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Cube-Type Nitrido Complexes Containing Titanium and Alkali/Alkaline-Earth Metals

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Synopsis:

Edge-linked double cube nitrido complexes $[M(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}]_2$ (M = Li, Na, K, Rb, Cs), or corner-shared double cube nitrido complexes $[M(\mu_3\text{-N})(\mu_3\text{-NH})_5\{Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}_2]$ (M = Na, K, Rb, Cs) have been obtained upon treatment of $[\{Ti(\eta^5\text{-C}_5Me_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with alkali metal bis(trimethylsilyl)amido derivatives $[M\{N(SiMe_3)_2\}]$ at different conditions. Analogous reactions of **1** with alkaline-earth derivatives $[M\{N(SiMe_3)_2\}_2(thf)_2]$ afford the corner-shared double cube nitrido complexes $[M\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}_2]$ (M = Mg, Ca, Sr, Ba) via single cube-type intermediates $[(thf)_x\{(Me_3Si)_2N\}M\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}]$.
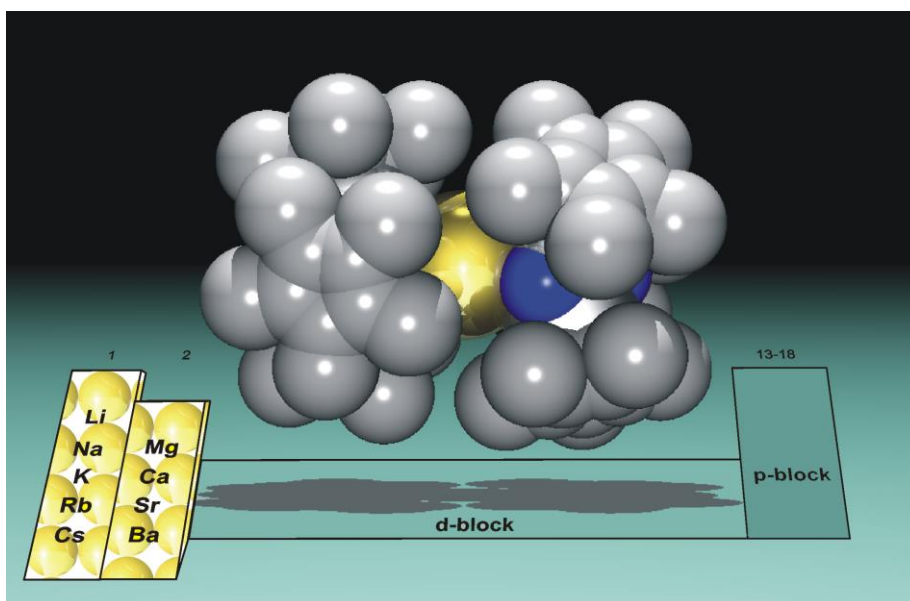
Abstract:

Treatment of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] with alkali metal bis(trimethylsilyl)amido derivatives [M{N(SiMe$_3$)$_2$}] in toluene afford edge-linked double cube nitrido complexes [M(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (M = Li, Na, K, Rb, Cs), or corner-shared double cube nitrido complexes [M(μ_3-N)(μ_3-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Na, K, Rb, Cs). Analogous reactions with 1/2 equivalent of alkaline-earth bis(trimethylsilyl)amido derivatives [M{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] give corner-shared double cube nitrido complexes [M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Mg, Ca, Sr, Ba). If one equivalent of the group 2 amido reagent is employed, single cube-type derivatives [(thf)$_x${(Me$_3$Si)$_2$N}M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Mg, x = 0; M = Ca, Sr, Ba, x = 1) can be isolated or identified. The tetrahydrofuran molecules are easily displaced with 4-*tert*-butylpyridine in toluene affording the analogous complexes [(*t*Bupy){(Me$_3$Si)$_2$N}M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Ca, Sr). The X-ray crystal structures of [M(μ_3-N)(μ_3-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = K, Rb, Cs) and [M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Ca, Sr) have been determined. The properties and solid-state structures of the azaheterometallocubane complexes bearing alkali and alkaline-earth metals are discussed.

Keywords: titanium · alkali metals · alkaline-earth metals · nitrido complexes · cage compounds

Introduction

Chalcogenide-bridged cube-type clusters containing M_4Q_4 (Q = S, Se) cores where M is a transition metal are quite common in the literature.[1] One of the most important strategies to access to that type of complexes is the building-block synthesis from lower nuclearity species, and it is especially convenient for the construction of heterometallic $M'_2M_2S_4$ and $M'M_3Q_4$ cluster complexes from dinuclear M_2S_2 or trinuclear M_3Q_4 aggregates.[2] Since the pioneering studies of Shibahara and co-workers on the incorporation of heterometals M' into M_3S_4 aggregates with incomplete cube structures,[3] the designated [3+1] strategy has been extensively used in the synthesis of heterobimetallic cube-type complexes (Chart 1).[2,4,5] Structures determined for those clusters reveal single cube [$M'M_3Q_4$], edge-linked double cube [$M'_2M_6Q_8$] or corner-shared double cube [$M'M_6Q_8$] central cores.
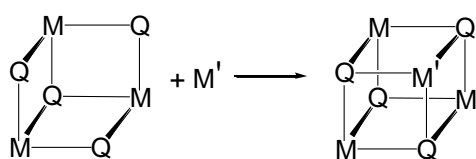
Chart 1. The [3 + 1] building-block synthesis of heterometallic cube-type complexes.

In 1995, we reported the synthesis and structure of a singular organometallic nitrido complex [{Ti(η^5-C$_5$Me$_5$)}$_4$(μ_3-N)$_4$], which contains an almost perfect [Ti$_4$N$_4$] cube-type core.[6] This compound can be also obtained by treatment of the trinuclear imido-nitrido complex [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)][7] (**1**) with [Ti(η^5-C$_5$Me$_5$)(NMe$_2$)$_3$].[8] Complex **1** shows an incomplete cube [Ti$_3$(μ-NH)$_3$(μ_3-N)] core (Chart 2), which strongly resembles those found in iron [Fe$_3$S$_4$] and Group 6 [M$_3$Q$_4$] chalcogenide clusters. Based on this similarity, we have been engaged in a project devoted to apply the [3+1] synthetic approach to incorporate different metal fragments into the preorganized structure of **1**. This methodology has allowed to access

to a new family of heterometallic nitrido compounds with cube-type $[MTi_3N_4]$ cores (Chart 2), which we have designated as azaheterometallocubanes.

Our initial work was focused on the incorporation of transition metal elements, and we have described the synthesis of several examples bearing single cube $[MTi_3N_4]$ (M = Ti,[8,9,10] Nb,[10] Ta,[10] Cr,[11] Mo,[11] W,[11] Rh,[12] Ir[12]) or corner-shared double cube $[MTi_6N_8]$ (M = Ti,[9,10] Zr,[9,10] Nb,[10] Ta[10]) central cores. We have also reported our preliminary results on the reactions with Group 1 and 2 amido and alkyl derivatives to give the first examples of edge-linked double cube $[M_2Ti_6N_8]$ (M = Li, Na, K) cores,[13] and magnesium and barium complexes with single cube or corner-shared double cube structures.[14] Herein, we present full details of our work with alkali and alkaline-earth elements, including the heavier *s*-block elements, and discuss the trends along the Groups 1 and 2 in structures and properties.

incomplete cube $[Ti_3N_4]$

single cube $[MTi_3N_4]$

edge-linked double cube $[M_2Ti_6N_8]$

corner-shared double cube $[MTi_6N_8]$

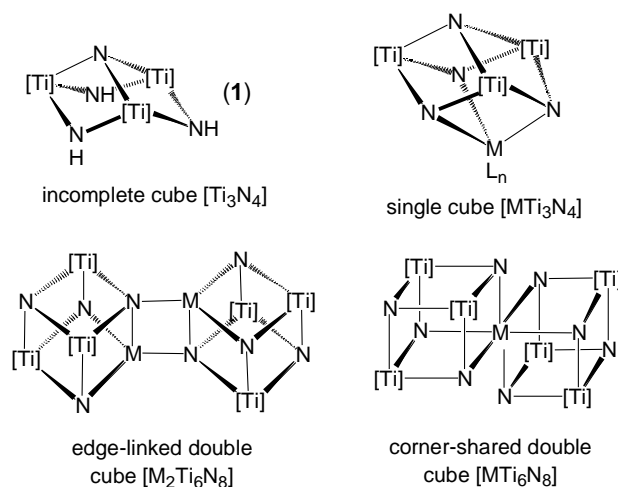**Chart 2.** Structural core of **1** and $[MTi_3N_4]$ cube-type complexes. $[Ti] = Ti(\eta^5\text{-}C_5Me_5)$

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene and tetrahydrofuran were freshly distilled from sodium or sodium/benzophenone. NMR solvents were dried with Na/K amalgam (C_6D_6) or

calcium hydride (C_5D_5N) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1 x 10^{-3} Torr) and subsequently filled with inert gas. [M{N(SiMe$_3$)$_2$}] (M = Li, Na, K) were purchased from Aldrich and used as received. 4-*tert*-butylpyridine was purchased from Aldrich and distilled from calcium hydride prior to use. [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**),[7,8] [M{N(SiMe$_3$)$_2$}] (M = Rb, Cs),[15] and [M{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (M = Mg, Ca, Sr, Ba)[16] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^{1}H and ^{13}C{^{1}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 microanalyzers.

Synthesis of [M(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (M = Li (2), Na (3), K (4)): The syntheses and characterization of complexes **2**-**4** have been reported previously.[13] However, in order to establish a comparison with the analogous rubidium (**6**) and cesium (**7**) derivatives, herein we include the synthetic procedure for **2** and new NMR data for **2**-**4**.

Synthesis of 2: A solution of [Li{N(SiMe$_3$)$_2$}] (0.14 g, 0.82 mmol) in toluene (5 mL) was carefully added to **1** (0.50 g, 0.82 mmol) in toluene (10 mL). The system was allowed to react without any stirring for 20 h. After decantation, the resultant orange crystals were vacuum-dried to afford **2·C$_7$H$_8$** (0.43 g, 80%). ^{1}H NMR (C$_5$D$_5$N, 20 °C, δ): 2.07 (s, 15H, C$_5$Me$_5$), 2.17 (s, 30H, C$_5$Me$_5$), 12.36 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_5$D$_5$N, 20 °C, δ): 11.9, 12.0 (C$_5$*Me*$_5$), 115.0, 116.4 (*C*$_5$Me$_5$).

NMR data for 3: ^{1}H NMR (C$_5$D$_5$N, 20 °C, δ): 2.04 (s, 15H, C$_5$Me$_5$), 2.16 (s, 30H, C$_5$Me$_5$), 12.83 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_5$D$_5$N, 20 °C, δ): 12.0, 12.1 (C$_5$*Me*$_5$), 113.8, 115.2 (*C*$_5$Me$_5$).

NMR data for 4: ^{1}H NMR (C$_5$D$_5$N, 20 °C, δ): 2.09 (s, 15H, C$_5$Me$_5$), 2.18 (s, 30H, C$_5$Me$_5$), 13.14 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_5$D$_5$N, 20 °C, δ): 12.0, 12.1 (C$_5$*Me*$_5$), 113.5, 114.9 (*C*$_5$Me$_5$).

Synthesis of [Rb(μ$_3$-N)(μ$_3$-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}]$_2$ (5): A 100-mL Schlenk flask was charged with **1** (0.15 g, 0.25 mmol), [Rb{N(SiMe$_3$)$_2$}] (0.06 g, 0.24 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 3 h to give a yellow precipitate and a yellow solution. After decantation, the yellow solid was vacuum-dried and characterized as **5** (0.10 g, 59%). IR (KBr, cm^{-1}): 3339 (w), 2908 (s), 2856 (s), 1496 (w), 1437 (m), 1373 (m), 1021 (w), 739 (vs), 705 (s), 653 (m), 616 (s), 541 (m), 471 (w), 437 (w); ^{1}H NMR (C$_5$D$_5$N, 20 °C, δ): 2.09 (s, 15H, C$_5$Me$_5$), 2.19 (s, 30H, C$_5$Me$_5$), 13.20 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_5$D$_5$N, 20 °C, δ): 12.1, 12.2 (C$_5$*Me*$_5$), 113.4, 114.8 (*C*$_5$Me$_5$). Anal. Calcd. for C$_{60}$H$_{94}$N$_8$Rb$_2$Ti$_6$ (%): C 51.99, H 6.85, N 8.09; found: C 52.25, H 6.81, N 7.27.

Synthesis of [Cs(μ$_3$-N)(μ$_3$-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}]$_2$ (6): In a fashion similar to the preparation of **5**, treatment of **1** (0.15 g, 0.25 mmol) with [Cs{N(SiMe$_3$)$_2$}] (0.07 g, 0.24 mmol) in toluene (20 mL) afforded **6** as a yellow solid (0.11 g, 61%). IR (KBr, cm^{-1}): 3342 (w), 2908 (s), 2856 (s), 1495 (w), 1437 (m), 1372 (m), 1021 (w), 739 (vs), 705 (s), 656 (m), 624 (s), 540 (m), 472 (w); ^{1}H NMR (C$_5$D$_5$N, 20 °C, δ): 2.09 (s, 15H, C$_5$Me$_5$), 2.20 (s, 30H, C$_5$Me$_5$), 13.25 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_5$D$_5$N, 20 °C, δ): 12.1, 12.2 (C$_5$*Me*$_5$), 113.4, 114.7 (*C*$_5$Me$_5$). Anal. Calcd. for C$_{60}$H$_{94}$Cs$_2$N$_8$Ti$_6$ (%): C 48.66, H 6.41, N 7.57; found: C 48.85, H 6.32, N 7.00.

Synthesis of [Na(μ$_3$-N)(μ$_3$-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}$_2$] (7): A 100-mL Schlenk flask was charged with **3** (0.13 g, 0.10 mmol), **1** (0.12 g, 0.20 mmol) and toluene (15 mL). The reaction mixture was stirred at 70 °C for 24 h. The resultant orange solid was isolated by filtration and vacuum-dried for 3 hours to give **7·C$_7$H$_8$** (0.21 g, 78%). IR (KBr, cm^{-1}): 3350 (m), 2967 (m), 2906 (s), 2854 (s), 1604 (w), 1495 (m), 1432 (m), 1375 (m), 1024 (w), 776 (m), 735 (vs), 704

(s), 672 (s), 656 (s), 635 (s), 623 (s), 578 (m), 540 (m), 473 (m). Anal. Calcd. for $C_{67}H_{103}N_8NaTi_6$ (%): C 60.45, H 7.81, N 8.42; found: C 60.86, H 8.14, N 8.07.

Synthesis of $[K(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (8): A toluene solution (20 mL) of **1** (0.30 g, 0.49 mmol) was carefully layered with a toluene solution (10 mL) of $[K\{N(SiMe_3)_2\}]$ (0.05 g, 0.25 mmol). The system was allowed to equilibrate for 2 days to afford dark green crystals of **8·C₇H₈** (0.24 g, 75%). IR (KBr, cm^{-1}): 3337 (w), 2907 (s), 2854 (s), 1492 (m), 1430 (m), 1374 (m), 1065 (w), 1023 (m), 736 (vs), 701 (s), 670 (s), 653 (s), 623 (s), 572 (m), 536 (m), 471 (m), 423 (m). Anal. Calcd. for $C_{67}H_{103}KN_8Ti_6$ (%): C 59.72, H 7.72, N 8.32; found: C 59.85, H 7.65, N 8.76.

Synthesis of $[Rb(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (9): A tetrahydrofuran solution (20 mL) of **1** (0.30 g, 0.49 mmol) was carefully layered with a toluene solution (10 mL) of $[Rb\{N(SiMe_3)_2\}]$ (0.06 g, 0.24 mmol). The system was allowed to equilibrate for 2 days to afford dark green crystals of **9** (0.21 g, 68%). IR (KBr, cm^{-1}): 3338 (m), 2908 (s), 2849 (s), 1489 (m), 1429 (s), 1374 (s), 1064 (w), 1022 (m), 737 (vs), 700 (s), 672 (s), 654 (s), 624 (s), 571 (m), 535 (m), 471 (m), 424 (m), 399 (s). Anal. Calcd. for $C_{60}H_{95}N_8RbTi_6$ (%): C 55.37, H 7.37, N 8.61; found: C 55.62, H 7.37, N 8.26.

Synthesis of $[Cs(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (10): In a fashion similar to the preparation of **9**, a tetrahydrofuran solution (20 mL) of **1** (0.30 g, 0.49 mmol) was carefully layered with a toluene solution (10 mL) of $[Cs\{N(SiMe_3)_2\}]$ (0.07 g, 0.24 mmol) to afford dark green crystals of **10** (0.19 g, 59 %). IR (KBr, cm^{-1}): 3339 (m), 2908 (s), 2854 (s), 1489 (m), 1429 (s), 1374 (s), 1064 (w), 1022 (m), 737 (vs), 700 (s), 674 (s), 655 (s), 625 (s), 569 (m), 534 (m), 471 (m), 426 (m), 396 (m). Anal. Calcd. for $C_{60}H_{95}CsN_8Ti_6$ (%): C 53.42, H 7.11, N 8.31; found: C 53.42, H 7.20, N 8.11.

Synthesis of $[(thf)\{(Me_3Si)_2N\}Ca\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (12): A 100-mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (0.25 g, 0.49

mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 3 h to give an orange solution. After filtration, the volatile components were removed under reduced pressure to afford **12** as an orange solid (0.38 g, 88%). IR (KBr, cm^{-1}): 3341 (w), 2941 (s), 2909 (s), 2860 (s), 1491 (w), 1437 (m), 1375 (m), 1246 (m), 1236 (m), 1057 (s), 1033 (m), 879 (m), 819 (s), 762 (m), 728 (vs), 710 (s), 661 (s), 637 (m), 623 (s), 587 (m), 533 (w), 475 (w), 445 (w), 418 (m); ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 0.25 (s, 18H, N(SiMe$_3$)$_2$), 1.32 (m, 4H, thf), 2.05 (s, 15H, C$_5$Me$_5$), 2.10 (s, 30H, C$_5$Me$_5$), 3.73 (m, 4H, thf), 12.43 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 6.0 (SiMe$_3$), 12.0, 12.3 (C$_5$*Me$_5$*), 25.0, 69.9 (thf), 116.4, 118.3 (*C$_5$*Me$_5$). Anal. Calcd. for C$_{40}$H$_{73}$CaN$_5$OSi$_2$Ti$_3$ (%): C 54.58, H 8.38, N 7.96; found: C 54.23, H 8.14, N 7.99.

Synthesis of [(thf){(Me$_3$Si)$_2$N}Sr{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (13): In a fashion similar to the preparation of **12**, treatment of **1** (0.30 g, 0.49 mmol) with [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.27 g, 0.49 mmol) in toluene (25 mL) afforded **13** as an orange solid (0.34 g, 76%). IR (KBr, cm^{-1}): 3335 (w), 2940 (s), 2909 (s), 2860 (s), 1492 (w), 1436 (m), 1375 (m), 1243 (s), 1086 (s), 1035 (m), 879 (m), 817 (s), 727 (vs), 704 (s), 658 (s), 637 (m), 622 (s), 603 (m), 573 (m), 531 (w), 474 (w), 445 (w), 417 (m); ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 0.24 (s, 18H, N(SiMe$_3$)$_2$), 1.31 (m, 4H, thf), 2.03 (s, 15H, C$_5$Me$_5$), 2.11 (s, 30H, C$_5$Me$_5$), 3.64 (m, 4H, thf), 12.67 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 5.9 (SiMe$_3$), 12.1, 12.3 (C$_5$*Me$_5$*), 25.2, 69.3 (thf), 116.1, 117.9 (*C$_5$*Me$_5$). Anal. Calcd. for C$_{40}$H$_{73}$N$_5$OSi$_2$SrTi$_3$ (%): C 51.78, H 7.95, N 7.55; found: C 51.26, H 7.80, N 6.87.

Synthesis of [Ca{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}$_2$] (16): A toluene solution (15 mL) of [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.12 g, 0.24 mmol) was slowly added to **1** (0.30 g, 0.49 mmol) in toluene (10 mL). The system was allowed to react without any stirring for 2 days to afford orange crystals of **16·2C$_7$H$_8$** (0.20 g, 59%). IR (KBr, cm^{-1}): 3341 (w), 2967 (m), 2907 (s), 2857 (m), 1606 (w), 1496 (w), 1434 (m), 1374 (m), 1026 (w), 726 (vs), 706 (s), 655 (m), 623

(s), 593 (s), 528 (w), 473 (w), 464 (w), 442 (w), 416 (m). Anal. Calcd. for $C_{74}H_{110}CaN_8Ti_6$ (%): C 61.74, H 7.72, N 7.79; found: C 61.36, H 7.69, N 7.82.

Synthesis of [Sr{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (17): In a fashion similar to the preparation of **16**, treatment of **1** (0.30 g, 0.49 mmol) with [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.14 g, 0.25 mmol) in toluene afforded orange crystals of **17·2C$_7$H$_8$** (0.22 g, 61%). IR (KBr, cm^{-1}): 3333 (w), 2098 (s), 2856 (m), 1491 (w), 1432 (m), 1374 (m), 1024 (w), 725 (vs), 700 (s), 655 (m), 623 (s), 587 (m), 529 (w), 473 (w), 442 (w), 416 (m). Anal. Calcd. for $C_{74}H_{110}N_8SrTi_6$ (%): C 59.77, H 7.47, N 7.54; found: C 59.22, H 7.49, N 7.08.

Synthesis of [(4-*t*Bupy){(Me$_3$Si)$_2$N}Ca{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (19): A 100-mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.25 g, 0.49 mmol), 4-*tert*-butylpyridine (0.07 g, 0.52 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 3 h to give an orange solution. After filtration, the volatile components were removed under reduced pressure to afford **19** as an orange solid (0.40 g, 87%). IR (KBr, cm^{-1}): 3339 (w), 3028 (w), 2949 (s), 2909 (s), 2861 (s), 1609 (m), 1498 (m), 1437 (m), 1375 (m), 1245 (m), 1231 (m), 1065 (s), 1024 (w), 1009 (m), 880 (m), 819 (s), 762 (s), 731 (vs), 715 (s), 660 (s), 623 (s), 585 (m), 572 (m), 535 (w), 476 (w), 444 (w), 418 (m); ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 0.35 (s, 18H, N(SiMe$_3$)$_2$), 0.90 (s, 9H, NC$_5$H$_4$C*Me$_3$*), 2.097 (s, 15H, C$_5$Me$_5$), 2.102 (s, 30H, C$_5$Me$_5$), 7.09 (m, 2H, NC$_5$*H$_4$*CMe$_3$), 9.11 (m, 2H, NC$_5$*H$_4$*CMe$_3$), 12.57 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 6.1 (SiMe$_3$), 12.0, 12.4 (C$_5$*Me$_5$*), 30.1 (NC$_5$H$_4$C*Me$_3$*), 34.6 (NC$_5$H$_4$*C*Me$_3$), 116.4, 118.4 (*C$_5$*Me$_5$), 120.8, 152.0, 162.4 (N*C$_5$*H$_4$CMe$_3$). Anal. Calcd. for $C_{45}H_{78}CaN_6Si_2Ti_3$ (%): C 57.30, H 8.35, N 8.91; found: C 58.12, H 8.39, N 7.76.

Synthesis of [(4-*t*Bupy){(Me$_3$Si)$_2$N}Sr{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (20): In a fashion similar to the preparation of **19**, treatment of **1** (0.30 g, 0.49 mmol) with [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.27 g, 0.49 mmol) and 4-*tert*-butylpyridine (0.07 g, 0.52 mmol) in

toluene (25 mL) afforded **20** as an orange solid (0.37 g, 77%). IR (KBr, cm^{-1}): 3334 (w), 3023 (w), 2944 (s), 2909 (s), 1607 (m), 1497 (m), 1436 (m), 1374 (m), 1242 (m), 1095 (s), 1023 (w), 1008 (m), 879 (m), 818 (s), 728 (vs), 708 (s), 658 (s), 637 (m), 623 (s), 603 (m), 572 (m), 533 (w), 475 (w), 464 (w), 445 (w), 418 (m); ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 0.35 (s, 18H, N(SiMe$_3$)$_2$), 0.89 (s, 9H, NC$_5$H$_4$C*Me$_3$*), 2.098 (s, 15H, C$_5$Me$_5$), 2.103 (s, 30H, C$_5$Me$_5$), 7.11 (m, 2H, NC$_5$*H*$_4$CMe$_3$), 9.17 (m, 2H, NC$_5$*H*$_4$CMe$_3$), 12.57 (s broad, 2H, NH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 6.0 (SiMe$_3$), 12.2, 12.4 (C$_5$*Me$_5$*), 30.2 (NC$_5$H$_4$C*Me$_3$*), 34.7 (NC$_5$H$_4$*C*Me$_3$), 116.1, 118.0 (*C*$_5$Me$_5$), 121.2, 150.8, 162.2 (N*C*$_5$H$_4$CMe$_3$). Anal. Calcd. for C$_{45}$H$_{78}$N$_6$Si$_2$SrTi$_3$ (%): C 54.55, H 7.95, N 8.48; found: C 54.04, H 7.88, N 6.76.

X-ray structure determination of 8, 9, 10, 16 and 17. Crystals of **9**, **10** and **16** were mounted in a glass capillary in a random orientation and transferred to an Enraf-Nonius CAD4 diffractometer for characterization and data collection at room temperature. Crystals of complexes **8** and **17** were grown as described in the experimental section, 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 1 (see page 24).

The structures were solved, using the WINGX package,[17] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[18]

All non-hydrogen atoms of **8**, **9** and **10** were anisotropically refined. All the hydrogen atoms of **8** and **9** were located in the difference Fourier map and refined isotropically, using a 5/6 factor of occupancy for the imido hydrogen. In the case of **10** all the hydrogen atoms were positioned

geometrically and refined by using a riding model, with the same 5/6 occupancy for the imido hydrogen atom.

Poor quality crystals of complexes **16** and **17** crystallized with two molecules of toluene. Complex **16** presented severe disorder in both solvent molecules, which only could be refined isotropically. The rest of all non-hydrogen atoms of **16**, except C22, C26, C27 C28 from one pentamethylcyclopentadienyl ring were anisotropically refined. Only the hydrogen atoms of the pentamethylcyclopentadienyl rings and the imido group (N23-H23) were included, positioned geometrically and refined by using a riding model.

On the other hand, complex **17** presented severe disorder in one of the toluene solvent molecules (C201-C204) while the other (C101-C103) only showed disorder in the methyl group (two sites, 50% occupancy). All non-hydrogen atoms except those of the C201-C204 toluene molecule were anisotropically refined. All hydrogen atoms were included, positioned geometrically and refined by using a riding model. Two imido hydrogen atoms statistically distribute over the four N13 nitrogen atoms linked to the central strontium (final 50% of occupancy) while the other two imido hydrogen atoms are positioned over the two N12 atoms. The highest peak found in the difference Fourier map of 3.167 eÅ^{-3} is located close to Sr1 (0.90 Å).

Results and Discussion

Cube-Type Complexes Containing Alkali Metals. The synthetic chemistry is outlined in Scheme 1. Treatment of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) with 1 equiv of Group 1 bis(trimethylsilyl)amido reagents [M{N(SiMe$_3$)$_2$}][15] in toluene at room temperature led to bis(trimethylsilyl)amine and precipitation of the alkali metal derivatives [M(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (M = Li (**2**), Na (**3**), K (**4**), Rb (**5**), Cs (**6**)). The preparation of **2-4** in high yields as orange (**2** and **3**) or yellow (**4**) crystals was carried out by careful layering

of toluene solutions of **1** with toluene solutions of the corresponding amido reagents.[13] However, the synthesis of the rubidium (**5**) and cesium (**6**) derivatives was performed under vigorous magnetic stirring to obtain the compounds as yellow solids in 60% yield. The stirring of the reaction mixture is crucial for the heavier Group 1 derivatives, otherwise dark green crystals identified by X-ray crystal structure determinations (vide infra) as the corner-shared double cube azaheterometallocubane complexes $[M(\mu_3\text{-N})(\mu_3\text{-NH})_5\{Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}_2]$ (M = Rb (**9**), Cs (**10**)) are isolated in poor yields. Accordingly, a more convenient synthesis for the complexes **9**-**10**, and the analogous potassium derivative $[K(\mu_3\text{-N})(\mu_3\text{-NH})_5\{Ti_3(\eta^5\text{-C}_5Me_5)_3(\mu_3\text{-N})\}_2]$ (**8**), involves the reaction of **1** with 0.5 equiv of the alkali metal amido reagents $[M\{N(SiMe_3)_2\}]$ at room temperature, isolating **8**, **9** and **10** as dark green crystals in 60-75% yields.
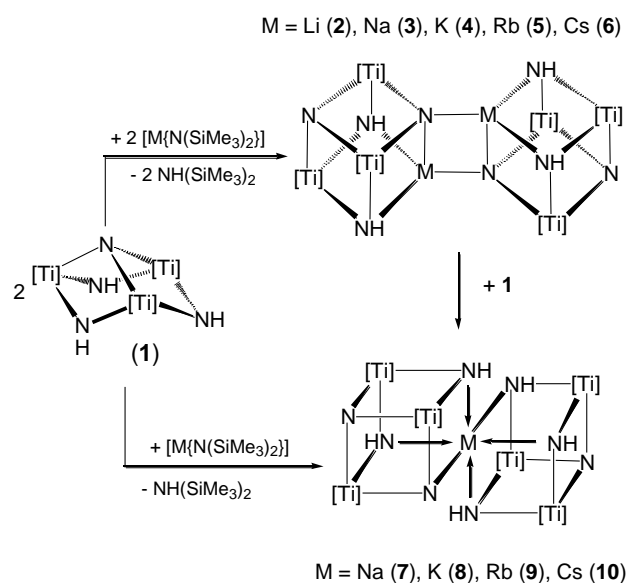
Scheme 1. Synthesis of the double cube nitrido complexes **2**-**10**. [Ti] = $Ti(\eta^5\text{-C}_5Me_5)$

The existence of both edge-linked and corner-shared double cube complexes for the heavier alkali metals moved us to try the preparation of corner-shared derivatives of lithium, sodium or potassium by treatment of **2**-**4** with complex **1**. While the potassium complex **4** reacts immediately with **1** in toluene at room temperature to give **8**, the sodium complex **3**

needs prolonged heating at 70 ºC to afford $[Na(\mu_3-N)(\mu_3-NH)_5\{Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}_2]$ (**7**) as an orange solid in elevated yield, and attempts to prepare a double cube complex of lithium failed since **2** did not react with **1** even at 100 ºC for several days.

Compounds **2**-**10** were characterized by infrared spectroscopy and C, H, N microanalysis, as well as by X-ray crystal structure determinations for **2**, **3**, **8**, **9** and **10**. Attempts to establish the degree of association of the compounds in the gas phase by mass spectrometry (EI, 70 eV) were unsuccessful due to the lack of volatility. IR spectroscopy (KBr) was not very informative to elucidate edge-linked or corner-shared structures since all the spectra are very similar, displaying only one absorption in the 3352-3336 cm^{-1} range for the ν_{NH} vibrations and several very strong bands at 739-611 cm^{-1} for the ν_{MN} vibrations in the molecules.

Once isolated in the solid state, all the compounds are virtually insoluble in benzene-d$_6$ or toluene-d$_8$, and decompose in chloroform-d$_1$. Fortunately, edge-linked compounds **2**-**6** are soluble in pyridine-d$_5$ and could be characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR data are consistent with a C$_s$ symmetry in solution for these complexes. ^1H NMR spectra reveal resonance signals for two η^5-C$_5$Me$_5$ groups in a 2:1 ratio and broad signals for equivalent NH groups. The $^{13}C\{^1H\}$ NMR spectra show also two sets of resonances for the η^5-C$_5$Me$_5$ ligands. On the other hand, complexes **7**-**10** are not soluble in pyridine-d$_5$ and attempts to gain insight into their structures by NMR spectroscopy failed.

The solid state structures of **2** and **3** revealed two azaheterometallocubane cores [MTi$_3$N$_4$] linked by metal nitrogen bonds.[13] The structures showed four coordinate lithium and sodium atoms, and were essentially identical with the differences due to the atomic radii of the alkali metal elements. Despite many attempts, we were not able to grow suitable crystals for the unambiguous structure determination in the solid-state of the potassium, rubidium or

cesium derivatives **4**-**6**. Therefore, we can only tentatively suggest an analogous composition in base to the similarities of the spectroscopic data and solubility properties.

Complexes **8**-**10** crystallize as solvent-free molecules. The structures confirm similar corner-shared double-cube [MTi$_6$N$_8$] cores to those found in our previous studies.[9,10,14] Selected distances and angles of the three structures are compared in Table 2. The molecular structure of **8** is shown in Figure 1, a simplified view of the core of **9** in Figure 2, and a Van der Waals model for the cesium complex **10** is given in Figure 3.

Table 2. Selected averaged lengths (Å) and angles (°) for complexes **1** and **8**-**10**.

	1	**8** (M = K)	**9** (M = Rb)	**10** (M = Cs)
M-N		2.958(2)	3.070(3)	3.219(4)
Ti-N	1.924(6)	1.930(2)	1.918(3)	1.925(4)
M···Ti		3.682(1)	3.808(2)	3.968(1)
Ti···Ti	2.802(3)	2.802(1)	2.795(1)	2.800(1)
Ti-N-Ti	93.7(3)	93.1(1)	93.6(1)	93.3(2)
N1-Ti-N	85.9(3)	86.6(1)	86.2(1)	86.5(1)
N-Ti-N	107.5(3)	104.1(1)	103.8(2)	104.1(2)
N-M-N[a]		62.0(1)	58.8(1)	56.2(1)
		118.0(1)	121.2(1)	123.8(1)
Ti-N-M		95.4(1)	96.8(1)	97.8(1)

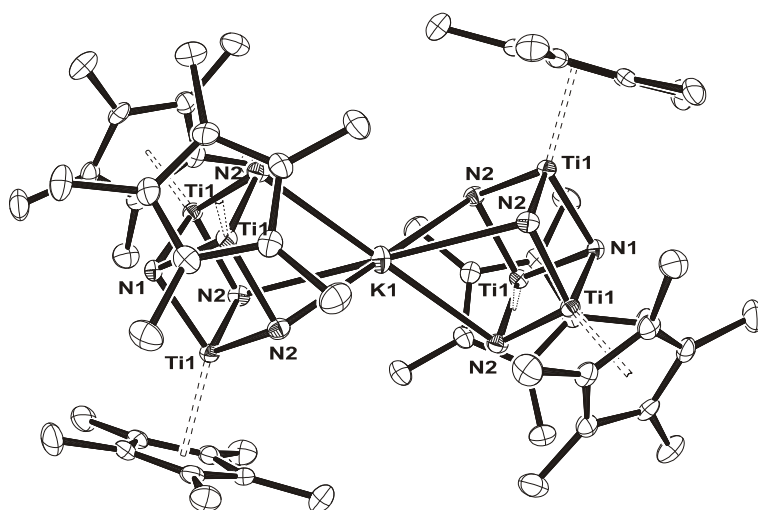[a] Narrower values correspond to intracube and wider to intercubes N-M-N angles.

Figure 1. Perspective view of [K(μ$_3$-N)(μ$_3$-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}$_2$] (**8**) with thermal ellipsoids at the 50% probability level.

Figure 2. Simplified view of $[Rb(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**9**) with thermal ellipsoids at the 50% probability level.

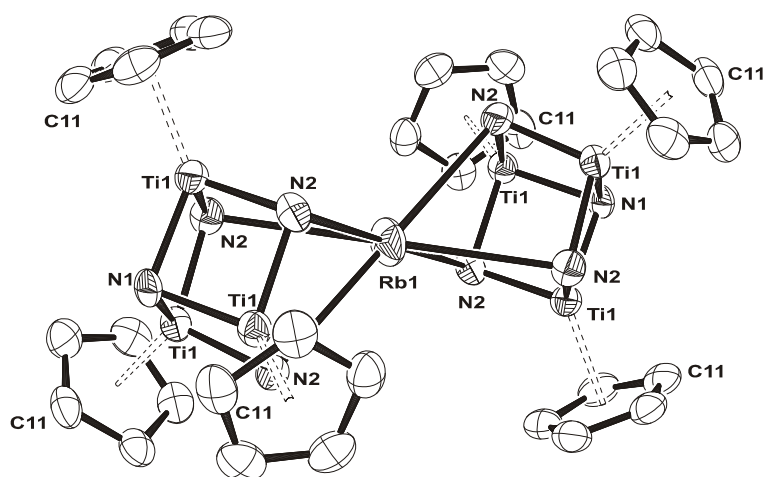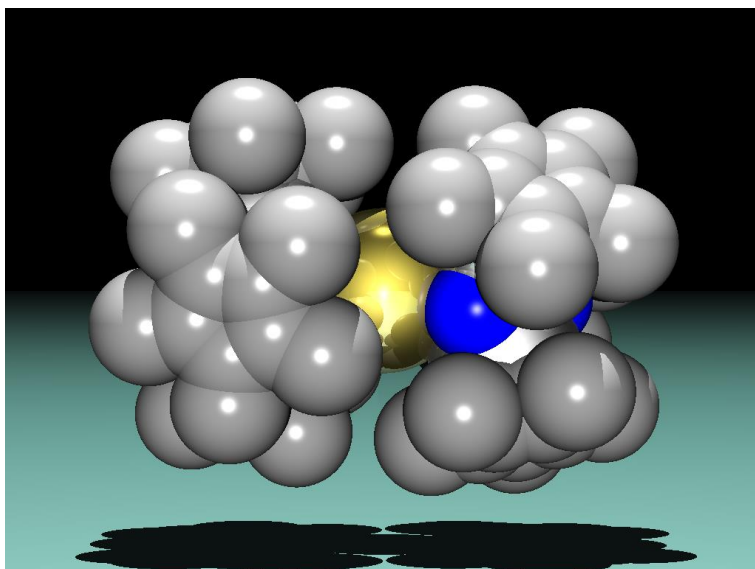**Figure 3.** Van der Waals model for $[Cs(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**10**). Hydrogen atoms are omitted.

Molecules of **8**, **9** and **10** lie on crystallographic inversion centers located on the alkali metal atoms and present a C_3 axis along the $N(1)\cdots M(1)$ line. The six-coordinate geometries around the potassium, rubidium and cesium centers are best described as trigonal antiprism where the two tridentate organometallic ligands adopt a mutually staggered conformation.

15

Within the tridentate ligands, the titanium-nitrogen bond lengths and the titanium-nitrogen-titanium angles in complexes **8-10** are very similar and compare well with those determined for **1**.[7]

As can be seen in Table 2, the alkali metal-nitrogen bond distances increase down the group (K 2.958(2) Å, Rb 3.070(3) Å, Cs 3.219(4) Å). The increments from K to Rb (0.112 Å) and Rb to Cs (0.149 Å) are very close to the difference among their ionic radii in six-coordinate geometries.[19] In agreement with those increments and geometries, the N-M-N intracube angles decrease with the higher cation size (K 62.0(1)º, Rb 58.8(1)º, Cs 56.2(1)º), whereas the N-M-N intercubes angles increase (K 118.0(1)º, Rb 121.2(1)º, Cs 123.8(1)º). For comparison, the M-N bond lengths in **8-10** are close to the averaged values found in the other polydentate anionic nitrogen ligands,[20] and also to the values reported for complexes containing tridentate neutral nitrogen ligands.[21]

Cube-Type Complexes Containing Alkaline-Earth Metals. The synthetic chemistry is outlined in Scheme 2. Treatment of **1** with one equivalent of Group 2 bis(trimethylsilyl)amido reagents $[M\{N(SiMe_3)_2\}_2(thf)_2]$[16] in toluene led to the alkaline-earth derivatives $[(thf)_x\{(Me_3Si)_2N\}M\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ [x = 0 M = Mg (**11**); x = 1 M = Ca (**12**), Sr (**13**)] via bis(trimethylsilyl)amine elimination. The reaction with the magnesium amido complex was very slow at room temperature and was carried out at 50 ºC, but the calcium and strontium derivatives reacted almost immediately. Complexes **11-13** were isolated as orange solids in 75-90% yields after workup and characterized by spectral and analytical techniques, as well as by an X-ray crystal structure determination for **11**. Whereas the structural data for **11** correspond to a solvent-free single-cube structure,[14] the presence of one tetrahydrofuran ligand in **12** and **13** was established through the spectroscopic and analytical data. The complexes are stable under argon atmosphere during months in the solid state but

their solutions exhibit a different behavior. Complex **11** is thermally stable in benzene-d_6 solutions at 150 ºC but the analogous calcium and strontium complexes **12** and **13** decompose within hours at room temperature via ligand redistribution reactions (vide infra). In the same way, although an analogous barium derivative $[(thf)_x\{(Me_3Si)_2N\}Ba\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**14**) was detected by NMR spectroscopy[14] following the reaction of **1** with 1 equiv of $[Ba\{N(SiMe_3)_2\}_2(thf)_2]$[16] in benzene-$d_6$, **14** decomposed within minutes and was not isolated in a pure form.
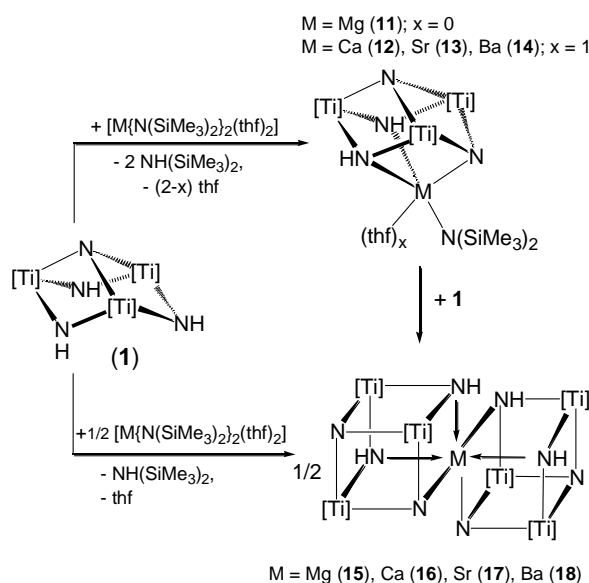
Scheme 2. Synthesis of single and double cube nitrido complexes **11**-**18**. $[Ti] = Ti(\eta^5\text{-}C_5Me_5)$

Analogous treatment of **1** with 0.5 equiv of Group 2 bis(trimethylsilyl)amido reagents in toluene at 20-50 ºC afforded the corner-shared double cube azaheterometallocubane complexes $[M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (M = Mg (**15**), Ca (**16**), Sr (**17**), Ba (**18**)). Complexes **15**-**18** were isolated in 45-60% yield as red or orange suitable crystals for X-ray diffraction studies directly from the reaction. Alternatively, **15**-**17** can be also prepared through the reaction of the single cube complexes **11**-**13** with 1 equiv of **1** in toluene at room temperature.

Complexes **15**-**18** were characterized by infrared spectroscopy and C, H, N microanalysis, as well as by X-ray crystal structure determinations. IR spectra showed a unique absorption at 3354-3318 cm^{-1} for the ν_{NH} vibrations and several strong bands at the 730-618 cm^{-1} range for the ν_{MN} vibrations in the molecules. None of the double cube complexes is soluble in arene, tetrahydrofuran or pyridine solvents; therefore, it was not possible to obtain their NMR spectra.

The molecular structures of $[Ca\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**16**) and $[Sr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**17**) are presented as examples in Figures 4 and 5. Selected distances and angles of complexes **15**[14], **16**, **17** and **18**[14] are compared in Table 3.
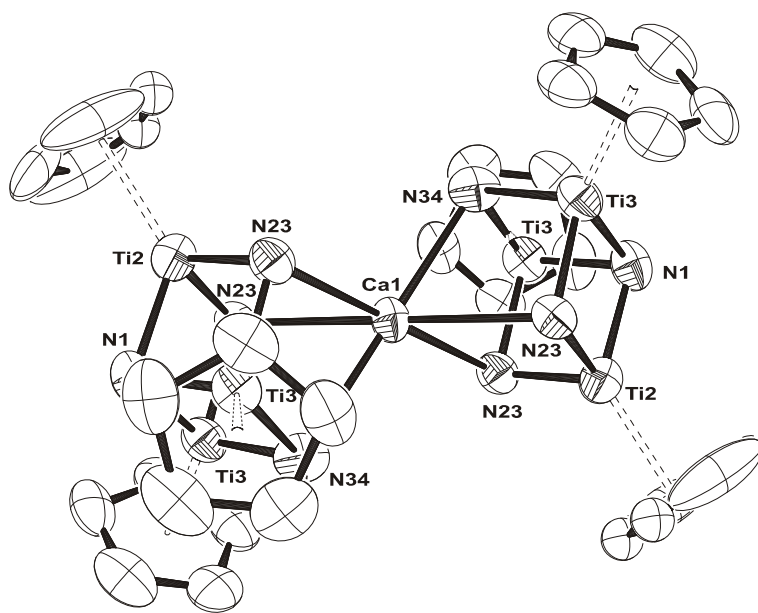

Figure 4. Simplified view of $[Ca\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**16**) with thermal ellipsoids at the 50% probability level.

Figure 5. Simplified view of $[Sr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**17**) with thermal ellipsoids at the 50% probability level.

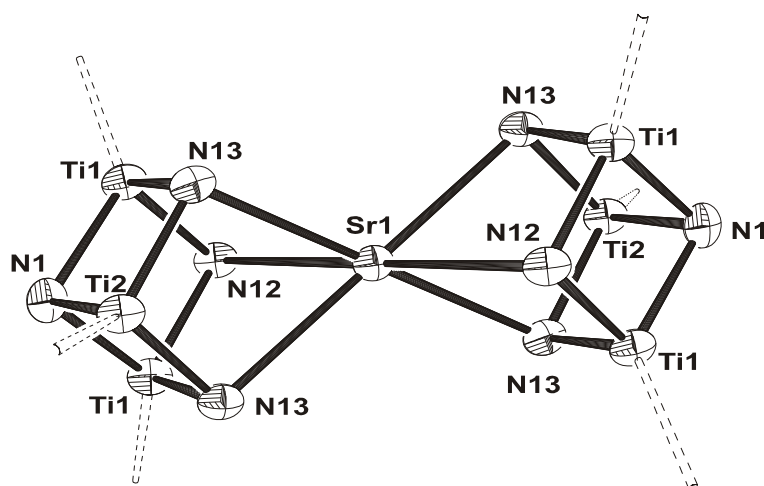**Table 3.** Selected averaged lengths (Å) and angles (°) for complexes **1** and **15-18**.

	1	**15** (M = Mg)	**16** (M = Ca)	**17** (M = Sr)	**18** (M = Ba)
M-N		2.304(8)	2.518(11)	2.686(6)	2.821(9)
Ti-N	1.924(6)	1.933(8)	1.924(10)	1.946(5)	1.925(9)
M···Ti		3.059(2)	3.282(2)	3.453(1)	3.594(2)
Ti···Ti	2.802(3)	2.815(3)	2.797(3)	2.817(2)	2.790(3)
Ti-N-Ti	93.7(3)	93.2(4)	93.1(5)	92.5(3)	92.8(4)
N1-Ti-N	85.9(3)	86.7(3)	86.8(4)	87.3(2)	87.0(4)
N-Ti-N	107.5(3)	97.0(4)	98.7(5)	100.1(3)	100.7(4)
N-M-N[a]		77.6(3)	70.7(3)	67.4(2)	63.3(2)
		102.4(3)	109.3(3)	112.6(2)	116.7(2)
Ti-N-M		92.2(3)	94.4(4)	95.2(2)	96.7(3)

[a] Narrower values correspond to intracube and wider to intercubes N-M-N angles.

Complexes **16** and **17** crystallize with two toluene molecules, and the structures confirm the expected corner-shared double-cube $[MTi_6N_8]$ cores. Molecules of **16** and **17** lie on crystallographic inversion centers on the M atoms, and present a mirror plane containing the central metal center, one titanium and also the apical N1 nitrogen atom. The calcium or strontium central atoms exhibit six-coordinate geometries in which the nitrogen atoms occupy the vertices of a trigonal antiprism. In that arrangement, the tridentate organometallic ligands

$\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$ force the pentamethylcyclopentadienyl groups to be into an alternate position.

The existence of structural data for the six-coordinate Mg-Ba complexes **15**-**18** allows making a comparison on bond lengths and angles along the Group 2. The N-M-N intracube angles decrease with the higher cation size (Mg 77.6(3)º, Ca 70.7(3)º, Sr 67.4(2)º, Ba 63.3(2)º), whereas the N-M-N intercubes angles increase with an inverse tendency (Mg 102.4(3)º, Ca 109.3(3)º, Sr 112.6(2)º, Ba 116.7(2)º). As can be observed in Table 3, the alkaline-earth metal-nitrogen bond distances increase down the group. The increments from Mg to Ca (0.214 Å), Ca to Sr (0. 168 Å) and Sr to Ba (0.135 Å) are close to the difference among their ionic radii in six-coordinate geometries.[19] The six-coordinate geometries around the alkaline-earth metals in complexes **15**-**18** resemble those determined for the bis(hydrotris(pyrazolyl)borato) complexes Tp_2M (M = Mg,[22,23] Ca,[23,24] Sr,[24] Ba[25]) but showing longer M-N bond lengths and narrower N-M-N intraligand angles.

The existence of crystal structures with corner-shared double cube cores for the Group 1 (**8**-**10**) and 2 (**15**-**18**) elements allows to compare bond lengths between elements of the same group or the same row, as it is illustrated in Figure 6.[26] As already pointed out for the compounds **8**-**10** or **15**-**18**, again the variance of the distances M···Ti for M = K to M = Ca (0.400 Å), Rb to Sr (0.355 Å), and Cs to Ba (0.374 Å) are similar to those expected from their ionic radii in six-coordinate geometries (K^+ - Ca^{2+} 0.380 Å, Rb^+ - Sr^{2+} 0.340 Å, Cs^+ - Ba^{2+} 0.320 Å).
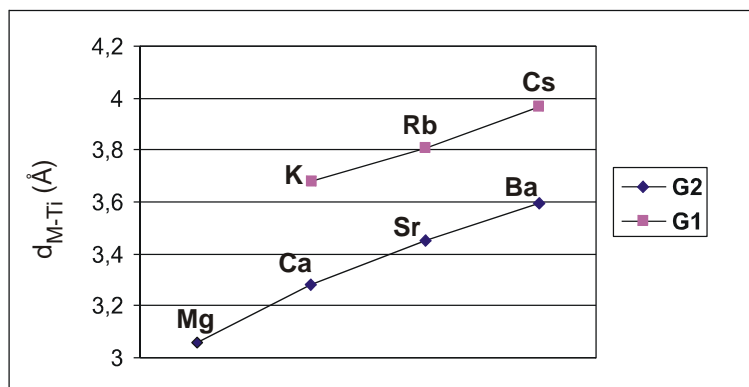
Figure 6. Periodic variation of the M···Ti distance for Group 1 and 2 elements in the corner-shared azaheterometallocubanes **8**-**10** and **15**-**18**.

On the other hand, the increase in the size of the metal center down the group 2 could be related with the different stability in solution exhibited by the single-cube complexes $[(thf)_x\{(Me_3Si)_2N\}M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**11**-**14**). The four-coordinate magnesium complex **11** is stable at high temperatures in benzene-d_6 but less crowded alkyl derivatives $[RMg\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (R = CH_2Ph, CH_2CMe_3)[14] undergo ligand redistribution reactions at room temperature to give the insoluble corner-shared double cube azaheterometallocube complex $[Mg\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**15**). Analogous processes from alkylmagnesium containing hydro(trispyrazolyl)borato ligands have been reported by Parkin et al. and compared with the Schlenk equilibrium (eq 1).[22]

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \quad (1)$$
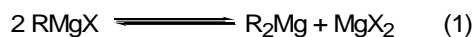
The calcium and strontium derivatives **12** and **13** present one tetrahydrofuran molecule in the coordination sphere, but the larger size of those metals allows their participation in Schlenk-type equilibriums to give the double cube complexes **16** and **17** at room temperature. In order to obtain single cube-type complexes with increased thermal stability, the replacement

of the tetrahydrofuran ligands by other neutral donors was examined. Treatment of **12** and **13,** prepared *in situ*, with 4-*tert*-butylpyridine in toluene at room temperature afforded the analogous compounds [(*t*Bupy){(SiMe$_3$)$_2$N}M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]] (M = Ca (**19**), Sr (**20**)) as orange solids (Scheme 3). The structural assignment of **19** and **20** was based on spectral and analytical data. Although **19** and **20** show an enhanced thermal stability when compared to the tetrahydrofuran adducts **12** and **13**, their solutions still decompose at room temperature within days to give the insoluble double cube complexes **16** and **17**. Preliminary studies on the reaction of **12** and **13** with polydentate amines (TMEDA, bipyridine,…) did not afford more stable adducts and were not pursued further.

M = Ca (**12**), Sr (**13**)   M = Ca (**19**), Sr (**20**)
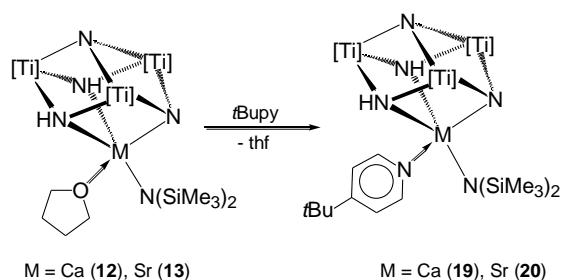
Scheme 3. Synthesis of the single cube complexes **19** and **20**.

Conclusion

The trinuclear complex [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) is capable to incorporate alkali and alkaline-earth metals into its incomplete cube structure to give cube-type derivatives. The titanium/alkali metal azaheterometallocubane complexes exhibit edge-linked double cube [M$_2$Ti$_6$N$_8$] or corner-shared double cube [MTi$_6$N$_8$] central cores. The former structures show the alkali metals in four-coordinate geometries and are preferred for the lighter elements (Li, Na), whereas the heavier elements (K, Rb, Cs) led to that containing six-coordinate alkali metals. In the same way, for the alkaline-earth metals derivatives single cube

structures [MTi$_3$N$_4$] are stable only for magnesium complexes bearing bulky anionic ligands. The less-crowded magnesium derivatives and those of the heavier Group 2 elements show a tendency to give corner-shared double cube azaheterometallocubane complexes, where the alkaline-earth atoms exhibit six-coordinate geometries.

Supporting Information Available: X-ray crystallographic files in CIF format for **8**, **9**, **10**, **16**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 1. Experimental data for the X-ray diffraction studies on compounds **8**, **9**, **10**, **16** and **17.**

Formula	$C_{60}H_{95}KN_8Ti_6$ (**8**)	$C_{60}H_{95}N_8RbTi_6$ (**9**)	$C_{60}H_{95}CsN_8Ti_6$ (**10**)	$C_{60}H_{94}CaN_8Ti_6$ (**16**) $2C_7H_8$	$C_{60}H_{94}N_8SrTi_6$ (**17**) $2C_7H_8$
M_r	1254.94	1301.31	1348.76	1439.18	1486.72
T [K]	100(2)	293(2)	293(2)	293(2)	100(2)
λ[Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	Trigonal	Trigonal	Trigonal	Orthorhombic	Orthorhombic
space group	R-3	R-3	R-3	Pnnm	Pnnm
a [Å]	18.523(2)	18.767(6)	18.799(5)	15.324(3)	14.590(3)
b [Å]	18.523(2)	18.767(6)	18.799(5)	14.731(3)	16.724(3)
c [Å]	15.474(2)	15.741(8)	16.115(5)	16.680(3)	15.165(3)
V [Å^3]	4597.5(7)	4801(3)	4932(2)	3765.3(13)	3700.5(11)
Z	3	3	3	2	2
ρ_{calcd} [g cm^{-3}]	1.360	1.350	1.362	1.269	1.334
$\mu_{MoK\alpha}$ [mm^{-1}]	0.856	1.510	1.280	0.718	1.375
$F(000)$	1986	2040	2094	1524	1560
crystal size [mm]	0.46 x 0.30 x 0.15	0.35 x 0.30 x 0.25	0.43 x 0.32 x 0.30	0.28 x 0.18 x 0.12	0.664 x 0.316 x 0.222
θ range	5.25 to 27.49°	1.80 to 22.49°.	1.78 to 22.97°.	1.80 to 24.96º	4.79 to 30.23
index ranges	-23≤h≤21, -23≤k≤24, -20≤l≤20	-16≤h≤20, -20≤k≤20, -17≤l≤12	-20≤h≤0, 0≤k≤20, 0≤l≤17	-18≤h≤0, -17≤k≤0, -19≤l≤0	-18≤h≤18, -19≤k≤19, -21≤l≤21
reflections collected	18910	4665	1675	3716	44388
Unique data	2322 [R_{int} = 0.151]	1493 [R_{int} = 0.106]	1529 [R_{int} = 0.021	3430 [R_{int} = 0.002]	4345 [R_{int} = 0.242]
obsd data [I>2σ(I)]	1901	1250	1202	1286	3496
goodness-of-fit on F^2	1.047	1.082	1.080	1.013	1.103
final R indices [I>2σ(I)]	R1 = 0.044, wR2 = 0.105	R1 = 0.038, wR2 = 0.092	R1 = 0.046, wR2 = 0.116	R1 = 0.105, wR2 = 0.269	R1 = 0.106, wR2 = 0.252
R indices (all data)	R1 = 0.059, wR2 = 0.114	R1 = 0.050, wR2 = 0.097	R1 = 0.068, wR2 = 0.126	R1 = 0.275, wR2 = 0.353	R1 = 0.129, wR2 = 0.276
largest diff. Peak/hole [e.Å^{-3}]	0.632/-0.633	0.514/-0.293	0.564/-0.409	1.320/-0.580	3.167/-1.459

[a] $R1=\Sigma||F_0|-|F_c||/[\Sigma|F_0|]$ $wR2= \{[\Sigma w(F_0^2 - F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$

Footnotes

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