Molecular Nitrides Containing Group 4 and 5 Metals: Single and Double Azatitanocubanes

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Abstract: Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with the imido complexes $[Ti(NAr)Cl_2(py)_3]$ (Ar = 2,4,6-$C_6H_2Me_3$) and $[Ti(NtBu)Cl_2(py)_3]$ in toluene affords the single azatitanocubanes $[\{Cl_2(ArN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot(C_7H_8)$ (**2**$\cdot C_7H_8$) and $[\{Cl_2Ti\}(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**), respectively. Similar reactions of complex **1** with the niobium and tantalum imido derivatives $[\{M(NtBu)(NHtBu)Cl_2(NH_2tBu)\}_2]$ (M = Nb, Ta) in toluene give the single azaheterometallocubanes $[\{Cl_2(tBuN)M\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Nb (**4**), Ta (**5**)), both complexes react with 2,4,6-trimethylaniline to yield the analogous species $[\{Cl_2(ArN)M\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot(C_7H_8)$ (Ar = 2,4,6-$C_6H_2Me_3$, M = Nb (**6**$\cdot C_7H_8$), Ta (**7**$\cdot C_7H_8$)). Also the azaheterodicubanes $[M\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\}_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]\cdot 2C_7H_8$ [M = Ti (**8**$\cdot 2C_7H_8$), Zr (**9**$\cdot 2C_7H_8$)], and $[M\{(\mu_3\text{-}N)_5(\mu_3\text{-}NH)\}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]\cdot 2C_7H_8$ (Nb (**10**$\cdot 2C_7H_8$), Ta (**11**$\cdot 2C_7H_8$)) were prepared from **1** and the homoleptic dimethylamido complex $[M(NMe_2)_x]$ ($x = 4$, M = Ti, Zr; $x = 5$, M = Nb, Ta) in toluene at 150 °C. X-ray crystal structure determinations were performed for **6** and **10**, which revealed a cube- and double-cube-type core, respectively. For complexes **2** and **4**–**7** we observed and studied by DNMR a rotation or trigonal-twist of the organometallic ligands $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) and $[(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]^{1-}$. Density functional theory calculations were carried out on model complexes of **2, 3**, and **8** to establish and understand their structures.

Keywords: cubanes · density functional calculations · N ligands · nitrido complexes · titanium

Introduction

The study of transition-metal nitrido complexes has been an area of interest over the last 20 years.[1] While extensive research has been carried out on mid-transition-metal complexes, which usually bear terminal nitrido ligands, the analogous treatment of early transition metals (Groups 4 and 5) has not received enough attention to make general statements. This is mainly a result of the tendency of the nitrido ligand to bridge two or more early transition-metal centers, which results in singular polynuclear structures, whose characterization can be extremely hard. A literature search shows crystallographically characterized examples of di-,[2] tri-,[3] tetra-,[4] penta-,[5] and hexanuclear[6] complexes with nitrido ligands bridging early transition-metal centers.

Polynuclear nitrido complexes might be of particular interest as building blocks in the synthesis of metal nitride materials.[7] Although the literature precedents are still scarce, Wolczanski and co-workers have demonstrated that the geometry of the nitridotantalum precursor $[(tBuCH_2)_2TaN]_5\cdot NH_3\cdot 2C_7H_8$ allows access to cubic TaN at 820 °C, instead of the hexagonal phase, which is more thermodinamically stable at that temperature.[5a, 8] Also it is interesting to consider that transition-metal nitrides produced with laser-induced plasma reactors are useful systems for studying the molecular details of the change from the gaseous to the condensed state.[9] Furthermore, polynuclear nitrido complexes are also of wide interest in theoretical studies.[10]

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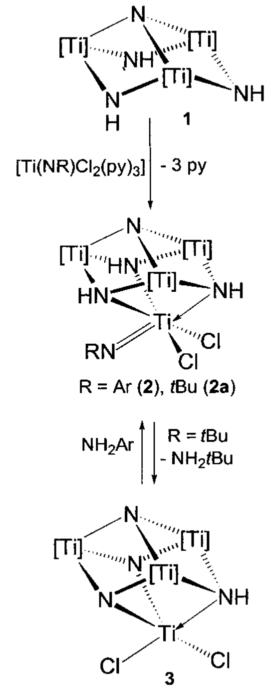
As part of our ongoing project devoted to the development of early transition-metal nitrido complexes, we reported the synthesis of several polynuclear titanium complexes containing nitrido ligands by the ammonolysis of mono(pentamethylcyclopentadienyl)titanium(IV) derivatives.[2j, 4a] Prior to our work, Roesky and co-workers prepared the trinuclear complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) by reaction of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ with ammonia.[3b] The crystal structure of **1** revealed an incomplete cube-type $[Ti_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$ core, and we were interested in the use of **1** as a potential starting material for the synthesis of cube-type heterometallic nitrido complexes.[11] Here we describe the syntheses, solid- and solution-state structures, and molecular orbital calculations for several azaheterometallocubane complexes obtained by the treatment of **1** with d^0 imido and amido Group 4 and 5 metal complexes. Part of this work has been communicated previously.[12]

Results and Discussion

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (1) with imido derivatives of Group 4 and 5 metals: Reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with the d^0 imidotitanium complexes $[Ti(NAr)Cl_2(py)_3]$ (Ar = 2,4,6-$C_6H_2Me_3$)[13] and $[Ti(NtBu)Cl_2(py)_3]$[13] in toluene at room temperature afforded brown crystals of $[\{Cl_2(ArN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot(C_7H_8)$ (**2**$\cdot C_7H_8$, 51 %) and green solid $[\{Cl_2Ti\}(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**, 82 %), respectively (Scheme 1). The reaction between **1** and $[Ti(NtBu)Cl_2(py)_3]$ in [D$_2$]dichloromethane was monitored by NMR spectroscopy. The NMR data after 10 min showed complete reaction and revealed resonances for free pyridine and the complex $[\{Cl_2(tBuN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2a**), analogous to **2**. NMR spectra showed the evolution of **2a** to give **3** and *tert*-butylamine at room temperature. Also, complex **3** reacts with 2,4,6-trimethylaniline in [D$_1$]chloroform to give **2** in quantitative yield after several days at room temperature.

Compounds **2** and **3** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, infrared spectrophotometry, microanalysis, and an X-ray structure determination for **2**.[12] The solid-state structure revealed a distorted $[Ti_4N_4]$ cube core, in which the imido-bonded titanium atom is six-coordinate with three *fac* sites occupied by the $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ organometallic ligand, and the remainder of the coordination sphere completed by two chloro and one arylimido group. The structural *trans* effect (STE)[14] of this ligand results in a titanium–nitrogen *trans* distance ($Ti{-}N_{trans}$, 2.602(7) Å) that is longer than the *cis* distance ($Ti{-}N_{cis}$, 2.284 Å).



Scheme 1. Reaction of **1** with imidotitanium(IV) complexes. [Ti] = Ti(η^5-C_5Me_5).

Abstract in Spanish: *La reacción de $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (1) con los imido complejos $[Ti(NAr)Cl_2(py)_3]$ (Ar = 2,4,6-$C_6H_2Me_3$) y $[Ti(NtBu)Cl_2(py)_3]$ en tolueno conduce a los azatitanocubanos $[\{Cl_2(ArN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot(C_7H_8)$ (**2**$\cdot C_7H_8$) y $[\{Cl_2Ti\}(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**) respectivamente. El tratamiento análogo del complejo **1** con los derivados $[\{M(NtBu)(NHtBu)Cl_2(NH_2tBu)\}_2]$ (M = Nb, Ta) permite preparar los azaheterometalocubanos $[\{Cl_2(tBuN)M\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Nb (**4**), Ta (**5**)), que reaccionan con 2,4,6-trimetilanilina para dar $[\{Cl_2(ArN)M\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot(C_7H_8)$ (Ar = 2,4,6-$C_6H_2Me_3$, M = Nb (**6**$\cdot C_7H_8$), Ta (**7**$\cdot C_7H_8$)). Los sistemas azametalodicubanos $[M\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\}_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]\cdot 2\,C_7H_8$ (M = Ti (**8**$\cdot 2\,C_7H_8$), Zr (**9**$\cdot 2\,C_7H_8$)) y $[M\{(\mu_3\text{-}N)_5(\mu_3\text{-}NH)\}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]\cdot 2\,C_7H_8$ (Nb (**10**$\cdot 2\,C_7H_8$), Ta (**11**$\cdot 2\,C_7H_8$)) son accesibles por tratamiento a 150 °C del complejo **1** con los derivados homolépticos $[M(NMe_2)_x]$ (x = 4, M = Ti, Zr; x = 5, M = Nb, Ta). El estudio cristalográfico de los complejos **6** y **10** demuestra la presencia de una unidad central tipo cubo o doble cubo de vértice compartido respectivamente. En disolución los derivados **2**, **4**–**7** ponen de manifiesto la existencia de rotación o torsión-trigonal de los ligandos organometálicos $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (1) y $[(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]^{1-}$. También se han llevado a cabo cálculos basados en la teoría del funcional (DFT) sobre modelos de los complejos **2, 3** y **8** para establecer y/o comprender sus estructuras.*

With the aim of understanding the electronic structure of the complexes mentioned above, DFT calculations were carried out on models $[\{Cl_2(PhN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$ (**2′**) and $[\{Cl_2(MeN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$ (**2′a**). Selected geometric parameters are given in Table 1. DFT calculations on model **2′** reproduced the experimental geometry well, and the calculated *trans* effect (STE)[14] of the imido ligand (elongation = 0.33 Å) is similar to that observed experimentally (0.32 Å).

Table 1. Selected computed bond lengths [Å] and angles [°] for $[Cl_2(RN)\mathit{Ti}\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$. Also experimental data for complex **2**.

	R = C_6H_5 (**2′**)	R = Me (**2′a**)	Complex **2**
$\mathit{Ti}{-}N_{ax}$	2.63	2.60	2.60
$\mathit{Ti}{-}N_{eq}$	2.30	2.31	2.28
$\mathit{Ti}{-}NR$	1.73	1.70	1.70
$\mathit{Ti}{-}Cl$	2.39	2.41	2.37
$N_{ax}\text{-}\mathit{Ti}\text{-}N_{eq}$	76.3	76.6	75.3
$N_{eq}\text{-}\mathit{Ti}\text{-}N_{eq}$	76.6	76.5	76.5
$N_{ax}\text{-}\mathit{Ti}\text{-}NR$	178.2	177.5	173.6
$N_{eq}\text{-}\mathit{Ti}\text{-}NR$	102.4	101.5	100.9
$Cl\text{-}\mathit{Ti}\text{-}Cl$	105.8	106.9	98.3

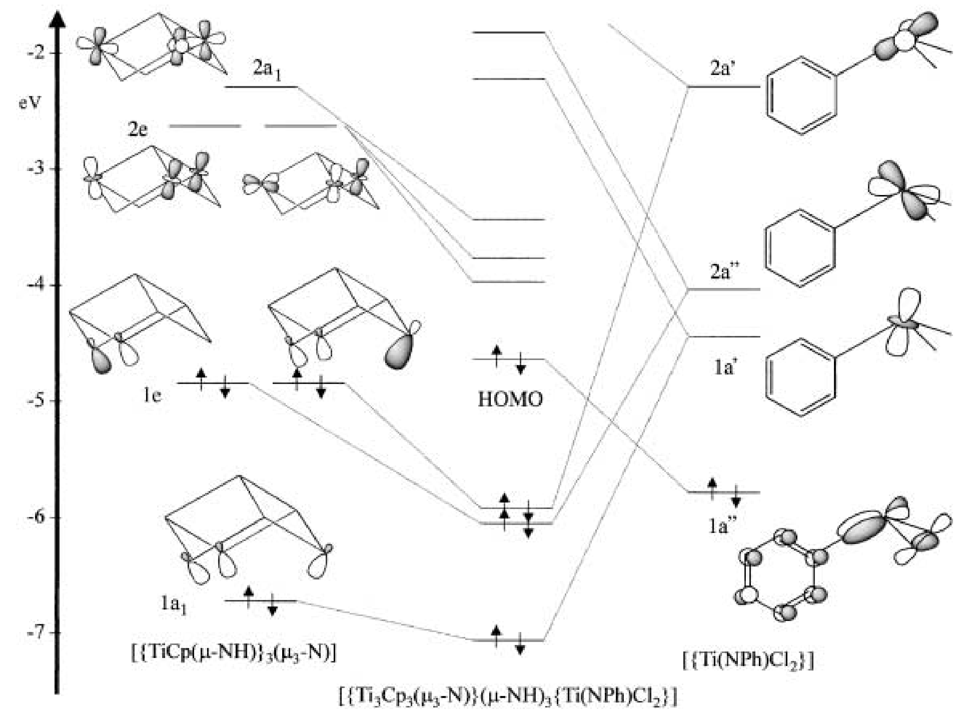


Figure 1. Interaction orbital diagram for the complex $[\{Cl_2(PhN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$ (**2′**).

A correlation diagram for **2′** is presented in Figure 1. Formation of these complexes is not accompanied by changes in the oxidation state of the metal centers (Ti^{IV}) and arises from the stabilization of the lone pair electrons of the tripodal ligand **1′**. On the other hand, the HOMO in complex **2′** is in essence an orbital of the $[TiCl_2NPh]$ fragment, which formally corresponds to the π bond between the metal and the phenylimido ligand. This orbital rises in energy in the formation of complex **2′**. Its destabilization is due to the increasing antibonding character between the Cl orbital contribution and the rest of the orbitals, with a change in the N-Ti-Cl angle from 111.6° in the isolated $[TiCl_2NPh]$ fragment to 103.6° in complex **2′**.

The energy for the dissociation of **2′**, to give the tridentate ligand **1′** and the $[TiCl_2NPh]$ fragment was computed to be $203\,kJ\,mol^{-1}$, whereas the fragment interaction energy[10c] between these same fragments is $-289\,kJ\,mol^{-1}$. Dissociation and fragment interaction energies are interconnected by the deformation energy necessary to transform the fragments from their optimal structure to the geometry adopted in the final compound. The dissociation energies computed for several azaheterometallocubane complexes $[(L_nM)(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$ are collected in Table 2. The values in this table clearly indicate that there is a relationship between the dissociation energy and the number of d electrons in the heterometal M. This is a consequence of the non-negligible mixing between the d orbitals of the metal center M and the d titanium orbital of the Ti_3N_3 core. In this way, the heterometal shares its d electrons with the other three titanium atoms. In complex **2′**, M is a Ti^{IV} without d electrons, therefore the bonding energy is only due to metal–ligand interactions, with the total absence of metal couplings. Consequently, this complex displays the lowest dissociation energy. These data are consistent with the very large *trans* effect (STE) found in the solid-state structure of **2** and its dynamic behavior in solution.

Table 2. Dissociation energy (ΔE_{Dis}) for azaheterometallocubane complexes $[(L_nM)(\mu_3\text{-}NH)_3\{Ti_3Cp_3(\mu_3\text{-}N)\}]$ ($Cp = \eta^5\text{-}C_5H_5$).

Complex	M	ΔE_{Dis} [$kJ\,mol^{-1}$]	Ref.
$[\{Cl_2(PhN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3Cp_3(\mu_3\text{-}N)\}]$ (**2′**)	Ti(d^0)	203	this work
$[\{(CO)_3M\}(\mu_3\text{-}NH)_3\{Ti_3Cp_3(\mu_3\text{-}N)\}]$	Cr(d^6)	376	[11a]
	Mo(d^6)	351	
	W(d^6)	445	
$[\{(cod)M\}(\mu_3\text{-}NH)_3\{Ti_3Cp_3(\mu_3\text{-}N)\}]^+$	Rh(d^8)	378	[11c]
	Ir(d^8)	445	

The ^1H NMR spectra of **3** in $[D_1]$chloroform at room temperature revealed resonances for two different $\eta^5\text{-}C_5Me_5$ ligands (1:2 ratio). The limited solubility and the low value of the ν_{NH} vibration in the IR spectrum could be indicative of the existence of strong inter/intramolecular N–H···Cl interactions[2j, 15] in this complex. Repeated attempts to obtain single crystals for an X-ray crystallographic study of **3** were unsuccessful, therefore DFT calculations were carried out to establish the structure for the model complex $[\{Cl_2Ti\}(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}]$ (**3′**). It shows two azatitanocubanes connected by symmetrical chloro bridges, with C_{2h} symmetry (Figure 2); in this way the titanium atoms adopt octahedral structures, in which the imido group >NH and the terminal chloro occupy the axial positions. The dissociation energy for this dimeric structure to give the monomeric units is $74\,kJ\,mol^{-1}$. Calculated bond lengths and angles are comparable to those found in the literature for complexes containing the $ClTi(\mu\text{-}Cl)_2TiCl$ structural motif.[16]

The analogous treatment of **1** in toluene at room temperature with the d^0 imidoniobium and -tantalum deriv-

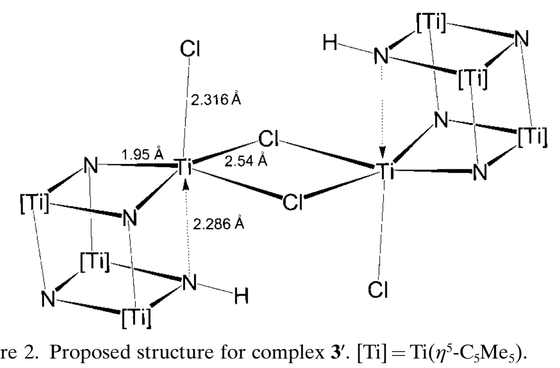
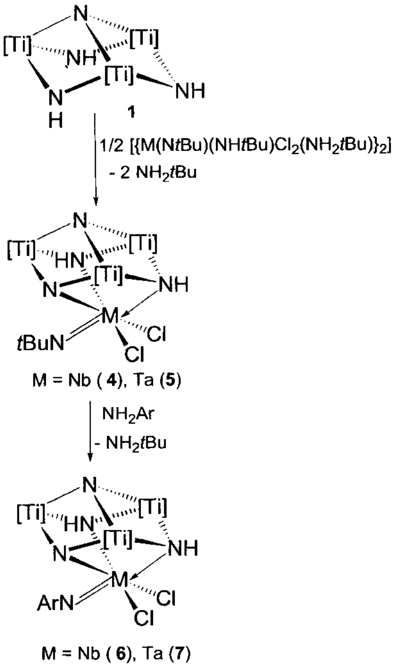


Figure 2. Proposed structure for complex **3′**. [Ti] = $Ti(\eta^5\text{-}C_5Me_5)$.

atives [{M(NtBu)(NHtBu)Cl$_2$(NH$_2$$t$Bu)}$_2$] (M = Nb, Ta)[17] (0.5 equiv) afforded [{Cl$_2$(tBuN)M}(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (M = Nb (**4**) 95 %, Ta (**5**) 88 %) as brown solids (Scheme 2). Attempts to detect intermediates by monitoring the reactions by ^{1}H NMR spectroscopy in [D$_6$]benzene failed and only *tert*-butylamine was observed along with the resonances of **4** and **5**. Treatment of **4** and **5** with 2,4,6-trimethylaniline in toluene at 70 °C afforded the analogous arylimido complexes [{Cl$_2$(ArN)M}(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] · (C$_7$H$_8$) (Ar = 2,4,6-C$_6$H$_2$Me$_3$, M = Nb (**6** · C$_7$H$_8$) 52 %, Ta (**7** · C$_7$H$_8$) 51 %) as brown crystals.



Scheme 2. Reaction of **1** with imidoniobium(v)/tantalum(v) complexes. [Ti] = Ti(η^5-C$_5$Me$_5$).

Compounds **4**–**7** were characterized by spectral and analytical methods, as well as by an X-ray structure determination in the case of **6** (vide infra). IR spectra of these complexes showed one medium intensity absorption in the 3346–3339 cm^{-1} range and several strong bands at 800–600 cm^{-1}, which we assigned to the ν_{NH} and ν_{MN} vibrational modes by comparison with those observed for **1**[3b] and other azametallocubanes reported previously.[2j, 11] In addition, the spectra revealed strong bands for the organoimido groups in the 1341–1237 cm^{-1} range.[18]

The molecular structure of [{Cl$_2$(ArN)Nb}(μ_3-N)(μ_3-NH)$_2$-{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] · (C$_7$H$_8$) (**6** · C$_7$H$_8$) is shown in Figure 3 and selected bond lengths and angles in Table 3. The X-ray structure confirms a distorted [NbTi$_3$N$_4$] cube core for **6** with average titanium–titanium and niobium–titanium distances of 2.824(3) Å and 3.113(2) Å respectively.

Thus, the niobium center is six-coordinate with three *fac* sites occupied by the anionic ligand [(μ_3-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$^{1-}$, and the remainder of the coordination sphere filled by two chloro and one arylimido groups. The anionic tridentate ligand coordinates to niobium through one nitrido and two >NH imido groups with angles spanning 77.9(3) to 102.8(4)°. The nitrido unit occupies a *cis* position with respect to the arylimido nitrogen atom, as could be expected because of the strong donor character of both groups. The structural *trans* effect (STE)[14] of the arylimido ligand results in a long niobium–nitrogen distance (2.542(8) Å) for the >NH group in the *trans* position (N2-Nb1-N5 174.2(3)°). For comparison, the remaining >NH group binds to niobium with a Nb1–N3 distance of 2.192(8) Å, whereas the niobium–nitrido (N4) bond length is 2.135(8) Å.

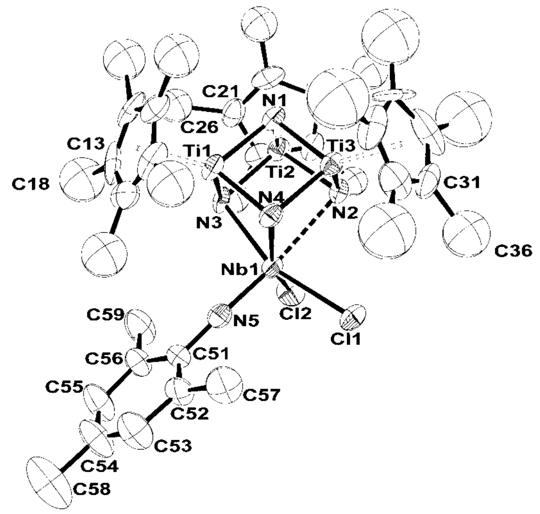


Figure 3. Molecular structure of **6** · C$_7$H$_8$. The C$_7$H$_8$ solvent molecules have been removed for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for **6** · C$_7$H$_8$.

Nb1–N5	1.760(9)	Nb1–N4	2.135(8)
Nb1–N3	2.192(8)	Nb1–Cl1	2.408(3)
Nb1–Cl2	2.427(3)	Nb1–N2	2.542(8)
Nb1–Ti1	3.012(2)	Nb1–Ti3	3.134(2)
Nb1–Ti2	3.193(2)	Ti1–N4	1.908(8)
Ti1–N3	1.935(8)	Ti1–N1	1.951(9)
Ti1–Ti3	2.817(3)	Ti1–Ti2	2.835(3)
Ti2–N1	1.911(8)	Ti2–N2	1.945(8)
Ti2–N3	1.975(9)	Ti2–Ti3	2.820(3)
Ti3–N1	1.922(8)	Ti3–N2	1.932(8)
Ti3–N4	1.947(9)	N5–C51	1.409(14)
N5-Nb1-N4	102.8(4)	N5-Nb1-N3	99.4(3)
N4-Nb1-N3	77.9(3)	N5-Nb1-Cl1	99.7(3)
N4-Nb1-Cl1	91.8(2)	N3-Nb1-Cl1	159.9(2)
N5-Nb1-Cl2	97.9(3)	N4-Nb1-Cl2	158.1(2)
N3-Nb1-Cl2	92.0(2)	Cl1-Nb1-Cl2	91.48(12)
N5-Nb1-N2	174.2(3)	N4-Nb1-N2	75.3(3)
N3-Nb1-N2	74.9(3)	Cl1-Nb1-N2	85.94(19)
Cl2-Nb1-N2	83.4(2)	N4-Ti1-N3	90.2(3)
N4-Ti1-N1	86.5(4)	N3-Ti1-N1	86.3(4)
Ti3-Ti1-Ti2	59.86(7)	N1-Ti2-N2	85.8(3)
N1-Ti2-N3	86.3(4)	N2-Ti2-N3	95.0(3)
Ti3-Ti2-Ti1	59.75(7)	N1-Ti3-N2	85.9(3)
N1-Ti3-N4	86.2(4)	N2-Ti3-N4	95.7(4)
Ti1-Ti3-Ti2	60.39(7)	Ti2-N1-Ti3	94.7(4)
Ti2-N1-Ti1	94.4(4)	Ti3-N1-Ti1	93.3(4)
Ti3-N2-Ti2	93.3(3)	Ti3-N2-Nb1	87.8(3)
Ti2-N2-Nb1	89.7(3)	Ti1-N3-Ti2	92.9(4)
Ti1-N3-Nb1	93.5(3)	Ti2-N3-Nb1	99.9(3)
Ti1-N4-Ti3	93.9(4)	Ti1-N4-Nb1	96.2(3)
Ti3-N4-Nb1	100.2(4)	C51-N5-Nb1	178.2(8)
N5-C51-C52	119.4(11)	N5-C51-C56	118.8(11)

The niobium–chloro and niobium–arylimido bond lengths are similar to other imidoniobium complexes.[18, 19] The Nb1–N5 bond length of 1.760(9) Å and the angle subtended at the arylimido nitrogen atom (Nb1-N5-C51 178.2(8)°) are consistent with a triple bond to niobium. On the other hand, for the titanium organometallic anionic ligand, coordination to the niobium center results in a very small distortion when compared with **1**.[3b]

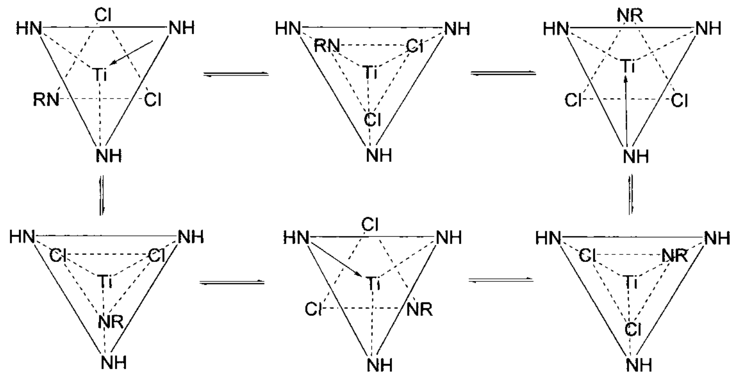


Figure 4. Proposed fluxional process for complex **2**.

Dynamic NMR study for complexes 2 and 4–7: The complexes **2** and **4–7** exhibit fluxional behavior on the NMR time scale. The ^1H NMR spectrum (11.7 T) in [D$_8$]toluene for **2** at room temperature showed equivalent NH and η^5-C_5Me_5 ligands, whereas at $-70\,^\circ C$ the spectrum revealed two types of μ_3-NH and η^5-C_5Me_5 ligands (2:1 ratio), consistent with the solid-state structure.

The room temperature ^1H NMR spectra for the *tert*-butylimido derivatives **4** and **5** showed one broad signal for the μ_3-NH groups, and two resonances for the η^5-C_5Me_5 ligands (2:1 ratio). Upon cooling to $-70\,^\circ C$ the more intense η^5-C_5Me_5 resonance gave two well-resolved signals.

On the other hand, the NMR data for complexes **6** and **7** are consistent with the solid-state X-ray structure determined for **6**. The ^1H NMR spectra (7.0 T) reveal two resonances for the μ_3-NH groups, three signals (1:1:1 ratio) for the η^5-C_5Me_5 ligands and the expected resonances for the arylimido groups. Two of the three signals for the η^5-C_5Me_5 ligands coalesce into one resonance at high temperature.

The kinetic parameters (Table 4) of the observed process were calculated on the basis of ^1H DNMR data with line shape analysis of the η^5-C_5Me_5 resonances using the gNMR program.[20] The results are in good agreement with an intramolecular process ($\log A = 12.5-14.0$) and support a nondissociative mechanism ($\Delta S^{\ddagger} = (-4.4)-(+4.6)$ e.u.).

The fluxional process in complex **2** can be visualized as rotation (octahedron–trigonal prism–octahedron) of the organometallic ligand around the [TiCl$_2$NPh] fragment (Figure 4). A similar rotation occurs in the [Ti(NR)(Me$_3$tach)Cl$_2$] (Me$_3$tach = 1,3,5-trimethyl-1,3,5-triazacyclohexane; R = *t*Bu or 2,6-*i*Pr$_2$C$_6$H$_3$) complexes previously described by Mountford et al.[21] The difference in the electronic energy between the prismatic and octahedral environments for model compound **2′** was estimated by DFT calculations to be 44 kJ mol^{-1} (10.5 kcal mol^{-1}).

Logically, the dynamic behavior of complexes **4–7** is also consistent with the mechanism proposed for the complex **2**. The trigonal twist of the anionic organometallic ligand $[(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]^{1-}$, modifies the octahedral arrangement around the Group 5 metals (octahedron–trigonal prism–octahedron). In that process, the nitrido bridge to niobium or tantalum would be exchanged between the sites *trans* to the chlorine atoms (Figure 5).

Table 4. Activation parameters for the exchange of η^5-C_5Me_5 resonances in complexes **2** and **4–7**.

Compound	log A	E_a [kcal mol^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [e.u.]	$\Delta G^{\ddagger\,298\,K}$ [kcal mol^{-1}]
2	14.00 ± 0.45 $r = 0.997$	14.45 ± 0.50	13.95 ± 0.50 $r = 0.997$	+3.9 ± 2.0	12.8
4	14.07 ± 0.24 $r = 0.999$	12.50 ± 0.25	12.00 ± 0.25 $r = 0.999$	−4.4 ± 1.0	10.7
5	12.50 ± 0.20 $r = 0.999$	12.80 ± 0.25	11.74 ± 0.25 $r = 0.998$	+4.6 ± 1.1	13.1
6	12.75 ± 0.15 $r = 0.999$	15.60 ± 0.20	15.00 ± 0.20 $r = 0.999$	−2.1 ± 0.6	15.6
7	12.60 ± 0.30 $r = 0.998$	17.50 ± 0.45	16.90 ± 0.46 $r = 0.998$	−2.9 ± 1.5	17.7

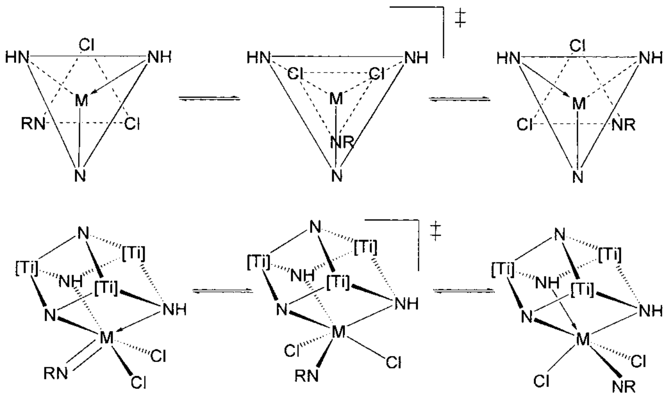
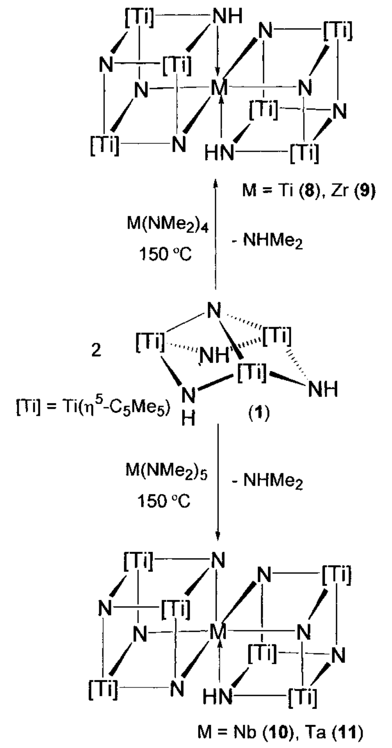


Figure 5. Proposed trigonal-twist process for complexes **4–7**. M = Nb or Ta; [Ti] = Ti(η^5-C_5Me_5).

Reaction of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (1) with amido derivatives of Group 4 and 5 metals: Treatment of **1** with 0.5 equivalents of [M(NMe$_2$)$_x$] ($x = 4$, M = Ti,[22] Zr;[23] $x = 5$, M = Nb,[24] Ta[25]) in toluene at 150 °C afforded the corner-shared double cube complexes $[M\{(\mu_3\text{-N})_2(\mu_3\text{-NH})\}_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}_2]\cdot 2\,C_7H_8$ (M = Ti (**8**·2 C$_7$H$_8$) 69 %, Zr (**9**·2 C$_7$H$_8$) 60 %)[12], and $[M\{(\mu_3\text{-N})_5(\mu_3\text{-NH})\}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}_2]\cdot 2\,C_7H_8$ (Nb (**10**·2 C$_7$H$_8$) 65 %, Ta (**11**·2 C$_7$H$_8$) 65 %) as dark green crystals (Scheme 3).

The reactions were monitored by NMR spectroscopy in [D$_6$]benzene. NMR spectra do not show changes in the composition of the initial solutions below 140 °C. Upon



Scheme 3. Reaction of **1** with homoleptic early transition-metal amido complexes.

heating above that temperature, ≈150 °C, the spectra revealed the formation of free dimethylamine as the only new product in the solutions. The fact that no reaction was observed on the treatment of **1** with [$Zr(NMe_2)_4$] until the temperature reached 140 °C, whereas **1** reacted with [$Zr(NAr')(NHAr')(py)_2$] (Ar' = 2,6-$C_6H_3iPr_2$)[26] at room temperature to give the complex **9**, suggests that the displacement of labile ligands joined to the metal center (Ti, Zr, Nb, Ta) might be the first step in the formation of these azametallodicubanes. We have reported that complex **1** reacts with [$Ti(\eta^5\text{-}C_5H_{5-n}R_n)(NMe_2)_3$] derivatives at 110–150 °C to give the cube-type nitrido complexes [$\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_{5-n}R_n)\}(\mu_3\text{-}N)_4$].[2j] This result is consistent with the decomposition of [$Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3$] at temperatures in the range between 120 and 150 °C in [D$_6$]benzene solutions.[27] Previously, Nugent et al. reported that [$M(NMe_2)_x$] (M = Zr, x = 4; M = Nb, Ta, x = 5; M = W, x = 6) complexes catalyze the incorporation of deuterium into the methyl groups of $NDMe_2$ at 140–180 °C.[28] The authors proposed that the amido derivatives decompose to give dimethylamine and azametallacyclopropane complexes in a reversible process. Therefore, we suggest that coordination of **1** to the metal center takes place once the homoleptic dialkylamido derivatives have decomposed and the subsequent N–H activation of the imido groups of **1** gives complexes **8**–**11** by dimethylamine elimination.

Complexes **8**–**11** were characterized by infrared spectroscopy and C, H, N microanalysis, as well as by an X-ray crystal structure determination for **8**–**10**. None of the double cube complexes is soluble in common organic solvents; therefore, it was not possible to obtain their NMR spectra. The IR spectra showed one absorption in the 3356–3345 cm^{-1} range, which is attributable to the ν_{NH} vibrations, and several very strong bands at 805–590 cm^{-1} for the ν_{MN} vibrations in the molecule.[2j, 3b, 11]

We have described the crystal structures of complexes **8** and **9** in a previous communication.[12] The molecular structure of [$Nb\{(\mu_3\text{-}N)_5(\mu_3\text{-}NH)\}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$] · 2 C_7H_8 (**10** · 2 C_7H_8) is depicted in Figure 6 and selected bond lengths and angles are in Table 5. Repeated attempts to obtain suitable single crystals for an X-ray determination of **11** were unsuccessful, although unit cell parameters obtained for several samples were consistent with those determined for **8**–**10**.

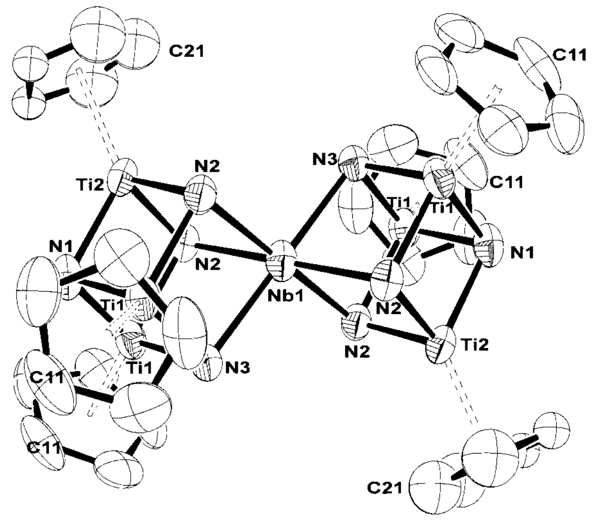


Figure 6. Molecular structure of **10** · 2 C_7H_8. The C_7H_8 solvent molecules have been removed for clarity.

Table 5. Selected bond lengths [Å] and angles [°] for **10** · 2 C_7H_8.

Nb1–N2	2.157(5)	Nb1–N3	2.158(8)
Nb1–Ti1	2.996(1)	Nb1–Ti2	3.009(2)
Ti1–N1	1.941(6)	Ti1–N3	1.944(5)
Ti1–N2	1.950(6)	Ti1–Ti1	2.811(2)
Ti1–Ti2	2.814(2)	Ti2–N2	1.948(5)
Ti2–N1	1.951(9)		
N2a-Nb1-N2b	180.0(1)	N2a-Nb1-N2c	80.2(3)
N2b-Nb1-N2c	99.8(3)	N2a-Nb1-N2	99.8(3)
N2b-Nb1-N2	80.2(3)	N2c-Nb1-N2	180.0(1)
N2a-Nb1-N3c	80.6(2)	N2b-Nb1-N3c	99.4(2)
N2c-Nb1-N3c	80.6(2)	N2-Nb1-N3c	99.4(2)
N2a-Nb1-N3	99.4(2)	N2b-Nb1-N3	80.6(2)
N2c-Nb1-N3	99.4(2)	N2-Nb1-N3	80.6(2)
N3c-Nb1-N3	180.0(1)	N1-Ti1-N3	87.3(2)
N1-Ti1-N2	87.6(3)	N3-Ti1-N2	91.6(3)
Ti1b-Ti1-Ti2	60.04(3)	N2-Ti2-N2b	91.0(3)
N2-Ti2-N1	87.4(2)	Ti1-Ti2-Ti1b	59.93(6)
Ti1-N1-Ti1b	92.7(4)	Ti1-N1-Ti2	92.6(3)
Ti2-N2-Ti1	92.4(2)	Ti2-N2-Nb1	94.2(2)
Ti1-N2-Nb1	93.5(2)	Ti1b-N3-Ti1	92.6(3)
Ti1-N3-Nb1	93.7(3)		

The X-ray structure determined for **10** confirms the expected corner-shared double cube [$NbTi_6N_8$] core. From the crystallographic point of view, molecules of **10** have a mirror plane and an inversion center located on the niobium atom. Niobium exhibits a six-coordinate geometry in which the nitrogen atoms occupy the vertices of a trigonal antiprism. In that arrangement, the tridentate organometallic ligands force the pentamethylcyclopentadienyl groups into an alternate position. All the niobium–nitrogen bond lengths are the same within experimental error (2.157(7) and 2.158(8) Å), and fall between those found for the niobium–nitrido and niobium–imido distances in complex **6** (2.135(8) and 2.192(8), respectively). The N-Nb-N angles established within each tridentate ligand span 80.2(3)–80.6(2)°, while the N-Nb-N *cis* angles between the two ligands range from 99.4(2) to 99.8(3)°.

All the structural data determined for **10** are fully comparable to those found for **8** and **9**. The differences in distances and angles correspond to the atomic radii of the corner-shared metal (covalent radius are 1.32 (Ti), 1.34 (Nb), and 1.45 Å(Zr)). Furthermore, inspection of the unit cell obtained for complexes **8**–**10** revealed a very similar arrangement in the solid state; see for example Figure 7, in which molecules of **10** are oriented along the *x* axis of the crystal with the toluene solvation molecules occupying the empty space between them.

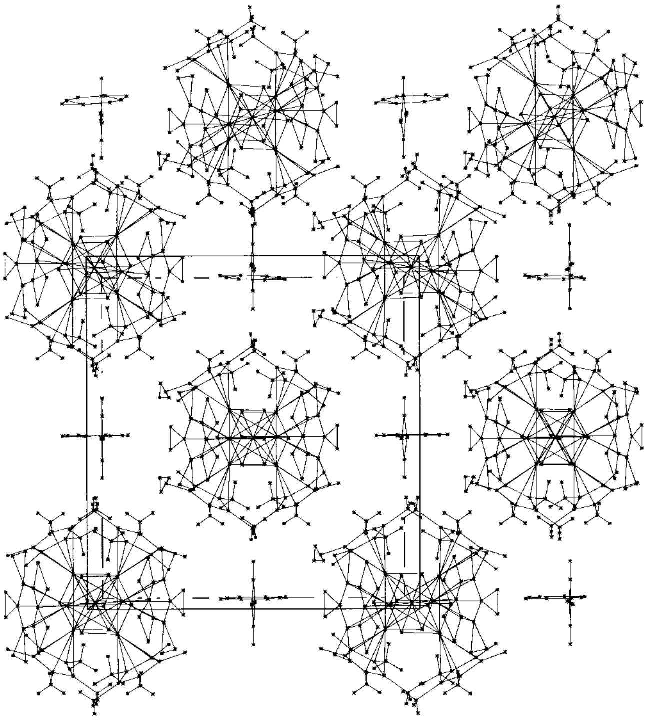


Figure 7. View normal to (100) of the unit cell of complex **10**, used as example for all of the double-cube compounds.

To determine the positions of the imido groups >NH in the [MTi_6N_8] (M = Ti, Zr, Nb, Ta) cores of the double azatitanocubanes **8**–**11**, DFT calculations were carried out on the model complex [$Ti\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)\}_2\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}N)\}_2$] (**8′**). Accepting that each cube has one >NH group, two structures are possible, one of C_{2h} symmetry with the two >NH ligands in a *trans* position and the other with C_2 symmetry, in which the two >NH are in a *cis* position (Figure 8).

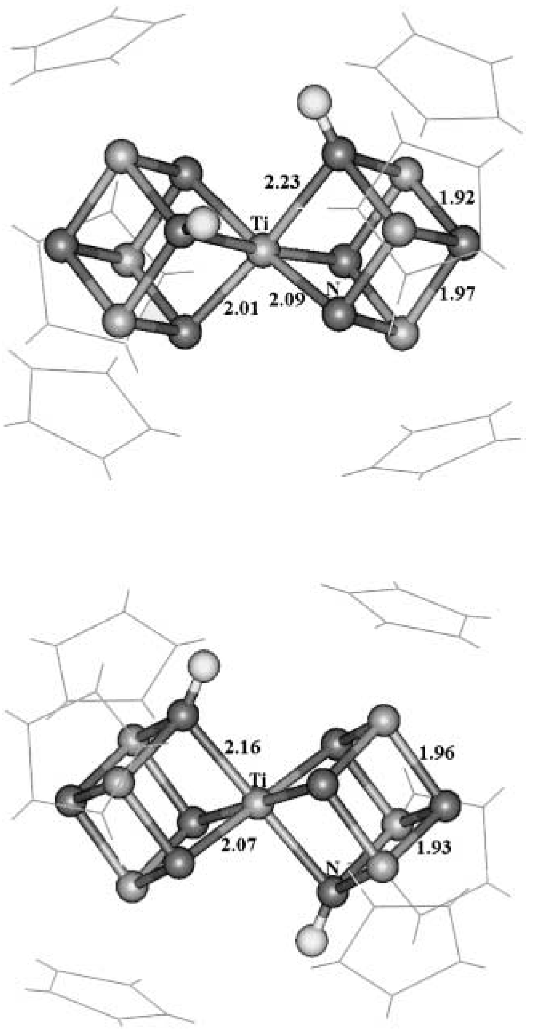


Figure 8. The *cis* (top) and *trans* conformers (bottom) for complex **8′**.

Both structures were optimized and the most relevant result is that they have similar energies, the computed difference being less than 3 kJ mol^{-1}. The other feature to note is that in both cases the $Ti_{central}$–NH bonds are longer than the $Ti_{central}$–N (see Figure 8) bonds. However, this result seems to be in contradiction to the crystal structure determination for complexes **8**–**10**, in which all the metal$_{central}$–nitrogen distances are the same in each compound. This discrepancy might be attributed to the steric effects induced by the pentamethylcyclopentadienyl ligands in the real complex **8** ($Ti_{central}$–N = 2.12 Å),[12] but the incorporation of the methyl groups into the calculations only generates a slight lengthening of all of the bonds around the central metal (≈0.02 Å).[29] In spite of this, we found that the energy difference between the complex optimized by keeping the six $Ti_{central}$–N distances fixed at the experimental value of 2.12 Å and the fully optimized compound is only 12 kJ mol^{-1}.

In conclusion, with the incorporation of metals from Groups 4 and 5, it has been well established that the [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] complex (**1**) is able to act as a neutral, mono-, di-, or trianionic ligand, which raises great expectations about its role in the design of new molecular heterometallic nitrides.

Experimental Section

General: All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Hexane was distilled from Na/K amalgam just prior to use. Toluene was freshly distilled from sodium. NMR solvents were dried with CaH_2 ($CDCl_3$) or Na/K amalgam (C_6D_6) and vacuum-distilled. 2,4,6-Trimethylaniline (purchased from Aldrich) was distilled from sodium. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[2j, 3b] $[\{M(NtBu)(NHtBu)Cl_2(NH_2tBu)\}_2]$ (M = Nb, Ta),[17] and $[M(NMe_2)_5]$ (M = Nb, Ta)[24, 25] were prepared according to literature methods.

Samples for infrared spectroscopy were prepared as KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 and/or Unity-500 Plus spectrometer. Chemical shifts (δ) are given relative to residual protons or to the carbon of the solvent. Microanalyses (C, H, N) were performed in a Heraeus CHN-O-Rapid microanalyzer.

$[\{Cl_2(tBuN)Nb\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (4): A 150-mL Schlenk flask was charged with **1** (1.00 g, 1.64 mmol), $[\{Nb(NtBu)(NHtBu)Cl_2(NH_2tBu)\}_2]$ (0.62 g, 0.82 mmol), and toluene (100 mL). After the mixture had been stirred at room temperature for 20 h, the volatile components were removed under reduced pressure. The resultant brown solid was washed with hexane (10 mL) and vacuum-dried to afford **4** (1.25 g, 95 %). ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.54$ (brs, 2H; NH), 2.06 (s, 30H; C_5Me_5), 1.94 (s, 15H; C_5Me_5), 1.50 ppm (s, 9H; CMe_3); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 122.9$, 121.5 (C_5Me_5), 68.0 (CMe_3), 31.2 (CMe_3), 12.6, 12.4 ppm (C_5Me_5); IR (KBr): $\tilde{\nu} = 3344$ (m), 2909 (s), 1431 (m), 1377 (m), 1354 (w), 1237 (s), 1127 (w), 1025 (w), 797 (vs), 748 (m), 723 (vs), 705 (vs), 654 (vs), 612 (vs), 532 (m), 450 (w), 429 (m) cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{56}N_5Cl_2NbTi_3$: C 48.48, H 6.70, N 8.32; found: C 48.13, H 6.66, N 7.75.

$[\{Cl_2(tBuN)Ta\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (5): In a similar fashion to the preparation of **4**, **1** (0.60 g, 0.99 mmol) and $[\{Ta(NtBu)(NHtBu)Cl_2(NH_2tBu)\}_2]$ (0.46 g, 0.49 mmol) were allowed to react in toluene (60 mL) to give **5** (0.81 g, 88 %). ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.17$ (brs, 2H; NH), 2.06 (s, 30H; C_5Me_5), 1.92 (s, 15H; C_5Me_5), 1.55 ppm (s, 9H; CMe_3); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C, TMS): $\delta = 123.0$ (C_5Me_5), 121.7 (brs; C_5Me_5), 64.8 (CMe_3), 33.2 (CMe_3), 12.6, 12.4 ppm (C_5Me_5); IR (KBr): $\tilde{\nu} = 3346$ (m), 2971 (s), 2911 (s), 1430 (m), 1378 (m), 1352 (w), 1260 (s), 1025 (w), 793 (vs), 767 (m), 730 (vs), 706 (s), 676 (s), 654 (vs), 611 (vs), 534 (m), 512 (w), 449 (w), 428 (m) cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{56}N_5Cl_2TaTi_3$: C 43.90, H 6.07, N 7.53; found: C 44.67, H 6.20, N 7.20.

$[\{Cl_2(ArN)Nb\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot C_7H_8$ ($6\cdot C_7H_8$): A 250-mL ampoule (Teflon stopcock) was charged with **4** (1.00 g, 1.19 mmol), 2,4,6-trimetylaniline (0.20 g, 1.50 mmol), and toluene (100 mL). After the mixture had been heated at 70 °C for five days, the volume of the solution was concentrated to about 50 mL under reduced pressure. The resulting brown solution was cooled to +5 °C for two days to afford single crystals of $\mathbf{6}\cdot C_7H_8$, which were collected by filtration. The filtrate was concentrated to a volume of about 25 mL and cooled to −10 °C for another two days to give a second crop of brown crystals. The combined yield of $\mathbf{6}\cdot C_7H_8$ was 0.61 g (52 %). ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.72$ (brs, 1H; NH), 11.42 (brs, 1H; NH), 6.66 (s, 2H; $C_6H_2Me_2Me$), 2.84 (s, 6H; $C_6H_2Me_2Me$), 2.14 (s, 3H; $C_6H_2Me_2Me$), 2.09 (brs, 15H; C_5Me_5), 1.96 (s, 15H; C_5Me_5), 1.88 ppm (brs, 15H; C_5Me_5); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 150.3$, 135.5, 132.9, 127.6 ($C_6H_2Me_2Me$), 123.6, 122.8, 121.5 (C_5Me_5), 21.0 ($C_6H_2Me_2Me$), 18.9 ($C_6H_2Me_2Me$), 12.6, 12.2, 11.7 ppm (C_5Me_5); IR (KBr): $\tilde{\nu} = 3339$ (m), 3023 (w), 2978 (m), 2912 (s), 2857 (m), 2727 (w), 1604 (w), 1494 (m), 1428 (s), 1377 (s), 1317 (s), 1290 (s), 1162 (w), 1081 (w), 1027 (m), 983 (m), 938 (w), 848 (m), 801 (m), 747 (s), 732 (s), 713 (vs), 669 (vs), 646 (vs), 610 (vs), 601 (s), 532 (s), 511 (m), 465 (m), 443 (m), 423 (m) cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{66}N_5Cl_2NbTi_3$: C 55.44, H 6.68, N 7.03; found: C 55.41, H 6.80, N 7.11.

$[\{Cl_2(ArN)Ta\}(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot C_7H_8$ ($7\cdot C_7H_8$): In a similar fashion to the preparation of $\mathbf{6}\cdot C_7H_8$, **5** (0.40 g, 0.43 mmol) and 2,4,6-trimethylaniline (0.11 g, 0.81 mmol) were heated at 70 °C to afford $\mathbf{7}\cdot C_7H_8$ as brown crystals (0.24 g, 51 %). ^1H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.40$ (brs, 1H; NH), 10.96 (brs, 1H; NH), 6.84 (s, 2H; $C_6H_2Me_2Me$), 2.89 (s, 6H; $C_6H_2Me_2Me$), 2.28 (s, 3H; $C_6H_2Me_2Me$), 2.07 (s, 15H; C_5Me_5), 1.94 (s, 15H; C_5Me_5), 1.88 ppm (s, 15H; C_5Me_5); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 149.8$, 135.3, 131.3, 127.1 ($C_6H_2Me_2Me$), 123.8, 123.0, 121.9 (C_5Me_5), 20.7 ($C_6H_2Me_2Me$), 18.7 ($C_6H_2Me_2Me$), 12.6, 12.2, 11.7 ppm (C_5Me_5); IR (KBr): $\tilde{\nu} = 3339$ (m), 2909 (s), 1604 (w), 1494 (m), 1471 (m), 1427 (m), 1377 (s), 1341 (s), 1292 (w), 1266 (w), 1234 (m), 1162 (w), 1081 (m), 1027 (m), 987 (w), 847 (m), 804 (s), 759 (s), 726 (vs), 710 (vs), 679 (vs), 647 (vs), 610 (vs), 535 (vs), 466 (m), 453 (w), 438 (m), 428 (w) cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{66}N_5Cl_2TaTi_3$: C 50.94, H 6.13, N 6.46; found: C 50.89, H 6.22, N 6.19.

$[Nb\{(\mu_3\text{-}N)_5(\mu_3\text{-}NH)\}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]\cdot 2C_7H_8$ ($10\cdot 2C_7H_8$): A 200 mL Carius tube was charged with **1** (0.30 g, 0.49 mmol), $[Nb(NMe_2)_5]$ (0.08 g, 0.26 mmol), and toluene (50 mL). The tube was flame sealed and

Table 6. Summary of the crystallographic data for complexes **6** and **10**.

	6	**10**
formula	$C_{39}H_{58}Cl_2N_5NbTi_3\cdot C_7H_8$	$C_{60}H_{91}N_8NbTi_6\cdot 2\,C_7H_8$
M_r	996.55	1488.99
T[K]	293(2)	293(2)
λ[Å]	0.71073	0.71073
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	Pnnm
a [Å]; α [°]	11.096(2); 101.6(1)	14.440(3)
b [Å]; β [°]	13.972(2); 91.1(1)	15.450(3)
c [Å]; γ [°]	16.605(3); 101.6(1)	16.587(3)
V [Å^3]	2464.5(7)	3700.5(12)
Z	2	2
ρ_{calcd} [g cm^{-3}]	1.343	1.336
$\mu_{MoK\alpha}$ [mm^{-1}]	0.839	0.809
$F(000)$	1036	1560
crystal size [mm]	0.40 × 0.35 × 0.30	0.45 × 0.35 × 0.33
θ range	3.00 to 20.00°	3.11 to 22.00°
index ranges	$0 \le h \le 10, -13 \le k \le 13, -15 \le l \le 15$	$-15 \le h \le 0, -16 \le k \le 16, 0 \le l \le 17$
reflections collected	4884	4594
unique data	4569	2356
observed data [$I > 2\sigma(I)$]	3266	1927
absorption correction	none	none
goodness-of-fit on F^2	0.965	1.038
final R indices [$I > 2\sigma(I)$]	$R1 = 0.064$, $wR2 = 0.172$	$R1 = 0.077$, $wR2 = 0.226$
R indices (all data)	$R1 = 0.106$, $wR2 = 0.202$	$R1 = 0.090$, $wR2 = 0.244$
largest diff. peak/hole [e Å^{-3}]	1.158/−0.599	1.143/−0.644

heated at 150 °C for 30 h. The reaction mixture was allowed to cool to ambient temperature overnight to afford green crystals of **10**·2C$_7$H$_8$ (0.24 g, 65%); IR (KBr): $\tilde{\nu} = 3352$ (m), 2971 (m), 2906 (vs), 2854 (s), 2718 (w), 1604 (w), 1494 (m), 1434 (s), 1373 (s), 1155 (w), 1079 (w), 1023 (m), 797 (s), 729 (s), 694 (s), 679 (s), 608 (vs), 521 (m), 464 (w), 427 (vs) cm^{-1}; elemental analysis calcd (%) for C$_{74}$H$_{107}$N$_8$NbTi$_6$: C 59.70, H 7.24, N 7.53; found: C 59.48, H 7.32, N 7.35.

[Ta{(μ_3-N)$_5$(μ_3-NH)}{Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$]·2C$_7$H$_8$ (11·2C$_7$H$_8$): In a similar way to the preparation of **10**·2C$_7$H$_8$, **1** (0.30 g, 0.49 mmol) and [Ta(NMe$_2$)$_5$] (0.10 g, 0.25 mmol) reacted to afford **11**·2C$_7$H$_8$ as green crystals (0.17 g, 44%); IR (KBr): $\tilde{\nu} = 3356$ (m), 3024 (w), 2907 (vs), 2854 (vs), 2718 (m), 1604 (w), 1494 (m), 1436 (s), 1373 (s), 1259 (w), 1155 (w), 1066 (w), 1022 (m), 793 (s), 770 (m), 729 (s), 678 (vs), 627 (s), 609 (s), 590 (s), 513 (s), 428 (vs) cm^{-1}; elemental analysis calcd (%) for C$_{74}$H$_{107}$N$_8$TaTi$_6$: C 56.36, H 6.84, N 7.11; found: C 56.08, H 7.12, N 6.89.

X-ray structure determination of complexes 6·C$_7$H$_8$ and 10·2C$_7$H$_8$: All data were collected on an ENRAF NONIUS CAD4 diffractometer at room temperature. Crystallographic data for complexes **6**·C$_7$H$_8$ and **10**·2C$_7$H$_8$ are presented in Table 6.

The structures were solved, using the WINGX package,[30] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[31] All non-hydrogen atoms of **6**, except the methyl carbon atoms of the pentamethylcyclopentadienyl C31–C40 unit and those of the solvent, were anisotropically refined. The hydrogen atoms were positioned geometrically and refined by using a riding model.

In the case of **10**, the pentamethylcyclopentadienyl C21–C26 ring was disordered, two sites with 50% occupancy were found for C23, C24, C25, and C26. Only the carbon atoms of the solvent and those of the disordered cyclopentadienyl ring were isotropically refined, the rest of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined by using a riding model, but only for the imido and nondisordered pentamethylcyclopentadienyl ring.

CCDC-197298 and CCDC-197299 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

Computational details: All DFT calculations were carried out with the ADF program[32] by using triple-ζ and polarization Slater basis sets to describe the valence electrons of C and N. For titanium, a frozen core composed of the 1s, 2s, and 2p orbitals was described by double-ζ Slater functions, the 3d and 4s orbitals by triple-ζ functions, and the 4p orbital by a single orbital. Hydrogen atoms were described by triple-ζ and polarization functions. The geometries and binding energies were calculated with gradient corrections. We used the local spin density approximation, characterized by the electron gas exchange (Xα with $\alpha = 2/3$) together with Vosko–Wilk–Nusair parametrization[33] for correlation. Becke's nonlocal corrections[34] to the exchange energy and Perdew's nonlocal corrections[35] to the correlation energy were added. Quasirelativistic corrections were employed by using the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC.[32]

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