Dinitrogen Cleavage

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Titanium-Promoted Dinitrogen Cleavage, Partial Hydrogenation, and Silylation**

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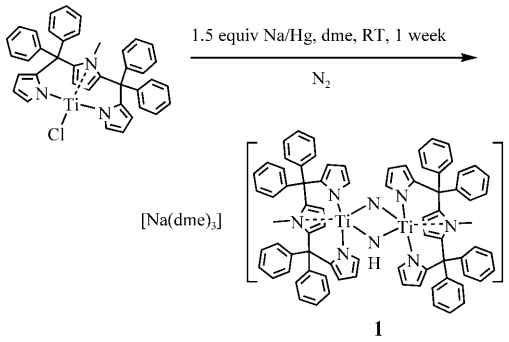
During the last decade, the chemistry of dinitrogen has experienced most spectacular progress in terms of activation,[1] transformation,[2] reduction,[1e,h,2a,e,f,3] and incorporation into molecular frames.[4] The series of steps through which this exceedingly stable molecule may be cleaved and protonated is now well established, having been elegantly demonstrated by the rational design of a catalytic cycle of reduction and hydrogenation.[1f,5a,b] The cleavage of N_2 to nitrides, as achieved with strongly reducing low-valent metals, is also documented.[1g,h,l,2q,6] Hydrogenation, as occurring during either the partial or complete cleavage, has been achieved in three conceptually different manners. The first is the direct protonation of the nitride during hydrolysis or protonolysis.[1b,f,h,j,l,2a–n,o,5] The second consists of the direct reaction of reduced forms of coordinated dinitrogen with hydrogen gas.[1c,e,t,2e,o,3a,7] The third is the attack of hydrides.[6b,8]

While attempting the synthesis of low-valent synthons of thorium (an element that has been reduced in only two instances),[9] a Th–NH_2 unit was serendipitously obtained.[10] Isotopic labeling studies clearly indicated that the nitrogen atom was derived from N_2, while the hydrogen atoms could in that case only be furnished by the solvent. In other words, by funneling electrons onto an element that is hard to reduce, it was possible not only to cleave dinitrogen but also to enable radical behavior of reduced fragments to extract hydrogen atoms from the solvent. Elements of the f-block series are versatile for this purpose, as most of the reactivity of reduced species may in fact be rationalized in terms of radical behavior.[6g,11]

The use of ligand systems containing either non-coordinated or weakly bonded π systems has been recently shown to be a viable strategy for augmenting the radical behavior of transition-metal complexes. In some instances, these ligands may act as electron storage units effectively permitting dinitrogen partial reduction,[12] cleavage, and even partial hydrogenation.[6b] We have therefore designed a ligand system based on pyrrolide anions containing an additional hemilabile π unit.[6c] In fact, the pyrrolide anions are isoelectronic with the cyclopentadienyl anions that have produced a number of dinitrogen complexes,[1c,d,e,h,m,l,p,13] including examples that facilitate dinitrogen reduction.[1c,d,e,h,m,l,p] By reducing a trivalent titanium complex of the 2,5-$\{(C_4H_3N)CPh_2\}_2C_4H_2N(Me)$ dianion, we recently obtained a toluene mixed-valence complex with inverted sandwich structure, which is an example of olefin coordination.[14] We find it puzzling that these clear signs of high reactivity were not accompanied by any apparent interaction with dinitrogen. By performing a reduction under nitrogen in dme instead of toluene and using a milder reducing agent, we have now obtained dinitrogen cleavage along with partial hydrogenation.

The reduction of the trivalent LTiCl (L = 2,5-$\{(C_4H_3N)CPh_2\}_2C_4H_2N(Me)$) complex[14] with the relatively mild reductant Na/Hg (1.5 equiv) in dme afforded a dark green solution. Crystallization yielded the dinuclear and diamagnetic complex $[Na(dme)_3][(LTi)_2(\mu\text{-}NH)(\mu\text{-}N)]$ (**1**) as pale green crystals (Scheme 1). The yield of the isolated product was improved to 25% if crystallization was carried out in thf after evaporation of dme. Surprisingly, identical reaction in thf afforded intractable materials from which only $[Na(dme)_3]_2[\{LNa\}_2]$ was isolated in crystalline form.[20]



Scheme 1.

By doubling the amount of Na/Hg or even using a larger excess, the diamagnetic complex $[Na(dme)_3]_4[\{LNa\}_2][(LTi)_2(\mu\text{-}N)_2]\cdot 2\,dme$ (**2**) was obtained (Scheme 2). Attempts to solubilize **2** in thf or dme for NMR spectroscopic characterization gave deposition of the insoluble $[Na(dme)_3]_2[(LTi)_2(\mu\text{-}N)_2]$ (**3**), while $[Na(dme)_3]_2[\{LNa\}_2]$ was retained in solution and subsequently crystallized.[20]

The connectivities of **1** and **2** were revealed by X-ray crystal structures (Figures 1 and 2). Complex **1** shows the monoanionic dimetallic unit as consisting of two identical [LTi] moieties bridged by one nitride and one NH unit

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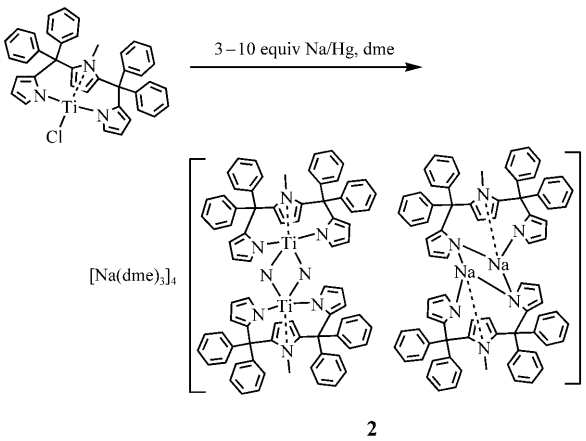


Scheme 2.

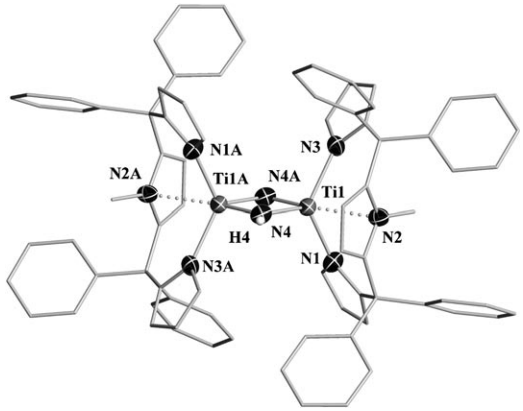


Figure 1. Thermal ellipsoid plot of the anion of **1** with selected ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Ti1···Ti1A 2.786(6), Ti1–N4A 1.837(6), Ti1–N4 1.878(7), Ti1–N1 2.112(6), Ti1–N3 2.118(6), Ti1–N2 2.582(7); N4A-Ti1-N4 82.8(2), N4A-Ti1-N1 97.2(2), N4-Ti1-N1 117.49(17), N4A-Ti1-N3 96.5(2), N4-Ti1-N3 118.3(2), N1-Ti1-N3 123.7(2), N4A-Ti1-N2 166.22(16), N4-Ti1-N2 110.95(18), N1-Ti1-N2 77.1(2), N3-Ti1-N2 76.9(2), Ti1A-N4-Ti1 97.2(2).[24]

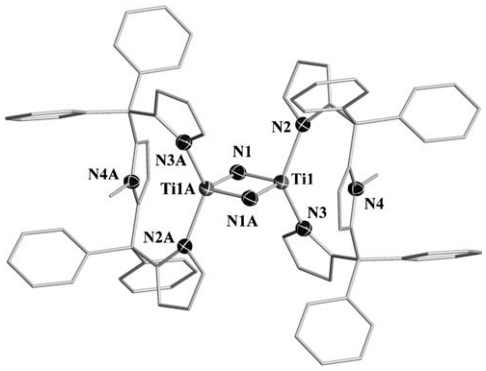


Figure 2. Thermal ellipsoid plot of **2** with selected ellipsoids drawn at 50% probability. Four [Na(dme)$_3$] cations and two [LNa] anions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1···Ti1A 2.642(2), N1···N1A 2.478(5), Ti1–N1 1.812(3), Ti1–N1A 1.810(3), Ti1–N3 2.150(3), Ti1–N2 2.157(3), N1-Ti1-N3 98.76(14), N1A-Ti1-N2 116.02(14), N1-Ti1-N2 99.21(13), N3-Ti1-N2 127.91(12).[24]

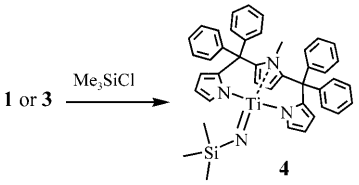
forming a planar Ti_2N_2 core. Identification of the two bridging atoms as nitrogen was initially suggested by the successful refinement of the crystallographic thermal parameters and analytical data. The identification of these bridging atoms as well as confirmation of the presence of one hydrogen atom was confirmed by NMR and IR spectroscopy, mass spectrometry, and chemical degradation, including that of the ^{15}N-labeled derivative. Complex **1** is diamagnetic, as expected for the proposed tetravalent titanium formulation. ^1H and ^{13}C NMR spectra showed the two expected sets of resonances for two magnetically non-equivalent ligands. One resonance, integrating for only one hydrogen atom per dimeric unit at $\delta = 13.11$ ppm, was not coupled to any carbon atoms, thus giving the first indication of the presence of an N–H function. To conclusively confirm the formulation, identical preparation was carried out under $^{15}N_2$ atmosphere. A crystalline product obtained in this manner, with identical cell parameters as **1**, was subjected to chemical degradation with HCl and subsequent precipitation with $NaBPh_4$ to confirm, with the formation of $^{15}NH_4BPh_4$, both the identity of the bridging atoms as nitrogen and their origin from atmospheric dinitrogen. Furthermore, the NMR spectra of the isotopically labeled compound were identical to those of **1**, except for the NH resonance at $\delta = 13.11$ ppm, which showed the doublet expected for coupling with the ^{15}N nucleus ($J(^{15}N\text{-}^1H) = 67$ Hz). In turn, the ^{15}N NMR spectrum showed two distinct resonances at $\delta = 542.0$ for Ti(μ-N)Ti and $\delta = 132.2$ ppm for Ti(μ-NH)Ti. The second resonance was particularly broad and could not be resolved into the expected doublet. It was confirmed to be coupled to the corresponding H atom at $\delta = 13.11$ ppm in the ^{15}N DEPT90 and ^1H-^{15}N HMQC spectra. The N–H stretch was also visible in the IR spectrum at 3373 cm^{-1} and shifted to 3337 cm^{-1} in the isotopically labeled sample.

The structure of **2** showed instead two separate dianionic $[\{LNa\}_2]^{2-}$ and $[\{(LTi)(\mu\text{-}N)\}_2]^{2-}$ moieties counterbalanced by four dme-solvated sodium cations. The Ti···Ti distances are substantially different in the two complexes (2.786(6) and 2.642(2) Å for **1** and **2**, respectively). A smaller and yet visible difference may be also observed among the Ti–N separations (1.837(6) and 1.878(7) Å in **1** and 1.812(3) Å for **2**). These distances compare well with those of Ti-(μ-$NR)_2$-Ti (1.830–1.997 Å, R = Me, *t*Bu, $SiMe_3$, Ph, etc.)[15] and are shorter than in cluster complexes containing the Ti-(μ-NH)-Ti moiety (1.94(2)–1.97(1) Å)[16] and bridging nitride (1.958(5)–1.993(4) Å).[17]

Complex **2** decomposes upon solubilization with deposition of **3**, thus preventing NMR spectroscopic characterization. Satisfactory elemental analysis data and ESI mass spectra were obtained in agreement with the proposed formulation. In addition, chemical degradation of a ^{15}N-enriched sample, carried out as in the case of **1** with HCl and subsequent precipitation with $NaBPh_4$, gave $^{15}NH_4BPh_4$. In turn, this result confirmed the identity and the origin of the bridging nitrides from gaseous nitrogen even in this case. The IR spectrum confirmed the absence of NH functions, which was also indicated by the diamagnetism of this compound. Complex **3** instead is sparingly soluble in thf, and a meaningful ^1H NMR spectrum could be obtained only upon partial

removal of $[Na(dme)_3]_2[\{LNa\}_2]$. Suitable crystals of **3** could not be grown.

Compounds **1** and **3**[22] are unreactive with MeI at room temperature but readily react with Me_3SiCl in thf to form NaCl and a yellow solution. Crystallization from toluene afforded yellow crystalline $LTiNSiMe_3$ (**4**) (Scheme 3).



Scheme 3.

The connectivity of **4** was revealed by an X-ray crystal structure (Figure 3), which shows the presence of a bent $TiNSiMe_3$ imido moiety. The Ti–N bond length (1.697(3) Å) is in the expected range.[18,19] The ^{1}H NMR spectrum of **4** is in

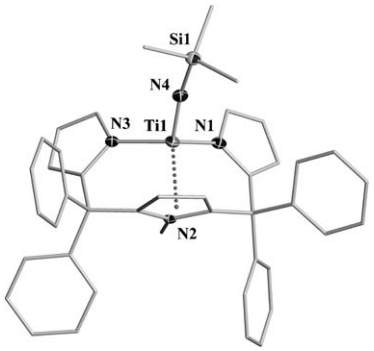
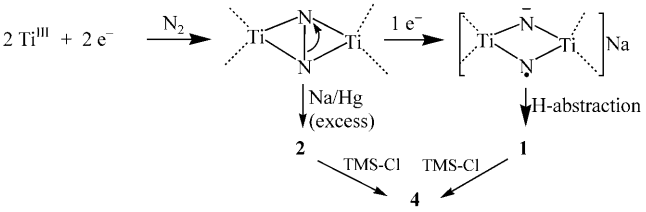


Figure 3. Thermal ellipsoid plot of **4** with selected ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.043(4), Ti1–N2 2.400(3), Ti1–N3 2.047(3), Ti1–N4 1.697(3), Si1–N4 1.733(4); N4-Ti1-N1 108.14(15), N4-Ti1-N3 110.69(15), N1-Ti1-N3 108.95(14), Ti1-N4-Si1 165.5(2).[24]

agreement with the established structure, showing the ligand and $SiMe_3$ group resonances in the normal positions. The ^{29}Si NMR spectrum shows a resonance at 17.12 ppm, while the ^{15}N–^{1}H HSQC NMR spectrum clearly shows the coupling of the Me_3Si methyl groups to a ^{15}N resonance at $\delta =$ 136.8 ppm.

The reactions forming **1** and **2** must be carried out exclusively in dme, as identical reactions in thf led to intractable mixtures from which only $[Na(dme)_3]_2[\{LNa\}_2]$[20] could be isolated. The formation of **1** required a careful control of the Ti/Na stoichiometric ratio. The oxidation of the two starting trivalent Ti centers, in combination with two additional electrons provided by the Na/Hg reductant, would initially lead to a neutral tetravalent side-on hydrazido complex in line with the reactive species isolated by Chirik,[1d] Fryzuk,[1c] and Sita[2f] with Group 4 elements (Scheme 4, TMS = Me_3Si). For **1** to be formed, it must be assumed that a simple one-electron attack on such an intermediate may



Scheme 4.

cleave the residual N–N single bond to generate one nitride (hence the necessity for the Na counteraction) and one nitrogen radical. As ethers are known to be attacked by radicals or by species with radical-type behavior affording a variety of fragmentation patterns,[21] it is conceivable that simple hydrogen-atom abstraction may readily form the final compound. However, it is also possible that the hydrogen atom has been provided by the ligand system of another molecule at the expense of the reaction yield. While a similar process has been observed during the reduction of thorium,[10] the origin of the proton from the solvent cannot be conclusively substantiated by isotope labeling experiments, given the stringent solvent requirement of the reaction. The formation of **2** is a more straightforward process. It is the typical six-electron reduction with two electrons provided by the two trivalent Ti atoms and the rest from Na/Hg. This transformation, however, has only one precedent in the chemistry of Ti,[4b] in which the reactive intermediate bis(nitride) moieties further reacted with the donor atoms of the ligand. Possible involvement of nitride was also claimed in the reduction of titanocene to form ammonia.[23] The cocrystallization with $[Na(dme)_3]_2[\{LNa\}_2]$ observed in **2** seems to indicate the presence even in dme of a degradation pattern similar to that occurring more extensively during reactions in thf.

The silylation of the nitride of **2** and **3** is rather straightforward, and it proceeds with elimination of NaCl and $[\{LNa\}_2]$ (for **2**). In the case of **1**, it is tempting to suggest that a $[LTiCl(NHSiMe_3)]$ compound may be the byproduct of this transformation, but at this stage we could not find conclusive evidence for it. Formation of imide species from dinitrogen has been observed only in the partial silylation of a tantalum nitride derivative[2e] performed by $PhSiH_3$ and in the Mo=NH unit, as detected in the catalytic cycle described by Schrock and co-workers.[5]

In conclusion, we have reported herein that five-electron reduction of dinitrogen may lead to nitride species displaying radical behavior and capable of abstracting hydrogen atoms from the reaction environment. Six-electron reduction instead afforded a standard bis(nitride) complex. The nucleophilic behavior of the nitride has enabled functionalization to a monomeric imido function.

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[20] Cell parameters of $[Na(dme)_3]_2[\{LNa\}_2]$: Monoclinic, *P*21/*c*, $a = 13.185(3)$ Å, $b = 26.470(5)$ Å, $c = 15.240(2)$ Å, $\beta = 116.074(14)°$, $V = 4777.5(15)$ Å^3, G. B. Nikiforov, S. Gambarotta, unpublished results.

[21] See for example: A. Arunachalampillai, P. Crewdson, I. Korobkov, S. Gambarotta, *Organometallics* **2006**, *25*, 3856, and references therein.

[22] Compound **4** may also be obtained from **3** using a similar experimental procedure.

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[24] CCDC 717594, 736290, and 736291 for **1**, **2**, and **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

