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Cube-Type Nitrido Complexes Containing Titanium and Zinc/Copper

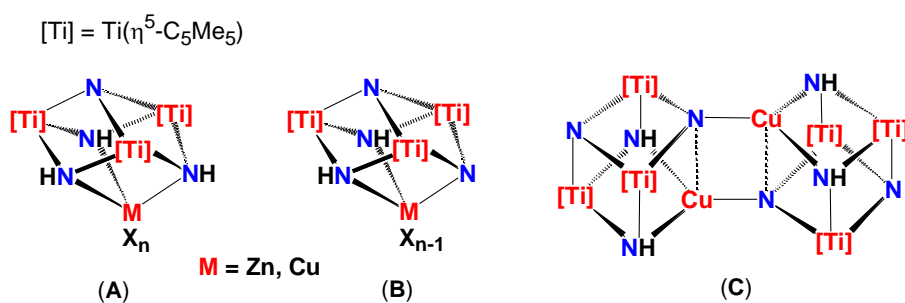
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Synopsis:

The imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) acts as a tridentate ligand towards zinc(II) or copper(I) $[\text{MX}_n]$ derivatives in its neutral $\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ (**A**) or monoanionic $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}^-$ (**B**) form. The new heterometallic nitrido compounds exhibit single cube structures, excepting the copper derivative $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (**C**) that shows an edge-linked double-cube structure with a $[\text{Cu}_2\text{Ti}_6\text{N}_8]$ core.



Abstract:

Several azaheterometallocubane complexes containing $[MTi_3N_4]$ cores have been prepared by the reaction of $[\{Ti(\eta^5-C_5Me_5)(\mu-NH)\}_3(\mu_3-N)]$ (**1**) with zinc(II) and copper(I) derivatives. Treatment of **1** with zinc dichloride in toluene at room temperature affords the adduct $[Cl_2Zn\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (**2**). Attempts to crystallize **2** in dichloromethane gave yellow crystals of the ammonia adduct $[(H_3N)Cl_2Zn\{(\mu_3-NH)Ti_3(\eta^5-C_5Me_5)_3(\mu-NH)_2(\mu_3-N)\}]$ (**3**). The analogous reaction of **1** with alkyl, (trimethylsilyl)cyclopentadienyl or amido zinc complexes $[ZnR_2]$ leads to the cube-type derivatives $[RZn\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ ($R = CH_2SiMe_3$ (**5**), CH_2Ph (**6**), Me (**7**), $C_5H_4SiMe_3$ (**8**), $N(SiMe_3)_2$ (**9**)) via RH elimination. The amido complex **9** decomposes in presence of ambient light to generate the alkyl derivative $[\{Me_3Si(H)N(Me)_2SiCH_2\}Zn\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (**10**). The chloride complex **2** reacts with lithium cyclopentadienyl or lithium indenyl reagents to give the cyclopentadienyl or indenyl zinc derivatives $[RZn\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ ($R = C_5H_5$ (**11**), C_9H_7 (**12**)). Treatment of **1** with copper(I) halides in toluene at room temperature leads to the adducts $[XCu\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ ($X = Cl$ (**13**), I (**14**)). Complex **13** reacts with lithium bis(trimethylsilyl)amido in toluene to give the precipitation of $[\{Cu(\mu_4-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}_2]$ (**15**). Complex **15** is prepared in higher yield through the reaction of **1** with $[\{CuN(SiMe_3)_2\}_4]$ in toluene at 150 °C. Addition of triphenylphosphane to **15** in toluene affords the single cube compound $[(Ph_3P)Cu\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (**16**). The X-ray crystal structures of **3**, **8**, **9** and **15** have been determined.

Introduction

An extensive coordination chemistry has been developed with tridentate nitrogen-based ligands. Representative examples are tris(pyrazolyl)borates,¹ tris(pyrazolyl)methanes,² triazacyclononanes,³ triazacyclohexanes,⁴ and other tripodal amido ligands,⁵ because of their ability to serve as facially coordinating six-electron donors. In this binding mode, the tris(pyrazolyl)hydroborate ligand is formally analogous to the cyclopentadienide (Cp^-) ligand, in that both are uninegative and isolobal. However, the electron-donating ability⁶ and the steric profile of tris(pyrazolyl)hydroborate (Tp) ligand, and substituted (Tp^x) derivatives thereof, are very different.⁷ At present, tris(pyrazolyl)hydroborates have become one of the most widely used class of ligand in inorganic chemistry, giving different reactivity patterns and frequently permitting the isolation of species whose cyclopentadienyl relatives are highly reactive.¹ In comparison, the chemistry of tris(pyrazolyl)methane ligands, the neutral analogous of the anionic tris(pyrazolyl)hydroborates, has been underdeveloped, although this area is a subject of active research in nowadays.² The neutral 1,4,7-triazacyclononane (R_3taccn)^{3a} and 1,3,5-triazacyclohexane (R_3tach)⁴ are also widely used as *fac*-coordinating N_3 -donor ligands in transition metal complexes, and more recently, monoanionic triazacyclononane (R_2taccn^-) ligands have demonstrated their ability to support novel organometallic chemistry with main group and early transition metals.^{3b}

In the last few years, we have been involved in the study of the coordination chemistry of the trinuclear titanium imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]^{8,9}$ (**1**). Nitrido complexes of the early transition metals (Groups 4 and 5) remain rare in the literature.^{10,11} This is possibly in part due to their polynuclear structures, which make extremely hard their characterization, and the lack of a systematic way of syntheses. The structure of complex **1** reveals a cyclic $[\text{Ti}_3(\mu\text{-NH})_3]$ system with three NH electron-donor imido groups and shows a strong resemblance to 1,4,7-triazacyclononane and, especially,

1,3,5-triazacyclohexane ligands. This similarity prompted us to explore its potential application as a tridentate, preorganized,¹² ligand towards different metal complexes and establish a rational strategy to prepare heterometallic nitrido complexes. This type of compounds might be of interest as building blocks in the synthesis of ternary metal nitride materials.¹³

Our initial work with transition metal derivatives has shown that **1** is capable of acting as a neutral ligand through the basal NH groups, but later those imido groups can also be deprotonated to give monoanionic, dianionic and even trianionic forms of **1** depending on the metal and the other ligands present in the coordination sphere.^{11,14,15} In main-group chemistry, we have demonstrated the ability of **1** to coordinate metal cyclopentadienides and halides to afford stable adducts $[X_nM\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$.¹⁶ However, the analogous treatment of **1** with alkyl and amido derivatives of the alkali and alkaline-earth metals gave immediately the elimination of alkane or amine. Thus, we have isolated Group 1 metal complexes with edge-linked $[\{M(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($M = \text{Li, Na, K}$) or corner-shared $[M\{(\mu_3\text{-N})(\mu_3\text{-NH})_5\text{Ti}_6(\eta^5\text{-C}_5\text{Me}_5)_6(\mu_3\text{-N})\}]$ ($M = \text{Na, K, Rb, Cs}$) double cube structures upon depending on the reagents ratio (1:1 or 2:1) of **1** and $[\text{MN}(\text{SiMe}_3)_2]$.^{17,18} Group 2 alkyl and amido $[\text{MR}_2]$ reagents react with **1** to give single-cube derivatives $[\text{RM}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$, but only the magnesium bis(trimethylsilyl)amido complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Mg}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ was stable in solution for long periods of time. In contrast, magnesium alkyls and derivatives bearing the heavier alkaline-earth elements, undergo ligand redistribution reactions at room temperature to give corner-shared complexes $[M\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($M = \text{Mg, Ca, Sr, Ba}$).^{18,19}

In view of these previous studies with s-block metals and as a logical continuation of our endeavor in the synthesis of new heterometallic nitrido complexes, we report here the results obtained in the treatment of **1** with analogous zinc(II) and copper(I) derivatives. The synthesis,

structures and properties of the new compounds are discussed and compared with other zinc and copper derivatives containing tridentate nitrogen-based ligands.²⁰

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. Dichloromethane was distilled from P₂O₅. NMR solvents were dried with Na/K alloy (C₆D₆, C₆D₅CD₃) or calcium hydride (CDCl₃), 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. Zinc(II) chloride (97%), copper(I) chloride (99.99%), copper(I) iodide (99.999%), [ZnMe₂] (2.0 M in toluene), PPh₃ and [LiN(SiMe₃)₂] were purchased from Aldrich and used as received. [{Ti(η⁵-C₅Me₅)(μ-NH)}₃(μ₃-N)] (**1**),^{8,9} [ZnR₂] (R = CH₂SiMe₃,²¹ CH₂Ph,²² N(SiMe₃)₂,^{23,24} C₅H₄SiMe₃,²⁵ C₅H₅²⁶), [LiCH₂SiMe₃],²⁷ [Li(C₅H₄SiMe₃)],²⁸ [Li(C₅H₅)],²⁹ [Li(C₉H₇)]³⁰ and [{CuN(SiMe₃)₂]₄^{31,32} were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Unity-300 and /or Unity-500 Plus 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. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzers.

Synthesis of [Cl₂Zn{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (2**):** A 100 mL Schlenk flask was charged with **1** (0.50 g, 0.82 mmol), ZnCl₂ (0.11 g, 0.81 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 3 h to give a yellow solid and a brown solution. The solid was isolated by filtration onto a glass frit, washed with toluene (5 mL) and vacuum-dried to give **2** as a yellow powder (0.41 g, 68%). IR (KBr, cm⁻¹): 3363 (w), 3291 (m), 2972 (w), 2908 (s), 2857 (m), 1618 (w), 1490 (w), 1429 (m), 1375 (m), 1260 (w), 1165

(w), 1025 (w), 743 (s), 719 (s), 704 (s), 653 (vs), 624 (m), 606 (s), 549 (w), 532 (m), 468 (m), 419 (m). ^1H NMR (CDCl_3 , 20 °C, δ): 11.51 (s broad, 3H; NH), 2.09 (s, 45H; C_5Me_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C, δ): 122.4 (C_5Me_5), 12.2 (C_5Me_5). MS (EI, 70 eV) m/z (%): 709 (2) $[\text{M}-\text{Cl}]^+$, 608 (1) $[\text{M}-\text{ZnCl}_2]^+$. Anal. Calcd for $\text{C}_{30}\text{H}_{48}\text{Cl}_2\text{N}_4\text{Ti}_3\text{Zn}$ ($M_w = 744.65$) (%): C 48.39, H 6.50, N 7.52. Found: C 48.22, H 6.60, N 7.26.

Reaction of 1 with $[\text{Zn}(\text{CH}_2\text{SiMe}_3)_2]$ in a NMR tube scale experiment: A 5 mm Valved-NMR tube was charged with **1** (0.010 g, 0.016 mmol), $[\text{Zn}(\text{CH}_2\text{SiMe}_3)_2]$ (0.004 g, 0.017 mmol) and benzene- d_6 (1.00 mL). The resultant brown solution was monitored by NMR spectroscopy. After 10 minutes at room temperature, the spectra showed complete reaction and the corresponding complex $[(\text{Me}_3\text{SiCH}_2)_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**4**) was characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Complex **4** decomposed completely within hours at room temperature to give a red solution containing **5** and SiMe_4 according to the NMR spectra.

NMR data for $[(\text{Me}_3\text{SiCH}_2)_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**4**): ^1H NMR (C_6D_6 , 20 °C, δ): 13.66 (s broad, 3H; NH), 1.99 (s, 45 H; C_5Me_5), 0.15 (s, 18H; CH_2SiMe_3), -0.67 (s, 4H; CH_2SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C, δ): 117.5 (C_5Me_5), 11.8 (C_5Me_5), 3.2 (CH_2SiMe_3), 2.7 (CH_2SiMe_3).

Synthesis of $[(\text{Me}_3\text{SiCH}_2)\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (5**):** *Method A:* A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), $[\text{Zn}(\text{CH}_2\text{SiMe}_3)_2]$ (0.12 g, 0.50 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h to give an orange solution. After filtration, the volatile components were removed under reduced pressure to afford **5** as a red solid (0.34 g, 92%). *Method B:* A 100 mL Schlenk flask was charged with **2** (0.15 g, 0.20 mmol), $[\text{LiCH}_2\text{SiMe}_3]$ (0.040 g, 0.42 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 20 h to give a red solution and a white precipitate. After filtration, the volatile components of the solution were removed under

reduced pressure to afford **5** as a red solid (0.11 g, 73%). IR (KBr, cm^{-1}): 3363 (w), 2911 (s), 2858 (s), 1491 (w), 1437 (m), 1376 (m), 1250 (w), 1239 (m), 1067 (w), 1024 (m), 937 (m), 857 (m), 819 (s), 787 (s), 722 (vs), 700 (s), 675 (s), 616 (s), 535 (w), 513 (w), 483 (w), 450 (w), 426 (m). ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 10.55 (s broad, 2H; NH), 2.08 (s, 30H; C_5Me_5), 1.88 (s, 15H; C_5Me_5), 0.22 (s, 9H; CH_2SiMe_3), -0.77 (s, 2H; CH_2SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 118.8, 117.8 (C_5Me_5), 11.9, 11.8 (C_5Me_5), 3.3 (CH_2SiMe_3), -13.3 (CH_2SiMe_3). MS (EI, 70 eV) m/z (%): 760 (2) $[\text{M}]^+$, 607 (5) $[\text{M}-\text{ZnCH}_2\text{SiMe}_3]^+$, 472 (7) $[\text{M}-\text{ZnCH}_2\text{SiMe}_3-\text{C}_5\text{Me}_5]^+$. Anal. Calcd for $\text{C}_{34}\text{H}_{58}\text{N}_4\text{SiTi}_3\text{Zn}$ ($M_w = 759.96$) (%): C 53.74, H 7.69, N 7.37. Found: C 53.62, H 7.54, N 6.69.

Synthesis of $[(\text{PhCH}_2)\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (6**):** In a fashion similar to the preparation of **5**, Method A, treatment of **1** (0.50 g, 0.82 mmol) with $[\text{Zn}(\text{CH}_2\text{Ph})_2]$ (0.20 g, 0.81 mmol) in toluene (25 mL) afforded **6** as a red solid (0.57 g, 92%). IR (KBr, cm^{-1}): 3361 (w), 2908 (s), 2856 (s), 1593 (m), 1486 (m), 1429 (m), 1374 (m), 1204 (w), 1178 (w), 1057 (w), 1025 (w), 997 (w), 889 (w), 798 (m), 749 (s), 723 (vs), 696 (vs), 664 (s), 613 (m), 539 (w), 483 (w), 451 (w), 427 (s). ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 10.39 (s broad, 2H; NH), 7.20-6.89 (m, 5H; $\text{CH}_2\text{C}_6\text{H}_5$), 2.08 (s, 2H; $\text{CH}_2\text{C}_6\text{H}_5$), 2.04 (s, 30H; C_5Me_5), 1.81 (s, 15H; C_5Me_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 151.5, 127.8, 126.9, 120.8 (C_6H_5), 119.1, 118.0 (C_5Me_5), 14.1 ($\text{CH}_2\text{C}_6\text{H}_5$), 11.8, 11.6 (C_5Me_5). MS (EI, 70 eV) m/z (%): 764 (6) $[\text{M}]^+$, 673 (11) $[\text{M}-\text{CH}_2\text{Ph}]^+$, 607 (21) $[\text{M}-\text{ZnCH}_2\text{Ph}]^+$. Anal. Calcd for $\text{C}_{37}\text{H}_{54}\text{N}_4\text{Ti}_3\text{Zn}$ ($M_w = 763.87$) (%): C 58.18, H 7.14, N 7.33. Found: C 57.87, H 7.42, N 7.05.

Synthesis of $[\text{MeZn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (7**):** In a fashion similar to the preparation of **6**, treatment of **1** (1.00 g, 1.64 mmol) with $[\text{ZnMe}_2]$ (2.0 M in toluene, 0.82 mL, 1.64 mmol) in toluene (50 mL) afforded **7** as a red solid (1.11 g, 98%). IR (KBr, cm^{-1}): 3365 (w), 2904 (s), 2856 (m), 2722 (w), 1489 (w), 1429 (m), 1375 (m), 1167 (w), 1066 (w), 1024 (w), 953 (w), 905 (w), 783 (m), 724 (vs), 699 (vs), 664 (s), 616 (s), 527 (m), 484 (w), 452 (w),

428 (s). ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 10.66 (s broad, 2H; NH), 2.08 (s, 30H; C_5Me_5), 1.86 (s, 15H; C_5Me_5), -0.37 (s, 3H; ZnMe). ^{13}C NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 118.8 (m; C_5Me_5), 117.8 (m; C_5Me_5), 11.8 (q, $^1\text{J}_{\text{C-H}} = 125$ Hz; C_5Me_5), 11.7 (q, $^1\text{J}_{\text{C-H}} = 126$ Hz; C_5Me_5), -20.8 (q, $^1\text{J}_{\text{C-H}} = 121$ Hz; ZnMe). MS (EI, 70 eV) m/z (%): 688 (35) $[\text{M}]^+$, 673 (4) $[\text{M-Me}]^+$, 607 (27) $[\text{M-ZnMe}]^+$, 472 (25) $[\text{M-ZnMe-C}_5\text{Me}_5]^+$, 337 (27) $[\text{M-ZnMe-2C}_5\text{Me}_5]^+$. Anal. Calcd for $\text{C}_{31}\text{H}_{50}\text{N}_4\text{Ti}_3\text{Zn}$ ($M_w = 687.77$) (%): C 54.14, H 7.33, N 8.15. Found: C 54.30, H 7.37, N 7.69.

Synthesis of $[\{(\text{Me}_3\text{Si})\text{H}_4\text{C}_5\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (8**):** In a fashion similar to the preparation of **5**, *Method A*, treatment of **1** (0.30 g, 0.49 mmol) with $[\text{Zn}\{\text{C}_5\text{H}_4(\text{SiMe}_3)_2\}]$ (0.17 g, 0.50 mmol) in toluene (20 mL) afforded **8** as a red solid (0.39 g, 98%). Also using *Method B*, treatment of **2** (0.30 g, 0.40 mmol) with $[\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)]$ (0.12 g, 0.83 mmol) in toluene (25 mL) afforded **8** as a red solid (0.25 g, 78%). IR (KBr, cm^{-1}): 3361 (w), 3344 (w), 3070 (w), 2948 (m), 2909 (s), 2860 (m), 1491 (w), 1430 (m), 1375 (m), 1246 (m), 1145 (w), 1063 (w), 1043 (w), 1019 (m), 888 (m), 833 (s), 741 (vs), 720 (vs), 699 (vs), 613 (s), 532 (m), 483 (w), 426 (m). ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 9.61 (s broad, 2H; NH), 6.88 (m, 2H; $\text{C}_5\text{H}_2\text{H}_2\text{SiMe}_3$), 6.67 (m, 2H; $\text{C}_5\text{H}_2\text{H}_2\text{SiMe}_3$), 2.06 (s, 30H; C_5Me_5), 1.85 (s, 15H; C_5Me_5), 0.19 (s, 9H; $\text{C}_5\text{H}_4(\text{SiMe}_3)$). ^{13}C NMR (C_6D_6 , 20 $^\circ\text{C}$, δ): 129.9 (m, $^1\text{J}_{\text{C-H}} = 163$ Hz; $\text{C}_4\text{H}_4\text{CSiMe}_3$), 121.5 (m, $^1\text{J}_{\text{C-H}} = 158$ Hz; $\text{C}_4\text{H}_4\text{CSiMe}_3$), 119.5 (m; C_5Me_5), 118.3 (m; C_5Me_5), 72.1 (m; $\text{C}_4\text{H}_4\text{CSiMe}_3$), 12.0 (q, $^1\text{J}_{\text{C-H}} = 125$ Hz; C_5Me_5), 11.8 (q, $^1\text{J}_{\text{C-H}} = 126$ Hz; C_5Me_5), 0.3 (q, $^1\text{J}_{\text{C-H}} = 117$ Hz; $\text{C}_4\text{H}_4\text{CSiMe}_3$). MS (EI, 70 eV) m/z (%): 810 (2) $[\text{M}]^+$, 673 (3) $[\text{M-C}_5\text{H}_4\text{SiMe}_3]^+$, 607 (4) $[\text{M-ZnC}_5\text{H}_4\text{SiMe}_3]^+$. Anal. Calcd for $\text{C}_{38}\text{H}_{60}\text{N}_4\text{SiTi}_3\text{Zn}$ ($M_w = 810.02$) (%): C 56.35, H 7.46, N 6.92. Found: C 56.27, H 7.32, N 6.61.

Synthesis of $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (9**):** In a fashion similar to the preparation of **5**, *Method A*, but using amber stained glassware, treatment of **1** (1.00 g, 1.64 mmol) with $[\text{Zn}\{\text{N}(\text{SiMe}_3)_2\}]$ (0.63 g, 1.63 mmol) in toluene (50 mL) afforded **9** as a red solid (1.19 g, 88%). Also through *Method B* but using amber stained glassware,

treatment of **2** (0.20 g, 0.27 mmol) with $[\text{LiN}(\text{SiMe}_3)_2]$ (0.090 g, 0.54 mmol) in toluene (20 mL) afforded **9** as a red solid (0.15 g, 68%). IR (KBr, cm^{-1}): 3383 (w), 3351 (w), 2909 (s), 1491 (w), 1435 (m), 1377 (m), 1239 (s), 1066 (w), 992 (s), 885 (s), 830 (s), 720 (vs), 703 (vs), 665 (s), 615 (s), 530 (w), 480 (w), 445 (w), 425 (m). ^1H NMR (C_6D_6 , 20 °C, δ): 10.24 (s broad, 2H; NH), 2.07 (s, 30H; C_5Me_5), 1.90 (s, 15H; C_5Me_5), 0.30 (s, 18H; $\text{N}(\text{SiMe}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 °C, δ): 119.6, 118.4 (C_5Me_5), 12.1, 12.0 (C_5Me_5), 6.7 (SiMe_3). MS (EI, 70 eV) m/z (%): 833 (2) $[\text{M}]^+$, 607 (2) $[\text{M}-\text{ZnN}(\text{SiMe}_3)_2]^+$, 472 (2) $[\text{M}-\text{ZnN}(\text{SiMe}_3)_2-\text{C}_5\text{Me}_5]^+$. Anal. Calcd for $\text{C}_{36}\text{H}_{65}\text{N}_5\text{Si}_2\text{Ti}_3\text{Zn}$ ($M_w = 833.13$) (%): C 51.90, H 7.86, N 8.41. Found: C 52.16, H 7.97, N 7.98.

Synthesis of $[\{\text{Me}_3\text{Si}(\text{H})\text{N}(\text{Me})_2\text{SiCH}_2\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (10**):** A 150 mL ampoule (Teflon stopcock) was charged with **9** (1.21 g, 1.45 mmol), toluene (50 mL) and a magnetic stir bar. The orange solution was stirred under irradiation with a sun lamp (Ultra-Vitalux E27/ES OSRAM, 300 W) for 20 h. The resultant brown solution was filtered, and the volatile components were removed under reduced pressure to afford **10** as a brown solid (0.96 g, 79%). IR (KBr, cm^{-1}): 3365 (m), 2948 (s), 2910 (s), 1494 (w), 1436 (m), 1376 (s), 1243 (s), 1168 (m), 1066 (w), 1023 (w), 922 (s), 838 (s), 800 (s), 774 (s), 723 (vs), 702 (vs), 678 (s), 616 (s), 529 (w), 483 (w), 451 (w), 427 (m). ^1H NMR (C_6D_6 , 20 °C, δ): 10.54 (s broad, 2H; NH), 2.08 (s, 30H; C_5Me_5), 1.86 (s, 15H; C_5Me_5), 0.30 (s, 6H; $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$), 0.28 (s, 9H; $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$), -0.69 (s, 2H; $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$), not observed $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$. ^{13}C NMR (C_6D_6 , 20 °C, δ): 118.9 (m; C_5Me_5), 117.9 (m; C_5Me_5), 12.0 (q, $^1J_{\text{C-H}} = 125$ Hz; C_5Me_5), 11.8 (q, $^1J_{\text{C-H}} = 126$ Hz; C_5Me_5), 5.6 (q, $^1J_{\text{C-H}} = 117$ Hz; $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$), 3.2 (q, $^1J_{\text{C-H}} = 117$ Hz; $\text{CH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$), -11.0 (t, $^1J_{\text{C-H}} = 115$ Hz; $\text{ZnCH}_2\text{Si}(\text{Me})_2\text{N}(\text{H})\text{SiMe}_3$). MS (EI, 70 eV) m/z (%): 833 (2) $[\text{M}]^+$, 607 (4) $[\text{M}-\text{ZnCH}_2\text{Si}(\text{Me})_2\text{NHSiMe}_3]^+$. Anal. Calcd for

$C_{36}H_{65}N_5Si_2Ti_3Zn$ ($M_w = 833.13$) (%): C 51.90, H 7.86, N 8.41. Found: C 52.33, H 7.96, N 7.52.

Synthesis of $[(H_5C_5)Zn\{\mu_3-N\}(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3\mu_3-N]$ (11**):** A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.40 mmol), $[Li(C_5H_5)]$ (0.060 g, 0.83 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 5 h to give a red solution and a white precipitate. After filtration, the volatile components were removed under reduced pressure to afford **11** as a red solid (0.22 g, 73%). IR (KBr, cm^{-1}): 3356 (w), 3334 (w), 2909 (s), 2857 (m), 1490 (w), 1431 (m), 1375 (m), 1261 (w), 1107 (w), 1067 (w), 1023 (w), 983 (w), 781 (s), 730 (s), 702 (vs), 665 (s), 613 (s), 533 (m), 481 (w), 448 (m), 427 (s). 1H NMR (C_6D_6 , 20 °C, δ): 9.56 (s broad, 2H; NH), 6.38 (s, 5H; C_5H_5), 2.04 (s, 30H; C_5Me_5), 1.85 (s, 15H; C_5Me_5). ^{13}C NMR (C_6D_6 , 20 °C, δ): 119.6 (m, C_5Me_5), 118.3 (m, C_5Me_5), 108.8 (m, $^1J_{C-H} = 160$ Hz; C_5H_5), 11.8 (q, $^1J_{C-H} = 125$ Hz; C_5Me_5), 11.7 (q, $^1J_{C-H} = 126$ Hz; C_5Me_5). MS (EI, 70 eV) m/z (%): 738 (3) $[M]^+$, 673 (11) $[M-C_5H_5]^+$, 607 (18) $[M-ZnC_5H_5]^+$, 472 (11) $[M-ZnC_5H_5-C_5Me_5]^+$. Anal. Calcd for $C_{35}H_{52}N_4Ti_3Zn$ ($M_w = 737.83$) (%): C 56.98, H 7.10, N 7.59. Found: C 57.16, H 6.86, N 7.32.

Synthesis of $[(H_7C_9)Zn\{\mu_3-N\}(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3\mu_3-N]$ (12**):** A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.40 mmol), $[Li(C_9H_7)]$ (0.10 g, 0.82 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 3 h to give a red solution and a white precipitate. After filtration, the volatile components were removed under reduced pressure and the resultant solid was washed with hexane (5 mL) to afford **12** as a red powder (0.23 g, 72%). IR (KBr, cm^{-1}): 3352 (w), 3055 (w), 2908 (m), 2856 (m), 1599 (w), 1491 (w), 1431 (m), 1375 (m), 1323 (w), 1261 (w), 1230 (w), 1198 (w), 1161 (w), 1143 (w), 1063 (w), 1024 (w), 992 (w), 924 (w), 887 (w), 865 (w), 809 (m), 774 (m), 735 (s), 721 (s), 699 (vs), 664 (s), 614 (m), 536 (w), 483 (w), 449 (w), 429 (m). 1H NMR (C_6D_6 , 20 °C, δ): 9.85 (s broad, 2H; NH), 7.67 (m, 2H; C_9H_7), 7.29 (m, 2H; C_9H_7), 7.05 (t, $^3J = 3$ Hz, 1H; C_9H_7), 5.63 (d, $^3J = 3$ Hz,

2H; C₉H₇), 2.03 (s, 30H; C₅Me₅), 1.68 (s, 15H; C₅Me₅). ¹³C NMR (C₆D₆, 20 °C, δ): 144.8 (s; C₉H₇), 137.2 (d, ¹J_{C-H} = 161 Hz; C₉H₇), 121.5 (m, ¹J_{C-H} = 151 Hz; C₉H₇), 121.3 (m, ¹J_{C-H} = 155 Hz; C₉H₇), 119.6 (m, C₅Me₅), 118.3 (m, C₅Me₅), 82.2 (m, ¹J_{C-H} = 152 Hz; C₉H₇), 11.8 (q, ¹J_{C-H} = 125 Hz; C₅Me₅), 11.5 (q, ¹J_{C-H} = 125 Hz; C₅Me₅). MS (EI, 70 eV) m/z (%): 788 (2) [M]⁺, 673 (24) [M-C₉H₇]⁺, 607 (27) [M-ZnC₉H₇]⁺, 472 (24) [M-ZnC₉H₇-C₅Me₅]⁺, 337 (41) [M-ZnC₉H₇-2C₅Me₅]⁺. Anal. Calcd for C₃₉H₅₄N₄Ti₃Zn (M_w = 787.89) (%): C 59.45, H 6.91, N 7.11. Found: C 59.59, H 6.72, N 7.20.

Synthesis of [ClCu{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (13): A 100 mL Schlenk flask was charged with **1** (0.70 g, 1.15 mmol), CuCl (0.11 g, 1.11 mmol) and toluene (40 mL). The reaction mixture was stirred at room temperature for 18 h to give a red solution. After filtration, the volatile components were removed under reduced pressure to give a red solid. The solid was washed with hexane (15 mL) and vacuum-dried to give **13** as a red powder (0.56 g, 72%). IR (KBr, cm⁻¹): 3362 (m), 3219 (broad, m), 2909 (s), 2857 (m), 2723 (w), 1489 (w), 1450 (m), 1428 (m), 1377 (s), 1067 (w), 1025 (m), 797 (m), 739 (s), 668 (s), 645 (vs), 639 (vs), 520 (w), 476 (w), 430 (m), 403 (m). ¹H NMR (C₆D₆, 20 °C, δ): 11.70 (s broad, 3H; NH), 1.87 (s, 45H; C₅Me₅). ¹³C{¹H} NMR (C₆D₆, 20 °C, δ): 119.4 (C₅Me₅), 11.6 (C₅Me₅). MS (EI, 70 eV) m/z (%): 706 (1) [M]⁺, 671 (4) [M-Cl]⁺. Anal. Calcd for C₃₀H₄₈ClCuN₄Ti₃ (M_w = 707.34) (%): C 50.94, H 6.84, N 7.92. Found: C 50.89, H 6.71, N 7.66.

Synthesis of [ICu{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (14): In a fashion similar to the preparation of **13**, treatment of **1** (0.50 g, 0.82 mmol) with CuI (0.16 g, 0.84 mmol) in toluene (30 mL) afforded **14** as a red solid (0.43 g, 65%). IR (KBr, cm⁻¹): 3363 (m), 2906 (s), 2857 (m), 1488 (w), 1427 (m), 1377 (m), 1024 (m), 746 (s), 735 (s), 685 (s), 670 (s), 644 (vs), 628 (s), 522 (w), 479 (w), 435 (m), 407 (m). ¹H NMR (C₆D₆, 20 °C, δ): 11.68 (s broad, 3H; NH), 1.87 (s, 45H; C₅Me₅). ¹³C{¹H} NMR (C₆D₆, 20 °C, δ): 119.5 (C₅Me₅), 11.7 (C₅Me₅). MS (EI,

70 eV) m/z (%): 671 (23) [M-I]⁺, 610 (5) [M-I-Cu]⁺. Anal. Calcd for C₃₀H₄₈CuIN₄Ti₃ (M_w = 798.78) (%): C 45.11, H 6.06, N 7.01. Found: C 45.41, H 5.77, N 6.63.

Synthesis of [Cu(μ₄-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)]₂ (15): *Method A:* A solution of [LiN(SiMe₃)₂] (0.047 g, 0.28 mmol) in toluene (5 mL) was carefully added to **13** (0.20 g, 0.28 mmol) in toluene (15 mL). The system was allowed to react without any stirring for 6 days to give the precipitation of huge red crystals of **15** and a fine white powder. After elimination of the solution by decantation, the crystals were rinsed with several portions of toluene (4 x 5 mL) to remove the powder and characterized as **15**·2C₇H₈ (0.11 g, 51%). *Method B:* A 100 mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), [CuN(SiMe₃)₂]₄ (0.11 g, 0.12 mmol) and toluene (30 mL). The tube was flame sealed and heated at 150 °C for 6 days. The reaction mixture was allowed to cool to room temperature overnight to afford red crystals of **15**·2C₇H₈ (0.27 g, 73%). IR (KBr, cm⁻¹): 3357 (m), 2902 (s), 1604 (w), 1494 (m), 1431 (s), 1373 (s), 1080 (w), 1023 (m), 729 (vs), 671 (vs), 629 (vs), 617 (vs), 509 (s), 478 (w), 464 (m). Anal. Calcd for C₇₄H₁₁₀Cu₂N₈Ti₆ (M_w = 1526.03) (%): C 58.24, H 7.26, N 7.34. Found: C 58.19, H 7.13, N 7.12.

Synthesis of [(Ph₃P)Cu{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**16**): A 100 mL Schlenk flask was charged with **13** (0.30 g, 0.42 mmol), PPh₃ (0.11 g, 0.42 mmol) and toluene (15 mL). After stirring at room temperature for 10 min., a solution of [Li{N(SiMe₃)₂}] (0.070 g, 0.42 mmol) in toluene (5 mL) was added. The reaction mixture was stirred at room temperature for 18 h to give an orange solution and a fine solid. After filtration, the volatile components were removed under reduced pressure to give **16** as an orange solid (0.34 g, 87%). IR (KBr, cm⁻¹): 3362 (m), 3050 (m), 2907 (s), 2855 (s), 1587 (w), 1573 (w), 1481 (m), 1434 (s), 1374 (m), 1185 (w), 1096 (m), 1026 (m), 997 (w), 744 (m), 707 (vs), 667 (vs), 613 (vs), 518 (s), 492 (m), 423 (m), 387 (m). ¹H NMR (C₆D₆, 20 °C, δ): 11.08 (s broad, 2H; NH), 7.59 (m, 6H; o-C₆H₅), 7.15-7.10 (m, 9H; m- and p-C₆H₅), 2.16 (s, 30H; C₅Me₅), 1.99 (s, 15H;

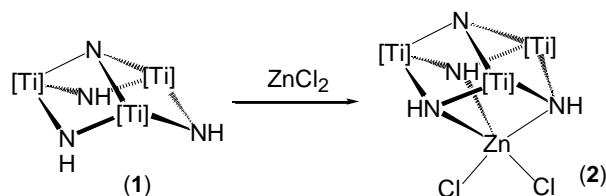
C₅Me₅). ¹³C{¹H} NMR (C₆D₆, 20 °C, δ): 135.5 (d, ¹J_{C-P} = 33.7 Hz; ipso-C₆H₅), 134.3 (d, ²J_{C-P} = 15.4 Hz; o-C₆H₅), 129.8 (d, ⁴J_{C-P} = 1.4 Hz; p-C₆H₅), 128.5 (d, ³J_{C-P} = 9.5 Hz; m-C₆H₅), 116.6 (C₅Me₅), 115.8 (C₅Me₅), 11.9 (C₅Me₅), 11.8 (C₅Me₅). MS (EI, 70 eV) m/z (%): 671 (3) [M-PPh₃]⁺, 608 (1) [M-PPh₃-Cu]⁺, 536 (2) [M-PPh₃-C₅Me₅]⁺, 400 (3) [M-PPh₃-2C₅Me₅]⁺, 262 (89) [PPh₃]⁺, 183 (100) [PPh₂]⁺, 108 (40) [PPh]⁺. Anal. Calcd for C₄₈H₆₂CuN₄PTi₃ (M_w = 933.17) (%): C 61.78, H 6.70, N 6.00. Found: C 61.62, H 6.54, N 5.36.

X-ray structure determination of 3, 8, 9 and 15. Crystals of complexes **3**, **8**, **9** and **15** were grown as described in the results and discussion 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 200K 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 34).

The structures were solved, using the WINGX package,³³ by direct methods (SHELXS-97) and refined by least-squares against F² (SHELXL-97).³⁴ All non-hydrogen atoms were anisotropically refined while the hydrogen atoms were positioned geometrically and refined by using a riding model. Crystals of compound **15** were of poor quality and also presented disorder for the carbon atoms C(16)-C(20) of the pentamethylcyclopentadienyl group linked to Ti(1), the PART tool and a free variable in the FVAR command of the SHELXL-97 program let to refine two positions for each carbon atom with 54.8% and 45.2% of occupancy respectively. The highest peak and hole found in the difference Fourier map of 1.58/-3.46 eÅ⁻³ are located close to Cu(1), 1.03 and 0.75 Å respectively.

Results and Discussion

Azaheterometallocubanes of zinc. Treatment of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with anhydrous zinc dichloride (1 equiv) in toluene at room temperature affords the adduct $[\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**2**) as a yellow solid in 68% yield (Scheme 1). Complex **2** is not soluble in aromatic solvents but exhibits a good solubility in chloroform or dichloromethane. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** in chloroform- d_1 at room temperature show resonances for equivalent NH and $\eta^5\text{-C}_5\text{Me}_5$ groups. The NH resonance signal ($\delta = 11.51$) in the ^1H NMR spectrum is shifted to higher field with respect to that found for **1** ($\delta = 13.40$), whereas the resonance signal for the ipso carbon of the pentamethylcyclopentadienyl groups ($\delta = 122.4$) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is shifted downfield with respect to that found for **1** ($\delta = 117.1$). These data are similar to those recently reported for several main-group metal adducts $[\text{X}_n\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$,¹⁶ and are consistent with a tridentate coordination of **1** to the zinc center or very fast exchange processes in solution.



Scheme 1. Reaction of **1** with ZnCl_2 . $[\text{Ti}] = \text{Ti}(\eta^5\text{-C}_5\text{Me}_5)$

Moreover, while the NMR data suggest a single-cube structure in solution, the insolubility of **2** in aromatic solvents might agree with a halide-bridged double cube structure in the solid state like that recently determined for the tin derivative $[\{\text{ISn}(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2(\mu\text{-I})_2]$.^{16b} Mass spectrum (EI, 70 eV) shows the ion $[\text{M-Cl}]^+$ as that of the higher relation mass/charge, suggesting a single-cube structure in the gas phase, but higher aggregates can not be ruled out. Attempts to grow suitable single crystals for a solid-state determination of **2** were failed, but a solution of **2** in dichloromethane at $-40\text{ }^\circ\text{C}$ rendered a

very small fraction of yellow crystals of the ammonia adduct $[(\text{H}_3\text{N})\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**). Complex **3** could not be obtained in a preparative scale experiment since reactions of **2** with an excess of ammonia in dichloromethane gave immediately **1** and a fine white precipitate of $[\text{ZnCl}_2(\text{NH}_3)_2]$.^{35,36} Furthermore, we did not observe any reaction between complex **1** and $[\text{ZnCl}_2(\text{NH}_3)_2]$ in dichloromethane or toluene even at high temperatures.

The X-ray crystal structure of $[(\text{H}_3\text{N})\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**) is presented in Figure 1 and selected bond lengths and angles in Table 2. The solid-state structure reveals a distorted tetrahedral geometry for the zinc center, comprising two chloride, one ammonia ligand and one NH imido group with angles spanning 123.3(1)-100.8(2)°. The Zn-Cl, average 2.283(2) Å, and Zn-N(ammonia), 2.044(5) Å, bond lengths compare well with those reported for $[\text{ZnCl}_2(\text{NH}_3)_2]$ ³⁶ and other $[\text{ZnCl}_2(\text{diamine})]$ ³⁷ complexes. The triaza ligand is bound to zinc by one NH group with a zinc-nitrogen bond length, Zn-N(13) 2.046(5) Å, very similar to that found for the ammonia ligand. Within the organometallic ligand, the average bond lengths and angles are similar to those determined in the free ligand **1**.⁸

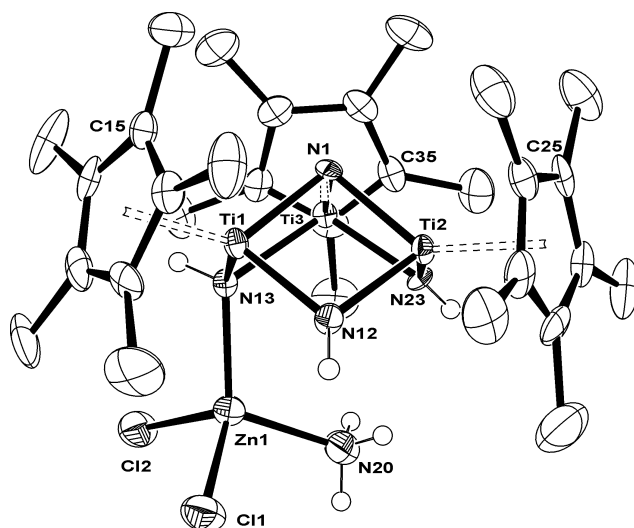


Figure 1. Perspective view of $[(\text{H}_3\text{N})\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (**3**) with thermal ellipsoids at the 50% probability level. The dichloromethane solvent molecule is omitted for clarity.

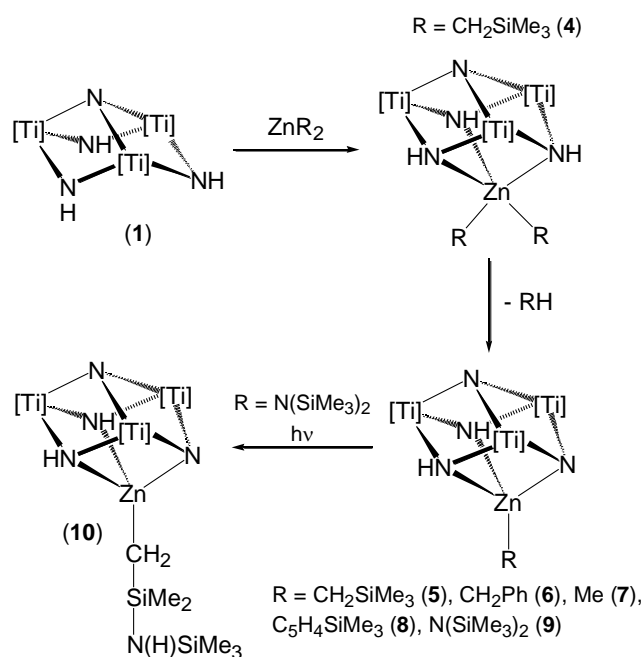
Table 2. Selected bond lengths (Å) and angles (°) for **3**.

Zn(1)-N(13)	2.046(5)	Zn(1)-N(20)	2.044(5)
Zn(1)-Cl(1)	2.274(2)	Zn(1)-Cl(2)	2.292(2)
Ti(1)-N(13)	2.009(4)	Ti(1)-N(12)	1.891(5)
Ti(1)-N(1)	1.908(4)	Ti(2)-N(12)	1.923(4)
Ti(2)-N(23)	1.927(4)	Ti(2)-N(1)	1.934(4)
Ti(3)-N(13)	2.009(4)	Ti(3)-N(23)	1.879(4)
Ti(3)-N(1)	1.922(4)	Ti...Ti av	2.815(1)
N(13)-Zn(1)-N(20)	111.9(2)	N(13)-Zn(1)-Cl(1)	123.3(1)
N(13)-Zn(1)-Cl(2)	103.4(1)	N(20)-Zn(1)-Cl(1)	100.8(2)
N(20)-Zn(1)-Cl(2)	108.3(2)	Cl(1)-Zn(1)-Cl(2)	108.7(1)
Ti(1)-N(1)-Ti(3)	95.9(2)	Ti(1)-N(1)-Ti(2)	93.9(2)
Ti(3)-N(1)-Ti(2)	93.0(2)	Ti(1)-N(12)-Ti(2)	94.8(2)
Ti(3)-N(13)-Ti(1)	90.1(2)	Ti(3)-N(13)-Zn(1)	120.0(2)
Ti(1)-N(13)-Zn(1)	113.0(2)	Ti(3)-N(23)-Ti(2)	94.6(2)
N(12)-Ti(1)-N(1)	86.2(2)	N(12)-Ti(1)-N(13)	103.6(2)
N(1)-Ti(1)-N(13)	87.0(2)	N(12)-Ti(2)-N(23)	107.3(2)
N(12)-Ti(2)-N(1)	84.6(2)	N(23)-Ti(2)-N(1)	85.0(2)
N(23)-Ti(3)-N(1)	86.7(2)	N(23)-Ti(3)-N(13)	105.3(2)
N(1)-Ti(3)-N(13)	86.7(2)		

Treatment of **1** with one equivalent of the zinc alkyl, trimethylsilylcyclopentadienyl or amido, complexes [ZnR₂] in toluene at room temperature leads to the cube-type derivatives [RZn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] [R = CH₂SiMe₃ (**5**), CH₂Ph (**6**), Me (**7**), C₅H₄SiMe₃ (**8**), N(SiMe₃)₂ (**9**)] via alkane/trimethylsilylcyclopentadiene/amine elimination (Scheme 2). However, the analogous treatment of **1** with dicyclopentadienylzinc [Zn(C₅H₅)₂]²⁶ gave the initial products unaltered, probably due to the insolubility of the zinc reagent in the reaction solvent.

The reactions most likely proceed via adducts similar to **2**, but only the bis(trimethylsilylmethyl)zinc derivative [(Me₃SiCH₂)₂Zn{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**4**) was stable for some minutes and clearly identified following the reaction course by ¹H and ¹³C{¹H} NMR spectroscopy. The spectra at room temperature of the reaction mixture in benzene-d₆ after 10 min. show shifted resonances with respect to those of the starting materials for equivalent NH, η⁵-C₅Me₅, and CH₂SiMe₃ groups. After some hours at room temperature,

the spectra revealed complete consumption of **4** to give complex **5** and the corresponding equivalent of tetramethylsilane.



Scheme 2. Reactions of **1** with ZnR₂. [Ti] = Ti(η^5 -C₅Me₅)

Complexes **5-9** were obtained in good yields (88-98%) as red solids, which are very soluble in hexane or toluene. These compounds were characterized by spectral and analytical methods, as well as by X-ray crystal structure determinations for **8** and **9**. Mass spectra (EI, 70 eV) show the expected molecular peaks suggesting a single-cube aggregation in the gas phase. ¹H and ¹³C NMR spectra in benzene-d₆ at room temperature show resonance signals for two η^5 -C₅Me₅ groups in a 2:1 ratio, one Zn-R fragment and a broad signal for the NH groups. These NMR data are consistent with a C_s symmetry in solution and tetrahedral geometries for the zinc centers, in a similar way to those recently reported for the analogous magnesium complexes [RMg{(μ₃-N)(μ₃-NH)₂Ti₃(η^5 -C₅Me₅)₃(μ₃-N)}]¹⁹ and several tris(pyrazolyl)hydroboratozinc derivatives.³⁸

In order to confirm the proposed structures in the Scheme 2 and establish unambiguously the coordination mode of the trimethylsilylcyclopentadienyl ligand in **8**, X-ray crystallographic studies were undertaken for crystals of **8**·C₇H₈ and **9** grown in saturated

toluene solutions. The X-ray structures are presented in Figures 2 and 3, while selected bond and angles are shown in Tables 3 and 4.

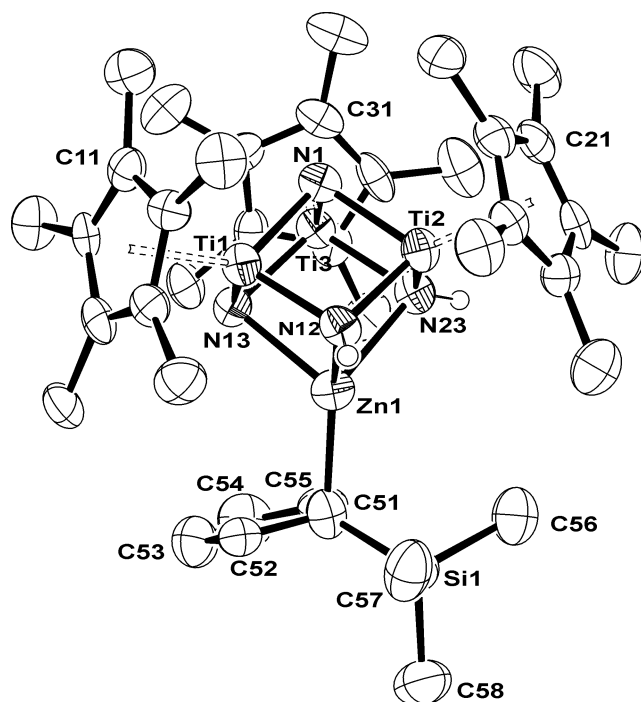


Figure 2. Perspective view of $[\{(Me_3Si)H_4C_5\}Zn\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (**8**) with thermal ellipsoids at the 50% probability level. The toluene solvent molecule is omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **8**.

Zn(1)-N(12)	2.148(8)	Zn(1)-N(13)	2.126(8)
Zn(1)-N(23)	2.147(8)	Zn(1)-C(51)	2.031(11)
Zn(1)···C(52)	2.753(11)	Zn(1)···C(53)	3.532(14)
Zn(1)···C(54)	3.482(15)	Zn(1)···C(55)	2.686(12)
C(51)-C(52)	1.461(14)	C(51)-C(55)	1.457(14)
C(52)-C(53)	1.372(16)	C(53)-C(54)	1.391(18)
C(54)-C(55)	1.376(16)	C(51)-Si(1)	1.855(11)
N(1)-Ti(3)	1.895(8)	N(1)-Ti(1)	1.922(8)
N(1)-Ti(2)	1.949(8)	N(12)-Ti(2)	1.857(7)
N(12)-Ti(1)	1.853(8)	N(13)-Ti(3)	1.961(8)
N(13)-Ti(1)	1.968(8)	N(23)-Ti(2)	1.946(8)
N(23)-Ti(3)	1.958(8)	Ti···Ti av	2.817(2)
N(12)-Zn(1)-N(13)	86.2(3)	N(12)-Zn(1)-N(23)	84.7(3)
N(13)-Zn(1)-N(23)	87.1(3)	N(12)-Zn(1)-C(51)	129.0(4)
N(13)-Zn(1)-C(51)	122.1(4)	N(23)-Zn(1)-C(51)	132.8(4)
Zn(1)-C(51)-Si(1)	107.9(5)	Zn(1)-C(51)-Cp	108.8(6)
Si(1)-C(51)-Cp	143.5(7)	Ti(3)-N(1)-Ti(1)	96.3(4)

Ti(3)-N(1)-Ti(2)	95.1(3)	Ti(1)-N(1)-Ti(2)	91.4(3)
Ti(2)-N(12)-Ti(1)	96.7(3)	Ti(2)-N(12)-Zn(1)	89.1(3)
Ti(1)-N(12)-Zn(1)	87.9(3)	Ti(3)-N(13)-Ti(1)	92.7(3)
Ti(3)-N(13)-Zn(1)	87.9(3)	Ti(1)-N(13)-Zn(1)	85.6(3)
Ti(2)-N(23)-Ti(3)	93.2(3)	Ti(2)-N(23)-Zn(1)	86.8(3)
Ti(3)-N(23)-Zn(1)	87.4(3)	N(12)-Ti(1)-N(1)	86.4(3)
N(12)-Ti(1)-N(13)	99.7(3)	N(1)-Ti(1)-N(13)	84.9(3)
N(12)-Ti(2)-N(1)	85.5(3)	N(12)-Ti(2)-N(23)	99.0(3)
N(1)-Ti(2)-N(23)	85.2(3)	N(1)-Ti(3)-N(23)	86.4(3)
N(1)-Ti(3)-N(13)	85.8(3)	N(23)-Ti(3)-N(13)	97.4(3)

Cp = centroid of the C(51)-C(55) ring

Compound **8** crystallizes with one toluene solvent molecule per cube-type complex. The structure shows a cube-type $[\text{ZnTi}_3\text{N}_4]$ core with angles M-N-M and N-M-N spanning 85.2(3)-99.7(3)°. The coordination sphere about the zinc atom is best described as distorted tetrahedral, comprising three nitrogen atoms of the tridentate organometallic ligand “ $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}^-$ ” and one carbon atom of the $\text{C}_5\text{H}_4\text{SiMe}_3$ group, with angles N-Zn-N 86.0(3) av. and C(51)-Zn-N 128.0(4)° av. The zinc-nitrogen bond lengths, average 2.140(8) Å, are slightly longer than that found for complex **3** but closer to those reported for several tris(pyrazolyl)hydroborates^{38a,39} where the zinc atom is also coordinated to three nitrogen atoms. The distance from the silyl-bearing carbon atom C(51) to the zinc atom [2.031(11) Å], typical for zinc-carbon covalent bonds,⁴⁰ is clearly shorter than those to the other carbon atoms of the trimethylsilylcyclopentadienyl ring, as can be seen in Table 3, in a fashion similar to those found in $[\text{Zn}(\text{C}_5\text{Me}_4\text{SiMe}_3)_2]$ ⁴¹ and $[\text{Zn}(\text{C}_5\text{H}_4\text{SiMe}_3)_2]$,^{25a} confirming an $\eta^1(\sigma)$ coordination mode. Moreover, the Zn-C(51)-Si and Zn-C(51)-ring angles [107.9(5) and 108.8(6)°, respectively] are very close to the ideal 109.5° value for a tetrahedral geometry, suggesting an sp^3 hybridization for C(51).

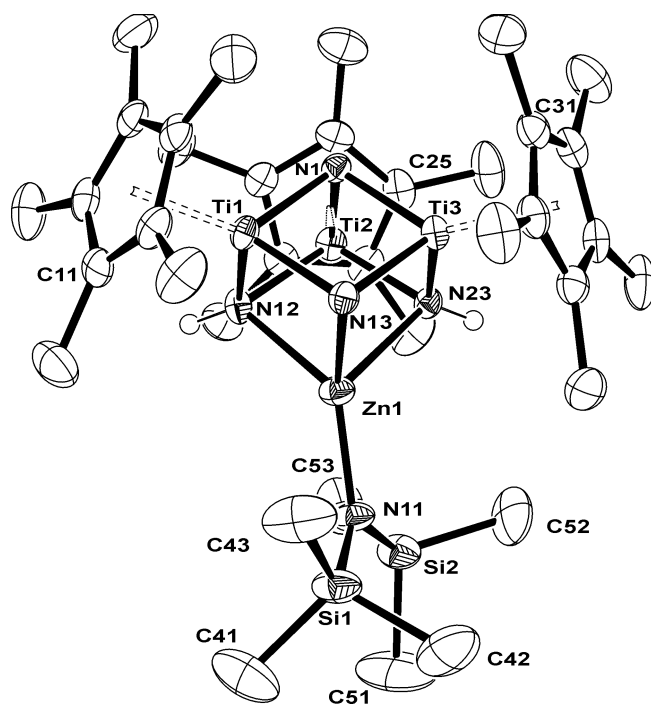


Figure 3. Perspective view of $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**9**)

with thermal ellipsoids at the 50% probability level.

Table 4. Selected lengths (Å) and angles (°) for **9**.

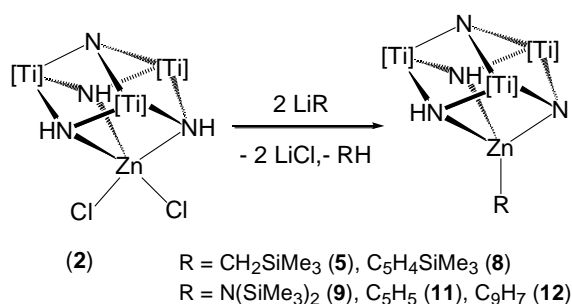
Zn(1)-N(12)	2.174(2)	Zn(1)-N(13)	2.132(2)
Zn(1)-N(23)	2.209(2)	Zn(1)-N(11)	1.916(2)
N(1)-Ti(1)	1.936(2)	N(1)-Ti(3)	1.939(2)
N(1)-Ti(2)	1.950(2)	N(11)-Si(2)	1.721(3)
N(11)-Si(1)	1.722(3)	N(12)-Ti(1)	1.961(2)
N(12)-Ti(2)	1.966(2)	N(13)-Ti(1)	1.957(2)
N(13)-Ti(3)	1.972(2)	N(23)-Ti(2)	1.923(2)
N(23)-Ti(3)	1.930(2)	Ti...Ti av	2.836(1)
N(12)-Zn(1)-N(13)	87.1(1)	N(12)-Zn(1)-N(23)	84.6(1)
N(13)-Zn(1)-N(23)	86.2(1)	N(12)-Zn(1)-N(11)	134.1(1)
N(13)-Zn(1)-N(11)	126.8(1)	N(23)-Zn(1)-N(11)	122.8(1)
Ti(1)-N(1)-Ti(3)	94.3(1)	Ti(1)-N(1)-Ti(2)	94.0(1)
Ti(3)-N(1)-Ti(2)	93.2(1)	Si(2)-N(11)-Si(1)	123.8(1)
Si(2)-N(11)-Zn(1)	112.9(1)	Si(1)-N(11)-Zn(1)	122.6(1)
Ti(1)-N(12)-Ti(2)	92.7(1)	Ti(1)-N(12)-Zn(1)	86.4(1)
Ti(2)-N(12)-Zn(1)	88.3(1)	Ti(1)-N(13)-Ti(3)	92.6(1)
Ti(1)-N(13)-Zn(1)	87.7(1)	Ti(3)-N(13)-Zn(1)	87.8(1)
Ti(2)-N(23)-Ti(3)	94.4(1)	Ti(2)-N(23)-Zn(1)	88.4(1)
Ti(3)-N(23)-Zn(1)	86.7(1)	N(1)-Ti(1)-N(13)	86.8(1)
N(1)-Ti(1)-N(12)	86.9(1)	N(13)-Ti(1)-N(12)	98.5(1)
N(23)-Ti(2)-N(1)	86.1(1)	N(23)-Ti(2)-N(12)	98.6(1)
N(1)-Ti(2)-N(12)	86.3(1)	N(23)-Ti(3)-N(1)	86.2(1)
N(23)-Ti(3)-N(13)	98.9(1)	N(1)-Ti(3)-N(13)	86.2(1)

The molecular structure of **9** confirms the azaheterometallobutane core [ZnTi₃N₄] of the complex and the tridentate coordination of the “{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}⁻” ligand to zinc. The geometry about the zinc center is best described as distorted tetrahedral, with intraligand N-Zn-N angles spanning 84.6(1)-87.1(1)° and interligand N-Zn-N(11) angles in the range 122.8(1)-134.1(1)°. The trimethylsilyl groups of the amido ligand are oriented in an alternate disposition with respect to the pentamethylcyclopentadienyl rings of the preorganized triaza ligand to decrease the steric repulsion. The zinc-nitrogen bond lengths within the cube core are in the range 2.132(2)-2.209(2) Å and are longer than that found for the amido ligand [Zn-N(11) 1.916(2) Å], in a similar way to the (guanidinato)(amido) complex [Zn(hpp){N(SiMe₃)₂}]₂ reported by Coles et al.⁴² The overall structure of **9** is very similar to that determined for the magnesium amido analogue [{(Me₃Si)₂N}Mg{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}]₂,¹⁹ but showing slightly shorter Zn-N bond lengths and wider N-Zn-N intraligand angles due to the smaller size of the zinc atom.

Alkyl complexes **5-8** are stable in benzene-d₆ solutions at ambient light or temperatures about 100 °C. In contrast, the magnesium analogous [RMg{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] undergo Schlenk-type redistribution reactions at room temperature to give the corner-shared nitrido complex [Mg{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}]₂.¹⁹ Furthermore, compounds **5-8** did not react with one equivalent of **1** even at high temperatures. On the other hand, the bis(trimethylsilyl)amido derivative **9** is light sensitive in solution and decomposes, slowly at room temperature and rapidly at higher temperatures, to give the alkyl derivative [{Me₃Si(H)N(Me)₂SiCH₂}Zn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**10**) (Scheme 2). No intermediates or secondary products were identified in the NMR spectra by monitoring the reaction course of a benzene-d₆ solution of **9** exposed to ambient light. Complex **10** was obtained as a brown solid in 79% yield by irradiation of toluene solutions of **9** with the light emitted by a sun lamp for 20 hours. ¹H and ¹³C NMR spectra of **10** reveal resonances for two

different η^5 -C₅Me₅ ligands in a 2:1 ratio and are consistent with a C_s symmetry in solution. The methylene CH₂ group of **10** shows a singlet resonance at -0.69 ppm in the ¹H NMR spectrum and a triplet resonance (¹J_{C-H} = 115 Hz) at -11.0 ppm in the ¹³C NMR spectrum. These chemical shifts are similar to those found for the methylene group in the spectra of [(Me₃SiCH₂)Zn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**5**), -0.77 (CH₂) and -13.3 (CH₂) ppm respectively. However, the ¹H NMR spectrum of **10** did not allow the unambiguous identification of the NH resonance for the CH₂Si(Me)₂N(H)SiMe₃ group.

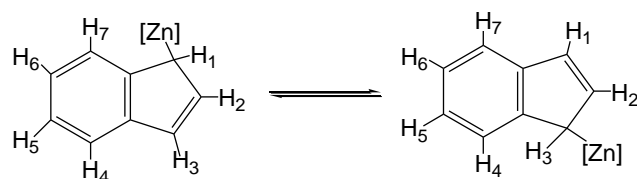
In order to test other ways to prepare the azaheterometallo-cubane complexes of zinc, we tried reactions of the dichloride complex [Cl₂Zn{(μ₃-NH)₃Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**2**) with several organolithium reagents (Scheme 3). Thus, treatment of **2** with 2 equiv of lithium (trimethylsilyl)methyl, (trimethylsilyl)cyclopentadienyl or bis(trimethylsilyl)amido derivatives in toluene at room temperature afforded the alkyl or amido zinc complexes [RZn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] [R = CH₂SiMe₃ (**5**), C₅H₄SiMe₃ (**8**), N(SiMe₃)₂ (**9**)] in good yields (68-78%). Analogous reactions of **2** with two equivalents of lithium cyclopentadienyl [Li(C₅H₅)] or lithium indenyl [Li(C₉H₇)] reagents at room temperature gave the new cyclopentadienyl or indenyl zinc derivatives [RZn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] [R = C₅H₅ (**11**), C₉H₇ (**12**)] as red solids in good yields (72-73%).



Scheme 3. Reactions of **2** with LiR. [Ti] = Ti(η⁵-C₅Me₅)

Complexes **11** and **12** exhibit a poor solubility in hexane but are very soluble in toluene or benzene, and the solutions are stable under argon atmosphere at ambient light and

temperature conditions. Compounds **11** and **12** were characterized by spectral and analytical methods. Mass spectra (EI, 70 eV) show the expected molecular peaks suggesting a single-cube aggregation for the complexes in the gas phase. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in benzene- d_6 at room temperature show resonance signals for two $\eta^5\text{-C}_5\text{Me}_5$ groups in a 2:1 ratio, one cyclopentadienyl or indenyl ligand and a broad signal for the NH groups. In order to investigate the coordination mode of the cyclopentadienyl or indenyl ligands to the zinc center, we studied a toluene- d_8 solution of complex **12** by low temperature ^1H NMR spectroscopy in a 500 MHz spectrometer. The room temperature ^1H NMR spectrum of **12** showed the following resonances for the indenyl group: one doublet ($^3J = 3.0$ Hz) at δ 5.53 for the H_1 and H_3 , one triplet at δ 6.98 for the H_2 and a sharp AA'BB' pattern at δ 7.59-7.23 for the H_4 , H_5 , H_6 and H_7 . Upon cooling at -20 °C the resonance signal at δ 5.53 began to broaden and at -94 °C gave two very broad resonances centered at approximately δ 4.6 and 7.0 which coalesced at about -89 °C. This nonequivalence of the protons of the indenyl ligand at low temperature is consistent with a $\eta^1(\sigma)$ coordination of the indenyl ligand by the C_1 or C_3 to the zinc center. The fluxional process observed can be explained by an intramolecular 1,3 migration of the zinc on the indenyl ligand that is very fast on the NMR time scale at room temperature and slower at -94 °C (Scheme 4).

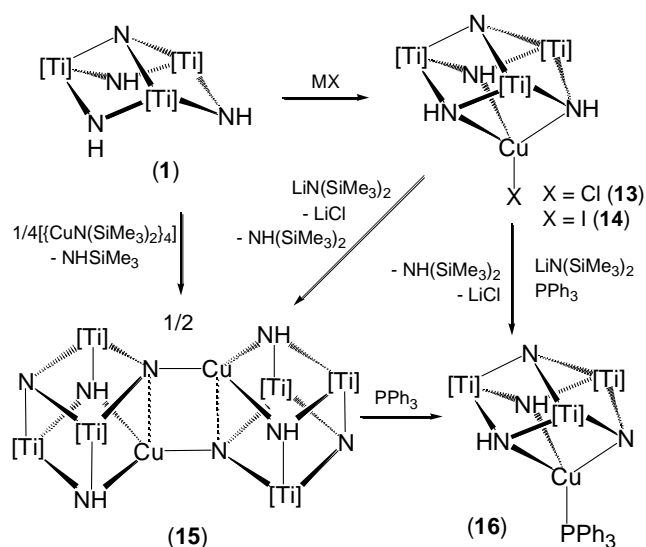


Scheme. 4. 1,3 Migration of the [Zn] fragment on the indenyl ligand in **12**.

An analogous 1,3 migration has been investigated in detail by Casey on several indenylrhenium derivatives.⁴³ In those studies on the fluxional processes, and in many others previously,⁴⁴ the authors observed a smaller barrier for η^1 -cyclopentadienyl systems compared with the η^1 -indenyl systems. Therefore, we did not study the fluxional process occurring on

complex **11**, but the NMR spectra are consistent with $\eta^1(\sigma)$ coordination of the cyclopentadienyl ligand bonded to zinc and a more rapid 1,2 migration of the zinc on the cyclopentadienyl ring.

Azaheterometallocubanes of copper(I). Treatment of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with anhydrous copper(I) halides (1 equiv) in toluene at room temperature affords the adducts $[\text{XCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ ($\text{X} = \text{Cl}$ (**13**), I (**14**)) in good yields (72 and 65%, respectively) (Scheme 5). Complexes **13** and **14** were obtained as red solids, which are very soluble in toluene and scarcely in hexane. Mass spectrum (EI, 70 eV) of **13** shows the molecular peak for a single cube structure whereas the spectrum of **14** reveals the ion $[\text{M-I}]^+$ as that of the higher relation mass/charge. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **13** and **14** in benzene- d_6 reveal resonances for equivalent NH and $\eta^5\text{-C}_5\text{Me}_5$ groups. The NH resonance signals ($\delta = 11.70$ and 11.68) are shifted to higher field than that found for **1** ($\delta = 13.40$), whereas the resonance signal for the C_5Me_5 groups ($\delta = 119.4$ and 119.5) are shifted downfield with respect to that found for **1** ($\delta = 117.1$). These NMR data are similar to those described above for **2** and are consistent with a tridentate coordination of **1** to the copper center and a C_{3v} symmetry in solution.



Scheme 5. Synthesis of copper(I) azaheterometallocubane complexes. $[\text{Ti}] = \text{Ti}(\eta^5\text{-C}_5\text{Me}_5)$

Treatment of the chloride derivative **13** with lithium bis(trimethylsilyl)amido in toluene at room temperature leads to bis(trimethylsilyl)amine and the precipitation of huge red crystals of the dicubane complex $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (**15**) together with a fine powder of LiCl. Lithium chloride can be removed from the mixture after rinsing with toluene for several times to give **15** in 51% yield. Complex **15** can be obtained in higher yield (73%) through the reaction of **1** with $[\{\text{CuN}(\text{SiMe}_3)_2\}_4]$ ^{31,32} (0.25 equiv) in toluene at 150 °C for 6 days. A mixture of **1** with $[\{\text{CuN}(\text{SiMe}_3)_2\}_4]$ in benzene-d₆ was monitored by NMR spectroscopy at different temperatures. After heating at 40 °C, red crystals precipitated at the bottom of the tube and resonances due to bis(trimethylsilyl)amine were detected in the spectra. However, the reaction rate was very slow at temperatures below 120 °C, probably due to the high stability of the tetranuclear structure determined for the copper amido reagent.^{32,45} Complex **15** was characterized by IR spectroscopy and C,H,N microanalysis, as well as by an X-ray crystal structure determination for suitable crystals of **15**·C₆D₆ grown in the treatment of **13** with LiN(SiMe₃)₂ in benzene-d₆ without any stirring.

The X-ray structure of **15** is presented in Figure 4 while selected bond and angles are shown in Table 5. Crystals of **15** bear one benzene solvent molecule per double cube complex. The molecule lies on an inversion center and shows an edge-linked double cube arrangement with two cube type [CuTi₃N₄] units, resembling the molybdenum-copper sulfido complex published by Shibahara and coworkers.⁴⁶ The two $\{\text{Cu}(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$ moieties adopt a mutually staggered disposition which minimizes the steric repulsion between the bulky pentamethylcyclopentadienyl ligands, in a similar way to the previously reported edge-linked Group 1 azaheterometallobucubane complexes.¹⁷

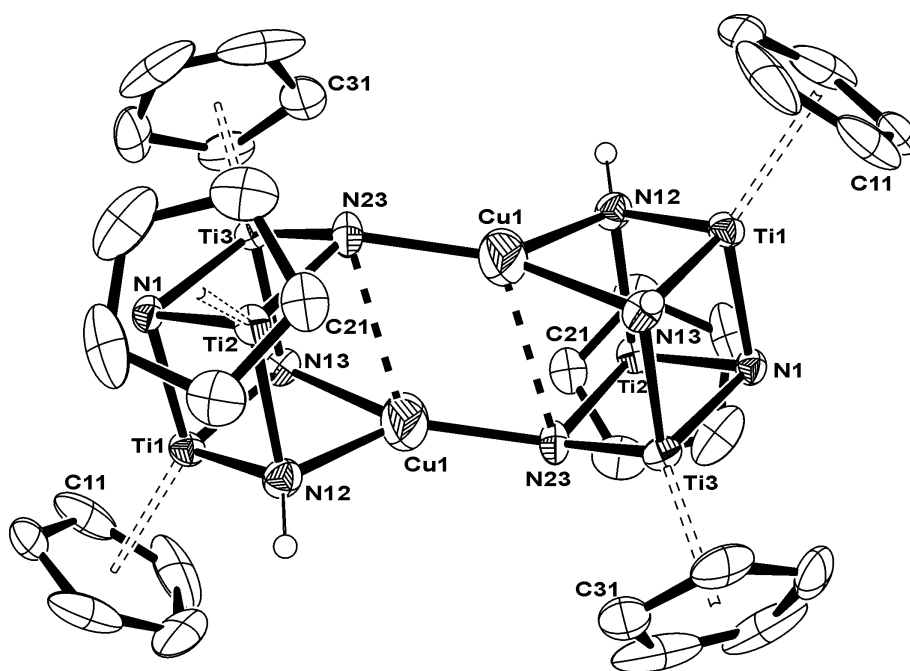


Figure 4. Perspective view of $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (**15**) with thermal ellipsoids at the 50% probability level. The benzene solvent molecule and methyl groups of the pentamethylcyclopentadienyl rings are omitted for clarity.

Table 5. Selected lengths (Å) and angles (°) for **15**.

Cu(1)-N(12)	2.218(5)	Cu(1)-N(13)	2.101(5)
Cu(1)-N(23) ^a	1.912(5)	Cu(1)···N(23)	2.690(5)
Cu(1)···Cu(1)	2.614(2)	N(1)-Ti(1)	1.916(4)
N(1)-Ti(3)	1.947(4)	N(1)-Ti(2)	1.952(4)
N(12)-Ti(1)	1.968(5)	N(12)-Ti(2)	2.007(5)
N(13)-Ti(1)	1.975(5)	N(13)-Ti(3)	1.987(5)
N(23)-Ti(2)	1.882(5)	N(23)-Ti(3)	1.891(5)
N(13)-Cu(1)-N(12)	89.4(2)	N(23) ^a -Cu(1)-N(13)	140.2(2)
N(23) ^a -Cu(1)-N(12)	130.0(2)	N(23) ^a -Cu(1)-N(23)	113.2(2)
Ti(1)-N(1)-Ti(2)	95.4(2)	Ti(1)-N(1)-Ti(3)	95.2(2)
Ti(2)-N(1)-Ti(3)	90.8(2)	Ti(1)-N(12)-Ti(2)	92.0(2)
Ti(1)-N(12)-Cu(1)	81.8(2)	Ti(2)-N(12)-Cu(1)	95.5(2)
Ti(1)-N(13)-Ti(3)	92.1(2)	Ti(1)-N(13)-Cu(1)	84.7(2)
Ti(3)-N(13)-Cu(1)	97.1(2)	Ti(2)-N(23)-Ti(3)	94.8(2)
Ti(2)-N(23)-Cu(1) ^a	121.0(3)	Ti(3)-N(23)-Cu(1) ^a	127.8(3)
N(1)-Ti(1)-N(12)	87.1(2)	N(1)-Ti(1)-N(13)	86.8(2)
N(12)-Ti(1)-N(13)	100.8(2)	N(1)-Ti(2)-N(23)	87.1(2)
N(1)-Ti(2)-N(12)	85.0(2)	N(23)-Ti(2)-N(12)	103.6(2)
N(1)-Ti(3)-N(23)	87.0(2)	N(1)-Ti(3)-N(13)	85.6(2)
N(23)-Ti(3)-N(13)	103.1(2)		

^a Intercube atoms

Each copper atom in **15** presents an almost trigonal environment (sum of angles 359.6°) with Cu-N bond distances from 1.912(5) to 2.218(5) Å. These lengths are in the same range than those found for other nitrogen polydentate ligands joined to copper⁴⁷ and slightly longer than those reported for several tris(pyrazolyl)hydroboratecopper(I) [$\{(\text{Tp}^x)\text{Cu}\}_2$] derivatives.⁴⁸ On the other hand, a triangular pyramidal environment could be proposed if the long range interaction of copper with the intracube N(23) atom (2.690(5) Å) is taken into consideration. Bond distances and angles involving titanium and nitrogen atoms of the same cube do not differ significantly with respect to the preorganized organometallic ligand **1**,⁸ with Ti-N 1.947(5) Å average [1.924(6) Å in **1**], Ti-N-Ti 93.4(2)° average [93.7(3)° in **1**], N1-Ti-N 87.0(2)° average [85.9(3)° in **1**] and only 5 degrees narrower N-Ti-N angles, 102.5(2)° average in **15** and 107.5(3)° in **1**. This latter deviation can be attributed to the coordination of the nitrogen atoms to copper.

Crystals of **15** are not soluble in common organic solvents (benzene-d₆, chloroform-d₁, pyridine-d₅,...) precluding its characterization by NMR spectroscopy. However, treatment of **15** with triphenylphosphane (2 equiv) in benzene-d₆ at 80 °C gave an orange solution where the single-cube complex $[(\text{Ph}_3\text{P})\text{Cu}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**16**) was characterized by NMR spectroscopy. Complex **16** was prepared in good yield (87%) by the direct reaction of a toluene solution of **13** and triphenylphosphane with $[\text{LiN}(\text{SiMe}_3)_2]$.

Compound **16** was obtained as an orange solid, which is very soluble in toluene and hexane, and was characterized by spectral and analytical techniques. ¹H and ¹³C{¹H} NMR spectra in benzene-d₆ at room temperature show resonance signals for two $\eta^5\text{-C}_5\text{Me}_5$ groups in a 2:1 ratio, one triphenylphosphane ligand and a broad signal for the NH groups. These data are consistent with a C_s symmetry and a single cube structure in solution. The tetrahedral environment around the copper center in **16** would be similar to those reported for several $\text{Tp}^x\text{Cu}(\text{PPh}_3)$ derivatives.⁴⁹

Conclusion

In summary, the imido-nitrido titanium complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) is capable of acting as a neutral ligand to give stable adducts with zinc(II) and copper(I) halides, while analogous derivatives with zinc and copper alkyl or amido groups undergo alkane or amine elimination to give complexes bearing the monoanionic $[\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]^-$ ligand. The coordination modes of **1** and its monoanionic form in those complexes resemble other well-established “non-organometallic” nitrogen-based ligands. The new heterometallic nitrido compounds here reported exhibit single-cube structures with $[\text{MTi}_3\text{N}_4]$ central cores, excepting the copper derivative $[\{\text{Cu}(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ that shows a double cube structure with a $[\text{Cu}_2\text{Ti}_6\text{N}_8]$ core.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **3**, **8**, **9** and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Experimental data for the X-ray diffraction studies on **3**, **8**, **9**, and **15**.

Formula	C ₃₁ H ₅₃ Cl ₄ N ₅ Ti ₃ Zn (3 ·CH ₂ Cl ₂)	C ₄₅ H ₆₈ N ₄ SiTi ₃ Zn (8 ·C ₇ H ₈)	C ₃₆ H ₆₅ N ₅ Si ₂ Ti ₃ Zn (9)	C ₆₆ H ₁₀₀ Cu ₂ N ₈ Ti ₆ (15 ·C ₆ D ₆)
<i>M_r</i>	846.65	902.19	833.18	1420.02
<i>T</i> [K]	200(2)	200(2)	200(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
space group	P2 ₁ /n	P2 ₁ /c	P-1	P2 ₁ /c
<i>a</i> [Å]; α [°]	11.595(2);	18.903(2);	11.645(3); 81.76(2)	12.397(2)
<i>b</i> [Å]; β [°]	23.461(2); 100.69(1)	11.069(2); 101.87(1)	11.906(3); 87.73(2)	14.963(3); 123.56(1)
<i>c</i> [Å]; γ [°]	14.608(2);	22.510(2);	17.621(4); 65.84(2)	22.185(2)
<i>V</i> [Å ³]	3904.7(8)	4609.2(9)	2205.6(9)	3429.3(9)
<i>Z</i>	4	4	2	2
ρ_{calcd} [g cm ⁻³]	1.440	1.300	1.255	1.375
$\mu_{\text{MoK}\alpha}$ [mm ⁻¹]	1.500	1.075	1.144	1.312
<i>F</i> (000)	1752	1904	880	1484
crystal size [mm ³]	0.3 x 0.3 x 0.3	0.3 x 0.1 x 0.1	0.33 x 0.29 x 0.21	0.41 x 0.29 x 0.27
θ range	5.00 to 25.01°	5.03 to 25.24°	3.05 to 27.50°	3.06 to 27.57°
index ranges	-13 to 13, -27 to 27, -17 to 17	-22 to 22, -13 to 13, -27 to 27	-15 to 15, -15 to 15, -22 to 22	-13 to 16, 0 to 19, -26 to 28
Reflections collected	23861	29828	18592	134861
Unique data	6817 [R _{int} = 0.122]	8271 [R _{int} = 0.186]	9997 [R _{int} = 0.042]	7908 [R _{int} = 0.118]
obsd data [I > 2 σ (I)]	4213	3773	7640	5418
Goodness-of-fit on <i>F</i> ²	1.042	1.092	1.065	1.087
final <i>R</i> indices [I > 2 σ (I)]	R1 = 0.062, wR2 = 0.114	R1 = 0.087, wR2 = 0.172	R1 = 0.047, wR2 = 0.127	R1 = 0.096, wR2 = 0.282
<i>R</i> indices (all data)	R1 = 0.127, wR2 = 0.135	R1 = 0.231, wR2 = 0.231	R1 = 0.067, wR2 = 0.137	R1 = 0.138, wR2 = 0.307
largest diff. Peak/hole [e.Å ⁻³]	0.449/-0.541	0.966/-1.113	0.763/-0.674	1.58/-3.461

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