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Partial hydrogenation of a tetranuclear titanium nitrido complex with ammonia borane.

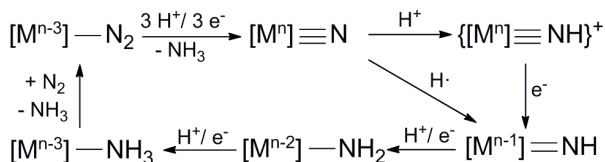
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ABSTRACT: Treatment of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ with NH_3BH_3 leads to the paramagnetic imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_3(\mu_3\text{-NH})]$ which can be also obtained by stepwise proton and electron transfers with HOTf and $[\text{K}(\text{C}_5\text{Me}_5)]$.

There is a tremendous interest in the development of molecular systems capable of performing the catalytic conversion of N_2 to NH_3 under mild conditions.¹ Nowadays, only three examples of molecular catalysis for N_2 reduction to ammonia in solution are known.² The methodology in those catalytic systems involves the addition of high excess of external acids and reducing agents to well-defined molybdenum^{2a,b} or iron^{2c} dinitrogen complexes. Proposed catalytic cycles for ammonia production in homogeneous systems (e.g. Chatt and Schrock cycles) are based on stepwise proton and electron transfers on metal complexes containing N_xH_y moieties.³ As shown in Scheme 1, three alternating proton and electron additions on a dinitrogen complex generate a metal nitrido $[\text{M}^n]\equiv\text{N}$ intermediate along with the release of the first equivalent of ammonia. A second equivalent of ammonia is produced by further protonation and reduction processes on the nitrido complex. To catalytic performance, the addition of protons to create N-H bonds in the nitrido complex has to be coupled with electrons to reduce the metal center for further dinitrogen incorporation and regeneration of the nitrido ligand. Thus, a metal nitrido complex $[\text{M}^n]\equiv\text{N}$ undergoes addition of a single proton and a single electron to form a reduced imido derivative $[\text{M}^{n-1}]=\text{NH}$, a process formally equivalent to the transfer of a hydrogen atom. While the reactivity of nitrido ligands with proton sources to generate NH imido groups is well documented in the literature,⁴ the direct hydrogen-atom transfer to a terminal nitrido ligand with an appropriate reagent has been only reported by Smith and co-workers.⁵

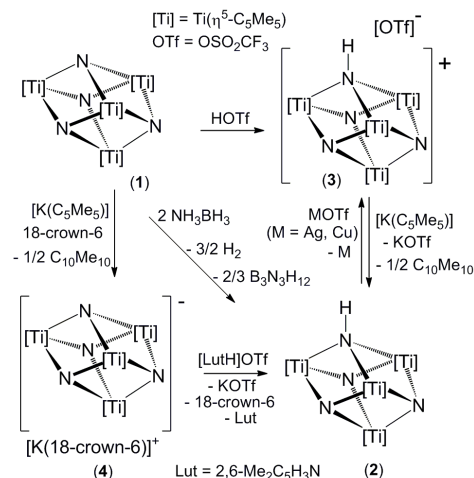
Scheme 1. Catalytic cycle for the reduction of dinitrogen to ammonia³



As part of a project devoted to develop new reactivity patterns of polynuclear nitrido complexes,⁶ we were interested in studying the hydrogenation of the tetranuclear titanium(IV) nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ (**1**). Compound **1** was prepared by

ammonolysis of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$,⁷ but related polynuclear titanium derivatives have been recently obtained by direct reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ with $\text{H}_2:\text{N}_2$ mixtures.⁸ While compound **1** does not react directly with H_2 , here we report the preliminary results on the reaction with NH_3BH_3 to generate the paramagnetic imido-nitrido cluster $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_3(\mu_3\text{-NH})]$ (**2**). In recent years, ammonia borane (NH_3BH_3) has attracted increasing attention mainly due to its potential use as portable source of hydrogen.⁹ Although it is commercially available, to our knowledge, the use of ammonia borane in the context of catalytic ammonia production is unprecedented. To gain insight into the formation of **2**, we have also prepared this complex either by protonation of **1** and subsequent one-electron reduction of the resultant cation or by reduction of **1** followed by proton transfer to the reduced specie (Scheme 2).

Scheme 2. Hydrogenation of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ (**1**)



Treatment of **1** with 2 equiv of NH_3BH_3 in tetrahydrofuran at 85 °C led to complex **2** as a dark blue precipitate in 64% yield. Similarly to **1**, compound **2** is poorly soluble in hydrocarbon solvents, pyridine or tetrahydrofuran at room temperature. However, complex **2** shows an enhanced solubility in those solvents at higher temperatures and, by slow cooling a heated toluene solution at 90 °C, suitable single-crystals for an X-ray crystal structure determination were obtained. The solid-state structure of **2** shows an almost perfect $[\text{Ti}_4\text{N}_4]$ cube core (Figure 1), with the Ti-N-Ti and the N-Ti-N angles very close to 90°, in an analogue disposition of the parent complex **1**.⁷ The imido hydrogen atom was not located in the difference Fourier map and was distributed over the four nitrogen atoms with 25% of occupancy for each position. Thus, all titanium-nitrogen and titanium-titanium distances are

within the narrow ranges of 1.948(4)-1.978(4) Å and 2.828(1)-2.846(1) Å, respectively. However, the averaged Ti-N (1.963(8) Å) and Ti-Ti (2.836(8) Å) separations in complex **2** are slightly longer than those found in **1**, 1.938(7) and 2.783(2) Å.¹⁰

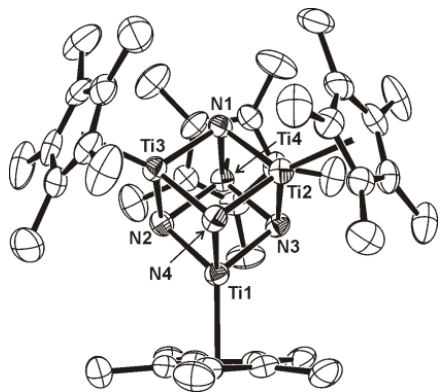


Figure 1. Perspective view of complex **2** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected averaged lengths (Å) and angles (deg): Ti-N 1.963(8), Ti...Ti 2.836(8), N-Ti-N 87.4(2), Ti-N-Ti 92.5(4).

Compound **2** exhibits a good solubility in chloroform-*d*₁, although it reacts slowly with this solvent to give **1** (ca. 5% conversion after 24 h at room temperature). The ¹H NMR spectrum of complex **2** in chloroform-*d*₁ shows two far-downfield and broad resonances in a 1:3 ratio at $\delta = 10.0$ ($\Delta\nu_{1/2} = 45$ Hz) and 8.7 ($\Delta\nu_{1/2} = 33$ Hz) attributable to the η^5 -C₅Me₅ ligands. We have recently found analogous resonance signals in the ¹H NMR spectra of paramagnetic titanium-yttrium cube-type species generated by one-electron reduction of the complex [Cl₃Y{(μ₃-NH)₃Ti₃(η^5 -C₅Me₅)₃(μ₃-N)}] with [K(C₅Me₅)].^{6c} DFT calculations showed that the incorporated electron in those complexes is delocalized among the three titanium atoms while maintaining the yttrium center as trivalent. The paramagnetic nature of **2** was confirmed by an Evans method determination of its magnetic susceptibility ($\mu_{\text{eff}} = 1.70 \mu_{\text{B}}$, 293 K, CDCl₃ solution), which is consistent with the presence of an unpaired electron in the complex. Although the presence of one resonance for the NH imido ligand was not detected in the ¹H NMR spectra of **2**, the N-H stretch was identified in the IR spectrum (KBr) at 3333 cm⁻¹.

The reaction of **1** with 2 equiv of NH₃BH₃ in tetrahydrofuran-*d*₈ was monitored by ¹H and ¹¹B NMR spectroscopy. No reaction was detected at room temperature, while spectra taken after heating at 85 °C for 3 days showed complete consumption of the ammonia borane adduct. The ¹¹B NMR spectrum of the resultant solution revealed one triplet resonance ($\delta = -10.5$, ¹J(B,H) = 102 Hz) assigned to cyclotriborazane (CTB, [NH₂BH₂]₃), along with minor resonance signals for borazine and polyborazylene.¹¹ The ¹H NMR spectrum showed the formation of molecular hydrogen in solution ($\delta = 4.54$) along with two broad resonances in a 1:3 ratio at $\delta = 9.9$ ($\Delta\nu_{1/2} = 48$ Hz) and 8.6 ($\Delta\nu_{1/2} = 34$ Hz) assignable to the η^5 -C₅Me₅ groups of the paramagnetic complex **2**. However, complex **1** in benzene-*d*₆ did not react under H₂ atmosphere at temperatures up to 120 °C and remained unaltered in its treatment with N,N-dimethylamineborane (NHMe₂BH₃), which decomposed at 85 °C with formation of molecular hydrogen and the cyclodiborazane [NMe₂BH₂]₂.¹² Interestingly, by using *in situ* multinuclear NMR spectroscopic studies, Shaw and co-workers have shown evidence for the formation of diammoniate of diborane, [BH₂(NH₃)₂]⁺[BH₄]⁻ (DADB), in glyme solutions of NH₃BH₃ heated at temperatures higher than 50 °C.^{11b} We speculate that hydrogenation of **1** might involve protonation and reduction processes with DADB and we have therefore examined step-

wise proton and electron transfers on **1** with separate acids and reducing agents.

Treatment of **1** with 1 equiv of triflic acid (HOTf) in toluene at room temperature led to the precipitation of the diamagnetic ionic derivative [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_4(\mu_3\text{-N})_3(\mu_3\text{-NH})\}[\text{OTf}]$] (**3**) (Scheme 2). Compound **3** was isolated in 78% yield as a red solid which is poorly soluble in hydrocarbon solvents but exhibits a good solubility and stability in halogenated solvents. Crystals of **3**·C₆H₆F were grown by diffusion of hexane into a fluorobenzene solution of this compound. The solid-state structure contains a cationic fragment with a [Ti₄(μ₃-N)₃(μ₃-NH)] cube-type core associated to the triflate anion through a hydrogen bonding interaction between the imido ligand and one of the oxygen atoms (N(4)···O(13) and H(4)···O(13) distances of 3.292(5) and 2.32(5) Å respectively, and N(4)-H(4)···O(13) angle of 167(4)°) (Figure 2). The protonation of one nitrido ligand results in a lengthening, approximately 0.1 Å, of the titanium-nitrogen and titanium-titanium distances of the {Ti₃(μ₃-NH)} fragment when compared with the Ti-N and Ti-Ti separations of the {Ti₃(μ₃-N)} units (average 1.937(11) and 2.787(5) Å). An analogous lengthening of those distances have been found in the {Ti₃(μ₄-N)MX} fragments of the Lewis acid-base adducts [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_4(\mu_3\text{-N})_{4-n}\{(\mu_4\text{-N})\text{MX}\}_n$] previously prepared in our group.^{6b} The IR spectrum (KBr) shows one broad band at 3237 cm⁻¹ for the ν_{NH} vibration and several strong absorptions in the range 1285-1032 cm⁻¹ for the triflate group.¹³ In particular, the ν_{as}(SO₃) vibration splits into two bands, at 1285 and 1255 cm⁻¹, in good agreement with the interaction of the triflate ion with the NH imido group^{13c} determined in the solid-state structure. The ¹H NMR spectrum of **3** in chloroform-*d*₁ at room temperature reveals a broad resonance signal at $\delta = 13.32$ for the NH group and two singlets in a 3:1 ratio for the C₅Me₅ ligands in accord with a C_{3v} symmetric structure in solution.

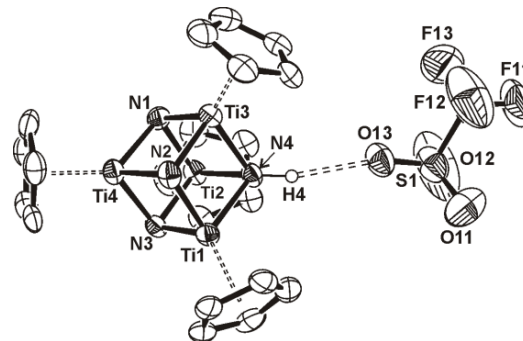


Figure 2. Perspective view of complex **3** (thermal ellipsoids at the 50% probability level). Methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity. Selected averaged lengths (Å) and angles (deg): Ti-N(4) 2.044(5), Ti-N 1.937(11), Ti(4)···Ti 2.787(5), Ti···Ti 2.875(1), Ti-N(4)-Ti 89.4(1), Ti-N-Ti 91.3(1)-96.7(1), N-Ti-N 87.6(6).

The ionic compound **3** reacted with 1 equiv of [K(C₅Me₅)] in toluene at room temperature to produce a dark blue precipitate containing **2** and potassium triflate. From this solid, complex **2** can be isolated in 65% yield if extraction with chloroform-*d*₁ and subsequent workup were performed within 15 min. The reaction of **3** with 1 equiv of [K(C₅Me₅)] in benzene-*d*₆ at room temperature was monitored by ¹H NMR spectroscopy. Immediately, the initial red suspension turned to a dark blue color and spectra taken after 10 min showed resonance signals for C₁₀Me₁₀ and the two minor far-downfield and broad resonances mentioned above for the η^5 -C₅Me₅ ligands of complex **2**. The exclusive formation of C₁₀Me₁₀ as organic byproduct, which is formed via coupling of pentamethylcyclopentadienyl radicals,^{14,6c} suggests that the reaction pathway for the synthesis of **2** consists of an electron transfer

from the $C_5Me_5^-$ anion to the cationic fragment of **3**. Interestingly, compound **2** readily reacts with copper(I) or silver(I) trifluoromethanesulfonate derivatives in chloroform- d_1 at room temperature to give solutions of **3**, while copper or silver metals were deposited at the bottom of the NMR tubes.

Treatment of **1** with 1 equiv of $[K(C_5Me_5)]$ and 18-crown-6 in toluene led to a dark purple precipitate of $[K(18\text{-crown-6})][Ti_4(\eta^5\text{-}C_5Me_5)_4(\mu_3\text{-}N)_4]$ (**4**) and a solution of $C_{10}Me_{10}$ (Scheme 2). The reaction was performed at 110 °C to ensure complete reaction of **1** which is poorly soluble in toluene. The presence of 18-crown-6 for stabilizing K^+ is crucial since treatments attempted without this macrocyclic polyether showed no reaction and the starting materials were recovered unaltered. Compound **4** was isolated in 67% yield as a dark purple solid which is only soluble in pyridine and reacts immediately with chloroform- d_1 to give **1** and 18-crown-6 as determined by NMR spectroscopy. The 1H NMR spectrum of **4** in pyridine- d_5 shows one broad signal at $\delta = 9.7$ ($\Delta\nu_{1/2} = 73$ Hz) assignable to the $\eta^5\text{-}C_5Me_5$ groups and a sharp singlet at $\delta = 3.44$ for one 18-crown-6 ligand. The paramagnetic nature with an unpaired electron of **4** was confirmed by an Evans method determination of its magnetic susceptibility ($\mu_{\text{eff}} = 1.80 \mu_B$, 293 K, C_5D_5N solution). Despite several data collections, the poor quality of crystals of **4** grown in pyridine at -35 °C has precluded an accurate determination of the solid-state structure by crystallographic methods, but the formation of well-separated $[K(18\text{-crown-6})(py)_2]^+$ and $[Ti_4(\eta^5\text{-}C_5Me_5)_4(\mu_3\text{-}N)_4]^-$ ions was unambiguously established. While the structural data in the cationic fragment were of low precision due to severe disorder, the cube-type anion shows averaged Ti-N and Ti-Ti separations of 1.936(7) and 2.772(6) Å respectively, which are essentially identical to those found in complex **1**.¹⁰ Most likely, the additional electron is delocalized among the titanium atoms in a fashion similar to those observed in the electronic structure of $[(RCC)Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}NCCR)\}]$ and $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]^-$ derivatives.^{6a,c} Addition of 1 equiv of 2,6-lutidinium trifluoromethanesulfonate ($[LuH]OTf$) to a benzene- d_6 suspension of **4** generated immediately complex **2** as determined by 1H NMR spectroscopy.

In summary, we have shown that hydrogenation of $[Ti(\eta^5\text{-}C_5Me_5)_4(\mu_3\text{-}N)_4]$ (**1**) with NH_3BH_3 in solution gives the paramagnetic imido-nitrido complex $[Ti(\eta^5\text{-}C_5Me_5)_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$. Since **1** does not react with H_2 or NH_3BH_3 at room temperature, the hydrogenation process appears to involve the formation of the ion pair $[BH_2(NH_3)_2]^+[BH_4]^-$ (DADB) by isomerization of ammonia borane in solution at higher temperatures. Thus, DADB could act as source of both a single proton and a single electron to **1** as shown in the stepwise proton and electron transfers with HOTf and $[K(C_5Me_5)]$. We are currently investigating the reactivity of **1** and other nitrido complexes with ammonia borane in different molar ratios.

ASSOCIATED CONTENT

Supporting Information

Experimental details and full characterization data for complexes **2-4**. IR spectra of complexes **1** and **2**, and crystallographic data of compounds **1-3**. X-ray crystallographic files in CIF format for complexes **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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- (10) For an appropriate comparison between the crystal structures, we have collected X-ray data for **1** at 200 K (see Supporting Information). The averaged lengths and angles of the structure of **1** determined at this temperature are virtually identical to those obtained at 295 K (see ref 7).
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SYNOPSIS TOC. Hydrogenation of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ with NH_3BH_3 leads to the paramagnetic imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_3(\mu_3\text{-NH})]$ which can also be obtained through stepwise protonation at one nitrido ligand and one-electron reduction of a titanium atom.

