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# Cleavage of Dinitrogen from Forming Gas by a Titanium Molecular System under Ambient Conditions

Mariano González-Moreiras, Miguel Mena, Adrián Pérez-Redondo and Carlos Yélamos\*

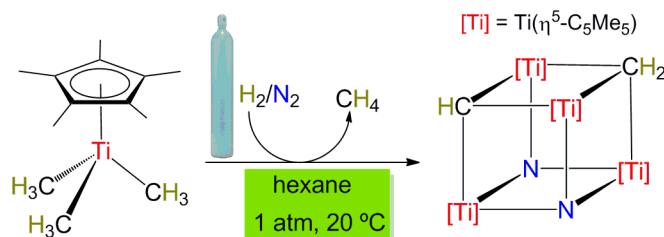
*Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá. 28805*

*Alcalá de Henares-Madrid (Spain). E-mail: [carlos.yelamos@uah.es](mailto:carlos.yelamos@uah.es)*

Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 70th birthday.

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Commercially available H<sub>2</sub>/N<sub>2</sub> mixture reacts with a hexane solution of [Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Me<sub>3</sub>] at ambient conditions to give a paramagnetic methylidene-methyldiylne-nitrido cube-type complex via dinitrogen cleavage.



**Abstract:**

Simple exposure of a hexane solution of  $[\text{TiCp}^*\text{Me}_3]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) to an atmosphere of commercially available and inexpensive forming gas ( $\text{H}_2/\text{N}_2$  mixture, 13.5–16.5% of  $\text{H}_2$ ) at room temperature leads to the methylidene-methylidyne-nitrido cube-type complex  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})(\mu_3\text{-CH}_2)(\mu_3\text{-N})_2]$  via dinitrogen cleavage. This paramagnetic compound reacts with  $[\text{D}_1]$ chloroform to give the titanium(IV) methylidyne-nitrido species  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})_2(\mu_3\text{-N})_2]$ , whereas its one-electron oxidation with  $\text{AgOTf}$  or  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2](\text{OTf})$  ( $\text{OTf} = \text{O}_3\text{SCF}_3$ ) yields the diamagnetic ionic derivative  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})(\mu_3\text{-CH}_2)(\mu_3\text{-N})_2](\text{OTf})$ . The  $\mu_3$ -nitrido ligands of the methylidyne-nitrido cubane complex can be protonated with  $[\text{LutH}](\text{OTf})$  ( $\text{Lut} = 2,6\text{-lutidine}$ ) or hydrogenated with  $\text{NH}_3\text{BH}_3$  to afford  $\mu_3\text{-NH}$  imido moieties.

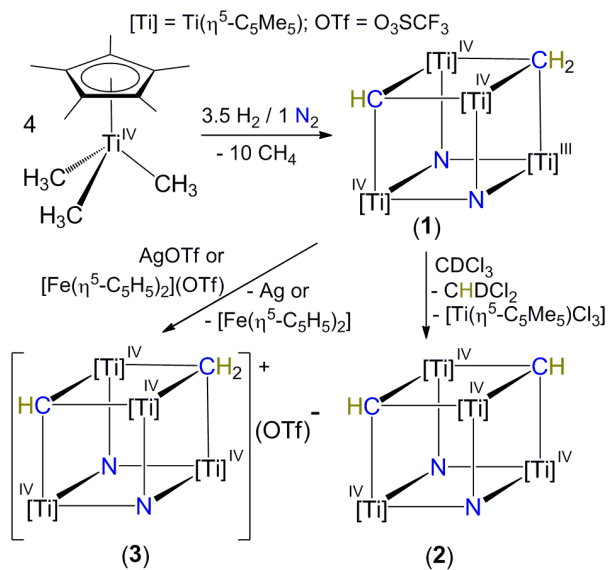
**Keywords:** cage compounds • methylidyne ligands • nitrides • nitrogen fixation • titanium

There is a tremendous interest in the development of molecular systems capable of performing the catalytic conversion of N<sub>2</sub> to NH<sub>3</sub> under mild conditions.<sup>[1]</sup> The industrial synthesis of ammonia in the Haber-Bosch process involves the treatment of a gas mixture of N<sub>2</sub> and H<sub>2</sub> under drastic pressure and temperature conditions using heterogeneous catalysts.<sup>[2]</sup> The first step is believed to be the homolytic splitting of dinitrogen on the surface of the catalyst to give chemisorbed nitrogen atoms bridging several metal centers.<sup>[3]</sup> Analogous reductive cleavage of N<sub>2</sub> to form nitrido (N<sup>3-</sup>) groups is now well-documented in molecular chemistry.<sup>[1]</sup> The active species that break the N≡N bond are low-valent transition metal complexes or derivatives generated by using strong reducing agents such as KC<sub>8</sub>, Na, K or KBHET<sub>3</sub>.<sup>[4]</sup> An alternative route to avoid such reagents is the preparation of hydride complexes that activate N<sub>2</sub> by elimination of H<sub>2</sub> and may provide an entry to homogeneous systems using H<sub>2</sub> as a reductant.<sup>[5]</sup> Nowadays, only a few examples of molecular catalysis for N<sub>2</sub> reduction to ammonia in solution are known.<sup>[6]</sup> The methodology in those catalytic systems involves the addition of a high excess of external acids and reducing agents to well-defined molybdenum<sup>[6a,b,d]</sup>, iron<sup>[6c,e]</sup> or cobalt<sup>[6f]</sup> dinitrogen or nitrido complexes. Nevertheless, molecular hydrogen represents the desirable source of both protons and electrons mimicking the heterogeneous Haber-Bosch process.

Noteworthy, Hou and co-workers recently reported the synthesis of a hydrido-imido tetranuclear titanium complex [(TiCp')<sub>4</sub>(μ-H)<sub>4</sub>(μ<sub>3</sub>-NH)<sub>2</sub>] (Cp' = η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>) by reaction of [TiCp'(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] with a 4:1 H<sub>2</sub>/N<sub>2</sub> mixture at 5 atm and 60 °C.<sup>[7]</sup> A combination of experimental and theoretical studies showed that NH imido groups are

formed by dinitrogen cleavage and subsequent partial hydrogenation on a trinuclear titanium polyhydrido complex. The hydrido-imido tetranuclear species is also capable of cleaving N<sub>2</sub> to give a imido-nitrido cube-type derivative [(TiCp<sup>\*</sup>)<sub>4</sub>(μ<sub>3</sub>-N)<sub>2</sub>(μ<sub>3</sub>-NH)<sub>2</sub>], which is a useful nitrogen source for the preparation of nitriles.<sup>[8]</sup> Here we report the preliminary results on the reaction of [TiCp<sup>\*</sup>Me<sub>3</sub>] (Cp<sup>\*</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) with forming gas (H<sub>2</sub>/N<sub>2</sub> mixture, 13.5–16.5% of H<sub>2</sub>) to produce the paramagnetic methyldiene-methyldiylne-nitrido cluster [(TiCp<sup>\*</sup>)<sub>4</sub>(μ<sub>3</sub>-CH)(μ<sub>3</sub>-CH<sub>2</sub>)(μ<sub>3</sub>-N)<sub>2</sub>] (**1**) via dinitrogen cleavage under ambient conditions. Forming gas is a common, cheap and safe source of a reducing atmosphere of hydrogen in many laboratories. To gain information into the composition and properties of **1**, we have studied its chemical oxidation to obtain diamagnetic derivatives and the subsequent functionalization by protonation and hydrogenation of the nitrido ligands.

The trimethyl derivative [TiCp<sup>\*</sup>Me<sub>3</sub>] in toluene is thermally stable under argon or dinitrogen atmosphere and decomposes at temperatures ≥ 95 °C to the methyldiylne cubane [(TiCp<sup>\*</sup>)<sub>4</sub>(μ<sub>3</sub>-CH)<sub>4</sub>] and methane.<sup>[9]</sup> However, exposure of a yellow hexane solution of [TiCp<sup>\*</sup>Me<sub>3</sub>] to 1 atm of forming gas at room temperature resulted in the precipitation of **1** as dark brown crystals in 40% yield (Scheme 1). A higher yield of **1** (63%) was obtained by heating the reaction mixture at 65 °C. Whereas single crystals of **1** were also isolated when the reaction was performed in other non-coordinating solvents (toluene, benzene or fluorobenzene), the analogous treatment of pyridine or tetrahydrofuran solutions of [TiCp<sup>\*</sup>Me<sub>3</sub>] with forming gas gave the starting mononuclear titanium complex unaltered.



**Scheme 1.** Reaction of [TiCp\*Me<sub>3</sub>] with forming gas.

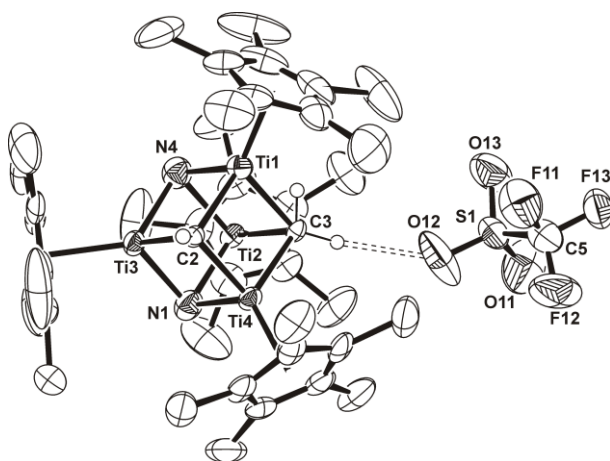
The crystal structure of **1** shows a Ti<sub>4</sub> tetrahedron with each face capped by one  $\mu_3$ -EH<sub>n</sub> (E = C or N) ligand (Figure S1 in the Supporting Information).<sup>[10]</sup> Thus, **1** contains an almost perfect [Ti<sub>4</sub>( $\mu_3$ -E)<sub>4</sub>] cube-type core, with averaged E–Ti–E and Ti–E–Ti angles of 89.3(5) and 90.7(9)°, respectively. The Ti–E and Ti–Ti separations (av. 2.005(18) and 2.854(16) Å respectively) range between those found in the cube-type methylidyne [(TiCp\*)<sub>4</sub>( $\mu_3$ -CH)<sub>4</sub>] (av. Ti–C = 2.052(7) and Ti···Ti = 2.893(2) Å)<sup>[9]</sup> and nitrido [(TiCp\*)<sub>4</sub>( $\mu_3$ -N)<sub>4</sub>] (av. Ti–N = 1.938(7) and Ti···Ti = 2.783(2) Å)<sup>[11]</sup> complexes. While the identity of the triply bridging ligands cannot be unambiguously established from the crystallographic data, they could be assigned as two  $\mu_3$ -N, one  $\mu_3$ -CH and one  $\mu_3$ -CH<sub>2</sub> groups according to spectroscopic data and reactivity studies. Thus, the <sup>1</sup>H NMR spectra in [D<sub>6</sub>]benzene or [D<sub>1</sub>]chloroform show three far-downfield ( $\delta$  = 10.6–8.3 ppm) and broad resonances for the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligands in a 1:1:2 ratio in accord with a C<sub>s</sub> symmetry in solution. We have recently reported comparable resonance signals in the <sup>1</sup>H NMR spectra of several paramagnetic tetrametallic species with [MTi<sub>3</sub>( $\mu_3$ -NH<sub>n</sub>)<sub>4</sub>] (M = Y, Ti, Zr) cube-

type cores where an unpaired electron is delocalized among the titanium atoms.<sup>[12]</sup> The analogous paramagnetic nature of **1** was confirmed by an Evans method determination of its magnetic susceptibility ( $\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$ , 293 K,  $\text{CDCl}_3$  solution). The IR spectrum (KBr) of **1** is apparently uninformative but the lack of N-H stretches ruled out the presence of NH functions in the compound. However, protonolysis of **1** with an excess of anhydrous hydrogen chloride (1M in  $\text{Et}_2\text{O}$ ) in toluene at 60 °C afforded a white precipitate of  $\text{NH}_4\text{Cl}$  (90% for 2 equiv) and a red solution of  $[\text{TiCp}^*\text{Cl}_3]$  (86% for 4 equiv). In addition, the treatment of **1** in  $[\text{D}_6]$ benzene with deuterotrifluoromethanesulfonic acid (DOTf) gave a solution where  $\text{CH}_2\text{D}_2$  ( $\delta = 0.12$  ppm, quint,  ${}^2J(^1\text{H}, {}^2\text{H}) = 2.0$  Hz) and  $\text{CHD}_3$  ( $\delta = 0.11$  ppm, sept,  ${}^2J(^1\text{H}, {}^2\text{H}) = 2.0$  Hz) were detected by  ${}^1\text{H}$  NMR spectroscopy.

Compound **1** is poorly soluble in hydrocarbon solvents, pyridine, or tetrahydrofuran but exhibits a good solubility in  $[\text{D}_1]$ chloroform, although it reacts slowly with this solvent at room temperature. The reaction of **1** with  $\text{CDCl}_3$  is faster at 85 °C, and analysis by  ${}^1\text{H}$  NMR spectroscopy of the resulting solution revealed resonance signals for  $\text{CHDCl}_2$  ( $\delta = 5.32$  ppm, t,  ${}^2J(^1\text{H}, {}^2\text{H}) = 1.0$  Hz),  $[\text{TiCp}^*\text{Cl}_3]$ , and the diamagnetic methylidyne-nitrido species  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})_2(\mu_3\text{-N})_2]$  (**2**). Complex **2** was isolated in 60% yield as a dark brown solid through the reaction of **1** with  $\text{CDCl}_3$  ( $\geq 2$  equiv) in toluene at 85 °C. The  ${}^1\text{H}$  NMR spectrum of **2** in  $[\text{D}_6]$ benzene shows two sharp singlets for the  $\eta^5\text{-C}_5\text{Me}_5$  ligands in a 1:1 ratio in accordance with a  $C_{2v}$  symmetry in solution. The methylidyne groups appear as a singlet at  $\delta = 15.24$  ppm in the  ${}^1\text{H}$  NMR spectrum, and the  ${}^{13}\text{C}\{^1\text{H}\}$  NMR signal of these ligands occurs at  $\delta = 393.7$  ppm. Similar downfield resonances have been reported for other polynuclear titanium(IV) complexes with  $\mu_3\text{-CH}$  ligands.<sup>[9,13]</sup>

The paramagnetic complex **1** readily reacted with 1 equiv of silver(I) trifluoromethanesulfonate in toluene at room temperature to produce a brown solution and a

dark precipitate containing the diamagnetic ionic derivative  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})(\mu_3\text{-CH}_2)(\mu_3\text{-N})_2](\text{OTf})$  (**3**) ( $\text{OTf} = \text{O}_3\text{SCF}_3$ ) and silver metal (Scheme 1). The solution was cooled to  $-30$  °C to give a few deep red crystals of  $\mathbf{3}\cdot\text{C}_7\text{H}_8$  suitable for an X-ray crystal structure determination.<sup>[10]</sup> The crystal structure of **3** contains a cationic fragment with a  $[\text{Ti}_4(\mu_3\text{-CH})(\mu_3\text{-CH}_2)(\mu_3\text{-N})_2]$  cube-type core associated with the triflate anion through a  $\text{C-H}\cdots\text{O}$  hydrogen-bonding interaction<sup>[14]</sup> between the methyldene ligand and one of the oxygen atoms ( $\text{C}(3)\cdots\text{O}(12)$  distance of  $3.391(7)$  Å)<sup>[15]</sup> (Figure 1). Furthermore, the methyldyne group is also involved in a  $\text{C-H}\cdots\text{O}$  hydrogen bond with an oxygen atom of another triflate anion ( $\text{C}(2)\cdots\text{O}(11)$  a length of  $3.485(7)$  Å) leading to zigzag chains (Figure S2). The existence of those interactions allows the unambiguous identification of all the triply bridging ligands in the cube-type  $[\text{Ti}_4(\mu_3\text{-CH})(\mu_3\text{-CH}_2)(\mu_3\text{-N})_2]$  units of **3**. Noteworthy, all Ti–N and Ti–C distances are within the narrow range of  $2.038(4)$ – $2.066(4)$  Å and the averaged Ti–E (E = C or N) and Ti $\cdots$ Ti separations of  $2.050(10)$  and  $2.844(13)$  Å respectively, compare well with those found in **1**.



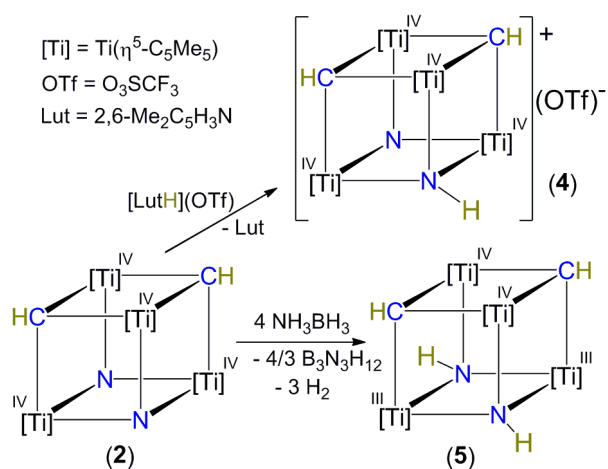
**Figure 1.** Perspective view of complex  $\mathbf{3}\cdot\text{C}_7\text{H}_8$  (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the  $\eta^5\text{-C}_5\text{Me}_5$  ligands and the toluene solvent molecule are omitted for clarity. Selected averaged lengths (Å) and angles (°): Ti–N  $2.050(12)$ , Ti–C(2)



2.053(9), Ti–C(3) 2.046(7), Ti···Ti 2.844(13), E–Ti–E 92.1(5), Ti–E–Ti 87.8(5) (E = C or N).

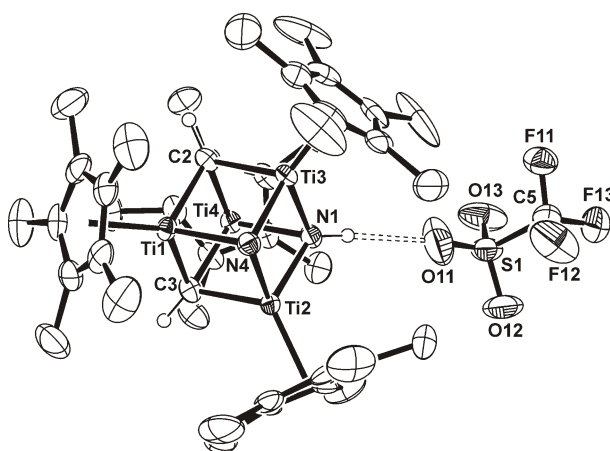
Compound **3** was isolated in higher yield (51%) as a dark brown precipitate by the treatment of **1** with 1 equiv of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2](\text{OTf})$  in toluene at room temperature. The ionic complex **3** is virtually insoluble in common organic solvents and reacts immediately with  $[\text{D}_1]$ chloroform. The  $^1\text{H}$  NMR spectrum of **3** in  $[\text{D}_6]$ benzene shows three sharp singlets for the  $\eta^5\text{-C}_5\text{Me}_5$  groups in a 1:2:1 ratio in accordance with a  $C_s$  symmetry in solution. In addition, the spectrum reveals two singlets at  $\delta = 15.05$  and 3.34 ppm attributable to one methylidyne and one methylene ligands, respectively. Unfortunately, the low solubility of **3** in non-reactive solvents precluded its characterization by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy and other NMR experiments. To our knowledge, compound **3** represents the first structurally documented example of a methylene bridging three group 4 metal centers,<sup>[16]</sup> although several polymetallic rare-earth metal complexes with  $\mu_3\text{-CH}_2$  ligands have been reported.<sup>[17,18]</sup>

Protonation of **2** with 1 equiv of 2,6-lutidinium trifluoromethanesulfonate in toluene at room temperature led to the ionic derivative  $[(\text{TiCp}^*)_4(\mu_3\text{-CH})_2(\mu_3\text{-N})(\mu_3\text{-NH})](\text{OTf})$  (**4**) (Scheme 2). Compound **4** was isolated in 56% yield as a green solid which is poorly soluble in hydrocarbon solvents at room temperature and reacts with  $[\text{D}_1]$ chloroform to give **2** and other unidentified products. However, complex **4** shows an enhanced solubility at higher temperatures, and through slow cooling of a heated benzene- $\text{d}_6$  solution at 80 °C, suitable single crystals of  $\mathbf{4}\cdot\text{C}_6\text{D}_6$  for an X-ray crystal structure determination were obtained.<sup>[10]</sup>



**Scheme 2.** Protonation and hydrogenation of **2**.

The solid-state structure of complex **4** contains a cationic fragment with a  $[\text{Ti}_4(\mu_3\text{-CH})_2(\mu_3\text{-N})(\mu_3\text{-NH})]$  cube-type core associated to the triflate anion through a  $\text{N-H}\cdots\text{O}$  hydrogen bonding interaction between the imido ligand and one of the oxygen atoms ( $\text{N}(1)\cdots\text{O}(11)$  and  $\text{H}(1)\cdots\text{O}(11)$  distances of 3.380(5) and 2.42(4) Å respectively, and  $\text{N}(1)\text{-H}(1)\cdots\text{O}(11)$  angle of 175(4)°) (Figure 2). The averaged  $\text{Ti-N}(1)$  bond lengths of 2.048(9) Å are similar to the remaining  $\text{Ti-E}$  ( $\text{E} = \text{C}$  or  $\text{N}$ ) distances within the cube-type core of 2.043(15) Å. The IR spectrum (KBr) shows one broad band at  $3210 \text{ cm}^{-1}$  for the  $\nu_{\text{NH}}$  vibration and several strong absorptions in the range  $1280\text{--}1030 \text{ cm}^{-1}$  for the triflate group. The  $^1\text{H}$  NMR spectrum of **4** in  $[\text{D}_6]$ benzene at room temperature reveals three singlets in a 2:1:1 ratio for the  $\eta^5\text{-C}_5\text{Me}_5$  ligands in accord with a  $C_s$  symmetric structure in solution. In addition, the spectrum shows a broad resonance signal at  $\delta = 14.72 \text{ ppm}$  for the NH group and a singlet at  $\delta = 15.59 \text{ ppm}$  for two methyldiylne ligands. The low solubility of **4** in non-reactive solvents precluded its characterization by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy.



**Figure 2.** Perspective view of complex **4**·C<sub>6</sub>D<sub>6</sub> (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligands and the benzene solvent molecule are omitted for clarity. Selected averaged lengths (Å) and angles (°): Ti–N(1) 2.048(9), Ti–E 2.044(13), Ti···Ti 2.842(8), E–Ti–E 91.9(8), Ti–E–Ti 88.0(6) (E = C or N).

The treatment of **2** with 4 equiv of ammonia borane in toluene at 85 °C led to the imido-methylidyne cluster [(TiCp\*)<sub>4</sub>( $\mu_3$ -CH)<sub>2</sub>( $\mu_3$ -NH)<sub>2</sub>] (**5**) as a dark brown precipitate in 50% yield (Scheme 2). We have recently reported the partial hydrogenation of the nitrido complex [(TiCp\*)<sub>4</sub>( $\mu_3$ -N)<sub>4</sub>] with NH<sub>3</sub>BH<sub>3</sub> (2 equiv) to give the paramagnetic imido-nitrido derivative [(TiCp\*)<sub>4</sub>( $\mu_3$ -N)<sub>3</sub>( $\mu_3$ -NH)].<sup>[12b]</sup> In a fashion similar to that transformation, the reaction of **2** with NH<sub>3</sub>BH<sub>3</sub> in [D<sub>8</sub>]tetrahydrofuran at 85 °C was monitored by <sup>11</sup>B NMR spectroscopy and the spectra showed one triplet resonance [ $\delta$  = –10.5 ppm; <sup>1</sup>J(B,H) = 101.4 Hz] assigned to cyclotriborazane (CTB; [NH<sub>2</sub>BH<sub>2</sub>]<sub>3</sub>) and minor resonance signals for borazine and polyborazylene.<sup>[19]</sup> However, the diamagnetic nature of **5** is consistent with the hydrogenation of the two  $\mu_3$ -nitrido ligands of **2** with concomitant two-electron reduction of the Ti<sub>4</sub> core similar to that observed in the electronic structure of [(RCC)Zn{( $\mu_3$ -NH)<sub>3</sub>Ti<sub>3</sub>Cp\*<sub>3</sub>( $\mu_3$ -NCCR)}].<sup>[20]</sup> The molecular structure of **5** shows a [Ti<sub>4</sub>( $\mu_3$ -E)<sub>4</sub>] cube-type core (Figure S3) similar to those found for complexes **1**, **3** and **4**, with

averaged Ti–E (E = C or N) and Ti–Ti distances of 2.040(4) and 2.809(1) Å, respectively.<sup>[10]</sup> The <sup>1</sup>H NMR spectrum of **5** in [D<sub>1</sub>]chloroform shows two sharp singlets for the η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> groups in a 1:1 ratio, one singlet at δ = 15.68 ppm for two methylidyne ligands and a broad resonance signal at δ = 12.72 ppm for the NH groups in accordance with a C<sub>2v</sub> symmetry in solution. The IR spectrum (KBr) shows the N–H stretching modes at 3309 and 3259 cm<sup>-1</sup> as the two absorptions expected for C<sub>2v</sub> symmetry (A<sub>1</sub> and B<sub>2</sub> vibrations).

In summary, we have shown that hydrocarbon solutions of [TiCp\*Me<sub>3</sub>] react with forming gas under ambient conditions to give the paramagnetic tetranuclear methylidene-methylidyne-nitrido complex [(TiCp\*)<sub>4</sub>(μ<sub>3</sub>-CH)(μ<sub>3</sub>-CH<sub>2</sub>)(μ<sub>3</sub>-N)<sub>2</sub>] (**1**) via dinitrogen cleavage. One-electron oxidation of **1** yielded titanium(IV) diamagnetic derivatives which are more amenable to detailed structural characterization and reactivity studies. Thus, the μ<sub>3</sub>-nitrido ligands of [(TiCp\*)<sub>4</sub>(μ<sub>3</sub>-CH)<sub>2</sub>(μ<sub>3</sub>-N)<sub>2</sub>] (**2**), derived from dinitrogen splitting, can be subsequently functionalized by partial protonation or hydrogenation to yield μ<sub>3</sub>-NH imido moieties. The presence of μ<sub>3</sub>-methylidene and μ<sub>3</sub>-methylidyne groups in **1** is indicative of the incomplete hydrogenolysis of all the titanium-carbon(methyl) bonds in the mononuclear [TiCp\*Me<sub>3</sub>] precursor.<sup>[21]</sup> We are currently investigating the reactivity of other early transition metal complexes with H<sub>2</sub>/N<sub>2</sub> mixtures with the aim to uncover more novel findings in the area of molecular nitrogen activation and functionalization.<sup>[22]</sup>

## Acknowledgements

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