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Partial Hydrogenation of a Tetranuclear Titanium Nitrido Complex with Ammonia Borane

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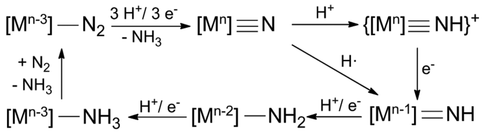
Supporting Information

ABSTRACT: The treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ with NH_3BH_3 leads to the paramagnetic imidonitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$, which can also be obtained by stepwise proton and electron transfer with HOTf and $[K(C_5Me_5)]$.

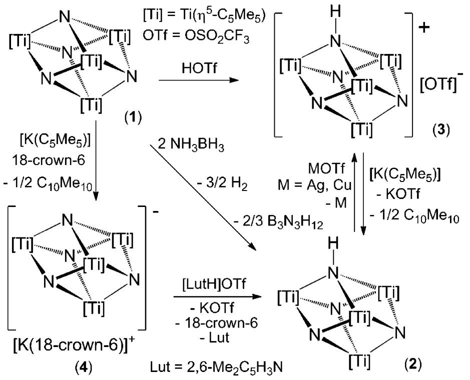
There is tremendous interest in the development of molecular systems capable of performing the catalytic conversion of N_2 to NH_3 under mild conditions.[1] Nowadays, only three examples of molecular catalysis for N_2 reduction to ammonia in solution are known.[2] The methodology in those catalytic systems involves the addition of a 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 transfer 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 $[M^n]{\equiv}N$ intermediate along with the release of the first 1 equiv of ammonia. A second 1 equiv of ammonia is produced by further protonation and reduction processes on the nitrido complex. To reach 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 $[M^n]{\equiv}N$ undergoes the addition of a single proton and a single electron to form a reduced imido derivative $[M^{n-1}]{=}NH$, 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 only been reported by Smith and co-workers.[5]

Scheme 1. Catalytic Cycle[3] for the Reduction of N_2 to NH_3



As part of a project devoted to developing new reactivity patterns of polynuclear nitrido complexes,[6] we were interested in studying the hydrogenation of the tetranuclear titanium(IV) nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**1**). Compound **1** was prepared by ammonolysis of $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$,[7] but related polynuclear titanium derivatives have been recently obtained by the direct reaction of $[Ti(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)_3]$ with H_2/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 imidonitrido cluster $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$ (**2**). In recent years, ammonia borane (NH_3BH_3) has attracted increasing attention mainly because of its potential use as a 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 1



The treatment of **1** with 2 equiv of NH_3BH_3 in tetrahydrofuran (THF) 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 THF at room temperature. However, complex **2** shows an enhanced solubility in those solvents at higher temperatures, and through slow cooling of a heated toluene solution at 90 °C, suitable single crystals for X-ray crystal structure determination were obtained. The solid-state structure of **2** shows an almost perfect $[Ti_4N_4]$ cube core (Figure 1), with the Ti−N−Ti and N−Ti−N angles very close to 90°, in

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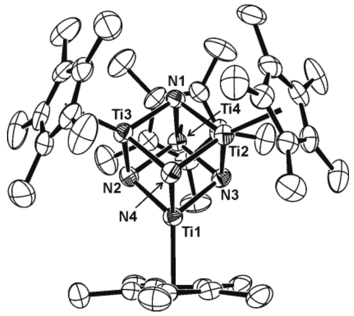

Figure 1. Perspective view of complex **2** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected average lengths (Å) and angles (deg): Ti−N 1.963(8), Ti···Ti 2.836(8); N−Ti−N 87.4(2), Ti−N−Ti 92.5(4).

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 the occupancy for each position. Thus, all Ti−N and Ti−Ti distances are within the narrow ranges of 1.948(4)−1.978(4) and 2.828(1)−2.846(1) Å, respectively. However, the average Ti−N [1.963(8) Å] and Ti−Ti [2.836(8) Å] separations in **2** are slightly longer than those found in **1**, 1.938(7) and 2.783(2) Å.[10]

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 ^{1}H NMR spectrum of complex **2** in chloroform-d_1 shows two far-downfield and broad resonances in a 1:3 ratio at δ 10.0 ($\Delta\nu_{1/2}$ = 45 Hz) and 8.7 ($\Delta\nu_{1/2}$ = 33 Hz) attributable to the η^5-C_5Me_5 ligands. We have recently found analogous resonance signals in the ^{1}H NMR spectra of paramagnetic titanium−yttrium cube-type species generated by one-electron reduction of the complex $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ with $[K(C_5Me_5)]$.[6c] Density functional theory 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 (μ_{eff} = 1.70 μ_B, 293 K, $CDCl_3$ 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 ^{1}H 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 NH_3BH_3 in THF-d_8 was monitored by ^{1}H and ^{11}B 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 ^{11}B NMR spectrum of the resultant solution revealed one triplet resonance [δ −10.5; ^1J(B,H) = 102 Hz] assigned to cyclotriborazane (CTB; $[NH_2BH_2]_3$), along with minor resonance signals for borazine and polyborazylene.[11] The ^{1}H NMR spectrum showed the formation of molecular H_2 in solution (δ 4.54) along with two broad resonances in a 1:3 ratio at δ 9.9 ($\Delta\nu_{1/2}$ = 48 Hz) and 8.6 ($\Delta\nu_{1/2}$ = 34 Hz) assignable to the η^5-C_5Me_5 groups of the paramagnetic complex **2**. However, complex **1** in benzene-d_6 did not react under a H_2 atmosphere at temperatures up to 120 °C and remained unaltered in its treatment with *N,N*-dimethylamineborane ($NHMe_2BH_3$), which decomposed at 85 °C with the formation of molecular H_2 and the cyclodiborazane $[NMe_2BH_2]_2$.[12] Interestingly, by using in situ multinuclear NMR spectroscopic studies, Shaw and co-workers have shown evidence for the formation of diammoniate of diborane, $[BH_2(NH_3)_2]^+[BH_4]^-$ (DADB), in glyme solutions of NH_3BH_3 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 stepwise proton and electron transfer on **1** with separate acids and reducing agents.

The treatment of **1** with 1 equiv of triflic acid (HOTf) in toluene at room temperature led to the precipitation of the diamagnetic ionic derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)][OTf]$ (**3**; Scheme 2). Compound **3** was isolated in 78% yield as a red solid, which is poorly soluble in hydrocarbon solvents but exhibits good solubility and stability in halogenated solvents. Crystals of $\mathbf{3}\cdot 3C_6H_5F$ were grown by diffusion of hexane into a fluorobenzene solution of this compound. The solid-state structure contains a cationic fragment with a $[Ti_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$ cube-type core associated with 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 a 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 Ti−N and Ti−Ti distances of the $\{Ti_3(\mu_3\text{-}NH)\}$ fragment compared with the Ti−N and Ti−Ti separations of the $\{Ti_3(\mu_3\text{-}N)\}$ units [average 1.937(11) and 2.787(5) Å]. An analogous lengthening of those distances has been found in the $\{Ti_3(\mu_4\text{-}N)MX\}$ fragments of the Lewis acid−base adducts $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_{4-n}\{(\mu_4\text{-}N)MX\}_n]$ 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 of 1285−1032 cm^{-1} for the triflate group.[13] In particular, the $\nu_{as}(SO_3)$ 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 ^{1}H NMR spectrum of **3** in chloroform-d_1 at room temperature reveals a broad resonance signal at δ 13.32 for the NH group and two singlets in a 3:1 ratio for the C_5Me_5 ligands in accordance with a C_{3v}-symmetric structure in solution.

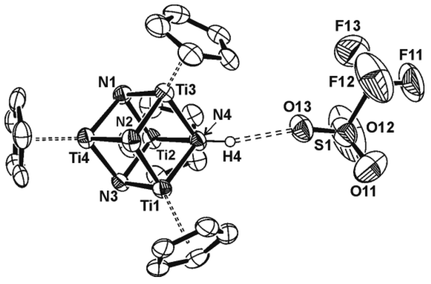

Figure 2. Perspective view of complex **3** (thermal ellipsoids at the 50% probability level). Methyl groups of the η^5-C_5Me_5 ligands are omitted for clarity. Selected average lengths (Å) and angles (deg): Ti−N(4) 2.044(5), Ti−N 1.937(11), Ti(4)···Ti 2.787(5), Ti···Ti 2.875(1); Ti−N(4)−Ti 89.4(1), Ti−N−Ti 91.3(1)−96.7(1), N−Ti−N 87.6(6).

The ionic compound **3** reacted with 1 equiv of $[K(C_5Me_5)]$ 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 a subsequent workup were performed within 15 min. The reaction of **3** with 1 equiv of $[K(C_5Me_5)]$ in benzene-d_6 at room temperature was monitored by ^{1}H NMR spectroscopy. Immediately, the initial red suspension turned dark blue, and spectra taken after 10 min showed resonance signals for $C_{10}Me_{10}$

and the two minor far-downfield and broad resonances mentioned above for the η^5-C_5Me_5 ligands of complex **2**. The exclusive formation of $C_{10}Me_{10}$ as an organic byproduct, which is formed via the coupling of pentamethylcyclopentadienyl radicals,[14,6c] suggests that the reaction pathway for the synthesis of **2** consists of 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 in the NMR tubes.

The 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 because 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 δ 9.7 ($\Delta\nu_{1/2}$ = 73 Hz) assignable to the η^5-C_5Me_5 groups and a sharp singlet at δ 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 (μ_{eff} = 1.80 μ_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 average Ti−N and Ti−Ti separations of 1.936(7) and 2.772(6) Å, respectively, which are essentially identical with 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 structures 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] The addition of 1 equiv of 2,6-lutidinium trifluoromethanesulfonate ([LutH]OTf) to a benzene-d_6 suspension of **4** immediately generated complex **2**, as determined by ^1H NMR spectroscopy.

In summary, we have shown that hydrogenation of **1** with NH_3BH_3 in solution gives the paramagnetic imidonitrido complex **2**. Because **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 DADB by isomerization of ammonia borane in solution at higher temperatures. Thus, DADB could act as the source of both a single proton and a single electron to **1**, as shown in the stepwise proton and electron transfer 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 for complexes **2**−**4**, IR spectra of **1** and **2**, crystallographic data of compounds **1**−**3**, and 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 interest.

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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 the Supporting Information). The average lengths and angles of the structure of **1** determined at this temperature are virtually identical with those obtained at 295 K (see ref 7).

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