The Niobaziridine−Hydride Functional Group: Synthesis and Divergent Reactivity

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Interest in the chemistry of three-coordinate trivalent niobium complexes supported by hard, anionic ligands has arisen from reports of their ability to mediate remarkable reactions including C−H[1] and C−N[2] bond cleavages and atom transfer reactions.[3] However, the high inherent reactivity of these complexes has made their isolation a challenging endeavor, with methodologies for stabilizing them having only recently become available.[1−4] Previously, we described the ability of the *N*-isopropylanilide ligand (N[^{i}Pr]Ar, Ar = 3,5-Me$_2$C$_6$H$_3$) to mask reactive, three-coordinate molybdenum trisamide complexes in a tautomeric molybdaziridine− hydride form via reversible β-H elimination.[5] Fascinated by an intriguing report of dinitrogen activation by a niobium trisamide complex,[6] chemistry we deemed explicable in terms of a niobaziridine−hydride intermediate, we adopted the latter as a synthetic target. Utilization of our *N*-isopropylanilide ligand toward this goal resulted at best in a borane adduct of the desired target.[7] Now we show that a new ligand variant, namely, the corresponding *N*-neopentyl version, permits isolation of the desired niobaziridine− hydride Nb(H)(η^2-^{t}Bu(H)C=NAr)(N[Np]Ar)$_2$ (**1**, Np = neopentyl), which serves as a reactive synthon for the trivalent niobium trisamide Nb(N[Np]Ar)$_3$ (**2**).

A multistep synthetic strategy provided the Nb(V) diiodide complex Nb(I)$_2$(N[Np]Ar)$_3$ (**3**) as an orange powder after diphenylacetylene deprotection of the corresponding η^2-alkyne complex with elemental iodine (25% yield over four steps starting from NbCl$_3$(DME); see Supporting Information). Treatment of a thawing THF solution of **3** with 1.25 equiv of Mg(THF)$_3$(anthracene) leads to the formation of diamagnetic **1** in 45−50% yield as orange blocks after recrystallization.[8] The ¹H NMR spectrum of **1**, consistent with its solid-state structure (Figure 1), indicates C_1 symmetry due to the formation of a stereogenic center at the carbon atom of the niobaziridine ring. A broad resonance observed at 9.24 ppm is assigned to the Nb−H moiety,[9] as is a stretch of moderate intensity at 1701 cm^{-1} in the infrared spectrum of **1**.

In an effort to observe reversible β-H elimination, complex **1** was studied by variable temperature ¹H NMR. The spectrum of **1** remained static up to 80 °C, at which temperature a new C_s symmetric product appeared. ¹H and ¹³C NMR data indicate the product of thermolysis to be the neopentylimido complex, Nb-(NNp)(Ar)(N[Np]Ar)$_2$ (**4**), formally the product of C−N bond oxidative addition by putative intermediate **2**, or alternatively the product of 1,2-aryl migration (N → Nb) via intermediate **2**. It is noteworthy that although **2** is also the likely precursor to **1**, crude reaction mixtures assayed during the synthesis of **1** do not indicate any formation of **4**. However, C$_6$D$_6$ solutions of pure **1** at room temperature do become enriched with **4** over time ($t_{1/2}$ = ca. 4.5 d), pointing to a slow conversion of **1** to **2** in solution. Furthermore, thermal rearrangement of **1** proceeds quantitatively to **4**, which retains its integrity at elevated temperatures. Thus, we hypothesize that **1** is a kinetic product while isomer **4** is the thermodynamic product.
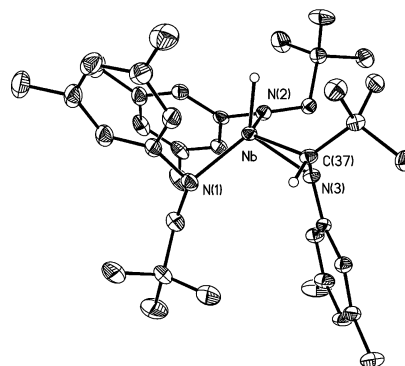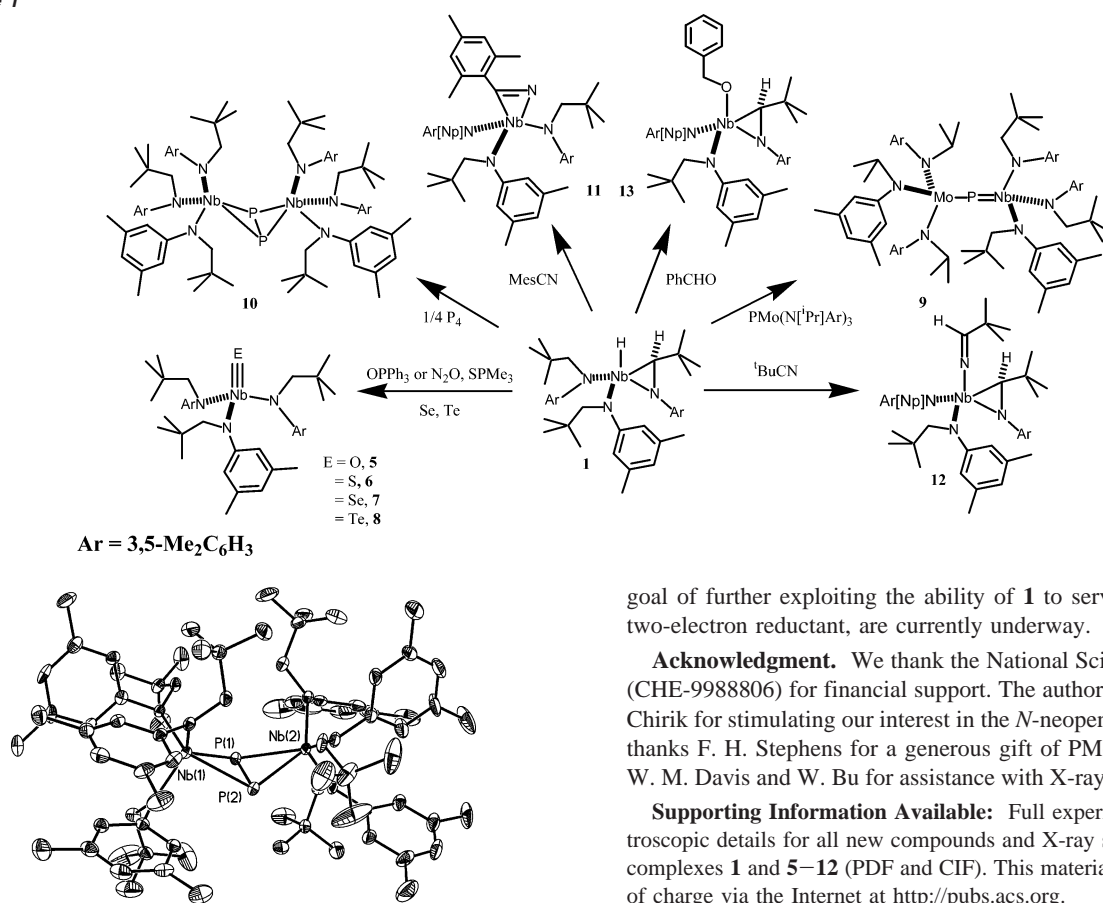

Figure 1. ORTEP diagram of **1** with 30% probability ellipsoids.

Whereas putative **2** was not observed directly, it was hoped that **1** would act as a functional equivalent of **2** when treated with appropriate substrates. Depicted in Scheme 1 are examples of 2e reductions effected by complex **1**, providing in high yields the crystalline species **5−10**. Worthy of mention is the deoxygenation of triphenylphosphine oxide by **1** leading to the oxo complex **5**, testifying to the ability of **1** to serve as a source of the potent twoelectron reductant **2**. In addition, **1** also proves to be a convenient route to the four-coordinate, terminal chalcogenide complexes[10] **6−8** when treated with an appropriate chalcogen atom source. Complex **1** can engage in incomplete atom transfer reactions as well.[11] Thus, upon addition of the terminal phosphide complex PMo(N[^{i}Pr]Ar)$_3$[12a] to C$_6$D$_6$ solutions of **1**, quantitative formation of the diamagnetic, hetero-dinuclear bridging phosphide complex (Ar[Np]N)$_3$Nb(μ-P)-Mo(N[^{i}Pr]Ar)$_3$ (**9**) is observed and further demonstrates the ability of **1** to reduce a diverse host of substrates.

In an additional display of reductive potency, **1** reacts with white phosphorus (P$_4$) to afford the dark green, bridging diphosphide complex (μ_2:η^2,η^2-P$_2$)[Nb(N[Np]Ar)$_3$]$_2$ (**10**) quantitatively as assayed by ¹H and ³¹P NMR. The reaction can be viewed as a 2e per Nb reduction of the P$_4$ tetrahedron and is reminiscent of the mild activation of P$_4$ reported for the Mo(III) trisamide system.[12] Formation of complex **10** from **1** and P$_4$ is selective inasmuch as it is the only new product obtained when either an excess or deficiency of P$_4$ is used. The molecular structure of **10** (Figure 2) shows the P$_2$ unit to be disposed in a side-on and butterfly conformation relative to the Nb−Nb vector (Nb−P−P−Nb dihedral angle = 135.61(5)°). The Nb−Nb distance of 4.2052(8) Å obviates the existence of a M−M bond and the observed diamagnetism of **10** substantiates the formulation of the P$_2$ unit as a (4−) ligand, a rarely documented functionality in early transition metal chemistry.[13] Furthermore, while N$_2$ is known to bridge two Nb(NCy$_2$)$_3$ (Cy = cyclohexyl) fragments in a linear fashion,[6] the P$_2$ bridge in complex **10** provides a striking contrast that is reminiscent of the structural chemistry of elemental nitrogen and phosphorus.[14]

With the ability of **1** to act as a source of **2** established, reactions with organic substrates were also probed. Treatment of **1** with 1.0

Scheme 1

Ar = 3,5-Me$_2$C$_6$H$_3$

Figure 2. ORTEP diagram of **10** with 30% probability ellipsoids.

equiv of mesitylnitrile (MesCN, Mes = 2,4,6-Me$_3$C$_6$H$_2$) leads exclusively to the η^2-nitrile complex (η^2-MesCN)Nb(N[Np]Ar)$_3$ (**11**), again demonstrating the accessibility of three-coordinate **2**. Crystallographic characterization confirmed the formulation of **11** as an η^2-nitrile complex possessing an elongated nitrile N−C bond of 1.258(4) Å, consistent with significant π-back-donation from a reducing metal center.[15]

In contrast, when **1** is treated with stoichiometric *tert*-butyl nitrile (tBuCN), sole formation of the nitrile insertion product **12** is obtained in which the niobaziridine ring remains *intact*. Likewise, treatment of **1** with benzaldehyde (PhCHO) leads exclusively to the benzyloxide complex **13**, highlighting the divergent reactivity accessible to the niobaziridine−hydride functional group. Indeed, insertion chemistry of this type has been encountered previously upon borane abstraction of our BH$_3$ adduct in the presence of benzophenone.[7] Extended heating of complexes **12** and **13** did not produce η^2-bound tautomers analogous to **11**,[16] an observation lending credence to the suggestion that dual pathways of reactivity are available to **1** depending on the substrate employed.

In conclusion, hints from the literature have suggested that the niobaziridine−hydride functional group is capable of tautomerization and subsequent small molecule activation chemistry,[6] with the present work confirming this hypothesis. However, and interestingly, no reaction of **1** with dinitrogen has yet been observed under ambient conditions. Whereas the molybdaziridine−hydride functionality has been shown conclusively to resist insertion into its Mo−H bond,[5] it is now shown for niobium that insertion pathways are accessible upon addition of certain unsaturated substrates. Investigations into the factors governing this dichotomy, with the

goal of further exploiting the ability of **1** to serve as a powerful two-electron reductant, are currently underway.

Supporting Information Available: Full experimental and spectroscopic details for all new compounds and X-ray structural data for complexes **1** and **5**−**12** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Thermolysis of **12** does proceed cleanly to a new cyclized product which will be the focus of an upcoming publication. Furthermore, complex **11** does not rearrange to an analogue of **12** when heated (C$_6$D$_6$, 100 °C, 3 d).

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