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Heterometallic Cube-Type Molecular Nitrides

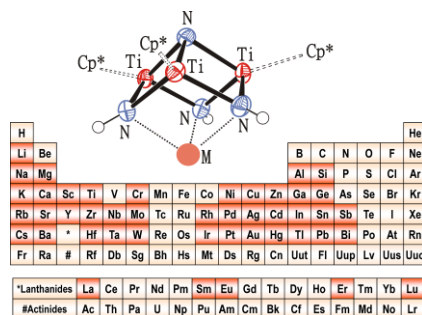
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MICROREVIEW

A wide family of heterometallic nitrido complexes with $[MTi_3N_4]$ cube-type cores has been prepared by incorporation of most of the metallic elements of the Periodic Table into the incomplete cube structure of $[\{TiCp^*(\mu-NH)\}_3(\mu_3-N)]$ ($Cp^* = \eta^5-C_5Me_5$).



Nitrido Cages

Miguel Mena, Adrián Pérez-Redondo, and Carlos Yélamos*

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Heterometallic Cube-Type Molecular Nitrides

Keywords: Cage compounds · Cubanes · Heterometallic complexes · Nitrides · Titanium

Abstract: Polynuclear transition metal nitrido complexes constitute a class of molecular cage compounds with fascinating structures and interesting bonding properties. However, there is a lack of systematic strategies for the rational construction of aggregates with desired structure and composition. This article provides a brief overview of the structure and bonding modes of polynuclear nitrido complexes, the most common synthetic approaches used to generate such aggregates, and a systematic review of the development of a family of heterometallic nitrido complexes with $[MTi_3N_4]$ cube-type cores. The rational entry to those well-defined systems is based on the incorporation of transition, lanthanides, and main-group metals into the incomplete cube structure of the trinuclear titanium(IV) imido-nitrido complex $[\{TiCp^*(\mu-NH)\}_3(\mu_3-N)]$ ($Cp^* = \eta^5-C_5Me_5$). The great versatility of $[\{TiCp^*(\mu-NH)\}_3(\mu_3-N)]$ as a preorganized metalloligand is also confirmed by the possibility of preparing complexes with heterometals in low (e.g. Mo^0 , Ir^I and Pt^0) or high oxidation states (e.g. Zr^{IV} , Ta^V and Pt^{IV}).

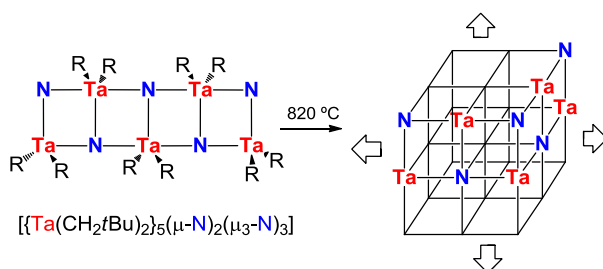
Introduction

Transition metal nitrido complexes constitute a large family of coordination compounds with a wide structural variety and diverse reactivity patterns.^[1,2,3,4] This is due principally to the numerous coordination possibilities of the monoatomic nitrido ligand (formally N^{3-}), which include the terminal functionality to a single metal site and many different (μ_n -N) bridging dispositions spanning anywhere from two to six metal centers.^[5] When acting in the terminal mode ($\equiv N$), the nitrido ligand forms a triple bond with a metal atom typically in a high oxidation state and behaves as a very strong σ - and π -electron donor. In consequence, the majority of complexes with this functionality are found for the mid transition metals (Groups 6-8), and particularly most nitrido species are formed with second- or third-row elements. However, significant efforts have been directed at the synthesis of rare examples with the terminal nitrido ligand bound to early transition metals (Ti,^[6] V^[7] and Nb^[8]) and Group 9 elements (Co,^[9] Rh^[10] and Ir^[11]).

The synthesis and reactivity of terminal transition metal nitrido complexes have been extensively covered in reviews by Abu-Omar, Berry, and recently Smith.^[12,13,14] However, transition metal complexes containing bridging nitrido ligands are not discussed in those articles and the last comprehensive review in this area by Dehnicke and Strähle dates back to 1992.^[4] Similarly, the review of organometallic nitrido clusters by Gladfelter was reported in 1985.^[15] Since then, only Lee and Holm have briefly outlined the structure and preparative routes to polynuclear nitrido complexes.^[16,17]

Molecular species with μ_n -nitrido groups are relevant to the bridging modes of the chemisorbed nitrogen atoms in heterogeneous catalytic reactions such as the Haber-Bosch process or the selective catalytic reduction of NO_x to give N_2 .^[18,19,20] Multimetallic nitrido

species are also implicated in the synthesis of ammonia by homogeneous systems where cooperation between multiple metal sites may be beneficial for dinitrogen activation.^[21,22,23] Furthermore, polynuclear nitrido complexes might serve as building blocks and precursors for the synthesis of metal nitride materials with different phases or compositions of those obtained by traditional methods.^[24] For instance, Wolczanski and co-workers demonstrated that the geometry of the nitrido tantalum precursor $[\{\text{Ta}(\text{CH}_2t\text{Bu})_2\}_5(\mu\text{-N})_2(\mu_3\text{-N})_3]$ allows access to cubic TaN at 820 °C (Scheme 1) rather than the thermodynamically expected hexagonal form.^[25,26]



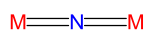
Scheme 1. Synthesis of TaN determined by the precursor structure.

The focus of this short review is to give a brief overview of the structural diversity of polynuclear nitrido complexes and to illustrate the most common synthetic approaches used to generate such aggregates. In addition, this article includes a systematic review of the development of a family of heterometallic nitrido complexes with $[\text{MTi}_3\text{N}_4]$ cube-type cores carried out in our laboratory over the last two decades.

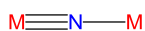
Polynuclear Nitrido Complexes

Structure and Bonding Modes

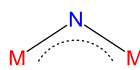
The nucleophilic behavior of the terminal nitrido moiety, particularly in early transition metal systems,^[3,12,27] may result in the formation of dimeric or oligomeric species with the nitrido ligand bridging two or more metal centers (Scheme 2). A search in the literature reveals many examples with the nitrido occurring as linear bridge, either in a symmetric $[M]=N=[M]$ or asymmetric $[M]\equiv N-[M]$ fashion, but also acting as bent bridge (μ -N) between two metals. In the symmetric bridging mode, the metal-nitrogen bonds exhibit double bond character and typical examples are found for oxidized early and middle transition metals.^[3,4,28] Alternatively, the asymmetric nitrido bridges feature localization of the triple bond while the long metal-nitrogen bond is usually a donor-acceptor $N\rightarrow[M]$ interaction. This asymmetric bridge is found in many structures of oligomeric or polymeric homometallic nitrido compounds such as $[\{MoCl_3(\mu-N)\}_4]^{[29]}$ and $[\{ReCl_4(\mu-N)\}_\infty]^{[30]}$. However, the majority of examples with $[M]\equiv N\rightarrow[M']$ nitrido bridges are heterometallic compounds formed by reaction of a basic terminal nitrido ligand with Lewis acidic metal halides or coordinatively unsaturated metal complexes.^[31,32,33]

Terminal:**Bridge to two metals:**

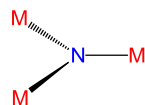
Linear Symmetric



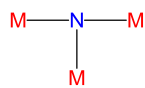
Linear Asymmetric



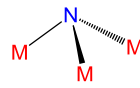
Bent

Bridge to three metals:

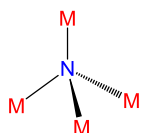
Trigonal planar



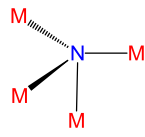
T-shaped



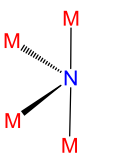
Pyramidal

Bridge to four metals:

Tetrahedral



Basal trigonal pyramidal



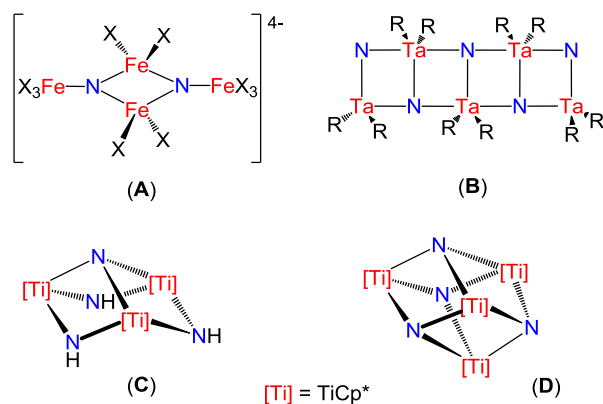
Butterfly

Scheme 2. Some coordination possibilities of the nitrido ligand.

For dinuclear $[(ML_5)_2(\mu-A)]$ ($A = p$ -block element) compounds with 0-8 electrons on the two metal atoms, extended Hückel calculations showed that the energy of the complexes depends very little on the $M-A-M$ angle and this is determined by intramolecular steric repulsion of the ML_5 units.^[34] Thus, although the most common dinuclear complexes with one μ -nitrido ligand are those containing a linear or almost linear disposition ($M-N-M$ $165-180^\circ$),^[3,4] a few examples with appreciable bent $M-N-M$ linkages have been also reported.^[35] Furthermore, angles notably smaller than 180° have been found in mono-bridged dinuclear nitrido species containing an additional intramolecular interaction. For instance, the titanium complex $[\{Ti_2Cl_5L_5\}(\mu-N)]$ ($L = 3,5$ -dimethylpyridine)^[36] shows a linear $Ti-N-Ti$ moiety whereas compound $[\{Ti_2Cp^*_2Cl_3(NH_3)\}(\mu-N)]$ ($Cp^* = \eta^5-C_5Me_5$)^[37] exhibits a $Ti-N-Ti$ angle of $153.1(2)^\circ$ due to the existence of an intramolecular hydrogen bonding $N-H \cdots Cl$ interaction. A more

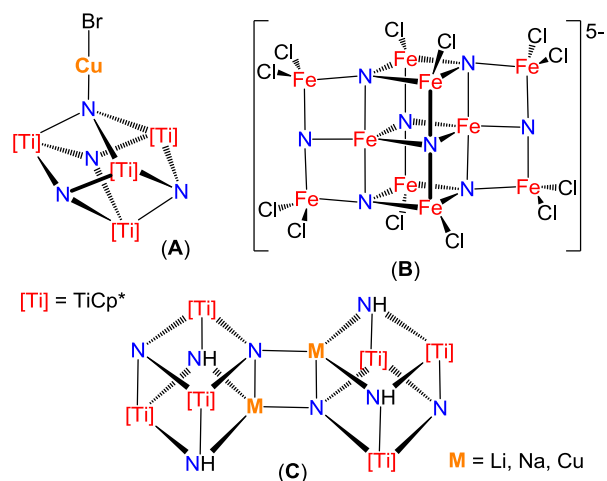
pronounced bending is found in complexes composed of two metals bridged by two μ -nitrido ligands adopting a $[M(\mu\text{-N})_2M]$ diamond core structure.^[38,39]

The nitrido ligand is also able to bridge three metal atoms ($\mu_3\text{-N}$) with different coordination modes as illustrated in the selected examples shown in Scheme 3. Although rare, the trigonal planar geometry around the nitrido ligand has been established in the structures of the trinuclear iridium anion $[\text{Ir}_3(\mu_3\text{-N})(\mu\text{-SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$,^[40] the tetranuclear iron complexes $[\text{Fe}_4(\mu_3\text{-N})_2\text{X}_{10}]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}$) (**A**),^[41] and some Group 6 clusters.^[42] The T-shaped arrangement has been described in several complexes containing metal–metal bonds,^[4,43] but also in the pentanuclear tantalum complex $[\{\text{Ta}(\text{CH}_2t\text{Bu})_2\}_5(\mu\text{-N})_2(\mu_3\text{-N})_3]^{[25]}$ (**B**) or the heterometallic titanium-sodium derivative $[\{\text{Ti}(i\text{Prtren})\}_2(\mu_3\text{-N})\text{Na}(\text{thf})]$ ($i\text{Prtren} = \text{N}(\text{CH}_2\text{CH}_2\text{NiPr}_2)_3$)^[44]. Lastly, the pyramidal geometry has been found in early transition metal complexes such as the trinuclear derivative $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]^{[45]}$ (**C**) or the cube-type tetranuclear species $[(\text{MCp}^*)_4(\mu_3\text{-N})_4]$ ($\text{M} = \text{Ti}$ (**D**),^[46] V ^[47]), as well as in the Group 8 clusters $[(\text{RuCp}^*)_3(\mu_3\text{-}\eta^1:\eta^3:\eta^1\text{-CHC}_6\text{H}_4)(\mu\text{-H})(\mu_3\text{-N})]^{[48]}$ and $[\text{Fe}_3(\text{tbsL})(\mu_3\text{-N})]^-$ ($\text{tbsL} = 1,3,5\text{-C}_6\text{H}_9(\text{NHPh-}o\text{-NSi}t\text{BuMe}_2)_3$)^[49].



Scheme 3. Some representative examples of complexes featuring μ_3 -nitrido ligands.

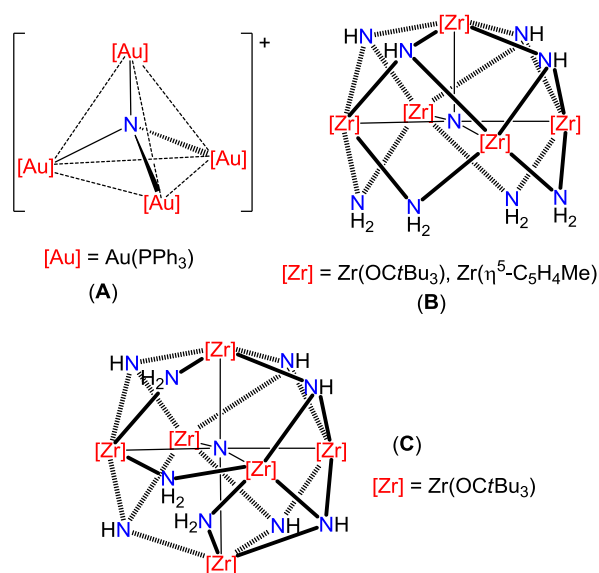
The μ_4 -bridging function for the nitrido ligand is also represented in different geometries as illustrated in Scheme 4. The tetrahedral environment for the nitrido ligand has been traditionally proposed in the mercury cation $[\{\text{Hg}(\text{Me})\}_4(\mu_4\text{-N})]^+$,^[50] and structurally characterized in several heterometallic titanium-copper complexes (e.g. $[(\text{TiCp}^*)_4(\mu_3\text{-N})_3\{(\mu_4\text{-N})\text{CuBr}\}]$)^[51] (**A**). The butterfly geometry (the metals surrounding the nitrogen are in nearly perfect octahedral geometry with two equatorial *cis* sites vacant) has been reported in several nitrido clusters (e.g. $[\text{Fe}_4(\mu_4\text{-N})(\text{CO})_{12}]^-$)^[52] and in the iron halide complexes $[\text{Fe}_{10}(\mu_3\text{-N})_2(\mu_4\text{-N})_6\text{X}_{12}]^{5-}$ (X = Cl, Br)^[41] (**B**). The latter species **B** contain also four $\mu_4\text{-N}$ units adopting the rare basal trigonal pyramidal geometry (a nitrido centered in the triangular basal face of a pyramidal coordination polyhedron),¹⁶ which is also found in several heterometallic double-cube species $[\{M(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (M = Li,^[53] Na,^[53] Cu^[54]) (**C**).



Scheme 4. Some representative examples of complexes featuring μ_4 -nitrido ligands.

Besides the well-defined bridging functions depicted in Scheme 2, the structure of several metal clusters has shown interstitial nitrogen atoms surrounded by four, five or six metal atoms (Scheme 5). In particular, gold(I) phosphine cations $[\text{Au}_4(\mu_4\text{-N})(\text{PR}_3)_4]^+$ (R =

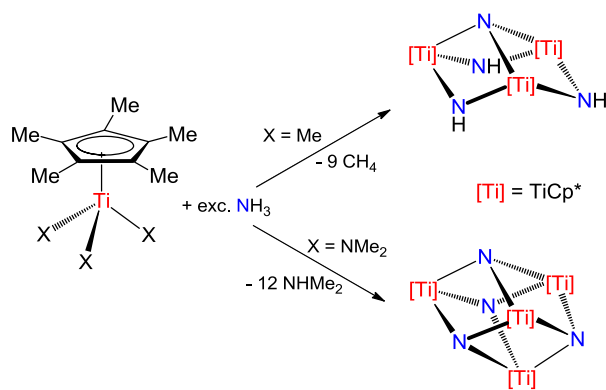
PPh₃, *t*Bu) contain N-atoms at the center of a tetrahedral metal polyhedron (A),^[55] while in cations [Au₅(μ₅-N)(PPh₃)₅]²⁺ the nitrogen atom is surrounded by five gold centers adopting polyhedral geometry between square pyramidal and trigonal bipyramidal.^[56] Aside from those gold(I) compounds with structures dominated by aurophilic interactions, classical examples of complexes with interstitial nitrogen atoms include homo- and heterometallic low-valent middle- to late-transition metal carbonyl clusters with μ₅- or μ₆-nitrido moieties.^[15] In addition, some pentanuclear early transition metal complexes with μ₅-N nitrido groups have been structurally characterized, [{ZrL}₅(μ₅-N)(μ₃-NH)₄(μ-NH₂)₄] (L = OC*t*Bu₃,^[57] η⁵-C₅H₄Me^[58]) (B) and [Ta₅(μ₅-N)(μ₃-N*i*Pr)₂(μ-N*i*Pr)₆(N*i*Pr)₄(NH*i*Pr)₂]⁵⁹, as well as a few hexanuclear zirconium aggregates where the μ₆-N moiety is encased in the center of an octahedral polyhedron, [{Zr(OC*t*Bu₃)₆(μ₆-N)(μ₃-NH)₆(μ-NH₂)₃]^[57] (C) and [Zr₆(μ₆-N)Cl₆(μ-Cl)₁₂]ⁿ⁻ (n = 3, 4)^[60].



Scheme 5. Some representative examples of complexes featuring interstitial N-atoms.

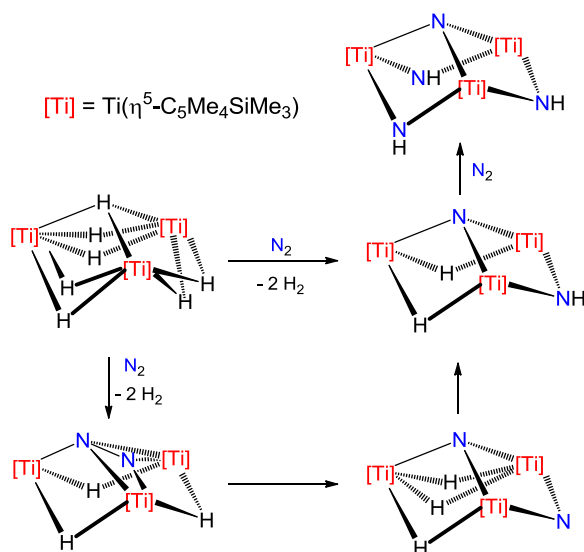
Common synthetic routes

The diverse synthetic methods used to prepare nitrido complexes have been described in previous reviews.^[2,4] In particular, preparative routes to terminal metal nitrido complexes have been recently reviewed,^[12,61] and many of those methods are also of application for the synthesis of polynuclear nitrido systems. For example, high-nuclearity early transition metal aggregates are usually prepared by acid/base chemistry using the reaction of a high-valent metal precursor with a fully reduced nitrogen source such as ammonia or amines NR_3 . Thus, the treatment of organometallic derivatives containing bulky ancillary ligands (e.g. cyclopentadienyl, alkoxido) with excess ammonia is an elegant and efficient entry to the synthesis of species with bridging nitrido (N^{3-}), imido (NH^{2-}) or amido (NH_2^-) ligands of titanium,^[37,45,46,62] zirconium,^[57,58,63] and tantalum^[25,64]. However, this methodology precludes the desired control in the composition and structure of the resultant polynuclear aggregates. For instance, Roesky and co-workers described the preparation of the trinuclear imido-nitrido complex $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) by ammonolysis of $[\text{TiCp}^*\text{Me}_3]$,^[45] whereas the analogous treatment of $[\text{TiCp}^*(\text{NMe}_2)_3]$ with NH_3 gave the cube-type tetranuclear nitrido derivative $[(\text{TiCp}^*)_4(\mu_3\text{-N})_4]$ (Scheme 6).^[46] Besides ammonia, the reaction of metal halide complexes with $\text{N}(\text{SnMe}_3)_3$ has been used to prepare tantalum^[65] and iron^[41,66] polynuclear nitrido species.



Scheme 6. Ammonolysis of $[\text{TiCp}^*\text{X}_3]$ ($\text{X} = \text{Me}, \text{NMe}_2$) derivatives.

Whereas those reactions do not involve changes in the oxidation state of the metal precursor, a second general procedure, and most appropriate for nitrido clusters of mid and late transition metals, is the reduction of an oxidized nitrogen source with a low-valent metal center or a reduced co-ligand. For instance, treatment of low-valent metal precursors with azides^[49,67] or reduction of nitrosyl ligands appended to metal clusters^[15] are typical entries to polynuclear species with $\mu_n\text{-N}$ ligands. Of particular relevance in the field of nitrogen fixation is the cleavage of dinitrogen by reduced complexes to afford nitrido ligands. Since the seminal work of Cummins on the activation of N_2 with the three-coordinate molybdenum(III) complex $[\text{Mo}\{\text{N}(t\text{Bu})\text{Ar}\}_3]$ ($\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) to give the mononuclear nitrido complex $[\text{Mo}(\equiv\text{N})\{\text{N}(t\text{Bu})\text{Ar}\}_3]$,^[68] many dinuclear nitrido species have been prepared by this route.^[39,69] However, isolated examples of polynuclear (nuclearity exceeding two) nitrido complexes derived from N_2 are rare.^[22] Notably, Hou and co-workers have recently characterized a trinuclear titanium hydride complex that cleaves molecular nitrogen to form $\mu_3\text{-N}$ and $\mu\text{-N}$ ligands bound to the metal centers (Scheme 7).^[23]



Scheme 7. Synthesis of nitrido complexes by activation of N_2 with a titanium hydride.

Lastly, other synthetic approaches to isolating dinuclear or polynuclear molecular nitrides are based on the derivatization of preexisting nitrido or imido complexes. As noted above, the addition of Lewis acidic metal centers to nitrido complexes with terminal nitrido ligands is a general route to the preparation of heterometallic complexes with $M\equiv N \rightarrow M'$ nitrido bridges.^[31-33] Other examples include the condensation reaction between vanadium silylimido compounds $[V(NSiR_3)(L)_n]$ and metal halides to form homometallic^[7b,70] and heterobimetallic^[71] nitrido-bridged complexes via SiR_3X elimination. Another series of heterometallic nitrido complexes were obtained through the reaction of $[V(NSiMe_3)(NPh_2)_3]$ with $[Li(NiPr_2)]$ to give the lithium salt $[(Ph_2N)_3V(\mu-N)Li(thf)_3]$, which subsequently reacts with Group 4 haloderivatives $[TiCpCl_3]$ and $[ZrCp_2Cl_2]$ to form compounds $[(Ph_2N)_3V(\mu-N)_2TiClCp]$ and $[(Ph_2N)_3V(\mu-N)ZrClCp_2]$ ($Cp = \eta^5-C_5H_5$), respectively.^[72]

Despite those examples, an examination of the literature reveals the lack of general and systematic strategies for the construction of high-nuclearity nitrido aggregates with

desired composition and structure. Consequently, our research over the last two decades has focused on developing a rational and versatile synthesis of heterometallic nitrido complexes using the incorporation reaction of a variety of inorganic fragments into the incomplete cube structure of the trinuclear titanium(IV) complex $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**). The imido-nitrido compound **1** was prepared in 1989 by H. W. Roesky and co-workers through the ammonolysis of $[\text{TiCp}^*\text{Me}_3]$ (Scheme 6).^[45] The molecular structure of **1** shows a six-membered $[\text{Ti}_3(\mu\text{-NH})_3]$ ring in chair conformation with the three titanium atoms also bridged by a further nitrogen atom (Figure 1). The pentamethylcyclopentadienyl ligands on the titanium centers are slightly tilted to the side of the apical nitrido ligand, enabling the coordination to Lewis acidic metal centers through the basal NH imido groups. Besides the capacity of acting as a neutral ligand through the imido groups, the N–H bonds of **1** can also be subsequently activated to give anionic systems coordinated to the heterometals.

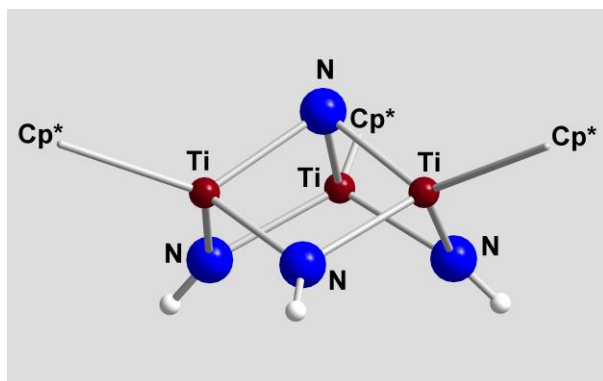


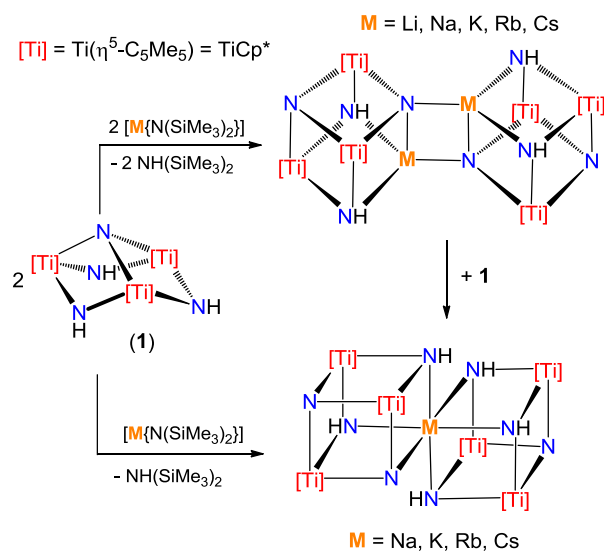
Figure 1. Molecular structure of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**). Adapted from the original report.^[45]

Heterometallic cube-type nitrido complexes

This section systematically reviews our studies on the synthesis and structure of heterometallic cube-type nitrido complexes derived from the incorporation of transition, lanthanides, and main-group metals into the preorganized structure of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**). The content of this survey is organized by group of the incorporated heterometals, paying particular attention to the structure and reactivity of these polynuclear aggregates.

Group 1 metal complexes

Treatment of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with 1 equiv. of Group 1 bis(trimethylsilyl)amido reagents at room temperature led to bis(trimethylsilyl)amine and precipitation of the alkali metal derivatives $[\{\text{M}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) (Scheme 8).^[53,73] These compounds exhibit edge-linked double-cube $[\text{M}_2\text{Ti}_6\text{N}_8]$ cores in the solid-state as determined by X-ray crystallographic studies for the lithium (Figure 2) and sodium complexes. The analogous reaction of **1** with 0.5 equiv. of the alkali metal amido reagents $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ gave the complexes $[\text{M}(\mu_3\text{-N})(\mu_3\text{-NH})_5\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$), which can also be obtained by treatment of the edge-linked derivatives with 1 equiv. of **1** at different temperatures.^[73] The resultant compounds contain corner-shared double-cube $[\text{MTi}_6\text{N}_8]$ cores as determined by X-ray crystal structure determinations for the potassium (Figure 3), rubidium, and cesium derivatives.



Scheme 8. Synthesis of Group 1 double-cube complexes.

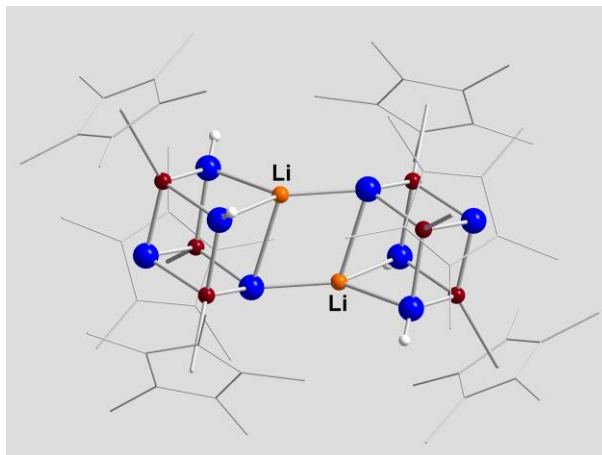


Figure 2. Crystal structure of complex $[Li(\mu_4-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)_2]$. Adapted from the original report.^[53]

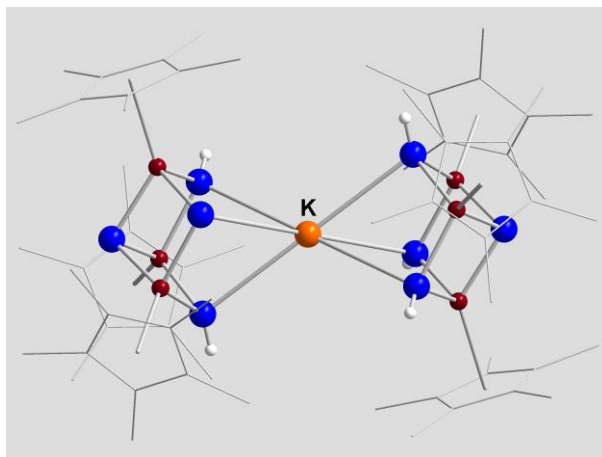
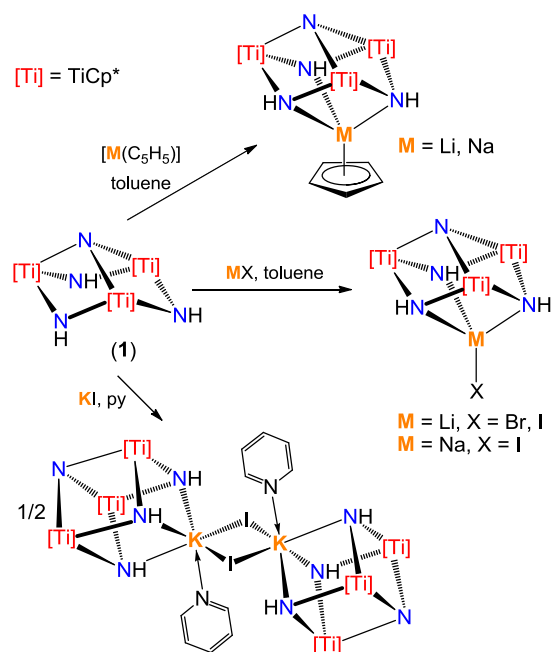


Figure 3. Crystal structure of complex $[\text{K}(\mu_3\text{-N})(\mu_3\text{-NH})_5\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_2$. Adapted from the original report.^[73]

While intermediates could not be observed in the reaction of **1** with $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ at room temperature, the analogous treatment with lithium and sodium cyclopentadienides gave the thermally stable cube-type adducts $[(\eta^5\text{-C}_5\text{H}_5)\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Li}, \text{Na}$) (Scheme 9).^[74] Related complexes $[\text{XM}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Li}, \text{X} = \text{Br}, \text{I}; \text{M} = \text{Na}, \text{X} = \text{I}$) were isolated in the direct reaction of **1** with the anhydrous metal halides in toluene.^[75] A series of Density Functional Theory (DFT) calculations were carried out to understand the adduct formation between metal halides and the metalloligand **1**. Calculations for alkali metal halides MX showed that the formation of $[\mathbf{1}\text{-MX}]$ in the gas phase is a largely exothermic process (from -55 to -162 kJ mol^{-1}), with values increasing going down the halogen group and going up the Group 1 metal. However, the reaction energies are significantly smaller in solution and the processes are less favorable when taken into account the dissolution energies of the LiX solids, in accordance with the lack of reactivity of **1** with LiCl, NaCl, NaBr, KBr, and KI salts in toluene or dichloromethane solvents. Indeed, later it was found that **1** reacts with KI in pyridine to give the adduct

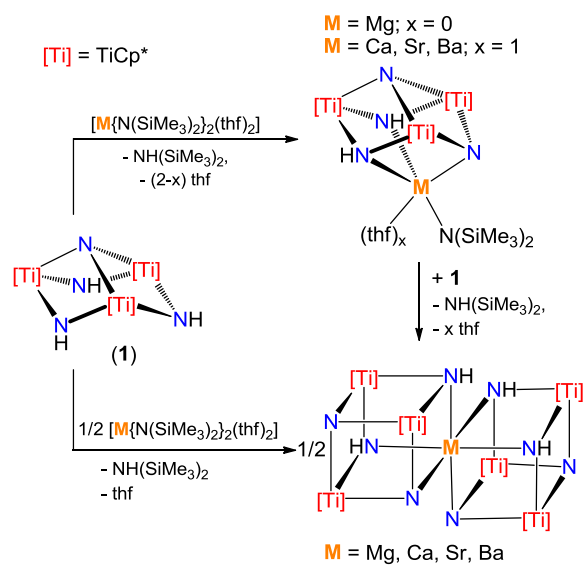
$[\{(\text{py})(\mu\text{-I})\text{K}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}\}_2]$ with a solid-state structure containing two $[\text{KTi}_3\text{N}_4]$ cube-type cores held together by two bridging iodine atoms.^[76]



Scheme 9. Synthesis of Group 1 adducts.

Group 2 metal complexes

The reaction of **1** with 0.5 equiv. of Group 2 bis(trimethylsilyl)amido reagents $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$ led to bis(trimethylsilyl)amine and the precipitation of corner-shared double-cube nitrido complexes $[\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) (Scheme 10).^[73,77] If 1 equiv. of the Group 2 amido reagent is used, single cube-type derivatives $[(\text{thf})_x\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Mg}, x = 0; \text{M} = \text{Ca}, \text{Sr}, \text{Ba}, x = 1$) can be isolated or identified. While the magnesium amido complex is stable in solution at high temperatures, the calcium and strontium analogues decompose slowly at room temperature, and the barium derivative was only detected by NMR spectroscopy.



Scheme 10. Synthesis of Group 2 cube-type complexes.

Similarly, magnesium complexes $[RMg\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}]$ ($R = \eta^5-C_5H_5, CH_2CMe_3, CH_2Ph$) exhibit very different thermal stability in solution depending on the steric bulk of the R group.^[77] Thus, whereas the cyclopentadienyl complex is stable at high temperatures, the neopentyl derivative decomposes within hours at room temperature and the benzyl analogue can only be detected by NMR spectroscopy. The thermal stabilities of $[(thf)_xRM\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}]$ may be rationalized by the steric crowding about the Group 2 metals. If R is relatively small or M is large, compounds undergo ligand redistribution reactions to give the insoluble corner-shared double-cube nitrido complexes $[M\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}_2]$ ($M = Mg, Ca, Sr, Ba$).

To obtain single cube-type complexes of the heavier Group 2 metals with increased thermal stability, the tetrahydrofuran ligands were displaced with 4-*tert*-butylpyridine but the resultant species $[(tBupy)\{(Me_3Si)_2N\}M\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}]$ ($M = Ca, Sr$) still decompose at room temperature. In the same vein, the treatment of $[(thf)_x\{(Me_3Si)_2N\}M\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}]$ with anilines afforded the arylamido

complexes $[(\text{ArHN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_n$ ($\text{M} = \text{Mg}$, $n = 1$, $\text{Ar} = 4\text{-C}_6\text{H}_4\text{Me}$; Ca , $n = 2$, $\text{Ar} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$).^[78] The magnesium compound has a single cube-type structure whereas the X-ray crystal structure of the analogous calcium derivative shows two cube-type azaheterometallocubane moieties $[\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ held together by two μ -2,4,6-trimethylanilido ligands (Figure 4). A related dinuclear magnesium derivative $[\{\text{Mg}_2(\mu_3\text{-N})(\mu_3\text{-NH})_5[\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})]_2\}(\mu\text{-NHAr})_3]$ which shows three 4-methylanilido ligands bridging two $[\text{MgTi}_3\text{N}_4]$ cube type cores was also structurally characterized.

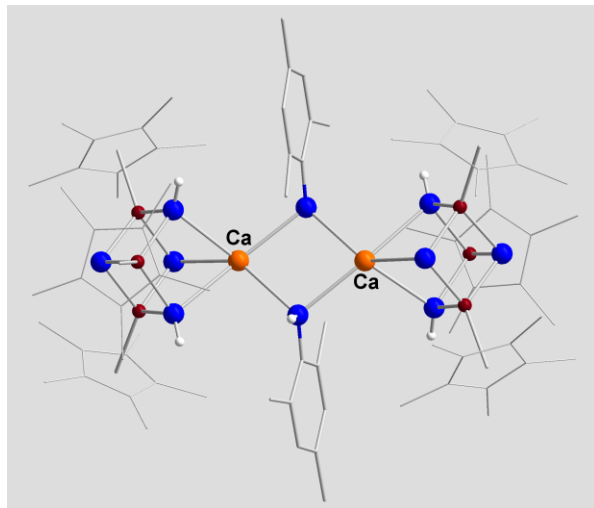


Figure 4. Crystal structure of complex $[(\text{ArHN})\text{Ca}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_2$.

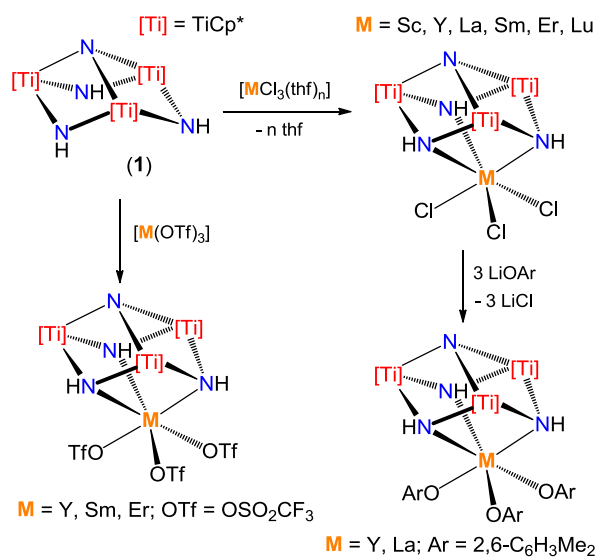
Adapted from the original report.^[78]

The arylamido complexes $[(\text{ArHN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_n$ react with chloroform- d_1 at room temperature to give the Group 2 chloride adducts $[\text{Cl}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Mg}$, Ca). Interestingly, those complexes cannot be prepared through the direct reaction of **1** with anhydrous magnesium or calcium dichlorides in chlorinated solvents. DFT calculations showed that the formation of $[\mathbf{1}\text{-MX}_2]$ complexes in the gas phase is a quite exothermic process, and similarly to Group 1 adducts, the greatest

formation energy was found for the iodide derivatives.^[75] Indeed, stable molecular adducts $[\text{I}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$) are easily prepared by reaction of **1** with Group 2 metal diiodides in dichloromethane at ambient temperature.

Group 3 metal and lanthanide complexes

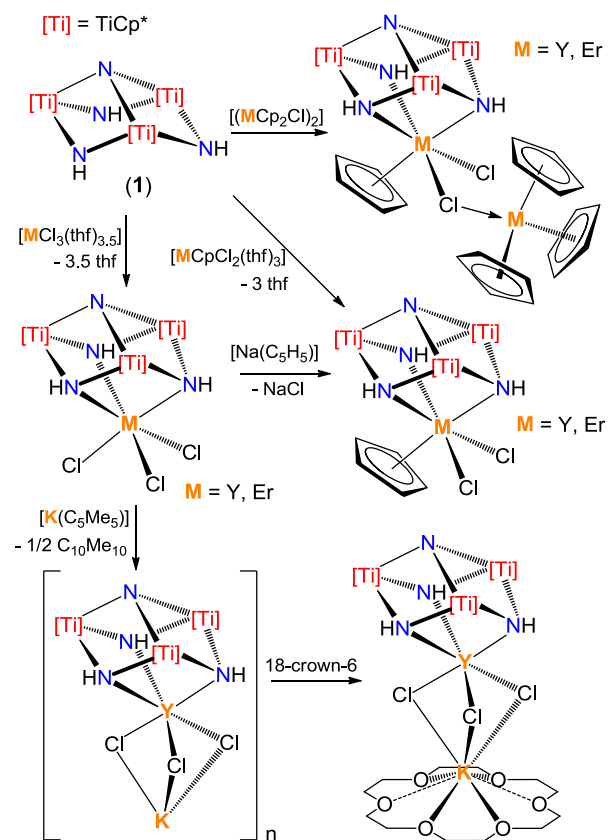
A series of titanium-Group 3/lanthanide metal cube-type adducts $[\text{X}_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{X} = \text{Cl}, \text{M} = \text{Sc}, \text{Y}, \text{La}, \text{Sm}, \text{Er}, \text{Lu}; \text{X} = \text{OTf}, \text{M} = \text{Y}, \text{Sm}, \text{Er}$) have been prepared by reaction of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with metal halide complexes $[\text{MCl}_3(\text{thf})_n]$ or metal trifluoromethanesulfonate derivatives $[\text{M}(\text{O}_3\text{SCF}_3)_3]$ (Scheme 11).^[79] The crystal structures of several isomorphous chloride complexes showed $[\text{MTi}_3\text{N}_4]$ ($\text{M} = \text{Sc}, \text{Er}, \text{Lu}$) cube-type cores with the neutral ligand $\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}$ coordinating in a tripodal fashion. In contrast, crystals of the triflate compounds presented severe disorder for an accurate determination of the structure, and analogous aryloxo derivatives $[(\text{ArO})_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Y}, \text{La}$) were prepared by treatment of yttrium or lanthanum chloride complexes with 3 equiv. of lithium 2,6-dimethylphenoxido LiOAr .



Scheme 11. Synthesis of Group 3 and lanthanides adducts.

The reaction of **1** with yttrium and erbium mono(cyclopentadienyl) derivatives $[\text{MCpCl}_2(\text{thf})_3]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) gave the adducts $[\text{CpCl}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Y, Er}$) (Scheme 12).^[80] Analogous treatment of **1** with bis(cyclopentadienyl) derivatives $[(\text{MCp}_2\text{Cl})_2]$ (0.5 or 1 equiv) in toluene at room temperature afforded complexes $[\text{Cp}_3\text{M}(\mu\text{-Cl})\text{ClCpM}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Y, Er}$). The monocyclopentadienyl adducts $[\text{CpCl}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Y, Er}$) were also obtained as orange solids by treatment of the trihalides with sodium cyclopentadienide (1 equiv.) in toluene at room temperature. In contrast, the analogous reaction of $[\text{Cl}_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with potassium pentamethylcyclopentadienide gave $\text{C}_{10}\text{Me}_{10}$ and $[\text{K}(\mu\text{-Cl})_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ as a green solid (Scheme 12).^[81] This species exhibits far-downfield and very broad resonances in the ^1H NMR spectrum and is paramagnetic, with one unpaired electron, according to magnetic moment measurements by the Evans method. This result, along with the exclusive formation of $\text{C}_{10}\text{Me}_{10}$ as byproduct, formed via coupling of pentamethylcyclopentadienyl radicals, suggests that the reaction pathway consists in an electron transfer from the C_5Me_5^- anion to the yttrium-titanium cube-type complex $[\text{Cl}_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. The resultant reduced species retains one potassium cation as part of the structure according to analytical data and reactivity studies. Crystallization of this compound in pyridine afforded the potassium-free $[\text{Cl}_2(\text{py})_2\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ complex with an yttrium center showing a distorted capped trigonal prismatic geometry. However, the reaction of $[\text{K}(\mu\text{-Cl})_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with 18-crown-6 or cryptand-222 leads to the molecular complex $[(18\text{-crown-6})\text{K}(\mu\text{-Cl})_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ or the ion pair $[\text{K}(\text{crypt-222})][\text{Cl}_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Figure 5), respectively. DFT calculations have elucidated the electronic structure of the

paramagnetic species, which should be regarded as containing trivalent yttrium bonded to the $\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}$ metalloligand radical anion.



Scheme 12. Synthesis of yttrium and erbium cyclopentadienyl complexes.

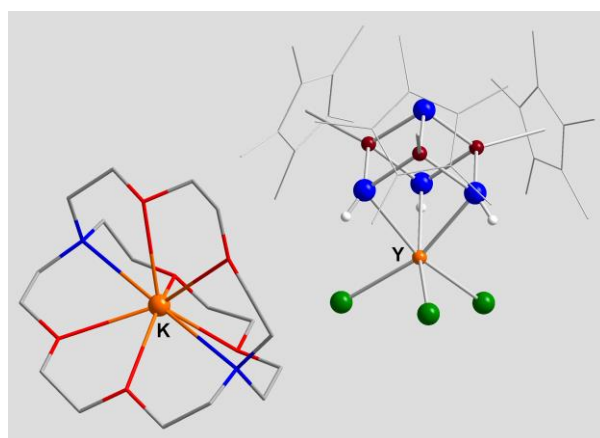
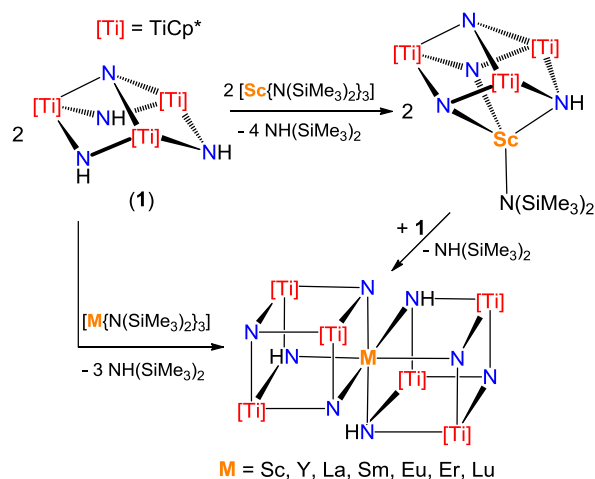


Figure 5. Crystal structure of complex $[\text{K}(\text{crypt-222})][\text{Cl}_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$.

Adapted from the original report.^[81]

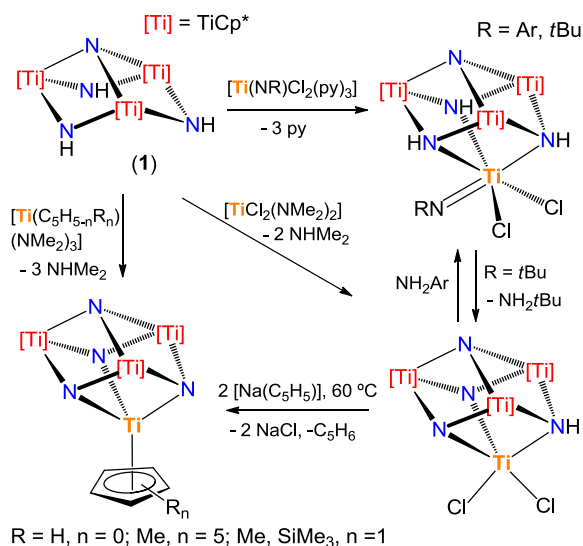
Complex **1** reacts with 0.5 equiv. of rare-earth bis(trimethylsilyl)amido derivatives $[M\{N(SiMe_3)_2\}_3]$ in toluene at 85-180 °C to afford the corner-shared double-cube nitrido compounds $[M(\mu_3-N)_3(\mu_3-NH)_3\{Ti_3Cp^*_3(\mu_3-N)\}_2]$ ($M = Sc, Y, La, Sm, Eu, Er, Lu$) via $NH(SiMe_3)_2$ elimination (Scheme 13).^[79] A single cube-type intermediate $[\{(Me_3Si)_2N\}Sc\{(\mu_3-N)_2(\mu_3-NH)Ti_3Cp^*_3(\mu_3-N)\}]$ was isolated in the treatment of **1** with 1 equiv. of the scandium bis(trimethylsilyl)amido derivative $[Sc\{N(SiMe_3)_2\}_3]$. The thermal decomposition in the solid state of several double-cube nitrido complexes was investigated by TGA/DTA measurements, as well as by pyrolysis experiments at 1100 °C under different atmospheres (Ar, H_2/N_2 , NH_3) for the yttrium complex. The ceramic yield and high carbon contents of the black residues obtained in the pyrolysis under argon and H_2/N_2 atmospheres indicated an inefficient removal of the pentamethylcyclopentadienyl groups in the precursor. However, the pyrolysis under a large flow of NH_3 led to the formation of a metal nitride material with a negligible carbon level.



Scheme 13. Synthesis of Group 3 and lanthanide double-cube complexes.

Group 4 and 5 metals

Reaction of **1** with the d^0 imidotitanium complexes $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ ($\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3, t\text{Bu}$) results in displacement of the pyridine (py) ligands and formation of the adducts $[\text{Cl}_2(\text{RN})\text{Ti}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Scheme 14).^[82,83] The *tert*-butylimido derivative decomposes in solution at room temperature to give NH_2tBu and $[\text{Cl}_2\text{Ti}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. This dichloride complex can also be obtained by treatment of **1** with $[\text{TiCl}_2(\text{NMe}_2)_2]$,^[84] and DFT calculations on a model compound suggested a structure with two azatitanocubanes connected by chloro bridges.^[83] A similar dimeric structure has been proposed for the monochloride complex $[(\text{Me}_2\text{NH})\text{ClTi}\{(\mu_3\text{-N})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, prepared by reaction of **1** with $[\text{TiCl}(\text{NMe}_2)_3]$, while its subsequent treatment with pyridine afforded the analogue complex $[(\text{py})_2\text{ClTi}\{(\mu_3\text{-N})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with a single cube-type structure.^[84]

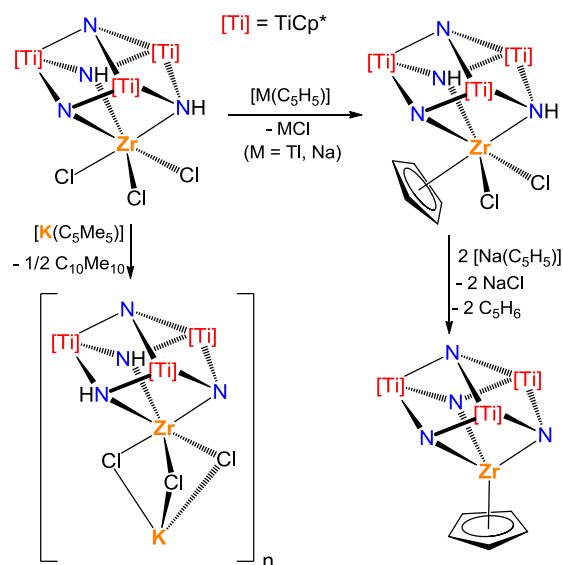


Scheme 14. Synthesis of titanium cube-type complexes.

The treatment of the chloride complexes $[\text{Cl}_{4-x}\text{Ti}\{(\mu_3\text{-N})_x(\mu_3\text{-NH})_{3-x}\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with $[\text{Na}(\text{C}_5\text{H}_5)]$ or $[\text{Li}\{\text{N}(\text{SiMe}_3)\}]$ afforded the titanium cyclopentadienyl or amido

derivatives $[\text{RTi}\{(\mu_3\text{-N})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \eta^5\text{-C}_5\text{H}_5, \text{N}(\text{SiMe}_3)_2$).^[84] A series of analogous cyclopentadienyl complexes $[(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)\text{Ti}\{(\mu_3\text{-N})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ were also obtained through the reaction of **1** with titanium tris(dimethylamido) derivatives $[\text{Ti}(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)(\text{NMe}_2)_3]$ at 110-150 °C (Scheme 14).^[37]

Zirconium and hafnium trichloride complexes $[\text{Cl}_3\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ were prepared by treatment of **1** with $[\text{MCl}_4(\text{thf})_2]$ reagents.^[84] The reaction of the zirconium trichloride complex with cyclopentadienyl thallium gave exclusively the dichloride-monocyclopentadienyl derivative $[(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Scheme 15), which exhibits a trigonal-twist rearrangement in solution as determined by dynamic NMR spectroscopy. However, the treatment with excess $[\text{Na}(\text{C}_5\text{H}_5)]$ causes further chloride replacement and subsequent cyclopentadiene elimination to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}\{(\mu_3\text{-N})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. The reaction in benzene- d_6 was monitored by NMR spectroscopy and the intermediates $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ClZr}\{(\mu_3\text{-N})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{ClZr}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ were characterized. The latter species was stabilized by incorporation of one $[\text{Mg}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ moiety in the magnesium complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mg}(\mu\text{-Cl})_2(\eta^5\text{-C}_5\text{H}_5)\text{Zr}\{(\mu_4\text{-N})(\mu_3\text{-N})(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Figure 6) prepared by reaction of $[\text{Cl}_3\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with $[\text{Mg}(\text{C}_5\text{H}_5)_2]$.



Scheme 15. Synthesis of zirconium cube-type complexes.

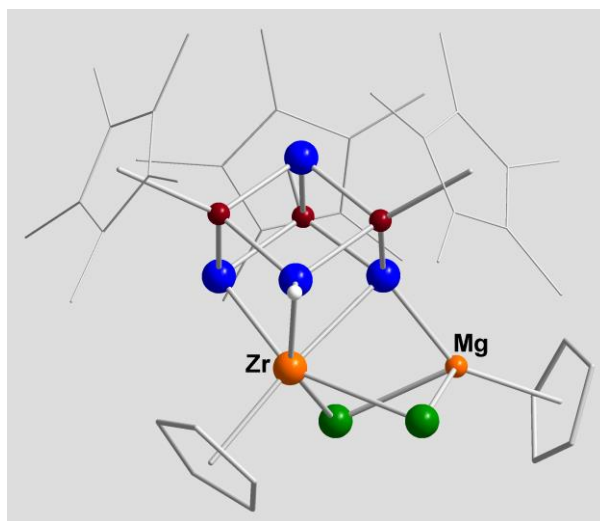


Figure 6. Crystal structure of complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mg}(\mu\text{-Cl})_2(\eta^5\text{-C}_5\text{H}_5)\text{Zr}\{(\mu_4\text{-N})(\mu_3\text{-N})(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. Adapted from the original report.^[84]

In contrast to the metathesis process with $[\text{M}(\text{C}_5\text{H}_5)_x]$ derivatives and subsequent C_5H_6 eliminations, the reaction of the zirconium trichloride complex with potassium pentamethylcyclopentadienide in toluene gave the paramagnetic derivative $[\text{K}(\mu\text{-Cl})_3\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ and $\text{C}_{10}\text{Me}_{10}$ (Scheme 15).^[84] This potassium complex has presumably a polymeric structure and reacts with one equivalent of 18-crown-

6 or cryptand-222 to give the molecular complex $[(18\text{-crown-}6)\text{K}(\mu\text{-Cl})_3\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Figure 7) or the ion pair $[\text{K}(\text{crypt-}222)][\text{Cl}_3\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, respectively.

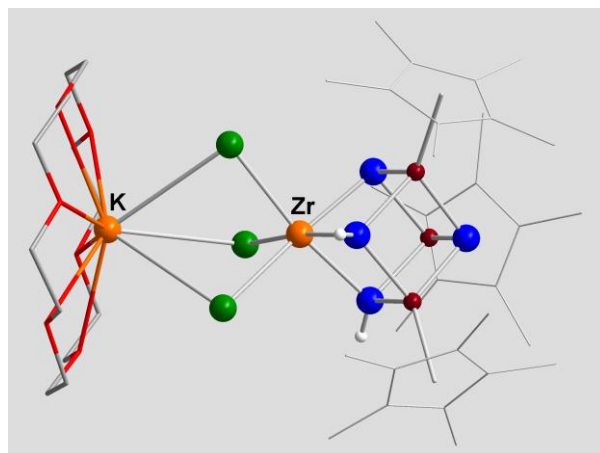
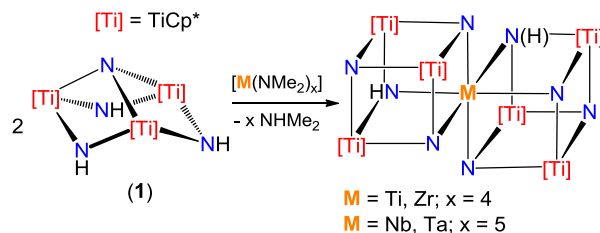


Figure 7. Crystal structure of complex $[(18\text{-crown-}6)\text{K}(\mu\text{-Cl})_3\text{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. Adapted from the original report.^[84]

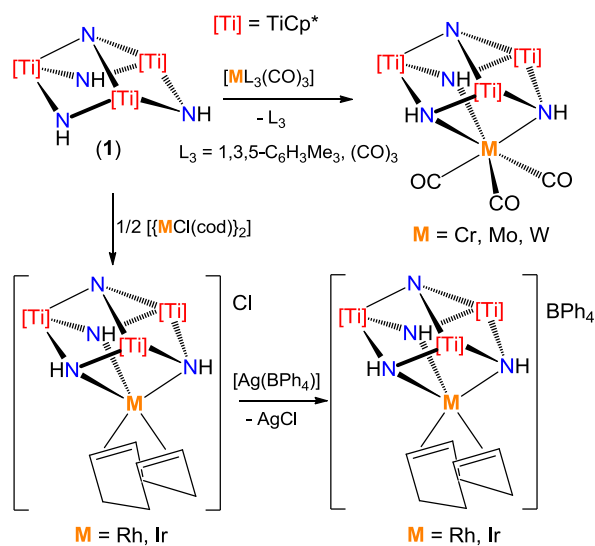
Finally, the reaction of compound **1** with 0.5 equiv. of homoleptic Group 4 and 5 amido complexes $[\text{M}(\text{NMe}_2)_x]$ ($x = 4$, $\text{M} = \text{Ti}, \text{Zr}$; $x = 5$, $\text{M} = \text{Nb}, \text{Ta}$) in toluene at $150\text{ }^\circ\text{C}$ gave the corner-shared double-cube derivatives $[\text{M}(\mu_3\text{-N})_x(\mu_3\text{-NH})_{6-x}\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Nb}, \text{Ta}$) (Scheme 16).^[82,83] Treatment of **1** with 0.5 equiv. of the d^0 imidoniobium and -tantalum derivatives $[\{\text{M}(\text{N}t\text{Bu})(\text{NH}t\text{Bu})\text{Cl}_2(\text{NH}_2t\text{Bu})\}_2]$ afforded complexes $[\text{Cl}_2(t\text{BuN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Nb}, \text{Ta}$), which react with 2,4,6-trimethylaniline at $70\text{ }^\circ\text{C}$ to form the analogous arylimido complexes.



Scheme 16. Synthesis of Group 4 and 5 corner-shared double-cube complexes.

Group 6-10 metals

The incorporation of $[\text{M}(\text{CO})_3]$ moieties ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) into the incomplete cube structure of **1** was performed by reaction at room temperature with $[\text{Mo}(\text{CO})_3(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)]$ or by irradiation with $[\text{M}(\text{CO})_6]$ (Scheme 17).^[85] The formation of the complexes $[(\text{CO})_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ is not accompanied by changes in the oxidation states of the metal centers but the metal carbonyl fragment shares electron density with the titanium atoms by means of metal–metal interactions according to DFT calculations (Figure 8).



Scheme 17. Synthesis of Group 6 and 9 cube-type complexes.

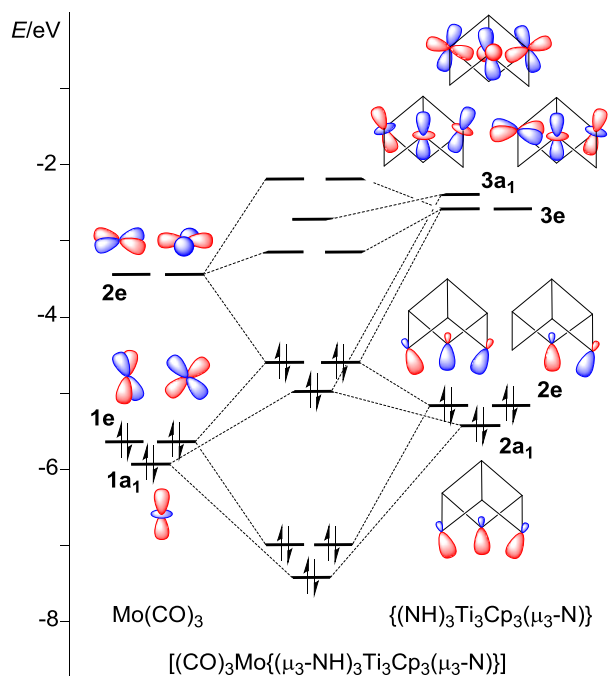
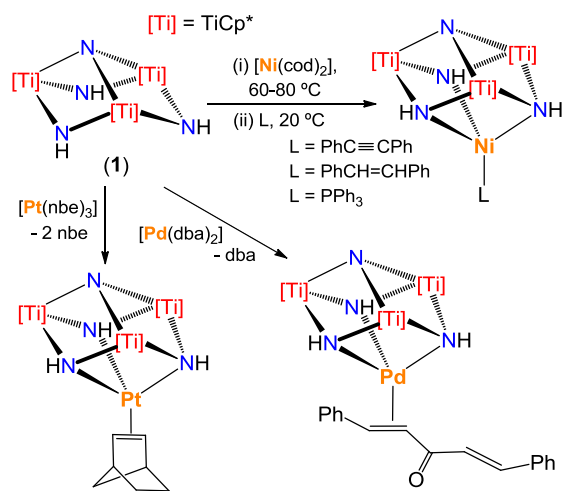


Figure 8. Interaction orbital diagram for complex $[(\text{CO})_3\text{Mo}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}_3(\mu_3\text{-N})\}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). Adapted from the original report.^[85]

The reaction of **1** with 0.5 equiv. of the Group 9 diolefin complexes $[\{\text{MCl}(\text{cod})\}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{cod} = 1,5\text{-cyclooctadiene}$) in toluene gave the precipitation of the ionic species $[(\text{cod})\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]\text{Cl}$ (Scheme 17).^[86] Their treatment with $[\text{Ag}(\text{BPh}_4)]$ led to anion metathesis and formation of the analogous compounds $[(\text{cod})\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}](\text{BPh}_4)$ which were characterized by X-ray crystallography in the case of iridium. Neutral Group 9-titanium complexes $[(\text{cod})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Rh}, \text{Ir}$) and $[(\text{C}_2\text{H}_4)_2\text{Rh}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ were obtained upon treatment of the diolefin complexes $[\{\text{MCl}(\text{cod})\}_2]$ and $[\{\text{RhCl}(\text{C}_2\text{H}_4)_2\}_2]$ with the lithium derivative $[\{\text{Li}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$. In a fashion similar to the d^6 Group 6 metal centers, DFT calculations showed that there is a sharing of the charge density between the d^8 metals and the Ti_3 core by means of metal–metal couplings.

Nickel(0) complexes $[\text{LNi}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ were prepared by treatment of **1** with $[\text{Ni}(\text{cod})_2]$ at 60-80 °C and subsequent addition of donor molecules L (PhC≡CPh, PhCH=CHPh, PPh₃) (Scheme 18).^[87] It appears that incorporation of Ni⁰ into the incomplete cube-type structure of **1** requires thermal decomposition of $[\text{Ni}(\text{cod})_2]$, whereas the analogous reactions of **1** with $[\text{Pd}(\text{dba})_2]$ (dba = dibenzylideneacetone) or $[\text{Pt}(\text{nbe})_3]$ (nbe = norbornene) proceed at room temperature to give the palladium(0) or platinum(0) complexes $[\text{LM}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (M = Pd, L = dba; M = Pt, L = nbe). IR and NMR spectroscopic data for the nickel complexes suggested a considerable sharing of electron density between the d¹⁰ metal center and the Ti₃ triangle.



Scheme 18. Synthesis of Group 10 cube-type complexes.

The oxidative addition with iodine of the toluene solution generated from heating **1** and $[\text{Ni}(\text{cod})_2]$ gave the nickel diiodide complex $[\text{I}_2\text{Ni}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. Similarly, the zerovalent palladium complex readily undergoes oxidative additions reactions with I₂ or dimethylacetylenedicarboxylate to give palladium(II) derivatives with the titanium metalloligand bound to the d⁸ metal center in a bidentate chelate fashion (Figure 9). The oxidation of the analogous platinum(0) species $[(\text{nbe})\text{Pt}\{(\mu_3\text{-}$

$(\text{NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}}]$ with excess iodine led to a cube-type $[\text{I}_3\text{Pt}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]^+$ cation with the Pt^{IV} (d^6) center stabilized by a *fac*-coordinating metalloligand **1**.

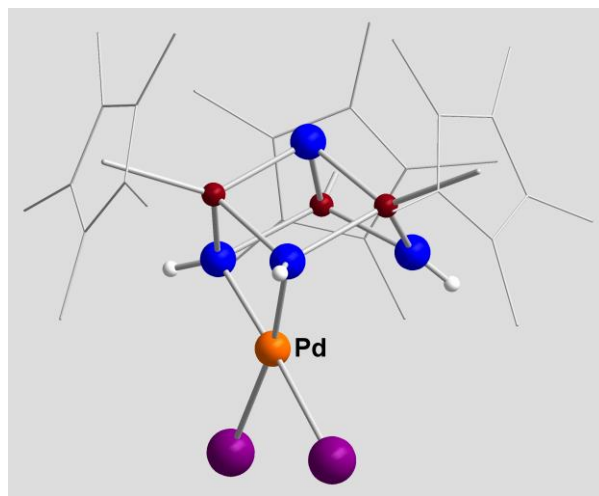
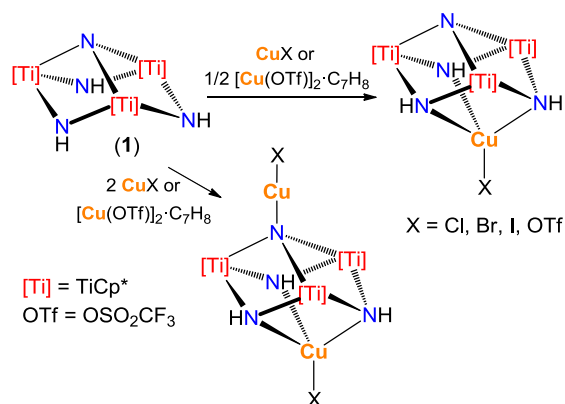


Figure 9. Crystal structure of complex $[\text{I}_2\text{Pd}\{(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})(\mu_3\text{-N})\}]$. Adapted from the original report.^[87]

Group 11 metals

Complex **1** entraps 1 equiv. of copper(I) halide or copper(I) trifluoromethanesulfonate through the basal NH imido groups to give cube-type adducts $[\text{XCu}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{X} = \text{Cl},^{[54]} \text{Br}, \text{I},^{[54]} \text{OSO}_2\text{CF}_3$) (Scheme 19).^[51] However, the treatment of **1** with an excess of copper reagents afforded complexes $[\text{XCu}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3\{(\mu_4\text{-N})\text{CuX}\}\}]$ by incorporation of an additional CuX fragment at the $\mu_3\text{-N}$ nitrido apical group.^[51] DFT calculations on model compounds confirmed the preference for the coordination through the three basal $\mu\text{-NH}$ groups over that by the apical $\mu_3\text{-nitrido}$ ligand. However, the energy differences are not too large ($\approx 25 \text{ kJ mol}^{-1}$), despite the higher coordination number in the first case, indicating that the copper-nitrogen apical bonds are stronger.



Scheme 19. Synthesis of copper(I) cube-type complexes.

Similarly, the tetranuclear nitrido derivative $[(\text{TiCp}^*)_4(\mu_3\text{-N})_4]$ is capable of incorporating one, two, or up to three CuX units at the $\mu_3\text{-N}$ ligands to give the complexes $[(\text{TiCp}^*)_4(\mu_3\text{-N})_{4-n}\{(\mu_4\text{-N})\text{CuX}\}_n]$ ($\text{X} = \text{Br}$, $n = 1$; $\text{X} = \text{Cl}$, $n = 2$; $\text{X} = \text{OSO}_2\text{CF}_3$, $n = 3$ (Figure 10)). DFT calculations demonstrated that the addition of MX units to $[(\text{TiCp}^*)_4(\mu_3\text{-N})_4]$ does not significantly reduce the Lewis basicity of the remaining $\mu_3\text{-nitrido}$ groups. Nevertheless, the incorporation of the fourth CuX fragment could not be obtained and the reaction of $[(\text{TiCp}^*)_4(\mu_3\text{-N})_4]$ with excess silver(I) trifluoromethanesulfonate produces only the incorporation of one $[\text{Ag}(\text{OSO}_2\text{CF}_3)]$ moiety.^[51] Indeed, complex **1** coordinates one equivalent of silver(I) halides at the basal positions to give cube-type adducts $[\text{XAg}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{X} = \text{Cl, I}$),^[88] but does not incorporate additional AgX fragments at the $\mu_3\text{-N}$ nitrido apical group. Furthermore, the analogous silver(I) triflate adduct $[(\text{CF}_3\text{SO}_2\text{O})\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ reacts with an excess of $\text{Ag}(\text{O}_3\text{SCF}_3)$ to give the triangular silver cluster $[(\text{CF}_3\text{SO}_2\text{O})_3\text{Ag}_3\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$, in which each face is capped by a titanium metalloligand (Figure 11), without participation of the $\mu_3\text{-N}$ ligands.^[89] In the same study, the reaction of **1** with a half equivalent of $\text{Ag}(\text{O}_3\text{SCF}_3)$ gave the ionic complex $[\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2](\text{O}_3\text{SCF}_3)$.

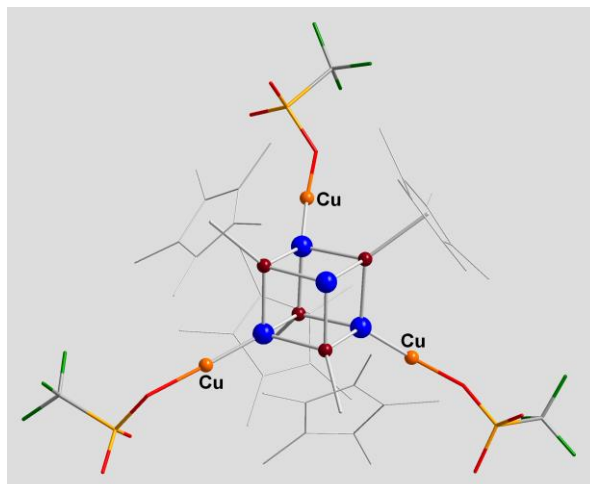


Figure 10. Crystal structure of complex $[(\text{TiCp}^*)_4(\mu_3\text{-N})\{(\mu_4\text{-N})\text{CuOSO}_2\text{CF}_3\}_3]$. Adapted from the original report.^[51]

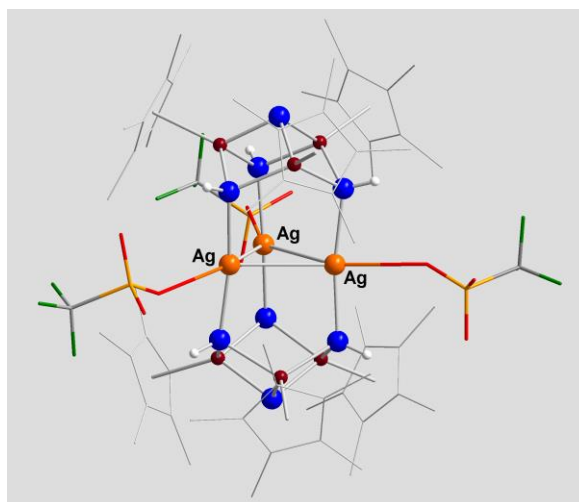
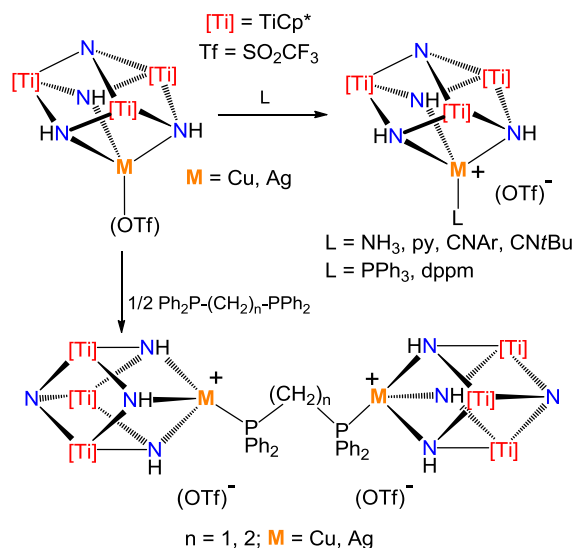


Figure 11. Crystal structure of complex $[(\text{CF}_3\text{SO}_2\text{O})_3\text{Ag}_3\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$. Adapted from the original report.^[89]

The trifluoromethanesulfonate ligand in complexes $[(\text{CF}_3\text{SO}_2\text{O})\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ is easily displaced by donor molecules L to give a series of copper(I) and silver(I) ionic compounds $[\text{LM}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}](\text{O}_3\text{SCF}_3)$ (L = NH₃, py, CNR, PPh₃) (Scheme 20).^[90] Similar reaction with methylenebis(diphenylphosphane) (dppm) in a 1:1 ratio led to the single cube-type complexes $[(\text{dppm})\text{M}\{(\mu_3\text{-$

$(\text{NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}](\text{O}_3\text{SCF}_3)$, whereas in a 2:1 ratio gave the bisphosphane-bridged double-cube compounds $[\{\text{M}(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2(\mu\text{-dppm})](\text{O}_3\text{SCF}_3)_2$ ($\text{M} = \text{Cu}, \text{Ag}$). Analogous double-cube complexes $[\{\text{M}(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2(\mu\text{-dppe})](\text{O}_3\text{SCF}_3)_2$ were obtained with a half equivalent of ethane-1,2-diylbis(diphenylphosphane) (dppe) and the copper ionic derivative was characterized by an X-ray crystallographic determination (Figure 12).



Scheme 20. Synthesis of copper(I) and silver(I) ionic compounds.

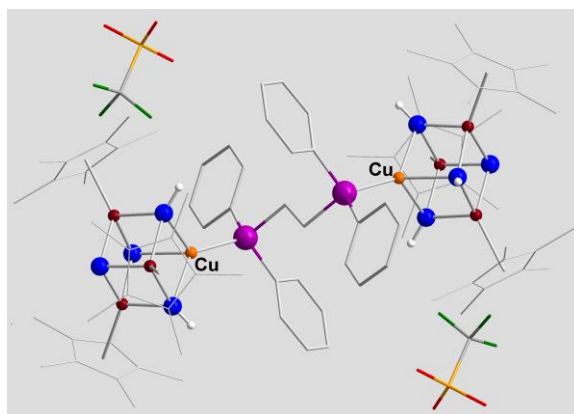
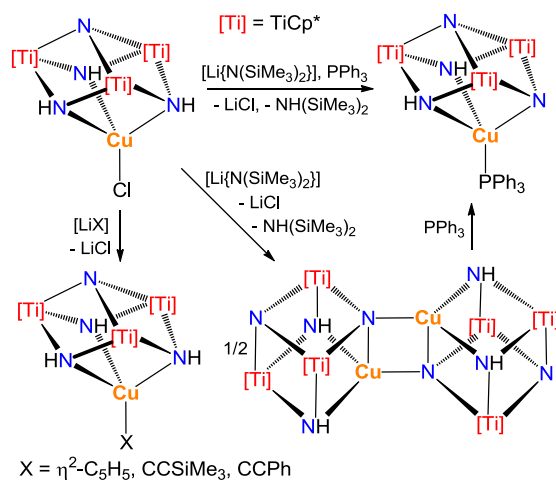


Figure 12. Crystal structure of complex $[\{\text{Cu}(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2(\mu\text{-dppe})](\text{O}_3\text{SCF}_3)_2$. Adapted from the original report.^[90]

Treatment of the copper(I) chloride derivative $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with lithium bis(trimethylsilyl)amide led to $\text{NH}(\text{SiMe}_3)_2$ and the precipitation of crystals of the edge-linked double-cube complex $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (Scheme 21).^[54] This compound was also prepared in higher yield through the reaction of **1** with $[\{\text{CuN}(\text{SiMe}_3)_2\}_4]$ at 150 °C. The addition of triphenylphosphane to the double-cube complex produced the single cube-type complex $[(\text{Ph}_3\text{P})\text{Cu}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$.



Scheme 21. Reactions of the copper(I) chloride adduct.

While intermediates could not be observed in the reaction of $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$, the analogous treatment with lithium cyclopentadienide or lithium acetylides gave the cube-type adducts $[\text{XCu}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{X} = \eta^2\text{-C}_5\text{H}_5, \text{C}\equiv\text{CSiMe}_3, \text{C}\equiv\text{CPh}$) (Scheme 21).^[91] The cyclopentadienyl derivative decomposed in solution to generate the edge-linked double-cube nitrido complex via C_3H_6 elimination. However, solutions of the alkynyl derivatives led to copper(I) acetylide-bridged double-cube complexes $[\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-}$

$C\equiv CR)Cu(\mu_4-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)_2]$ ($R = SiMe_3, Ph$) (Figure 13) along with **1** and $RC\equiv CH$.

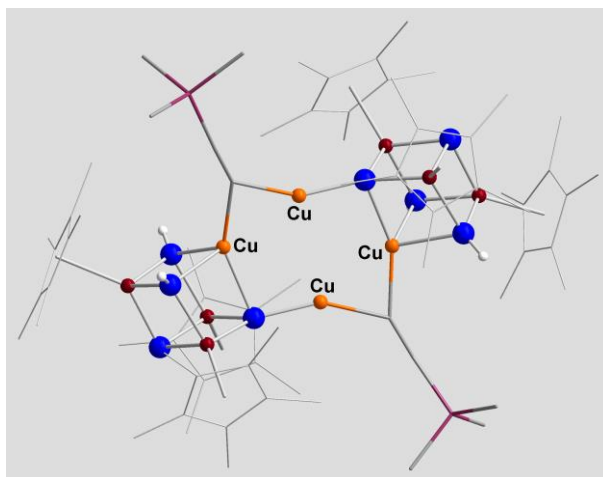


Figure 13. Crystal structure of complex $[\{Cu(\mu-1\kappa C^1:2\kappa C^1-C\equiv CSiMe_3)Cu(\mu_4-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)_2\}]_2$. Adapted from the original report.^[91]

The molecular silver(I) chloride adduct $[ClAg\{(\mu_3-NH)_3Ti_3Cp^*_3(\mu_3-N)\}]$ reacted with $[Li\{N(SiMe_3)_2\}]$ to afford the nitrido complex $[Ag_2\{(\mu_3-N)(\mu_3-NH)Ti_3Cp^*_3(\mu-NH)(\mu_3-N)_2\}]$ where two $[Ti_3N_4]$ units are linked by two silver atoms in a linear geometry (Figure 14).^[88] The Ag–Ag separation of 2.966(1) Å and the outward angle N–Ag–N of 165.1(1)° could be indicative of metallophilic attraction.

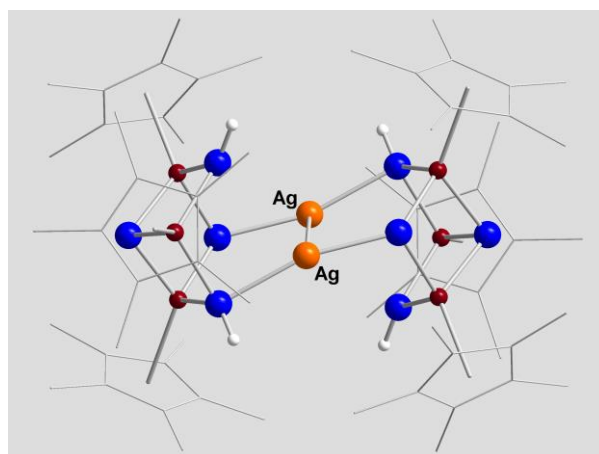
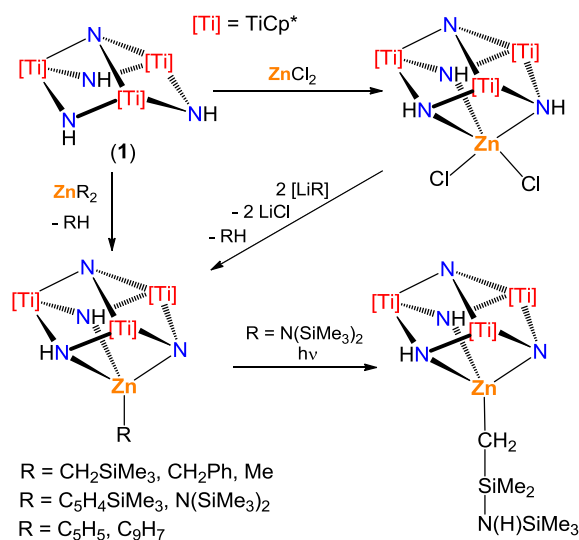


Figure 14. Crystal structure of complex $[\text{Ag}_2\{(\mu_3\text{-N})(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})(\mu_3\text{-N})\}_2]$.

Adapted from the original report.^[88]

Group 12 metals

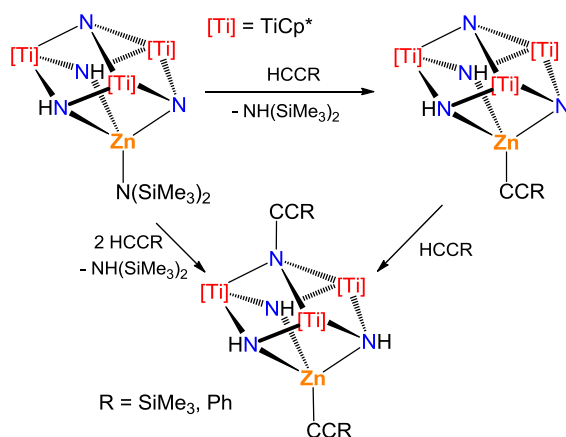
Treatment of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with zinc complexes ZnR_2 led to $[\text{RZn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2, \text{CH}_2\text{SiMe}_3, \text{Me}, \text{CH}_2\text{Ph}, \text{C}_5\text{H}_4\text{SiMe}_3$) via RH elimination (Scheme 22).^[54] The reactions most likely involve the formation of adducts, but only the derivative $[(\text{Me}_3\text{SiCH}_2)_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ was identified by NMR spectroscopy. The amido compound decomposed in the presence of ambient light to generate the isomeric alkyl species $[(\text{Me}_3\text{Si})\text{HN}(\text{Me})_2\text{SiCH}_2]\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$.



Scheme 22. Synthesis of zinc cube-type complexes.

The metalloligand **1** reacted with zinc dichloride in toluene at room temperature to produce the adduct $[\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, which upon treatment with lithium reagents $[\text{LiR}]$ provided an alternative route to zinc derivatives $[\text{RZn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Scheme 22). The reaction of the amido compound

$[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ with 1 equiv. of terminal alkyne $\text{RC}\equiv\text{CH}$ in toluene gives the expected zinc acetylides $[(\text{RC}\equiv\text{C})\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{SiMe}_3, \text{Ph}$) via amine elimination (Scheme 23).^[92] Surprisingly, these complexes are able to react with 1 equiv. of terminal alkyne affording the alkynylimido clusters $[(\text{RC}\equiv\text{C})\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-NC}\equiv\text{CR})\}]$ ($\text{R} = \text{SiMe}_3, \text{Ph}$). DFT calculations demonstrate that this process involves a two-electron reduction of the Ti_3 fragment. The proposed mechanism consists of a concerted C-H bond activation leading to an alkynyltitanium complex, followed by alkynyl migration to the apical nitrido ligand.



Scheme 23. Synthesis of zinc alkynyl complexes.

In a way similar to zinc, the reaction of the preorganized ligand **1** with cadmium halides in toluene afforded the molecular adducts $[\text{X}_2\text{Cd}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{X} = \text{Cl}, \text{I}$).^[93] The X-ray structural analysis of the iodide complex reveals two cube-type units associated by long-range interactions between the cadmium atom of one fragment and the iodine atom of the other (Figure 15). Treatment of the cadmium chloride adduct with 2 equiv. of lithium amido, alkyl, cyclopentadienyl and alkynyl derivatives $[\text{LiR}]$ afforded the cube-type compounds $[\text{RCd}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2, \text{CH}_2\text{SiMe}_3, \text{C}_5\text{H}_4\text{SiMe}_3, \text{C}\equiv\text{CSiMe}_3$). The amido derivative reacted with 1 equiv. of complex **1** to give

the corner-shared double-cube complex $[\text{Cd}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ by means of $\text{NH}(\text{SiMe}_3)_2$ elimination.

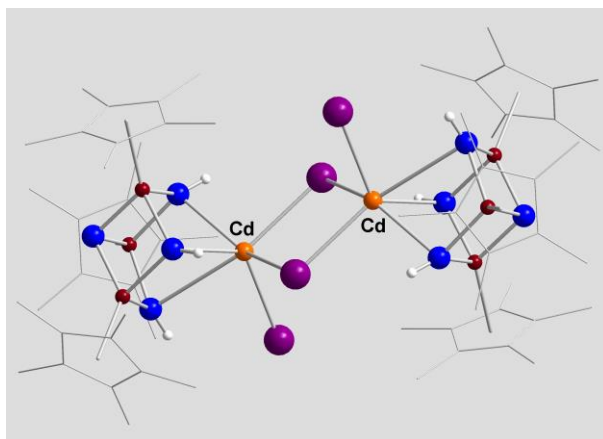
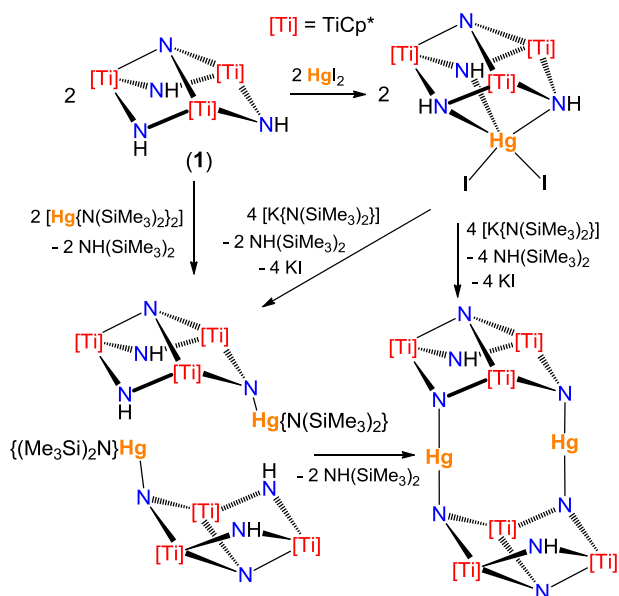


Figure 15. Crystal structure of complex $[\text{I}_2\text{Cd}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$. Adapted from the original report.^[93]

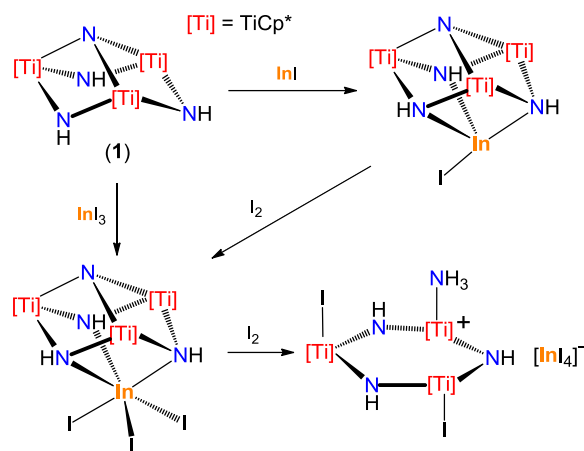
Lastly, treatment of the metalloligand **1** with mercury(II) iodide gave the adduct $[\text{I}_2\text{Hg}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, which reacted with $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ to afford $[\text{Hg}_2\{(\mu_3\text{-N})_2\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})(\mu_3\text{-N})\}_2]$ through the amido mercury intermediate $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Hg}\{(\mu_3\text{-N})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ (Scheme 24).^[93] The X-ray crystal structure of the $[\text{Hg}_2\{(\mu_3\text{-N})_2\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})(\mu_3\text{-N})\}_2]$ shows two linear mercury atoms bridging two incomplete cube $[\text{Ti}_3\text{N}_4]$ units.^[88] An analogous compound $[\text{Hg}\{(\mu_3\text{-N})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}_2]$ with one mercury atom between two titanium trinuclear systems was obtained upon treatment of HgI_2 with the potassium derivative $[\{\text{K}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$.



Scheme 24. Synthesis of mercury complexes.

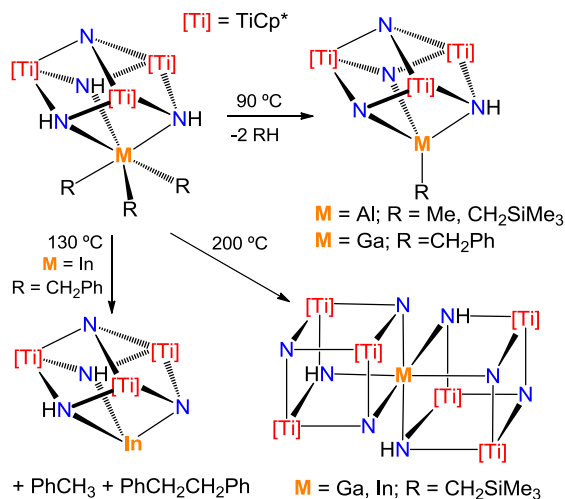
Group 13-15 metals

Complex **1** is able to break the polymeric chain structure of cyclopentadienyl thallium in toluene to afford the adduct $[(\eta^5\text{-C}_5\text{H}_5)\text{Tl}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]\cdot\text{C}_7\text{H}_8$ whereas in hexane gives $[(\eta^5\text{-C}_5\text{H}_5)\text{Tl}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)\text{Tl}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ where the metalloligand coordinates to a dimeric thallium fragment $[\text{Tl}(\eta^5\text{-C}_5\text{H}_5)]_2$.^[74] Analogous treatment of **1** with Group 13 monoiodides MI or indium triiodide led to single cube-type complexes $[\text{IM}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (M = In, Tl) or $[\text{I}_3\text{In}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (Scheme 25).^[75] The latter complex can also be prepared through the oxidative addition of iodine to the indium(I) derivative $[\text{In}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, but with excess iodine gave the ionic complex $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\text{I})_2(\text{NH}_3)][\text{InI}_4]$.^[94] The ionic complex $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\text{I})_2(\text{NH}_3)][\text{I}_3]$, with the same trinuclear titanium cation, was obtained in the treatment of **1** with an excess of iodine.



Scheme 25. Synthesis of indium complexes.

Treatment of **1** with trialkyl derivatives of aluminum, gallium or indium $[\text{MR}_3]$ or chloromethylaluminum $[\text{AlCl}_{3-n}\text{Me}_n]$ ($n = 1, 2$) at room temperature afforded the adducts $[\text{R}_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{M} = \text{Al, Ga, In}$; $\text{R} = \text{CH}_2\text{Ph}$, $\text{M} = \text{Ga, In}$) or $[\text{Me}_n\text{Cl}_{3-n}\text{Al}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$.^[95] The analogous reaction of **1** with $[\text{AlMe}_3]$ at 90 °C gave the methylaluminum derivative $[\text{MeAl}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ via methane elimination (Scheme 26). The thermal decomposition of adducts $[\text{R}_3\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ afforded further examples of Group 13 monoalkyl complexes $[\text{RM}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Al}$, $\text{R} = \text{CH}_2\text{SiMe}_3$; $\text{M} = \text{Ga}$, $\text{R} = \text{CH}_2\text{Ph}$) or corner-shared double-cube complexes $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Ga, In}$). However, the heating of the tribenzyl indium(III) derivative led to $[\text{In}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$, toluene and bibenzyl in a 1:1:1 ratio. This indium(I) compound and also the analogous thallium(I) derivative $[\text{Tl}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ could be prepared through the metathesis reaction of indium or thallium monochlorides with $[\{\text{Li}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$.^[53]



Scheme 26. Thermal behavior of adducts with Group 13 trialkyl derivatives.

The reaction of **1** with $[\text{Al}\{\text{N}(\text{SiMe}_3)_2\}_3]$ in toluene at 110 °C gave the monoamido complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Al}\{\mu_3\text{-N}\}_2\{\mu_3\text{-NH}\}\text{Ti}_3\text{Cp}^*_3\{\mu_3\text{-N}\}]$, whereas the analogous treatment with the gallium or indium derivatives $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3]$ at 200 °C led to the precipitation of the corner-shared double-cube complexes $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (M = Ga, In).^[96] Interestingly, the reaction of **1** with $[\{\text{Ga}(\text{NMe}_2)_3\}_2]$ at 110 °C afforded the novel digallane $[\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\}\text{Ti}_3\text{Cp}^*_3\{\mu_3\text{-N}\}]_2$ complex in which two $[\text{GaTi}_3\text{N}_4]$ units are linked through a gallium-gallium single bond (Figure 16). A singular aluminum-titanium square-pyramidal aggregate $[\{(\text{Me}_3\text{Si})_2\text{N}\}\text{Cl}_3\text{Al}_2\{\mu_3\text{-N}\}(\mu_3\text{-NH})_2\{\text{Ti}_3\text{Cp}^*_3(\mu\text{-Cl})(\mu_3\text{-N})\}]$ was obtained by reaction of **1** with the aluminum chloroamido derivative $[\text{AlCl}_2\{\text{N}(\text{SiMe}_3)_2\}(\text{OEt}_2)]$.

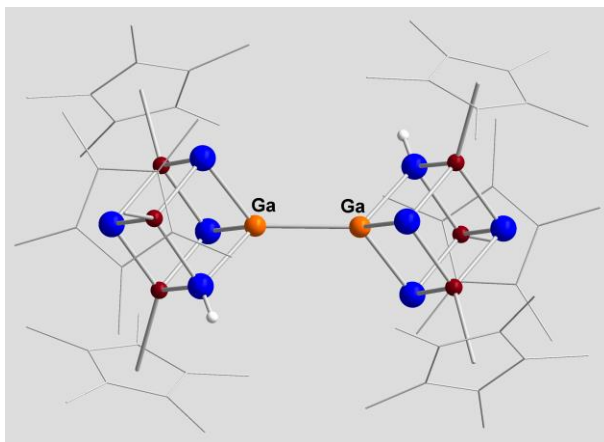


Figure 16. Crystal structure of complex $[\{\text{Ga}(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$. Adapted from the original report.^[96]

On the other hand, Group 14 alkyl complexes $[\text{Me}_3\text{M}\{(\mu_3\text{-N})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) were prepared through the reaction of the lithium compound $[\{\text{Li}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ with silicon, germanium and tin chlorotrimethyl derivatives MClMe_3 .^[53,95] The compounds exhibit incomplete cube structures in the solid state as determined by X-ray crystallographic studies (see Figure 17 for the germanium complex) as well as in solution according to NMR data.

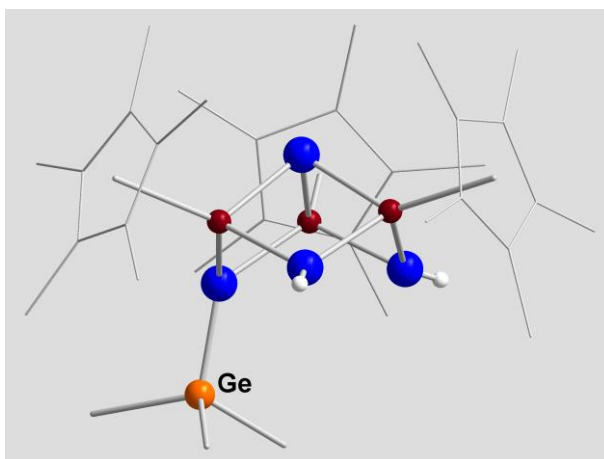
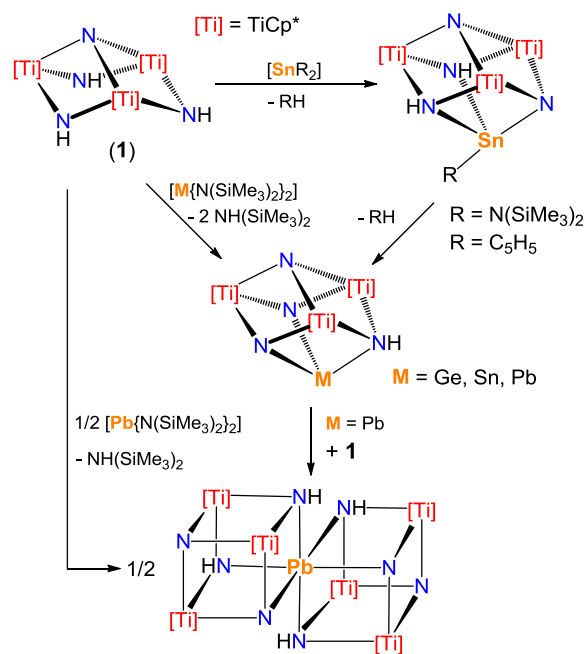


Figure 17. Crystal structure of complex $[\text{Me}_3\text{Ge}\{(\mu_3\text{-N})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$. Adapted from the original report.^[95]

Complex **1** reacted with 1 equiv. of divalent germanium, tin or lead amido complexes $[M\{N(SiMe_3)_2\}_2]$ to give the cube-type derivatives $[M\{(\mu_3-N)_2(\mu_3-NH)Ti_3Cp^*_3(\mu_3-N)\}]$ ($M = Ge, Sn, Pb$) (Scheme 27).^[96] Monitoring the reaction of **1** with $[Sn\{N(SiMe_3)_2\}_2]$ and $[Sn(\eta^5-C_5H_5)_2]$ by NMR spectroscopy allowed the identification of the intermediates $[RSn\{(\mu_3-N)(\mu_3-NH)_2Ti_3Cp^*_3(\mu_3-N)\}]$ ($R = N(SiMe_3)_2, \eta^5-C_5H_5$). Stable tin(II) and lead(II) adducts $[X_2M\{(\mu_3-NH)_3Ti_3Cp^*_3(\mu_3-N)\}]$ ($M = Sn, X = Cl, I; M = Pb, X = Cl$) were isolated in the treatment of **1** with dihalides MX_2 .^[75] The X-ray crystal structure determination for the tin dichloride adduct shows two molecules associated by a $Sn\cdots Sn$ interaction (Figure 18), while the solid-state structure for the analogous tin diiodide complex reveals two cube-type $[SnTi_3N_4]$ units linked by two bridging iodine atoms.



Scheme 27. Synthesis of Group 14 cube-type complexes.

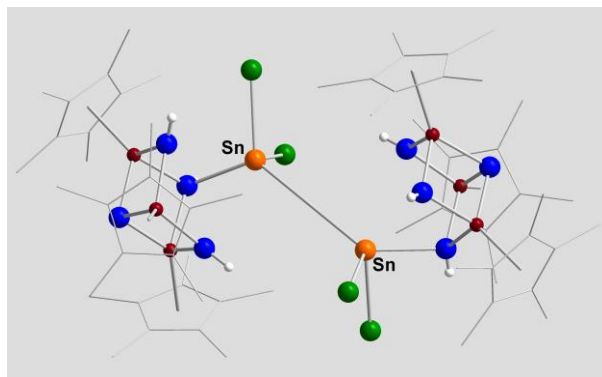


Figure 18. Crystal structure of complex $[\text{Cl}_2\text{Sn}\{(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu\text{-NH})_2(\mu_3\text{-N})\}]$. Adapted from the original report.^[75]

Finally, addition of 1 equiv. of the metalloligand **1** to a solution of the lead(II) derivative $[\text{Pb}\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ or the treatment of **1** with a half equivalent of $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ afforded the corner-shared double-cube compound $[\text{Pb}(\mu_3\text{-N})_2(\mu_3\text{-NH})_4\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (Scheme 27). Analogous Group 15 derivatives $[\text{M}(\mu_3\text{-N})_3(\mu_3\text{-NH})_3\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Sb}, \text{Bi}$) were obtained through the reaction of **1** with the antimony and bismuth tris(dimethylamido) reagents $[\text{M}(\text{NMe}_2)_3]$. X-ray crystal structures of the lead(II) and bismuth(III) double-cube complexes show trigonal antiprismatic geometries around the Group 14 and 15 atoms, and consequently the lone pair on those metal centers appears to be stereochemically inactive.^[96]

Conclusion

The research on polynuclear nitrido complexes derived from the trinuclear titanium(IV) imido-nitrido species $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) has uncovered a diverse spectrum of chemical structure and reactivity. The enormous potential of **1** to form heterometallic complexes with cube-type $[\text{MTi}_3\text{N}_4]$ cores is illustrated by the possibility of

incorporating most of the metallic elements of the Periodic Table into its incomplete cube structure. Further indication of the versatility of the titanium metalloligand is the capacity of stabilizing complexes with metal centers in low (e.g. Mo⁰, Ir^I and Pt⁰) or high oxidation states (e.g. Zr^{IV}, Ta^V and Pt^{IV}). Although the main driving force in the coordination of **1** is the electron donation of the nitrogen atom lone pair of the NH imido ligands to the incorporated metals, theoretical calculations performed on complexes of low-valent transition metals showed that the presence of Ti^{IV} centers in the metalloligand produces an additional stabilization through metal–metal couplings. Furthermore, while the preorganized structure of **1** appears to be particularly appropriated for coordinating in a conventional tridentate chelate mode to a single metal center, examples of metal complexes with titanium imido-nitrido metalloligands binding in monodentate or bidentate fashion have been also described. In addition to the possibility of acting as a neutral ligand, the N–H bonds in **1** can also be subsequently activated to give nitrido groups bridging different metal centers. Most of these heterometallic species feature triply bridging nitrido moieties adopting a pyramidal geometry. However, a few cage compounds contain μ_4 -nitrido ligands in the rare tetrahedral or basal trigonal pyramidal arrangements.

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to the understanding of our polynuclear systems and their contributions are thanked. Finally, and most importantly, the authors save the greatest gratitude for the graduate and undergraduate students who have been the backbone of this research effort. Their names are given in the appropriate references below.

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