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García-Castro, M. et al., 2009. Molecular Nitrides with Titanium and Group 13–15 Elements. *Chemistry – A European Journal*, 15(29), pp.7180–7191.

Available at <https://doi.org/10.1002/chem.200900660>

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Molecular Nitrides with Titanium and Group 13-15 Elements

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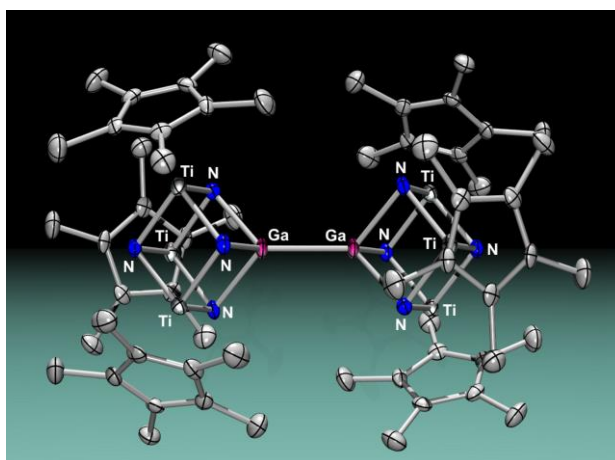
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Text for the Table of Contents

Eye-Catching Headline: Cage Compounds

Text: Heterometallic nitrido complexes containing single-cube $[\text{MTi}_3\text{N}_4]$, corner-shared double-cube $[\text{MTi}_6\text{N}_8]$ or the unprecedented (see picture) corner-linked double-cube $[\text{Ga}_2\text{Ti}_6\text{N}_8]$ cores have been obtained by reaction of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ with amido $[\text{M}(\text{NR}_2)_x]$ group 13-15 derivatives.



Keywords: cage compd. ... cubanes ... main-group elem. ... nitrides ... titanium

Abstract:

Several heterometallic nitrido complexes have been prepared by reaction of the imido-nitrido titanium complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with amido derivatives of group 13-15 elements. Treatment of **1** with bis(trimethylsilyl)amido $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3]$ derivatives of aluminum, gallium or indium in toluene at 150-190 °C affords the single-cube amidoaluminum complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Al}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**2**) or the corner-shared double-cube compounds $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Ga}$ (**3**), In (**4**)). Complexes **3** and **4** are also obtained by treatment of **1** with the trialkyl derivatives $[\text{M}(\text{CH}_2\text{SiMe}_3)_3]$ ($\text{M} = \text{Ga}$, In) at high temperatures. The analogous reaction of **1** with $[\{\text{Ga}(\text{NMe}_2)_3\}_2]$ at 110 °C leads to $[\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (**5**), where two $[\text{GaTi}_3\text{N}_4]$ cube-type moieties are linked through a gallium-gallium bond. Complex **1** reacts with one equivalent of germanium, tin or lead bis(trimethylsilyl)amido derivatives $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in toluene at room temperature to give cube-type complexes $[\text{M}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Ge}$ (**6**), Sn (**7**), Pb (**8**)). Monitoring the reaction of **1** with $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and $[\text{Sn}(\text{C}_5\text{H}_5)_2]$ by NMR spectroscopy allows the identification of intermediates $[\text{RSn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**9**), C_5H_5 (**10**)) in the formation of **7**. Addition of one equivalent of the metalloligand **1** to a solution of lead derivative **8** or the treatment of **1** with a half equivalent of $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ afford the corner-shared double-cube compound $[\text{Pb}(\mu_3\text{-N})_2(\mu_3\text{-NH})_4\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (**11**). Analogous antimony and bismuth derivatives $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Sb}$ (**12**), Bi (**13**)) are obtained through the reaction of **1** with the tris(dimethylamido) reagents $[\text{M}(\text{NMe}_2)_3]$. Treatment of **1** with $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$ affords the precipitation of the singular aluminum-titanium square pyramidal aggregate $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Cl}_3\text{Al}_2\}(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})]$ (**14**).

$\text{NH}_2\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-Cl})(\mu_3\text{-N})\}$ (**14**). The X-ray crystal structures of **5**, **11**, **13**, **14**, and $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ have been determined.

Abstract in Spanish:

La reacción del complejo imido-nitruro de titanio [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})$] (**1**) con derivados amido de los grupos 13-15 permite preparar diversos complejos nitruro heterometálicos. El tratamiento de **1** con los derivados bis(trimetilsilil)amido de aluminio, galio o indio [$\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3$] en tolueno a 150-190 °C produce el complejo amido de aluminio de estructura de cubo-sencillo [$\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Al}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$] (**2**) o los compuestos de estructura dicubano de vértice compartido [$\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$] ($\text{M} = \text{Ga}$ (**3**), In (**4**)). Además, los complejos **3** y **4** se pueden obtener por tratamiento de **1** con los derivados trialquilo [$\text{M}(\text{CH}_2\text{SiMe}_3)_3$] ($\text{M} = \text{Ga}$, In) a altas temperaturas. La reacción análoga de **1** con [$\{\text{Ga}(\text{NMe}_2)_3\}_2$] a 110 °C conduce a [$\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$] (**5**), donde dos unidades [GaTi_3N_4] tipo-cubo están unidas mediante un enlace galio-galio. El complejo **1** reacciona con un equivalente de los derivados bis(trimetilsilil)amido de germanio, estaño y plomo [$\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$] en tolueno y a temperatura ambiente para dar los compuestos tipo-cubo [$\text{M}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$] ($\text{M} = \text{Ge}$ (**6**), Sn (**7**), Pb (**8**)). El seguimiento de la reacción de **1** con [$\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$] y [$\text{Sn}(\text{C}_5\text{H}_5)_2$] por espectroscopía de RMN permite la identificación de los intermedios [$\text{RSn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$] ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**9**), C_5H_5 (**10**)) en la formación de **7**. La adición de un equivalente del metaloligando **1** a una disolución del derivado de plomo **8** o el tratamiento de **1** con medio equivalente de [$\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$] produce el compuesto dicubano de vértice compartido [$\text{Pb}(\mu_3\text{-N})_2(\mu_3\text{-NH})_4\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$] (**11**). Los derivados análogos de antimonio y bismuto [$\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$] ($\text{M} = \text{Sb}$ (**12**), Bi (**13**)) se obtienen mediante la reacción de **1** con los reactivos tris(dimetilamido) [$\text{M}(\text{NMe}_2)_3$]. El tratamiento de **1** con [$\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)$] da lugar a la precipitación de un singular agregado con estructura de pirámide de base cuadrada de titanio y aluminio [$\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Cl}_3\text{Al}_2\}(\mu_3\text{-$

$\text{N}(\mu_3\text{-NH})_2\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-Cl})(\mu_3\text{-N})\}$ (**14**). Las estructuras cristalinas de los complejos **5**, **11**, **13**, **14** y $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ se han determinado mediante difracción de rayos-X de monocristal.

Introduction

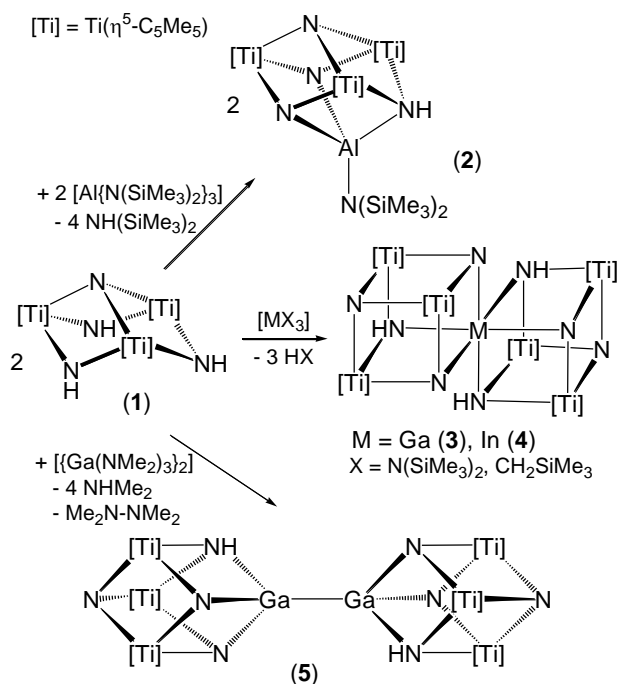
The chemistry of molecular cages and clusters of the main-group elements is receiving an increasing attention in the last years.^[1] This is motivated by their fascinating structures and unusual bonding properties, which differ significantly from those of transition-metal cluster compounds. Furthermore, well-defined molecular main-group compounds are attractive candidates to serve as building blocks and precursors for functional materials.^[2] In particular, complexes having preformed metal-nitrogen bonds are ideal systems as precursors of metal nitride MN materials. A common synthetic route to metal-nitrogen polynuclear compounds is based on the reaction of alkyl or amido main-group derivatives with primary amines.^[3,4,5] In those reactions, imido species with diverse degree of aggregation (dimeric, trimeric, tetrameric,...) are obtained upon depending on the steric demand of the ligands at the metal and nitrogen atoms, the temperature and the solvent used.^[6,7,8]

Nitrido complexes of the early transition metals (groups 4 and 5) constitute also a class of molecular compounds with singular polynuclear structures.^[9] An elegant and efficient entry to the synthesis of these polynuclear complexes involves the treatment of organometallic derivatives with ammonia to give species with bridging amido (NH_2^-), imido (NH^{2-}) and nitrido (N^{3-}) ligands.^[10,11,12,13,14] In those reactions, aggregates with diverse nuclearity of titanium,^[10-12] zirconium,^[13] and tantalum^[14] containing bulky ancillary ligands (cyclopentadienyl, alkoxido, etc) at the metal centers have been isolated. In particular, the ability of cyclopentadienyl groups to support metallonitrido oligomers has been proved in vanadium^[15] and tantalum^[16] compounds prepared by distinct routes. However, a review of the literature shows the lack of systematic strategies for the rational construction of aggregates with desired metal composition.

In the last years, we have been studying the coordination chemistry of the trinuclear titanium imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) obtained in 1989 by Roesky and co-workers by reaction of $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3]$ with ammonia.^[10] The structure of **1** shows an incomplete cube-type $[\text{Ti}_3(\mu\text{-NH})_3(\mu_3\text{-N})]$ core, and we have extensively studied the incorporation of heterometals M into this core for the synthesis of cube-type heterometallic nitrido complexes.^[17,18] In particular, we have recently reported the reactivity of **1** toward alkyl derivatives of group 13 and 14 elements.^[19] In a fashion similar to organic macrocyclic amines,^[20] complex **1** acts as chelate to a single group 13 center forming adducts $[\text{R}_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (M = Al, Ga, In). These adduct complexes further react at room or high temperatures to give heterometallic cube-type nitrido derivatives via elimination of alkane molecules. With the aim to extend that previous study, herein we report the results obtained in the treatment of **1** with amido derivatives of group 13-15 elements.

Results and Discussion

Reactions with Group 13 Tri(amido) Derivatives. The synthetic chemistry is outlined in Scheme 1. Treatment of $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with 1 equiv of $[\text{Al}\{\text{N}(\text{SiMe}_3)_2\}_3]$ in toluene at 190 °C afforded the monoamido complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Al}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (**2**) via bis(trimethylsilyl)amine elimination. Compound **2** was obtained as an extremely air sensitive red solid, and could not be isolated in a pure form due to the presence of small impurities (ca. 5% by ^1H NMR spectroscopy) of the oxotitanium derivative $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\mu\text{-O})_6]$,^[21] which shows similar solubility in common solvents. The ^1H NMR spectrum of **2** in $[\text{D}_6]$ benzene at room temperature reveals two resonance signals for $\eta^5\text{-C}_5\text{Me}_5$ ligands in a 1:2 ratio, a singlet for one $\text{N}(\text{SiMe}_3)_2$ group and a broad signal for the NH imido ligand. These NMR data are consistent with a C_s -symmetric structure in solution as those reported for the monoalkyl aluminum(III) derivatives $[\text{RAl}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{Me}$, CH_2SiMe_3).^[19]



Scheme 1. Reactions of **1** with $[\text{M}(\text{NR}_2)_3]$ group 13 derivatives.

The analogous treatment of **1** with gallium(III) or indium(III) bis(trimethylsilyl)amido derivatives $[M\{N(SiMe_3)_2\}_3]$ (0.5 or 1 equiv) in toluene at 150 °C afforded the precipitation of the corner-shared double-cube nitrido complexes $[M(\mu_3-N)_3(\mu_3-NH)_3\{Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}_2]$ (M = Ga (**3**), In (**4**)). Compounds **3**·2C₇H₈ and **4**·2C₇H₈ were isolated as orange crystals in poor yields (10-20% for **3** and 35% for **4**). The gallium complex **3**·2C₇H₈ was prepared in higher yield by treatment of a mixture (2:1 ratio) of **1** and the trialkyl $[Ga(CH_2SiMe_3)_3]$ derivative in toluene at 200 °C (34%), or by heating of the trimethylsilylmethylgallium adduct $[(Me_3SiCH_2)_3Ga\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]^{[19]}$ at 200 °C (52%).

Compounds **3** and **4** are not soluble in common NMR solvents ($[D_8]$ toluene, $[D_1]$ chloroform, $[D_5]$ pyridine, $[D_8]$ tetrahydrofuran,...), and their lack of volatility precludes the characterization by mass spectrometry (EI, 70 eV). Therefore, the compounds were only characterized by IR spectroscopy and C, H, N microanalysis. Repeated attempts to obtain suitable single crystals for an X-ray determination of **3** and **4** complexes were unsuccessful, although unit cell parameters obtained for several samples were consistent with those determined for previously published corner-shared double-cube nitrido complexes,^[17] and analogous lead(II) and bismuth(III) compounds with this structure (*vide infra*).

The reaction of **1** with $[M\{N(SiMe_3)_2\}_3]$ (M = Ga, In) in $[D_6]$ benzene was monitored by NMR spectroscopy. No soluble intermediates could be detected at different temperatures. After heating at 150 °C for 2-3 days, orange crystals of **3** and **4** were grown at the bottom of the NMR tubes. The analysis of the solution contents by ¹H NMR spectroscopy revealed resonances assigned to free bis(trimethylsilyl)amine and, in the case of the indium derivative, those for the indium(I) complex $[In\{(\mu_3-N)(\mu_3-NH)_2Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]^{[22]}$ along with other unidentified species. We have reported the clean

formation of this indium(I) compound and bibenzyl in the thermal decomposition of $[(C_6H_5CH_2)_3In\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$.^[19]

The analogous treatment of **1** with $[\{Ga(NMe_2)_3\}_2]$ (0.5 equiv) in toluene at 110 °C afforded the precipitation of $[\{Ga(\mu_3-N)_2(\mu_3-NH)Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}_2]$ (**5**) as orange crystals in 39% yield (Scheme 1). Following of the reaction course in $[D_6]$ benzene by ¹H NMR spectroscopy allows the unambiguous characterization of NHMe₂, along with other minor resonances in the range 3.0-2.0 ppm.^[23] Compound **5** is not soluble in common organic solvents and was characterized by IR spectroscopy and microanalysis, as well as by an X-ray crystal structure determination. The molecular structure of complex **5** is showed in Figure 1, while selected distances and angles are given in Table 1. The structure shows two almost perfect $[GaTi_3N_4]$ cubes joined by a gallium-gallium bond. The angles M-N-M, N-Ga-N, and N-Ti-N within each cube are all close to 90°. Molecules of **5** lie on a crystallographic inversion center located on the midpoint of the two gallium atoms, and also present a C_3 axis which crosses the N(1) and Ga(1) atoms. The coordination environment of gallium is best described as distorted tetrahedral with angles spanning 90.7(1)-124.8(1)°. The gallium-nitrogen distances of 2.057(2) Å compare well with those found in the adduct $[(C_6H_5CH_2)_3Ga\{(\mu_3-NH)Ti_3(\eta^5-C_5Me_5)_3(\mu-NH)_2(\mu_3-N)\}]$ (2.094(2) Å)^[19] and aminogallane derivatives.^[24] The gallium-gallium bond length of 2.397(2) Å is similar to those found in the complex $[\{Ga(N\{SiMe_3\}CH_2)_2CMe_2\}_2]$ (2.385(1) Å), reported by Linti and co-workers,^[25] and other analogous complexes containing a Ga-Ga single bond.^[26]

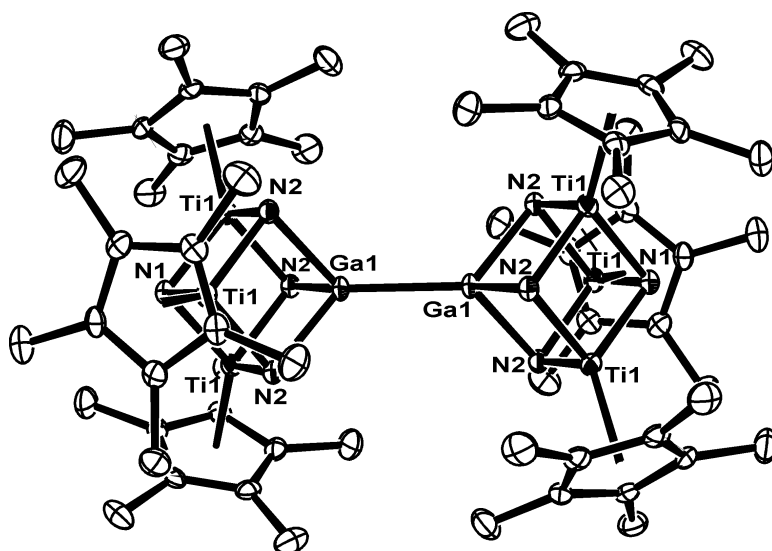


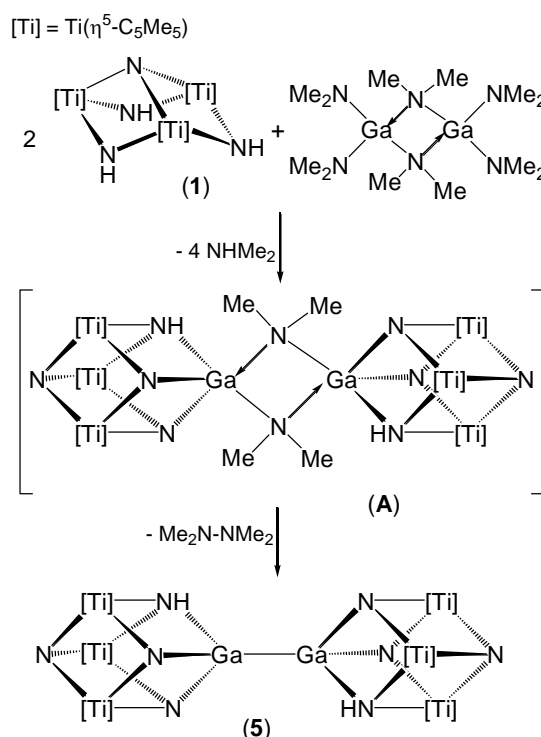
Figure 1. Perspective view of **5** with thermal ellipsoids at the 50% probability level.

Table 1. Selected Averaged Lengths (Å) and Angles (deg) for **5**.

Ga(1)-Ga(1)	2.397(2)	Ga(1)-N(2)	2.057(2)
Ti(1)-N(1)	1.961(2)	Ti(1)-N(2)	1.967(6)
Ti...Ti	2.852(2)		
N(2)-Ga(1)-N(2)	90.7(1)	N(2)-Ga(1)-Ga(1)	124.8(1)
N(1)-Ti(1)-N(2)	86.8(2)	N(2)-Ti(1)-N(2)	96.1(1)
Ti(1)-N(1)-Ti(1)	93.3(2)	Ti(1)-N(2)-Ti(1)	93.0(2)
Ga(1)-N(2)-Ti(1)	86.6(2)		

The unexpected formation of the digallane **5** instead of the corner-shared double-cube complex **3** is most likely due to the different aggregation of the triamido $[\text{Ga}(\text{NR}_2)_3]$ reagents. While tris(dimethylamido)gallium has a dinuclear structure with dimethylamido bridges in solution^[27] and in the solid-state,^[28] the steric hindrance of the bis(trimethylsilyl)amido ligands prevent the association of $[\text{Ga}\{\text{N}(\text{SiMe}_3)_2\}_3]$.^[27,29,30,31] We propose that the dinuclear nature of the tris(dimethylamido)gallium reagent could be maintained during the reaction with **1** to give a double-cube intermediate with bridging dimethylamido groups $[\{\text{Ga}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}(\mu\text{-NMe}_2)\}_2]$ (**A**, Scheme 2). This intermediate would be structurally similar to the calcium complex $[\{\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}(\mu\text{-NHAr})\}_2]$ (Ar = 2,4,6-Me₃C₆H₂),^[32] and

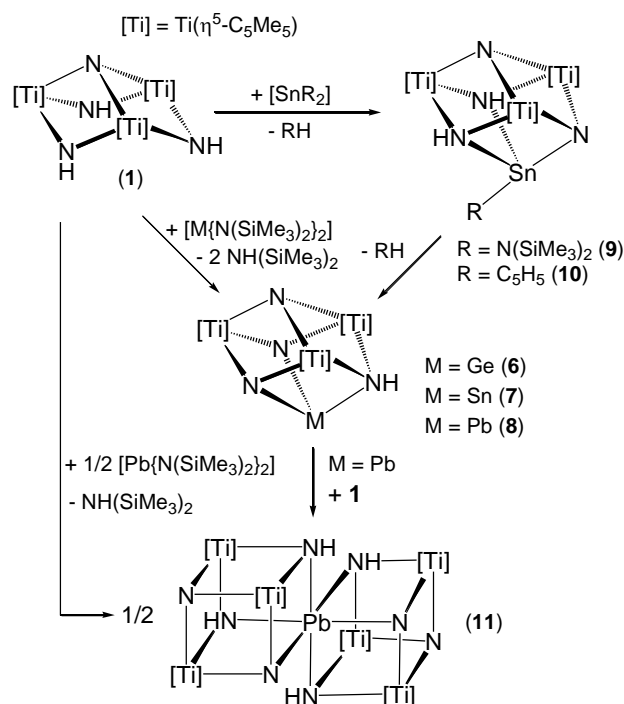
the amido-bridged dimeric gallium azagallatrane $[\{Ga(MeNCH_2CH_2)_3N\}_2]$ derivative.^[33] Finally, the reductive elimination of tetramethylhydrazine could take place with generation of the gallium-gallium bond. The formation of $(C_5Me_5)_2$ and the digallane $[\{Ga\{NRC(H)\}_2\}_2]$ bearing a Ga-Ga bond has been reported by Jutzi and co-workers in the photochemical treatment of $[(\eta^1-C_5Me_5)Ga\{NRC(H)\}_2]$ ($R = 2,6-iPr_2C_6H_3$; $2,6-Et_2C_6H_3$).^[26b]



Scheme 2. Plausible way of formation of **5**.

Compound **1** reacted with $[\{Al(NMe_2)_3\}_2]$ at 20-60 °C in $[D_6]$ benzene or toluene giving an intractable mixture of products, from which none compound could be isolated after many attempts. In contrast, complex **1** did not react with tris(dimethyl)amido $[B(NMe_2)_3]$ or trialkyl $[BR_3]$ ($R = C_6H_5, Et$) boron derivatives even after prolonged heating at 200 °C in $[D_6]$ benzene solutions. The latter result could be attributed to the small size of the boron atom, which precludes the coordination of the NH groups of **1**.

Reactions with Group 14 and 15 Amido Derivatives. Treatment of [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})$] (**1**) with 1 equiv of germanium, tin or lead bis(trimethylsilyl)amido [$\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$] reagents in toluene afforded the cube-type derivatives [$\text{M}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$] ($\text{M} = \text{Ge}$ (**6**), Sn (**7**), Pb (**8**)) via bis(trimethylsilyl)amine elimination (Scheme 3). The reaction of **1** with the germanium amido reagent is very slow at room temperature and was carried out at 55 °C, but the tin and lead analogues reacted within hours at room temperature. Complex **7** was prepared in higher yield by treatment of **1** with a half equivalent of the bis(dimethyl)amido reagent [$\{\text{Sn}(\text{NMe}_2)_2\}_2$]. Following of the reactions of **1** with [$\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$] or [$\text{Sn}(\eta^5\text{-C}_5\text{H}_5)_2$] in [D_6]benzene at room temperature allowed us to characterize the amido or cyclopentadienyl intermediates [$\text{RSn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}$] ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**9**), $\eta^5\text{-C}_5\text{H}_5$ (**10**)) by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The ^1H NMR spectra show two resonance signals for $\eta^5\text{-C}_5\text{Me}_5$ groups in a 2:1 ratio, those due to one $\text{N}(\text{SiMe}_3)_2$ or $\eta^5\text{-C}_5\text{H}_5$ groups, and a broad signal for the NH imido ligands. The NMR data for complexes **9** and **10** are consistent with C_s -symmetric structures in solution. Despite many attempts we did not obtain a pure sample of complexes **9** and **10** for a complete characterization.



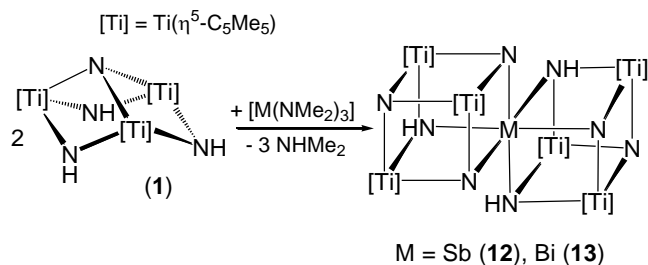
Scheme 3. Reactions of **1** with [M(NR₂)₂] group 14 derivatives.

Complexes **6-8** were isolated as orange solids in good yields (74-87%) which are soluble in toluene or hexane. Compounds **6-8** were characterized by spectral and analytical methods. The mass spectra of these complexes (EI, 70 eV) show the expected molecular peaks suggesting a single-cube structure in the gas phase. IR spectra (KBr) of complexes **6-8** reveal one ν_{NH} vibration in the range 3361-3349 cm^{-1} similar to the value determined for **1**,^[11] 3352 cm^{-1} . ¹H NMR spectra of complexes **6-8** in [D₆]benzene show two resonance signals for η^5 -C₅Me₅ groups in a 1:2 ratio and a broad signal for the NH imido ligand. The NMR data are consistent with C_s-symmetric structures in solution.

Germanium and tin complexes **6** and **7** are stable in [D₆]benzene solutions at 150 °C, but the lead derivative **8** decomposes in solution, upon standing at room temperature and ambient light for several days, to give orange crystals of the corner-shared double-cube complex [Pb(μ_3 -N)₂(μ_3 -NH)₄{Ti₃(η^5 -C₅Me₅)₃(μ_3 -N)}₂] (**11**), along with a mixture of products where lead metal is visually observed. Complex **11**·C₇H₈ can be prepared in

better yield by treatment of **1** with a half equivalent of $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in toluene at room temperature (45%), or by reaction of the single-cube complex **8** with one equivalent of **1** (54%) (Scheme 3). Importantly, complexes **6** or **7** did not react with an additional equivalent of **1** to give analogous germanium or tin double-cube complexes.

The treatment of **1** with antimony and bismuth amido $[\text{M}(\text{NMe}_2)_3]$ derivatives (0.5 or 1 equiv) in toluene at room temperature gave the corner-shared double-cube complexes $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Sb}$ (**12**), Bi (**13**)) via dimethylamine elimination (Scheme 4). Compounds **12**· $2\text{C}_7\text{H}_8$ and **13**· $2\text{C}_7\text{H}_8$ were isolated as orange crystals in good yields (55 and 60%, respectively). Complex **13**· $2\text{C}_7\text{H}_8$ can be obtained in a similar yield (62%) by the reaction of **1** with $[\text{Bi}\{\text{N}(\text{SiMe}_3)_2\}_3]$ at room temperature. We also examined the treatment of **1** with the dinuclear antimony imido derivative $[\{\text{Sb}(\text{NMe}_2)\}_2(\mu\text{-N}t\text{Bu})_2]$. No intermediates were detected by NMR spectroscopy in $[\text{D}_6]$ benzene, and only complex **12**· C_6D_6 was obtained as orange crystals in 54% yield when the reaction was performed at preparative scale.



Scheme 4. Reactions of **1** with $[\text{M}(\text{NR}_2)_3]$ group 15 derivatives.

Double-cube complexes **11-13** are not soluble in common solvents, precluding characterization by NMR spectroscopy, and were characterized by IR spectroscopy and C, H, N microanalysis, as well as by X-ray crystal structure determinations for **11**· C_7H_8 and **13**· $2\text{C}_7\text{H}_8$. The molecular structures of complexes **11** and **13** are presented in Figures 2 and 3, while selected distances and angles for both compounds are given in Table 2. The solid-state structures show corner-shared double-cube $[\text{MTi}_6\text{N}_8]$ cores similar to those found in

our previous studies.^[17] From the crystallographic point of view, molecules of **11** and **13** have a mirror plane bearing the Pb(1), N(1), Ti(1) and N(2) (**11**) or Bi(1), N(1), Ti(2) and N(3) (**13**) core atoms, and an inversion center located on the lead or bismuth atoms. The six-coordinate geometry around the lead or bismuth center is best described as trigonal antiprismatic, where the two tridentate organometallic ligands adopt a mutually staggered disposition. The coordination environment about the lead center in **11** and the Pb-N bond distances, average 2.677(3) Å, resemble those determined for bis(tris(pyrazolyl)methane), [Pb{HC(3,5-Me₂pz)₃}₂][BF₄]₂ (2.635(7) Å)^[34] and [Pb{HC(3,5-Me₂pz)₃}₂][B{(3,5-(CF₃)₂C₆H₃)₄}₂] (av. 2.59 Å)^[35], and bis(hydrotris(pyrazolyl)borato) [Pb{HB(3,5-Me₂pz)₃}₂] (av. 2.61 Å)^[36] lead(II) derivatives. Thus, in a fashion similar to those complexes, the lone pair on the lead center in **11** appears to be stereochemically inactive.^[37] The isoelectronic and isostructural compound **13** shows bismuth-nitrogen bond lengths of average 2.62(2) Å, which falls in the range, 2.256(5)-2.837(5) Å, determined for the asymmetric formamidinate ligands of the bismuth(III) complex [Bi{RNC(H)NR}₃] (R = C₆H₃-2,6-Et₂).^[38] Within the tridentate ligands, the titanium-nitrogen bond lengths and the titanium-nitrogen-titanium angles in complexes **11** and **13** are very similar and compare well with those determined for **1**.^[10]

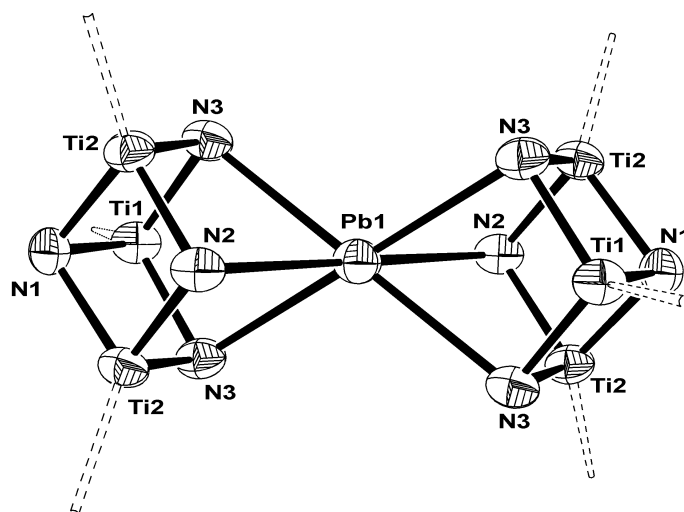


Figure 2. Simplified view of **11** with thermal ellipsoids at the 50% probability level.

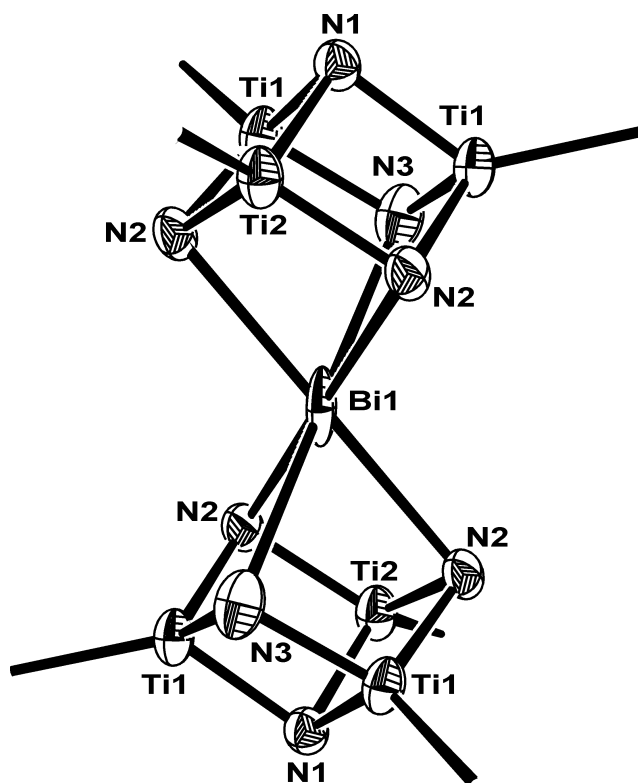


Figure 3. Simplified view of **13** with thermal ellipsoids at the 50% probability level.

Table 2. Selected Averaged Lengths (Å) and Angles (deg) for **11**·C₇H₈ and **13**·2C₇H₈.

	M = Pb (11)	M = Bi (13)
M-N	2.677(3)	2.62(2)
Ti-N	1.927(5)	1.932(7)
Ti···Ti	2.801(1)	2.800(2)
N-M-N (intracube)	67.7(1)	70.0(6)
N-M-N (<i>cis</i> -intercube)	112.2(1)	110.0(6)
N-M-N (<i>trans</i> -intercube)	180.0(1)	180.0(4)
N-Ti-N	101.5(3)	102.7(9)
N(1)-Ti-N	86.6(1)	86.9(2)
Ti-N(1)-Ti	93.0(1)	92.5(3)
Ti-N-Ti	93.4(2)	93.2(2)
Ti-N-M	94.2(2)	93(1)

Finally, we have also examined the reaction of **1** with amido derivatives of group 16 elements [E{N(SiMe₃)₂}]₂ (E = Se, Te). However, an extensive decomposition of the starting materials was observed within a few minutes at room temperature to give a mixture of unknown compounds. For instance, the treatment of **1** with [Te{N(SiMe₃)₂}]₂ gave an abundant grey solid due to tellurium(0) formation.

Reactions with Aluminum Chloroamido Derivatives. The reaction of **1** with aluminum chloroamido derivatives $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$ has been also investigated. The $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ reagent was prepared by treatment of AlCl_3 with 2 equiv of $[\text{LiN}(\text{SiMe}_3)_2]$ in diethyl ether, in a fashion similar to a reported procedure.^[39] Suitable colorless crystals for an X-ray crystal structure determination (Figure 4 and Table 3) were grown on the distillation of the yellow liquid obtained from the reaction. The molecular structure shows a tri-coordinated aluminum center in a trigonal planar geometry (angles $\text{N}(1)\text{-Al}(1)\text{-N}(2)$ $126.4(2)^\circ$, $\text{N}(1)\text{-Al}(1)\text{-Cl}(1)$ $117.3(2)^\circ$ and $\text{N}(2)\text{-Al}(1)\text{-Cl}(1)$ $116.3(2)^\circ$). This geometry and the $\text{Al}(1)\text{-Cl}(1)$ and $\text{Al}(1)\text{-N}$ bond lengths, $2.078(2)$ and $1.812(3)$ Å respectively, are similar to those reported in the literature for $[\text{AlCl}(\text{tmp})_2]$ (tmp = 2,2,6,6-tetramethylpiperidino).^[40]

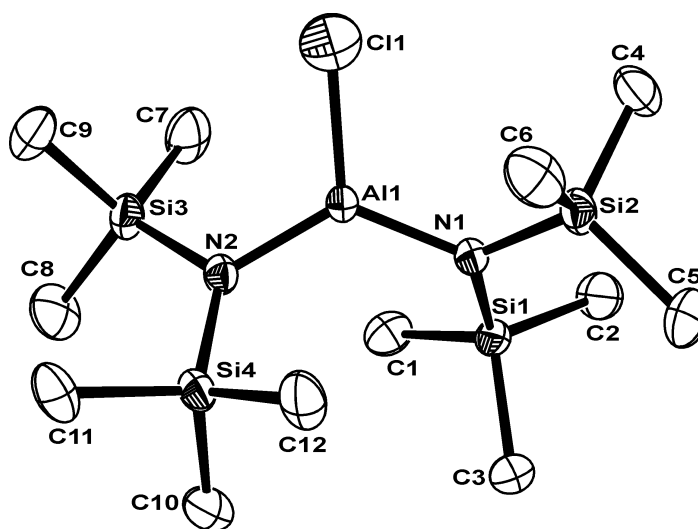


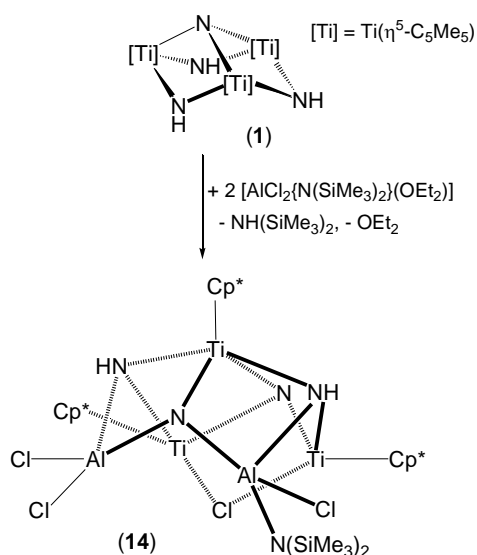
Figure 4. Perspective view of $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [AlCl{N(SiMe₃)₂}₂].

Al(1)-N(1)	1.812(3)	Al(1)-N(2)	1.812(3)
Al(1)-Cl(1)	2.078(2)	N(1)-Si(1)	1.744(3)
N(1)-Si(2)	1.762(3)	N(2)-Si(3)	1.751(3)
N(2)-Si(4)	1.744(3)	Si-C (av.)	1.877(9)
N(1)-Al(1)-N(2)	126.4(2)	N(1)-Al(1)-Cl(1)	117.3(2)
N(2)-Al(1)-Cl(1)	116.3(2)	Al(1)-N(1)-Si(1)	121.4(2)
Al(1)-N(1)-Si(2)	117.7(2)	Si(1)-N(1)-Si(2)	120.8(2)
Al(1)-N(2)-Si(3)	117.8(2)	Al(1)-N(2)-Si(4)	118.9(2)
Si(3)-N(2)-Si(4)	122.6(2)	N-Si-C (av.)	111(1)

An analogous reaction of AlCl₃ with 1 equiv of [LiN(SiMe₃)₂] in diethyl ether gave the dichloroamido [AlCl₂{N(SiMe₃)₂}(OEt₂)] complex as a colorless solid in 64% yield. The new compound [AlCl₂{N(SiMe₃)₂}(OEt₂)], which is similar to the reported [AlCl₂{N(SiMe₃)₂}(NEt₃)],^[39] was characterized by spectral and analytical methods. This extremely moisture sensitive aluminum complex is very soluble in all common organic solvents and its solutions in [D₆]benzene remain unaltered at high temperatures (below 160 °C).

Treatment of **1** with [AlCl₂{N(SiMe₃)₂}(OEt₂)] (2 equiv) in [D₆]benzene at 120 °C afforded the precipitation of [{{(Me₃Si)₂N}Cl₃Al₂}(μ₃-N)(μ₃-NH)₂{Ti₃(η⁵-C₅Me₅)₃(μ-Cl)(μ₃-N)}}]·C₆D₆ (**14**·C₆D₆) as orange crystals in 64% yield (Scheme 5). Analysis of the solution by NMR spectroscopy revealed resonances for free OEt₂ and NH(SiMe₃)₂, along with other unidentified signals. Analogous reaction of **1** with [AlCl{N(SiMe₃)₂}₂] in [D₆]benzene gave a complicated mixture of products in solution, where only resonances for NH(SiMe₃)₂ and [{{(Me₃Si)₂N}Al{(μ₃-N)₂(μ₃-NH)Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}}] (**2**) were unambiguously assigned by NMR spectroscopy.



Scheme 5. Reaction of **1** with $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$.

Complex **14** is not soluble in benzene or toluene and decomposes immediately in $[\text{D}_1]$ chloroform, $[\text{D}_2]$ dichloromethane, $[\text{D}_8]$ tetrahydrofuran, or $[\text{D}_5]$ pyridine, precluding its characterization by NMR spectroscopy. The IR (KBr) spectrum shows two bands, at 3330 and 3302 cm^{-1} , for the ν_{NH} vibrations and several absorptions typical for the $\text{N}(\text{SiMe}_3)_2$ group.^[29] The molecular structure of **14**· C_6D_6 is presented in Figure 5, while selected distances and angles are given in Table 4. The central core of **14** consists of two aluminum and three titanium atoms forming a distorted square pyramid (Figure 6). The almost planar base of this pyramid contains the Al(1), Al(2), Ti(1) and Ti(2) core atoms while the apical position is occupied by the Ti(3) atom. The Al(1)···Al(2), Al(1)···Ti(1) and Al(2)···Ti(2) edges of the square range 3.416(3)-3.516(3) Å, while the remaining Ti(1)···Ti(2) edge is shorter, 3.055(2) Å, maybe due to the μ -chloride group between the titanium atoms. The distances between the basal metal atoms and the apical Ti(3) atom fall in the range 2.875(2)-2.968(2) Å. The four triangular faces of the pyramid are capped by two μ_3 -N nitrido ligands, N(1) and N(2), and two μ_3 -NH imido groups, N(13) and N(23), in alternating positions.

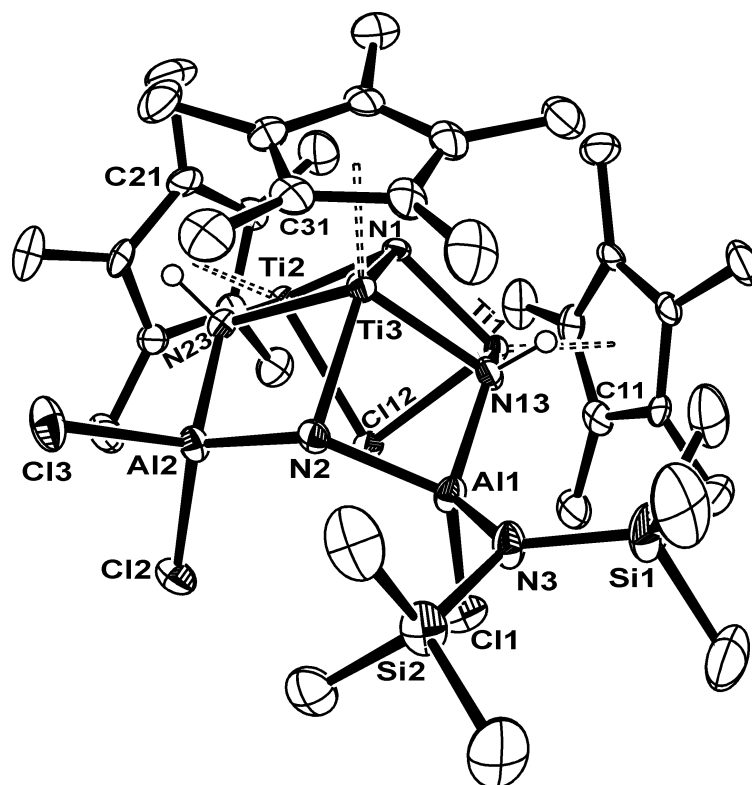


Figure 5. Perspective view of **14** with thermal ellipsoids at the 50% probability level.

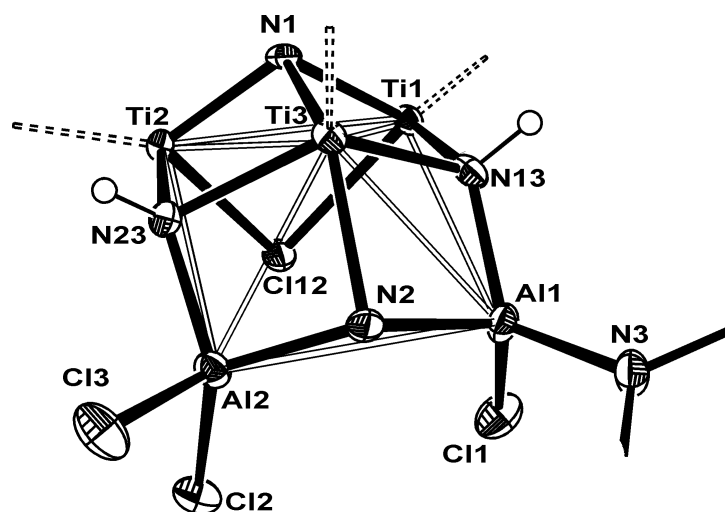


Figure 6. Simplified view of **14** with thermal ellipsoids at the 50% probability level.

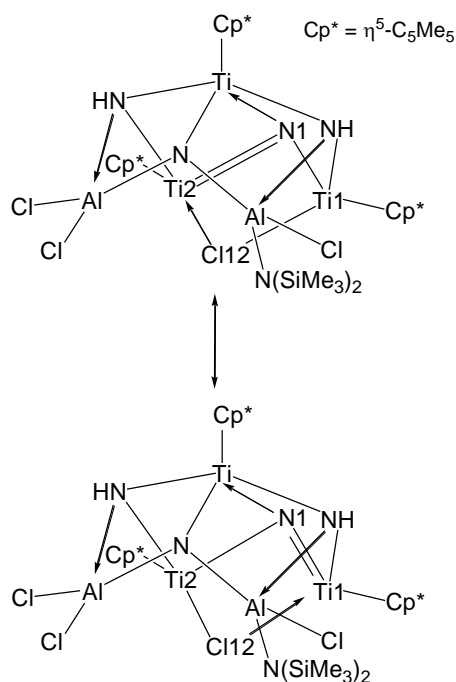
Table 4. Selected Lengths (Å) and Angles (deg) for **14**·C₆D₆.

Al(1)-Cl(1)	2.186(3)	Al(1)-N(3)	1.843(6)
Al(1)-N(2)	1.896(6)	Al(1)-N(13)	1.900(5)
Al(2)-Cl(2)	2.141(3)	Al(2)-Cl(3)	2.168(3)
Al(2)-N(2)	1.851(6)	Al(2)-N(23)	1.884(6)
Ti(1)-N(1)	1.899(5)	Ti(1)-N(13)	1.854(6)
Ti(1)-Cl(12)	2.443(2)	Ti(2)-N(1)	1.856(5)
Ti(2)-N(23)	1.924(5)	Ti(2)-Cl(12)	2.366(2)
Ti(3)-N(1)	2.123(5)	Ti(3)-N(2)	2.229(5)
Ti(3)-N(13)	2.016(5)	Ti(3)-N(23)	2.154(5)
Si(1)-N(3)	1.734(6)	Si(2)-N(3)	1.731(6)
Al(1)···Al(2)	3.416(3)	Ti(1)···Ti(2)	3.055(2)
Al(1)···Ti(1)	3.434(3)	Al(2)···Ti(2)	3.516(3)
Al(1)···Ti(3)	2.966(2)	Al(2)···Ti(3)	2.958(2)
Ti(1)···Ti(3)	2.875(2)	Ti(2)···Ti(3)	2.968(2)
Cl(1)-Al(1)-N(3)	108.8(2)	Cl(1)-Al(1)-N(2)	118.1(2)
Cl(1)-Al(1)-N(13)	103.2(2)	N(3)-Al(1)-N(2)	109.2(3)
N(3)-Al(1)-N(13)	126.7(3)	N(2)-Al(1)-N(13)	90.7(2)
Cl(2)-Al(2)-Cl(3)	107.3(2)	Cl(2)-Al(2)-N(2)	117.5(2)
Cl(2)-Al(2)-N(23)	114.7(2)	Cl(3)-Al(2)-N(2)	112.1(2)
Cl(3)-Al(2)-N(23)	109.4(2)	N(2)-Al(2)-N(23)	95.4(2)
N(1)-Ti(1)-N(13)	91.0(2)	N(1)-Ti(1)-Cl(12)	84.5(2)
N(13)-Ti(1)-Cl(12)	107.3(2)	N(1)-Ti(2)-N(23)	91.3(2)
N(1)-Ti(2)-Cl(12)	87.7(2)	N(23)-Ti(2)-Cl(12)	101.9(2)
N(1)-Ti(3)-N(2)	134.2(2)	N(1)-Ti(3)-N(13)	80.5(2)
N(1)-Ti(3)-N(23)	78.4(2)	N(2)-Ti(3)-N(13)	78.8(2)
N(2)-Ti(3)-N(23)	78.2(2)	N(13)-Ti(3)-N(23)	121.2(2)
Ti(1)-N(1)-Ti(2)	108.9(2)	Ti(1)-N(1)-Ti(3)	91.1(2)
Ti(2)-N(1)-Ti(3)	96.2(2)	Al(1)-N(2)-Al(2)	131.5(3)
Al(1)-N(2)-Ti(3)	91.6(2)	Al(2)-N(2)-Ti(3)	92.4(2)
Al(1)-N(13)-Ti(1)	132.4(3)	Al(1)-N(13)-Ti(3)	98.4(2)
Ti(1)-N(13)-Ti(3)	95.9(2)	Al(2)-N(23)-Ti(2)	134.8(3)
Al(2)-N(23)-Ti(3)	93.9(2)	Ti(2)-N(23)-Ti(3)	93.2(2)
Ti(1)-Cl(12)-Ti(2)	78.9(1)		

Each aluminum atom has a distorted tetrahedral geometry (angles 90.7(2)-126.7(3)°) comprising one chlorine, one nitrogen atom N(3) of a bis(trimethyl)amido ligand, one nitrido N(2) group and one NH imido N(13) ligand for Al(1) and two chlorine atoms, one nitrido N(2) group and one NH imido N(23) ligand for Al(2). The Al-Cl (average 2.16(2) Å) and Al(1)-N(3) 1.843(6) bond lengths are longer than those described above for the tri-coordinated aluminum center of [AlCl{N(SiMe₃)₂}]₂. The Al-N distances associated with the nitrido or imido groups range 1.851(6)-1.900(5) Å and compare well with that found in

the adduct $[\text{MeCl}_2\text{Al}\{\mu_3\text{-NH}\}\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (1.902(2) Å).^[19] The Ti(1) and Ti(2) atoms have a classical three-legged piano-stool arrangement, where the legs are occupied by one μ -chloride, one nitrido N(1) and one NH imido N(13)/N(23) ligands. The chloride group bridges Ti(1) and Ti(2) in an asymmetric fashion, Ti(1)-Cl(12) 2.443(2) Å and Ti(2)-Cl(12) 2.366(2) Å, with an acute Ti(1)-Cl(12)-Ti(2) angle of 78.9(1)°. The Ti(1)-N and Ti(2)-N bond lengths range 1.854(6)-1.924(5) Å and are slightly shorter than the Ti-N found in **1** (av. 1.92 Å).^[10] The Ti(3) atom exhibits a classical four-legged piano-stool arrangement, where the legs are occupied by two nitrido N(1) and N(2) ligands and two NH imido N(13) and N(23) groups in an alternate position. The Ti(3)-N bond lengths of 2.016(5)-2.229(5) Å are clearly longer than those associated with Ti(1) and Ti(2). The geometry about the μ_3 -nitrido groups is best described as trigonal pyramidal, sum of angles M-N(1)-M = 296.2° and M-N(2)-M = 315.5°, whereas that about the μ_3 -NH imido ligands is close to tetrahedral, sum of angles M-N(13)-M = 326.7° and M-N(23)-M = 321.9°.

A plausible interpretation of the bonding in complex **14** is illustrated in Scheme 6. The bonding system can be described between two resonance forms in valence bond theory terms involving a titanium-nitrogen double bond within the flat ring containing the Ti(2), Ti(1), N(1) and Cl(12) atoms. The first of the contributing structures represents a double bond between the Ti(2) and N(1) atoms with concomitant dative Cl(12)→Ti(2) bond, while the second structure comprises Ti(1)=N(1) and Cl(12)→Ti(1) units.



Scheme 6. Schematic representation of the bond situation in **14**.

The synthesis of **14** has been successfully repeated on a number of occasions by using benzene or toluene as the reaction solvents. It seems probable that the isolation of **14** is due to its insolubility in those solvents. All attempts to gain structural information of the compound in solution were failed by its immediate decomposition in chlorinated or polar organic solvents.

Conclusion

The trinuclear imido-nitrido complex $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) reacts with homoleptic amido derivatives of group 13-15 elements to give heterometallic nitrido complexes via amine elimination. These molecular nitrides exhibit structures bearing single-cube $[\text{MTi}_3\text{N}_4]$ or corner-shared double cube $[\text{MTi}_6\text{N}_8]$ cores. Interestingly, the treatment of **1** with $[\{\text{Ga}(\text{NMe}_2)_3\}_2]$ affords the novel digallane $[\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ complex where two $[\text{GaTi}_3\text{N}_4]$ units are linked through a

gallium-gallium single bond. The reactions of **1** with aluminum chloroamido derivatives are more complicated, although the singular square pyramidal aggregate $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Cl}_3\text{Al}_2\}_{(\mu_3\text{-N})(\mu_3\text{-NH})_2}\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-Cl})(\mu_3\text{-N})\}]$ was isolated due to its insolubility in the reaction solvent.

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane and toluene were distilled from Na/K alloy just before use. Diethyl ether was distilled from purple solution of sodium/benzophenone ketyl immediately prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Thermolyses in solution at high temperatures were carried out by heating flame-sealed NMR or Carius tubes in a Roth autoclave model III. $[Ge\{N(SiMe_3)_2\}_2]$ was purchased from ABCR and used as received. $AlCl_3$ and $[LiN(SiMe_3)_2]$ were purchased from Aldrich and used as received. $[Ti(\eta^5-C_5Me_5)(\mu-NH)]_3(\mu_3-N)$ (**1**),^[10,11] $[(Me_3SiCH_2)_3Ga\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$,^[19] $[Ga(CH_2SiMe_3)_3]$,^[41] $[M\{N(SiMe_3)_2\}_3]$ ($M = Al$,^[29] Ga ,^[29,30] In ,^[29] Bi ^[42]), $[M(NMe_2)_3]_2$ ($M = Al$,^[28] Ga ^[27,28]), $[M\{N(SiMe_3)_2\}_2]$ ($M = Sn, Pb$),^[43] $[Sn(NMe_2)_2]_2$,^[44] $[Sn(C_5H_5)_2]$,^[43] $[M(NMe_2)_3]$ ($M = B$,^[43] Sb ,^[45] Bi ^[42]), $[Sb(NMe_2)_2(\mu-NtBu)_2]$,^[46] $[E\{N(SiMe_3)_2\}_2]$ ($E = Se, Te$)^[47] and $[AlCl\{N(SiMe_3)_2\}_2]$ ^[39] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. 1H and ^{13}C NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts (δ) 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 5988A mass spectrometer. Melting points were determined in sealed capillary tubes under argon and are uncorrected. Microanalysis (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzers.

Synthesis of $[{(Me_3Si)_2N}Al\{(\mu_3-N)_2(\mu_3-NH)\}\{Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (2**).** A 100 mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), $[Al\{N(SiMe_3)_2\}_3]$ (0.25 g, 0.49 mmol) and toluene (30 mL). The tube was flame-sealed and heated at 190 °C for 3 days to

give a red solution. The tube was opened in the glovebox and the solution was filtered through a coarse glass frit. The volatile components were removed under reduced pressure and the resultant sticky red solid was extracted with hexane (20 mL). Filtration of the hexane extract, followed by removal of the solvent under reduced pressure, afforded a deep red solid. The solid was washed with hexane (2×5 mL) and vacuum-dried to give **2** (ca. 95% purity by ^1H NMR spectroscopy) as a red solid (0.10 g, 25%). ^1H NMR (300 MHz, C_6D_6 , 20 °C, TMS): δ = 8.69 (s br., 1H; NH), 2.17 (s, 15H; C_5Me_5), 2.03 (s, 30H; C_5Me_5), 0.32 ppm (s, 18H; SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 20 °C, TMS): δ = 119.1 (C_5Me_5), 118.4 (C_5Me_5), 12.2 (C_5Me_5), 12.1 (C_5Me_5), 6.2 ppm (SiMe_3); IR (KBr): $\tilde{\nu}$ = 3405 (w), 3367 (w), 2945 (s), 2909 (vs), 2856 (s), 1494 (w), 1436 (m), 1376 (s), 1261 (s), 1246 (vs), 1065 (w), 1023 (w), 933 (vs), 897 (vs), 839 (vs), 753 (m), 732 (vs), 703 (vs), 678 (vs), 651 (vs), 623 (s), 582 (m), 549 (w), 482 (w), 455 (w), 437 (m) cm^{-1} ; MS (70 eV): m/z (%): 794 (19) [M^+]; elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{64}\text{AlN}_5\text{Si}_2\text{Ti}_3$ ($M_w = 793.69$): C 54.48, H 8.13, N 8.82; found: C 55.21, H 8.06, N 8.01.

Synthesis of $[\text{Ga}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (3**).** **Method A.** A 100 mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), $[\text{Ga}(\text{CH}_2\text{SiMe}_3)_3]$ (0.082 g, 0.25 mmol) and toluene (15 mL). The tube was flame-sealed and heated at 200 °C for 3 days. The reaction mixture was allowed to cool to ambient temperature overnight to afford orange crystals. The tube was opened in the glovebox and the crystals were collected by filtration and characterized as **3**· $2\text{C}_7\text{H}_8$ (0.12 g, 34%).

Method B. A 100 mL Carius tube was charged with $[(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (0.30 g, 0.33 mmol) and toluene (15 mL). The tube was flame-sealed and heated at 200 °C for 2 days. After decantation, the dark orange crystalline solid was characterized as **3**· $2\text{C}_7\text{H}_8$ (0.12 g, 52%).

IR (KBr): $\tilde{\nu} = 3354$ (w), 2970 (m), 2906 (vs), 2855 (vs), 2718 (w), 1604 (w), 1494 (w), 1435 (m), 1374 (s), 1066 (w), 1023 (w), 881 (w), 780 (w), 730 (vs), 694 (vs), 639 (s), 618 (vs), 526 (w), 475 (w), 464 (w), 417 (s) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{109}\text{GaN}_8\text{Ti}_6$ ($M_w = 1467.66$): C 60.56, H 7.48, N 7.63; found: C 60.67, H 7.22, N 7.92.

Synthesis of $[\text{In}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (4**).** In a fashion similar to the preparation of **3** (method A), treatment of **1** (0.30 g, 0.49 mmol) with $[\text{In}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (0.15 g, 0.25 mmol) in toluene (15 mL) at 150 °C for 3 days afforded **4**·2C₇H₈ as dark orange crystals (0.13 g, 35%). IR (KBr): $\tilde{\nu} = 3352$ (w), 2905 (vs), 2854 (s), 1604 (w), 1494 (m), 1433 (s), 1373 (s), 1080 (w), 1023 (w), 728 (vs), 712 (vs), 660 (s), 633 (s), 619 (s), 520 (w), 464 (m), 415 (m) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{109}\text{InN}_8\text{Ti}_6$ ($M_w = 1512.75$): C 58.75, H 7.26, N 7.41; found: C 58.79, H 7.82, N 8.45.

Synthesis of $[\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ (5**).** In a fashion similar to the preparation of **3**, a mixture of **1** (0.30 g, 0.49 mmol) and $[\{\text{Ga}(\text{NMe}_2)_3\}_2]$ (0.10 g, 0.25 mmol) in toluene (20 mL) was heated at 110 °C for 4 days. The reaction mixture was allowed to cool to ambient temperature overnight to yield **5** as dark orange crystals (0.13 g, 39%). IR (KBr): $\tilde{\nu} = 3367$ (w), 2910 (vs), 2857 (s), 1487 (w), 1430 (m), 1374 (m), 1261 (w), 1100 (w), 1024 (w), 800 (m), 736 (s), 712 (vs), 694 (vs), 664 (vs), 641 (m), 612 (vs), 539 (m), 503 (w), 454 (w), 437 (s) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{92}\text{Ga}_2\text{N}_8\text{Ti}_6$ ($M_w = 1352.09$): C 53.30, H 6.86, N 8.29; found: C 53.48, H 6.94, N 7.74.

Synthesis of $[\text{Ge}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ (6**).** A 100 mL ampoule (Teflon stopcock) was charged with **1** (0.30 g, 0.49 mmol), $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.21 g, 0.53 mmol) and toluene (40 mL). The reaction mixture was stirred at 55 °C for two days to give an orange solution. The ampoule was opened in a glovebox, and the volatile components of the solution were removed under reduced pressure. The resultant solid was washed with hexane (5 mL) and vacuum-dried to afford **6** as an orange solid (0.25 g, 76%). ¹H NMR

(300 MHz, C₆D₆, 20 °C, TMS): δ = 9.22 (s br., 1H; NH), 2.18 (s, 15H; C₅Me₅), 1.97 ppm (s, 30H; C₅Me₅); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C, TMS): δ = 118.6 (C₅Me₅), 118.2 (C₅Me₅), 11.9 (C₅Me₅), 11.8 ppm (C₅Me₅); IR (KBr): $\tilde{\nu}$ = 3361 (w), 2908 (vs), 2856 (s), 1492 (w), 1437 (m), 1375 (s), 1260 (w), 1024 (w), 803 (s), 758 (s), 716 (vs), 686 (vs), 662 (vs), 615 (vs), 544 (w), 496 (w), 466 (w), 437 (vs) cm⁻¹; MS (70 eV): *m/z* (%): 681 (4) [*M*⁺], 545 (7) [*M*⁺-C₅Me₅], 409 (17) [*M*⁺-2C₅Me₅], 272 (22) [*M*⁺-3C₅Me₅]; elemental analysis calcd (%) for C₃₀H₄₆GeN₄Ti₃ (*M_w* = 678.93): C 53.07, H 6.83, N 8.25; found: C 52.72, H 7.22, N 7.11.

Synthesis of [Sn{(μ₃-N)₂(μ₃-NH)Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (7). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [{Sn(NMe₂)₂]₂] (0.10 g, 0.25 mmol) and toluene (40 mL). The reaction mixture was stirred at room temperature for 20 h to give an orange solution. The volatile components were removed under reduced pressure to afford **7** as an orange solid (0.31 g, 87%). ¹H NMR (300 MHz, C₆D₆, 20 °C, TMS): δ = 10.05 (s br., 1H; NH), 2.21 (s, 15H; C₅Me₅), 1.99 ppm (s, 30H; C₅Me₅); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C, TMS): δ = 117.9 (C₅Me₅), 117.5 (C₅Me₅), 12.1 (C₅Me₅), 12.0 ppm (C₅Me₅). IR (KBr): $\tilde{\nu}$ = 3355 (w), 2908 (vs), 2856 (s), 1495 (w), 1436 (m), 1375 (s), 1067 (w), 1024 (w), 797 (m), 717 (vs), 686 (vs), 663 (vs), 611 (vs), 539 (m), 478 (w), 455 (w), 428 (vs) cm⁻¹; MS (70 eV): *m/z* (%): 725 (4) [*M*⁺], 589 (7) [*M*⁺-C₅Me₅], 453 (35) [*M*⁺-2C₅Me₅], 320 (55) [*M*⁺-3C₅Me₅]; elemental analysis calcd (%) for C₃₀H₄₆N₄SnTi₃ (*M_w* = 725.03): C 49.70, H 6.39, N 7.73; found: C 49.52, H 6.73, N 6.94.

Synthesis of [Pb{(μ₃-N)₂(μ₃-NH)Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (8). A 100 mL Schlenk flask was charged with **1** (0.60 g, 0.99 mmol), [Pb{N(SiMe₃)₂]₂] (0.52 g, 0.99 mmol) and toluene (40 mL). The reaction mixture was stirred at room temperature for 8 h. The volatile components were removed under reduced pressure and the resultant solid was washed with hexane (15 mL) to give **8** as an orange solid (0.59 g, 74%). ¹H NMR (300 MHz, C₆D₆, 20

°C, TMS): δ = 11.08 (s br., 1H; NH), 2.24 (s, 15H; C₅Me₅), 2.03 ppm (s, 30H; C₅Me₅); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C, TMS): δ = 117.0 (C₅Me₅), 116.5 (C₅Me₅), 12.1 (C₅Me₅), 12.0 ppm (C₅Me₅); IR (KBr): $\tilde{\nu}$ = 3349 (w), 2908 (s), 2855 (s), 2718 (w), 2203 (w), 2157 (w), 1495 (w), 1436 (m), 1375 (s), 1258 (w), 1166 (w), 1066 (w), 1024 (w), 953 (w), 865 (w), 800 (m), 710 (vs), 683 (vs), 662 (vs), 613 (vs), 536 (m), 477 (w), 447 (w), 420 (vs) cm⁻¹; MS (70 eV): *m/z* (%): 813 (1) [*M*⁺], 680 (3) [*M*⁺-C₅Me₅], 543 (5) [*M*⁺-2C₅Me₅], 407 (10) [*M*⁺-3C₅Me₅]; elemental analysis calcd (%) for C₃₀H₄₆N₄PbTi₃ (*M_w* = 813.52): C 44.29, H 5.70, N 6.89; found: C 44.95, H 5.35, N 5.94.

Reaction of 1 with [Sn{N(SiMe₃)₂]₂] in a NMR Tube-scale Experiment. A 5-mm valved NMR tube was charged with **1** (0.015 g, 0.025 mmol), [Sn{N(SiMe₃)₂]₂] (0.011 g, 0.025 mmol) and [D₆]benzene (1.00 mL). The reaction course was monitored by NMR spectroscopy. After 1 h at room temperature, the spectra revealed new resonances assigned to [{"(Me₃Si)₂N}Sn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**9**) and NH(SiMe₃)₂ as the major products (ca. 70%), along with minor resonances for the starting compounds and **7**. Complex **9** decomposed completely after 24 h at room temperature to give an orange solution containing **7** and NH(SiMe₃)₂ according to the NMR spectra.

NMR data for [{"(Me₃Si)₂N}Sn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**9**): ¹H NMR (300 MHz, C₆D₆, 20 °C, TMS): δ = 11.47 (s br., 2H; NH), 2.09 (s, 30H; C₅Me₅), 1.85 (s, 15H; C₅Me₅), 0.39 ppm (s, 18H; SiMe₃); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C, TMS): δ = 118.7 (C₅Me₅), 118.6 (C₅Me₅), 12.3 (C₅Me₅), 11.9 (C₅Me₅), 6.5 ppm (SiMe₃).

Reaction of 1 with [Sn(C₅H₅)₂] in a NMR Tube-scale Experiment. A 5-mm valved NMR tube was charged with **1** (0.020 mg, 0.033 mmol), [Sn(C₅H₅)₂] (0.008 mg, 0.033 mmol) and [D₆]benzene (1.00 mL). The reaction course was monitored by NMR spectroscopy. After 3 h at room temperature, the spectra showed resonances for [{"(H₅C₅)Sn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**10**) and C₅H₆ as the major products

(ca. 60%), along with minor resonances for the starting compounds and **7**. Complex **10** decomposed completely after 3 days at room temperature to give cleanly **7** and C₅H₆ according to the NMR spectra.

NMR data for [(H₅C₅)Sn{(μ₃-N)(μ₃-NH)₂Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}] (**10**): ¹H NMR (300 MHz, C₆D₆, 20 °C, TMS): δ = 11.52 (s br., 2H; NH), 6.23 (s, 5H; C₅H₅), 2.03 (s, 30H; C₅Me₅), 1.76 ppm (s, 15H; C₅Me₅); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C, TMS): δ = 118.6 (C₅Me₅), 118.3 (C₅Me₅), 109.5 (C₅H₅), 12.2 (C₅Me₅), 11.9 ppm (C₅Me₅).

Synthesis of [Pb(μ₃-N)₂(μ₃-NH)₄{Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}₂] (11**). Method A.** A solution of **8** (0.40 g, 0.49 mmol) in toluene (15 mL) was carefully added to **1** (0.30 g, 0.49 mmol) in toluene (20 mL). The system was allowed to react at ambient temperature without any stirring for 7 days. After decantation, the resultant orange crystals were vacuum-dried to give **11**·C₇H₈ (0.34 g, 45%).

Method B. In a fashion similar to Method A, a solution of [Pb{N(SiMe₃)₂}₂] (0.13 g, 0.25 mmol) in toluene (10 mL) was carefully added to **1** (0.30 g, 0.49 mmol) in toluene (20 mL). After decantation, the resultant orange crystals were vacuum-dried to afford **11**·C₇H₈ (0.20 g, 54%).

IR (KBr): $\tilde{\nu}$ = 3344 (w), 2960 (w), 2907 (s), 2853 (s), 1608 (m), 1493 (w), 1432 (m), 1374 (m), 1261 (w), 1023 (w), 791 (s), 714 (vs), 695 (m), 678 (m), 657 (m), 620 (s), 522 (m), 418 (m) cm⁻¹; elemental analysis calcd (%) for C₆₇H₁₀₂N₈PbTi₆ (*M_w* = 1514.00): C 53.15, H 6.66, N 7.40; found: C 53.47, H 6.64, N 6.94.

Synthesis of [Sb(μ₃-N)₃(μ₃-NH)₃{Ti₃(η⁵-C₅Me₅)₃(μ₃-N)}₂] (12**). Method A.** In a fashion similar to the preparation of **11**, a solution of [Sb(NMe₂)₃] (0.07 g, 0.28 mmol) in toluene (5 mL) was added to **1** (0.30 g, 0.49 mmol) in toluene (20 mL). The system was allowed to react without any stirring for 20 h. After that time, orange crystals of **12**·2C₇H₈ (0.12 g) were isolated by decantation. From the solution a second crop of orange crystals was

obtained after 7 days at room temperature. The combined yield for $\mathbf{12} \cdot 2\text{C}_7\text{H}_8$ was 0.24 g (55%). IR (KBr): $\tilde{\nu} = 3351$ (w), 2966 (m), 2907 (s), 2855 (s), 1604 (w), 1494 (w), 1432 (m), 1374 (m), 1067 (w), 1025 (w), 791 (m), 728 (s), 694 (w), 669 (vs), 638 (w), 602 (s), 572 (w), 547 (w), 465 (w), 439 (m), 421 (w) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{109}\text{N}_8\text{SbTi}_6$ ($M_w = 1519.69$): C 58.49, H 7.23, N 7.37; found: C 58.44, H 7.17, N 6.99.

Method B. A 25 mL ampoule (Teflon stopcock) was charged with $\mathbf{1}$ (0.15 g, 0.25 mmol), $[\{\text{Sb}(\text{NMe}_2)\}_2(\mu\text{-N}t\text{Bu})_2]$ (0.06 g, 0.13 mmol) and $[\text{D}_6]\text{benzene}$ (10 mL). The reaction mixture was stirred at 100 °C for two days, and the solution was allowed to cool to ambient temperature overnight to afford orange crystals of $\mathbf{12} \cdot \text{C}_6\text{D}_6$ (0.095 g, 54%). IR (KBr): $\tilde{\nu} = 3350$ (w), 2966 (m), 2906 (s), 2854 (s), 1490 (w), 1431 (m), 1374 (s), 1329 (w), 1265 (w), 1024 (w), 801 (m), 720 (s), 669 (vs), 639 (m), 602 (s), 571 (m), 547 (m), 501 (m), 469 (w), 439 (s), 431 (m) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{66}\text{H}_93\text{D}_6\text{N}_8\text{SbTi}_6$ ($M_w = 1419.56$): C 55.84, H 7.03, N 7.89; found: C 56.10, H 6.82, N 7.71.

Synthesis of $[\text{Bi}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ ($\mathbf{13}$). In a fashion similar to the preparation of $\mathbf{11}$, treatment of $\mathbf{1}$ (0.30 g, 0.49 mmol) with $[\text{Bi}(\text{NMe}_2)_3]$ (0.09 g, 0.26 mmol) or $[\text{Bi}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (0.17 g, 0.25 mmol) in toluene (25 mL) at room temperature afforded orange crystals of $\mathbf{13} \cdot 2\text{C}_7\text{H}_8$ (0.24 g, 60%; or 0.25 g, 62%). IR (KBr): $\tilde{\nu} = 3346$ (w), 2905 (s), 2853 (s), 1604 (w), 1494 (w), 1431 (m), 1374 (m), 1066 (w), 1024 (w), 787 (m), 728 (s), 694 (m), 667 (vs), 617 (m), 588 (vs), 545 (m), 523 (m), 465 (m), 429 (s) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{109}\text{BiN}_8\text{Ti}_6$ ($M_w = 1606.90$): C 55.31, H 6.84, N 6.97; found: C 54.99, H 6.87, N 6.55.

Synthesis of $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$. A solution of AlCl_3 (2.00 g, 0.015 mol) in diethyl ether (100 mL) was slowly added to a solution of $[\text{LiN}(\text{SiMe}_3)_2]$ (2.50 g, 0.015 mol) in diethyl ether (100 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. After filtration, the volatile components were

removed under reduced pressure to afford a yellow oil (4.70 g). Distillation at 120 °C under vacuum (0.01 mmHg) gave $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$ (3.20 g, 64%) as a colorless solid. m. p. 41-43 °C; ^1H NMR (300 MHz, C_6D_6 , 20 °C, TMS): δ = 3.62 (q, $^3J_{\text{H-H}} = 7$ Hz, 4H; OCH_2CH_3), 0.74 (t, $^3J_{\text{H-H}} = 7$ Hz, 6H; OCH_2CH_3), 0.39 ppm (s, 18H; SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 20 °C, TMS): δ = 68.5 (OCH_2CH_3), 12.8 (OCH_2CH_3), 5.6 ppm (SiMe_3); IR (KBr): $\tilde{\nu}$ = 2980 (m), 2955 (m), 2900 (w), 1448 (w), 1394 (m), 1252 (s), 1193 (w), 1150 (w), 1093 (w), 1011 (m), 906 (vs), 842 (s), 765 (s), 674 (m), 619 (w), 544 (m), 510 (s) cm^{-1} ; MS (70 eV): m/z (%): 333 (1) [M^+], 242 (35) [$M^+ - \text{Me} - \text{Et}_2\text{O}$]; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{28}\text{AlCl}_2\text{NOSi}_2$ ($M_w = 332.40$): C 36.13, H 8.49, N 4.21; found: C 35.80, H 8.06, N 4.40.

Synthesis of $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Cl}_3\text{Al}_2\}(\mu_3\text{-N})(\mu_3\text{-NH})_2\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu\text{-Cl})(\mu_3\text{-N})\}]$ (14): A 10-mm valved NMR tube was charged with **1** (0.30 g, 0.49 mmol), $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$ (0.33 g, 0.99 mmol) and $[\text{D}_6]$ benzene (5 mL). The reaction mixture was heated at 120 °C for 2 h. The resultant dark red solution was allowed to cool to ambient temperature overnight to afford orange crystals of **14**· C_6D_6 (0.30 g, 64%). IR (KBr): $\tilde{\nu}$ = 3330 (w), 3302 (w), 2948 (s), 2910 (s), 2278 (w), 1491(w), 1437 (m), 1379 (s), 1330 (w), 1245 (vs), 1067 (w), 1023 (m), 915 (vs), 887 (vs), 834 (vs), 752 (vs), 710 (w), 678 (s), 657 (s), 631 (s), 585 (s), 557 (w), 517 (w), 498 (s), 451 (vs) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{65}\text{Al}_2\text{Cl}_4\text{D}_6\text{N}_5\text{Si}_2\text{Ti}_3$ ($M_w = 1047.64$): C 48.15, H 6.83, N 6.68; found: C 49.58, H 7.01, N 6.47.

X-ray structure determination of **5, **11**, **13**, **14** and $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$.** Orange crystals of **5**, **11**· C_7H_8 , **13**· $2\text{C}_7\text{H}_8$, and **14**· C_6D_6 were grown in toluene or $[\text{D}_6]$ benzene at room temperature as described in the experimental section. Suitable colorless crystals of $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ for single crystal X-ray diffraction were grown by distillation of the crude product obtained from the reaction of AlCl_3 with two equiv of $[\text{LiN}(\text{SiMe}_3)_2]$ as

described in the literature.^[39] Crystals were removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, attached to a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. The molybdenum radiation was used in all cases, graphite monochromated and enhanced with a MIRACOL collimator. Crystallographic data for all the complexes are presented in Table 5 (see page 36).

The structures were solved, using the WINGX package,^[48] by direct methods (SHELXS-97)^[49] and refined by least-squares against F^2 (SHELXL-97).^[49]

All non-hydrogen atoms of **5** were anisotropically refined. The hydrogen atoms were positioned geometrically and refined by using a riding model, and the two imido hydrogen atoms statistically distributed over the six N2 nitrogen atoms linked to the gallium atoms (final 33% of occupancy).

Compounds **11** and **13** crystallized with one and two molecules of toluene respectively, several tries to model the solvent molecules were performed but were unsuccessful, so Squeeze^[50] procedure was applied to remove its contribution to the structure factors. Both complexes presented some disorder in the pentamethylcyclopentadienyl groups, so C11 and C16 in complex **11** and C23 and C28 in **13** were refined in two different positions with a 50% of occupancy. Also the bismuth central atom in complex **13** presented disorder, being Bi1 with a 40% of occupancy and two positions for Bi1' with a 30% of occupancy for each. All non-hydrogen atoms were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model. The corresponding imido hydrogen atoms statistically distribute

over the six nitrogen atoms linked to the central atoms (final occupancy: 66% in **11** and 50% in **13**).

All non-hydrogen atoms of **14** and $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ were anisotropically refined. The hydrogen atoms were positioned geometrically and refined by using a riding model.

CCDC 722848 – 722852 for **5**, **11**, **13**, **14** and $[\text{AlCl}\{\text{N}(\text{SiMe}_3)_2\}_2]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements. We are grateful to the Spanish MEC (CTQ2005-00238/BQU), Comunidad de Madrid and the Universidad de Alcalá (CCG06-UAH/PPQ-0665), and Factoría de Cristalización (CONSOLIDER-INGENIO 2010) for financial support of this research.

Table 5. Experimental Data for the X-ray Diffraction Studies on **5**, **11**·C₇H₈, **13**·2C₇H₈, **14**·C₆D₆ and [AlCl{N(SiMe₃)₂}₂]

	5	11 ·C ₇ H ₈	13 ·2C ₇ H ₈	14 ·C ₆ D ₆	[AlCl{N(SiMe ₃) ₂ } ₂]
formula	C ₆₀ H ₉₂ Ga ₂ N ₈ Ti ₆	C ₆₇ H ₁₀₂ N ₈ PbTi ₆	C ₇₄ H ₁₀₉ BiN ₈ Ti ₆	C ₄₂ H ₇₁ Al ₂ Cl ₄ N ₅ Si ₂ Ti ₃	C ₁₂ H ₃₆ AlClN ₂ Si ₄
<i>M_r</i>	1352.26	1514.16	1607.07	1041.68	383.22
<i>T</i> [K]	200(2)	100(2)	200(2)	200(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal syst	trigonal	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	<i>R</i> -3	<i>Pnmm</i>	<i>Pnmm</i>	<i>P2₁/c</i>	<i>P2₁2₁2₁</i>
<i>a</i> [Å]; α [deg]	18.852(3); 90	14.8966(4); 90	14.7443(6); 90	14.669(4); 90	11.737(4); 90
<i>b</i> [Å]; β [deg]	18.852(3); 90	15.4021(5); 90	15.324(3); 90	19.614(6); 101.10(2)	16.0533(14); 90
<i>c</i> [Å]; γ [deg]	15.784(3); 120	16.7373(4); 90	16.5713(16); 90	18.702(5); 90	12.839(3); 90
<i>V</i> [Å ³]	4857.8(14)	3840.19(19)	3744.1(8)	5280(3)	2419.0(9)
<i>Z</i>	3	2	2	4	4
ρ_{calcd} [g cm ⁻³]	1.387	1.309	1.425	1.310	1.052
$\mu_{\text{MoK}\alpha}$ [mm ⁻¹]	1.560	2.815	2.993	0.757	0.388
<i>F</i> (000)	2106	1548	1648	2184	832
cryst size [mm]	0.28 x 0.22 x 0.12	0.49 x 0.33 x 0.27	0.26 x 0.15 x 0.15	0.30 x 0.30 x 0.10	0.20 x 0.20 x 0.20
θ rang [deg]	3.55 to 27.60	5.03 to 27.51	3.07 to 27.52	3.01 to 25.01	3.07 to 27.50
index ranges	-24<= <i>h</i> <=24, -24<= <i>k</i> <=24, -20<= <i>l</i> <=20	-19<= <i>h</i> <=19, -19<= <i>k</i> <=20, 0<= <i>l</i> <=21	-18<= <i>h</i> <=19, -19<= <i>k</i> <=19, -21<= <i>l</i> <=18	-17<= <i>h</i> <=17, -23<= <i>k</i> <=22, -21<= <i>l</i> <=22	-14<= <i>h</i> <=15, -20<= <i>k</i> <=20, -16<= <i>l</i> <=16
reflns collected	35756	59000	44754	62786	54809
unique data	2494 [<i>R</i> _{int} = 0.149]	4537 [<i>R</i> _{int} = 0.029]	4447 [<i>R</i> _{int} = 0.102]	9279 [<i>R</i> _{int} = 0.150]	5568 [<i>R</i> _{int} = 0.054]
obsd data [<i>I</i> > 2 σ (<i>I</i>)]	1589	3587	2848	5708	4497
GOF on <i>F</i> ²	1.026	1.106	1.049	1.171	1.068
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>RI</i> = 0.046, <i>wR2</i> = 0.088	<i>RI</i> = 0.036, <i>wR2</i> = 0.112	<i>RI</i> = 0.085, <i>wR2</i> = 0.254	<i>RI</i> = 0.077, <i>wR2</i> = 0.146	<i>RI</i> = 0.064, <i>wR2</i> = 0.166
<i>R</i> indices (all data)	<i>RI</i> = 0.104, <i>wR2</i> = 0.101	<i>RI</i> = 0.049, <i>wR2</i> = 0.120	<i>RI</i> = 0.122, <i>wR2</i> = 0.276	<i>RI</i> = 0.141, <i>wR2</i> = 0.167	<i>RI</i> = 0.084, <i>wR2</i> = 0.181
largest diff. Peak/hole [e.Å ⁻³]	0.513/-0.783	1.547/-0.477	1.261/-1.799	0.701/-0.496	0.432/-0.963

$$^a RI = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad wR2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{1/2}$$

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