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Martín, A. et al., 2005. Amido-bridged double-cube nitrido complexes containing titanium and magnesium/calcium. Dalton Transactions, 12, pp. 2116-2119.

Available at <https://doi.org/10.1039/B503405A>

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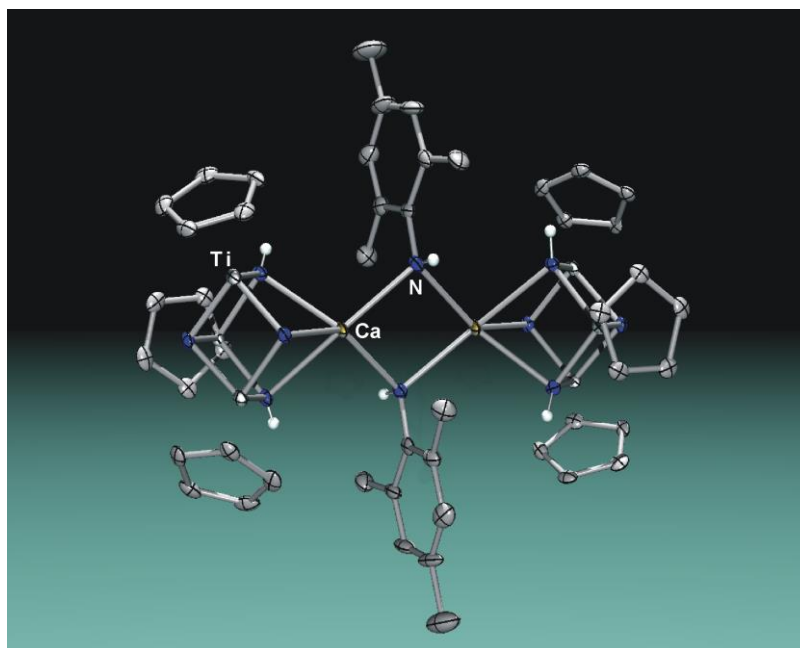
Amido-bridged double cube nitrido complexes containing titanium and magnesium/calcium.

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Graphical contents entry:

The first examples of cube-type $[MTi_3N_4]$ nitrido complexes held together by amido ligands have been isolated and structurally characterized.



Summary:

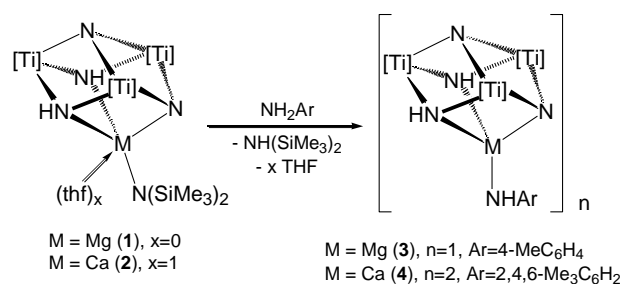
Treatment of the single cube nitrido complexes $[(\text{thf})_x\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]]$ ($\text{M} = \text{Mg}$, $x = 0$; Ca , $x = 1$) with one equivalent of anilines NH_2Ar in toluene affords the arylamido complexes $[(\text{ArHN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]_n$ [$\text{M} = \text{Mg}$ (**3**), $n = 1$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$; Ca (**4**), $n = 2$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$]. The magnesium complex **3** has a single cube structure whereas the X-ray crystal structure of the analogous calcium derivative **4** shows two cube-type azaheterometallobutane moieties “ $\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ ” held together by two μ -2,4,6-trimethylanilido ligands. Complexes **3** and **4** react with chloroform- d_1 at room temperature to give the metal halide adducts $[\text{Cl}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Mg}$, Ca). A solution of **3** in n-hexane gave complex $[\{\text{Mg}_2(\mu_3\text{-N})(\mu_3\text{-NH})_5[\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})]_2\}(\mu\text{-NHAr})_3]$ which shows three μ -4-methylanilido ligands bridging two $[\text{MgTi}_3\text{N}_4]$ cube type cores according to an X-ray crystal structure determination.

Introduction

Polynuclear transition metal nitrido complexes remain rare in the literature due to their difficult characterization and, maybe more important, the lack of a systematic way of syntheses.¹ Over the last few years, we have been actively involved in the development of a new family of heterometallic nitrido complexes with cube-type structures. Our synthetic methods are based on the use of the incomplete cube structure of the trinuclear imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]^2$ to incorporate different metal derivatives with the possible deprotonation of the NH groups. Thus, we have recently characterized complexes with titanium and alkali/alkaline-earth metals showing single-cube, edge-linked double cube or corner-shared double cube central cores.^{3,4} Herein, we report the synthesis and structure of a new class of metal nitrido complexes containing amido-bridged double cube cores.

Results and discussion

The synthetic chemistry is outlined in Scheme 1. Treatment of the single-cube Group 2 metal complexes $[(\text{thf})_x\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (M = Mg (**1**), x = 0; Ca (**2**), x = 1)⁴ with one equivalent of 4-methylaniline or 2,4,6-trimethylaniline in toluene at room temperature led to bis(trimethylsilyl)amine and the arylamido complexes $[(\text{ArHN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]_n$ [M = Mg (**3**), n = 1, Ar = 4-MeC₆H₄; Ca (**4**), n = 2, Ar = 2,4,6-Me₃C₆H₂]. On the other hand, complex **1** did not react with 2,4,6-trimethylaniline at the same conditions and the reaction of **2** with 4-methylaniline gave an intractable mixture of products.



Scheme 1. Synthesis of the amido-bridged azaheterometallocubanes. [Ti] = Ti(η^5 -C₅Me₅)

After workup, complex **3** was isolated in 59% yield as an orange solid that is very soluble in toluene or benzene. Compound **3** was characterized by analytical and spectroscopic methods. The ¹H and ¹³C{¹H} NMR spectra in benzene-d₆ at room temperature revealed resonance signals for two η^5 -C₅Me₅ groups in a 2:1 ratio, resonance signals for one 4-MeC₆H₄NH arylamido ligand and a broad signal for the NH groups. The NMR data are consistent with a tetrahedral geometry around the magnesium centre as determined previously in the single cube-type structure of **1**.⁴ Complex **4** was isolated in 69% yield as red crystals directly from the reaction, and characterized by IR spectroscopy and C,H,N microanalysis. Compound **4** is not soluble in unreactive solvents suggesting a higher aggregation state, being the double cube structure confirmed by an X-ray crystal structure determination. The molecular structure of **4** is shown in Figure 1, while selected lengths and angles are provided in Table 1. The structural analysis reveals two cube-type azaheterometallocubane moieties “Ca{(μ₃-N)(μ₃-NH)₂Ti₃(η^5 -C₅Me₅)₃(μ₃-N)}” held together by two μ-2,4,6-trimethylanilido ligands. The compound is close to be centrosymmetric. The central rhomboid Ca₂N₂ ring is nearly planar with all the Ca-N distances identical within the experimental error, average 2.441(3) Å, and N-Ca-N of 83.4(1)° and Ca-N-Ca 96.5(1)° averaged angles. These distances and angles compare well with those found in [(Me₄EtC₅)Ca{μ-N(SiMe₂CH₂)₂}]₂,⁵ and [Ca{(NDippCMe)₂CH}{μ-NH(CH₂)₂OMe}]₂

(Dipp = C₆H₃ⁱPr₂-2,6).⁶ The distorted trigonal bipyramidal geometry around calcium is completed by three nitrogen atoms of the organometallic ligand $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ showing slightly longer Ca-N bond lengths (2.467(3)-2.543(3) Å) and narrower N-Ca-N angles (average 72.0(1)°) than those of the bridging moiety and similar to those recently reported by us for the corner-shared double cube complex $[\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ [average Ca-N 2.518(11) Å and N-Ca-N 70.7(3)°].^{4b}

Table 1. Selected lengths (Å) and angles (°) for complex **4**.

Ca(1)-N(10)	2.438(3)	Ca(1)-N(20)	2.447(3)
Ca(1)-N(12)	2.467(3)	Ca(1)-N(23)	2.496(3)
Ca(1)-N(13)	2.525(3)	Ca(2)-N(10)	2.442(3)
Ca(2)-N(20)	2.438(3)	Ca(2)-N(45)	2.477(3)
Ca(2)-N(46)	2.487(4)	Ca(2)-N(56)	2.543(3)
Ca(1)⋯Ca(2)	3.642(1)	Ti-N av	1.932(3)
N(10)-Ca(1)-N(20)	83.4(1)	N(10)-Ca(1)-N(12)	138.1(1)
N(10)-Ca(1)-N(23)	137.9(1)	N(10)-Ca(1)-N(13)	90.0(1)
N(20)-Ca(1)-N(12)	121.0(1)	N(20)-Ca(1)-N(23)	105.2(1)
N(20)-Ca(1)-N(13)	165.5(1)	N(12)-Ca(1)-N(23)	72.5(1)
N(12)-Ca(1)-N(13)	72.0(1)	N(23)-Ca(1)-N(13)	71.4(1)
N(10)-Ca(2)-N(20)	83.5(1)	N(10)-Ca(2)-N(45)	119.8(1)
N(10)-Ca(2)-N(46)	107.3(1)	N(10)-Ca(2)-N(56)	167.7(1)
N(20)-Ca(2)-N(45)	137.3(1)	N(20)-Ca(2)-N(46)	138.3(1)
N(20)-Ca(2)-N(56)	89.5(1)	N(45)-Ca(2)-N(46)	72.4(1)
N(45)-Ca(2)-N(56)	71.9(1)	N(46)-Ca(2)-N(56)	71.6(1)
Ca(1)-N(10)-Ca(2)	96.6(1)	Ca(1)-N(10)-C(101)	119.6(2)
Ca(2)-N(10)-C(101)	118.7(2)	Ca(1)-N(20)-Ca(2)	96.4(1)
Ca(1)-N(20)-C(201)	118.3(2)	Ca(2)-N(20)-C(201)	119.5(2)
Ti-N-Ti av	92.8(1)	N-Ti-N av	98.8(1)
N(1)-Ti-N av	87.4(1)	N(2)-Ti-N av	87.6(1)

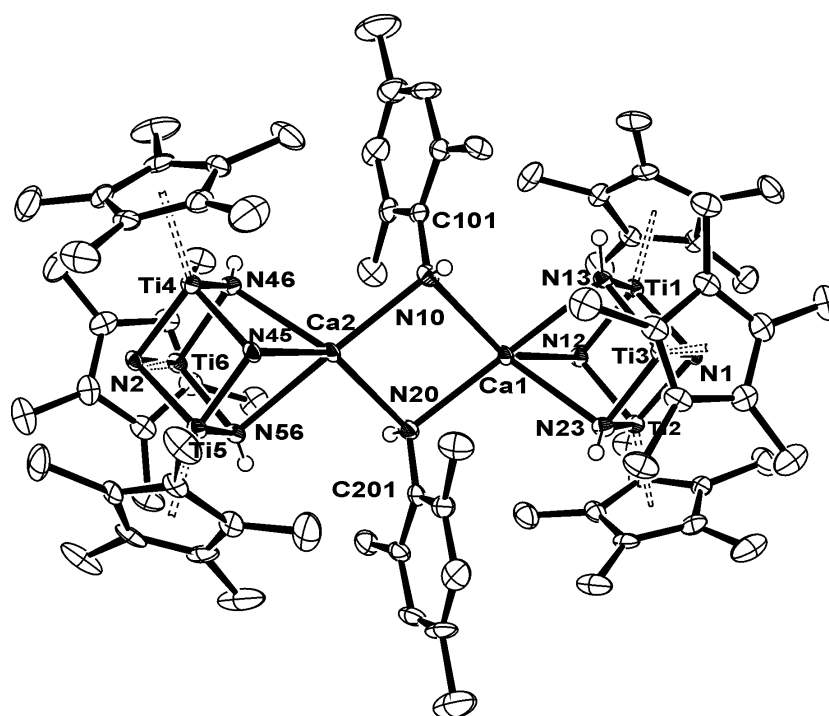


Figure 1. Molecular structure of complex **4**.

The lack of solubility of **4** in unreactive organic solvents (toluene, tetrahydrofuran, pyridine) precluded its characterization by NMR spectroscopy. On the other hand, it is not soluble but reacts with chloroform- d_1 or dichloromethane- d_2 within minutes to give $[\text{Cl}_2\text{Ca}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**5**) and free 2,4,6-trimethylaniline. Complex **5** was isolated as a yellow powder in 38% yield after workup. Similarly, complex **3** reacts immediately with chloroform- d_1 to give cleanly the analogous complex $[\text{Cl}_2\text{Mg}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**6**) as a yellow powder in 28% isolated yield. Compounds **5** and **6** are soluble in dichloromethane or chloroform, but scarcely soluble in arene solvents, and were characterized by spectral and analytical techniques. Their ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at room temperature show resonances for equivalent NH and $\eta^5\text{-C}_5\text{Me}_5$ groups. The spectroscopic data are similar to those determined for other Group 2 metal halides adducts and are consistent with a tridentate coordination of the organometallic ligand $\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ to the alkaline-earth metal

centres.⁷ Interestingly, complexes **5** and **6** can not be prepared through the direct reaction of [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})$] with magnesium or calcium dichlorides.

A solution of **3** in n-hexane at $-40\text{ }^\circ\text{C}$ for 7 days gave red crystals identified by an X-ray crystal structure determination as the amido-bridged double cube complex [$\{\text{Mg}_2(\mu_3\text{-N})(\mu_3\text{-NH})_5[\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})_2](\mu\text{-NHAr})_3\}$] (**7**) presumably via reaction of **3** with traces of NH_2Ar . Despite many attempts we were not able to reproduce this result in a preparative experiment. The molecular structure of complex **7** is shown in Figure 2 and selected lengths and angles are summarised in Table 2. The molecular structure of **7** resembles that of the dinuclear cation $[(\text{tacn})\text{Mg}(\mu\text{-Me})_3\text{Mg}(\text{tacn})]^+$,⁸ and shows three μ -4-methylanilido ligands bridging two $[\text{MgTi}_3\text{N}_4]$ cube type cores. Both magnesium atoms exhibit six coordinate geometries, the coordination environment around Mg(1) is best described as trigonal prismatic and that of Mg(2) corresponds to trigonal antiprismatic. Furthermore, Mg(1) is bonded to the nitrogen atoms of the arylamido groups [Mg(1)-N 2.219(3) Å, av.] and those of the anionic ligand $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}^-$ [Mg(1)-N 2.381(3) Å, av.]. On the other side, Mg(2)-nitrogen arylamido bond lengths [Mg(2)-N 2.176(3) Å, av.] are slightly shorter than those of Mg(1) while distances to the neutral organometallic ligand $\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ [Mg(2)-N 2.410(3) Å, av.] are vaguely longer. We have not found precedents in the literature for dinuclear magnesium complexes with three amido bridges, and the reported examples with two arylamido groups exhibit shorter Mg-N bond lengths (2.08 - 2.14 Å) and wider angles Mg-N-Mg ($89 - 92^\circ$)⁹ than those determined for **7**.

Within the $[\text{MgTi}_3\text{N}_4]$ cores complex **7** shows longer Mg-N bond lengths and narrower N-Mg-N angles (average $75.9(1)^\circ$) than those recently determined for the

corner-shared double cube complex $[\text{Mg}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$
 [average values Mg-N 2.304(8) Å and N-Mg-N 77.6(3)°].⁴

Table 2. Selected lengths (Å) and angles (°) for complex **7**.

Mg(1)-N(3)	2.208(3)	Mg(1)-N(4)	2.226(3)
Mg(1)-N(5)	2.224(3)	Mg(1)-N(12)	2.419(3)
Mg(1)-N(13)	2.375(3)	Mg(1)-N(23)	2.350(3)
Mg(2)-N(3)	2.174(3)	Mg(2)-N(4)	2.175(3)
Mg(2)-N(5)	2.180(3)	Mg(2)-N(45)	2.424(3)
Mg(2)-N(46)	2.406(3)	Mg(2)-N(56)	2.400(3)
Mg(1)···Mg(2)	2.826(2)	Ti-N av	1.931(3)
N(3)-Mg(1)-N(4)	82.0(1)	N(3)-Mg(1)-N(5)	83.1(1)
N(4)-Mg(1)-N(5)	81.2(1)	N(3)-Mg(1)-N(12)	85.3(1)
N(3)-Mg(1)-N(13)	143.5(1)	N(3)-Mg(1)-N(23)	128.2(1)
N(4)-Mg(1)-N(12)	144.5(1)	N(4)-Mg(1)-N(13)	130.5(1)
N(4)-Mg(1)-N(23)	86.4(1)	N(5)-Mg(1)-N(12)	129.9(1)
N(5)-Mg(1)-N(13)	86.0(1)	N(5)-Mg(1)-N(23)	144.3(1)
N(12)-Mg(1)-N(13)	75.3(1)	N(12)-Mg(1)-N(23)	75.8(1)
N(13)-Mg(1)-N(23)	76.8(1)	N(3)-Mg(2)-N(4)	83.9(1)
N(3)-Mg(2)-N(5)	84.9(1)	N(4)-Mg(2)-N(5)	83.4(1)
N(3)-Mg(2)-N(45)	91.3(1)	N(3)-Mg(2)-N(46)	163.0(1)
N(3)-Mg(2)-N(56)	110.9(1)	N(4)-Mg(2)-N(45)	163.3(1)
N(4)-Mg(2)-N(46)	112.0(1)	N(4)-Mg(2)-N(56)	92.1(1)
N(5)-Mg(2)-N(45)	112.1(1)	N(5)-Mg(2)-N(46)	90.9(1)
N(5)-Mg(2)-N(56)	163.0(1)	N(45)-Mg(2)-N(46)	75.1(1)
N(45)-Mg(2)-N(56)	74.7(1)	N(46)-Mg(2)-N(56)	75.6(1)
Mg(1)-N(3)-Mg(2)	80.3(1)	Mg(1)-N(3)-C(301)	124.1(2)
Mg(2)-N(3)-C(301)	127.3(2)	Mg(1)-N(4)-Mg(2)	79.9(1)
Mg(1)-N(4)-C(401)	123.7(2)	Mg(2)-N(4)-C(401)	126.9(2)
Mg(1)-N(5)-Mg(2)	79.9(1)	Mg(1)-N(5)-C(501)	123.9(2)
Mg(2)-N(5)-C(501)	125.8(2)	Ti-N-Ti av	93.5(1)
N-Ti-N av	98.8(1)	N(1)-Ti-N av	86.7(1)
N(2)-Ti-N av	86.3(1)		

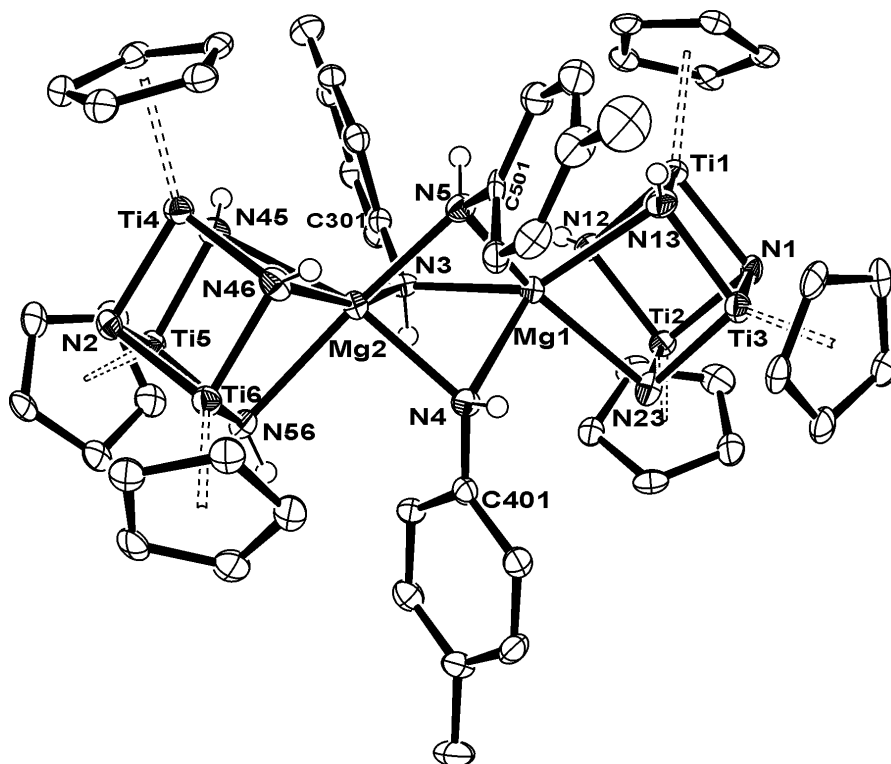


Figure 2. Simplified view of the molecular structure of **7**. The methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity.

In conclusion, the structures here reported represent a new class of polynuclear nitrido complexes, where the amido ligands connect $[MTi_3N_4]$ cube-type cores. We are currently working on the development of similar systems using other bridging moieties.

Experimental

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just prior to use. Toluene was freshly distilled from sodium. NMR solvents were dried with CaH_2 ($CDCl_3$) or Na/K alloy (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. 4-Methylaniline was purchased from Aldrich and sublimed under

vacuum prior to use. 2,4,6-Trimethylaniline was purchased from Aldrich and distilled from calcium hydride prior to use. $[(\text{thf})_x\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (M = Mg (**1**),^{4a} $x = 0$; Ca (**2**),^{4b} $x = 1$) were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts (δ , ppm) are given relative to residual protons or to carbon of the solvent. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzer.

Synthesis of $[(\text{4-MeC}_6\text{H}_4)\text{HN}]\text{Mg}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ (3**):** A 100-mL Schlenk flask was charged with $[(\text{Me}_3\text{Si})_2\text{N}]\text{Mg}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ (0.30 g, 0.38 mmol), 4-methylaniline (0.040 g, 0.37 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 4 h to give an orange solution. The volatile components were removed under reduced pressure, and the resultant orange solid was washed with hexane (5 mL) and vacuum-dried for 3 h to yield **3** as an orange powder (0.16 g, 59%). IR (KBr, cm^{-1}): 3342 (m), 3313 (w), 2908 (s), 2858 (s), 1608 (m), 1571 (w), 1504 (s), 1433 (m), 1376 (m), 1297 (w), 1261 (m), 1250 (m), 1189 (w), 1180 (w), 1108 (w), 1066 (w), 1024 (w), 819 (s), 732 (vs), 711 (vs), 652 (vs), 626 (s), 423 (s). $^1\text{H-NMR}$ (C_6D_6 , 20 °C, δ): 11.16 (s broad, 2H, NH), 7.09 (m, 2H, $\text{C}_6\text{H}_2\text{H}_2\text{Me}$), 6.54 (m, 2H, $\text{C}_6\text{H}_2\text{H}_2\text{Me}$), 2.31 (s, 3H, $\text{C}_6\text{H}_2\text{H}_2\text{Me}$), 2.11 (s, 30H, C_5Me_5), 1.84 (s, 15H, C_5Me_5), 1.77 (s broad, 1H, $\text{NHC}_6\text{H}_4\text{Me}$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 20 °C, δ): 152.9, 130.0, 124.9, 120.4 ($\text{C}_6\text{H}_4\text{Me}$), 118.4, 117.1 (C_5Me_5), 20.6 ($\text{C}_6\text{H}_4\text{Me}$), 12.1, 11.7 (C_5Me_5). Anal. Calcd. for $\text{C}_{37}\text{H}_{55}\text{MgN}_5\text{Ti}_3$ (%): C 60.21, H 7.53, N 9.49; found: C 60.07, H 7.44, N 8.47.

Synthesis of $[\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}(\mu\text{-NHAr})_2]$ (4**):** A toluene solution (10 mL) of 2,4,6-trimethylaniline (0.060 g, 0.44 mmol) was carefully added to

2 (0.40 g, 0.45 mmol) in toluene (20 mL). The system was allowed to equilibrate at room temperature for 3 days to give red crystals. After decantation, the crystals were dried under vacuum and characterized as **4·C₇H₈** (0.25 g, 69%). IR (KBr): 3337 (w), 3324 (w), 2966 (m), 2907 (s), 2856 (s), 2721 (w), 1605 (w), 1494 (m), 1470 (m), 1432 (m), 1374 (m), 1288 (m), 1239 (m), 1208 (w), 1156 (w), 1024 (w), 998 (w), 957 (w), 853 (m), 778 (m), 722 (vs), 698 (s), 658 (m), 621 (s), 573 (m), 532 (w), 491 (w), 473 (w), 463 (w), 440 (w), 417 (m) cm⁻¹. Anal. Calcd. for C₈₅H₁₂₆Ca₂N₁₀Ti₆ (%): C 61.65, H 7.68, N 8.46; found: C 61.59, H 7.76, N 8.15.

Synthesis of [Cl₂Ca{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (5**):** A 50-mL Schlenk flask was charged with **4·C₇H₈** (0.30 g, 0.18 mmol) and CDCl₃ (10 mL). After being stirred for 3 h at room temperature, the volatile components were removed under reduced pressure. The resultant orange solid was washed with toluene (3 x 5 mL) to afford **5** as a yellow powder (0.10 g, 38 %). IR (KBr, cm⁻¹): 3342 (w), 3330 (m), 3221 (w), 2909 (s), 2858 (m), 2469 (w), 2394 (w), 2098 (w), 1490 (m), 1451 (m), 1428 (m), 1378 (s), 1067 (w), 1026 (m), 767 (s), 728 (s), 662 (vs), 533 (w), 465 (w), 437 (w). ¹H-NMR (CDCl₃, 20 °C, δ): 13.15 (s broad, 3H, NH), 2.09 (s, 45H, C₅Me₅). ¹³C{¹H}-NMR (CDCl₃, 20 °C, δ): 121.2 (C₅Me₅), 12.1 (C₅Me₅). Anal. Calcd. for C₃₀H₄₈CaCl₂N₄Ti₃ (%): C 50.08, H 6.74, N 7.79; found: C 49.18, H 6.56, N 6.83.

Synthesis of [Cl₂Mg{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (6**):** In a fashion similar to the preparation of **5**, treatment of **3** (0.30 g, 0.41 mmol) with CDCl₃ (10 mL) afforded **6** as a yellow powder (0.080 g, 28 %). IR (KBr, cm⁻¹): 3342 (m), 3232 (m), 2909 (s), 2858 (s), 2726 (w), 2477 (w), 2406 (w), 1492 (m), 1429 (s), 1377 (s), 1259 (w), 1154 (w), 1100 (w), 1067 (w), 1026 (m), 764 (m), 727 (s), 671 (vs), 638 (s), 623 (s), 531 (w), 478 (w), 465 (w), 428 (m). ¹H-NMR (CDCl₃, 20 °C, δ): 12.06 (s broad, 3H, NH), 2.09 (s, 45H,

C_5Me_5). $^{13}C\{^1H\}$ -NMR ($CDCl_3$, 20 °C, δ): 121.7 (C_5Me_5), 12.3 (C_5Me_5). Anal. Calcd. for $C_{30}H_{48}Cl_2MgN_4Ti_3$ (%): C 51.20, H 6.89, N 7.96; found: C 50.73, H 7.20, N 8.24.

X-ray structure determination of 4 and 7. X-ray crystals of **4** were grown in toluene as described in the experimental section. Crystals of **7** were grown at -40 °C from a n-hexane solution of **3**. The crystals were removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin[®]Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 100K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit.

Crystallographic data for all the complexes are presented in Table 3. The structures were solved, using the WINGX package,¹⁰ by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).¹¹

Compound **4** crystallizes with two very disordered toluene solvent molecules per double cube complex. Several attempts to obtain chemical sensible models for the solvent were failed, so PLATON¹² squeeze procedure was used to remove their contribution to the structure factors. All non-hydrogen atoms of **4** were anisotropically refined. All the hydrogen atoms were positioned geometrically and refined by using a riding model.

Crystals of **7** bear two and a half n-hexane solvent molecules per double cube complex. Attempts to model the solvent in a sensible way were also failed and similarly to **4**, PLATON¹² squeeze procedure was applied. All the non-hydrogen atoms of **7** were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model.

Table 3. Selected crystallographic and data collection parameters for complexes **4** and **7**.

Compound	4·(2C₇H₈)	7·(5/2C₆H₁₄)
Empirical formula	C ₉₂ H ₁₃₄ Ca ₂ N ₁₀ Ti ₆	C ₉₆ H ₁₅₄ Mg ₂ N ₁₁ Ti ₆
Formula weight	1747.65	1798.32
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
<i>a</i> (Å); α (°)	11.794(3); 81.03(1)	42.934(8)
<i>b</i> (Å); β (°)	14.532(1); 87.91(1)	20.209(4); 127.48(1)
<i>c</i> (Å); γ (°)	27.051(5); 69.38(1)	28.592(6)
Volume (Å ³)	4285.3(13)	19686(7)
Z	2	8
Density (calculated) (Mg/m ³)	1.354	1.214
Absorption coefficient (mm ⁻¹)	0.704	0.524
F(000)	1856	7704
Crystal size (mm ³)	0.73 x 0.49 x 0.42	0.40 x 0.36 x 0.28
Theta range for data collection	5.0 to 27.5°	5.0 to 27.5°
Index ranges	-15<= <i>h</i> <=15, -17<= <i>k</i> <=18, -35<= <i>l</i> <=35	-55<= <i>h</i> <=55, -26<= <i>k</i> <=26, -37<= <i>l</i> <=37
Reflections collected	36741	65898
Independent reflections	19499 [R(int) = 0.079]	22091 [R(int) = 0.108]
Completeness to $\theta = 27.5^\circ$	99.0 %	97.6 %
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19499 / 0 / 865	22091 / 0 / 901
Goodness-of-fit on F ²	0.961	0.968
Final R indices [I>2 σ (I)]	R1 = 0.061, wR2 = 0.148	R1 = 0.067, wR2 = 0.168
R indices (all data)	R1 = 0.118, wR2 = 0.168	R1 = 0.135, wR2 = 0.188
Largest diff. peak and hole (e.Å ⁻³)	0.685 and -0.731	0.510 and -0.475

Acknowledgements

We thank the Spanish MCYT (BQU2001-1499) and DGICAM (07N/0091/2002) for financial support of this research.

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