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Inorganic Chemistry Article

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

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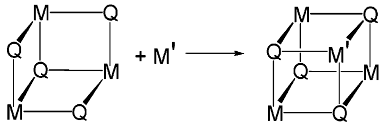
Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with alkali-metal bis(trimethylsilyl)amido derivatives $[M\{N(SiMe_3)_2\}]$ in toluene affords edge-linked double-cube nitrido complexes $[M(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (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). Analogous reactions with 1/2 equiv of alkaline-earth bis(trimethylsilyl)amido derivatives $[M\{N(SiMe_3)_2\}_2(thf)_2]$ give 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). If 1 equiv of the group 2 amido reagent is employed, single-cube-type derivatives $[(thf)_x\{(Me_3Si)_2N\}M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (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 $[(tBupy)\{(Me_3Si)_2N\}M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Ca, Sr). The X-ray crystal structures of $[M(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (M = K, Rb, Cs) and $[M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (M = Ca, Sr) have been determined. The properties and solid-state structures of the azaheterometallocubane complexes bearing alkali and alkaline-earth metals are discussed.

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 that type of complex 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. [3 + 1] Building-Block Synthesis of Heterometallic Cube-Type Complexes



In 1995, we reported the synthesis and structure of a singular organometallic nitrido complex, $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$, which contains an almost perfect $[Ti_4N_4]$ cube-type core.[6] This compound can also be obtained by treatment of the trinuclear imido−nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}$

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(1) For reviews, see: (a) Coucouvanis, D. *Acc. Chem. Res.* **1991**, *24*, 1−8. (b) Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1−71. (c) Dance, I.; Fisher, K. *Prog. Inorg. Chem.* **1994**, *41*, 637−803. (d) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093−2121.

(2) (a) Hidai, M.; Kuwata, S.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46−52. (b) Llusar, R.; Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271−1290.

(3) (a) Shibahara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143−173. (b) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73−147.

(4) For reviews, see: (a) Hernández-Molina, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1999**, 3137−3148. (b) Hernández-Molina, R.; Sokolov, M. N.; Sykes, A. G. *Acc. Chem. Res.* **2001**, *34*, 223−230.

(5) For selected recent examples, see: (a) Zhou, J.; Raebiger, J. W.; Crawford, C. A.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 6242−6250. (b) Herbst, K.; Rink, B.; Dahlenburg, L.; Brorson, M. *Organometallics* **2001**, *20*, 3655−3660. (c) Herbst, K.; Zanello, P.; Corsini, M.; D'Amelio, N.; Dahlenburg, L.; Brorson, M. *Inorg. Chem.* **2003**, *42*, 974−981. (d) Takei, I.; Suzuki, K.; Enta, Y.; Dohki, K.; Suzuki, T.; Mizobe, Y.; Hidai, M. *Organometallics* **2003**, *22*, 1790−1792. (e) Seino, H.; Kaneko, T.; Fujii, S.; Hidai, M.; Mizobe, Y. *Inorg. Chem.* **2003**, *42*, 4585−4596.

(6) Gómez-Sal, P.; Martín, A.; Mena, M.; Yélamos C. *J. Chem. Soc., Chem. Commun.* **1995**, 2185−2186.

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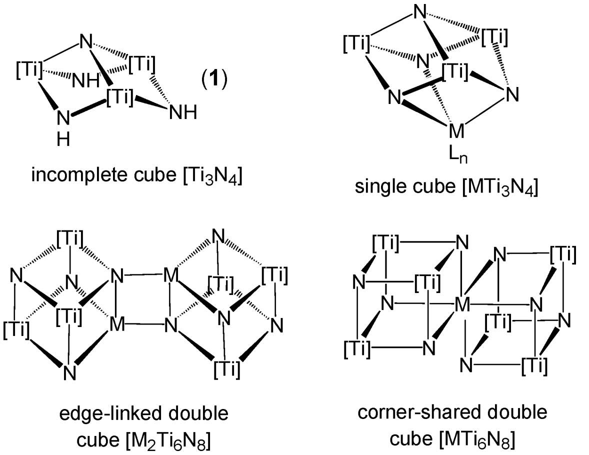
Chart 2. Structural Core of **1** and $[MTi_3N_4]$ Cube-Type Complexes ($[Ti] = Ti(\eta^5\text{-}C_5Me_5)$)



NH)}$_3$(μ_3-N)]^7 (**1**) with $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$.[8] Complex **1** shows an incomplete cube $[Ti_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$ core (Chart 2), which strongly resembles those found in iron $[Fe_3S_4]$ and group 6 $[M_3Q_4]$ chalcogenide clusters. On the basis of 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 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,[8−10] 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 groups 1 and 2 in structures and properties.

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 alloy (C_6D_6) or calcium hydride (C_5D_5N) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. $[M\{N(SiMe_3)_2\}]$ (M = Li, Na, K) complexes were purchased from Aldrich and used as received. 4-*tert*-Butylpyridine was purchased from Aldrich and distilled from calcium hydride prior to use. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**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. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts (δ, ppm) are given relative to the peak for residual protons or carbon of the solvent. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzer.

Synthesis of $[M(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (M = Li (2), Na (3), K (4)). The syntheses and characterization of complexes **2**−**4** have been reported previously.[13] However, 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 $\mathbf{2}\cdot C_7H_8$ (0.43 g, 80%). ^1H NMR (C_5D_5N, 20 °C, δ): 2.07 (s, 15H, C_5Me_5), 2.17 (s, 30H, C_5Me_5), 12.36 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_5D_5N, 20 °C, δ): 11.9, 12.0 (C_5*Me*$_5$), 115.0, 116.4 (*C*$_5$Me$_5$).

NMR Data for 3. ^1H NMR (C_5D_5N, 20 °C, δ): 2.04 (s, 15H, C_5Me_5), 2.16 (s, 30H, C_5Me_5), 12.83 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_5D_5N, 20 °C, δ): 12.0, 12.1 (C_5*Me*$_5$), 113.8, 115.2 (*C*$_5$Me$_5$).

NMR Data for 4. ^1H NMR (C_5D_5N, 20 °C, δ): 2.09 (s, 15H, C_5Me_5), 2.18 (s, 30H, C_5Me_5), 13.14 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_5D_5N, 20 °C, δ): 12.0, 12.1 (C_5*Me*$_5$), 113.5, 114.9 (*C*$_5$Me$_5$).

Synthesis of $[Rb(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (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). ^1H NMR (C_5D_5N, 20 °C, δ): 2.09 (s, 15H, C_5Me_5), 2.19 (s, 30H, C_5Me_5), 13.20 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_5D_5N, 20 °C, δ): 12.1, 12.2 (C_5*Me*$_5$), 113.4, 114.8 (*C*$_5$Me$_5$). Anal. Calcd for $C_{60}H_{94}N_8Rb_2Ti_6$: C, 51.99; H, 6.85; N, 8.09. Found: C, 52.25; H, 6.81; N, 7.27.

Synthesis of $[Cs(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (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). ^1H NMR

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(7) Roesky, H. W.; Bai, Y.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 754−755.

(8) Abarca, A.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J. M.; Yélamos, C. *Inorg. Chem.* **2000**, *39*, 642−651.

(9) Abarca, A.; Martín, A.; Mena, M.; Yélamos, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 3460−3463.

(10) Abarca, A.; Galakhov, M. V.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J. M.; Sarasa, J. P.; Yélamos, C. *Chem.*—*Eur. J.* **2003**, *9*, 2337−2346.

(11) Abarca, A.; Galakhov, M.; Gómez-Sal, P.; Martín, A.; Mena, M.; Poblet, J. M.; Santamaría, C.; Sarasa, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 534−537.

(12) Freitag, K.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J. M.; Sarasa, J. P.; Yélamos, C. *Chem.*—*Eur. J.* **2001**, *7*, 3644−3651.

(13) García-Castro, M.; Martín, A.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Chem.*—*Eur. J.* **2001**, *7*, 647−651.

(14) Martín, A.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Organometallics* **2002**, *21*, 3308−3310.

(15) The unsolvated rubidium and cesium amido derivatives were prepared according to the procedure described by Edelmann et al.: Edelmann, F. T.; Pauer, F.; Wedler, M.; Stalke, D. *Inorg. Chem.* **1992**, *31*, 4143−4146. The analogous $[M\{N(SiMe_3)_2\}]$ (M = Li, Na, K) complexes are commercially available.

(16) Bradley, D. C.; Hurthouse, M. B.; Ibrahim, A. A.; Malik, K. M. A.; Montevalli, M.; Möseler, R.; Powell, H.; Runnacles, J. D.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 2959−2964.

(C_5D_5N, 20 °C, δ): 2.09 (s, 15H, C_5Me_5), 2.20 (s, 30H, C_5Me_5), 13.25 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_5D_5N, 20 °C, δ): 12.1, 12.2 ($C_5\textit{Me}_5$), 113.4, 114.7 ($\textit{C}_5Me_5$). Anal. Calcd for $C_{60}H_{94}Cs_2N_8Ti_6$: 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 h to give **7**$\cdot C_7H_8$ (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(μ_3-N)(μ_3-NH)$_5$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-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**$\cdot C_7H_8$ (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(μ_3-N)(μ_3-NH)$_5$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-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(μ_3-N)(μ_3-NH)$_5$\{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-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$_3$Si)$_2$N\}Ca\{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-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). ^1H NMR (C_6D_6, 20 °C, δ): 0.25 (s, 18H, N(SiMe$_3$)$_2$), 1.32 (m, 4H, thf), 2.05 (s, 15H, C_5Me_5), 2.10 (s, 30H, C_5Me_5), 3.73 (m, 4H, thf), 12.43 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 6.0 (SiMe$_3$), 12.0, 12.3 ($C_5\textit{Me}_5$), 25.0, 69.9 (thf), 116.4, 118.3 ($\textit{C}_5Me_5$). Anal. Calcd for $C_{40}H_{73}CaN_5OSi_2Ti_3$: 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). ^1H NMR (C_6D_6, 20 °C, δ): 0.24 (s, 18H, N(SiMe$_3$)$_2$), 1.31 (m, 4H, thf), 2.03 (s, 15H, C_5Me_5), 2.11 (s, 30H, C_5Me_5), 3.64 (m, 4H, thf), 12.67 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 5.9 (SiMe$_3$), 12.1, 12.3 ($C_5\textit{Me}_5$), 25.2, 69.3 (thf), 116.1, 117.9 ($\textit{C}_5Me_5$). Anal. Calcd for $C_{40}H_{73}N_5OSi_2SrTi_3$: 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**$\cdot 2C_7H_8$ (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**$\cdot 2C_7H_8$ (0.22 g, 61%). IR (KBr, cm^{-1}): 3333 (w), 2908 (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). ^1H NMR (C_6D_6, 20 °C, δ): 0.35 (s, 18H, N(SiMe$_3$)$_2$), 0.90 (s, 9H, $NC_5H_4C\textit{Me}_3$), 2.097 (s, 15H, C_5Me_5), 2.102 (s, 30H, C_5Me_5), 7.09 (m, 2H, $NC_5\textit{H}_4CMe_3$), 9.11 (m, 2H, $NC_5\textit{H}_4CMe_3$), 12.57 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 6.1 (SiMe$_3$), 12.0, 12.4 ($C_5\textit{Me}_5$), 30.1 ($NC_5H_4C\textit{Me}_3$), 34.6 ($NC_5H_4\textit{C}Me_3$), 116.4, 118.4 ($\textit{C}_5Me_5$), 120.8, 152.0, 162.4 ($N\textit{C}_5H_4CMe_3$). 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). ^1H NMR (C_6D_6, 20 °C, δ): 0.35 (s, 18H, N(SiMe$_3$)$_2$), 0.89 (s, 9H, $NC_5H_4C\textit{Me}_3$), 2.098 (s, 15H, C_5Me_5), 2.103 (s, 30H, C_5Me_5), 7.11 (m, 2H, $NC_5\textit{H}_4CMe_3$), 9.17 (m, 2H, $NC_5\textit{H}_4CMe_3$), 12.57 (s br, 2H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 6.0 (SiMe$_3$), 12.2, 12.4 ($C_5\textit{Me}_5$), 30.2 ($NC_5H_4C\textit{Me}_3$), 34.7 ($NC_5H_4\textit{C}Me_3$), 116.1,

Table 1. Experimental Data for the X-ray Diffraction Studies on Compounds **8**−**10**, **16**, and **17**

empirical 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**)$\cdot 2C_7H_8$	$C_{60}H_{94}N_8SrTi_6$ (**17**)$\cdot 2C_7H_8$
mol wt	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
cryst syst	trigonal	trigonal	trigonal	orthorhombic	orthorhombic
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	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
$\mu_{Mo\ K\alpha}$ (mm^{-1})	0.856	1.510	1.280	0.718	1.375
F(000)	1986	2040	2094	1524	1560
cryst size (mm)	0.46 × 0.30 × 0.15	0.35 × 0.30 × 0.25	0.43 × 0.32 × 0.30	0.28 × 0.18 × 0.12	0.664 × 0.316 × 0.222
θ range (deg)	5.25−27.49	1.80−22.49	1.78−22.97	1.80−24.96	4.79−30.23
index ranges	$-23 \le h \le +21$, $-23 \le k \le +24$, $-20 \le l \le +20$	$-16 \le h \le +20$, $-20 \le k \le +20$, $-17 \le l \le +12$	$-20 \le h \le 0$, $0 \le k \le +20$, $0 \le l \le +17$	$-18 \le h \le 0$, $-17 \le k \le 0$, $-19 \le l \le 0$	$-18 \le h \le +18$, $-19 \le k \le +19$, $-21 \le l \le +21$
no. of reflns collected	18910	4665	1675	3716	44388
no. of unique data	2322 ($R_{int} = 0.151$)	1493 ($R_{int} = 0.106$)	1529 ($R_{int} = 0.021$)	3430 ($R_{int} = 0.002$)	4345 ($R_{int} = 0.242$)
no. of obsd data [$I > 2\sigma(I)$]	1901	1250	1202	1286	3496
GOF on F^2	1.047	1.082	1.080	1.013	1.103
final R indices[a] [$I > 2\sigma(I)$]	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[a] (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] $R1 = \sum||F_o| - |F_c||/[\sum|F_o|]$. $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

118.0 (C_5Me$_5$), 121.2, 150.8, 162.2 (N$C_5H_4CMe_3$). Anal. Calcd for $C_{45}H_{78}N_6Si_2SrTi_3$: C, 54.55; H, 7.95; N, 8.48. Found: C, 54.04; H, 7.88; N, 6.76.

X-ray Structure Determination of 8−10, 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 (FomblinY). 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 100 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 1.

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**−**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 could only be refined isotropically. The rest of the non-hydrogen atoms of **16**, except C22, C26, C27, and 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 e Å^{-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_4-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(μ_3-N)(μ_3-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Rb (**9**), Cs (**10**)) are isolated in poor yields. Accordingly, a more convenient synthesis for complexes **9** and **10**, and the analogous potassium derivative [K(μ_3-N)(μ_3-NH)$_5${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-

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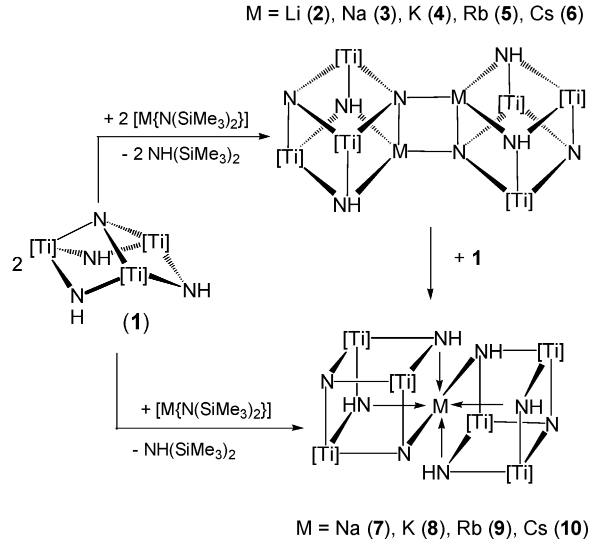
(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(18) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Analysis*, Release 97-2; Universität Göttingen: Göttingen, Germany, 1998.

Scheme 1. Synthesis of the Double-Cube Nitrido Complexes **2**−**10** ([Ti] = Ti(η^5-C_5Me_5))



$N)\}_2]$ (**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**−**10** as dark green crystals in 60−75% yields.

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 °C to afford $[Na(\mu_3\text{-}N)(\mu_3\text{-}NH)_5\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**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 °C 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**, and **8**−**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_5Me_5 groups in a 2:1 ratio and broad signals for equivalent NH groups. The $^{13}C\{^1H\}$ NMR spectra also show two sets of resonances for the η^5-C_5Me_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.

Table 2. Selected Averaged Lengths (Å) and Angles (deg) 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 values to intercube N−M−N angles.

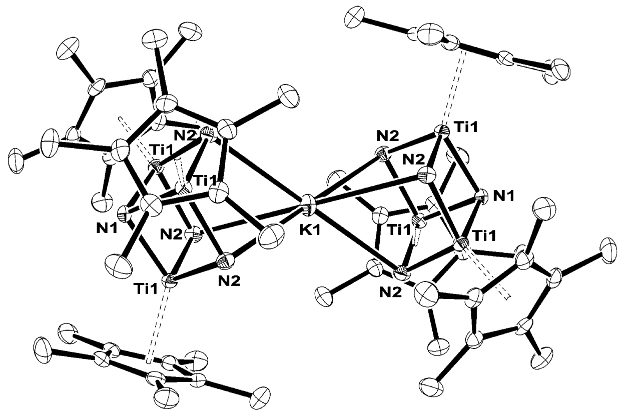


Figure 1. Perspective view of **8** with thermal ellipsoids at the 50% probability level.

The solid-state structures of **2** and **3** revealed two azaheterometallocubane cores $[MTi_3N_4]$ 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 on the basis of the similarities of the spectroscopic data and solubility properties.

Complexes **8**−**10** crystallize as solvent-free molecules. The structures confirm corner-shared double-cube $[MTi_6N_8]$ cores similar 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** in Figure 3.

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

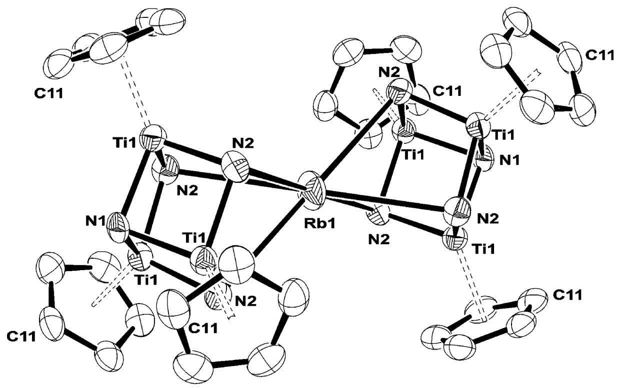


Figure 2. Simplified view of **9** with thermal ellipsoids at the 50% probability level.

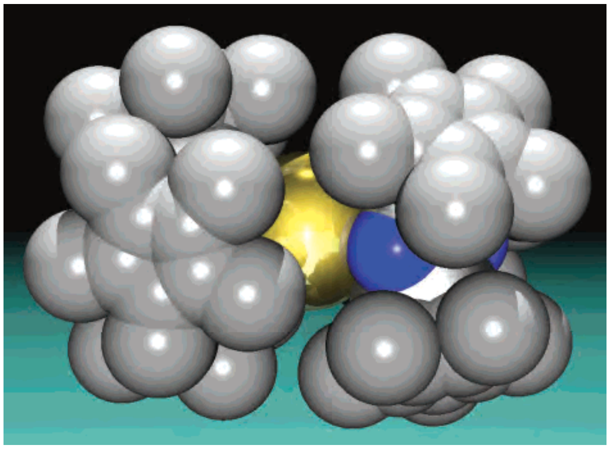
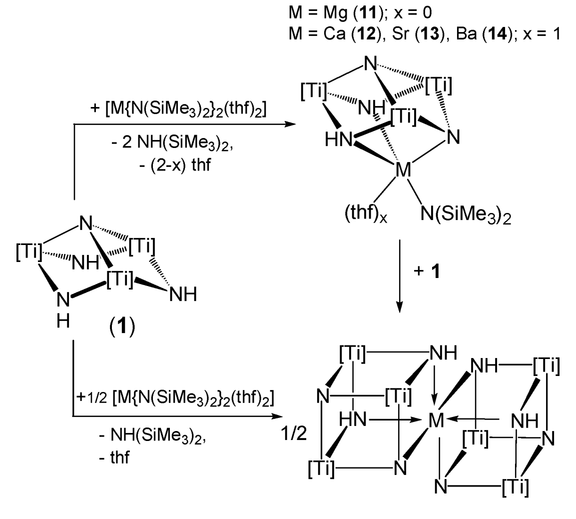


Figure 3. van der Waals model for **10**. Hydrogen atoms are omitted.

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 differences among their ionic radii in six-coordinate geometries.[19] In agreement with those increments and geometries, the N−M−N intracube angles decrease with higher cation size (K, 62.0(1)°; Rb, 58.8(1)°; Cs, 56.2(1)°), whereas the N−M−N intercubes angles increase (K, 118.0(1)°; Rb, 121.2(1)°; Cs, 123.8(1)°). 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.

Scheme 2. Synthesis of Single- and Double-Cube Nitrido Complexes **11**−**18** ([Ti] = Ti(η^5-C$_5$Me$_5$))



Treatment of **1** with 1 equiv 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$_3$Si)$_2$N}M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_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 °C, 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 °C, 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$_3$Si)$_2$N}Ba{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-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.

Analogous treatment of **1** with 0.5 equiv of group 2 bis(trimethylsilyl)amido reagents in toluene at 20−50 °C afforded the corner-shared double-cube azaheterometallocubane complexes [M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Mg (**15**), Ca (**16**), Sr (**17**), Ba (**18**)). Complexes **15**−**18** were isolated in 45−60% yield as red or orange crystals suitable for X-ray diffraction studies directly from the reaction. Alternatively, **15**−**17** can also be 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

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(19) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(20) (a) Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127−145. (b) Steiner, A.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 1977−1981. (c) Kottke, T.; Stalke, D. *Organometallics* **1996**, *15*, 4552−4558. (d) Liddle, S.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2001**, 402−408.

(21) (a) Hoffmann, D.; Bauer, W.; Schleyer, P. v R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193−1200. (b) Hithcock, P. B.; Lappert, M. F.; Leung, W.-P.; Diansheng, L.; Shun, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1386−1387. (c) Hoffmann, D.; Hampel, F.; Schleyer, P. v R. *J. Organomet. Chem.* **1993**, *456*, 13−17. (d) Hoffmann, D.; Bauer, W.; Hampel, F.; van Eikema Hommes, N. J. R.; Schleyer, P. v R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528−536. (e) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Tian, S. *Organometallics* **2000**, *19*, 4030−4035.

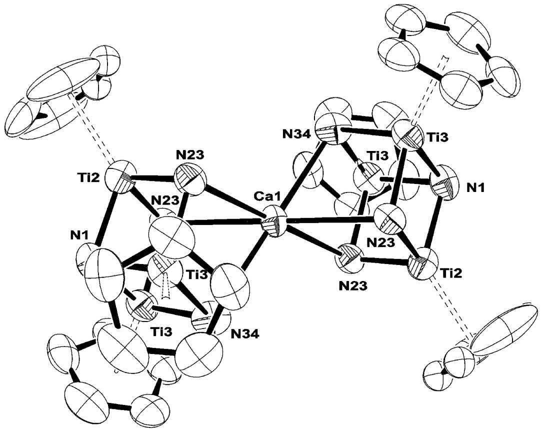

Figure 4. Simplified view of **16** with thermal ellipsoids at the 50% probability level.

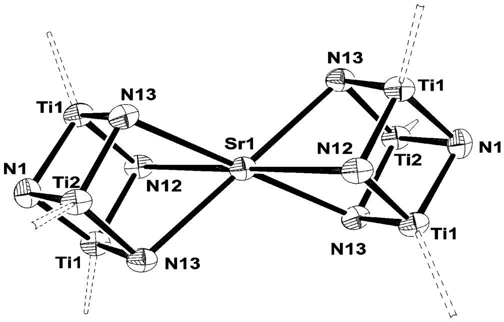

Figure 5. Simplified view of **17** with thermal ellipsoids at the 50% probability level.

Table 3. Selected Averaged Lengths (Å) and Angles (deg) 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 values to intercube N−M−N angles.

crystal structure determinations. IR spectra showed a unique absorption at 3354−3318 cm^{-1} for the ν_{NH} vibrations and several strong bands in the 730−618 cm^{-1} range for the ν_{MN} vibrations in the molecules. None of the double-cube complexes are soluble in arene, tetrahydrofuran, or pyridine solvents; therefore, it was not possible to obtain their NMR spectra.

The molecular structures of **16** and **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.

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 vertexes of a trigonal antiprism. In that arrangement, the tridentate organometallic ligands {(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)} force the pentamethylcyclopentadienyl groups into an alternate position.

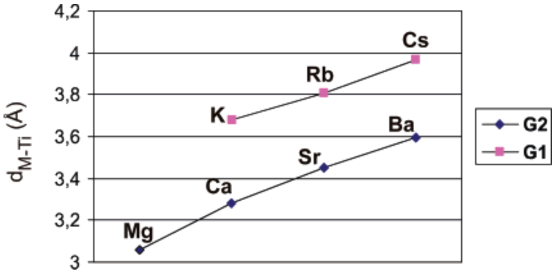

Figure 6. Periodic variation of the M···Ti distance for group 1 and 2 elements in the corner-shared azaheterometallocubanes **8**−**10** and **15**−**18**.

The existence of structural data for the six-coordinate Mg−Ba complexes **15**−**18** allows making a comparison on bond lengths and angles along group 2. The N−M−N intracube angles decrease with higher cation size (Mg, 77.6(3)°; Ca, 70.7(3)°; Sr, 67.4(2)°; Ba, 63.3(2)°), whereas the N−M−N intercubes angles increase with an inverse tendency (Mg, 102.4(3)°; Ca, 109.3(3)°; Sr, 112.6(2)°; Ba, 116.7(2)°). 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 differences 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$_2$M (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 comparison of bond lengths between elements of the same group or the same row, as illustrated in Figure 6.[26] As already pointed out for compounds **8**−**10** or **15**−**18**, again the variances of the distances M···Ti for M = K to 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$^+$ to Ca^{2+}, 0.380 Å; Rb$^+$ to Sr^{2+}, 0.340 Å; Cs$^+$ to Ba^{2+}, 0.320 Å).

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(22) (a) Han, R.; Parkin, G. *J. Organomet. Chem.* **1990**, *393*, C43−C46. (b) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 748−757.

(23) Shorin, Y.; Kokusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4128−4136.

(24) Shorin, Y.; Matsui, M.; Hata, Y.; Hasegawa, H.; Kokusen, H. *Inorg. Chem.* **1994**, *33*, 4376−4383.

(25) (a) Dutremez, S. G.; Leslie, D. B.; Streib, W. E.; Chisholm, M. H.; Caulton, K. G. *J. Organomet. Chem.* **1993**, *462*, C1−C2. (b) Belderraín, T. R.; Contreras, L.; Paneque, M.; Carmona, E.; Monge, A.; Ruiz, C. *Polyhedron* **1996**, *15*, 3453−3463.

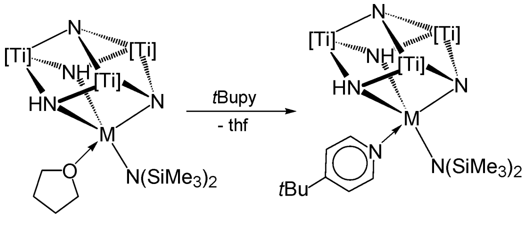
(26) To minimize the differences between the quality of the crystals, we have chosen the distance from the central metal atom to the titanium atoms as the parameter to study, which is always the magnitude with the minimum standard deviation.

On the other hand, the increase in the size of the metal center down group 2 could be related to the different stability in solution exhibited by the single-cube complexes **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 azaheterometallocubane complex **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]

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

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. 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 $[(t\text{Bupy})\{(SiMe_3)_2N\}M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (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.

Scheme 3. Synthesis of the Single-Cube Complexes **19** and **20**



M = Ca (**12**), Sr (**13**)   M = Ca (**19**), Sr (**20**)

Conclusion

The trinuclear complex **1** is capable of incorporating 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 $[M_2Ti_6N_8]$ or corner-shared double-cube $[MTi_6N_8]$ 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 structures containing six-coordinate alkali metals. In the same way, for the alkaline-earth metal derivatives single-cube structures $[MTi_3N_4]$ 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.

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

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