Titanium Alkali Metal Nitrido Complexes

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Abstract: Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with alkali metal bis(trimethylsilyl)amido reagents in toluene afforded the 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 (**2**), Na, (**3**), K (**4**)). The molecular structures of **2** and **3** have been determined by X-ray crystallographic studies and show two azaheterometallocubane cores $[MTi_3N_4]$ linked by metal–nitrogen bonds. Reaction of the lithium derivative **2** with chlorotrimethylsilane or trimethyltin chloride in toluene gave the incomplete cube nitrido complexes $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu\text{-}NMMe_3)(\mu_3\text{-}N)]$ (M = Si (**5**), Sn (**6**)). A similar reaction with indium(I) or thallium(I) chlorides yielded cube-type derivatives $[M(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}N)]$ (M = In (**7**), Tl (**8**)).

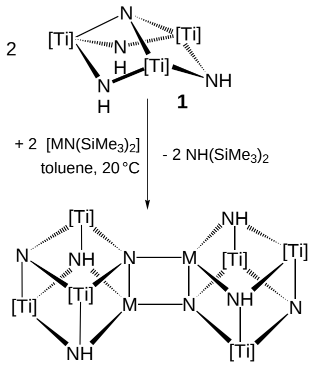
Keywords: alkali metals · cubanes · nitrido complexes · titanium

Introduction

In our investigations on polynuclear nitrido complexes, we reported the preparation of the first cube-type nitrido derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ by reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ with ammonia.[1, 2] Prior to our work, Roesky et al. had described the imido–nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) obtained by the ammonolysis of $[\{Ti(\eta^5\text{-}C_5Me_5)Me_3]$.[3] We have recently showed that **1** is capable of displacing labile ligands (mesitylene, carbonyls) coordinated to Group 6 metals to give d^0–d^6 azaheterometallocubane compounds.[4] Moreover, if other highly reactive metal–ligand bonds are present in the incorporated metal, as in the case of Group 4 amido and imido complexes, N–H bond activation occurs in **1** to give titanium and zirconium corner-shared double cube complexes.[5] Although this methodology provides a great number of potential sources for the synthesis of heterometallic molecular precursors of ternary nitrides MTi_xN_y, we are exploring other alternative pathways which may offer more possibilities. Herein we report the synthesis, structure, and preliminary reactivity studies of alkali metal derivatives of **1**.

Results and Discussion

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with Group 1 bis(trimethylsilyl)amido reagents (1 equiv) in toluene at room temperature led to bis(trimethylsilyl)amine and precipitation of the alkali metal derivatives $[M(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ (M = Li (**2**), Na (**3**), K (**4**)) (Scheme 1).



M = Li (**2**), 80%; Na (**3**), 73%; K (**4**), 57%

Scheme 1. Synthesis of the edge-linked double azaheterometallocubane complexes **2**–**4**. [Ti] = $Ti(\eta^5\text{-}C_5Me_5)$.

Complexes **2**–**4** were isolated as orange or yellow crystals in good yields (57–80%), and were characterized by IR spectroscopy and C,H,N microanalysis.[6] Owing to the low solubility of **2**–**4** in nonreactive solvents, it was not possible to obtain ^1H and $^{13}C\{^1H\}$ NMR data. However, complex **3** was found to be slightly soluble in $[D_6]$benzene, and its ^1H NMR spectrum in this solvent reveals resonance signals for two η^5-

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C_5Me_5 ligands (2:1 ratio) and a broad signal for the NH groups. These data are consistent with C_s symmetry in solution. Attempts to elucidate 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.

The X-ray crystal structure analyses of **2** and **3** revealed the geometry and aggregation in the solid state. The crystal structure of the lithium complex **2** showed an unprecedented edge-linked double azaheterometallocubane core [$LiTi_3N_4$] (Figure 1).[7]

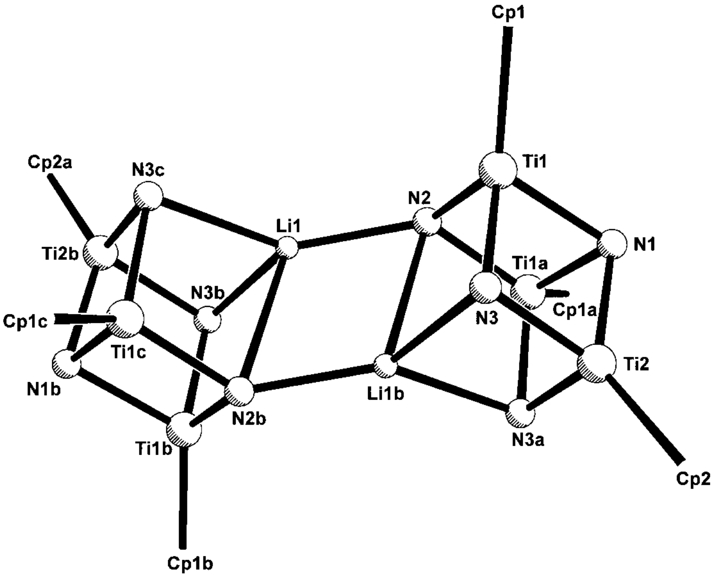


Figure 1. Simplified view of the molecular structure of **2**. The pentamethylcyclopentadienyl ligands are omitted for clarity. The C_7H_8 solvent molecules are also excluded. Selected lengths [Å] and angles [°]: Li1–N2 2.03(2), Li1–N3b 2.13(2), Li1–N2b 2.42(2), Li1 ··· Li1b 2.64(3), Ti1–N2 1.855(5), Ti1–N1 1.931(6), Ti1–N3 1.970(5), Ti2–N1 1.912(7), Ti2–N3 1.925(6); N2-Li1-N2b 107.8(8), N2-Li1-N3b 136.3(4), N3b-Li1-N3c 87.1(7), N3b-Li1-N2b 80.4(5).

Molecules of **2** lie on a crystallographic inversion center and also present a mirror plane bearing the Li1, Li1b, N2, N2b, N1, N1b, Ti2, and Ti2b core atoms. The two "Li(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}" units adopt a mutually staggered conformation which may correspond to the minimization of the steric repulsion of the bulky pentamethylcyclopentadienyl ligands. The lithium atoms are four-coordinate; the angles range from 80.4(5) to 136.3(4)°. The N-Li-N angles in the same [$LiTi_3N_4$] unit are smaller than 90° (80.4(5) and 87.1(7)°), whereas those between the cubes are 107.8(8) and 136.3(4)°. The four-coordination of the lithium (L1) atom is achieved by bonding to the nitrido (N2) group at 2.03(2) Å, two dative imido ligands (N3b and N3c) at 2.13(2) Å, and a long-range interaction with the nitrido group (N2b) at 2.42(2) Å. The L1–N2, Li1–N3b and Li1–N3c distances are similar to those reported for both complexed and uncomplexed lithium amido derivatives.[8, 9]

Complex **3** shows a similar geometry to that of **2** (Figure 2). There is a center of symmetry on the midpoint of the two sodium atoms, but the molecule does not possess a mirror plane. The double cube-type structure of **3** is more distorted owing to the different atomic radii of the sodium and the lithium atoms. Thus, complex **3** shows longer sodium–nitrogen bonds (ca. 0.35 Å), narrower angles between sodium and the nitrogen atoms of the cubes (69.2(1) – 75.1(1)°), and wider angles between the nitrogen atoms of different cubes (105.6(1) – 145.7(1)°). The Na1–N12a, Na1–N13 and Na1–N23 distances are similar to those reported for sodium amido derivatives.[10]

The utility of **2** as a transfer reagent of the "(μ_3-N)(μ-NH)$_2$-{Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}" system was explored (Scheme 2). Treatment of MMe_3Cl (M = Si, Sn) with **2** (0.5 equiv) in toluene for 40 h afforded the new complexes [Ti$_3$(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ-NMMe$_3$)(μ_3-N)] (M = Si (**5**, 59 %), Sn (**6**, 63 %)) as orange crystals. Analogous treatment of indium(I) chloride or thallium(I) chloride with **2** (0.5 equiv) gave orange crystals of [M(μ_3-N)(μ_3-NH)$_2${Ti(η^5-C_5Me_5)}$_3$(μ_3-N)] (M = In (**7**, 55 %), Tl (**8**, 62 %)). The metathesis reactions progress cleanly at room temperature and, once isolated, the new compounds appear to be invariable to UV radiation and high temperatures (> 150 °C) in [D$_6$]benzene solutions.

The compositions of **5** – **8** were established from their spectral and analytical data. ^{1}H NMR spectra in [D$_6$]benzene reveal resonance signals for two η^5-C_5Me_5 groups in a 2:1 ratio and broad signals for equivalent NH fragments. These data are consistent with C_s-symmetric structures in solution. Interestingly, the NH resonance signals of complexes **5** (δ = 14.22) and **6** (δ = 14.13) are shifted to lower field than those found in **1** (δ = 13.80), while complexes **7** and **8** exhibit NH resonance signals shifted to higher field (δ = 11.61 and 12.14, respectively). We have observed an analogous shift to high field in **3**, and in several transition azaheterometallocubane derivatives,[4, 5] where the coordination of the NH groups to the metal (Na or Ti) have been demonstrated. Furthermore, the ^{1}H NMR spectrum of **8** reveals ^{1}H – ^{203,205}Tl couplings ($^2J_{H,Tl}$ = 78 Hz) for the imido groups, suggesting the presence of important Tl ← :NH= covalent interactions in this complex. These data led us to propose a cube-type structure with three-coordinate indium[11]/thallium[12, 13] centers for **7** and **8** (Scheme 2). However, the NMR data of **5** and **6** are in agreement with an incomplete cube structure similar to the organometallic ligand **1**,[3] and rule out a six-coordinate tin center in solution as that determined in the solid state for the complex [{HB(pz)$_3$}SnMe$_3$] (pz = pyrazole).[14]

Abstract in Spanish: *El complejo [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$-(μ_3-N)] reacciona con bis(trimetilsilil)amiduros de metales alcalinos para dar los compuestos [M(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}]$_2$ (M = Li (**2**), Na (**3**), K (**4**)). Las estructuras de los derivados **2** y **3** han sido determinadas por difracción de rayos-X y muestran dos unidades azaheterometalocubano conectadas por aristas a través de enlaces metal-nitrógeno. La reacción del complejo **2** con los derivados de silicio y estaño [MMe$_3$Cl] conduce a la preparación, con altos rendimientos, de las especies [Ti$_3$(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ-NMMe$_3$)(μ_3-N)] (M = Si (**5**), Sn (**6**)) con una estructura de cubo incompleto. El tratamiento análogo utilizando los cloruros de indio(I) y talio(I) da lugar a los complejos tipo cubo [M(μ_3-N)-(μ_3-NH)$_2${Ti(η^5-C_5Me_5)}$_3$(μ_3-N)] (M = In (**7**), Tl (**8**)).*

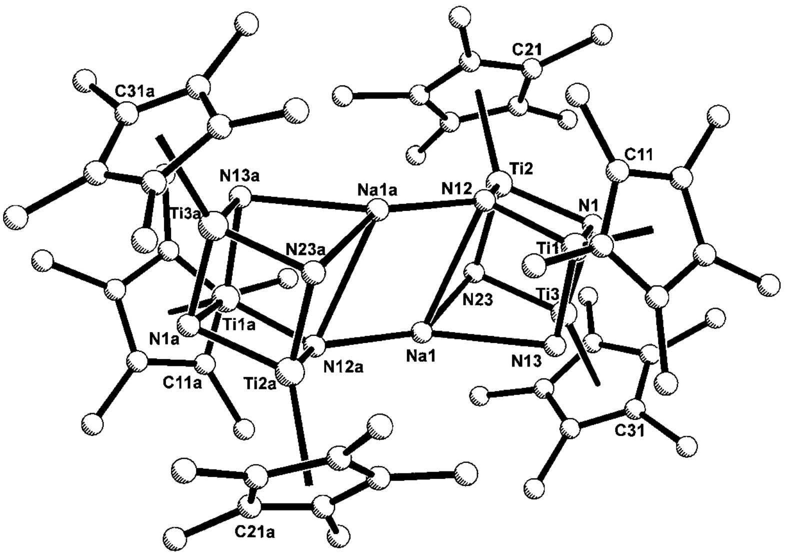
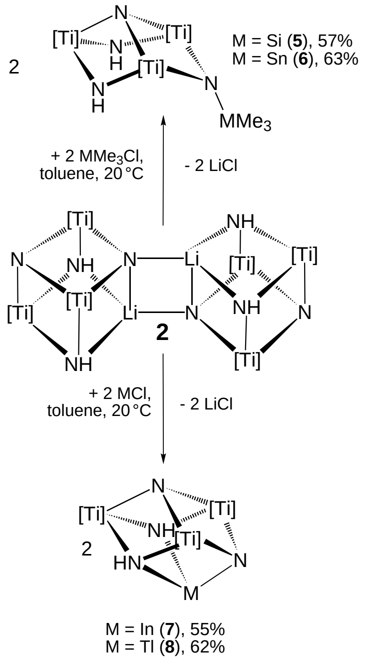


Figure 2. Molecular structure of **3**. Selected lengths [Å] and angles [°]: Na1–N12a 2.337(4), Na1–N13 2.477(4), Na1–N23 2.486(4), Na1–N12 2.785(4), Na1 ··· Na1a 3.118(4), Ti1–N12 1.860(4), Ti1–N1 1.934(3), Ti1–N13 1.970(4), Ti2–N12 1.860(4), Ti2–N1 1.944(3), Ti2–N23 1.981(4), Ti3–N1 1.911(4), Ti3–N23 1.942(4), Ti3–N13 1.948(4); N12-Na1-N12a 105.6(1), N12a-Na1-N13 136.5(1), N12a-Na1-N23 145.7(1), N13-Na1-N23b 75.1(1), N12-Na1-N13 69.2(1), N12-Na1-N23 69.3(1).



Scheme 2. Behavior of complex **2** as a metathesis reagent. [Ti] = Ti(η^5-C_5Me_5).

In summary, the complexes $[M(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-N})]_2$ (M = Li (**2**), Na (**3**)) feature an unusual edge-linked double cube structure with nitrido groups among the titanium and alkali metal centers. Compound **2** is very useful in the synthesis of new titanium nitrido derivatives (**5**–**8**) containing silicon, tin, indium, or thallium atoms. We are currently exploring the reactivity of these systems as mild reagents to introduce the incomplete cube "$(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-N})$" in other inorganic and organometallic halides.

Experimental Section

General considerations: All manipulations were carried out under an argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K amalgam prior to use. Toluene was freshly distilled from sodium. NMR solvent (C_6D_6) was dried with Na/K amalgam and vacuum-distilled. $[MN(SiMe_3)_2]$ (M = Li, Na, K), $[MMe_3Cl]$ (M = Si, Sn), and [MCl] (M = In, Tl) were purchased from Aldrich and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) was prepared as described in the literature.[2, 3]

Samples for IR 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 residual protons or to carbon of the solvent. Electron impact mass spectra were obtained at 70 eV on a Hewlett-Packard 5988 spectrometer. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of $[Li(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]_2$ (2): A solution of $[LiN(SiMe_3)_2]$ (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 %). IR (KBr): $\tilde{\nu}$ = 3352 (w), 2906 (s), 2855 (s), 2718 (w), 1605 (w), 1495 (m), 1436 (s), 1375 (s), 1065 (w), 1024 (m), 956 (w), 839 (w), 719 (vs), 695 (s), 658 (m), 643 (s), 634 (s), 621 (m), 586 (s), 478 (w), 464 (m), 415 (s) cm^{-1}; elemental analysis calcd for $C_{67}H_{102}N_8Li_2Ti_6$ (%): C 60.93, H 7.78, N 8.48; found: C 60.82, H 7.75, N 8.09.

Synthesis of $[Na(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]_2$ (3): In a fashion similar to the preparation of **2**, $[NaN(SiMe_3)_2]$ (0.15 g, 0.82 mmol) and **1** (0.50 g, 0.82 mmol) were allowed to react in toluene (40 mL) to afford orange crystals of **3** (0.38 g, 74 %). IR (KBr): $\tilde{\nu}$ = 3336 (m), 2968 (m), 2908 (s), 2856 (s), 2719 (w), 1493 (m), 1436 (s), 1374 (s), 1248 (w), 1167 (w), 1110 (w), 1064 (w), 1023 (m), 953 (w), 802 (w), 727 (vs), 655 (s), 636 (s), 624 (s), 572 (s), 522 (w), 477 (m), 438 (w), 410 (s) cm^{-1}; ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): δ = 12.67 (s br., 2 H; NH), 2.10 (s, 30 H; C_5Me_5), 1.98 (s, 15 H; C_5Me_5); elemental analysis calcd for $C_{60}H_{94}N_8Na_2Ti_6$ (%): C 57.17, H 7.51, N 8.89; found: C 57.59, H 7.52, N 8.29.

Synthesis of $[K(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]_2$ (4): In a similar way to the preparation of **2**, $[KN(SiMe_3)_2]$ (0.16 g, 0.82 mmol) and **1** (0.50 g, 0.82 mmol) in toluene (40 mL) gave **4** as yellow crystals (0.30 g, 57 %). IR (KBr): $\tilde{\nu}$ = 3338 (w), 2907 (s), 2855 (s), 2716 (w), 1495 (m), 1434 (s), 1372 (s), 1240 (w), 1231 (w), 1065 (w), 1020 (m), 949 (w), 804 (w), 738 (vs), 704 (s), 658 (m), 611 (vs), 543 (s), 468 (w), 436 (w), 405 (s) cm^{-1}; elemental analysis calcd for $C_{60}H_{94}N_8K_2Ti_6$ (%): C 55.74, H 7.33, N 8.67; found: C 55.36, H 7.32, N 7.92.

Synthesis of $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-NH})_2(\mu\text{-NSiMe}_3)(\mu_3\text{-N})]$ (5): Chlorotrimethylsilane (0.092 mL, 0.73 mmol) was added dropwise to $\mathbf{2}\cdot C_7H_8$ (0.40 g, 0.30 mmol) in toluene (30 mL) at ambient temperature. After stirring for 40 h, the volatile components were removed under vacuum. The orange solid was extracted with hexane (40 mL), filtered, and the volume of the resultant orange solution was reduced under vacuum to about 10 mL. Cooling at −40 °C for two days gave orange crystals of **5** (0.24 g, 59 %). IR (KBr): $\tilde{\nu}$ = 3351 (m), 2971 (s), 2907 (s), 2856 (s), 2720 (w), 1494 (m), 1432 (s), 1374 (s), 1238 (s), 1166 (w), 1099 (w), 1065 (w), 1023 (m), 918 (vs), 830 (s), 790 (m), 758 (s), 711 (s), 665 (vs), 646 (vs), 550 (w), 522 (s), 481 (w), 453 (m), 410 (s) cm^{-1}; ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): δ = 14.22 (s br., 2 H; NH), 2.09 (s, 30 H; C_5Me_5), 1.88 (s, 15 H; C_5Me_5), 0.15 (s, 9 H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C, TMS): δ = 118.2 (C_5Me_5), 117.8

(C_5Me$_5$), 12.5 (C$_5$*Me*$_5$), 11.8 (C$_5$*Me*$_5$), 7.0 (Si*Me*$_3$); MS (EI, 70 eV): *m/z* (%): 681 (21) [M^+], 666 (12) [$M-\mathrm{Me}^+$], 546 (16) [$M-\mathrm{C_5Me_5}^+$], 531 (11) [$M-\mathrm{Me}-\mathrm{C_5Me_5}^+$], 516 (17) [$M-2\,\mathrm{Me}-\mathrm{C_5Me_5}^+$]; elemental analysis calcd for $C_{33}H_{56}N_4SiTi_3$ (%): C 58.24, H 8.29, N 8.23; found: C 58.69, H 8.32, N 7.26.

Synthesis of [Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ-NSnMe$_3$)(μ_3-N)] (6): A 100-mL Schlenk flask was charged with **2**$\cdot C_7H_8$ (0.30 g, 0.23 mmol), trimethyltin chloride (0.09 g, 0.45 mmol), and toluene (40 mL). The mixture was stirred for 40 h at room temperature. The volatile components were removed under vacuum to give an orange solid. This solid was extracted with hexane (50 mL) and filtered to afford an orange solution. After reducing the volume to about 10 mL, the solution was cooled to $-40\,^\circ$C for three days to afford orange crystals of **6** (0.22 g, 63 %). IR (KBr): $\tilde{\nu} = 3349$ (m), 2971 (s), 2909 (s), 2856 (s), 2719 (w), 1493 (m), 1433 (s), 1374 (s), 1189 (w), 1182 (w), 1174 (w), 1065 (w), 1023 (m), 948 (w), 852 (m), 747 (s), 712 (vs), 669 (vs), 657 (vs), 645 (vs), 636 (s), 592 (m), 550 (w), 524 (s), 508 (s), 473 (w), 450 (m), 410 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 14.13$ (s br., 2 H; NH), 2.09 (s, 30 H; C$_5$Me$_5$), 1.91 (s, 15 H; C$_5$Me$_5$), 0.21 (s, ^2J(H,Sn) = 54.3 Hz, 9 H; SnMe$_3$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 117.5$ (C_5Me$_5$), 117.2 (C_5Me$_5$), 12.3 (C$_5$*Me*$_5$), 11.8 (C$_5$*Me*$_5$), 1.1 (Sn*Me*$_3$); MS (EI, 70 eV): *m/z* (%): 756 (1) [$M-\mathrm{Me}^+$], 622 (2) [$M-\mathrm{SnMe_2}^+$], 607 (11) [$M-\mathrm{SnMe_3}^+$], 591 (7) [$M-\mathrm{NH_2SnMe_3}^+$], 472 (7) [$M-\mathrm{SnMe_3}-\mathrm{C_5Me_5}^+$], 456 (20) [$M-\mathrm{NH_2SnMe_3}-\mathrm{C_5Me_5}^+$], 321 (23) [$\mathrm{M}-\mathrm{NH_2SnMe_3}-2\,\mathrm{C_5Me_5}^+$]; elemental analysis calcd for $C_{33}H_{56}N_4SnTi_3$ (%): C 51.40, H 7.32, N 7.27; found: C 51.60, H 7.48, N 6.60.

Table 1. Summary of the crystallographic data for complexes **2** and **3**.

	2	**3**
formula	$C_{60}H_{94}Li_2N_8Ti_6 \cdot 2\,C_7H_8$	$C_{60}H_{94}N_8Na_2Ti_6$
M_r	1412.8	1260.82
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
crystal system	orthorhombic	triclinic
space group	*Pnnm*	$P\bar{1}$
a [Å]; α [°]	15.027(1)	11.306(8);106.42(4)
b [Å]; β [°]	15.444(1)	11.384(4);94.54(3)
c [Å]; γ [°]	16.344(1)	15.188(4);113.96(4)
V [Å^3]	3793.1(4)	1671.0(14)
Z	2	1
ρ_{calcd} [g cm^{-3}]	1.223	1.253
$\mu\mathrm{Mo}_{K\alpha}$ [mm^{-1}]	0.645	0.736
F(000)	1464	664
crystal size [mm]	$0.42 \times 0.35 \times 0.28$	$0.34 \times 0.30 \times 0.26$
θ range	2.26 to 23.41°	3.12 to 21.98°
index ranges	$0 \le h \le 16$, $-17 \le k \le 0$, $0 \le l \le 18$	$-11 \le h \le 0$, $-10 \le k \le 11$, $-15 \le l \le 15$
reflections collected	2892	4298
unique data	2892	4050
obsd data [$I > 2\sigma(I)$]	1551	3424
absorption correction	N/A	
goodness-of-fit on F^2	0.999	1.028
final R indices [$I > 2\sigma(I)$]	$R1 = 0.069$, $wR2 = 0.190$	$R1 = 0.050$, $wR2 = 0.137$
R indices (all data)	$R1 = 0.172$, $wR2 = 0.238$	$R1 = 0.061$, $wR2 = 0.148$
largest diff. peak/hole [e Å^{-3}]	1.040/ – 0.424	0.427/ – 0.349

Synthesis of [In(μ_3-N)(μ_3-NH)$_2${Ti(η^5-C$_5$Me$_5$)}$_3$(μ_3-N)] (7): Similarly to the preparation of **6**, **2**$\cdot C_7H_8$ (0.30 g, 0.23 mmol), indium(I) chloride (0.068 g, 0.45 mmol) and toluene (40 mL) reacted to afford **7** as orange crystals (0.18 g, 55 %). IR (KBr): $\tilde{\nu} = 3353$ (m), 2908 (s), 2855 (s), 1491 (m), 1430(m), 1375 (m), 1260 (m), 1095 (w), 1024 (m), 782 (s), 718 (vs), 700 (vs), 687 (s), 664 (s), 620 (s), 531 (m), 480 (w), 452 (w), 421 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.61$ (s br., 2 H, NH), 2.09 (s, 30 H; C$_5$Me$_5$), 1.86 (s, 15 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 117.9$ (C_5Me$_5$), 117.2 (C_5Me$_5$), 12.0 (C$_5$*Me*$_5$), 11.9 (C$_5$*Me*$_5$); MS (EI, 70 eV): *m/z* (%): 722 (3) [M^+], 607 (1) [$M-\mathrm{In}^+$], 587 (2) [$M-\mathrm{C_5Me_5}^+$], 472 (1) [$M-\mathrm{In}-\mathrm{C_5Me_5}^+$], 452 (3) [$M-2\,\mathrm{C_5Me_5}^+$], 115 (100) [In$^+$]; elemental analysis calcd for $C_{30}H_{47}N_4InTi_3$ (%): C 49.90, H 6.56, N 7.76; found: C 50.19, H 6.64, N 6.69.

Synthesis of [Tl(μ_3-N)(μ_3-NH)$_2${Ti(η^5-C$_5$Me$_5$)}$_3$(μ_3-N)] (8): In a fashion similar to the preparation of **6**, **2**$\cdot C_7H_8$ (0.30 g, 0.23 mmol), thallium(I) chloride (0.11 g, 0.45 mmol), and toluene (40 mL) reacted to afford **8** as orange crystals (0.23 g, 63 %). IR (KBr): $\tilde{\nu} = 3348$ (m), 2907 (s), 2854 (s), 1493 (m), 1431 (s), 1374 (s), 1023 (m), 714 (vs), 687 (s), 659 (s), 640 (s), 620 (s), 528 (m), 478 (w), 449 (w), 417(s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 12.14$ (d, ^2J(H,Tl) = 78.0 Hz, 2 H; NH), 2.12 (s, 30 H; C$_5$Me$_5$), 1.89 (s, 15 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 117.3$ (C_5Me$_5$), 116.4 (C_5Me$_5$), 12.1 (C$_5$*Me*$_5$), 12.0 (C$_5$*Me*$_5$); MS (EI, 70 eV): *m/z* (%): 812 (1) [M^+], 677 (1) [$M-\mathrm{C_5Me_5}^+$], 608 (3) [$M-\mathrm{Tl}^+$], 542 (2) [$M-2\,\mathrm{C_5Me_5}^+$], 473 (9) [$M-\mathrm{Tl}-\mathrm{C_5Me_5}^+$]; elemental analysis calcd for $C_{30}H_{47}N_4Ti_3Tl$ (%): C 44.39, H 5.84, N 6.90; found: C 45.47, H 6.05, N 6.28.

X-ray structure determination of 2 and 3: Orange crystals of **2** and **3** were obtained by slow crystallization from saturated toluene solutions. Data were collected on an Enraf Nonius CAD4 diffractometer at room temperature. Crystallographic data for complexes **2** and **3** are presented in Table 1. Intensity measurements for **2** were performed by $\omega - 2\theta$ scans in the range $4^\circ < 2\theta < 46^\circ$. Of the 3187 measured reflections, 2892 were independent; $R1 = 0.069$ and $wR2 = 0.190$ (for 1551 reflections with $F > 4\sigma(F)$). Intensity measurements for **3** were performed by $\omega - \theta$ scans in the range $6^\circ < 2\theta < 44^\circ$. Of the 4298 measured reflections, 4050 were independent; $R1 = 0.050$ and $wR2 = 0.137$ (for 3424 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined $R1 = \Sigma \| F_0 | - | F_c \| / [\Sigma | F_0 |]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Both structures were solved by direct methods (SHELXS-97), using the WINGX package[15] and refined by least-squares against F^2 (SHELXL-97).[16] Compound **2** crystallized with two molecules of toluene, which were disordered, but this disorder did not affect the location of the core of the molecule. All non-hydrogen atoms, except those of the solvent, were refined anisotropically. The hydrogen atoms of the molecule were positioned geometrically and refined by using a riding model except that linked to N3 which was located and refined isotropically, those of the solvent were not added. All non-hydrogen atoms of **3** refined anisotropically and hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-147372 (**2**) and CCDC-147373 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] P. Gómez-Sal, A. Martín, M. Mena, C. Yélamos, *J. Chem. Soc. Chem. Commun.* **1995**, 2185–2186.

[2] A. Abarca, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet, C. Yélamos, *Inorg. Chem.* **2000**, *39*, 642–651.

[3] H. W. Roesky, Y. Bai, M. Noltemeyer, *Angew Chem.* **1989**, *101*, 788–789; *Angew Chem. Int. Ed. Engl.* **1989**, *28*, 754–755.

[4] A. Abarca, M. Galakhov, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet, C. Santamaría, J. P. Sarasa, *Angew Chem.* **2000**, *112*, 544–547; *Angew Chem. Int. Ed.* **2000**, *39*, 534–537.

[5] A. Abarca, A. Martín, M. Mena, C. Yélamos, *Angew Chem.* **2000**, *112*, 3602–3605; *Angew Chem. Int. Ed.* **2000**, *39*, 3460–3463.

[6] Combustion analysis for the complexes reported in this paper gave always low values of nitrogen (0.4–1 %).

[7] For X-ray crystal structures of edge-linked double cube sulfido clusters see: a) T. Shibahara, H. Akashi, H. Kuroya, *J. Am. Chem. Soc.* **1988**, *110*, 3313–3314; b) T. Shibahara, H. Akashi, M. Yamasaki, K. Hashimoto, *Chem. Lett.* **1991**, 689–692; c) T. Murata, H. Gao, Y. Mizobe, F. Nakano, S. Motoruma, T. Tanase, S. Yano, M. Hidai, *J. Am. Chem. Soc.* **1992**, *114*, 8287–8288; d) T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, S. Motoruma, *J. Am. Chem. Soc.* **1994**, *116*, 3389–3398; e) T. Shibahara, T. Yamamoto, G. Sakane, *Chem. Lett.* **1994**, 1231–1234; f) L. Cai, B. M. Segal, J. R. Long, M. J. Scott, R. H. Holm, *J. Am. Chem. Soc.* **1995**, *117*, 8863–8864; g) K. D. Demadis, C. F. Campana, D. Coucouvanis, *J. Am. Chem. Soc.* **1995**, *117*, 7832–7833; h) C. Goh, B. M. Segal, J. Huang, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 11844–11853; i) F. Osterloh, B. M. Segal, C. Achim, R. H. Holm, *Inorg. Chem.* **2000**, *39*, 980–989.

[8] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, West Sussex, UK, **1980**.

[9] For structures of nitrogen-lithium compounds, see: a) K. Gregory, P. von R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47–142; b) R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167–209; c) R. E. Mulvey, *Chem. Soc. Rev.* **1998**, *27*, 339–346.

[10] See for example: a) K. Gregory, M. Bremer, W. Bauer, P. von R. Schleyer, N. P. Lorenzen, J. Kopf, E. Weiss, *Organometallics* **1990**, *9*, 1485–1492; b) N. Kuhn, G. Henkel, J. Kreutzberg, *Angew. Chem.* **1990**, *102*, 1179; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1143–1144; c) P. C. Andrews, W. Clegg, R. E. Mulvey, *Angew. Chem.* **1990**, *102*, 1480; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1440–1441; d) N. P. Lorenzen, J. Kopf, F. Olbrich, U. Schümann, E. Weiss, *Angew. Chem.* **1990**, *102*, 1481; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1441–1444.

[11] For crystal structures of tris(pyrazolyl)borate indium(I) complexes, see for example: a) A. Frazer, B. Piggott, *J. Am. Chem. Soc.* **1994**, *116*, 4127–4128; b) H. V. Rasika Dias, L. Huai, W. Jin, S. G. Bott, *Inorg. Chem.* **1995**, *34*, 1973–1974; c) M. C. Kuchta, H. V. Rasika Dias, S. G. Bott, G. Parkin, *Inorg. Chem.* **1996**, *35*, 943–948; d) H. V. Rasika Dias, W. Jin, *Inorg. Chem.* **1996**, *35*, 267–268.

[12] For crystal structures of tris(pyrazolyl)borate thallium(I) complexes, see for example: a) A. H. Cowley, R. L. Geerts, C. M. Nunn, S. Trofimenko, *J. Organomet. Chem.* **1989**, *365*, 19–22; b) E. Libertini, K. Yoon, G. Parkin, *Polyhedron* **1993**, *12*, 2539–2542; c) A. J. Amoroso, J. C. Jeffery, P. L. Jones, J. A. McCleverty, E. Psillakis, M. D. Ward, *J. Chem. Soc. Chem. Commun.* **1995**, 1175–1176; d) D. L. Reger, J. E. Colins, R. Layland, R. D. Adams, *Inorg. Chem.* **1996**, *35*, 1372–1376; e) R. Han, P. Ghosh, P. J. Desrosiers, S. Trofimenko, G. Parkin, *J. Chem. Soc. Dalton Trans.* **1997**, 3713–3717; f) T. Fillebeen, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, *36*, 3787–3790; g) E. Herdtweck, F. Peters, W. Scherer, M. Wagner, *Polyhedron* **1998**, *17*, 1149–1157.

[13] For a 1,4,7-triazacyclononane thallium(I) complex, see: K. Wieghardt, M. Kleine-Boymann, B. Nuber, J. Weiss, *Inorg. Chem.* **1986**, *25*, 1309–1313.

[14] B. K. Nicholson, *J. Organomet. Chem.* **1984**, *265*, 153–157.

[15] L. J. Farrugia, WinGX—A Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, **1998**.

[16] G. M. Sheldrick, SHELX97, Program for Crystal Structure Analysis (Release 97–2), Universität Göttingen, Germany, **1998**.

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