

## Ligand Non-Innocence Allows Isolation of a Neutral and Terminal Niobium Nitride

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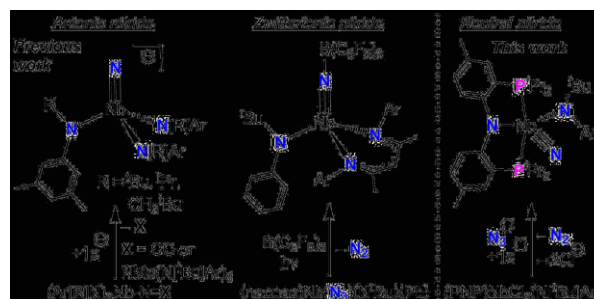
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Complex (PNP)NbCl<sub>2</sub>(N[<sup>t</sup>Bu]Ar) (1) (PNP<sup>-</sup> = N[2-PiPr<sub>2</sub>-4-methylphenyl]<sub>2</sub>; Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) reacts with one equiv of NaN<sub>3</sub> to form a mixture of (PNPN)NbCl<sub>2</sub>(N[<sup>t</sup>Bu]Ar) (2) and (PNP)Nb≡N(N[<sup>t</sup>Bu]Ar) (3), both of which have been spectroscopically and crystallographically characterized, including <sup>15</sup>N isotopic labelling studies. Complex 3 represents the first structurally characterized example of a neutral and mononuclear Nb nitride. Independent studies established 3 to form via two-electron reduction of 2, whereas oxidation of 3 by two-electrons reversed the process. Computational studies suggest that the transmetalation step to produce the intermediate [(PNP)NbCl(N<sub>3</sub>)(N[<sup>t</sup>Bu]Ar)] (A) extrudes N<sub>2</sub> to form the phosphinimide [(PNPN)NbCl(N[<sup>t</sup>Bu]Ar)] (B) followed by disproportionation to 2 and low-valent [(PNPN)Nb(N[<sup>t</sup>Bu]Ar)] (C). The latter then undergoes intramolecular N-atom transfer to form the nitride moiety in 3.

Although niobium nitride (NbN) has found widespread use as a thermally robust superconducting thin film in electronic devices<sup>1–4</sup> and as supercapacitors,<sup>5,6</sup> little is known about the nature of the neutral NbN functionality. One approach is to prepare discrete monomers having this functional group on Nb,<sup>7–10</sup> but given the high charge of N<sup>3-</sup>, its nucleophilic nature,<sup>7,11</sup> and its tendency to bridge,<sup>12–16</sup> only a handful of molecules displaying terminally bound Nb nitrides are known.<sup>17–20</sup> Cummins and co-workers reported three examples of anionic niobium nitrides (Fig. 1, left), all of which derived from reductive routes using Nb<sup>IV</sup> precursors such as ClNb(N[R]Ar)<sub>3</sub> (R = <sup>t</sup>Bu, <sup>i</sup>Pr, CH<sub>2</sub><sup>t</sup>Bu) by either splitting N<sub>2</sub> using heterobimetallic systems<sup>18,20</sup> or via decarbonylation of isocyanate.<sup>17</sup> In an interesting twist,

Arnold and co-workers found access to a zwitterionic Nb nitride (Fig. 1, center) by taking advantage of a photochemically driven process where the Nb<sup>V</sup> does not formally change oxidation state during the reaction.<sup>19</sup> Instead, their strategy involves photochemically promoting N<sub>2</sub> extrusion from a Nb<sup>V</sup>-N<sub>3</sub>, with the required 2e<sup>-</sup> equivalents coming from the reductive coupling of Nb–phenyl and Nb=N<sup>t</sup>Bu moieties to form an anilide Nb–N[<sup>t</sup>Bu]Ph (Fig. 1). In other words, the ligands provide the 2e<sup>-</sup> needed to achieve the reductive splitting of N<sub>3</sub><sup>-</sup> into N<sup>3-</sup> and N<sub>2</sub>. Unfortunately, this procedure relies on a borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to cap and trap the elusive neutral nitride ligand, resulting in the formation of a zwitterionic nitrido borate.<sup>19</sup>



**Fig. 1** Examples of structurally characterized anionic and zwitterionic mononuclear Nb nitrides (previous studies) along with the neutral and terminal Nb nitride reported in this work.

These two distinct routes share in common the use of hard nitrogen donors to stabilize the nitrido ligand as well as the necessity of a transient and highly reducing Nb<sup>III</sup> ion. Learning from these approaches we hypothesized that an anilide was not only an ideal ligand to stabilize a nitride, but that the ubiquitous N<sub>3</sub><sup>-</sup> could be the nitride source under reducing conditions, while taking advantage of a redox-active ligand. Recently, we found that the pincer ligand [PNP]<sup>-</sup> was indeed suitable for stabilizing the methylidyne (PNP)Nb≡CH(OAr) (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and that such system could undergo cross-metathesis with NC<sup>t</sup>Bu or NCAd to form (PNP)Nb≡N(OAr) and the terminal alkyne.<sup>21</sup> Despite obtaining <sup>15</sup>N isotopic labeling studies for the neutral

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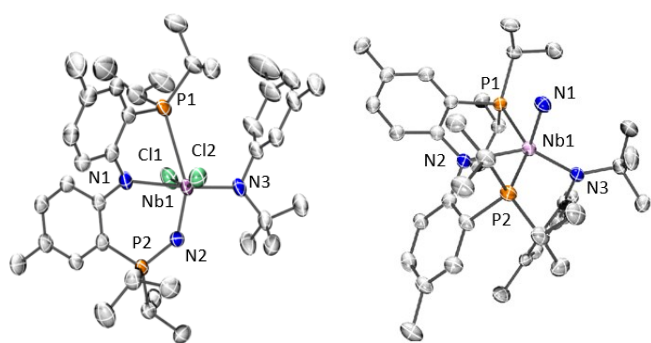
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nitride, we were unable to crystallographically characterize and unambiguously confirm its terminal nature. This feature along with the multistep process required to make its methylidyne precursor rendered this approach synthetically cumbersome. Hence, in order to stabilize a terminal and neutral nitride on Nb, a square pyramidal geometry seemed appropriate to use in combination with both an anilide and redox-active pincer scaffold. In this work we show how the Nb<sup>IV</sup> precursor (PNP)NbCl<sub>2</sub>(N<sup>[t</sup>Bu]Ar)<sup>22</sup> (**1**) can be the source of a terminal and neutral nitride ligand directly from azide reduction, and we establish that the PNP ligand plays a crucial non-redox innocent role, whereas the anilide ligand assists the N-atom transfer to Nb. Independent synthetic routes in combination with computational studies were used to probe the mechanism of formation of the neutral nitride ligand on Nb<sup>V</sup>, which was spectroscopically and structurally characterized including <sup>15</sup>N enriched isotopic labelling studies.

Recently, we reported the formation of complex **1** from the transmetalation of (PNP)NbCl<sub>3</sub> and Li(N<sup>[t</sup>Bu]Ar).<sup>22</sup> When **1** was treated with one equiv of NaN<sub>3</sub> in THF over 16 h, two diamagnetic Nb compounds were observed in approximately 1:1 ratio based on a combination of <sup>1</sup>H and <sup>31</sup>P NMR spectral studies (Fig. S16 and Fig. S17). The <sup>1</sup>H NMR spectrum also revealed two C<sub>1</sub>-symmetric complexes in solution. Notably, the <sup>31</sup>P NMR spectrum shows one compound to contain an intact PNP ligand (two broad phosphorus environments at 35.36 and 36.58 ppm) whereas the second species has two distinct phosphorus doublets at 41.57 and 11.83 ppm with *J*<sub>PP</sub> = 44 and 40 Hz respectively (Fig. S17). In addition to NMR spectral characterization, fractional crystallization from a pentane solution followed by a single crystal X-ray diffraction study allowed for the identification of these two species as (PNPN)NbCl<sub>2</sub>(N<sup>[t</sup>Bu]Ar) (**2**) and (PNP)Nb≡N(N<sup>[t</sup>Bu]Ar) (**3**) in 56% combined yield<sup>23</sup> as shown in Fig. 2 and Scheme 1. Whereas the structural study (Fig. 2) confirmed oxidation of one P-arm of the PNP ligand and transoid orientation of the two Cl<sup>-</sup> in the case of **2**, complex **3** represents the first example of a terminal and neutral Nb nitrido complex with a short Nb≡N bond length of 1.698(2) Å.<sup>18,20</sup> For **2**, the Nb center resides in a highly distorted octahedral geometry, while for **3** the geometry value is more in accord with a square pyramidal structure (*τ*<sub>5</sub> = 0.03)<sup>24</sup> akin to what was observed for (PNP)Nb≡CH(OAr) (*τ*<sub>5</sub> = 0.03).<sup>21</sup> The <sup>15</sup>N NMR spectrum of the <sup>15</sup>N enriched **2**-<sup>15</sup>N evinced a resonance at 351 ppm (*Δ**v*<sub>1/2</sub> = 11 Hz) while **3**-<sup>15</sup>N has a further downfield resonance at 824 ppm (*Δ**v*<sub>1/2</sub> = 10 Hz; referenced to AdCN at 242 ppm vs. NH<sub>3</sub>(l) at 0 ppm).

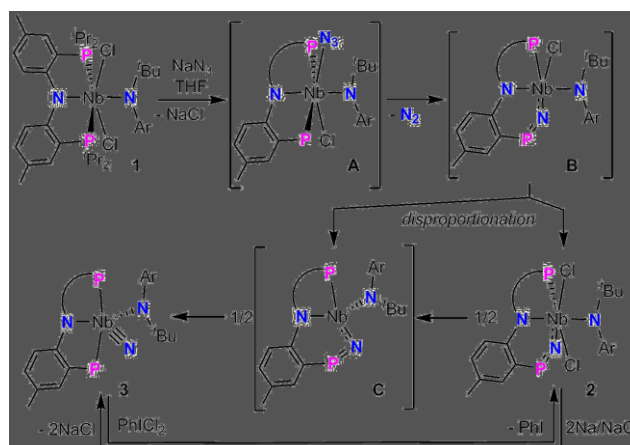


**Fig. 2** Molecular structures of complexes **2** (left) and **3** (right) with thermal ellipsoids at the 50% probability level. All

hydrogen atoms and co-crystallized pentane from **2** have been omitted for clarity.

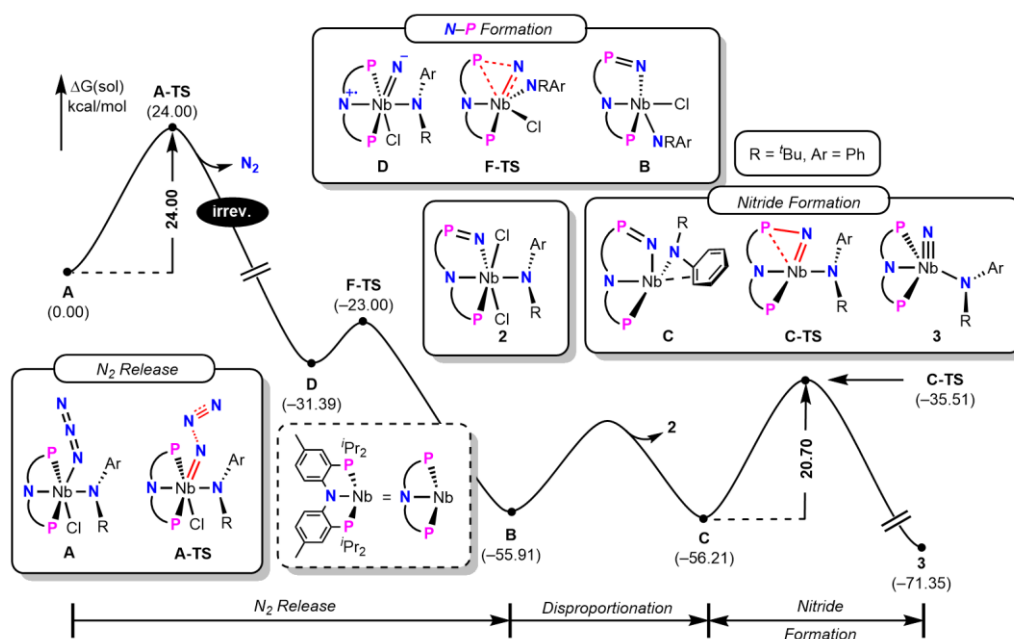
Despite having similar solubilities, compound **2** recrystallizes first after workup from a concentrated pentane solution at -35 °C. Further recrystallization of the pentane supernatant allows for the separation and isolation of **3**. Compounds **2** and **3** are likely formed from an initial transmetalation step to produce [(PNP)NbCl(N<sub>3</sub>)(N<sup>[t</sup>Bu]Ar)] (**A**), followed by N<sub>2</sub> ejection and PNP ligand oxidation to form the phosphinimide [(PNPN)NbCl(N<sup>[t</sup>Bu]Ar)] (**B**). Disproportionation of **B** most likely produces **2** and the unstable Nb<sup>III</sup> species [(PNPN)Nb(N<sup>[t</sup>Bu]Ar)] (**C**), which intramolecularly splits the P=N bond to form the nitrido complex **3** as outlined in Scheme 1. Since a disproportionation step relates **2** and **3**, we decided to chemically reduce **2** by two e<sup>-</sup> via putative **C** to **3**, inasmuch as oxidize **3** by the same amount of e<sup>-</sup> to promote PNP oxidation to yield **2**.

Accordingly, chemical reduction of **2** using 2 equiv Na/NaCl resulted in the formation of **3** along with some PNP and NaPNP that was confirmed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.<sup>23</sup> Similarly, chemical oxidation of **3** with PhICl<sub>2</sub> formed **2** along with other intractable side products.<sup>23</sup>



**Scheme 1** Synthesis of complexes **2** and **3** and proposed mechanism.

We used density functional theory calculations at the B3LYP-D3/cc-pVTZ(-f)/LACV3P//6-31G\*\*/LACVP level of theory<sup>25-32</sup> to gain further insight into the detailed mechanism to formation of **2** and **3** (see ESI for details) and understand the differing reactivity of **1** with the analogous P-atom transfer reagent, Na(OCP)<sup>22</sup> (Fig. S25). As illustrated in Fig. 3, the reaction begins with the transmetalation step resulting in the azide-bound complex **A**. N<sub>2</sub> release from **A** forms the N-centered radical cation complex **D** and traverses the transition state **A-TS** which involves three consecutive intramolecular electron transfer steps (Fig. S20–S23) to afford a barrier of 24.0 kcal/mol. The redox non-innocent nature of the PNP ligand enables the formation of a strong Nb–N bond, thus rendering it to be a PNP N-centered radical cation (**D**), and this is the driving force that makes the N<sub>2</sub> release highly exergonic by 31.4 kcal/mol. The following N–P bond formation (**F-TS**) from **D** involves energetically low isomerization steps between the anilide and the chloride ligand (Fig. S24). The resulting intermediate **B** undergoes thermoneutral disproportionation to form **2** and **C**.



**Fig. 3** Solvation-corrected Gibbs free energy profile for the conversion of **A** into **2** and **3**.

As shown in Fig. 3, the anilide aryl also plays a crucial role (Fig. S26) in stabilizing the intermediate **C** and in facilitating the complete intramolecular N-atom transfer from P to Nb via **C-TS** to form the nitride **3** with a barrier of 20.7 kcal/mol.

In summary, we shown that a redox active pincer ligand is critical for assembling the neutral and terminal niobium nitride and it can be directly accessed using  $\text{NaN}_3$  as the N-atom source. Theoretical studies suggest that the initial transmetallation followed by  $\text{N}_2$  release forms an unprecedented ligand-based niobium nitride with a ligand centered radical cation, whereby the redox non-innocent character of the pincer ligand drives the reaction to be highly exergonic. The following ligand-assisted coupling of the nitride affords a  $\text{Nb}^{\text{IV}}$  phosphinimide, which undergoes disproportionation to yield an isolable  $\text{Nb}^{\text{V}}$  phosphinimide and a highly reducing  $\text{Nb}^{\text{III}}$  phosphinimide intermediate. Finally, reductive cleavage of the P–N bond of the  $\text{Nb}^{\text{III}}$  phosphinimide, via assistance from the anilide ligand, furnishes the fully characterized neutral  $\text{Nb}^{\text{V}}$  nitride. Further reactivity studies disclose that P–N bond formation is promoted upon  $2e^-$  oxidation of the nitride whereas  $\text{Nb}^{\text{V}}$  nitride formation can be accomplished via  $2e^-$  reduction of **2**.

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### Conflicts of interest

There are no conflicts to declare.

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