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Cadmium and mercury complexes containing trinuclear titanium imido-nitrido metalloligands

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Dedicated to the memory of Professor Francisco Urbanos, who passed away in May 28, 2011

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Several nitrido metallocubanes and incomplete cube-type compounds have been prepared by the reaction of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) with cadmium and mercury derivatives.
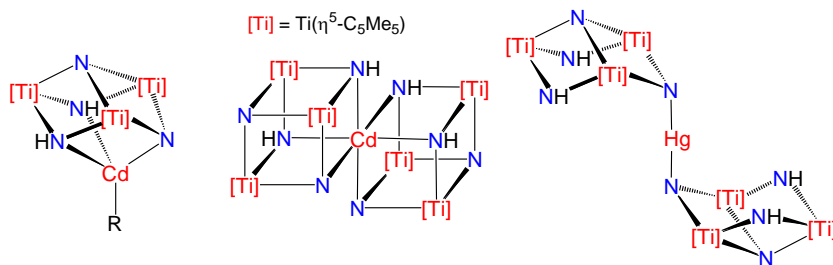
Keywords: Cadmium / Cage Compounds / Mercury / Nitrides / Titanium

Abstract:

Several heterometallic nitrido complexes have been prepared by the reaction of the trinuclear titanium imido-nitrido complex [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) with cadmium and mercury derivatives. Treatment of **1** with cadmium dichloride or cadmium diiodide in toluene afforded the adducts [X$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] [X = Cl (**2**), I (**3**)]. Complex **2** reacted with lithium reagents [LiR] in toluene to give the cube-type derivatives [RCd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] [R = CH$_2$SiMe$_3$ (**4**), C≡CSiMe$_3$ (**5**), C$_5$H$_4$(SiMe$_3$) (**6**), N(SiMe$_3$)$_2$ (**7**)]. The amido complex **7** reacted with one equivalent of **1** to give the corner-shared double-cube complex [Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (**8**) via bis(trimethylsilyl)amine elimination. Treatment of **1** with mercury(II) iodide in toluene gave the adduct [I$_2$Hg{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**9**) which reacted with [K{N(SiMe$_3$)$_2$}] to afford [Hg{(μ_3-N)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}]$_2$ (**10**) via the mercury amido intermediate [{(Me$_3$Si)$_2$N}Hg{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] (**11**). Compound **11** and the analogue alkyl derivative [(Me$_3$SiCH$_2$)Hg{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] (**12**) were characterized by NMR spectroscopy on the treatment of **1** with [Hg{N(SiMe$_3$)$_2$}R] (R = N(SiMe$_3$)$_2$, CH$_2$SiMe$_3$) reagents. Complex [Hg{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}$_2$] (**13**), with one bridging mercury atom between two titanium trinuclear systems, was obtained upon treatment HgI$_2$ with the potassium derivative [K(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$. Complexes **3**, **5** and **8** have been characterized by single-crystal X-ray diffraction analysis.
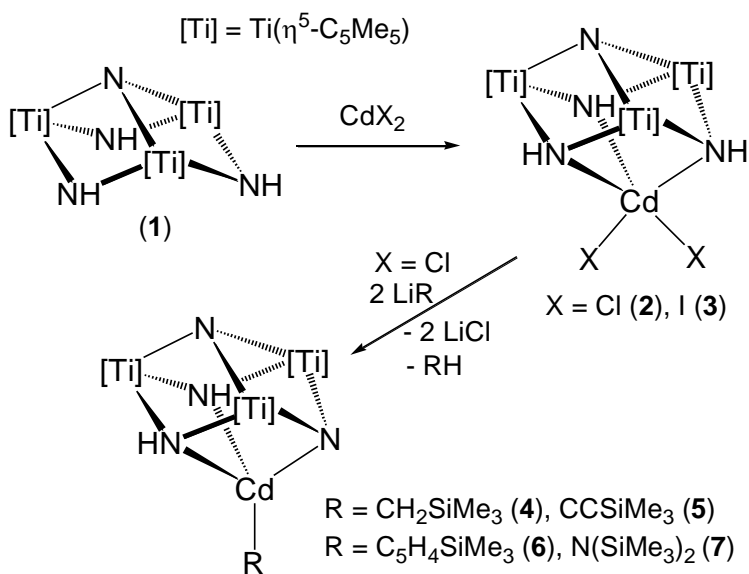
Introduction

We are interested in the study of the coordination chemistry of the trinuclear titanium imido-nitrido complex $[\{Ti(\eta^5-C_5Me_5)(\mu-NH)\}_3(\mu_3-N)]$[1,2] (**1**). The structure of complex **1** shows an incomplete cube-type $[Ti_3N_4]$ core with three NH electron-donor imido groups in the base, which resembles that of other tridentate nitrogen-based ligands such as tris(pyrazolyl)borates,[3] tris(pyrazolyl)methanes,[3b,4] 1,4,7-triazacyclononanes,[5] 1,3,5-triazacyclohexanes[6] and other tripodal amido ligands,[7] whose extensive coordination chemistry is known. This similarity prompted us to explore its potential application as a tridentate ligand toward different metal complexes and design a rational strategy to prepare cube-type heterometallic nitrido compounds. Polynuclear nitrido complexes are rare in the literature because the difficult characterization of their singular structures and, maybe more important, the lack of systematic strategies for the construction of aggregates with desired metal composition.[8] Our previous work has shown that **1** is capable of acting as a neutral tridentate chelate ligand through the basal NH imido groups toward transition[9] and main-group[10] metal derivatives. However, once the adducts $[(\mathbf{1})ML_n]$ are formed, the NH imido groups can be deprotonated leading to monoanionic, dianionic or even trianionic forms of **1** depending on the metal and the other ligands present in the coordination sphere.[10b,11]

As part of this general study, we have reported the formation of several azaheterometallocubane complexes by the reaction of the metalloligand **1** with zinc(II) reagents,[12] and we present here the results obtained in the treatment of this preorganized system with cadmium and mercury derivatives. Part of the mercury chemistry has been recently communicated.[13]

Results and Discussion

Cadmium Compounds. Treatment of [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) with one equivalent of anhydrous cadmium(II) chloride or iodide in toluene afforded the cube-type adducts [X$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] [X = Cl (**2**), I (**3**)] in good yields (70 and 73%, respectively) (Scheme 1). Compounds **2** and **3** were isolated as air-sensitive yellow or orange solids which are poorly soluble in toluene or benzene but exhibit a good solubility in chloroform or dichloromethane. Halide complexes **2** and **3** are stable in [D$_1$]chloroform at room temperature but the solution of **2** at higher temperatures affords a gray insoluble material, which we presume to be cadmium metal.

Complexes **2** and **3** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for **3**. The IR spectra (KBr) reveal two ν_{NH} vibrations, between 3341 and 3234 cm^{-1}, in a range similar to the value determined for compound **1**,[2] 3352 cm^{-1}. ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **2** and **3** in [D$_1$]chloroform at room temperature show resonance signals for equivalent NH and η^5-C$_5$Me$_5$ ligands, suggesting the existence of a dynamic behavior in solution, as in other metal dihalide adducts of **1**.[10a] The NH resonance signals (δ = 11.91 and 11.46) are shifted to a higher field than that found for **1** (δ = 13.40), whereas the resonance for the *ipso* carbon of the C_5Me$_5$ groups (δ = 121.6 and 122.4) in the ^{13}C NMR spectrum are shifted downfield with respect to that found for **1** (δ = 117.1). In previous works we have used those data to propose the tridentate chelate coordination of the NH groups to the metal centers.[9,10]

[Ti] = Ti(η^5-C$_5$Me$_5$)

(**1**) $\xrightarrow{\text{CdX}_2}$

X = Cl (**2**), I (**3**)

X = Cl
2 LiR
- 2 LiCl
- RH

R = CH$_2$SiMe$_3$ (**4**), CCSiMe$_3$ (**5**)
R = C$_5$H$_4$SiMe$_3$ (**6**), N(SiMe$_3$)$_2$ (**7**)

Scheme 1. Synthesis of cadmium complexes.

The molecular structure of **3** is presented in Figure 1, and selected bond lengths and angles are given in Table 1. The structural analysis reveals two [I$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] units related by a center of inversion located on the midpoint between the two cadmium atoms. The two units are associated by long-range interactions between the cadmium atom of one fragment and the iodine atom I(2) of the other moiety. If this Cd$\cdots$I interaction is considered, the geometry around the Cd(1) center can be defined as distorted trigonal prismatic, with three iodine atoms (I(1), I(2) and I(2)a) placed in an eclipsed position with respect to the three imido-nitrogen atoms (N(12), N(13) and N(23)). The distances N(23)$\cdots$I(1) (3.440(5) Å) and N(13)$\cdots$I(2)a (3.754(5) Å) are similar to the sum of the van der Waal radii of nitrogen and iodine atoms (3.7 Å)[14] and could be indicative of the existence of weak hydrogen bonding interactions. The Cd(1)-I(1) and Cd(1)-I(2) bond lengths (terminal 2.755(2) Å and bridging 2.791(1) Å, respectively) are similar to the values found in other compounds containing μ-I bridged Cd$_2$I$_4$ units.[15] These Cd-I bond lengths are approximately 0.8 Å shorter than the Cd(1)-I(2)a distance of 3.548(1) Å, which

may be considered as a long-range interaction distance. Whereas the Cd(1)–N(12) (2.598(5) Å) and Cd(1)–N(13) (2.319(5) Å) bond lengths are similar to those found in six-coordinated cadmium tris(pyrazolyl)methane complexes,[16] the distance Cd(1)–N(23) (3.098(5) Å) is much longer but it is still shorter than the sum of the van der Waals radii.[14] This asymmetric coordination of the imido groups to the cadmium atom produces an angle N(12)–Ti(1)–N(13) (99.8(2)°) narrower than the angles N(12)–Ti(2)–N(23) (105.1(2)°) and N(13)–Ti(3)–N(23) (104.3(2)°). The rest of the structural parameters of the metalloligand in **3** do not differ significantly with respect to those of the free complex **1**.[1]
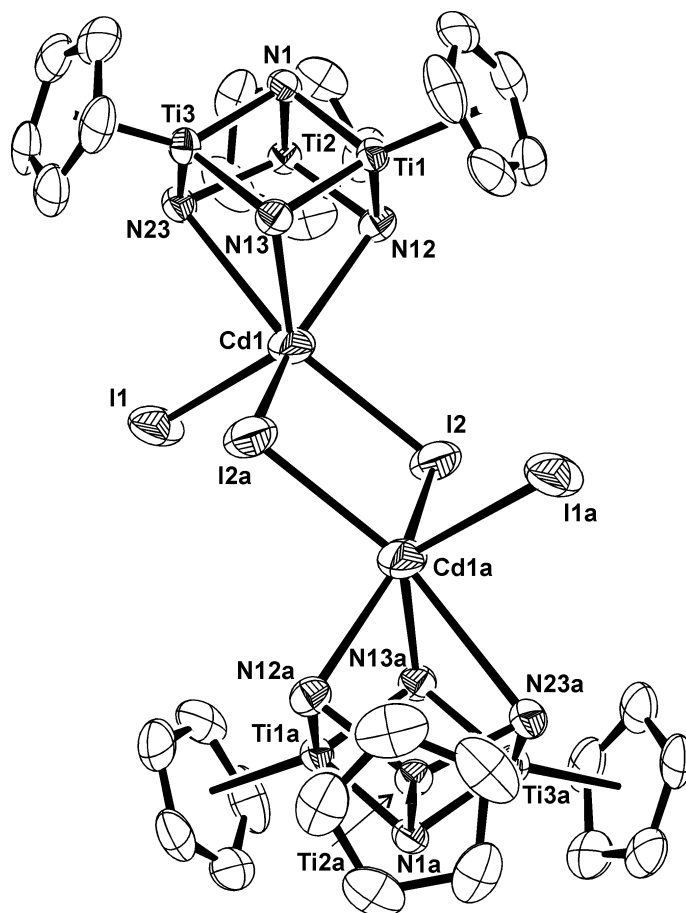

Figure 1. Perspective view of the dimeric disposition of complex [I$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the methyl groups of the pentamethylcyclopentadienyl rings are omitted for clarity. Symmetry transformation: (a) –x + 1, –y + 2, –z + 2.

Table 1. Selected lengths (Å) and angles (°) for **3**.

Cd(1)–I(1)	2.755(2)	Cd(1)–I(2)	2.791(1)
Cd(1)–I(2)a	3.548(1)	Cd(1)–N(12)	2.598(5)
Cd(1)–N(13)	2.319(5)	Cd(1)–N(23)	3.098(5)
Ti(1)–N(1)	1.908(5)	Ti(1)–N(12)	1.942(5)
Ti(1)–N(13)	1.962(5)	Ti(2)–N(1)	1.931(5)
Ti(2)–N(12)	1.958(5)	Ti(2)–N(23)	1.915(5)
Ti(3)–N(1)	1.920(5)	Ti(3)–N(13)	1.992(5)
Ti(3)–N(23)	1.892(5)		
N(12)–Cd(1)–N(13)	74.6(2)	N(13)–Cd(1)–N(23)	67.2(2)
N(12)–Cd(1)–N(23)	64.6(1)	N(12)–Cd(1)–I(1)	119.4(1)
N(12)–Cd(1)–I(2)	93.5(1)	N(12)–Cd(1)–I(2)a	141.3(2)
N(13)–Cd(1)–I(1)	123.3(1)	N(13)–Cd(1)–I(2)	126.0(1)
N(13)–Cd(1)–I(2)a	76.4(2)	N(23)–Cd(1)–I(1)	71.7(1)
N(23)–Cd(1)–I(2)	152.1(1)	N(23)–Cd(1)–I(2)a	124.6(2)
I(1)–Cd(1)–I(2)	108.6(5)	I(1)–Cd(1)–I(2)a	97.8(5)
I(2)–Cd(1)–I(2)a	83.3(5)	Cd(1)–I(2)–Cd(1)a	96.7(5)
Cd(1)–N(12)–Ti(1)	86.1(2)	Cd(1)–N(12)–Ti(2)	102.3(2)
Cd(1)–N(13)–Ti(1)	93.9(2)	Cd(1)–N(13)–Ti(3)	104.4(2)
Cd(1)–N(23)–Ti(2)	87.5(2)	Cd(1)–N(23)–Ti(3)	82.5(2)
N(12)–Ti(1)–N(13)	99.8(2)	N(1)–Ti(1)–N(12)	86.9(2)
N(1)–Ti(1)–N(13)	87.1(2)	N(12)–Ti(2)–N(23)	105.1(2)
N(1)–Ti(2)–N(12)	85.9(2)	N(1)–Ti(2)–N(23)	84.6(2)
N(13)–Ti(3)–N(23)	104.3(2)	N(1)–Ti(3)–N(13)	85.9(2)
N(1)–Ti(3)–N(23)	85.6(2)	Ti(1)–N(1)–Ti(2)	94.5(2)
Ti(1)–N(1)–Ti(3)	95.4(2)	Ti(2)–N(1)–Ti(3)	93.7(2)
Ti(1)–N(12)–Ti(2)	92.5(2)	Ti(1)–N(13)–Ti(3)	91.5(2)
Ti(2)–N(23)–Ti(3)	95.2(2)		

Symmetry transformation: (a) –x + 1, –y + 2, –z + 2.

Reaction of **2** with two equivalents of lithium reagents [LiR] in toluene at room temperature gave the alkyl, alkynyl, cyclopentadienyl or amido derivatives [RCd{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] [R = CH$_2$SiMe$_3$ (**4**), C≡CSiMe$_3$ (**5**), C$_5$H$_4$(SiMe$_3$) (**6**), N(SiMe$_3$)$_2$ (**7**)] (Scheme 1). Complexes **4**-**7** were isolated in good yields (57-86%) as red solids which are soluble in toluene or hexane. Compounds **4**-**7** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for **5**. Mass spectra (EI, 70 eV) show the expected molecular peaks for a single-cube

aggregation in the gas phase. IR spectra (KBr) of complexes **4**-**7** reveal one ν_{NH} absorption, between 3358 and 3349 cm^{-1}, similar to the value found for **1**, 3352 cm^{-1}. In addition, the IR spectrum of **5** shows a weak absorption at 2061 cm^{-1} for the $\nu_{C\equiv C}$ vibration, which is typical of a terminal alkynyl ligand bound to a single metal center.[17] ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **4**-**7** in [D$_6$]benzene at room temperature show resonance signals for two η^5-C$_5$Me$_5$ groups in a 2:1 ratio, one R ligand, and a broad signal for the NH groups. These NMR data are consistent with a C_s symmetry in solution and tetrahedral geometries for the cadmium centers. The C$_5$H$_4$(SiMe$_3$) ligand of **6** shows three resonance signals at δ = 6.94, 6.74 and 0.20 in the ^{1}H NMR spectrum and four resonances at δ = 124.8, 121.1, 79.5 and 0.7 in the ^{13}C{^{1}H} NMR spectrum. These chemical shifts are consistent with a σ-coordination mode of the trimethylsilylcyclopentadienyl ligand in **6**, in a similar manner to that determined in the zinc analogue [{(Me$_3$Si)C$_5$H$_4$}Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}],[12] and several crystallographically documented cadmium cyclopentadienyl derivatives.[18]

The X-ray crystal structure of [(Me$_3$SiC$\equiv$C)Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**5**) is presented in Figure 2, and selected lengths and angles are given in Table 2. The molecular structure shows a cube-type [CdTi$_3$N$_4$] core with the cadmium atom bound to three nitrogen atoms of the tridentate organometallic ligand and one alkynyl carbon atom. The geometry about the cadmium center is best described as distorted tetrahedral with angles N−Cd−N = 79.5(1)° (av) and N−Cd−C(41) = 132(1)° (av). The cadmium−nitrogen bond lengths (av 2.367(8) Å) are slightly longer than those found for several cadmium tris(pyrazolyl)borate derivatives (range 2.22-2.35 Å),[19] while the Cd−C(41) bond distance of 2.103(4) Å compares well with those reported for the alkynyl complexes [Cd(C$\equiv$CPh)$_2$(tmeda)] (av 2.142(7) Å)[20] and [Cd(C$\equiv$CSiMe$_3$)(μ_3-NPEt$_3$)]$_4$ (av 2.134(5)

8

Å).[21] The alkynyl ligand is linear with an angle Cd(1)-C(41)-C(42) of 179.5(4)° and a

C(41)≡C(42) bond length of 1.208(5) Å, all of which are typical for these ligands.[17]

Within the organometallic ligand, the average bond lengths and angles are similar to those

determined in the free ligand **1**.[1]
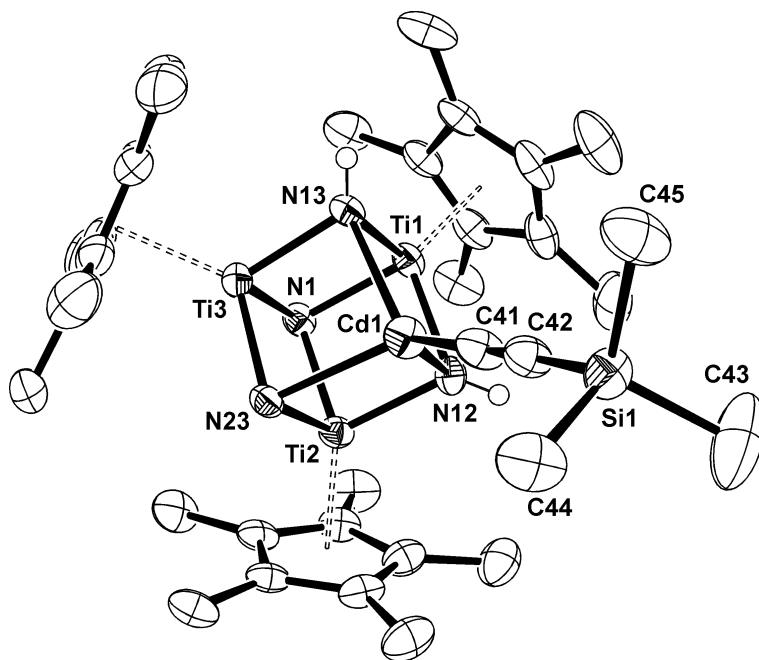
Figure 2. Perspective view of complex [(Me$_3$SiC≡C)Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**5**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the methyl groups are omitted for clarity.

Table 2. Selected lengths (Å) and angles (°) for **5**.

Cd(1)–C(41)	2.103(4)	Cd(1)–N(13)	2.361(3)
Cd(1)–N(23)	2.364(3)	Cd(1)–N(12)	2.376(3)
C(41)–C(42)	1.208(5)	Ti–N av	1.952(9)
Ti···Ti av	2.835(5)	Cd···Ti av	3.051(7)
N–Cd(1)–N av	79.5(1)	N(12)–Cd(1)–C(41)	131.1(1)
N(13)–Cd(1)–C(41)	132.5(1)	N(23)–Cd(1)–C(41)	133.8(1)
Cd(1)–C(41)–C(42)	179.5(4)	C(41)-C(42)-Si(1)	178.2(4)
Cd(1)–N–Ti av	89.2(3)	N(1)–Ti–N av	86.6(2)
N(12)–Ti(1)–N(13)	101.7(1)	N(12)–Ti(2)–N(23)	101.4(1)
N(13)–Ti(3)–N(23)	100.9(1)	Ti–N(1)–Ti av	93.7(2)
Ti(1)–N(12)–Ti(2)	93.6(1)	Ti(1)–N(13)–Ti(3)	92.9(1)
Ti(2)–N(23)–Ti(3)	92.3(1)		

The alkyl complex **4** is stable in [D$_6$]benzene solution at 90 ºC, but solutions of compounds **5**-**7** decompose at that temperature to give an insoluble gray solid, presumably cadmium metal. The cadmium amido complex **7** is stable to ambient light in solution in contrast to the behavior observed for the zinc analogue [{(Me$_3$Si)$_2$N}Zn{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}].[12] Additionally, this zinc amido derivative did not react with **1** even at high temperatures while the treatment of the analogue cadmium compound **7** with one equivalent of **1** in toluene at room temperature gives the corner-shared double-cube complex [Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (**8**) (Scheme 2).
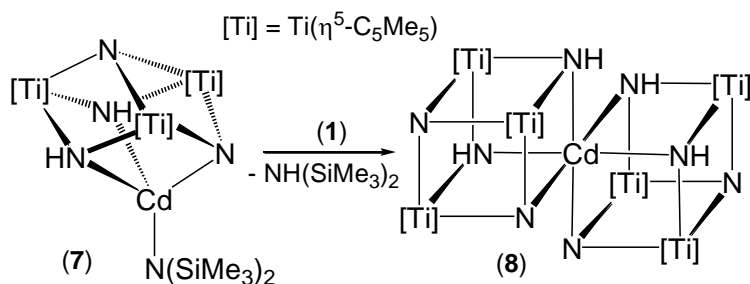
Scheme 2. Synthesis of the double-cube cadmium complex **8**.

Compound **8** was isolated in high yield as red crystals which are not soluble in common solvents, precluding its characterization by NMR spectroscopy, but it was characterized by IR spectroscopy and C, H, N microanalysis, as well as by an X-ray crystal structure determination. Attempts to establish the degree of association of the compound in the gas phase by mass spectrometry (EI, 70 eV) were unsuccessful due to the lack of volatility. The IR spectrum (KBr) of complex **8** reveals one ν_{NH} vibration at 3357 cm^{-1} similar to the value determined for **1**, 3352 cm^{-1}.

The molecular structure of **8** is presented in Figure 3, and selected lengths and angles are given in Table 3. The crystal structure shows a corner-shared double-cube

[CdTi$_6$N$_8$] core similar to those determined for the analogous group 2 double-cube derivatives [M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (M = Mg, Ca, Sr, Ba).[11c] Molecules of **8** lie on a crystallographic inversion center on the cadmium atom and also present a mirror plane bearing the Cd(1), N(1), N(22), and Ti(1) core atoms. The cadmium central atom exhibits a six-coordinate geometry in which the nitrogen atoms occupy the vertexes of a trigonal antiprism. In that arrangement, the tridentate organometallic ligands {(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$^-$ force the pentamethylcyclopentadienyl groups to be into an alternate position. The coordination environment around cadmium in **8** resembles those determined for cadmium bis(tris(pyrazolyl)borate) complexes,[22] but showing longer Cd-N bond lengths (av 2.490(3) Å) and narrower N−Cd−N intraligand angles (av 74.3(1)º).
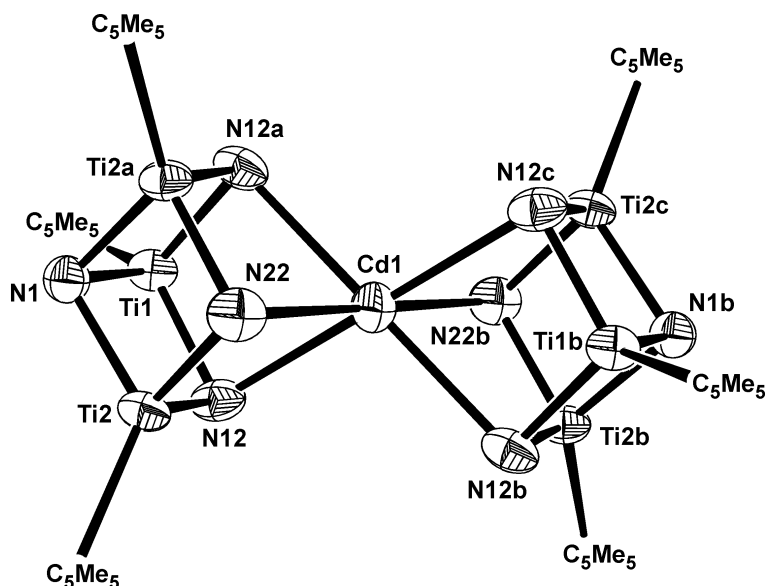
Figure 3. Perspective view of [Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (**8**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the pentamethylcyclopentadienyl groups are omitted for clarity. Symmetry transformations: (a) x, y, −z; (b) −x + 2, −y, z; (c) −x + 2, −y, −z.

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

Cd(1)–N(12)	2.492(5)	Cd(1)–N(22)	2.486(6)
Ti(1)–N(1)	1.962(6)	Ti(2)–N(1)	1.964(4)
Ti(1)–N(12)	1.954(4)	Ti(2)–N(12)	1.940(4)
Ti(2)–N(22)	1.942(5)	Ti···Ti av	2.837(2)
Cd···Ti av	3.20(1)		
N(12)–Cd(1)–N(12)a	74.4(2)	N(12)–Cd(1)–N(22)	74.2(2)
N(12)–Cd(1)–N(12)b	105.6(2)	N(12)–Cd(1)–N(22)b	105.8(2)
Cd(1)–N(12)–Ti(1)	91.7(2)	Cd(1)–N(12)–Ti(2)	91.4(2)
Cd(1)–N(22)–Ti(2)	91.6(2)	Ti(1)–N(12)–Ti(2)	93.4(2)
Ti(2)–N(22)–Ti(2)a	93.9(3)	Ti(1)–N(1)–Ti(2)	92.5(2)
Ti(2)–N(1)–Ti(2)a	92.6(3)	N(12)–Ti(1)–N(12)a	100.8(3)
N(12)–Ti(2)–N(22)	101.3(2)	N(1)–Ti(1)–N(12)	86.7(2)
N(1)–Ti(2)–N(12)	87.0(2)	N(1)–Ti(2)–N(22)	86.5(2)

Symmetry transformations: (a) x, y, −z; (b) −x + 2, −y, z.

Mercury Compounds. The synthetic chemistry is outlined in Scheme 3. The reaction of **1**

with one equivalent of anhydrous mercury(II) iodide in toluene at room temperature led to

the cube-type adduct $[I_2Hg\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**), as an air-sensitive yellow

solid in good yield (78%).[13] Subsequent treatment of complex **9** with two equivalents of

potassium bis(trimethylsilyl)amide in toluene at room temperature affords $[Hg_2\{(\mu_3\text{-}$

$N)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}_2]$ (**10**), as a red solid in a 45% yield.[13] The reaction of

compound **9** with $[K\{N(SiMe_3)_2\}_2]$ (2 equiv) in [D$_6$]benzene was monitored by NMR

spectroscopy at room temperature. Spectra taken within 5 min revealed resonances assigned

to the mercury amido complex $[\{(Me_3Si)_2N\}Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$

(**11**) along with those due to free bis(trimethylsilyl)amine. After leaving the NMR tube

without any stirring for 1 h, the NMR analysis of the solution showed complete

consumption of **11** and complex **10** precipitated as a red solid. The formation of **10** from

the amido derivative **11** could take place by an intermolecular elimination of $NH(SiMe_3)_2$

as depicted in Scheme 3.
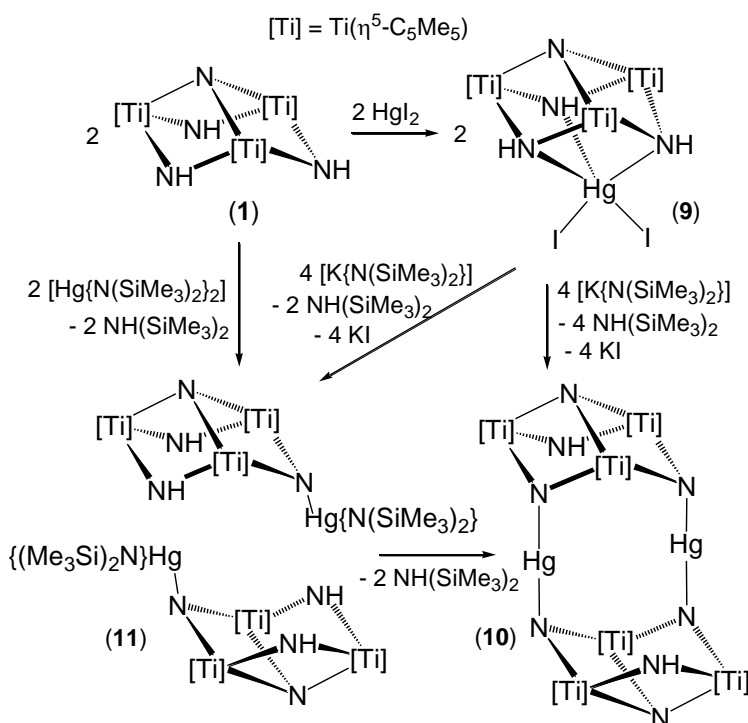
Scheme 3. Synthesis of mercury complexes.

Complex **11** was also identified by NMR spectroscopy by following the reaction of **1** with one equivalent of $[Hg\{N(SiMe_3)_2\}_2]$ in $[D_6]$benzene. No reaction was found at room temperature, and after heating at 60 ºC the spectra showed resonance signals for **11** as the major product, along with minor resonances due to the starting materials and $NH(SiMe_3)_2$. Despite many attempts at preparative scale reactions, it was not possible to isolate compound **11** in a pure form for a complete characterization. Because complex **1** did not react with the bis(trimethylsilymethyl) analogue $[Hg(CH_2SiMe_3)_2]$ in $[D_6]$benzene even at 100 ºC, we synthesized the previously unknown alkyl-amido derivative $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$ and tried to prepare a more stable alkyl analogue to complex **11**. Thus, treatment of **1** with $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$ in $[D_6]$benzene at 60 ºC allowed the characterization by NMR spectroscopy of the alkyl compound

[(Me₃SiCH₂)Hg{(μ₃-N)Ti₃(η⁵-C₅Me₅)₃(μ-NH)₂(μ₃-N)}] ($[(Me_3SiCH_2)Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$) (**12**). Unfortunately, again despite many attempts, we could not obtain a pure sample of **12**.

The NMR spectroscopic data of **11** and **12** are consistent with a C_s symmetry in solution for these compounds. ^{1}H NMR spectra show resonance signals for two $\eta^5\text{-}C_5Me_5$ groups in a 2:1 ratio, one bis(trimethylsilyl)amido or trimethylsilylmethyl ligand, and a broad signal for the NH groups. The NH resonance signals of complexes **11** ($\delta = 13.87$) and **12** ($\delta = 13.86$) are slightly shifted to lower field than those found in **1** ($\delta = 13.80$), suggesting the absence of coordination of the NH groups to the mercury center. These data are in agreement with an incomplete cube-type structure, similar to the free organometallic ligand **1** and the derivatives of group 14 elements $[Me_3M\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (M = Si, Ge, Sn),[10b] and lead us to rule out a four-coordinate mercury center in solution.

Moreover, the existence of compound **10**, in which two trinuclear systems are linked by two mercury atoms, moved us to examine the preparation of a complex where two metalloligand units were connected by one mercury atom. Thus, the reaction of the potassium[11a] derivative $[K(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ with one equivalent of mercury diiodide in toluene at room temperature afforded $[Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}_2]$ (**13**) (Scheme 4).
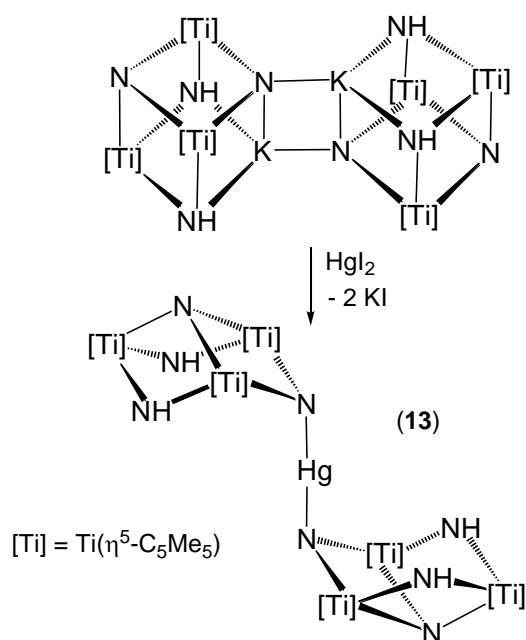
Scheme 4. Synthesis of the mercury complex **13**.

Complex **13** was obtained in good yield (89%) as an orange solid, which is very soluble in toluene and slightly soluble in hexane. This compound was characterized by spectroscopic and analytical methods. NMR spectroscopic data are consistent with a C_{2h} symmetric structure in solution. The ^{1}H NMR spectrum in [D$_6$]benzene at room temperature reveals resonances for two different η^5-C$_5$Me$_5$ ligands in a 2:1 ratio, and a broad signal for equivalent NH groups. The NH resonance signal at 13.96 ppm is shifted to lower field than that found in compound **1** ($\delta = 13.80$), suggesting again the absence of coordination of the NH ligands to the mercury center in solution, in a fashion similar to that determined for complex **10** by single-crystal X-ray diffraction analysis.

Conclusions

The reaction of the organometallic ligand [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] with cadmium and mercury dihalides gives the molecular adducts [X$_2$M{(μ_3-NH)$_3$Ti$_3$(η^5-

$C_5Me_5)_3(\mu_3\text{-}N)\}]$. Treatment of these complexes with alkali metal reagents leads to titanium/cadmium nitrido derivatives with single-cube $[CdTi_3N_4]$ central cores or titanium/mercury compounds with incomplete cube-type structures. Whereas a cadmium center with a six-coordinate geometry was determined in the corner-shared double-cube complex $[Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$, the analogue mercury derivative shows two titanium metalloligands connected by one mercury atom in a linear geometry.

Experimental Section

General Considerations and Starting Materials: All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. Tetrahydrofuran (THF) was distilled from purple solutions of sodium benzophenone just prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. $CdCl_2$ (99.9%), CdI_2 (99.999%), HgI_2 (99.999%) and $[Li\{N(SiMe_3)_2\}]$ were purchased from Aldrich, and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[1,2] $[Li(CH_2SiMe_3)]$,[23] $[Li(C\equiv CSiMe_3)]$,[24] $[Li\{C_5H_4(SiMe_3)\}]$,[25] $[Hg\{N(SiMe_3)_2\}_2]$,[26] $[Hg(CH_2SiMe_3)_2]$,[27] $[Hg(CH_2SiMe_3)Cl]$,[27] and $[K(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$,[11a] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 or a Varian Mercury-300 spectrometers. Chemical shifts (δ) are given relative to residual protons or to carbon of the solvent.

Electron impact mass spectra were obtained at 70 eV. Microanalysis (C, H, N) were performed in a Leco CHNS-932 or a Fisons CHNS-O-EA 1108.

Synthesis of [Cl$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (2). A 100 mL Schlenk flask was charged with **1** (0.60 g, 0.99 mmol), CdCl$_2$ (0.18 g, 0.98 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h. The volatile components were removed under reduced pressure to give a yellow solid. This solid was washed with toluene (5 mL) and vacuum-dried to afford **2** as a yellow powder (0.55 g, 70%). IR (KBr) $\tilde{v}$: 3341 (m), 3234 (m), 2907 (s), 2857 (m), 1489 (w), 1428 (m), 1378 (s), 1207 (w), 1066 (w), 1025 (w), 764 (m), 712 (s), 695 (s), 659 (vs), 525 (w), 421 (w) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 11.91 (s br, 3H, NH), 2.09 (s, 45H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 20 °C): δ = 121.6 (*C$_5$*Me$_5$), 12.2 (C$_5$*Me$_5$*). EI MS: m/z (%) 608 (6) [M − CdCl$_2$]$^+$. C$_{30}$H$_{48}$CdCl$_2$N$_4$Ti$_3$ (791.65): calcd. C 45.52, H 6.11, N 7.08; found C 45.08, H 6.24, N 6.68.

Synthesis of [I$_2$Cd{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (3). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), CdI$_2$ (0.18 g, 0.49 mmol) and toluene (20 mL). The reaction mixture was stirred at 90 °C for two days. The volatile components were removed under reduced pressure to give a brown solid. This solid was washed with toluene (5 mL) and vacuum-dried to afford **3** as an orange powder (0.35 g, 73%). X-ray quality crystals of complex **3** were obtained in a NMR tube by slow cooling to room temperature a mixture of **1** and CdI$_2$ in [D$_6$]benzene heated at 90 °C for 20 h. IR (KBr) $\tilde{v}$: 3338 (w), 3307 (w), 2909 (s), 2855 (m), 1488 (w), 1426 (m), 1377 (s), 1261 (w), 1094 (w), 1067 (w), 1023 (w), 764 (vs), 721 (s), 655 (vs), 621 (s), 528 (m), 478 (m), 429 (m), 402 (m) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 11.46 (s br, 3H, NH), 2.11 (s, 45H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75

MHz, CDCl$_3$, 20 ºC): δ = 122.4 (C_5Me$_5$), 12.4 (C$_5$$Me_5$). C$_{30}H_{48}CdI_2N_4Ti_3$ (974.55): calcd. C 36.96, H 4.96, N 5.75; found C 35.77, H 4.54, N 5.17.

Synthesis of [(Me$_3$SiCH$_2$)Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (4). A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.38 mmol), [Li(CH$_2$SiMe$_3$)] (0.070 g, 0.74 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 20 h to give a red solution and a white precipitate. After filtration, the volatile components of the solution were removed under reduced pressure to afford **4** as a red solid (0.25 g, 83%). IR (KBr) $\tilde{v}$: 3358 (w), 2944 (s), 2910 (s), 2858 (s), 1490 (w), 1435 (m), 1375 (m), 1252 (w), 1240 (m), 1094 (w), 1067 (w), 1024 (w), 924 (m), 854 (m), 820 (s), 799 (m), 719 (vs), 698 (s), 662 (s), 618 (s), 531 (w), 447 (w), 421 (m) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): δ = 11.14 (s br, 2H, NH), 2.10 (s, 30H, C$_5$Me$_5$), 1.89 (s, 15H, C$_5$Me$_5$), 0.20 (s, 9H, CH$_2$SiMe_3), -0.36 (s, 2H, CH_2SiMe$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): δ = 118.5, 117.4 (C_5Me$_5$), 12.0, 11.9 (C$_5$$Me_5$), 3.3 (CH$_2SiMe_3$), -11.6 (CH$_2$SiMe$_3$). EI MS: m/z (%) 807 (4) [M]$^+$, 607 (22) [M − Cd(CH$_2$SiMe$_3$)]$^+$. C$_{34}$H$_{58}$CdN$_4$SiTi$_3$ (806.95): calcd. C 50.61, H 7.24, N 6.94; found C 50.94, H 7.32, N 6.29.

Synthesis of [(Me$_3$SiC≡C)Cd{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (5). A 100 mL Schlenk flask was charged with **2** (0.85 g, 1.07 mmol), [Li(C≡CSiMe$_3$)] (0.22 g, 2.11 mmol) and toluene (30 mL). The reaction mixture was stirred at room temperature for 4 h to give a red solution and a white precipitate. After filtration, the volume of the solution was concentrated to about 5 mL under reduced pressure, and the resultant solution was cooled at -25 ºC. After 24 h, red crystals were collected by filtration and vacuum-dried to afford **5** (0.49 g, 57%). IR (KBr) $\tilde{v}$: 3354 (m), 2954 (s), 2909 (s), 2859 (s), 2061 (w), 1491 (w), 1430 (m), 1376 (m), 1244 (m), 1067 (w), 1025 (w), 857 (s), 840 (s), 759 (m), 719 (vs), 695 (vs), 668 (vs), 616 (s), 531 (w), 445 (w), 423 (m) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20

ºC): $\delta = 10.80$ (s br, 2H, NH), 2.00 (s, 30H, C$_5$Me$_5$), 1.81 (s, 15H, C$_5$Me$_5$), 0.24 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): $\delta = 122.2$ (CCSiMe$_3$), 119.2, 118.1 (C_5Me$_5$), 117.6 (CCSiMe$_3$), 11.8, 11.7 (C$_5$$Me_5$), 0.9 (CCSi$Me_3$). EI MS: m/z (%) 817 (4) [M]$^+$, 607 (6) [M − Cd(CCSiMe$_3$)]$^+$. C$_{35}$H$_{56}$CdN$_4$SiTi$_3$ (816.94): calcd. C 51.46, H 6.91, N 6.86; found C 51.57, H 6.90, N 6.44.

Synthesis of [{(Me$_3$Si)C$_5$H$_4$}Cd{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (6). In a fashion similar to the preparation of **4**, the treatment of **2** (0.30 g, 0.38 mmol) with [Li{C$_5$H$_4$(SiMe$_3$)}] (0.11 g, 0.76 mmol) in toluene (30 mL) afforded **6** as a red solid (0.23 g, 72%). IR (KBr) $\tilde{v}$: 3353 (w), 3064 (w), 2946 (m), 2909 (s), 2856 (m), 1440 (w), 1430 (m), 1375 (s), 1259 (w), 1247 (m), 1148 (w), 1062 (w), 1041 (w), 1018 (m), 952 (w), 884 (m), 833 (s), 792 (m), 741 (vs), 720 (vs), 698 (vs), 661 (vs), 616 (s), 530 (w), 423 (m) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): $\delta = 10.30$ (s br, 2H, NH), 6.94 (m, 2H, C$_5$$H_2H_2$SiMe$_3$), 6.74 (m, 2H, C$_5H_2$$H_2$SiMe$_3$), 2.06 (s, 30H, C$_5Me_5$), 1.85 (s, 15H, C$_5Me_5$), 0.20 (s, 9H, C$_5H_4SiMe_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): $\delta = 124.8$, 121.1 (C_4H$_4$CSiMe$_3$), 119.2, 117.9 (C_5Me$_5$), 79.5 (C$_4$H$_4$$C$SiMe$_3$), 12.0, 11.8 (C$_5$$Me_5$), 0.7 (C$_5H_4SiMe_3$). EI MS: m/z (%) 607 (9) [M − Cd{C$_5$H$_4$(SiMe$_3$)}]$^+$. C$_{38}$H$_{60}$CdN$_4$SiTi$_3$ (857.01): calcd. C 53.26, H 7.06, N 6.54; found C 53.52, H 6.96, N 6.12.

Synthesis of [{(Me$_3$Si)$_2$N}Cd{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (7). In a fashion similar to the preparation of **4**, the treatment of **2** (0.53 g, 0.67 mmol) with [Li{N(SiMe$_3$)$_2$}] (0.22 g, 1.31 mmol) in toluene (25 mL) for 3 h afforded **7** as a red solid (0.50 g, 86%). IR (KBr) $\tilde{v}$: 3349 (w), 2944 (s), 2909 (s), 2858 (s), 1493 (w), 1437 (m), 1376 (m), 1251 (m), 1240 (s), 1179 (w), 1011 (s), 932 (w), 879 (s), 830 (s), 779 (m), 717 (vs), 693 (vs), 666 (s), 615 (s), 527 (w), 442 (w), 421 (m) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): $\delta = 10.72$ (s br, 2H, NH), 2.07 (s, 30H, C$_5$Me$_5$), 1.89 (s, 15H, C$_5$Me$_5$), 0.29 (s, 18H, N(SiMe$_3$)$_2$). ^{13}C{^{1}H}

NMR (75 MHz, C_6D_6, 20 ºC): δ = 119.3, 118.1 (C_5Me_5), 12.1, 12.0 (C_5Me_5), 6.7 (SiMe_3).

EI MS: m/z (%) 880 (1) [M]$^+$, 607 (3) [M – Cd{N(SiMe_3)_2}]$^+$. $C_{36}H_{65}CdN_5Si_2Ti_3$ (880.12): calcd. C 49.13, H 7.44, N 7.96; found C 48.46, H 7.30, N 7.64.

Synthesis of [Cd{(μ_3-N)(μ_3-NH)_2Ti_3(η^5-C_5Me_5)_3(μ_3-N)}_2] (8). A solution of **1** (0.21 g, 0.34 mmol) in toluene (5 mL) was carefully added to **7** (0.30 g, 0.34 mmol) in toluene (20 mL). The system was allowed to react without any stirring for 2 days. After decantation, the resultant red crystals were vacuum-dried to afford **8·**1.5C_7H_8 (0.40 g, 80%). IR (KBr) $\tilde{v}$: 3357 (w), 2968 (m), 2905 (s), 2854 (m), 2717 (w), 1604 (w), 1494 (w), 1433 (m), 1373 (m), 1079 (w), 1023 (w), 855 (w), 719 (vs), 694 (s), 658 (m), 632 (m), 618 (s), 518 (m), 475 (w), 464 (w), 437 (w), 413 (m) cm^{-1}. $C_{70.5}H_{106}CdN_8Ti_6$ (1465.27): calcd. C 57.79, H 7.29, N 7.65; found C 57.74, H 7.56, N 7.19.

Reaction of 1 with [Hg{N(SiMe_3)_2}_2]. A 5 mm NMR tube was charged with **1** (0.010 g, 0.016 mmol), [Hg{N(SiMe_3)_2}_2] (0.008 g, 0.017 mmol) and [D_6]benzene (1.00 mL). The course of the reaction was followed by NMR spectroscopy. After 20 h at 60 ºC, the spectra showed resonances assigned to complex [{(Me_3Si)_2N}Hg{(μ_3-N)Ti_3(η^5-C_5Me_5)_3(μ-NH)_2(μ_3-N)}] (**11**) along with those due to free NH(SiMe_3)_2. Upon heating the solution for longer periods of time or higher temperatures, a red solid corresponding to complex **10** precipitated at the bottom of the tube.

NMR data for **11**: ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ = 13.87 (s br, 2H, NH), 2.08 (s, 30H, C_5Me_5), 1.94 (s, 15H, C_5Me_5), 0.20 (s, 18H, N(SiMe_3)_2). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ºC): δ = 117.8, 117.4 (C_5Me_5), 12.2, 11.8 (C_5Me_5), 5.4 (SiMe_3).

Synthesis of [Hg(CH_2SiMe_3){N(SiMe_3)_2}]. This compound was prepared in a fashion similar to those reported for the analogous complexes [Hg{N(SiMe_3)_2}R] (R = Me, Et).[28] A 100 mL Schlenk flask was charged with [Hg(CH_2SiMe_3)Cl] (0.35 g, 1.08 mmol),

[Li{N(SiMe$_3$)$_2$}] (0.18 g, 1.08 mmol) and THF (25 mL). The reaction mixture was stirred at room temperature for 20 h to give a colorless solution. The volatile components were removed under reduced pressure, and the resultant oil was extracted with hexane (20 mL). After filtration, the volatile components were removed under reduced pressure to afford [Hg(CH$_2$SiMe$_3$){N(SiMe$_3$)$_2$}] as a colorless liquid (0.42 g, 88%). IR (KBr) $\tilde{v}$: 2951 (s), 2893 (w), 1623 (w), 1444 (w), 1407 (w), 1356 (w), 1247 (vs), 1019 (m), 989 (s), 880 (s), 851 (vs), 831 (vs), 790 (m), 769 (m), 751 (m), 711 (m), 689 (m), 674 (m), 615 (w) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ℃): δ = 0.24 (s, 18H, N(SiMe$_3$)$_2$), 0.16 (s, 2H, CH_2SiMe$_3$), 0.00 (s, 9H, CH$_2$SiMe_3). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ℃): δ = 13.6 (CH$_2$SiMe$_3$), 5.5 (N(SiMe$_3$)$_2$), 1.8 (CH$_2$SiMe_3). EI MS: m/z (%) 450 (2) [M + H]$^+$, 162 (17) [N(SiMe$_3$)$_2$ + 2H]$^+$, 88 (100) [CH$_2$SiMe$_3$ + H]$^+$.

Reaction of 1 with [Hg(CH$_2$SiMe$_3$){N(SiMe$_3$)$_2$}]. A 5 mm NMR tube was charged with **1** (0.010 g, 0.016 mmol), [Hg(CH$_2$SiMe$_3$){N(SiMe$_3$)$_2$}] (0.007 g, 0.016 mmol) and [D$_6$]benzene (1.00 mL). The course of the reaction was followed by NMR spectroscopy. After 20 h at 60 ℃, the spectra showed resonances assigned to complex [(Me$_3$SiCH$_2$)Hg{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] (**12**) along with those due to free NH(SiMe$_3$)$_2$. Upon heating the solution for longer periods of time or higher temperatures, complex **12** decomposed to give a mixture of unidentified products.

NMR data for **12**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ℃): δ = 13.86 (s br, 2H, NH), 2.12 (s, 30H, C$_5$Me$_5$), 1.97 (s, 15H, C$_5$Me$_5$), 0.24 (s, 2H, CH_2SiMe$_3$), 0.04 (s, 9H, CH$_2$SiMe_3). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ℃): δ = 117.4, 116.9 (C$_5$Me$_5$), 14.3 (CH$_2$SiMe$_3$), 12.2, 11.9 (C$_5$Me$_5$), 1.9 (CH$_2$SiMe_3).

Synthesis of [Hg{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}$_2$] (13). A 100 mL Schlenk flask was charged with [K(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (0.27 g, 0.21 mmol), HgI$_2$

(0.090 g, 0.20 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature for 5 h to give an orange solution and a white precipitate. After filtration, the volatile components of the solution were removed under reduced pressure to afford **13** as an orange solid (0.25 g, 89%). IR (KBr) $\tilde{v}$: 3354 (w), 2906 (s), 2854 (m), 1492 (w), 1431 (m), 1374 (m), 1258 (w), 1065 (w), 1023 (w), 798 (s), 712 (vs), 678 (vs), 649 (vs), 636 (s), 624 (s), 550 (w), 526 (m), 454 (w), 415 (w) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC): δ = 13.96 (s br, 4H, NH), 2.08 (s, 60H, C$_5$Me$_5$), 1.99 (s, 30H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 20 ºC): δ = 117.2, 117.1 (*C*$_5$Me$_5$), 12.3, 11.9 (C$_5$*Me*$_5$). C$_{60}$H$_{94}$HgN$_8$Ti$_6$ (1415.23): calcd. C 50.92, H 6.69, N 7.92; found C 50.83, H 6.97, N, 6.49.

X-ray Crystal Structure Determination of Complexes 3, 5 and 8. Crystals of **3**, **5** and **8** were obtained as described in the Experimental Section. Crystals were removed from the NMR tube or Schlenk flasks, and covered with a layer of a viscous perfluoropolyether (Fomblin Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit, K_α(Mo) = 0.71073 Å. Crystallographic data for all the complexes are presented in Table 4 (see page 25).

The structures were solved, using the WINGX package,[29] by direct methods (SHELXS-97[30] for **3** and **8**; SIR2002[31] for **5**), and refined by least-squares against F^2 (SHELXL-97).[30] Crystals of compound **3** presented disorder for the iodine atoms, I(1) and I(2). The PART tool allowed two positions for each iodine atom to be refined with a fixed occupancy of 90 and 10%, respectively. All non-hydrogen atoms of **3** were anisotropically refined,

while the hydrogen atoms were positioned geometrically and refined using a riding model in the last cycles of refinement.

In the crystallographic study of complex **5**, all non-hydrogen atoms were anisotropically refined. The imido hydrogen atoms (NH) were located in the difference Fourier map and refined isotropically, while the rest of the hydrogen atoms in the molecule were positioned geometrically and refined using a riding model.

Compound **8** crystallized with two molecules of toluene, which were found in the difference Fourier map, but it was not possible to get a chemically sensible model for them, so Squeeze procedure[32] was used to remove their contribution to the structure factors. Two carbon atoms of one pentamethylcyclopentadienyl ring (C(13) and C(18), both on the crystallographic mirror plane) were disordered and refined in two sites with occupancy 25%. All non-hydrogen atoms, except C(13), C(13)', C(16), C(17), C(18) and C(18)' from the disordered C_5Me_5 group, were anisotropically refined. All hydrogen atoms were included, positioned geometrically and refined by using a riding model. Two imido hydrogen atoms were statistically distributed over the nitrogen atoms N(12), N(12)a, N(12)b and N(12)c linked to the central cadmium (final 50% occupancy), while the other two imido hydrogen atoms were positioned over the atoms N(22) and N(22)b.

CCDC-835865 (for **3**), -835866 (for **5**), -835867 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Experimental data for the X-ray diffraction studies on **3**, **5** and **8**.

	3	**5**	**8**·2C$_7$H$_8$
Formula	C$_{30}$H$_{48}$CdI$_2$N$_4$Ti$_3$	C$_{35}$H$_{56}$CdN$_4$SiTi$_3$	C$_{74}$H$_{110}$CdN$_8$Ti$_6$
M	974.62	817.03	1511.50
T [K]	200(2)	200(2)	200(2)
λ[Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P-1$	$Pnnm$
a [Å]; α [°]	11.051(3)	11.521(1); 91.60(1)	14.727(3)
b [Å]; β [°]	18.824(4); 100.6(1)	12.134(2); 108.67(1)	15.504(3)
c [Å]; γ [°]	17.851(3)	15.259(3); 91.28(1)	16.716(3)
V [Å^3]	3650(1)	2019.0(5)	3816(1)
Z	4	2	2
ρ_{calcd} [g cm^{-3}]	1.774	1.344	1.315
$\mu_{MoK\alpha}$ [mm^{-1}]	2.923	1.148	0.913
$F(000)$	1904	844	1580
Crystal size [mm^3]	$0.18 \times 0.17 \times 0.16$	$0.24 \times 0.19 \times 0.10$	$0.45 \times 0.37 \times 0.20$
θ range [deg]	3.17 – 27.51	3.10 – 27.50	3.06 – 27.51
Index ranges	–14 to 14, –23 to 24, –23 to 23	–14 to 14, –15 to 15, –19 to 19	–16 to 19, –19 to 20, –21 to 21
Refl. collected	68936	48031	47187
Unique data	8376 (R_{int} = 0.156)	9134 (R_{int} = 0.086)	4533 (R_{int}=0.071)
Reflections [I>2σ(I)]	5555	6328	2997
Goodness-of-fit on F^2	1.073	1.019	1.030
Final R indices [I>2σ(I)]	R1 = 0.056 wR2 = 0.104	R1 = 0.044 wR2 = 0.103	R1 = 0.080 wR2 = 0.238
R indices (all data)	R1 = 0.117 wR2 = 0.145	R1 = 0.077 wR2 = 0.114	R1 = 0.115 wR2 = 0.238
Largest diff. peak/hole [e·Å^{-3}]	1.331/–1.712	0.766/–0.990	1.386/–0.709

[a] R1 = Σ||F$_0$|-|F$_c$||/[Σ|F$_0$|]; wR2 = $\{[\Sigma w(F_0^2 - F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$

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