

MOLECULAR NITRIDES CONTAINING TITANIUM AND GROUP 1, 2 OR 12 ELEMENTS

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Chapter 1. Introduction

Transition-metal nitrido complexes have been studied extensively in the past few decades.^[1] Besides complexes with a terminal nitrido functionality $[M]\equiv N$, there are also polynuclear compounds with nitrido bridges. Polynuclear nitrido complexes are promising precursors in the synthesis of metal nitride materials.^[2] Moreover, these compounds are referred as models or intermediates in dinitrogen fixation and activation processes.^[3] Finally, nitrido complexes are also of wide interest in theoretical studies.^[4]

In this context, early transition-metal nitrido complexes usually exhibit complicated polynuclear structures, whose characterization can be extremely hard.^[5] In many cases, the nitrido (N^{3-}) group is accompanied by amido (NH_2^-) or imido (NH^{2-}) ligands, like those found in the imido-nitrido titanium complex $[TiCp^*(\mu-NH)]_3(\mu_3-N)$ (**1**) ($Cp^* = \eta^5-C_5Me_5$).^[6] The structure determined for **1** shows an incomplete cube $[Ti_3N_4]$ core with three NH electron donor imido groups in the base, which resembles those found in chalcogenide-bridged compounds with $[M_3Q_4]$ cores. These M_3Q_4 aggregates are useful precursors on the synthesis of cube-type $[M'M_3Q_4]$ clusters via incorporation of heterometals M' into their incomplete cube structure.^[7] On the basis of this similarity, our initial work has shown that **1** is capable of acting as a neutral tridentate ligand to d^0 , d^6 and d^8 transition metal centers through the basal NH groups.^[8,9] These imido groups can also be deprotonated if the coordination sphere of the incorporated metal contains imido, amido or alkyl ligands, to give anionic forms of **1**, via elimination of amine or alkane.^[9,10] In main-group chemistry, we have demonstrated the ability of **1** to coordinate metal halides and cyclopentadienides to yield stable adducts.^[11]

In this way, our group has reported a new family of polynuclear nitrido complexes with cube-type structures (azaheterometallobucubanes), and in this Thesis, we describe a systematic study on the incorporation of s-block metals and Group 12 elements into the preorganized structure of complex **1**.

Chapter 2. Azaheterometallocubanes of Titanium with Group 1 or 2 elements

Treatment of $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) with alkali-metal bis(trimethylsilyl)amido derivatives $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ affords edge-linked double-cube nitrido complexes $[\text{M}(\mu_4\text{-N})(\mu_3\text{-NH})_2\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_2$ ($\text{M} = \text{Li}$ (**2**), Na (**3**), K (**4**), Rb (**5**), Cs (**6**)) or corner-shared double-cube nitrido complexes $[\text{M}(\mu_3\text{-N})(\mu_3\text{-NH})_5\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ ($\text{M} = \text{Na}$ (**7**), K (**8**), Rb (**9**), Cs (**10**)) depending on reagents ratio (1:1 or 2:1) and reaction conditions.

The preorganized ligand **1** reacts with one equivalent of magnesium amido-, alkyl- and cyclopentadienyl compounds $[\text{MgR}_2(\text{thf})_n]$ to give single cube-type molecular nitrides $[\text{RMg}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**11**), CH_2CMe_3 (**12**), CH_2Ph (**13**), Cp (**14**)). Analogous reactions with the heavier alkaline-earth bis(trimethylsilyl)amido derivatives $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$ allow to isolate or identify new single cube-type complexes $[(\text{thf})\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Ca}$ (**16**), Sr (**17**), Ba (**18**)).

The magnesium amido **11** and cyclopentadienyl **14** complexes are stable in solution for long periods of time, but magnesium alkyls (**12** and **13**) and derivatives bearing the heavier alkaline-earth elements (**16**, **17** and **18**) undergo ligand redistribution reactions to give corner-shared metallodibicubanes $[\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_2$ ($\text{M} = \text{Mg}$ (**15**), Ca (**19**), Sr (**20**), Ba (**21**)). Those compounds were also prepared through the reaction of the metalloligand **1** with the corresponding Group 2 amido reagent on a 2:1 ratio.

The tetrahydrofuran molecules of calcium and strontium derivatives **16** and **17** are easily displaced with 4-*tert*-butylpyridine, affording the analogous compounds $[(t\text{Bupy})\{(\text{Me}_3\text{Si})_2\text{N}\}\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Ca}$ (**22**), Sr (**23**)) with an enhanced thermal stability, but their solutions still decompose at room temperature to give the insoluble double-cube complexes **19** and **20**.

On the other hand, treatment of **16** and **11** with anilines NH_2Ar in toluene affords the arylamido complexes $[(\text{ArHN})\text{M}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_n$ ($\text{M} = \text{Ca}$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $n = 2$ (**24**); $\text{M} = \text{Mg}$, $\text{Ar} = 4\text{-MeC}_6\text{H}_4$, $n = 1$ (**25**)). Derivatives **24** and **25** react with chloroform- d_1 at room temperature to give the

metal halide adducts $[\text{Cl}_2\text{M}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{M} = \text{Ca}$ (**26**), Mg (**27**)). A solution of **25** in *n*-hexane gave complex $[\{\mu\text{-NH}(4\text{-MeC}_6\text{H}_4)\}_3\text{Mg}_2\{(\mu_3\text{-N})(\mu_3\text{-NH})_5[\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})]_2\}]$ (**28**), which shows three μ -4-methylanilido ligands bridging two $[\text{MgTi}_3\text{N}_4]$ cube-type cores according to an X-ray crystal structure determination.

Chapter 3. Azaheterometallocubanes of Titanium with Group 12 elements

Part I. Azaheterometallocubanes of Titanium with Zinc

Treatment of **1** with zinc complexes $[\text{ZnR}_2]$ leads to $[\text{RZn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**29**), CH_2SiMe_3 (**30**), Me (**31**), CH_2Ph (**32**), $\text{C}_5\text{H}_4(\text{SiMe}_3)$ (**34**)) via RH elimination. The reactions most likely involve the formation of adducts, but only the derivative $[(\text{Me}_3\text{SiCH}_2)_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**33**) has been identified by NMR spectroscopy. The amido compound **29** decomposes in the presence of ambient light to generate the alkyl complex $[\{(\text{Me}_3\text{Si})\text{HN}(\text{Me})_2\text{SiCH}_2\}\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**35**).

The metalloligand **1** reacts with zinc dichloride in toluene at room temperature to produce the adduct $[\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**36**). Attempts to crystallize **36** in dichloromethane gave yellow crystals of the ammonia compound $[(\text{H}_3\text{N})\text{Cl}_2\text{Zn}\{(\mu_3\text{-NH})(\mu\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**36b**). Treatment of chloride complex **36** with lithium reagents $[\text{LiR}]$ provides an alternative route to **29**, **30**, **34** or the new cyclopentadienyl and indenyl zinc derivatives $[\text{RZn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{C}_5\text{H}_5$ (**37**), C_9H_7 (**38**)).

The reaction of the amido compound **29** with one equivalent of terminal alkyne $\text{RC}\equiv\text{CH}$ in toluene gives the expected zinc acetylides $[(\text{RC}\equiv\text{C})\text{Zn}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{CMe}_3$ (**39**), SiMe_3 (**40**), Ph (**41**)) via amine elimination. Surprisingly, complexes **40** and **41** are able to react with one equivalent of terminal alkyne affording the first alkynylimido clusters $[(\text{RC}\equiv\text{C})\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-NC}\equiv\text{CR})\}]$ ($\text{R} = \text{SiMe}_3$ (**42**), Ph (**43**)). DFT calculations performed by the research group of Josep Maríà Poblet (Department de Química Física i Inorgànica, Universitat Rovira i Virgili, Tarragona) 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. Compounds **41** and **43** can also be prepared by the treatment of the metalloligand **1** with $[\text{Zn}(\text{C}\equiv\text{CPh})_2]$. In addition, the methyl derivative **31** reacts with terminal alkynes to give $[\text{MeZn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-NC}\equiv\text{CR})\}]$ ($\text{R} = \text{SiMe}_3$ (**44a**), Ph (**44b**)), but these alkynylimido clusters have been only identified by NMR spectroscopy.

Part II. Azaheterometallocubanes of Titanium with Cadmium/Mercury

The reaction of the preorganized ligand **1** with cadmium dichloride in toluene at room temperature affords $[\text{Cl}_2\text{Cd}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**45**). Treatment of the adduct **45** with two equivalents of lithium amido-, alkyl-, cyclopentadienyl- and alkynyl derivatives $[\text{LiR}]$ produces the cube-type compounds $[\text{RCd}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**46**), CH_2SiMe_3 (**47**), $\text{C}_5\text{H}_4(\text{SiMe}_3)$ (**48**), $\text{C}\equiv\text{CSiMe}_3$ (**49**)). The amido compound **46** reacts with one equivalent of complex **1** to give the corner-shared metallodicubane $[\text{Cd}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (**50**).

On the other hand, mercury compounds with incomplete cube structure $[\text{RHg}\{(\mu_3\text{-N})(\mu\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ ($\text{R} = \text{N}(\text{SiMe}_3)_2$ (**51a**), CH_2SiMe_3 (**51b**)) have been identified by NMR spectroscopy. These complexes are formed by the reaction of the trinuclear system **1** with the mercury(II) derivatives $[\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2]$ or $[\text{Hg}(\text{CH}_2\text{SiMe}_3)\{\text{N}(\text{SiMe}_3)_2\}]$, respectively.

Treatment of the metalloligand **1** with mercury diiodide in toluene at room temperature leads to the adduct $[\text{I}_2\text{Hg}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]$ (**52**). The reaction of complex **52** with $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ gives the compound $[\text{Hg}_2\{(\mu_3\text{-N})_2(\mu\text{-NH})\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (**53**), which shows two mercury atoms bridging two incomplete cube moieties according to an X-ray crystal structure determination. Finally, the potassium azametallodicubane $[\text{K}(\mu_4\text{-N})(\mu_3\text{-NH})_2\{\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}]_2$ (**4**) reacts with one equivalent of mercury diiodide to produce $[\text{Hg}\{(\mu_3\text{-N})(\mu\text{-NH})_2\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-N})\}_2]$ (**54**).

The experimental procedures for the synthesis of the complexes are described in **Chapter 4**. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Solvents were refluxed over an appropriate drying agent and distilled. The starting reagents were purchased commercially or prepared according to published methods.

The structural characterization of the new compounds was performed by IR spectroscopy, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, mass spectrometry and microanalysis (C, H, N). In addition, complexes **2**, **3**, **8 - 11**, **15**, **19 - 21**, **24**, **28**, **29**, **34**, **36b**, **42**, **49**, **50** and **53** were also characterized by X-ray single crystal structure determinations, carried out by Dr. Avelino Martín at the Universidad de Alcalá.

Conclusions

1. Complex $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) reacts with alkali-metal amido compounds to afford edge-linked or corner-shared double-cube molecular nitrides.

2. Treatment of the metalloligand with alkaline-earth derivatives gives single cube-type nitrido complexes. Most of them undergo ligand redistribution reactions to yield corner-shared azaheterometallocubanes, which are also prepared through the reaction of **1** with Group 2 disilylamides in a 2:1 ratio. Magnesium or calcium double-cube compounds with $[\text{MTi}_3\text{N}_4]$ cores linked by arylamido ligands can be synthesized by treatment of the single cube derivatives with anilines.

3. Azaheterometallocubanes containing single cube $[\text{Ti}_3\text{ZnN}_4]$ cores are prepared through the reaction of complex **1** with zinc(II) derivatives or by treatment of the zinc chloride adduct $[\text{Cl}_2\text{Zn}(\textbf{1})]$ with the corresponding lithium reagents.

4. The novel alkynylimido clusters $[(\text{RC}\equiv\text{C})\text{Zn}\{(\mu_3\text{-NH})_3\text{Ti}_3\text{Cp}^*_3(\mu_3\text{-NC}\equiv\text{CR})\}]$ are formed by reaction of alkynyl metallocubane complexes with terminal alkynes. The process involves a two-electron reduction of the Ti_3 system.

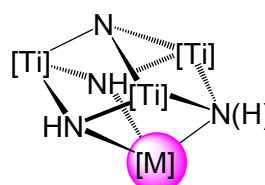
5. The metathesis reaction of the cadmium chloride adduct $[\text{Cl}_2\text{Cd}(\mathbf{1})]$ with lithium derivatives produces single cube nitrido complexes bearing $[\text{CdTi}_3\text{N}_4]$ cores. A corner-shared azametallodibutane with cadmium at the common vertex was also synthesized.

6. Complex **1** incorporates mercury(II) derivatives showing a tendency to form incomplete cube compounds with a linear geometry about the mercury atoms.

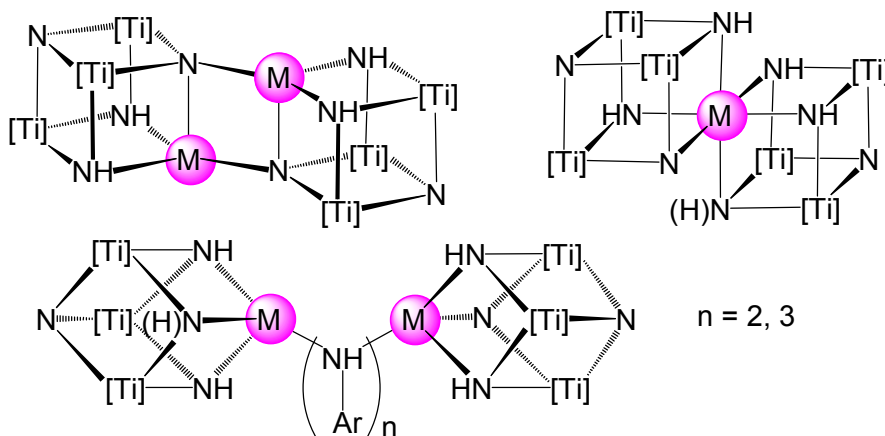
7. The preorganized ligand $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**1**) allows synthesize compounds with a large structural diversity due to its capability of building open or close cube-type systems as depicted below.

$[\text{Ti}] = \text{TiCp}^*$ $[\text{M}] = \text{Inorganic fragment}$

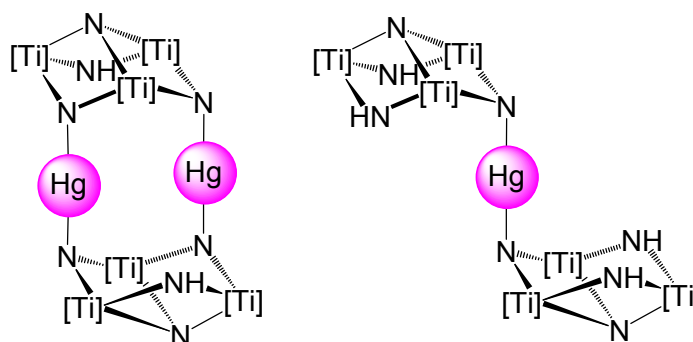
AZAHETEROMETALLOCUBANES



AZAHETEROMETALLODIBUTANES



OPEN CUBE-TYPE COMPOUNDS



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