Communication

Dinitrogen Activation at Ambient Temperatures: New Modes of H and PhSiH Additions for an “End-On-Bridged” [Ta(IV)](□-□:□-N) Complex and for the Bis(□-nitrido) [Ta(V)(□-N)] Product Derived from Facile N#N Bond Cleavage

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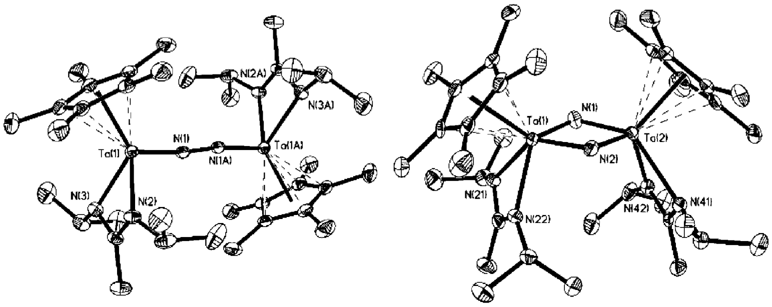

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Dinitrogen Activation at Ambient Temperatures: New Modes of H_2 and $PhSiH_3$ Additions for an "End-On-Bridged" $[Ta(IV)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ Complex and for the Bis(μ-nitrido) $[Ta(V)(\mu\text{-}N)]_2$ Product Derived from Facile N≡N Bond Cleavage

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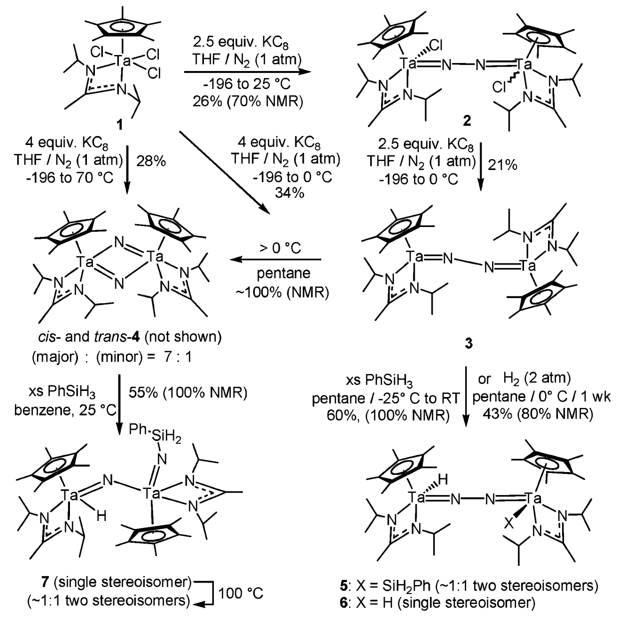
Elucidation of mechanistic underpinnings that can support the design of transition-metal-based catalysts for the direct conversion of N_2 and H_2 to ammonia (NH_3) at, or near, ambient temperatures still presents important experimental and theoretical challenges now into the 21st century.[1−3] Indeed, although substantial advances toward this goal have been made, the number of well-defined inorganic and organometallic complexes that can ligate N_2 in such a fashion that ultimately leads to facile N≡N bond cleavage and N-atom functionalization remains extremely small.[1,2] Herein, we report experimental results that serve to establish a new midvalent bimetallic, "end-on-bridged" $[Ta(IV)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ complex that is sufficiently activating for these processes to occur at, and below, room temperature.

Scheme 1 summarizes results obtained for chemical reduction of the Ta(V) trichloride **1**, which includes structural characterization of all new compounds by crystallographic analysis.[4] To begin, under an atmosphere of N_2 (1 atm), reduction of **1** employing a slurry of 2.5 equiv of potassium graphite (KC_8) in tetrahydrofuran (THF) at low temperatures served to reliably provide a 26% isolated yield (70% by NMR) of a new diamagnetic crystalline material that on the basis of ^1H NMR spectroscopy was shown to be composed of a 60:40 mixture of two non-interconverting stereoisomers. Fractional crystallization, followed by single-crystal X-ray analysis, identified the major species as being the racemic (*rac*) diastereoisomer of the bimetallic $[Ta]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ dichloride **2** shown in Scheme 1.[4] Molecular bond lengths and bond angles obtained for *rac*-**2** include Ta−N, N−N, and Ta−N−N values of 1.813(5) Å, 1.288(10) Å, and 178.5(6)°, respectively, that are in keeping with other known $[Ta]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ complexes for which a strong degree of hydrazido (diimido) $[\mu\text{-}N_2]^{4-}$ character and formal Ta(V) oxidation states for the two metal centers have been proposed.[5] Also in keeping with prior observations,[5] **2** proved to be thermally robust in toluene solution up to 100 °C; showing no propensity to engage in final N−N bond cleavage at these elevated temperatures. Fortunately, by utilizing 4 equiv of KC_8 and keeping the reaction mixture and isolated product at, or below, 0 °C, reduction of **1** under N_2 (1 atm) now provided a 34% isolated yield of a new paramagnetic, dark purple crystalline material for which only broadened ^1H NMR resonances were observed in solution, but for which, single-crystal X-ray analysis determined the solid-state structure to be the end-on-bridged $[Ta]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ complex **3** (see Scheme 1).[4] It was subsequently determined that **2** can also be reduced to provide **3** in comparable yield under identical conditions using 2.5 equiv of KC_8.

Figure 1 presents the molecular structure of **3** which adopts a C_{2h}-symmetric geometry in the solid-state, with Ta(1)−N(1), N(1)−N(1A), and Ta(1)−N(1)−N(1A) values of 1.807(2) Å, 1.313(4) Å, and 172.7(3)°, respectively.[4] As these bond length parameters are shorter and longer, respectively, relative to those of **2**, it might be concluded that **3** possesses a significantly greater degree of $[\mu\text{-}N_2]^{4-}$ character that is possibly coupled with an associated weaker N−N bonding interaction. Indeed, while **3** proved to be stable in solution at 0 °C for extended periods of time (∼1 week), as Scheme 1 reveals, above this temperature, it quantitatively converted to a new diamagnetic pale-yellow material comprising a 7:1 mixture of two non-interconverting stereoisomers as determined by ^1H NMR spectroscopy. Once more, fractional crystallization, followed by crystallographic analysis, determined the two species to be the *cis* (major) and *trans* (minor) stereoisomers of the bis(μ-nitrido) complex **4**.[4] Figure 1 presents the molecular structure of *cis*-**4** in which the four-membered $[Ta(V)(\mu\text{-}N)]_2$ ring adopts a planar geometry with Ta(1)−N(1) and Ta(1)−N(2) bond distances of 1.894(4) and 1.924(4) Å, respectively, and a transannular N⋯N nonbonding distance of 2.574 Å.[4]

Scheme 1



Although cyclic bis(μ-nitrido) species, such as **4**, have previously been reported as the product of bimetallic N_2 activation under reducing conditions,[1,2d] to the best of our knowledge, the **3** → **4** transformation is the only well-documented example of thermally induced rearrangement of a linear $[M]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ structure to a $[M(\mu\text{-}N)]_2$ diamond core that proceeds with complete N≡N bond cleavage and without participation of the supporting ligand framework.[2d,e,6,7] In this regard, the electronic structure of **3** as well as the nature of the mechanism (e.g., intramolecular vs fragmentation/recombination) are of particular interest for any new insights they might shed on the specific steps and criteria that are required for this process to occur with minimal energy barriers. Experimentally, preliminary solid-state magnetic susceptibility (SQUID) data

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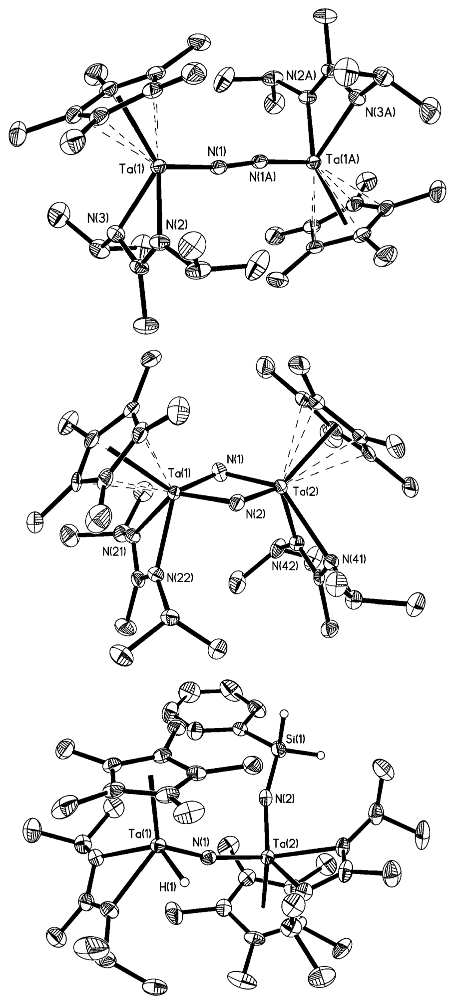

Figure 1. Molecular structures (30% thermal ellipsoids) for (top to bottom): **3**, *cis*-**4**, and **7**. Hydrogen atoms, except for selected ones in **7**, have been removed for the sake of clarity.[4]

for **3** recorded between 2 and 300 K are consistent with the material approaching a singlet ground state (GS) below 2 K and, above, the existence of antiferromagnetic exchange occurring between two formal d^1 Ta(IV) centers in a manner similar to that reported by Fryzuk and co-workers[6] for a structurally characterized $[Nb(IV)]_2(\mu$-η^1:η^1-$N_2)$ complex.[4] On the theory side, high level DFT studies of C_{2h}-symmetric $[M]_2(\mu$-η^1:η^1-$N_2)$ complexes appear supportive of the likelihood of a singlet GS and a thermally populated triplet state for **3**.[3] However, it is also recognized that many factors, such as spin−orbit coupling, mixing of electronic states, and spin surface crossings, serve to complicate formulation of a simple picture of N_2 activation and N≡N bond cleavage for the present system in the absence of additional theoretical and experimental studies regarding electronic structure and mechanism now underway.

Compound **3** exhibits a pattern of chemical reactivity toward hydrogenation and hydrosilylation at (sub)ambient temperatures that is distinct from that observed previously for other $[Ta]_2(\mu$-η^1:η^1-$N_2)$ complexes[5d] and by Fryzuk and co-workers[8] for an "end-on, side-on"-bridged $[Ta(IV)]_2(\mu$-η^1:η^2-$N_2)$ complex. Thus, as Scheme 1 reveals, both $PhSiH_3$ and H_2 undergo "1,4-addition" across the Ta═N−N═Ta framework to provide, with the former reagent at 25 °C, a 60% isolated yield (100% by NMR) of the new diamagnetic product **5** as a ~1:1 mixture of two non-interconverting stereoisomers. With H_2, **3** reacted more slowly, but stereospecifically, at 0 °C over a 1 week period to provide a 43% yield (80% by NMR) of the single diastereomeric dihydride product **6**, along with a 20% yield of **4**.[4] The molecular structures of **5** and **6**, as determined by single-crystal X-ray analyses, reveals the absence of bridging hydrides in both cases, along with Ta−N, N−N, and Ta−N−N metrical parameters that are again consistent with Ta(V) formal oxidation states and significant $[\mu$-$N_2]^{4-}$ character.[4,5] Both **5** and **6** also proved to be thermally stable in solution up to 100 °C. Finally, although **4** is chemically inert toward hydrogenation (2 atm) at ambient and elevated temperatures to 60 °C, *cis*-**4**, but not *trans*-**4**, was found to readily react with $PhSiH_3$ at 25 °C in benzene to cleanly provide a 55% isolated yield (100% by NMR) of the "ring-opened" product **7** through stereospecific σ-bond metathesis of a Ta−N single bond, rather than the anticipated 1,2-addition across a Ta═N double bond.[8] Single-crystal X-ray analysis of **7** (see Figure 1), along with ^1H and ^{15}N NMR spectra of $^{15}N(1)$ and $^{15}N(2)$-labeled **7**, confirm the stereochemistry of ring-opening and the absence of bridging hydrides in both solution and the solid state.[4] Unfortunately, attempts to induce a second Ta−N σ-bond metathesis of **7** with $PhSiH_3$ up to temperatures of 100 °C only achieved metal-centered epimerization to produce a 1:1 mixture of two diastereoisomers as Scheme 1 reveals. This epimerization process was also found to occur at the same rate in the absence of silane. With this new lead, however, we are presently exploring different silane derivatives and other reagents that might be capable of more readily engaging in multiple Ta−N σ-bond metatheses to provide mononuclear metal imido end-products.

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Supporting Information Available: Experimental details, including CIF reports for *rac*-**2**, **3**, *cis*- and *trans*-**4**, and **5**−**7**, SQUID data for **3**, and ^{15}N NMR chemical shift data for *cis*- and *trans*-**4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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