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Ammonia Activation by μ_3-Alkylidyne Fragments Supported on a Titanium Molecular Oxide Model

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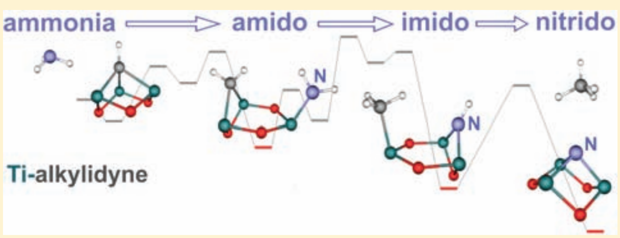
Supporting Information



ABSTRACT: Ammonolysis of the μ_3-alkylidyne derivatives $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] produces a trinuclear oxonitride species, $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)]$ (**3**), via methane or ethane elimination, respectively. During the course of the reaction, the intermediates amido μ-alkylidene $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHR)(NH_2)]$ [(R = H (**4**), Me (**5**)] and μ-imido ethyl species $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}NH)Et]$ (**6**) were characterized and/or isolated. This achievement constitutes an example of characterization of the three steps of successive activation of N−H bonds in ammonia within the same transition-metal molecular system. The N−H σ-bond activation of ammonia by the μ_3-alkylidyne titanium species has been theoretically investigated by DFT method on $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ model complex. The calculations complement the characterization of the intermediates, showing the multiple bond character of the terminal amido and the bridging nature of imido ligand. They also indicate that the sequential ammonia N−H bonds activation process goes successively downhill in energy and occurs via direct hydron transfer to the alkylidyne group on organometallic oxides **1** and **2**. The mechanism can be divided into three stages: (i) coordination of ammonia to a titanium center, in a trans disposition with respect to the alkylidyne group, and then the isomerization to adopt the cis arrangement, allowing the direct hydron migration to the μ_3-alkylidyne group to yield the amido μ-alkylidene complexes **4** and **5**, (ii) hydron migration from the amido moiety to the alkylidene group, and finally (iii) hydron migration from the μ-imido complex to the alkyl group to afford the oxo μ_3-nitrido titanium complex **3** with alkane elimination.

INTRODUCTION

The activation of the ammonia molecule has attracted considerable interest because it is a synthetic precursor for a wide range of commercially useful products. Most of the chemistry of ammonia is dominated by its nucleophilicity due to the presence of a lone pair at nitrogen, the high N−H bond dissociation energy ($\sim 104 \pm 2$ kcal mol^{-1}),[1] and the scarce tendency to form N−H σ complexes.[2] In consequence, the majority of the reactions of ammonia with transition metal complexes generate Lewis acid−base adducts,[3] the activation of its N−H bonds still being unusual.[4−6]

Relatively few examples of ammonia N−H bond activation processes by direct use of ammonia have been reported to synthesize amido complexes (M−NH$_2$). Most of them have been prepared via the oxidative addition of ammonia to a transition-metal complex (Scheme 1, path a).

Only recently have Hartwig and co-workers reported the first stable mononuclear amido hydride species via cleavage of one of the N−H bonds of ammonia molecule by a Ir(I) complex with an aliphatic PCP ligand.[5] Interestingly, the same authors showed that in the case of an aromatic PCP ligand the reverse reaction to give a σ-bonded NH$_3$ complex via reductive elimination takes place.[7] More recently have Turculet and co-workers detailed the formation of an isolable complex of the type $[\{CyPSiP\}Ir(H)(NH_2)]$ (Cy-PSiP = κ^3-$(2\text{-}Cy_2PC_6H_4)_2SiMe$),[8] significantly more resistant to N−H bond reductive elimination than the (PCP)Ir pincer systems previously mentioned.[5,7] The groups of Mindiola and Ozerov have achieved the activation of ammonia via a binuclear oxidative addition using a dinuclear palladium (PNP) pincer species to give monomeric species.[9] Alternatively, the H$_2$N−H bond-breaking processes can also lead to the formation of dinuclear bridging amido species such as $[\{Ir(\mu\text{-}NH_2)(PEt_3)\}_2]$[3a] and *cis*-$[\{Ir(PEt_3)_2(NH_3)H(\mu\text{-}NH_2)\}_2]$[10] reported by Milstein, and $[Ir(4\text{-}C_5NF_4)(H)(\mu\text{-}NH_2)(NH_3)\{PPr^i_3\}]_2$ reported by Braun.[11] There have been examples of oxidative addition of ammonia to trimetallic systems with a cooperative action of the metal centers. The osmium trinuclear carbonyl cluster, $[Os_3(CO)_{11}(L)]$ (L = *c*-C$_6$H$_8$ or CH$_3$CN), reacts with ammonia to produce the complex $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NH_2)]$, where two osmium centers support a μ-amido moiety.[12]

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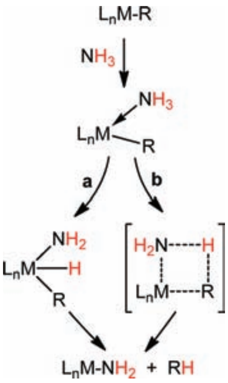
Scheme 1



The oxidative addition can be also achieved by main group elements. Bertrand and co-workers[13] published a facile splitting of ammonia using cyclic and acyclic (alky)(amino)carbenes and their strong nucleophilic character. Research on carbene type species, involving oxidative addition of NH_3 and creating an amide fragment and a terminal hydride ligand, has been further expanded to other group 14 elements by the groups of Power,[14] Roesky,[15] and Stephan.[16] The latter reported a N−H bond cleavage by a frustrated Lewis pairs (FLP) as *N*-heterocyclic carbene/$B(C_6F_5)_3$.

As an alternative to oxidative addition, the N−H bond can be also activated via metal−ligand cooperation without involving oxidative addition of the metal center (Scheme 1, path b).[17] Some complexes containing d^0 early transition metal centers, such as $[(\eta^5\text{-}C_5Me_5)_2MH_2]$ (M = Zr, Hf)[18] and $[(\eta^5\text{-}C_5Me_5)_2ScR]$ (R = H, Me)[17c] or $[\{(Me_3Si)_2N\}_3MCl]$,[19] react with ammonia to yield amide complexes and H_2, methane, or hydrogen halide elimination, respectively. Carbene type derivatives $[Ar_2M]$ (M = Sn,[20] Mn, Fe;[21] Ar = bulky terphenyl ligands) afford bridging μ-amide complexes with arene elimination. Milstein and co-workers have reported a novel type of reversible N−H bond activation by ruthenium complexes modified with pyridine-based PNP pincer ligand that involves hydrogen transfer to an unsaturated bond of the ligand, leading to aromaticity of the central pyridine ring.[22] Very recently have Driess and co-workers reported an ammonia N−H bond activation by a silylene ligand in a $LSi(II) \rightarrow Ni(CO)_3$ complex.[23]

Apart from single N−H activation, further N−H bond cleavage to yield imide and nitride complexes has been also reported; however, these examples are still rare. Some tantalum complexes promote a second N−H bond cleavage of ammonia to yield imide complexes of the type $[(\eta^5\text{-}C_5Me_5)_2Ta({=}NH)H]$[24] and $[\{(Me_3SiNCH_2CH_2)_3N\}Ta{=}NH]$.[25] Another interesting example, which constitutes a bridge of knowledge between the organometallic chemistry and the surface chemistry, was reported by Basset, Emsley, Quadrelli, and co-workers.[26] The authors showed that a solid-supported tantalum hydrido $[(\equiv SiO)_2TaH]$ converts into the imido amido surface complex $[(\equiv SiO)_2Ta(NH)(NH_2)]$ by reaction with ammonia. Similar to the osmium trinuclear cluster mentioned above, Suzuki and co-workers reported the ammonia oxidative addition over the triruthenium complex $[\{(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2]$ to form the μ_3-imido cluster $[\{(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)\}_3(\mu_3\text{-}NH)]$.[27]

Finally, the activation of ammonia via cleavage of the three N−H bonds leading to nitrido species is rather scarce.[28] The first example of such a process was reported by Roesky and co-workers, who synthesized the titanium imido nitrido $[\{(\eta^5\text{-}C_5Me_5)Ti(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$, by reaction of $[(\eta^5\text{-}C_5Me_5)TiMe_3]$ with excess of ammonia and loss of methane at room temperature.[29] Ammonia N−H bonds activation was further expanded by Wolczanski to other tantalum[30,31] and zirconium[32] nitrido derivatives. Some linear nitrido complexes of the type $[X(NH_3)_4OsNOs(NH_3)_4X]Cl_n$ (X = NH_3, Cl)[33] were prepared by reaction of $(NH_4)_2[OsCl_6]$ with hydrazine hydrate involving disproportionation of hydrazine into N_2 and NH_3. A similar result is obtained in the thermal treatment of $(NH_4)_2[OsCl_6]$ with concentrated aqueous ammonia.[34] In the 1990s, our research group succeeded in synthesizing the first nitrido organometallic with metalocubane structure $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}N)\}_4]$ by ammonolysis of the amido derivative $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$.[35,36] Similar ammonolysis reactions from $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ or $[Ti(\eta^5\text{-}C_5Me_5)Cl_2(NMe_2)]$ led to the isolation of the species $[Ti_2(\eta^5\text{-}C_5Me_5)_2Cl_3(\mu\text{-}N)(NH_3)]$.[37] Also, ammonolysis of homoleptic metal amide complexes[38] $[M(NR_2)_n]$ provides access to nitrido solids with ammonia as coprecursor.

Besides the studies on synthetic chemistry, quantum mechanical methods have provided some insight into this complex reactivity. The interactions of bare metals and bare metal cations with ammonia, where the N−H activation occurs via oxidative addition to the metal, have been the subject of a number of theoretical investigations.[39,40] To extrapolate the results of ion chemistry in gas phase to organometallic chemistry in solution, one has to analyze the trends from the variation of transition-metal center. Sicilia and co-workers have systematically analyzed the species expected in the dehydrogenation process of ammonia by bare first-row transition-metal cations ($M^+{-}NH_3$, $H{-}M^+{-}NH_2$, $M^+{-}NH_2$, $M^+{-}NH$).[39] For early transition metals, such as Ti^+, the metal−amido and imido binding energies are larger, which can be explained in terms of multiple bond character; that is, the NH_2 and the NH groups are doubly and triply bonded to the metal.[39c] Moreover, the relative energy of the transition states for N−H bond-breaking correlates with the stability of intermediate products, and, consequently in the case of Ti^+, the process does not require energy in excess of reactants. Analogously for bare second row transition metals, Sigbhan and co-workers found that for the metal atoms on the left the ammonia activation has lower barriers than for metals on the right.[40a] However, in both cases, the authors considered gas-phase collisionless conditions, in which the energy of reactants is considered to be the threshold energy. Consequently, the formation of low-energy lying intermediates via ammonia coordination does not affect the kinetics of the system because the excess of energy cannot dissipate in the media. This is not the case in solution chemistry, where the stability of ammonia complex can prevent its N−H activation. Morokuma and co-workers have analyzed the activation of N−H bonds by the organometallic complex CpRh(L), focusing on the trends among different H−R bonds.[41] For this late transition metal complex, the oxidative addition of N−H bond is significantly more difficult than for other model H−R bonds such as $H{-}SiH_3$, H−H, $H{-}CH_3$, or H−OH, because of the depth energy level of the NH_3 complex. Thus, in solution conditions, it will be very difficult to activate the N−H bond of ammonia, explaining why the reported examples of oxidative addition of N−H bond of ammonia are relatively scarce.

Some theoretical studies have alternatively focused on the N−H bond activation via addition across M═X multiple bonds.

Matsubara investigated the hypothetical activation of the N—H bond of ammonia at the double bond between palladium and the ligand, Pd═X (X = Sn, Si, C).[42] Sakaki and co-workers also investigated a hypothetical process, in which the N—H bond is activated by Ti—imido and Ti—alkylidyne complexes, comparing them with the activation of C—H bond of methane.[43] Both groups proposed mechanisms involving coordination of NH_3 by donation of its lone pair, followed by heterolytic breaking of the N—H bond and migration of the hydrogen as hydron. Very interestedly, Sakaki and co-workers predicted that the N—H bond activation of ammonia can be achieved by terminal alkylidyne—titanium complexes. To the best of our knowledge, such process had been never observed until now. Here, we will show that ammonia activation is accomplished by a related bridging μ_3-alkylidyne titanium complex, further supporting previous theoretical prediction. This type of chemistry can also be related to the above-mentioned N—H bond activation by PNP—Ru complexes,[22] with the hydrogen transfer to a multiple bond of the pyridine ligand. The authors complemented their study with DFT calculations to support their claims.[22] Finally, our previous theoretical work on group 4 molecular oxide models has provided us with some insight into the activation of σ bonds such as O—H.[44,45] For the same $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ complexes reported here, calculations showed that the activation of O—H bonds of silanols and alcohols occurs easily via heterolytic bond-breaking with the assistance of titanium bridging oxygen atoms.[45]

Herein, we report the reactions of ammonia with $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)][46] to give rise to the first example of ammonia N—H bonds activation by μ_3-alkylidyne transition metal derivatives. It includes the isolation and structural characterization of the nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)]$ (**3**), corresponding to the complete ammonia N—H bond activation processes. Also, the amido μ-alkylidene $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHR)NH_2]$ [R = H (**4**), Me (**5**)] and the μ-imido-alkyl $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}NH)Et]$ (**6**) intermediates were isolated or detected. According to the DFT calculations performed on the $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**A**) model, the ammonia degradation occurs via direct hydron transfer to the alkylidyne group on the organometallic titanium oxide. To our knowledge, there is no other reported process in which the sequential activation of the three N—H bonds in ammonia has been studied within the same molecular system.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed with use of either glovebox or high vacuum line techniques. Toluene was freshly distilled under argon from sodium. Benzene-d_6 was dried with Na/K alloy, vacuum distilled, and stored under argon. NH_3(g) was purchased from Air Liquide (N-47, 99.999%) and used as supplied. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] was synthesized according to the published procedures.[46]

Elemental analysis (C, H, N) was performed with a Leco CHNS-932 analyzer. NMR spectra were obtained by using Varian NMR System spectrometers, Unity-300 or Mercury-VX, amounts of protonated solvents or carbon of the solvent were used as references, and chemical shifts are reported relative to TMS, benzene-d_6 (^{1}H, δ 7.15; ^{13}C, δ 128.0). Infrared spectra were acquired for samples in KBr pellets on a FT-IR Perkin-Elmer SPECTRUM 2000 spectrophotometer. Mass spectrometry analysis (Electron Impact, EI) was conducted at 70 eV on a Hewlett-Packard 5988 spectrometer.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)]$ (3). Thermal treatment of complexes **1** and **2** with ammonia leads to the formation of the same compound **3**. A 100 mL Carius tube was charged with $[\{Ti\{\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CMe)]$ (**2**) (0.80 g, 1.28 mmol) and 30 mL of toluene. The argon atmosphere was replaced by ammonia while cooling the solution with liquid nitrogen, and then the solution was heated at 75 °C for 72 h. After that, the Carius tube was opened in a glovebox, and the solvent was removed in a vacuum to yield a brown green solid identified as **3** (0.65 g, 83%). A fraction of solid was redissolved in toluene, and the solution was then allowed to slowly evaporate at room temperature to give dark green crystals suitable for X-ray diffraction studies. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): δ = 2.07 (s, 45H, C_5Me_5). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C, TMS): δ = 11.6 (q, J_{CH} = 125.7 Hz, C_5Me_5), 120.7 (m, C_5Me_5). IR (KBr, cm^{-1}): $\bar{\nu}$ = 2909 (s), 2856 (s), 1492 (m), 1435 (m), 1374 (s), 1259 (w), 1101 (w), 1067 (w), 1024 (s), 789 (vs), 687 (vs), 606 (s), 476 (m), 413 (s). EI mass spectrum: m/z (%) 611 (52) $[M]^+$. Anal. Calcd (%) for $C_{30}H_{45}NO_3Ti_3$ (611.30): C, 58.94; H, 7.42; N, 2.29. Found: C, 59.11; H, 7.42; N, 2.30.

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CH_2)NH_2]$ (4). 0.40 g (0.65 mmol) of $[\{Ti\{\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) was placed in an amber-stained 100 mL Carius tube with a Young valve and dissolved in 30 mL of toluene. The argon atmosphere was replaced by ammonia while the solution was maintained at 0 °C. After 16 h of stirring at room temperature, the solvent was removed in a vacuum, and the solid residue was extracted with ~20 mL of hexane. The solution was filtered and dried to afford a red solid identified as **4** (0.14 g, 34%). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): δ = 2.02 (s, 30H, C_5Me_5), 2.06 (s, 15H, C_5Me_5), 5.11 (bs, 2H, NH_2), 5.99, 6.38 (AB spin system, 2H, $^2J_{HH}$ = 9.3 Hz, μ-CH_2). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C, TMS): δ = 11.7, 11.8 (q, J_{CH} = 125.3 Hz, C_5Me_5), 119.8, 121.8 (m, C_5Me_5), 185.5 (t, J_{CH} = 124.8 Hz, μ-CH_2). IR (KBr, cm^{-1}): $\bar{\nu}$ = 3402 (w, N—H), 3310 (w, N—H), 2907 (s), 2854 (m), 1508 (m), 1431 (m), 1375 (m), 1166 (w), 1068 (w), 1024 (w), 766 (vs), 679 (s), 648 (s), 626 (m), 607 (m), 490 (w), 470 (w), 417 (m), 389 (m). EI mass spectrum: m/z (%) 611 (32) $[M - CH_4]^+$. Anal. Calcd (%) for $C_{31}H_{49}NO_3Ti_3$ (627.34): C, 59.35; H, 7.87; N, 2.23. Found: C, 59.92; H, 8.05; N, 2.48.

Characterization of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHMe)NH_2]$ (5). Twenty milligrams (0.03 mmol) of **2**, placed in an amber-stained NMR tube with a Young valve, was dissolved in benzene-d_6 (0.6 mL), and the argon atmosphere was replaced by ammonia while the solution was cooled with liquid nitrogen. After 5 min, the reaction was checked by ^{1}H NMR, allowing the detection of complex **5**. ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): δ = 1.98 (s, 30H, C_5Me_5), 2.02 (s, 15H, C_5Me_5), 2.27 (d, 3H, $^3J_{HH}$ = 7.8 Hz, μ-CHMe), 5.26 (bs, 2H, NH_2), 6.27 (q, 1H, $^3J_{HH}$ = 7.8 Hz, μ-CHMe).

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}NH)Et]$ (6). The preparation was similar to that for **4**, but with **2** (0.30 g, 0.48 mmol) in toluene (30—40 mL) and stirring 25 h at room temperature to give **5** as a violet solid (0.26 g, 83%). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C, TMS): δ = 0.98 (q, 2H, $^3J_{HH}$ = 7.8 Hz, CH_2Me), 1.55 (t, 3H, $^3J_{HH}$ = 7.8 Hz, CH$_2Me$), 1.97 (s, 30H, C_5Me_5), 2.07 (s, 15H, C_5Me_5), 10.77 (bs, 1H, μ-NH). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C, TMS): δ = 11.5, 11.7 (q, J_{CH} = 124.8 Hz, C_5Me_5), 18.1 (q, J_{CH} = 123.7 Hz, CH$_2Me$), 58.7 (t, J_{C-H} = 120.2 Hz, CH_2Me), 120.1, 120.9 (m, C_5Me_5). IR (KBr, cm^{-1}): $\bar{\nu}$ = 3376 (w, N—H), 2909 (vs), 2854 (s), 2720 (m), 1495 (m), 1434 (s), 1375 (s), 1260 (w), 1165 (w), 1066 (m), 1025 (m), 779 (vs), 710 (vs), 628 (vs), 605 (s), 515 (m), 478 (w), 417 (s), 400 (s), 368 (m). EI mass spectrum: m/z (%) 611 (23) $[M - C_2H_6]^+$. Anal. Calcd (%) for $C_{32}H_{51}NO_3Ti_3$ (641.37): C, 59.93; H, 8.02; N, 2.18. Found: C, 59.78; H, 7.57; N, 1.80.

X-ray Analysis of Complex 3. *Crystal Data.* $C_{30}H_{45}NO_3Ti_3$, orange prism 0.29 × 0.27 × 0.20 mm^3, orthorhombic, *Pnam*, a = 11.839(2) Å, b = 13.792(3) Å, c = 19.361(3) Å, from 19 degrees of data,

T = 200(2) K, V = 3161.6(10) Å^3, Z = 4, M_r = 611.37, D_c = 1.284 Mg m^{-3}, μ = 0.768, F(000) = 1288. Data collection and processing: Bruker Nonius KappaCCD diffractometer, Mo Kα λ = 0.71073 Å, graphite monochromator, MiraCol optics, $-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-24 \leq l \leq 24$, $2\theta_{max}$ = 55°, 48 272 reflections collected, 3739 independent reflections (R_{int} = 0.106). The structure was solved, using the WINGX package,[47] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97),[48] 267 parameters with 0 restraints, final R_1 = 0.0494 (for 2879 data with $I > 2\sigma(I)$) and R_1 = 0.0722 for all data, GOF on F^2 = 1.102, largest electron density peak =0.837 e Å^{-3}, and hole = −0.588 e Å^{-3}.

Pentamethylcyclopentadienyl ring linked to Ti(2) presented disorder; it was modeled and refined by using the Shelxl PART command in two different positions with occupancies of 0.553 for C(21)−C(30) and 0.447 for C(31)−C(40) carbon atoms. All non-hydrogen atoms were anisotropically refined, but the mentioned disorder atoms still presented high thermal factors. Hydrogen atoms were positioned geometrically and refined by using a riding model.

CCDC 810704 (**3**) contains the supplementary crystallographic data for this Article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All calculations were performed with the Gaussian 03 series of programs[49] within the framework of the Density Functional Theory (DFT)[50] using the B3LYP functional.[51] A quasi-relativistic effective core potential operator was used to represent the 10 innermost electrons of the Ti atom.[52] The basis set for Ti atoms was that associated with the pseudopotential,[52] with a standard double-ξ LANL2DZ contraction.[49] The 6-31G(d) basis set was used for C, N, and O atoms,[53] the 6-31G(p) basis set was used for the hydrogen of ammonia and the alkylidyne group,[53] whereas the 6-31G basis set was used for the other hydrogens.[53] Geometry optimizations were carried out without any symmetry restrictions, and all stationary points were optimized with analytical first derivatives. Transition states were characterized by single imaginary frequency, whose normal mode corresponded to the expected motion

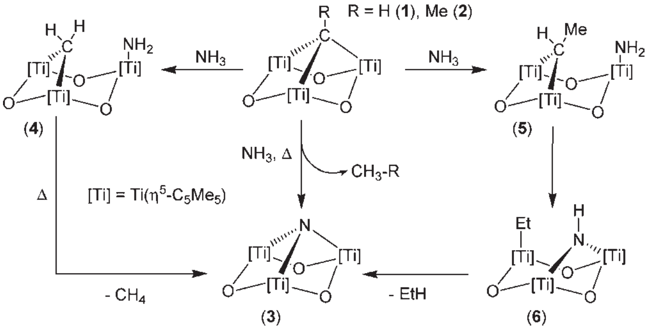
RESULTS AND DISCUSSION

Synthesis of Species Derived from Ammonia NH Bonds Activation. Upon monitoring the ammonolysis of [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-CR)] [R = H (**1**), Me (**2**)] by ^{1}H NMR in benzene-d_6 solutions at room temperature, the presence of the intermediate amido μ-alkylidene species [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ-CHR)(NH$_2$)] [R = H (**4**), Me (**5**)], μ-imido ethyl [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ-NH)Et] (**6**), and the final μ_3-nitrido product [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-N)] (**3**) was revealed as a result of the sequential ammonia N−H bond activation process. A later thermal treatment of the mixture reaction at ∼75 °C for 3 days afforded [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-N)] (**3**) as the unique product (see Scheme 2).

The μ_3-nitrido complex **3** was isolated as green crystals by thermal treatment of **1** or **2** in toluene with an excess of ammonia at 75 °C for 72 h in 83% yield. Complex **3** probed to be stable under argon atmosphere at room temperature and practically soluble in most common solvents (e.g., toluene, hexane, tetrahydrofurane, chloroform). It is noteworthy the single set of signals corresponding to the η^5-C$_5$Me$_5$ ligands indicating the equivalence of all of them in the ^{1}H and ^{13}C NMR spectra of complex **3**, retaining the C_{3v} symmetry of the starting materials **1** and **2**.

As it was mentioned above, during the course of the reaction, the species corresponding to the single and double ammonia N−H bond activation were detected by NMR spectroscopy. In an attempt to isolate them, the reaction conditions (temperature, time of reaction, ammonia exposure, etc.) were modified. Toluene solutions of **1** or **2** placed in an amber-stained Carius tube were treated with ammonia while maintaining the solution at 0 °C. After the excess of NH$_3$ was removed and the mixture was stirred at room temperature, complete conversion was achieved overnight to afford the amido μ-alkylidene complexes [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ-CHR)(NH$_2$)] [(R = H (**4**), Me (**5**)], as a result of the activation of one N−H bond. Compound **4** was isolated as a red solid in 34% yield, probed to be soluble in the habitual solvents (e.g., toluene, hexane), but it is unstable both in solution and in the solid state evolving to provide **3** and other uncharacterized species. The analogous compound **5** was only detected by ^{1}H NMR.

Scheme 2. Ammonolysis of the μ_3-Alkylidyne Complexes [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-CR)] [R = H (1), Me (2)]



The NMR spectra of complexes **4** and **5** display two types of η^5-C$_5$Me$_5$ groups in a 2:1 ratio, consistent with a C_s symmetry and in contrast with the C_{3v} symmetry of the starting materials **1** and **2**. In the ^{1}H NMR spectra, **4** exhibits an AB spin system at δ = 5.99 and 6.38 ($^2J_{H-H}$ = 9.3 Hz) assigned to a μ-methylene moiety, while complex **5** shows a doublet at δ = 2.27 and a quartet at δ = 6.27 ($^3J_{H-H}$ = 7.8 Hz) corresponding to a μ-ethylidene group. Also, narrow signals at δ = 5.11 and 5.26 attributed to the amido fragment Ti−NH$_2$ were observed for complexes **4** and **5**, respectively.

The ^{13}C NMR spectrum of **4** reveals as an important feature the resonance of the μ-methylidene group as a triplet at δ = 185.5, demonstrating a strong high field shift with respect to the starting μ_3-methylidyne product **1** [μ_3-CH, δ = 383.8]. The chemical shift of the signal due to the μ-alkylidene carbon in **4** follows a trend similar to those observed for homo-[45,46b,54,55] and heterodinuclear[56] μ-methylene titanium systems reported in the literature.

In an attempt to isolate the compounds derived of the double ammonia N−H bonds activation, we used a synthetic approach similar to that of **4**, increasing the reaction time. The reaction of **2** with ammonia allowed us to obtain the μ-imido ethyl compound [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ-NH)Et] (**6**) as a violet solid in 83% yield. The preparation of the analogous μ-imido methyl compound from the corresponding amounts of **1** and ammonia affords a mixture of products in which we were able to identify the μ-imido methyl compound together with **3** and another ammonolysis process derivatives. All of our efforts to isolate the analogous to complex **6** were unsuccessful, and no further characterization was possible.

In the ^{1}H NMR spectrum of **6**, two signals corresponding to the η^5-C$_5$Me$_5$ ligands in a 2:1 ratio indicate a C_s symmetry for this species. In addition, a quartet at $\delta = 0.98$ and a triplet at $\delta = 1.55$, assigned to an ethyl bonded to a titanium atom, together with a broad signal at $\delta = 10.77$, attributed to a μ-NH group, were detected. The ^{13}C NMR spectra display as the most remarkable feature the resonance of the alkyl (C_α) moiety as a triplet at $\delta = 58.7$, strong high field shifted with respect to the μ_3-ethylidyne starting material **2** [$\delta(\mu_3\text{-CMe}) = 401.7$].[57]

Structural Study of [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)$] (3). Green crystals of [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)$] (**3**) were obtained in a glovebox at room temperature from a concentrated toluene solution after slow evaporation. The molecular structure of **3** is shown in Figure 1, while Table 1 contains the selected data for **3**, the starting compound **2**, and the isoelectronic species [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$].[29]

Complex **3** has a crystallographic mirror plane, which contains Ti(1), N(1), and O(22). The three pseudotetrahedral titanium atoms are the apexes of a hypothetical equilateral triangle capped by a μ_3-nitride moiety and bridged by the three oxygen atoms to form a six-membered [Ti_3O_3] ring in a chair disposition. As it can be seen in Table 1, the Ti−N bond distances [av 2.066(4) Å] in **3** are clearly longer than those found for the isoelectronic azaderivative [av 1.912(1) Å].[29] The steric restrictions imposed by the [Ti_3O_3] ring make the Ti−N−Ti angles clearly narrower than those found for the tertiary organic amines (~115°) and also than those of the mentioned azaderivative. The nitrogen atom is located 1.27(1) Å above the plane formed by the titanium atoms. This distance is slightly shorter than that observed in the starting μ_3-alkylidine product **2** [1.35(1) Å][46] but longer than that presented by the apical nitrido fragment in [$(\{Ti\{\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (1.03(1) Å).[29]

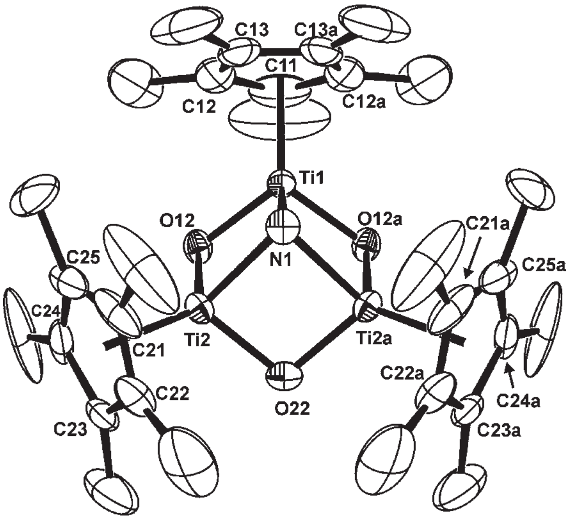


Figure 1. Molecular structure of complex **3** depicting thermal ellipsoids at the 50% probability level. Symmetry transformations used to generate equivalent atoms: a $x,y,-z+{}^1/_2$.

Table 1. Averaged Distances (Å) and Angles (deg) in Isoelectronic and Isostructural Compounds

	[$\{Ti(\eta^5\text{-}C_5Me_5)$ $(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$]	2	3
Ti−(μ_3-N/C_α)	1.912(1)	2.116(1)	2.066(4)
Ti··Ti	2.802(1)	2.818(1)	2.820(1)
Ti−NH/O	1.930(6)	1.829(1)	1.853(1)
Ti−(NH/O)−Ti	93.1(4)	100.8(1)	99.0(1)
O−Ti−O		104.0(7)	104.9(4)
(HN)−Ti−(NH)	107.5(7)		
Ti−(N/C_α)−Ti	94.2(1)	83.5(1)	86.1(1)
N/C_α−Ti−O		86.8(1)	86.5(1)
N−Ti−NH	85.9(1)		

On the other hand, the Ti−O bond distances [av 1.853(1) Å] in **3** are very similar to those observed in other not only trinuclear,[46a,55] but also dinuclear, [$\{Ti(\eta^5\text{-}C_5Me_5)Me(\eta^2\text{-}MeNNCPh_2)\}(\mu\text{-}O)(Ti(\eta^5\text{-}C_5Me_5)Me_2)$] (1.83 Å),[58] and tetranuclear oxocomplexes, [$\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}O)_6\}$] (1.84 Å).[59] Additionally, Ti−O−Ti angles [av 99.0(1)°] are similar to those found in the precubane **2** [av 100.8°][46a] or in the cube-type derivative [$\{Mo(CO)_3\}(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CMe)$] (100.7),[60] but remarkably narrower than those observed in other titanium trinuclear systems where the metal centers are only bridged by oxygen atoms, as, for example, in [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)X\}_3$] (X = Cl 133.9°,[61] Br 134.0°)[62] and [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Me\}_3$] (132.9°).[63]

Structural, Electronic, and Energetic Analysis of the Amido−, Imido−, and Nitrido−Titanium Species. To investigate the successive N−H σ-bond activation of ammonia by the molecular oxides **1** and **2** at a mechanistic level, a theoretical analysis was carried out on the model complex [$\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)$] (**A**). The study of the reaction was started with the search for minimum energy configurations at different intermediates of the ammonolysis process of complex **A**. Thus, we found three minima **D**, **E**, and **F**, which correspond respectively to the three experimentally characterized species, that is, the amido−titanium complex **4**, the μ-imido−titanium complex **6**, and the μ_3-nitrido−titanium complex **3**. Figure 2 shows the molecular structures and the main geometric parameters of **D** and **E**, optimized without any symmetry constraints.

The first N−H bond activation via hydron transfer to the alkylidyne group leads to a μ-alkylidene amido complex. As commented above, the N−H bond activation of ammonia by

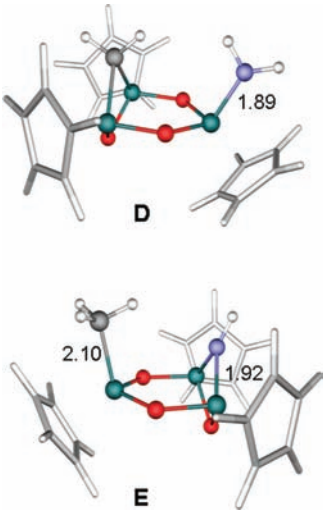


Figure 2. Computed molecular structures (Å) of the amido (**D**) and μ-imido (**E**) intermediates involved in successive N−H bonds activation of ammonia.

Ti—alkylidyne complexes was predicted by theoretical calculations,[43] but it had not been observed until now. In structure **D**, we have considered a ligand arrangement analogous to that obtained by reaction of **1** with diphenylamine to give the X-ray characterized μ-ethylidene diphenylamido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHMe)(NPh_2)]$.[55] Both the alkylidene group bridging two titanium atoms and the amido ligand located on the third titanium center are situated on the same side of the plane formed by the three Ti atoms. The nature as a minimum of this proposed species **D** was confirmed by vibrational analysis showing no imaginary frequencies. Moreover, the formation of **D** from **A** and NH_3 is computed to be energetically favorable by 62 kJ mol^{-1}.

The $[Ti_3O_3]$ core in **D** resembles that of the diphenylamido complex $[\{Ti\{\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CHMe)NPh_2]$,[55] the calculated Ti—O—Ti angle (100.2°) corresponding to the titanium atoms bridged by the μ-alkylidene group is smaller than the other Ti—O—Ti angles (av 128.4°), the values being very close to those of the diphenylamido complex (99.4(1)° and av 127.4°, respectively). Also, the computed average Ti—O (1.83 Å) and Ti—μ-C (2.10 Å) bond lengths in **D** are close to those of the diphenylamido complex (1.84 and 2.11 Å, respectively). On the other hand, **D** exhibits a Ti—N bond length of 1.894 Å, which is somewhat shorter than that for the diphenylamido ligand (2.007 (4) Å). The Ti—N bond elongation in the latter complex can be related to the steric repulsion between the phenyl substituents of the amido ligand and the pentamethylcyclopentadienyl ligands; this steric repulsion is clearly weaker in the ammonia-derived complex. The nitrogen atom in **D** shows a planar environment, allowing a strong p_π—d_π bonding interaction between a vacant d orbital at the Ti center and the amido N-atom lone pair, perpendicular to the NH_2 plane. Indeed, we found a molecular orbital (HOMO−4) formally corresponding to this interaction (see Figure 3). Thus, the NH_2 moiety acts as a four electron donor ligand, the amido group being doubly bonded to titanium as previously suggested by calculations on bare early transition-metal cations.[39c]

The second N—H bond activation leads to an alkyl μ-imido complex via migration of a hydron from the amido ligand to the μ-alkylidene group. In **E**, the methyl group and the imido moiety bridging the other titanium atoms are in a cis disposition (see Figure 2). The nitrogen atom shows a planar environment with Ti—N distances of 1.92 Å (av), close to the value of 1.95 Å (av) found in the phenyl imido moiety of the complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(CH{=}CHPh)(\mu\text{-}NPh)]$.[64] The analysis of frontier molecular orbitals of **E** shows that the first set of unoccupied orbitals are combinations of titanium d atomic orbitals, indicating that the titanium centers remain formally fully oxidized. The HOMO−1 and HOMO−2 orbitals are mixtures between π orbitals of Cp ligands and a nonbonding nitrogen p-type orbital perpendicular to the plane of μ-imido group. This orbital assessment indicates the presence of a lone-pair at the imido group, which is not involved in the Ti—N bonds. On going from **D** to **E**, calculations predict a stabilization energy of 48 kJ mol^{-1} and confirm the nature as a minimum of **E** via frequency analysis.

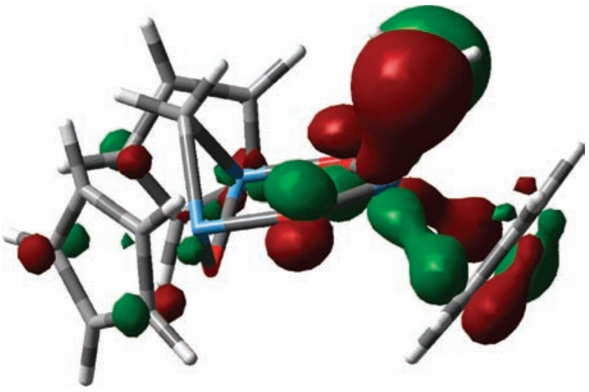


Figure 3. Representation of the p_π—d_π-type orbital HOMO−4 for the amido group in intermediate **D**.

Third, the final step in the sequential N—H bonds activation process leads to methane elimination and the μ_3-nitrido oxo model **F**, already characterized by X-ray analysis as complex **3**. The computed geometry for **F** compares reasonably well with the crystallographic data. The computed Ti—O, Ti—N, and Ti$\cdots$Ti distances in **F** (av 1.84, 1.92, and 2.75 Å), as well as the Ti—O—Ti and Ti—N—Ti angles (av 96.6° and 91.2°), follow the same trend as the experimental values (av 1.854, 2.066, and 2.820 Å; and 99.1° and 86.5°, respectively). The formation of the final complex **F** from **E** is also computed to be exothermic (−62 kJ mol^{-1}). We can conclude that, starting at **A**, the successive N—H activation of ammonia proceed through different stages (**A** → **D** → **E** → **F**), which go downhill in energy (0.0, −62, −110, and −172 kJ mol^{-1}) providing the thermodynamic driving force for the reaction.

Mechanism for the Three N—H Bonds' Activation of Ammonia. The energy profiles of the different studied mechanisms are summarized in Figure 4. For the activation of the first N—H bond, we initially examined a mechanism analogous to that previously reported for the hydron transfer processes between silanols (or alcohols) and the μ_3-methylidyne complex **A**.[45] The first step of this mechanism would involve the hydron transfer from the substrate to one of the oxygen atoms of the Ti_3O_3 ring. Yet the results show qualitative differences with respect to those previously found in the analogous processes involving silanols and alcohols. The approach of NH_3 to the complex **A** does not form any adduct by hydrogen bonding N—H$\cdots$O, but a complex **B** (see Figure 4) with the ammonia coordinated to titanium (Ti—N bond distance 2.39 Å). The short Ti—NH_3 distance indicates that a typical coordinative bond has been formed, in contrast with the weak initial interactions between the titanium atoms and the silanols[45a] or alcohols.[45b] The coordination of NH_3 stabilizes the complex by 49 kJ mol^{-1}.

From **B** (see Figure 4), the computed energy barrier for the ammonia hydron transfer to one oxo group is relatively high (111 kJ mol^{-1}), 2-folds higher than those computed for the CH_3OH (56 kJ mol^{-1}) or SiH_3OH (42 kJ mol^{-1}). Also, the process from **B** to the amido intermediate **C** is computed to be quite endothermic +107 kJ mol^{-1}, leading to a very low inverse energy barrier of about 4 kJ mol^{-1}. All of these data indicate that, in this case, the hydron transfer to one of the oxygen atoms is unlikely. The differences found can be explained from the lower acidity of the hydrogen atoms in ammonia in comparison with those of alcohols and silanols.

Alternatively, we considered a mechanism, in which the hydron transfer to the alkylidyne group occurs directly from the coordinated ammonia. Actually, we located two ammonia titanium intermediates, **B** and **B′**, which result from the approach of the ammonia to two different sides of the titanium center. The ammonia ligand in **B** is located trans with respect to the alkylidyne group, whereas in **B′** it is cis. The trans disposition of the ligand is quite stable, but the cis is not; their energies relative to the reactants are −49 and +15 kJ mol^{-1}, respectively

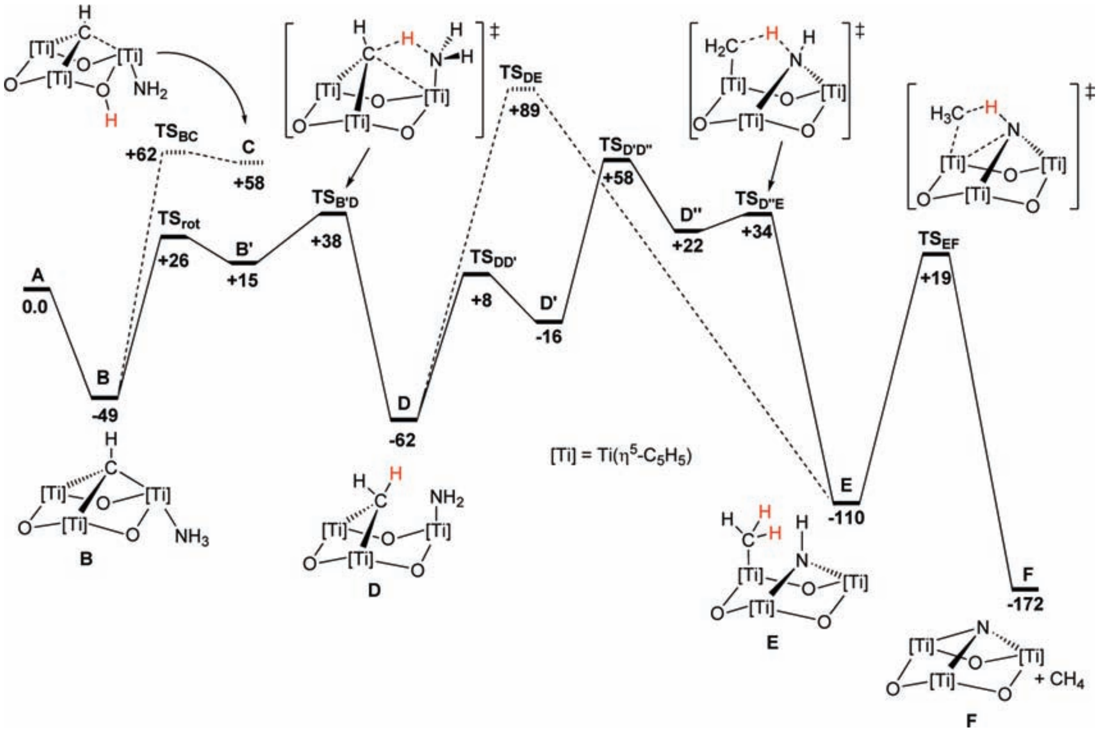


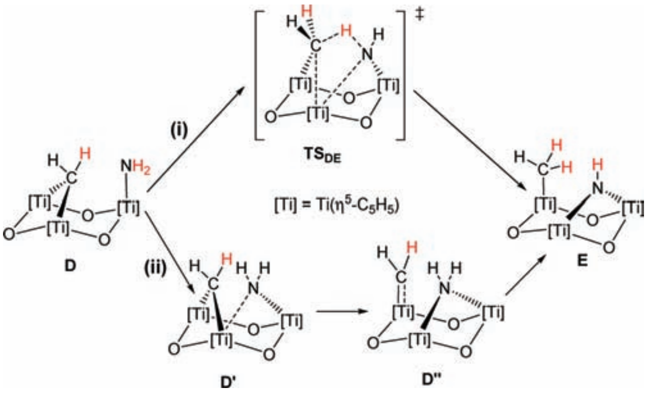
Figure 4. Potential energy profile (kJ mol^{-1}) for the successive N−H bonds activation of NH_3 by [{Ti(η^5-C_5H_5)(μ-O)}$_3$(μ_3-CH)] (**A**).

(see Figure 4). Moreover, the NH_3 approach through the basal region of [{Ti(η^5-C_5H_5)(μ-O)}$_3$(μ_3-CH)] (**A**) complex yielding the trans isomer would be less sterically demanding than the approach through the apical one yielding the cis isomer. Thus, although the hydron migration to the μ_3-alkylidyne group should occur from **B′**, the interaction of NH_3 and **A** most probably forms the trans ammonia intermediate **B**. Next, the **B** complex can undergo an intramolecular rearrangement of the ammonia and the cyclopentadienyl ligands that are not involved in the Ti_3 skeleton to yield **B′**. In both complexes, the ammonia titanium center can be regarded as a trigonal bipyramid structure, with the NH_3 and Cp ligands in axial-equatorial positions for **B** and equatorial-axial for **B′**. The transition state connecting **B** and **B′** species (**TS$_{rot}$**) is a square-based pyramid-type structure, in which the NH_3 and Cp ligands occupy basal positions. The computed energy barrier for the NH_3 rearrangement is modest, amounting 75 kJ mol^{-1} (see Figure 4). Note that an analogous process was proposed for the rearrangement of alkynyl and cyclopentadienyl ligands in a trinuclear imido-nitrido titanium complex, the energy barrier being of the same order of magnitude (62 kJ mol^{-1}).[65] Once **B′** is formed, the hydrogens of ammonia are facing to its neighboring alkylidyne group, allowing the hydron migration to form the amido μ-alkylidene−titanium complex **D**. The estimated migration energy barrier is only 23 kJ mol^{-1}. Thus, the estimated energy barrier for the overall process involving ligand rearrangement and direct hydron transfer from NH_3 amounts to 87 kJ mol^{-1}. This value is significantly lower than that computed for hydron transfer to the oxo groups (111 kJ mol^{-1}), and consequently in this case, we can discard the participation of the oxo groups in the N−H activation.

The interaction of NH_3 with the titanium center in **B′** elongates the Ti−C$_{apical}$ bond length with respect to that in the reactant **A** by 0.28 Å. On going from **A** to **B′**, we also observed that the energy of the HOMO, which is mainly formed by a bonding combination of p orbitals of the bridging carbon atom and d orbitals of the Ti atoms in **B′**, rises significantly from −6.5 to −5.5 eV. This suggests an increase of the basicity of the alkylidyne carbon atom, enough to trap the relatively low acidic hydrogen of ammonia. Recently, Sakaki and co-workers have computationally investigated the hypothetical N−H σ-bond activation by the titanium alkylidyne complex [(PNP)Ti≡$CSiMe_3$] (PNP = *N*-[2-(PH_2)$_2$-phenyl]$_2$$^-$), reporting an activation barrier of 31 kJ mol^{-1} at DFT level,[43] similar to that computed here for the transformation of **B′** to **D** (23 kJ mol^{-1}). The authors concluded that the N−H activation can be easily achieved by the titanium alkylidyne complex, although to the best of our knowledge it had not been yet experimentally observed. Our experimental and computational evidence provides a further proof that the Ti(IV) alkylidyne complexes activate the N−H bonds of ammonia.

In the second N−H activation, the hydrogen atom at the amido group of **D** could directly migrate to the hydrocarbon moiety to afford the μ-imido−titanium complex **E** (Scheme 3i and dashed lines in Figure 4). The energy barrier (**TS$_{DE}$**) for the step from **D** to **E** is calculated to be 151 kJ mol^{-1}, which seems to be too high for a reaction occurring under mild experimental conditions. To achieve this transformation, several processes should occur simultaneously: breaking of the N−H and Ti−C$_{alkylidene}$ bonds, the formation of new C−H and Ti−N bonds, and the rotation of the μ-alkylidene group. In the transition state **TS$_{DE}$**, the breaking N−H and Ti−C bond distances lengthen 0.38 and 0.44 Å, respectively, and the formed C−H (1.40 Å) and Ti−N (2.21 Å) bond distances are significantly shorter than those of the reactants. The μ-alkylidene rotation process is required to allow the hydron migration from the NH_2 ligand. Note that in the reactant **D**, the μ-alkylidene CH_2 ligand is within the same plane of NH_2 ligand with two hydrogen atoms from the two different ligands facing each other (see Figure 2). We have already evaluated the full rotation of the

Scheme 3



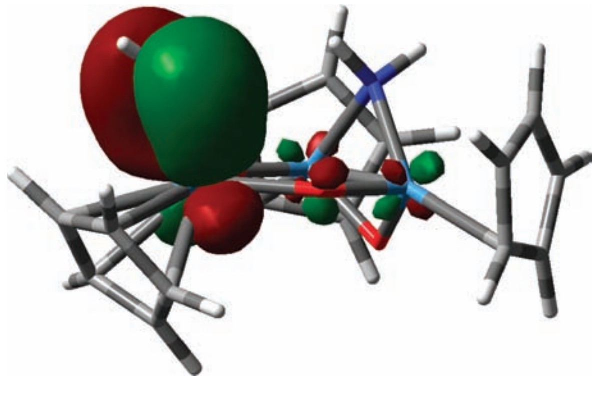


Figure 5. Representation of the p_π−d_π-type orbital HOMO for the alkylidene group in intermediate **D**$''$.

μ-ethylidene ligand in a closely related system amounting to about 129 kJ mol^{-1}.[45a] The latter value together with the other simultaneous processes could explain the high computed energy barrier.

In another possible mechanism for the second N−H activation, the ligands could rearrange previously to the hydron migration, following a stepwise mechanism to reduce the overall energy cost (Scheme 3ii). We located two new intermediates with different rearrangements of the alkylidene and amido ligands: the μ-alkylidene μ-amido−titanium complex **D**$'$ and the alkylidene μ-amido−titanium complex **D**$''$ (for molecular structures, see the Supporting Information). The relative energies of **D**$'$ and **D**$''$ with respect to the intermediate **D** are +46 and +84 kJ mol^{-1}. In the first place, the terminal amido in **D** rearranges into a two-titanium bridging amido ligand in **D**$'$, with the energy cost to reach the **TS**$_{\mathbf{DD'}}$ being a modest 70 kJ mol^{-1}. In **D**$'$, the former Ti−N bond distance lengthens to 2.05 Å, while the new Ti−N bond at the four-legs piano stool Ti center is 2.31 Å. The formation of the new Ti−N bond increases the saturation of the Ti center and in turn weakens the Ti−C$_{\text{alkylidene}}$ bond to be broken in the next step (lengthening of about 0.08 Å). Second, the bridging alkylidene in **D**$'$ rearranges to a terminal alkylidene ligand, with the energy cost to reach the **TS**$_{\mathbf{D'D''}}$ again being a modest 74 kJ mol^{-1}. In **D**$''$, the bond distance between the titanium and the alkylidene carbon is 1.87 Å, significantly shorter than in **D** (2.11 Å). The alkylidene carbon atom shows a strictly planar environment, suggesting that the group acts as a four-electron donor similar to the NH$_2$ moiety in **D** discussed above. In accordance, the HOMO molecular orbital corresponds mainly to a p-type orbital of the alkylidene carbon atom perpendicular to the CH$_2$ plane. At the HOMO, we also observe some stabilizing π-type overlapping with the titanium d orbitals (see Figure 5). Its energy is quite high (−4.6 eV), even higher than for **B**$'$ (−5.5 eV), suggesting an even higher basicity of the carbon atom. Next, once **D**$''$ is formed, an amido hydrogen can easily migrate as hydron to the alkylidene carbon via rotation of the terminal alkylidene ligand. The energy cost to reach **TS**$_{\mathbf{D''E}}$ is a very low 12 kJ mol^{-1}, in agreement with the predicted high basicity of the terminal alkylidene carbon. In **TS**$_{\mathbf{D''E}}$, the calculated Ti−H distance is significantly larger (2.38 Å) than that found in the hydron migration from oxo to alkylidyne group in related complexes (1.88 Å),[45a] suggesting that the titanium center plays a minor role.

As observed in our previous reactivity studies on these trinuclear titanium molecular systems,[45,65] the available empty low-energy titanium d orbitals could play an important role in this reaction via stabilization of the ligands such as the terminal amido, the bridging amido, and the terminal alkylidene ligands. Nevertheless, in the case of the terminal alkylidene complex **D**$''$, the very low energy barrier calculated for the hydron migration shows that the **D**$''$ species is not a very stable minimum and suggests that the existence or nonexistence of the terminal alkylidene complex as a reaction intermediate in the overall mechanism will depend on the particular nature of the system. A slight destabilization of this intermediate would cause the hydron transfer to pass from a three-step to a two-step process. In summary, the overall energy barrier for the stepwise mechanism of the second N−H activation is determined by the energy difference between the lowest energy intermediate **D** and the highest energy point **TS**$_{\mathbf{D'D''}}$, amounting to 120 kJ mol^{-1}. The ligands of complex **D** rearrange intramolecularly (**D** → **D**$'$ → **D**$''$), climbing the energetic ladder (−62 → −16 → +22 kJ mol^{-1}) to reach a ligand disposition favorable for the hydron migration. This new estimation of the energy barrier is in better agreement with experimental observations than that for the direct hydron transfer (**TS**$_{\mathbf{DE}}$).

Finally, in the last N−H bond activation, the hydrogen atom at the imido group of **E** directly migrates to the alkyl group, releasing methane and forming the μ_3-nitrido titanium complex **F**. The process is exothermic (−62 kJ mol^{-1}), and the energy barrier (**TS**$_{\mathbf{EF}}$) is computed to be 129 kJ mol^{-1}, similar to that computed for the previous step (120 kJ mol^{-1}). This last step can be regarded as the inverse process of the methane C−H σ-bond activation by metal nitride complexes.[66] Interestingly, there are several reported examples of arene or alkane C−H σ-bond activation[67,68] via addition of the C−H bond across metal−nitrogen multiple bonds by early transition metal complexes, which include the titanium−imido complex [(^{t}Bu$_3$SiO)$_2$Ti(≡NSi^{t}Bu$_3$)].[69] Moreover, the reactivity of this latter complex has been theoretically investigated by the groups of Cundari[70] and Sakaki.[43] Our studied system, containing a nitrogen atom bridging two titanium atoms instead of Ti═N multiple bonds, shows a transition state geometry similar to those previously calculated for mononuclear Ti−imido complexes. In **TS**$_{\mathbf{EF}}$, the breaking Ti−C bond distance lengths to 2.43 Å and the migrating H atom is at the middle position between C and N atoms, 1.39 and 1.28 Å for C−H and N−H distances, respectively. For the corresponding transition state in the mononuclear Ti−imido complex, the Ti−C, C−H, and N−H distances are qualitatively similar at 2.27, 1.44, and 1.39 Å, respectively.[43] These similarities

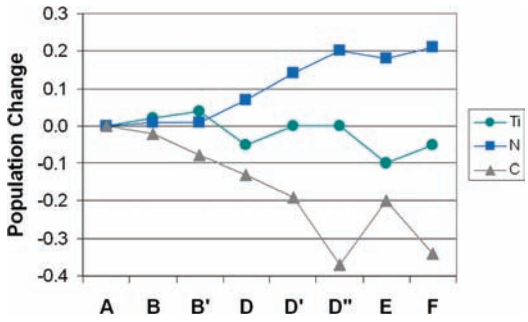


Figure 6. Population changes along the reaction coordinate for the atomic centers involved in the successive hydron transfer (Ti, average value of the three centers). The positive value represents the increase in Mulliken electron population, and the negative value represents the decrease.

suggest that the hydron transfer has the same nature in both complexes. Thus, as in previous studies,[43,70] we also propose that the bond cleavage occurs through a heterolytic manner.

To further clarify the nature of the successive N—H bonds activation of ammonia, we have analyzed the electron population changes along the reaction coordinate. Figure 6 shows the variation of atomic Mulliken electron population at the C and N atoms involved in hydron migration, as well as of the Ti centers (average values). As the reaction proceeds, the electron population of the C atom considerably decreases whereas the N atomic population increases. In both cases, it varies steadily, except in the case of the intermediate **D**″, where the formation of an unstable terminal Ti—alkylidene group causes an abrupt variation of electron population at the alkylidene carbon atom. On the other hand, the average population of the three Ti centers remains relatively unchanged. In the overall reaction, it slightly decreases, but in the ammonia intermediates, **B** and **B**′, it moderately increases, which is attributed to the charge transfer from the ammonia to the Ti center. These results further support that the N—H activation by the polynuclear Ti complex can be understood in terms of heterolytic N—H activation, in which Ti-alkylidyne, -alkylidene, and -alkyl groups act as the basic centers promoting the bond cleavage.

CONCLUSIONS

In this work, we have demonstrated, experimentally and theoretically, that the titanium μ_3-alkylidyne complexes $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ [R = H (**1**), Me (**2**)] can promote the N—H bonds activation of ammonia to give the compound μ_3-nitride $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}N)]$ (**3**). Moreover, it has been possible to isolate and/or characterize the intermediates derived from the sequential ammonia N—H bonds activation, amide-μ-alkylidene $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}CHR)NH_2]$ [R = H (**4**), Me (**5**)] and μ-imide alkyl complexes $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu\text{-}N)Et]$ (**6**), highlighting a marked cooperative effect between the three titanium atoms in the activation of discrete molecules like ammonia. DFT calculations have shown that upon successive N—H activation of ammonia, and the resulting species amide-μ-alkylidene, μ-imide alkyl, and μ_3-nitride with methane elimination, the energy of the system goes downhill (−62, −110, and −172 kJ mol^{-1}), providing the thermodynamic driving force for the reaction.

The mechanism for this sequential N—H bonds activation can be described as follows (see solid line in Figure 4): (i) first, the ammonia coordinates to a titanium center trans to the alkylidyne group, and then isomerizes to adopt the cis arrangement, allowing the direct hydron transfer to the μ_3-alkylidyne group yielding a μ-alkylidene amido titanium complex, (ii) next, the alkylidene and amido ligands rearrange to a favorable disposition for the hydron migration from the amido group to the alkylidene group, and (iii) finally, in the μ-imido complex the hydron directly migrates to the alkyl group releasing methane and forming a μ_3-nitrido oxo titanium complex. All N—H bond activations occur via direct hydron transfer to carbon atom without direct participation of the titanium metal centers. The computed energy barriers of the successive steps are high enough to provide kinetic stability to the different intermediates, allowing their characterization.

The N—H bond activation of ammonia by terminal alkylidyne—titanium complexes had been predicted theoretically,[43] but was never observed. Here, we report a very closely related example, which supports previous predictions and promotes further investigations in titanium—alkylidyne species as potential catalysts in processes involving N—H activation.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information file (CIF) for **3** and tables containing *xyz* coordinates for the most relevant computed structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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