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Communication

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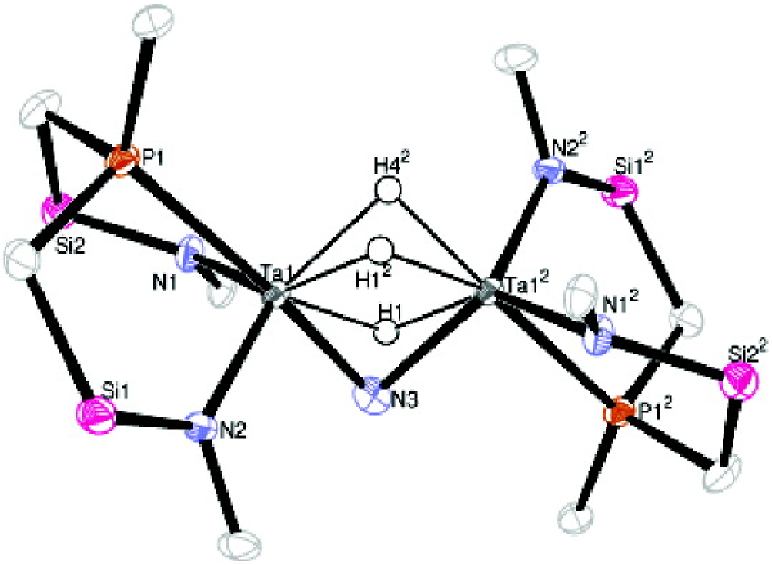

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Cleavage of Hydrazine and 1,1-Dimethylhydrazine by Dinuclear Tantalum Hydrides: Formation of Imides, Nitrides, and *N*,*N*-Dimethylamine

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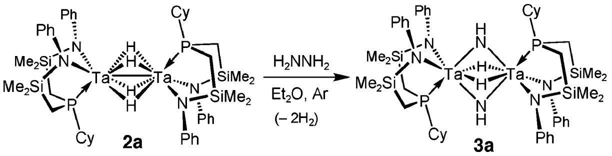
We recently reported the facile formation of the side-on end-on dinitrogen complexes (^{RPh}[NPN]Ta)$_2$(μ-η^1:η^2-N$_2$)(μ-H)$_2$ (**1a**, R = Cy; **1b**, R= Ph) (where ^{RPh}[NPN] = RP(CH$_2$SiMe$_2$NPh)$_2$) by reaction of N$_2$ with the dinuclear tetrahydride derivative (^{RPh}[NPN]-Ta)$_2$(μ-H)$_4$ (**2a**, R = Cy; **2b**, R= Ph).[1,2] Given the intrinsic inertness of dinitrogen, to generate a complex where the coordinated N$_2$ is activated without the use of strong reducing agents is quite remarkable.[3,4] To achieve such an activated N$_2$ unit, it is necessary that tetrahydride **2** or its reactive intermediate be strongly reducing. Four electrons are transferred to the N$_2$ from the reductive loss of H$_2$ and from a HOMO that is Ta−Ta bond in character. It is noteworthy that the N$_2$ moiety in **1** undergoes hydroboration[5] and hydrosilylation[6] with formation of new N−B and N−Si bonds along with N−N bond cleavage. Given the importance of N−N bond breaking to the formation of ammonia from N$_2$ both industrially via the Haber−Bösch process and biologically via nitrogenase, along with the longstanding use of hydrazine to model dinitrogen cleavage,[7−9] we have examined the ability of tetrahydrides **2a** and **2b** to cleave N−N bonds in hydrazine derivatives. In this work, we report our studies on the formation of dinuclear tantalum nitrides and imides via the cleavage of N−N single bonds. Of particular importance is the elimination of amine from these systems under certain circumstances.

Addition of 1 equiv of hydrazine, H$_2$NNH$_2$, to (^{CyPh}[NPN]Ta)$_2$-(μ-H)$_4$ gave clean conversion to (^{CyPh}[NPN]Ta)$_2$(μ-NH)$_2$(μ-H)$_2$, **3a**, a compound that contains two bridging imides and two bridging hydrides. This new product is identified spectroscopically by its ^{1}H{^{31}P} NMR spectrum that shows two peaks of interest, each integrating to 2 H and coupling weakly to one another, which are observed at 15.1 and 3.4 ppm. They can be assigned to bridging hydride Ta$_2$(μ-H)$_x$ and N−H environments, respectively. A ^{1}H−^{15}N HSQC experiment showed strong coupling between the resonance at 3.4 ppm and a ^{15}N resonance (−24.5 ppm) within the structure, suggesting that this proton is nitrogen-bound. The symmetry of this complex in solution is high, as equivalent phosphines and only two silyl methyl resonances are observed. Unfortunately, attempts to confirm this structure by X-ray crystallography were unsuccessful. This reaction is shown in eq 1.



(1)

In an effort to generate suitable crystals for X-ray analysis, the reaction of hydrazine with the P-phenyl derivative **2b** was examined. However, in this case, this process is complicated by the formation of free ligand ^{PhPh}[NPN]H$_2$ as the major product along with approximately 30% yield of the analogue of **3a**, the diimide (^{PhPh}[NPN]Ta)$_2$(μ-NH)$_2$(μ-H)$_2$, **3b**. The NMR spectroscopic characteristics of **3b** closely match that of **3a**, in particular, the observation of peaks in the ^{1}H{^{31}P} NMR spectrum for the bridging N−H and bridging hydrides. Crystals suitable for X-ray analysis could be obtained by rapid cooling of a toluene/hexanes solution of the crude mixture; Figure 1 shows an ORTEP depiction of the solid-state molecular structure of **3b**.

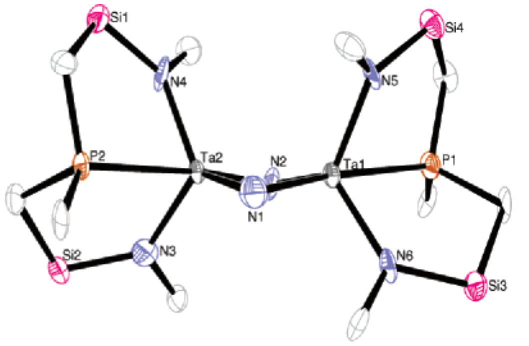


Figure 1. ORTEP representation of the molecular structure of **3b**; silyl methyl and phenyl ring carbons other than ipso positions have been omitted for clarity.

Reduction of hydrazine by (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$ has cleaved the N−N bond. The dihedral angle for Ta(1)−N(1)−Ta(2)−N(2) of −15.6(3)° shows the two bridging nitrogen atoms are bent down from the equatorial plane. The nitrogen atoms, N(1) and N(2), are symmetrically bound between the two metals, and bond lengths are consistent with bridging imides; for example, the Ta(1)−N(2) and Ta(2)−N(2) interatomic distances of 2.027(11) and 2.002(11) Å are similar to each other and also to the average Ta−N bond length of the bis(silylimide) complex (^{PhPh}[NPN]Ta)$_2$(μ-NSiH$_2$^{n}Bu)$_2$ of 2.008 Å.[6] Unfortunately, the N−H and bridging hydrides were not located within the diffraction pattern, and crystal size has so far prohibited the use of neutron diffraction. The atom connectivity, symmetrical Ta−N bond lengths, and NMR evidence support the formation of bis(imide)dihydride bimetallic tantalum complexes **3a** and **3b**.

The addition of 1,2-disubstituted hydrazines could access stable complexes of the type (^{PhPh}[NPN]Ta)$_2$(μ-NR)$_2$(μ-H)$_2$ (R = Ph, Me). Unfortunately, addition of 1,2-dimethylhydrazine or 1,2-diphenylhydrazine gave highly complicated product distributions; no traceable products were isolated.

Moving to a 1,1-disubstituted hydrazine promoted a different transformation. Addition of Me$_2$NNH$_2$ to (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ resulted in the formation of an asymmetric bimetallic product evidenced by two singlets at 12.8 and 14.8 ppm in the ^{31}P{^{1}H} NMR spectra. Two hydridic resonances were also observed at 8.4 (integrating to 2 H) and 14.3 ppm (integrating to 1 H). Crystals of this product were grown from a saturated toluene/hexanes solution and analyzed by X-ray crystallography. An ORTEP depiction of the solid-state molecular structure of (^{CyPh}[NPN]Ta)$_2$(μ-N)(μ-H)$_3$, **4**, is shown in Figure 2. The structure is a mononitride complex,

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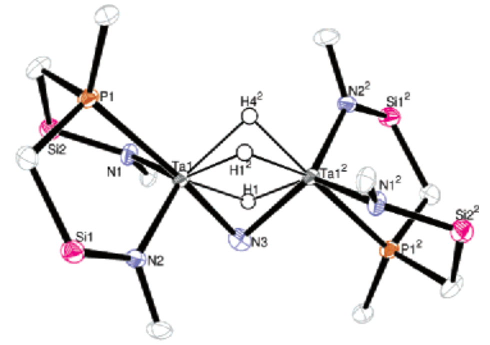
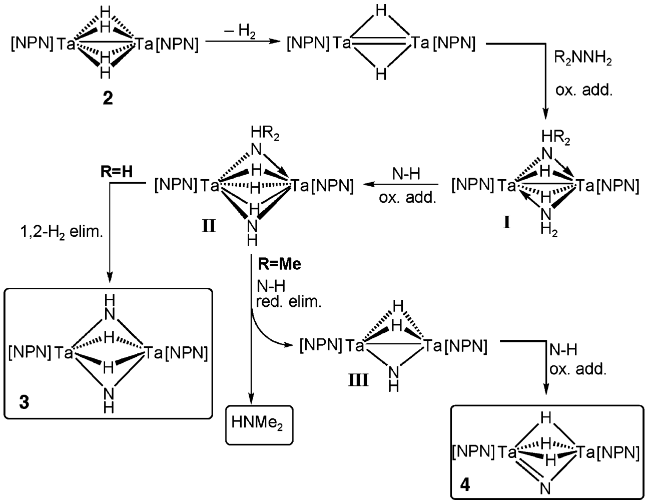


Figure 2. ORTEP representation of the molecular structure of **4**; silyl methyl, N-phenyl, and P-cyclohexyl (except ipso) carbons have been omitted for clarity.

Scheme 1



where the N(3) atom is disordered over two locations; a 50% occupancy is placed on N(3). Four hydrides were located within the diffraction pattern. Hydrides H4 and H4^2 were set at half occupancy to match the disorder in the bridging nitride. The bridging nitrogen atom is no longer positioned symmetrically. The Ta(1)−N(3) distance of 1.973(8) Å is shorter than the Ta(1)^2−N(3) distance of 2.059(7) Å and from the bond lengths in structure **3b**, suggesting nitride formation. The hydride positions were confirmed using the X-HYDEX mapping program. The structure is the mononitride−trihydride complex, **4**, and is in agreement with solution NMR studies.

How does this mononitride form, and why do we get a different product with this substituted hydrazine? A proposed pathway that accounts for the formation of both **3** and **4** is shown in Scheme 1. Initial loss of H_2 would generate a previously proposed Ta=Ta double bond. Reaction of this species with R_2NNH_2 and cleavage of the N−N bond would generate a bis(amide) complex (**I**). Oxidative addition of an N−H bond would give an imide−amide−trihydride intermediate (**II**). For R = H, a 1,2-H_2 elimination from the remaining amide would generate the final product (**3**).[10] In the reaction with *N*,*N*-dimethylhydrazine, a reductive elimination of the amide as $HNMe_2$ would generate an imide−dihydride complex (**III**). Oxidative addition of the remaining N−H imide bond would generate the observed nitride−trihydride complex (**4**). In support of this mechanism, GC−MS of the headspace above the reaction to form complex **3** indicates the presence of $HNMe_2$.

Group 5 nitrides have been prepared from molecular nitrogen.[11−15] The activation and cleavage of the N−N bond in hydrazines have been previously reported.[16−21] Of particular interest, the addition of hydrazines to $(Cp^*Ru)_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ promotes the formation of bis(μ_3-imido) complexes,[20] while the addition of 1,1-methylphenylhydrazine to $Mo_2M_2S_4$ (M = Rh, Ir) clusters, followed by addition of 2,6-lutidinium chloride as a proton source and cobaltocene as an external electron source, promotes the formation of *N*-methylaniline.[21] To facilitate these reactions, however, harsh conditions, external proton sources, and external reductions are required.

Promoting the formation and elimination of a functionalized nitrogen-containing product (Me_2NH) without harsh conditions or additives is surprising. The 1,1-substituted hydrazine could not form the thermodynamically favorable imide as no N−H bonds were available for activation. These ideas can hopefully be extended to current work with molecular nitrogen. For example, upon addition of primary silanes to the dinitrogen complex **1b**, bis(imido) complexes $(^{PhPh}[NPN]Ta)_2(\mu\text{-}NSiH_2R)_2$ are formed[6]. Doubly functionalizing one nitrogen atom prior to cleavage would shut down the formation of imide and potentially eject HNR_2 species derived from molecular nitrogen. Current work is focused on extending these ideas toward molecular nitrogen-based activation and investigating the reactivity of **4** with E−H bonds.

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Supporting Information Available: Complete experimental details for the synthesis of **1**−**3**. Information on X-ray data collection and processing and X-ray crystallographic data for **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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