

Ammonolysis of Mono(pentamethylcyclopentadienyl) Titanium(IV) Derivatives[§]

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Ammonolyses of mono(pentamethylcyclopentadienyl) titanium(IV) derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3]$ ($\text{X} = \text{NMe}_2$, Me, Cl) have been carried out in solution to give polynuclear nitrido complexes. Reaction of the tris(dimethylamido) derivative $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$ with excess of ammonia at 80–100 °C gives the cubane complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_4(\mu_3\text{-N})_4\}]$ (**1**). Treatment of the trimethyl derivative $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Me}]$ with NH_3 at room temperature leads to the trinuclear imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**2**) via the intermediate $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-NH})\}_2]$ (**3**). The analogous reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Me}]$ with 2,4,6-trimethylaniline (ArNH_2) gives the dinuclear imido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-NH})\}_2]$ (**4**) which reacts with ammonia to afford $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NH}_2)\}_2(\mu\text{-NAr})_2]$ (**5**). Complex **2** has been used, by treatments with the tris(dimethylamido) derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5\text{-}n\text{R}_n)(\text{NMe}_2)_3]$, as precursor of the cubane nitrido systems $[\{\text{Ti}_4(\eta^5\text{-C}_5\text{Me}_5)_3(\eta^5\text{-C}_5\text{H}_5\text{-}n\text{R}_n)(\mu_3\text{-N})_4\}]$ [$\text{R} = \text{Me}$ $n = 5$ (**1**), $\text{R} = \text{H}$ $n = 0$ (**6**), $\text{R} = \text{SiMe}_3$ $n = 1$ (**7**), $\text{R} = \text{Me}$ $n = 1$ (**8**)] via dimethylamine elimination. Reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3]$ or $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_2\text{Cl}_2]$ with excess of ammonia at room temperature gives the dinuclear complex $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)(\mu\text{-N})\}]$ (**9**) where an intramolecular hydrogen bonding and a nonlinear nitrido ligand bridge the “ $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}(\text{NH}_3)$ ” and “ $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2$ ” moieties. The molecular structures of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-NAr})_2]$ (**4**) and $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)(\mu\text{-N})\}]$ (**9**) have been determined by X-ray crystallographic studies. Density functional theory calculations also have been conducted on complex **9** to confirm the existence of an intramolecular $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bond and to evaluate different aspects of its molecular disposition.

Introduction

Tremendous interest exists in the use of chemical processing routes to ceramics.^{1–5} Traditional synthetic methods to refractory metal nitrides involve high-temperature combinations of the elements or treatment of anhydrous metal halides with ammonia. Recent synthetic strategies to new and existing metal nitrides involve the use of molecular precursors, which reduce the energy requirements to produce the desired materials. For instance, titanium nitride [TiN] is a refractory, gold-colored material that has been used in several industrial applications because of its important properties, including extreme hardness, excellent chemical resistance, desirable optical properties, and good electrical conductivity.⁶ These characteristics have motivated its use as coatings in several technological applications. Thin

films of [TiN] have been prepared with chemical vapor deposition (CVD) techniques involving a variety of precursors, especially amido complexes.^{7–9} The presence of ammonia is crucial to the growth of pure [TiN] in order to remove significant amounts of carbon from the precursors.

In this context, it is important to understand the reaction mechanism of metal amido and halide compounds with ammonia.^{10,11} Gas-phase studies on the reaction of $[\text{Ti}(\text{NR}_2)_4]$ and NH_3 provided mechanistic insight, suggesting transamination reactions as the rate-limiting step in the deposition of TiN.^{7–9,12} Intermediates involving amido NH_2 and imido NH groups have been postulated in those processes. Often references to solution-chemistry studies are used to understand the intermediate stages and to explain spectroscopic data obtained in the gas phase.^{7–9,13–15} The reactivity of amido complexes with second-

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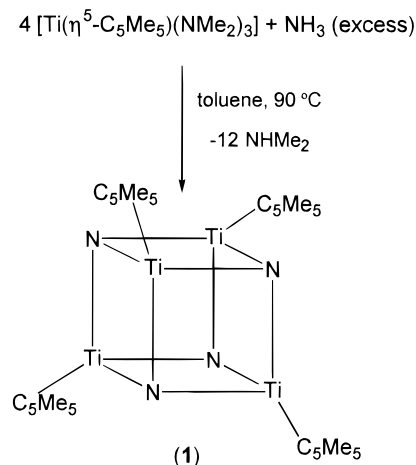
ary and primary amines has been studied extensively in solution,^{16–18} but analogous reactions with ammonia have received little attention. Brown and Maya¹⁹ studied the reaction between $[\text{Ti}(\text{NMe}_2)_4]$ and liquid ammonia to produce an insoluble polymeric material formulated as $[\text{Ti}_3(\text{NMe}_2)(\text{NH}_2)_2(\text{N})_3]$ on the basis of analytical and IR data. Thermolysis of this material yielded bulk titanium nitride at 800 °C. More recently, Chisholm and co-workers reported the treatment of $[\text{Ti}(\text{NRR}')_4]$ with NH_3 in hydrocarbon solvents to give insoluble precipitates which yielded titanium nitride upon heating.²⁰

Several polynuclear early transition metal nitrido complexes have been obtained in the solution ammonolysis of organometallic derivatives^{21–27} and the structural characterization revealed the presence of nitrido (N^{3-}), imido (NH^{2-}), and amido (NH_2^{1-}) ligands bridging the metal centers. The solubility and stability of this group of titanium,²² zirconium,^{23,24} and tantalum^{25–27} compounds arise from the bulky ancillary ligands (cyclopentadienyl, alkoxido, etc.) at the metal centers. In particular, the ability of cyclopentadienyl groups to support metallonitrido oligomers has been proved in Ta ^{28,29} and V ^{30,31} compounds prepared by distinct routes. We have previously communicated the synthesis and structural characterization of the first organometallic nitrido cubane $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ by treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$ with NH_3 .³² Herein we report the solution treatment with ammonia of amido, alkyl, and chlorocomplexes of titanium containing the pentamethylcyclopentadienyl ligand. Several polynuclear nitrido derivatives have been characterized in these processes, and interesting spectroscopic and structural data are offered. Density functional theory (DFT) calculations on the complex $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**) were performed to confirm the intramolecular $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bond and to explain the geometrical features found in the crystal structure determination.

Results and Discussion

Treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$ with excess of ammonia in hexane, toluene, or tetrahydrofuran (THF) at 80–100 °C afforded $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ (**1**) as a dark green crystalline solid (Scheme 1). We have previously communicated the cubane structure for **1** and established the geometrical relationship between the Ti_4N_4 core of this complex and the rock-salt

Scheme 1. Ammonolysis of the Complex $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$



structure of cubic TiN .³² More recently, Bottomley and co-workers described the preparation of a vanadium nitrido cluster $[\{\text{V}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ with a very similar structure.³¹

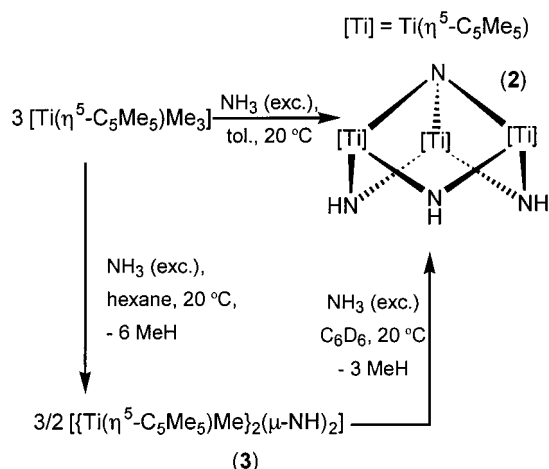
Attempts to detect or isolate any intermediate in the formation of **1** failed. A NMR tube experiment of a sample of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$ in benzene- d_6 sealed under NH_3 atmosphere was monitored by ^1H NMR spectroscopy. At temperatures close to 55 °C resonances for NHMe_2 clearly appeared as the only new species present in solution. Compound **1** exhibits good solubility in chloroform and very poor solubility in other common solvents. Solutions of **1** in chloroform- d_1 remain unaltered under argon atmosphere for long periods even after heating at 100 °C for several days. Nevertheless, it is very sensitive to hydrolysis in solid state and solution to give the oxoderivative $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu\text{-O})_6]$.^{33,34}

The ^{15}N NMR spectrum of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-}^{15}\text{N})_4]$ (**1**- ^{15}N) showed a singlet at 500.6 ppm (CH_3NO_2 used as external reference). To our knowledge, this shift is unusual in the literature for organometallic or inorganic diamagnetic compounds.^{21–27,35–37} We recently reported that the methylidyne groups of the isoelectronic complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-CH})_4]$ appear at very low field in ^{13}C NMR spectroscopy ($\delta = 490.8$ ppm).³⁸ The strong deshielding in both cases is evident and consistent with the parallelism proposed in the literature between ^{15}N and ^{13}C chemical shifts.³⁹

We next sought to study the similar reaction of complex $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with NH_3 (Scheme 2). Treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with excess of ammonia in toluene at room temperature gave $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**2**) as a yellow solid. Heating of the reaction mixture at 150 °C did not lead to a different result, and only compound **2** was isolated. Furthermore, a benzene- d_6 solution of **2** heated at 200 °C did not show any detectable change in the ^1H NMR spectrum. This

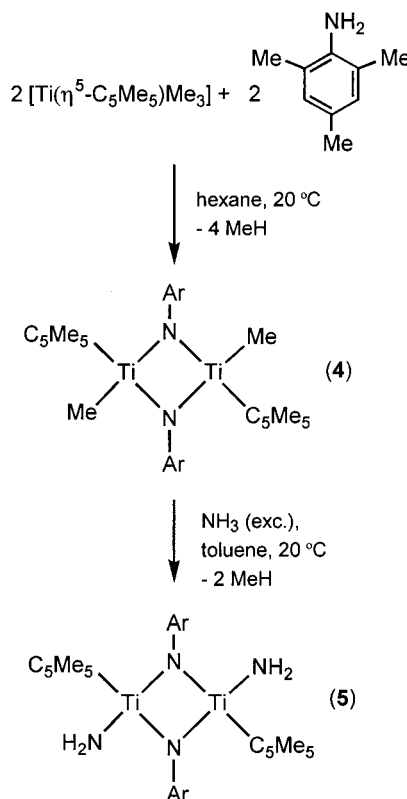
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Scheme 2. Ammonolysis of the Complex $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ 

complex has been previously prepared and characterized by Roesky and co-workers.²² However, to compare it with other complexes, we report its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR in C_6D_6 , mass spectra (EI), and full-detailed IR data (see the Experimental Section). The ^{15}N NMR spectrum reported for **2** was a doublet ($^1J_{\text{N-H}} = 63.5$ Hz) at 90.7 ppm corresponding to the three $\mu\text{-NH}$ groups.²² In addition to this resonance, analysis of a sample prepared with isotopically enriched NH_3 (10% ^{15}N) revealed a singlet at 461.9 ppm assignable to the nitrido which bridges the three titanium centers. The chemical shift for the nitrido groups in the ^{15}N NMR spectra of **1** (500.6 ppm) and **2** (461.9 ppm) are rare in the literature and could offer insight in other studies. For example, the magic-angle spinning (MAS) ^{15}N solid-state NMR spectrum of $[\{\text{Ta}(\text{CH}_2\text{tBu})_2(\text{N})\}_5]$ revealed resonances at $\delta = 406$ and 397 which were not assigned by the authors.²⁷

Complex **2** was initially prepared in hexane.²² Nevertheless, reactions run in this solvent without any magnetic stirring lead to the precipitation of orange crystals from the solution. The composition of these crystals as $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}\}_2(\mu\text{-NH})_2]$ (**3**) was established by spectroscopic and analytical data. The mass spectrum was consistent with a dimeric formulation for **3**, in good agreement to the well-known tendency of titanium imido complexes.^{16–18,40–52} The IR spectrum shows one ν_{NH} absorption at 3349 cm^{-1} , in a range similar to that found in **2**

Scheme 3. Reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with 2,4,6-Trimethylaniline

(KBr, 3352 cm^{-1}). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra reveal a symmetric arrangement for both the terminal methyl and pentamethylcyclopentadienyl ligands with respect to the central $\text{Ti}_2(\mu\text{-NH})_2$ core, showing also a broad signal at $\delta = 10.90$ for the NH groups in the ^1H NMR spectrum.

Compound **3** is stable in solid state under argon at $-30\text{ }^\circ\text{C}$ for at least several months, but it decomposes in a few hours in hexane, benzene, or toluene solutions to give an unidentified dark solid insoluble in common solvents. When a recently prepared benzene- d_6 solution of **3** was exposed to ammonia, the ^1H NMR showed the quantitative transformation in **2** and concomitant loss of methane within a few minutes. The characterization of complex **3** by ^{15}N NMR spectroscopy was not possible because of its lack of stability. However, the ^1H spectrum from a ^{15}N isotopically enriched sample displays a coupling constant ($^1J_{\text{NH}} = 63.0$ Hz) analogous to that found in **2**. Despite many attempts, suitable single crystals of complex **3** for an X-ray structure determination were not obtained.

The IR spectra recorded in the gas-phase ammonolysis of $[\text{Ti}(\text{NMe}_2)_4]$ showed absorptions assigned to NH_x fragments of oligomeric intermediates with $[\text{Ti}_2(\mu\text{-NH})_2]$ cores.^{7,8} Furthermore, prominent bands in the range $3350\text{--}3190\text{ cm}^{-1}$ have been described for the insoluble precipitates obtained in the analogous solution reaction.^{19,20} It is very likely that species with NH bridging fragments, similar to the existing in complexes **2** and **3**, are formed during the ammonolysis process.

The treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with a primary amine was studied to gain insight into the ammonolysis process and also the structure of **3** (Scheme 3). Reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with 2,4,6-trimethylaniline (NH_2Ar) in hexane at room

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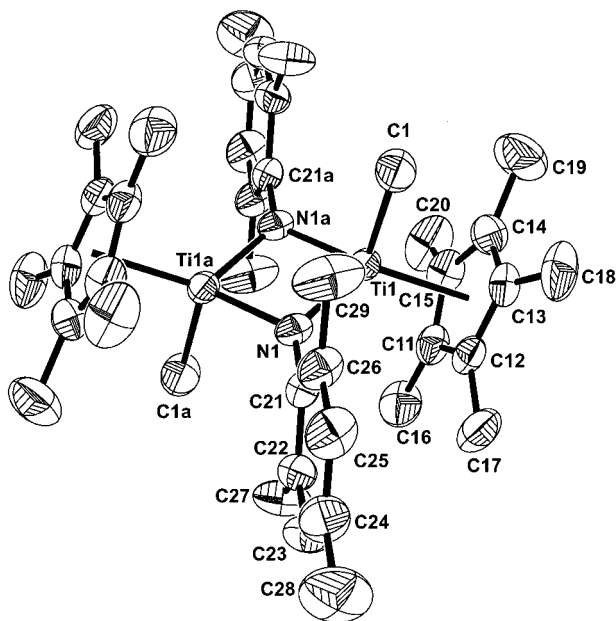


Figure 1. Perspective view of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}\}_2(\mu\text{-NAr})_2]$ (**4**). Thermal ellipsoids correspond to 50% of probability.

Table 1. Selected Lengths (Å) and Angles (deg) for Complex **4**^a

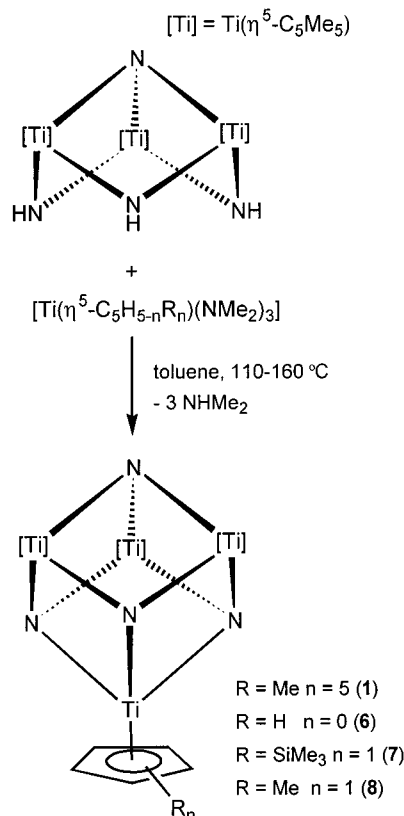
Ti(1)–N(1)	1.946(3)	Ti(1)–N(1)a	1.953(3)
Ti(1)–C(1)	2.129(4)	Ti(1)···Ti(1)a	2.829(1)
N(1)–C(21)	1.422(4)	Ti(1)–C ₅ Me ₅ (1)	2.097
N(1)–Ti(1)–N(1)a	87.0(1)	N(1)–Ti(1)–C(1)	102.8(2)
N(1)a–Ti(1)–C(1)	102.3(1)	C(21)–N(1)–Ti(1)	134.3(2)
C(21)–N(1)–Ti(1)a	132.7(2)	Ti(1)–N(1)–Ti(1)a	93.0(1)
C ₅ Me ₅ (1)–Ti(1)–N(1)	126.9	C ₅ Me ₅ (1)–Ti(1)–C(1)	105.3
C ₅ Me ₅ (1)–Ti(1)–N(1)a	128.3		

^a Symmetry transformations used to generate equivalent atoms: a, $-x, -y, -z + 1$. C₅Me₅ is the centroid of the $\eta^5\text{-C}_5\text{Me}_5$ ligand ring.

temperature gave the dinuclear imido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}\}_2(\mu\text{-NAr})_2]$ (**4**) as a brown precipitate in 40% yield after workup.

The composition of **4** was established by a combination of spectral and analytical data. NMR spectra showed a symmetric structure in solution and the *trans* arrangement of the terminal groups was confirmed by an X-ray crystal structure determination (Figure 1). Selected distances and angles are presented in Table 1. Compound **4** is a dimer, with one pentamethylcyclopentadienyl, one methyl, and one imido ligand per metal atom. The two titanium centers are held together $[\text{Ti1} \cdots \text{Ti1a} = 2.829(1)]$ by the two bridging imido ligands. Each molecule of **4** lies on a crystallographic inversion center and the titanium atoms possess a classical three-legged piano-stool arrangement. The titanium–C₅Me₅(centroid) (2.097 Å) and titanium–carbon–(Me) (2.129(4) Å) bond lengths are in the normal range for this type of complex.^{53–57} Bond lengths and angles associated with the imido linkages $[\text{Ti}(1)\text{--N}(1) 1.946(3), \text{Ti}(1)\text{--N}(1a) 1.953(3) \text{ Å}, \text{Ti}(1)\text{--N}(1)\text{--Ti}(1a) 93.0(1)^\circ]$ are similar to those found in other structurally characterized complexes containing

Scheme 4. Reaction of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**2**) with $[\text{Ti}(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)(\text{NMe}_2)_3]$



an undistorted $\text{Ti}(\mu\text{-NR})_2\text{Ti}$ fragment.^{40,44,45,47,48,52} The geometry at the bridging nitrogen atoms is trigonal planar [sum of angles = $360.0(2)^\circ$] and perpendicular to the Ar imido groups.

Treatment of complex **4** with ammonia in toluene at room temperature afforded the dinuclear imido derivative $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NH}_2)\}_2(\mu\text{-NAr})_2]$ (**5**) as a light brown precipitate in 88% yield. Complex **5** is only soluble in chloroform and can be washed with other solvents without significant waste of product. The IR spectrum shows two bands at 3394 and 3321 cm^{-1} for the NH_2 stretching vibrations and one absorption at 1537 cm^{-1} consistent with an NH_2 bending mode.⁵⁸ The ^1H NMR spectrum manifested the symmetric arrangement of the molecule and also the presence of NH_2 groups affording a broad signal at $\delta = 3.78$ (4H). Complex **5** might be similar to an intermediate “ $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NH}_2)\}_2(\mu\text{-NH})_2]$ ” hypothetically formed in the ammonolysis of **3** to give **2** (Scheme 2).

A striking feature in our ammonolysis studies is the different products, **1** and **2**, obtained under similar conditions from $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_3]$ and $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$. For this reason, the relationship between **1** and **2** has been investigated. We have found that treatment of **2** with proportional amounts (1:1) of tris(dimethylamido) titanium derivatives^{59–61} $[\text{Ti}(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)(\text{NMe}_2)_3]$ in benzene or toluene at 110–160 °C affords the cubane nitrido complexes $[\{\text{Ti}_4(\eta^5\text{-C}_5\text{Me}_5)_3(\text{C}_5\text{H}_{5-n}\text{R}_n)\}(\mu_3\text{-N})_4]$ $[\text{R} = \text{Me } n = 5$ (**1**), $\text{R} = \text{H } n = 0$ (**6**), $\text{R} = \text{SiMe}_3 n = 1$ (**7**), $\text{R} = \text{Me } n = 1$ (**8**)] via dimethylamine elimination. As shown in Scheme 4, these reactions formally represent the addition of

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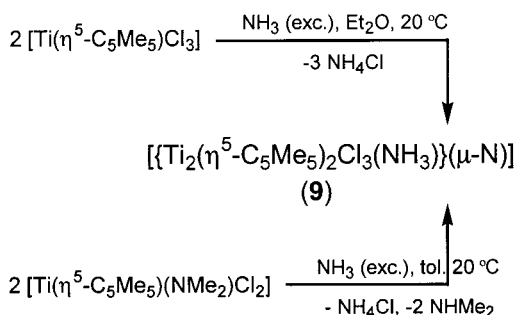
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Scheme 5. Ammonolysis of the Complexes $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_x\text{Cl}_{3-x}]$ 

the fourth metal vertex to the precubane structure complex **2**. We are currently exploring this reaction path with a variety of other metal complexes.

Complexes **6–8** were isolated in 41–51% yields as dark crystalline solids soluble in aromatic and aliphatic solvents. The extreme air sensitivity of these complexes did not allow us to obtain analytically pure samples of **7** and **8**, but spectroscopic data for all the compounds agreed with a cubane nitrido structure similar to that reported for $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-N})_4]$ (**1**).³² IR spectra of the cubane complexes **1** and **6–8** show very strong absorptions in the range 651–644 cm^{-1} , assignable to the titanium–nitrogen bonds. Analogous bands have been reported for amido^{60,62,63} and bridging imido^{64,65} titanium complexes, and even binary nitrides MN_2 .⁶⁶ Very strong bands at 590¹⁹ and 630²⁰ cm^{-1} also have been reported for the insoluble precipitates obtained in the solution ammonolysis of $[\text{Ti}(\text{NMe}_2)_4]$.

It is very interesting to consider the Ti_4N_4 fragment of complexes **1** and **6–8** as building blocks in the gas phase to form a film of titanium nitride on a surface (CVD).⁶⁷ Chen and Castleman⁶⁸ showed the particular stability of clusters $(\text{TiN})_x$ in the gas phase when the clusters corresponded to a piece of the cubic NaCl structure ($x = 2, 3, 4, 6, 9, \dots$, the so-called “magic numbers”). Significantly, the most stable structures of the clusters are cuboids.

We next examined the reaction of the chloroderivatives $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_x\text{Cl}_{3-x}]$ with ammonia (Scheme 5). Treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ with NH_3 in toluene, diethyl ether, or THF at room temperature gave the dinuclear complex $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**) with concomitant ammonium chloride formation. Although the ammonolysis reaction seemed to proceed quantitatively, the presence of NH_4Cl and small amounts of the oxoderivative $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-O})]$ ⁶⁹ complicated the isolation of **9** and only low yields were obtained (25%). Reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)\text{Cl}_2]$ with NH_3 in toluene produces **9** in 40% isolated yield with dimethylamine and ammonium chloride as secondary species. Analogous treatment of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)_2\text{Cl}]$ afforded an intractable mixture of products.

The resultant compound **9** was isolated as an orange solid very soluble in chloroform and dichloromethane but scarcely

soluble in aromatic and aliphatic solvents. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra revealed resonances for two different $(\eta^5\text{-C}_5\text{Me}_5)$ groups and a broad signal at $\delta = 2.70$ (3H) in the proton spectrum assigned to an NH_3 ligand. ^{15}N NMR spectrum showed a singlet at $\delta = 431.6$ for the nitrido ligand and a broad signal at $\delta = -360.8$ for the NH_3 molecule. This chemical shift of the ammonia present in compound **9** is similar to the values found in the complexes $[\text{TiCl}_4(\text{NH}_3)_2]$ (-361.2 ppm),¹¹ and $[\text{Ta}_5(\text{CH}_2\text{-}^t\text{Bu})_{10}(\mu_3\text{-N})_3(\mu\text{-N})_2\text{NH}_3]$ (-360 ppm).²⁶ Mass spectrometry showed the easy elimination of NH_3 from a dinuclear structure. The infrared spectrum presents weak ν_{NH} bands at values (3286, 3227, 3144, and 3040 cm^{-1}) similar to those reported for $[\text{TiCl}_4(\text{NH}_3)_2]$ where $\text{N-H}\cdots\text{Cl}$ hydrogen bonding was proposed.¹¹ Also the IR spectrum showed a very strong absorption at 931 cm^{-1} assigned to the $\text{Ti}=\text{N}=\text{Ti}$ fragment established by an X-ray structure determination.

The molecular structure of $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**) is shown in Figure 2 and selected distances and angles in Table 2. Inspection of the unit cell reveals molecular association along the crystal by intermolecular hydrogen bonding between one of the hydrogen atoms in the NH_3 ligand and the chlorine atom Cl(1) of other molecules [length $\text{N}(2)\cdots\text{Cl}(1) = 3.478$ Å]. Complex **9** is a dimer, with two asymmetric moieties “ $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2$ ” held together by a bridging nitrido ligand. Each titanium atom has a classical three-legged piano-stool arrangement, with two chlorine, and the nitrido for Ti(1), and one chlorine, one ammonia, and one nitrido ligand for Ti(2). The pseudotetrahedral angles around the titanium atoms span 95.2–117.2°. The titanium– C_5Me_5 (centroid) and titanium–chlorine bond lengths are in the normal range,^{53–57,70–72} and those for Ti(2) [Ti(2)–(C_5Me_5)(2) 2.036 Å, and Ti(2)–Cl(3) 2.283(2) Å] are slightly shorter than the corresponding Ti(1) [Ti(1)–(C_5Me_5)(1) 2.050 Å, Ti(1)–Cl(1) 2.326(1) Å, and Ti(1)–Cl(2) 2.320(2) Å]. The titanium–nitrogen(ammonia) distance of 2.158(4) Å exceeds the sum of the covalent radii for Ti and N ($1.32 + 0.75 = 2.07$ Å)⁷³ but is shorter than those found in amine titanium(IV) adducts.^{74,75} To our knowledge, there are no other crystallographic characterized titanium organometallic complexes with ammonia and the only group 4 structurally documented example is $[\text{Zr}(\eta^8\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)(\text{NH}_3)]$.⁷⁶

The bridging nitrido ligand of **9** is characterized by titanium–nitrogen bond lengths of 1.784(4) [Ti(2)–N(1)] and 1.792(3) Å [Ti(1)–N(1)]. Monomeric titanium imido complexes reported to date show titanium–nitrogen bond lengths in the range 1.65–1.74 Å consistent with a formal triple bond.^{77–80} The Ti(2)–N(1) distance in the nitrido group is longer and it should be

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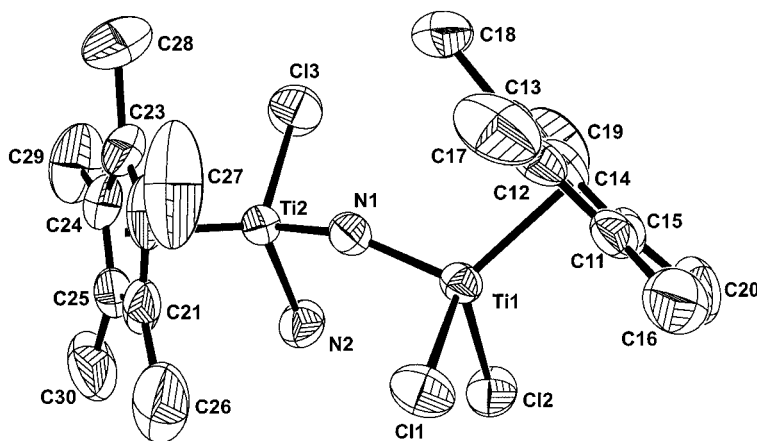


Figure 2. Perspective view of $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**). Thermal ellipsoids correspond to 50% of probability.

Table 2. Selected Lengths (Å) and Angles (deg) for Complex **9**^a

Ti(1)–N(1)	1.792(3)	Ti(1)–Cl(2)	2.320(2)
Ti(1)–Cl(1)	2.326(1)	Ti(2)–N(1)	1.784(4)
Ti(2)–N(2)	2.158(4)	Ti(2)–Cl(3)	2.283(2)
Ti(1)–C ₅ Me ₅ (1)	2.051	Ti(2)–C ₅ Me ₅ (2)	2.036
N(2)–Cl(2)	3.404(5)		
N(1)–Ti(1)–Cl(2)	103.2(1)	N(1)–Ti(1)–Cl(1)	105.4(1)
Cl(2)–Ti(1)–Cl(1)	100.4(1)	N(1)–Ti(2)–N(2)	101.6(2)
N(1)–Ti(2)–Cl(3)	108.1(1)	N(2)–Ti(2)–Cl(3)	95.2(2)
Ti(2)–N(1)–Ti(1)	153.1(2)	C ₅ Me ₅ (1)–Ti(1)–Cl(1)	114.7
C ₅ Me ₅ (1)–Ti(1)–Cl(2)	115.8	C ₅ Me ₅ (1)–Ti(1)–N(1)	115.5
C ₅ Me ₅ (2)–Ti(2)–Cl(3)	116.0	C ₅ Me ₅ (2)–Ti(2)–N(1)	117.1
C ₅ Me ₅ (2)–Ti(2)–N(2)	115.9		

^a C₅Me₅ are the centroids of the $\eta^5\text{-C}_5\text{Me}_5$ ligand rings.

considered as a double bond, $\text{Ti}=\text{N}$. An analogous distance [1.81(1) Å] has been reported for the complex $[\{\text{Cp}_2(\text{PMe}_3)\text{-Ti}=\text{NC}(\text{Ar})\text{C}(\text{Ar})\text{N}=\text{TiCp}_2(\text{PMe}_3)\}]$.⁸¹ On the other hand, $\text{Ti}(1)\text{--N}(1)$ bond length is shorter than the usual bond length in amido^{18,72} and bridging imido^{40–52} titanium complexes, and can be rationalized by an important donation of the nitrogen lone pair to this metal center. A similar argument has been proposed to explain the $\text{Ti}\text{--N}$ distance [1.800(1) Å] in the amido derivative $[\text{TiCl}\{\text{N}(\text{SnMe}_3)\}(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2]$.⁸² From these features, we suggest that the bonding for the bridging fragment can be described as $\text{Ti}(2)=\text{N}(1)=\text{Ti}(1)$ similar to those reported for $[\{\text{N}(\text{CH}_2\text{CH}_2\text{N}^i\text{Pr})_3\text{Ti}\}_2(\mu_3\text{-N})\text{Na}(\text{THF})]$,⁸³ $[(\eta^5\text{-C}_5\text{Me}_5)\text{-Me}_3\text{W}(\mu\text{-N})\text{WMe}_3(\eta^5\text{-C}_5\text{Me}_5)]$,³⁶ $[(\text{Ph}_4\text{P})\{\text{Cl}_5\text{W}(\mu\text{-N})\text{WCl}_5\}]$,²¹ and $[(\text{NH}_4)_3\{\text{X}_5\text{Ta}(\mu\text{-N})\text{TaX}_5\}]$ ($\text{X} = \text{Br}, \text{I}$).²¹ The titanium–nitrogen–titanium angle in our case [153.1(2)°] is narrower than the almost linear disposition found in those complexes ($\text{M}\text{--N}\text{--M} = 170\text{--}180^\circ$, $\text{M} = \text{Ti}, \text{W}, \text{Ta}$). Angles also notably smaller than 180° have been described for the compounds $[\text{Cl}_3\text{-OW}(\mu\text{-N})(\mu\text{-O}_2\text{PCl}_2)\text{WOC}_2\text{H}_5]^{2-}$ (166.2°),²¹ $[\text{Cl}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\mu\text{-N})(\mu\text{-N}_2\text{CCH}_3)\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ (161.4°),⁸⁴ and $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3(\mu\text{-N})_3\}]$ ($\text{X} = \text{Cl}$,²⁸ 128°, $\text{X} = \text{Me}$,²⁵ 127°) where an additional bridging ligand is always present. Furthermore, in complex **9** the planarity of the $\text{Ti}(1)\text{Ti}(2)\text{N}(1)\text{N}(2)\text{Cl}(2)$ system and a $\text{N}(2)\cdots\text{Cl}(2)$ distance [3.404(5) Å] slightly longer than the sum of the van der Waals radii of the N and Cl atoms (1.50

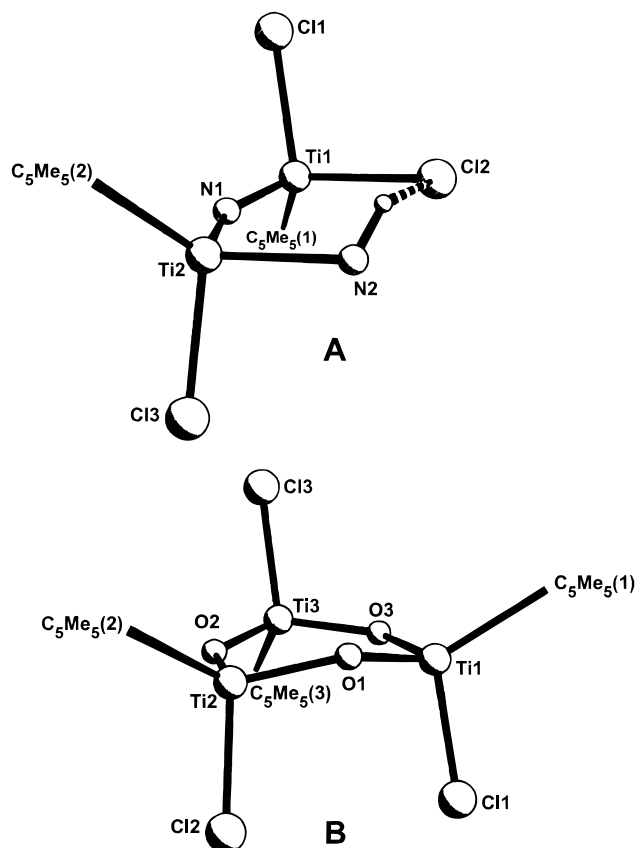


Figure 3. View of the molecular structures of $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**) (A) and $[(\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl})_3(\mu\text{-O})_3]$ (B) without the $(\eta^5\text{-C}_5\text{Me}_5)$ ligands.

and 1.80 Å,⁸⁵ respectively) suggest an intramolecular hydrogen bonding interaction between $\text{N}(2)$ and $\text{Cl}(2)$ atoms. The structural disposition of cyclopentadienyl and chlorine ligands with respect to the fragment $\text{Ti}(1)\text{Ti}(2)\text{N}(1)\text{N}(2)\text{Cl}(2)$ is shown in Figure 3A and compares well with that found for analogous groups in the trinuclear complexes $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3(\mu\text{-O})_3\}]$ [$\text{X} = \text{Cl}$ (Figure 3B),⁸⁶ Br ,⁸⁷ Me ,⁵³ crotyl⁸⁸] and $[\{\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3(\mu\text{-N})_3\}]$ ($\text{X} = \text{Cl}$,²⁸ Me ,²⁵).

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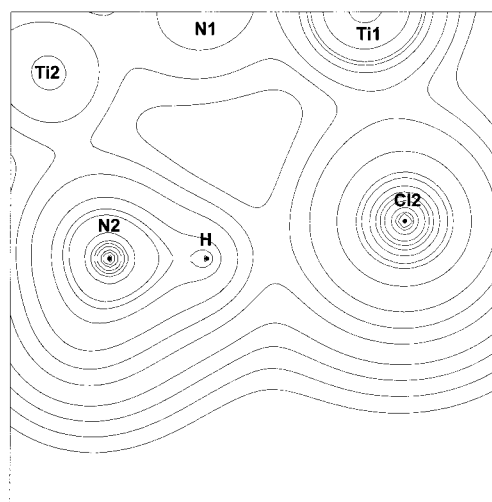
Table 3. Some Computed and Experimental Bond Lengths and Angles for **9** and the Model **10**

	DFT		X-ray
	10	9	9
Ti(1)–N(1)	1.835	1.837	1.792(3)
Ti(2)–N(1)	1.768	1.787	1.784(4)
Ti(2)–N(2)	2.199	2.194	2.158(4)
Ti(1)–Cl(2)	2.353	2.367	2.320(2)
Ti(1)–N(1)–Ti(2)	151.1	150.7	153.1(2)

Theoretical Study of Complex 9. DFT calculations were conducted to characterize these N–H···Cl and Ti=N=Ti intramolecular interactions and to explain the molecular disposition found for compound **9**. The first series of calculations were conducted on $[\{\text{Ti}_2\text{Cp}_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**10**), as the model complex for **9**. Although the methyl groups were substituted by hydrogen atoms, the DFT calculations reproduced the molecular structure of **9** very well (Table 3). The major discrepancies between the experimental and the theoretical bond lengths appear in the N(1)–Ti(1) bond distance and in the long Ti(2)–N(2) bond length. In both cases the deviation is approximately 0.04 Å. The computed Ti(1)–N(1)–Ti(2) angle (151.1°) also compares very reasonably with the experimental one (153.1°).

Bottomley and Goh analyzed the structure of 283 complexes of the $[(\text{ML}_m)(\mu\text{-A})(\text{M}'\text{L}'_n)]$ type by statistical methods.⁸⁹ For compounds $[\{\text{M}(\eta^5\text{-C}_5\text{R}_5)\text{L}_2\}_2(\mu\text{-A})]$, a special case of the $[(\text{ML}_5)_2(\mu\text{-A})]$ complexes, they showed from the extended Hückel calculations that the energy of the complexes depends very little on the M–A–M angle (180–140°) when the number of metal electrons is less than 9. Our calculations for model compound **10** seems to confirm this hypothesis, because the energy of the linear complex with the Ti–N–Ti angle fixed to 180° was computed to be higher than the bent complex by only 7.5 kJ·mol^{−1}.

Another feature that deserves attention in molecules of the $[\{\text{M}(\eta^5\text{-C}_5\text{R}_5)\text{L}_2\}_2(\mu\text{-A})]$ type is the relative arrangement between the two cyclopentadienyl ligands. In this article, we specify the relative orientation of the two “TiCpL₂” halves using the dihedral angle ϕ defined by the two centroids of the Cp groups and the titanium atoms. In the structure of minimum energy for **10**, the value of this torsion angle ϕ was 148°. The energy of this compound in the staggered conformation ($\phi = 180^\circ$, the most common arrangement of the $\eta^5\text{-C}_5\text{R}_5$ ligands with linear M–A–M units) is 26.4 kJ·mol^{−1} higher than the minimum. What is the origin of this relatively important difference in energy between the minimum (or bent structure) and the staggered conformation? To answer this question, we have also analyzed these two conformations for the still unknown anion $[\{\text{TiCpCl}_2\}_2(\mu\text{-N})]^-$. In this case, the linear and bent structures have similar energies ($\Delta E \approx 1.3$ kJ·mol^{−1}), which shows that the energy of the molecule does not change rotating one “TiCpL₂” fragment by $\approx 30^\circ$. This result, which is completely consistent with the two observed conformations for $[\{\text{TiCpCl}_2\}_2(\mu\text{-O})]$,^{90,91} an analogue complex of $[\{\text{TiCpCl}_2\}_2(\mu\text{-N})]^-$, suggests that the steric repulsion between the two Cp’s does not increase when going from the staggered structure to the bent one. However, the rotation moves the ammonia in complex **10** away from the Cp ligand of the other half, thus lowering the steric repulsion between the two “TiCpL₂”

**Figure 4.** Electron density plot for the DFT optimized model complex $[\{\text{Ti}_2(\text{Cp})_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**10**) in its optimal structure.

fragments. The formation of the six-membered ring via attractive N–H···Cl interaction also stabilizes the bent conformation when a Cl[−] is substituted by a NH₃. The short distance (2.163 Å) between one of the hydrogen atoms in the NH₃ ligand and the chlorine atom Cl(2) (Figure 3A) clearly suggests the existence of an intramolecular hydrogen bond. Stabilization by the formation of a hydrogen bond is also suggested, because the alternative geometry with two hydrogens of the NH₃ group oriented toward the chlorine is higher than the minimum by 5 kJ·mol^{−1}. In this new conformation the H···Cl(2) separations are now 2.65 and 2.82 Å.

According to the theory of “atoms in molecules” (AIM), the presence of a bond critical point (bcp) in the charge density distribution linking two nuclei at the equilibrium geometry is a necessary and sufficient condition for the existence of a bond.^{92,93} The basic idea of the AIM scheme is that atomic nuclei correspond to electron density maxima, and a bond path, characterized by a bcp, can be rigorously defined between each bound pair of atoms. The AIM scheme seems *particularly suitable* for cases in which chemical bonding between atoms cannot be clearly assigned only from geometrical features. Figure 4 shows the electron density plot for the DFT optimized complex **10** in its optimal structure in a plane defined by N(2), Cl(2), and the H in the NH₃ ligand closest to the Cl(2) atom. Although a larger scale would be more appropriate for a general view, we have chosen this illustration because it highlights the particular interaction among these three atoms. In the charge density distribution, we can clearly identify a maximum charge density on each of the three nuclei. The maximum on the hydrogen atom is less pronounced, because this atom has only 1 e[−]. When going from hydrogen to chlorine, the density decreases, reaches a minimum in this direction, and then increases again. The minimum point in this particular direction corresponds to a density maximum in the perpendicular direction. It would also correspond to a maximum in the third dimension, which is perpendicular to the plane of the drawing. The point at which the gradient of the charge density is zero and the density is minimum in one direction and maximum in the other two is called the bcp in the AIM theory. Such a point in the charge distribution of complex **10** linking the chlorine and hydrogen nuclei confirms the previously mentioned formation of a six-membered ring via a hydrogen bond. The values of the charge density (ρ) and laplacian of the charge density ($\nabla^2\rho$) at the bcp define the topological properties of a bond in the AIM theory. In this case, the values of ρ and $\nabla^2\rho$ (0.028

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and 0.069 au, respectively) are in the range reported for other hydrogen bonds.⁹⁴

Although incorporating the methyl groups into the calculations does not modify significantly the geometry of the complex (see Table 3), the new structure has two short distances between the chlorine atoms Cl(1) and Cl(2) and one methyl hydrogen of the other half of the molecule. The computed C—H...Cl distances (2.707 and 2.531 Å, respectively) are clearly longer than the N—H...Cl(2) distance (2.167 Å). Scholz et al. recently characterized intramolecular C—H...Cl hydrogen bonds in titanium and niobium complexes, with distances between 2.59 and 2.69 Å.⁹⁵ All these distances are significantly shorter than the sum of the van der Waals radii of chlorine and hydrogen (≈ 3 Å⁹⁵). The existence of three hydrogen bonds in **9** is confirmed by analyzing the charge density. Besides the bcp associated with the N—H...Cl(2) hydrogen bond, two additional bcp's were found associated with C—H...Cl interactions. In these hydrogen bonds, the values of ρ at the bcp's were lower than in the hydrogen bond that forms Cl(2) with one hydrogen of ammonia because of the existing inverse correlation between the bond distance and the density at the bcp.⁹⁶

The staggered conformation was also computed for **9**. Substituting hydrogen atoms by methyl groups in the Cp ligands did not change our general conclusions for complex **10**. The energy difference between the bent and staggered conformations in complex **9** (27.2 kJ·mol⁻¹) is almost identical with the energy computed for **10** (26.4 kJ·mol⁻¹). This similarity can be attributed to the fact that in the staggered conformation of **9** there are also two short C—H...Cl distances, whose values are 2.62 and 2.72 Å. So, the new interactions that appear with the methyl groups do not produce a further stabilization of the bent structure. Opening the Ti—N—Ti angle from 151° to 180° in complex **9** requires an energy of ~ 4 kJ·mol⁻¹, which is somewhat less than for **10**.

Another interesting feature of complex **9** mentioned above is the presence of two short titanium—nitrido distances, which suggests that there are two π Ti—N bonds. Analysis of the molecular orbitals fully confirms this interpretation for the Ti—N—Ti interaction. Figure 5A shows a plot of the highest occupied molecular orbital (HOMO)-2 in the plane defined by the two titaniums and the bridging nitrogen. If we consider that the two metals define the z -axis and that the bridging nitrogen is in the xz -plane, from Figure 5A we can clearly identify the π -donation from the $p_x(\text{N})$ orbital to the d_{xz} orbitals of the two metals. The π interaction in the plane yz is also delocalized between the three atoms and appears in the HOMO, a plot of which is presented in Figure 5B in a plane defined by the two titaniums and the Cl(3) atom. Notice that this plane is approximately perpendicular to the plane that contains the atoms Ti(1), Ti(2), and N(1) (the dihedral angle between the two planes is 83°).

Conclusions

We have described that the ammonolysis of mono(pentamethylcyclopentadienyl) titanium(IV) derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{X}_3]$ ($\text{X} = \text{NMe}_2, \text{Me}, \text{Cl}$) in solution is a suitable route to obtain polynuclear nitrido complexes as $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu_3\text{-}$

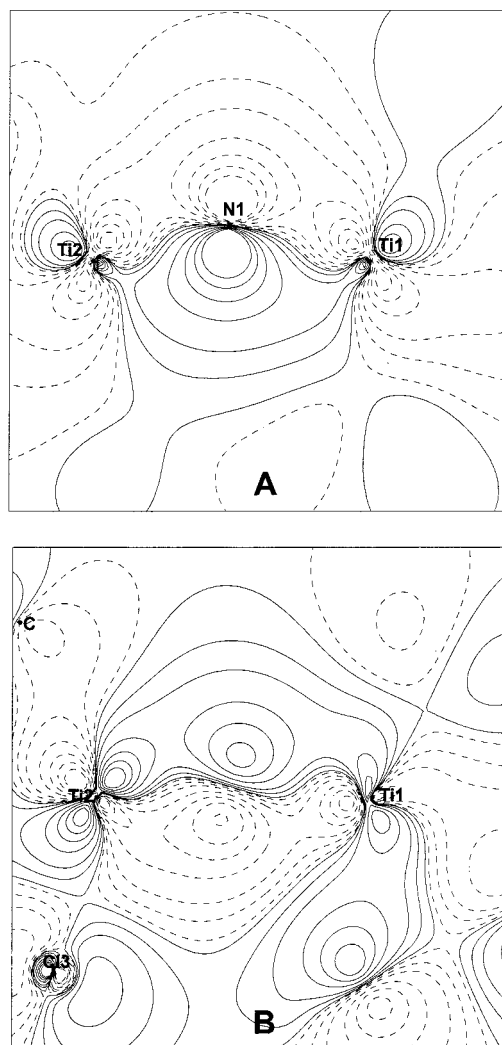


Figure 5. Plot of the π orbitals HOMO-2 (A) and HOMO (B) in the planes defined by the two metals and N(1), and the two metals and Cl(3), respectively.

N_4) (**1**), $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**2**), and $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (**9**). The precubane structure of **2** is capable of incorporating the fourth metal vertex by reaction with tris(dimethylamido) titanium(IV) derivatives, and generating a family of tetranuclear nitrido complexes containing different cyclopentadienyl groups: $[\{\text{Ti}_4(\eta^5\text{-C}_5\text{Me}_5)_3(\eta^5\text{-C}_5\text{H}_5\text{-}n\text{R}_n)\}(\mu_3\text{-N})_4]$ (**6–8**). The crystal structure of the unprecedented ammonia titanium organometallic adduct **9** shows a bent disposition around the nitrido ligand and suggests the existence of inter/intramolecular hydrogen bond interactions N—H...Cl. DFT calculations carried out on this complex show that the structure of minimum energy (bent conformation with $\phi = 144^\circ$, ϕ is the dihedral angle defined by the two centroids of the $\eta^5\text{-C}_5\text{Me}_5$ ligands and the metal atoms) is 27.2 kJ·mol⁻¹ less than the staggered conformation ($\phi = 180^\circ$) with a linear Ti—N—Ti unit. In the most stable arrangement, N—H...Cl and C—H...Cl hydrogen bonds were characterized by means of the topology of the charge density.

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane and pentane were distilled from Na/K amalgam just before use. Toluene was freshly distilled from sodium. Tetrahydrofuran and diethyl ether were distilled from purple solutions of sodium/benzophenone ketyl

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immediately before use. NMR solvents were dried with P_2O_5 ($CDCl_3$) or Na/K amalgam (C_6D_6) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. 2,4,6-Trimethylaniline (purchased from Aldrich Chemical Co.) was distilled from sodium. Electronic grade ammonia (purity > 99.995%, O_2 < 2 ppm, and H_2O < 10 ppm) was purchased from Sociedad Española del Oxígeno and used as received. NH_3 (^{15}N 10%) was purchased from Cambridge Isotope Laboratories (1-L glass ampules) and used without further purification. $[Ti(\eta^5-C_5H_5-nR_n)(NMe_2)_3]$,^{59,60} $[Ti(\eta^5-C_5Me_5)(NMe_2)_3Cl_3]$,⁶¹ and $[Ti(\eta^5-C_5Me_5)Me_3]$ ⁹⁷ were prepared by known procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 and/or Unity-500 Plus spectrometer. Chemical shifts (δ , ppm) are given relative to residual protons or to carbon of the solvent. ^{15}N NMR spectra were recorded on a Varian Unity-500 Plus (50.7 MHz) in 10-mm NMR tubes sealed by flame. Chemical shifts (δ , ppm) were measured with respect to CH_3NO_2 (δ = 0.0 ppm) as external reference. Electron impact mass spectra were obtained at 70 eV. Microanalysis (C, H, N) were performed in a Heraeus CHN—O—Rapid microanalyzer.

Synthesis of $[Ti(\eta^5-C_5Me_5)_4(\mu_3-N)_4]$ (1). We have communicated the preparation, spectroscopic, analytic, and crystallographic data for **1**.³² The synthesis of **1**- ^{15}N isotopically enriched 10% in ^{15}N was carried out in a similar procedure. A solution of $[Ti(\eta^5-C_5Me_5)(NMe_2)_3]$ (1.75 g, 5.55 mmol) in hexane (50 mL) was transferred into a Carius tube (capacity, 200 mL). The argon atmosphere was changed to ammonia (1 L, ^{15}N 10%) and cooled to $-78^\circ C$, and the Carius tube was flame-sealed. After being heated for 3 days at $90^\circ C$, the tube was opened, and the resultant dark green crystals were washed with hexane (2×25 mL) to yield 0.77 g (77%). ^{15}N NMR ($CDCl_3$, $20^\circ C$, δ): 500.6 (s).

Synthesis of $[Ti(\eta^5-C_5Me_5)(\mu-NH)_3(\mu_3-N)]$ (2). Although Roesky and co-workers have reported a synthesis for **2**,²² we used a procedure similar to the one described for **1**. A solution of $[Ti(\eta^5-C_5Me_5)Me_3]$ (0.63 g, 2.76 mmol) in toluene (20 mL) was transferred via cannula into a Carius tube (capacity, 120 mL) equipped with a stir bar. The argon atmosphere was changed to ammonia and cooled to $-78^\circ C$, and the Carius tube was flame-sealed. The reaction mixture was stirred at room temperature for 24 h. The Carius tube was opened in a glovebox, and the volatile components were removed under reduced pressure to give an orange powder. The orange powder was washed with cold hexane (20 mL) and then dried under vacuum to yield yellow **2** (0.41 g, 73%). IR (KBr, cm^{-1}): 3352m, 2910vs, 2722w, 1669w, 1490w, 1433s, 1374s, 1255w, 1160w, 1064w, 1023m, 955w, 869w, 797s, 711vs, 674vs, 654vs, 532s, 505s, 453m, 415m, 391s; 1H NMR (C_6D_6 , $20^\circ C$, δ): 13.80 (s broad, 3H, $\mu-NH$), 2.01 (s, 45H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6 , $20^\circ C$, δ): 117.1 (C_5Me_5), 11.8 (C_5Me_5); MS (70 eV) m/e [assignment, relative intensity (rel int.) (%): 608 [M^+ , 68], 591 [($M - NH_3$) $^+$, 9], 473 [($M - C_5Me_5$) $^+$, 11], 456 [($M - NH_3 - C_5Me_5$) $^+$, 23], 438 [($M - 2NH_3 - C_5Me_5H$) $^+$, 22], 319 [($M - 2NH_3 - 2C_5Me_5H$) $^+$, 36], 200 [($M - 3C_5Me_5H$) $^+$, 24].

^{15}N (^{15}N 10%) was prepared in the same way from 1.60 g (7.01 mmol) of $[Ti(\eta^5-C_5Me_5)Me_3]$ and 1 L of NH_3 (^{15}N , 10%) to give 1.02 g (72%). ^{15}N NMR ($CDCl_3$, $20^\circ C$, δ): 461.9 (s, μ_3-N), 89.5 (d, $^1J_{NH}$ = 63.0 Hz, $\mu-NH$).

Synthesis of $[Ti(\eta^5-C_5Me_5)Me_2(\mu-NH)_2]$ (3). A 200-mL ampule (Teflon stopcock) was charged with $[Ti(\eta^5-C_5Me_5)Me_3]$ (0.90 g, 3.94 mmol) and hexane (20 mL). The argon atmosphere was changed to ammonia and cooled to $-78^\circ C$. The reaction mixture was allowed to warm to room temperature for 12 h. Orange crystals were collected by filtration, washed with cold hexane (20 mL), and vacuum-dried to yield **3** (0.20 g, 24%). The filtrate was pump-dried to afford an orange solid. Analysis of this solid by 1H NMR showed that it was a mixture of compounds **2** and **3**. Spectral and analytical data for **3**: IR (KBr, cm^{-1}): 3349m, 2912s, 1489w, 1431s, 1375s, 1238w, 1100w, 1022m, 787vs, 735s, 650vs, 500s, 385s; 1H NMR (C_6D_6 , $20^\circ C$, δ): 10.90 (s broad, 2H, $\mu-NH$), 1.95 (s, 30H, C_5Me_5), 0.78 (s, 6H, $TiMe$); $^{13}C\{^1H\}$ NMR (C_6D_6 , $20^\circ C$, δ): 120.1 (C_5Me_5), 35.8 ($TiMe$), 11.8 (C_5Me_5); MS (70 eV) m/e [assignment, rel int. (%): 425 [($M - H$) $^+$, 3], 411 [($M -$

Me) $^+$, 2], 396 [($M - 2CH_3$) $^+$, 33]. Anal. Calcd for $C_{22}H_{38}N_2Ti_2$ (426.36): C, 61.98; H, 8.98; N, 6.57. Found: C, 62.17; H, 8.89; N, 6.84.

Synthesis of $[Ti(\eta^5-C_5Me_5)Me_2(\mu-NAr)_2]$ (4). 2,4,6-Trimethylaniline (0.30 g, 2.22 mmol) was added to a solution of $[Ti(\eta^5-C_5Me_5)Me_3]$ (0.50 g, 2.19 mmol) in hexane (20 mL). After 20 h at room temperature a brown solution was separated from brown crystals by filtration. The crystals were isolated, washed with hexane (5 mL), and dried under vacuum to yield **4** (0.30 g, 41%). IR (KBr, cm^{-1}): 2981s, 2911s, 2726w, 1464vs, 1376s, 1301w, 1203vs, 1152vs, 1062w, 1020m, 956m, 853s, 734m, 637s, 586s, 519vs, 476s, 377s; 1H NMR (C_6D_6 , $20^\circ C$, δ): 6.72 (s, 4H, $C_6H_2Me_2Me$), 2.42 (s, 12H, $C_6H_2Me_2Me$), 2.13 (s, 6H, $C_6H_2Me_2Me$), 1.62 (s, 30H, C_5Me_5), 1.34 (s, 6H, $TiMe$); $^{13}C\{^1H\}$ NMR (C_6D_6 , $20^\circ C$, δ): 155.5, 131.0, 128.6, 127.3 ($C_6H_2Me_2Me$), 121.9 (C_5Me_5), 53.4 ($TiMe$), 23.0 ($C_6H_2Me_2Me$), 20.5 ($C_6H_2Me_2Me$) 11.1 (C_5Me_5); MS (70 eV) m/e [assignment, rel int. (%): 647 [($M - MeH$) $^+$, 9], 631 [($M - 2MeH$) $^+$, 46], 496 [($M - 2MeH - C_5Me_5$) $^+$, 26], 316 [($Ti(\eta^5-C_5Me_5)(NAr)$) $^+$, 75]. Anal. Calcd for $C_{40}H_{58}N_2Ti_2$ (662.71): C, 72.50; H, 8.82; N, 4.23. Found: C, 72.86; H, 8.86; N, 4.19.

Synthesis of $[Ti(\eta^5-C_5Me_5)(NH_2)_2(\mu-NAr)_2]$ (5). A 150-mL ampule (Teflon stopcock) was charged with $[Ti(\eta^5-C_5Me_5)Me_2(\mu-NAr)_2]$ (**4**) (0.17 g, 0.26 mmol), toluene (25 mL), and a stir bar. The argon atmosphere was changed to ammonia and cooled at $-78^\circ C$. After stirring at room temperature for 20 h, the brown solution was separated from a fine light brown powder. The powder was vacuum-dried for 6 h to afford **5** (0.15 g, 88%). IR (KBr, cm^{-1}): 3394m, 3321w, 1538m, 1462vs, 1415s, 1376w, 1305vs, 1284vs, 1161w, 1024w, 971m, 929w, 849m, 791w, 739m, 676vs, 631w, 620w, 595w, 572w, 510w, 478vs, 414m, 385w; 1H NMR ($CDCl_3$, $20^\circ C$, δ): 6.64 (s, 4H, $C_6H_2Me_2Me$), 3.78 (s broad, 4H, NH_2), 2.18 (s, 6H, $C_6H_2Me_2Me$), 2.12 (s, 12H, $C_6H_2Me_2Me$), 1.95 (s, 30H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, $20^\circ C$, δ): 154.8, 131.3, 127.7, 127.6 ($C_6H_2Me_2Me$), 118.6 (C_5Me_5), 20.9 ($C_6H_2Me_2Me$), 19.1 ($C_6H_2Me_2Me$), 11.1 (C_5Me_5); MS (70 eV) m/e [assignment, rel int. (%): 665 [M^+ , 9], 530 [($M - C_5Me_5$) $^+$, 7], 513 [($M - C_5Me_5 - NH_3$) $^+$, 60], 496 [($M - C_5Me_5 - 2NH_3$) $^+$, 13]. Anal. Calcd for $C_{38}H_{56}N_4Ti_2$ (664.69): C, 68.67; H, 8.49; N, 8.43. Found: C, 68.11; H, 8.60; N, 7.81.

Reaction of $[Ti(\eta^5-C_5Me_5)(\mu-NH)_3(\mu_3-N)]$ (2) with $[Ti(\eta^5-C_5Me_5)(NMe_2)_3]$. A 5-mm NMR tube was charged with **2** (0.008 g, 0.013 mmol), $[Ti(\eta^5-C_5Me_5)(NMe_2)_3]$ (0.004 g, 0.0013 mmol), and benzene- d_6 (0.80 mL). The tube was flame-sealed, and the course of the reaction at different temperatures was monitored by 1H NMR. After heating at temperatures near $160^\circ C$, the spectra showed resonances for $NHMe_2$ with concomitant minor intensity for those of the starting complexes. The temperature was maintained for 2 days until the complete consumption of the initial products to afford green crystals and a red solution. The 1H and $^{13}C\{^1H\}$ NMR spectra of the crystals in chloroform- d were identical with those of $[Ti(\eta^5-C_5Me_5)_4(\mu_3-N)_4]$ (**1**). 1H NMR ($CDCl_3$, $20^\circ C$, δ): 1.99 (s, 60H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, $20^\circ C$, δ): 119.1 (C_5Me_5), 12.0 (C_5Me_5).

Synthesis of $[Ti_4(\eta^5-C_5Me_5)_3(\eta^5-C_5H_5)_3(\mu_3-N)_4]$ (6). A 120-mL Carius tube was charged with **2** (0.50 g, 0.82 mmol), $[Ti(\eta^5-C_5H_5)(NMe_2)_3]$ (0.20 g, 0.82 mmol), and hexane (50 mL). The tube was flame-sealed and heated at $135^\circ C$ for 2 days. The Carius tube was opened in a glovebox, and the dark green solution was concentrated to a volume of about 10 mL. Crystallization at $-40^\circ C$ for 24 h afforded **6** as green crystals (0.25 g, 42%). IR (KBr, cm^{-1}): 2964s, 2909s, 1437s, 1374s, 1261s, 1197vs, 1019vs, 782vs, 650vs, 451s; 1H NMR (C_6D_6 , $20^\circ C$, δ): 6.12 (s, 5H, C_5H_5), 2.03 (s, 45H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6 , $20^\circ C$, δ): 119.7 (C_5Me_5), 110.3 (C_5H_5), 11.9 (C_5Me_5); MS (70 eV) m/e [assignment, rel int. (%): 718 [M^+ , 0.3], 583 [($M - C_5Me_5$) $^+$, 4], 518 [($M - C_5Me_5 - Cp$) $^+$, 0.2], 448 [($M - 2C_5Me_5$) $^+$, 9], 383 [($M - 2C_5Me_5 - Cp$) $^+$, 2], 313 [($M - 3C_5Me_5$) $^+$, 32], 248 [($M - 3C_5Me_5 - Cp$) $^+$, 8]. Anal. Calcd for $C_{35}H_{50}N_4Ti_4$ (718.41): C, 58.52; H, 7.02; N, 7.80. Found: C, 58.44; H, 7.26; N, 7.63.

Synthesis of $[Ti_4(\eta^5-C_5Me_5)_3(\eta^5-C_5H_4SiMe_3)_3(\mu_3-N)_4]$ (7). In a fashion similar to the preparation of **6**, **2** (0.80 g, 1.32 mmol) and $[Ti(\eta^5-C_5H_4SiMe_3)(NMe_2)_3]$ (0.42 g, 1.32 mmol) were heated at $140^\circ C$ to afford **7** as green crystals (0.53 g, 51%). IR (KBr, cm^{-1}): 2912s, 2860s, 2722w, 2207w, 1633w, 1493w, 1441s, 1375s, 1246s, 1171m, 1070m, 1041s, 904m, 837s, 789vs, 651vs, 623s, 451s; 1H NMR (C_6D_6 ,

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Table 4. Crystal Data and Structure Refinement for Complexes **4** and **9**^a

	4	9
color	brown	orange
empirical formula	$\text{C}_{40}\text{H}_{58}\text{N}_2\text{Ti}_2$	$\text{C}_{20}\text{H}_{33}\text{Cl}_3\text{N}_2\text{Ti}_2$
fw	662.68	503.63
temp (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P1$	$C2/c$
a (Å); α (deg)	8.684(1); 66.11(1)	28.272(6); 90
b (Å); β (deg)	11.074(1); 71.44(1)	8.452(2); 111.85(3)
c (Å); γ (deg)	11.174(1); 87.92(1)	22.260(4); 90
vol (Å ³)	926.1(2)	4937(2)
Z	1	8
ρ calcd (g/cm ³)	1.188	1.355
μ (mm ⁻¹)	0.460	0.979
$F(000)$	356	2096
GOF on F^2	0.577	0.966
final R indices [$I > 2\sigma(I)$]	$R1 = 0.048$, $wR2 = 0.137$	$R1 = 0.033$, $wR2 = 0.081$
R indices (all data)	$R1 = 0.076$, $wR2 = 0.177$	$R1 = 0.076$, $wR2 = 0.095$
largest diff peak and hole (e Å ⁻³)	0.393 and -0.304	0.277 and -0.224

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$. $GOF = \{\sum [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$. n is the number of reflections, and p is the total number of parameters refined.

20 °C, δ): 6.44, 6.22 (m, A_2B_2 spin system, 4H, $\text{C}_5\text{H}_4\text{SiMe}_3$), 2.05 (s, 45H, (C_5Me_5)), 0.41 (s, 9H, $\text{C}_5\text{Me}_4\text{SiMe}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C, δ): 119.7 (C_5Me_5), 119.2, 115.4, 115.3 ($\text{C}_5\text{H}_4\text{SiMe}_3$), 12.1 (C_5Me_5), 0.8 ($\text{C}_5\text{H}_4\text{SiMe}_3$). Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{N}_4\text{SiTi}_4$ (790.59): C, 57.73; H, 7.40; N, 7.09. Found: C, 58.24; H, 7.88; N, 5.93.

Synthesis of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_3(\eta^5\text{-C}_5\text{H}_4\text{Me})\}(\mu_3\text{-N})_4]$ (8**).** In a way similar to the preparation of **6**, **2** (0.80 g, 1.32 mmol) and $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{NMe}_2)_3]$ (0.34 g, 1.31 mmol) were heated at 140 °C to afford **8** as green crystals (0.40 g, 42%). IR (KBr, cm^{-1}): 2911s, 2858s, 2721w, 1494w, 1437m, 1373m, 1259w, 1083m, 1029m, 932w, 829m, 779vs, 728m, 649vs, 621s, 453s; ^1H NMR (C_6D_6 , 20 °C, δ): 6.05, 5.84 (m, A_2B_2 spin system, 4H, $\text{C}_5\text{H}_4\text{Me}$), 2.25 (s, 3H, $\text{C}_5\text{H}_4\text{Me}$), 2.04 (s, 45H, C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C, δ): 119.6 (C_5Me_5), 119.1, 110.9, 110.4 ($\text{C}_5\text{H}_4\text{Me}$), 12.3 ($\text{C}_5\text{H}_4\text{Me}$), 12.0 (C_5Me_5). Anal. Calcd for $\text{C}_{36}\text{H}_{52}\text{N}_4\text{Ti}_4$ (732.43): C, 59.04; H, 7.16; N, 7.65. Found: C, 58.52; H, 7.31; N, 6.55.

Synthesis of $[\{\text{Ti}_2(\eta^5\text{-C}_5\text{Me}_5)_3\text{Cl}_3(\text{NH}_3)\}(\mu\text{-N})]$ (9**).** **Method A.** A Carius tube (capacity, 200 mL) was charged with $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$ (1.00 g, 3.45 mmol), diethyl ether (70 mL), and a stir bar. The argon atmosphere was changed to ammonia and cooled to -78 °C, and the Carius tube was flame-sealed. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The orange solution was separated from an orange solid by filtration. The orange solid was extracted with THF (2 \times 25 mL) until it became white, and the THF extracts were combined with the diethyl ether filtrate. The volatile

components were removed under reduced pressure, and the resultant orange solid was washed with toluene (3 \times 20 mL) to afford **9** (0.22 g, 25%).

Method B. In a fashion similar to method A, $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{NMe}_2)\text{-Cl}_2]$ (2.00 g, 6.71 mmol) in toluene (50 mL) was treated with ammonia for 2 days. An orange solution was filtered off from an orange solid. The solid was extracted with THF (75 mL), and the resultant solution was carried out to dryness to give an orange solid. The orange solid was washed with toluene (20 mL) and then dried under vacuum to yield **9** (0.67 g, 40%). IR (KBr, cm^{-1}): 3286w, 3227w, 3144w, 3040w, 2911s, 1595w, 1483w, 1428m, 1409w, 1379s, 1272s, 1068w, 1024 m, 931vs, 788m, 761m, 729w, 682w, 663w, 622w, 465w, 441s, 412m, 363w, 347m, 316m; ^1H NMR (CDCl_3 , 20 °C, δ): 2.70 (s broad, 3H, NH_3), 2.123 (s, 15H, C_5Me_5), 2.117 (s, 15H, C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C, δ): 127.8 (C_5Me_5), 125.9 (C_5Me_5), 12.8 (C_5Me_5), 12.3 (C_5Me_5); MS (70 eV) m/e [assignment, rel int. (%): 487 $[(\text{M} - \text{NH}_3)^+]$, 40], 451 $[(\text{M} - \text{NH}_3 - \text{HCl})^+]$, 3], 351 $[(\text{M} - \text{NH}_3 - \text{C}_5\text{Me}_5\text{H})^+]$, 87], 315 $[(\text{M} - \text{NH}_3 - \text{C}_5\text{Me}_5\text{H} - \text{HCl})^+]$, 17]. Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{-Cl}_3\text{Ti}_2$ (503.65): C, 47.70; H, 6.60; N, 5.56. Found: C, 47.61; H, 6.55; N, 4.84.

^{15}N (^{15}N 10%) was prepared following method B in the amounts and yields described above. ^{15}N NMR (CDCl_3 , 20 °C, δ): 431.6 (s, $\mu\text{-N}$), -360.8 (broad, NH_3).

X-ray Crystal Structure Determination of Complexes **4** and **9**.

Brown crystals of compound **4** were crystallized from a hexane solution at room temperature, whereas the orange crystals of **9** were obtained from toluene. Table 4 provides a summary of the crystal data and refinement parameters for complexes **4** and **9**. Both data were collected on an ENRAF NONIUS CAD4 diffractometer at room temperature. Intensity measurements were performed by ω - 2θ scans in the range $6^\circ < 2\theta < 50^\circ$ for **4**, and ω scans in the range $6^\circ < 2\theta < 44^\circ$ for **9**. Of the 3474 measured reflections for **4**, 3243 were independent; $R1 = 0.048$ and $wR2 = 0.137$ [for 2561 reflections with $F > 4\sigma(F)$]. Of the 5999 measured reflections for **9**, 3005 were independent; $R1 = 0.033$ and $wR2 = 0.081$ [for 2032 reflections with $F > 4\sigma(F)$]. The structures were solved by direct methods (SHELXS-90)⁹⁸ and refined by least-squares against F^2 (SHELXL-93).⁹⁹ All non-hydrogen atoms were refined anisotropically and the hydrogen atoms positioned geometrically and refined by using a riding model in the last cycles of refinement, except those linked to N(2) in complex **9**, which were located and refined isotropically.

Computational Details. All the DFT calculations were carried out with the ADF program^{100–103} using triple- ζ + polarization Slater basis set to describe the valence electrons of C, N, and Cl. For titanium a frozen core composed of the 1s, 2s, and 2p was described by double- ζ Slater functions, 3d and 4s by triple- ζ functions, and 4p by a single orbital. Hydrogens were described by triple- ζ + polarization functions. The geometries and binding energies were calculated using gradient corrections. We used the local spin density approximation characterized by the electron gas exchange ($X\alpha$ with $\alpha = 2/3$) together with Vosko–Wilk–Nusair parametrization¹⁰⁴ for correlation. Becke's nonlocal corrections¹⁰⁵ to the exchange energy and Perdew's nonlocal corrections¹⁰⁶ to the correlation energy were added. The topological properties of the charge density were computed with a modified version of the AIMPAC package¹⁰⁷ and the Xaim software.¹⁰⁸

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **4** and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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