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# Cadmium and Mercury Complexes Containing Trinuclear Titanium Imido-Nitrido Metalloligands

**Avelino Martín,[a] Miguel Mena,[a] Adrián Pérez-Redondo,[a] and Carlos Yélamos*[a]**

*Dedicated to the memory of Professor Francisco Urbanos*[‡]

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Several heterometallic nitrido complexes have been prepared from the reaction of the trinuclear imido-nitrido titanium complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with cadmium and mercury derivatives. Treatment of **1** with cadmium dichloride or cadmium diiodide in toluene afforded the adducts $[X_2Cd\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [X = Cl (**2**), I (**3**)]. Complex **2** reacted with lithium reagents [LiR] in toluene to give the cube-type derivatives $[RCd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [R = $CH_2SiMe_3$ (**4**), $C{\equiv}CSiMe_3$ (**5**), $C_5H_4(SiMe_3)$ (**6**), $N(SiMe_3)_2$ (**7**)]. The amido complex **7** reacted with 1 equiv. of **1** to give the corner-shared double-cube complex $[Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**8**) by means of bis(trimethylsilyl)amine elimination. Treatment of **1** with mercury(II) iodide in toluene gave the adduct $[I_2Hg\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**9**), which reacted with $[K\{N(SiMe_3)_2\}]$ to afford $[Hg\{(\mu_3\text{-}N)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}]_2$ (**10**) through the amido mercury intermediate $[\{(Me_3Si)_2N\}Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (**11**). Compound **11** and the analogous alkyl derivative $[(Me_3SiCH_2)Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (**12**) were characterised by NMR spectroscopy upon the treatment of **1** with $[Hg\{N(SiMe_3)_2\}R]$ [R = $N(SiMe_3)_2$, $CH_2SiMe_3$]. Complex $[Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}_2]$ (**13**), with one bridging mercury atom between two titanium trinuclear systems, was obtained upon treatment of $HgI_2$ with the potassium derivative $[K(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$. Complexes **3**, **5** and **8** were characterised by single-crystal X-ray diffraction analysis.

## Introduction

We are interested in the coordination chemistry of the trinuclear titanium imido-nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[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] the extensive coordination chemistry of which is known. This similarity prompted us to explore its potential application as a tridentate ligand towards different metal complexes and the design of a rational strategy for preparing cube-type heterometallic nitrido compounds. Polynuclear nitrido complexes are rare in the literature because of the difficult characterisation of their singular structures and, perhaps more importantly, the lack of systematic strategies for the construction of aggregates with the desired metal composition.[8] Our previous work has shown that **1** is capable of acting as a neutral tridentate chelating 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 from studies of the treatment of this preorganised system with cadmium and mercury derivatives. Part of the mercury chemistry has been recently communicated.[13]

## Results and Discussion

### Cadmium Compounds

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with 1 equiv. of anhydrous cadmium(II) chloride or iodide in toluene afforded the cube-type adducts $[X_2Cd\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [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,

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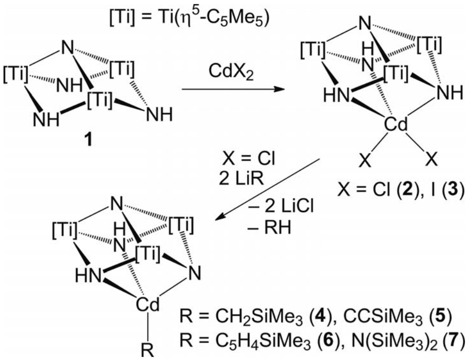
[a] Departamento de Química Inorgánica, Universidad de Alcalá
28871 Alcalá de Henares-Madrid, Spain
Fax: +34-91-8854683
E-mail: carlos.yelamos@uah.es

[‡] Passed away on May 28, 2011

which are poorly soluble in toluene or benzene but exhibit 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** affords a gray insoluble material at higher temperatures, which we presume to be cadmium metal.



Scheme 1. Synthesis of cadmium complexes.

Complexes **2** and **3** were characterised by spectroscopic and analytical methods and, in addition, **3** was further characterised by single-crystal X-ray diffraction. The IR spectra (KBr) revealed two $\nu_{NH}$ vibrations, between 3341 and 3234 cm$^{-1}$, which are similar to the value of 3352 cm$^{-1}$ determined for compound **1**.[2] The $^1$H and $^{13}$C{$^1$H} NMR spectra of complexes **2** and **3** in [D$_1$]chloroform at room temperature show signals for equivalent NH and η$^5$-C$_5$Me$_5$ ligands, suggesting the existence of dynamic behaviour in solution as seen in other metal dihalide adducts of **1**.[10a] The NH resonances ($\delta$ = 11.91 and 11.46 ppm) are shifted to a higher field than that found for **1** ($\delta$ = 13.40 ppm), whereas the resonances for the *ipso* carbon atom of the *C*$_5$Me$_5$ groups ($\delta$ = 121.6 and 122.4 ppm) in the $^{13}$C NMR spectrum are shifted downfield with respect to that found for **1** ($\delta$ = 117.1 ppm). In previous work we have used those data to propose a tridentate chelating coordination mode of the NH groups to the metal centres.[9,10]

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 centre 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···I interaction is considered, the geometry around the Cd(1) centre can be defined as distorted trigonal-prismatic, with three iodine atoms [I(1), I(2) and I(2)a] located in an eclipsed position with respect to the three imido-nitrogen atoms [N(12), N(13) and N(23)]. The distances N(23)···I(1) [3.440(5) Å] and N(13)···I(2)a [3.754(5) Å] are similar to the sum of the van der Waals radii of the 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 bonds 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-coordinate [tris(pyrazolyl)methane]cadmium 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]

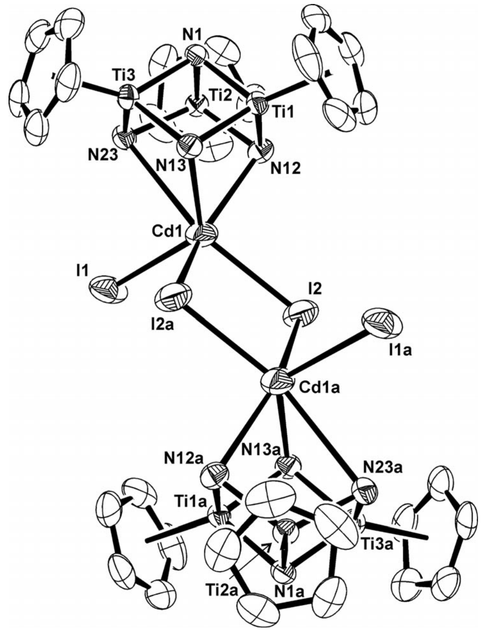


Figure 1. Perspective view of the dimeric disposition of complex [I$_2$Cd{(μ$_3$-NH)$_3$Ti$_3$(η$^5$-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the methyl groups of the pentamethylcyclopentadienyl rings are omitted for clarity. Symmetry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

The reaction of **2** with 2 equiv. of the 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 characterised 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 $\nu_{NH}$ absorption, between 3358 and 3349 cm$^{-1}$, similar to the value of 3352 cm$^{-1}$ found for **1**. In addition, the IR

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) | | |

spectrum of **5** shows a weak absorption at 2061 cm$^{-1}$ for the $\nu_{C\equiv C}$ vibration, and this is typical for a terminal alkynyl ligand bound to a single metal centre.[17] The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of compounds **4**–**7** in [D$_6$]benzene at room temperature show resonance signals for two $\eta^5$-$C_5Me_5$ groups in a 2:1 ratio, one R ligand and a broad signal for the NH groups. These NMR spectroscopic data are consistent with $C_s$ symmetry in solution and tetrahedral geometries for the cadmium centres. The $C_5H_4(SiMe_3)$ ligand of **6** shows three resonances at $\delta$ = 6.94, 6.74 and 0.20 ppm in the $^1H$ NMR spectrum and four resonances at $\delta$ = 124.8, 121.1, 79.5 and 0.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum. These chemical shifts are consistent with a σ-coordination mode of the (trimethylsilyl)cyclopentadienyl ligand in **6**, in a similar manner to that determined in the zinc analogue $[\{(Me_3Si)C_5H_4\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$[12] and several crystallographically documented cyclopentadienylcadmium derivatives.[18]

The X-ray crystal structure of $[(Me_3SiC\equiv C)Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**5**) is presented in Figure 2 with selected lengths and angles given in Table 2. The molecular structure shows a cube-type $[CdTi_3N_4]$ 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 centre 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 bonds [av. 2.367(8) Å] are slightly longer than those found in several [tris(pyrazolyl)borato]cadmium derivatives (range 2.22–2.35 Å),[19] while the Cd–C(41) bond length 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 $[Cd(C\equiv CSiMe_3)(\mu_3\text{-}NPEt_3)]_4$ [av. 2.134(5) Å].[21] The alkynyl ligand is linear with a Cd(1)–C(41)–C(42) angle 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 uncoordinated ligand **1**.[1]

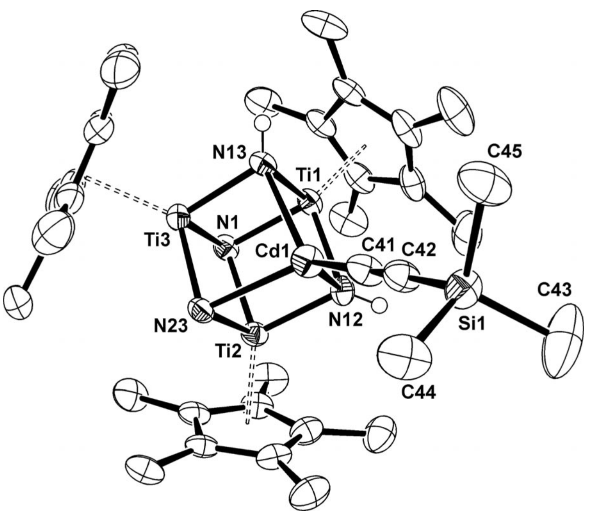


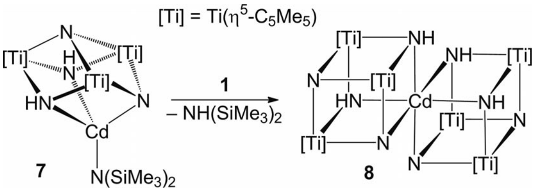
Figure 2. Perspective view of $[(Me_3SiC\equiv C)Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\text{-}Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**5**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the methyl groups are omitted for clarity.

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 °C, but solutions of compounds **5**–**7** decompose at that temperature to give an insoluble gray solid, presumably cadmium metal. The amido cadmium complex **7** is stable to ambient light in solution in contrast to the behaviour observed for the zinc analogue $[\{(Me_3Si)_2N\}Zn\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.[12] Additionally, this amido zinc derivative did not react with **1** even at high temperatures, while the treatment of the analogous cadmium compound **7** with 1 equiv. of **1** in toluene at room temperature gave the corner-shared double-cube complex $[Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**8**) (Scheme 2).

Compound **8** was isolated in high yield as red crystals, which are insoluble in common solvents, precluding its characterisation by NMR spectroscopy, but it was charac-



Scheme 2. Synthesis of the double-cube cadmium complex **8**.

terised 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 its lack of volatility. The IR spectrum (KBr) of complex **8** reveals one $\nu_{NH}$ vibration at 3357 cm$^{-1}$ similar to the value of 3352 cm$^{-1}$ determined for **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 [$CdTi_6N_8$] core similar to those determined for the analogous group 2 double-cube derivatives [$M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\text{-}Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$] (M = Mg, Ca, Sr, Ba).[11c] Molecules of **8** lie on a crystallographic inversion centre at the cadmium atom and also exhibit a mirror plane bearing the Cd(1), N(1), N(22) and Ti(1) core atoms. The central cadmium 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 $\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}^-$ force the pentamethylcyclopentadienyl groups into alternate positions. The coordination environment around the cadmium atom in **8** resembles those determined for bis[tris(pyrazolyl)borato]-cadmium complexes[22] but showing longer Cd–N bonds [av. 2.490(3) Å] and narrower N–Cd–N intraligand angles [av. 74.3(1)°].

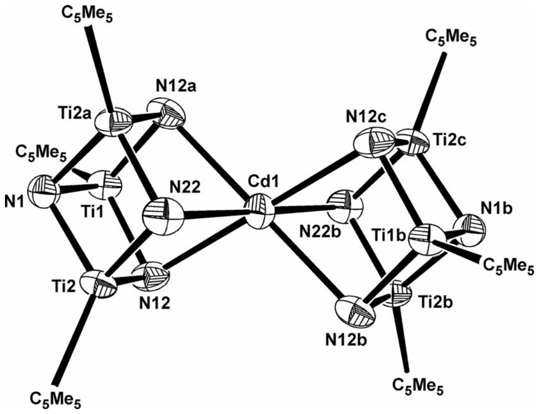


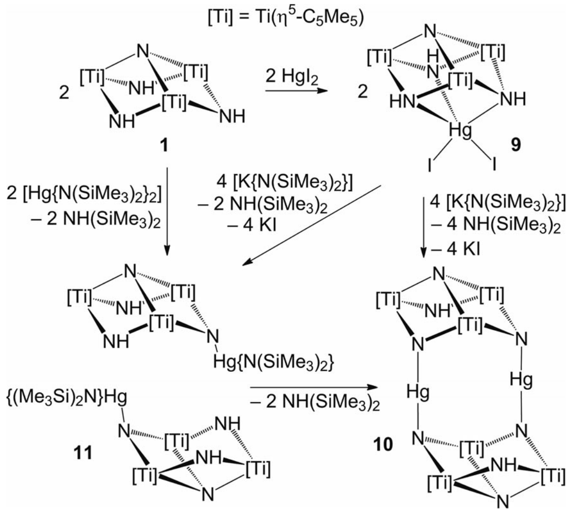
Figure 3. Perspective view of [$Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3\text{-}(\mu_3\text{-}N)\}_2$] (**8**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the pentamethylcyclopentadienyl groups are omitted for clarity. Symmetry transformations: (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) |

## Mercury Compounds

The synthetic chemistry is outlined in Scheme 3. The reaction of **1** with 1 equiv. 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 2 equiv. 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 equiv.) in [D$_6$]benzene was monitored by NMR spectroscopy at room temperature. Spectra taken within 5 min revealed resonances assigned to the amido mercury complex [$\{(Me_3Si)_2N\}Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3\text{-}(\mu\text{-}NH)_2(\mu_3\text{-}N)\}$] (**11**) along with those due to free bis(trimethylsilyl)amine. After leaving the NMR tube without any stirring for 1 h, the NMR spectroscopic 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.

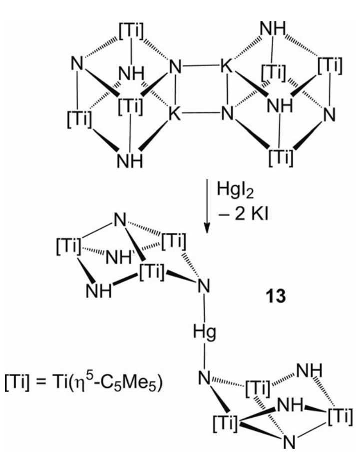


Scheme 3. Synthesis of mercury complexes.

Complex **11** was also identified by NMR spectroscopy according to the reaction of **1** with 1 equiv. of [$Hg\{N(SiMe_3)_2\}_2$] in [D$_6$]benzene. No reaction was found at room temperature and, after heating at 60 °C, 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 complete characterisation. Because complex **1** did not react with the bis(trimethylsilymethyl) analogue $[Hg(CH_2SiMe_3)_2]$ in [D$_6$]benzene even at 100 °C, we synthesised the previously unknown alkyl amido derivative $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$ and tried to prepare a more stable alkyl analogue of complex **11**. Thus, treatment of **1** with $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$ in [D$_6$]benzene at 60 °C allowed the characterisation, by NMR spectroscopy, of the alkyl compound $[(Me_3SiCH_2)Hg\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (**12**). Unfortunately, despite many attempts again, we could not obtain a pure sample of **12**.

The NMR spectroscopic data of **11** and **12** are consistent with $C_s$ symmetry in solution for these compounds. $^1$H NMR spectra show resonance signals for two $\eta^5$-$C_5Me_5$ 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 ppm) and **12** ($\delta$ = 13.86 ppm) are slightly shifted to lower field than those found in **1** ($\delta$ = 13.80 ppm), suggesting the absence of coordination of the NH groups to the mercury centre. 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] This leads us to rule out a four-coordinate mercury centre 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 1 equiv. 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 characterised 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 $\eta^5$-$C_5Me_5$ ligands in a 2:1 ratio and a broad signal for equivalent NH groups. The NH resonance signal at $\delta$ = 13.96 ppm is shifted to lower field than that found in compound **1** ($\delta$ = 13.80 ppm), again suggesting the absence of coordination of the NH ligands to the mercury centre 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 $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with cadmium and mercury dihalides gives the molecular adducts $[X_2M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$. Treatment of these complexes with alkali metal reagents leads to nitrido titanium/cadmium derivatives with single-cube $[CdTi_3N_4]$ central cores or titanium/mercury compounds with incomplete cube-type structures. Whereas a cadmium centre 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 analogous 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 by 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. $1\times10^{-3}$ 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 $[K(\mu_4\text{-}N)(\mu_3\text{-}NH)_2\text{-}\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$[11a] were prepared according to published procedures. Samples for IR spectroscopy were prepared as KBr pellets. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded with a Varian Unity-300 or a Varian Mercury-300 spectrometer. Chemical shifts ($\delta$) are given relative to residual protons or to carbon of the solvent. Electron impact mass spectra were obtained at 70 eV. Microanalyses (C, H, N) were performed with a Leco CHNS-932 or a Fisons CHNS-O-EA 1108 instrument.

**Synthesis of $[Cl_2Cd\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (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): ṽ =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): $\delta$ = 11.91 (br. s, 3 H, NH), 2.09 (s, 45 H, $C_5Me_5$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta$ = 121.6 ($\mathit{C}_5Me_5$), 12.2 ($C_5\mathit{Me}_5$) ppm. EI MS: *m/z* (%) = 608 (6) $[M - CdCl_2]^+$. $C_{30}H_{48}CdCl_2N_4Ti_3$ (791.65): calcd. C 45.52, H 6.11, N 7.08; found C 45.08, H 6.24, N 6.68.

**Synthesis of $[I_2Cd\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (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 2 d. 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 an 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): $\tilde{\nu}$ =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): $\delta$ = 11.46 (br. s, 3 H, NH), 2.11 (s, 45 H, $C_5Me_5$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta$ = 122.4 ($\mathit{C}_5Me_5$), 12.4 ($C_5\mathit{Me}_5$) ppm. $C_{30}H_{48}CdI_2N_4Ti_3$ (974.55): calcd. C 36.96, H 4.96, N 5.75; found C 35.77, H 4.54, N 5.17.

**Synthesis of $[(Me_3SiCH_2)Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (4):** A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.38 mmol), $[Li(CH_2SiMe_3)]$ (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): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 11.14 (br. s, 2 H, NH), 2.10 (s, 30 H, $C_5Me_5$), 1.89 (s, 15 H, $C_5Me_5$), 0.20 (s, 9 H, $CH_2Si\mathit{Me}_3$), –0.36 (s, 2 H, $C\mathit{H}_2SiMe_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 118.5, 117.4 ($\mathit{C}_5Me_5$), 12.0, 11.9 ($C_5\mathit{Me}_5$), 3.3 ($CH_2Si\mathit{Me}_3$), –11.6 ($\mathit{C}H_2SiMe_3$) ppm. EI MS: *m/z* (%) = 807 (4) $[M]^+$, 607 (22) $[M - Cd(CH_2SiMe_3)]$. $C_{34}H_{58}CdN_4SiTi_3$ (806.95): calcd. C 50.61, H 7.24, N 6.94; found C 50.94, H 7.32, N 6.29.

**Synthesis of $[(Me_3SiC{\equiv}C)Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (5):** A 100 mL Schlenk flask was charged with **2** (0.85 g, 1.07 mmol), $[Li(C{\equiv}CSiMe_3)]$ (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 to –25 °C. After 24 h, red crystals were collected by filtration and vacuum-dried to afford **5** (0.49 g, 57%). IR (KBr): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 10.80 (br. s, 2 H, NH), 2.00 (s, 30 H, $C_5Me_5$), 1.81 (s, 15 H, $C_5Me_5$), 0.24 (s, 9 H, $SiMe_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 122.2 ($C\mathit{C}SiMe_3$), 119.2, 118.1 ($\mathit{C}_5Me_5$), 117.6 ($\mathit{C}CSiMe_3$), 11.8, 11.7 ($C_5\mathit{Me}_5$), 0.9 ($CCSi\mathit{Me}_3$) ppm. EI MS: *m/z* (%) = 817 (4) $[M]^+$, 607 (6) $[M - Cd(CCSiMe_3)]^+$. $C_{35}H_{56}CdN_4SiTi_3$ (816.94): calcd. C 51.46, H 6.91, N 6.86; found C 51.57, H 6.90, N 6.44.

**Synthesis of $[\{(Me_3Si)C_5H_4\}Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (6):** In a fashion similar to the preparation of **4**, the treatment of **2** (0.30 g, 0.38 mmol) with $[Li\{C_5H_4(SiMe_3)\}]$ (0.11 g, 0.76 mmol) in toluene (30 mL) afforded **6** as a red solid (0.23 g, 72%). IR (KBr): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 10.30 (br. s, 2 H, NH), 6.94 (m, 2 H, $C_5\mathit{H}_2H_2SiMe_3$), 6.74 (m, 2 H, $C_5H_2\mathit{H}_2SiMe_3$), 2.06 (s, 30 H, $C_5Me_5$), 1.85 (s, 15 H, $C_5Me_5$), 0.20 (s, 9 H, $C_5H_4Si\mathit{Me}_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 124.8, 121.1 ($\mathit{C}_4H_4CSiMe_3$), 119.2, 117.9 ($\mathit{C}_5Me_5$), 79.5 ($C_4H_4\mathit{C}SiMe_3$), 12.0, 11.8 ($C_5\mathit{Me}_5$), 0.7 ($C_5H_4Si\mathit{Me}_3$) ppm. EI MS: *m/z* (%) = 607 (9) $[M - Cd\{C_5H_4(SiMe_3)\}]^+$. $C_{38}H_{60}CdN_4SiTi_3$ (857.01): calcd. C 53.26, H 7.06, N 6.54; found C 53.52, H 6.96, N 6.12.

**Synthesis of $[\{(Me_3Si)_2N\}Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (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): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 10.72 (br. s, 2 H, NH), 2.07 (s, 30 H, $C_5Me_5$), 1.89 (s, 15 H, $C_5Me_5$), 0.29 [s, 18 H, $N(SiMe_3)_2$] ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 119.3, 118.1 ($\mathit{C}_5Me_5$), 12.1, 12.0 ($C_5\mathit{Me}_5$), 6.7 ($SiMe_3$) ppm. 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 $[Cd\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (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 mixture was allowed to react without any stirring for 2 d. After decantation, the resultant red crystals were vacuum-dried to afford **8**·$1.5C_7H_8$ (0.40 g, 80%). IR (KBr): $\tilde{\nu}$ =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 monitored by NMR spectroscopy. After 20 h at 60 °C, the spectra showed resonances assigned to 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 $NH(SiMe_3)_2$. 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 spectroscopic data for **11**: $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ = 13.87 (br. s, 2 H, NH), 2.08 (s, 30 H, $C_5Me_5$), 1.94 (s, 15 H, $C_5Me_5$), 0.20 [s, 18 H, $N(SiMe_3)_2$] ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 117.8, 117.4 ($\mathit{C}_5Me_5$), 12.2, 11.8 ($C_5\mathit{Me}_5$), 5.4 ($SiMe_3$) ppm.

**Synthesis of $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$:** This compound was prepared in a similar manner to 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 colourless 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 $[Hg(CH_2SiMe_3)\{N(SiMe_3)_2\}]$ as a colourless liquid (0.42 g, 88%). IR (KBr): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 0.24 [s, 18 H, N(SiMe$_3$)$_2$], 0.16 (s, 2 H, C*H*$_2$SiMe$_3$), 0.00 (s, 9 H, CH$_2$Si*Me*$_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 13.6 (*C*H$_2$SiMe$_3$), 5.5 [N(SiMe$_3$)$_2$], 1.8 (CH$_2$Si*Me*$_3$) ppm. EI MS: *m*/*z* (%) = 450 (2) [M + H]$^+$, 162 (17) [N(SiMe$_3$)$_2$ + 2 H]$^+$, 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 monitored by NMR spectroscopy. After 20 h at 60 °C, the spectra showed resonances assigned to complex [(Me$_3$SiCH$_2$)Hg{($\mu_3$-N)Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu$-NH)$_2$($\mu_3$-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 spectroscopic data for **12**: $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ = 13.86 (br. s, 2 H, NH), 2.12 (s, 30 H, C$_5$Me$_5$), 1.97 (s, 15 H, C$_5$Me$_5$), 0.24 (s, 2 H, C*H*$_2$SiMe$_3$), 0.04 (s, 9 H, CH$_2$Si*Me*$_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 117.4, 116.9 (*C*$_5$Me$_5$), 14.3 (*C*H$_2$SiMe$_3$), 12.2, 11.9 (C$_5$*Me*$_5$), 1.9 (CH$_2$Si*Me*$_3$) ppm.

**Synthesis of [Hg{($\mu_3$-N)Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu$-NH)$_2$($\mu_3$-N)}$_2$] (13):** A 100 mL Schlenk flask was charged with [K($\mu_4$-N)($\mu_3$-NH)$_2${Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu_3$-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): $\tilde{\nu}$ =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, $C_6D_6$, 20 °C): $\delta$ = 13.96 (br. s, 4 H, NH), 2.08 (s, 60 H, C$_5$Me$_5$), 1.99 (s, 30 H, C$_5$Me$_5$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ = 117.2, 117.1 (*C*$_5$Me$_5$), 12.3, 11.9 (C$_5$*Me*$_5$) ppm. $C_{60}H_{94}HgN_8Ti_6$ (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 above. 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 fibre, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K with a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit and Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Crystallographic data for all the complexes are presented in Table 4. The structures were solved by direct methods (SHELXS-97[29] for **3** and **8**; SIR2002[30] for **5**) using the WINGX package[31] and refined by least squares against $F^2$ (SHELXL-97).[29] 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 nonhydrogen atoms of **3** were anisotropically refined, whereas the hydrogen atoms were positioned geometrically and refined by using a riding model in the last cycles of refinement. In the crystallographic study of complex **5**, all nonhydrogen atoms were anisotropically refined. The imido hydrogen atoms (NH) were located in the difference Fourier map and refined isotropically, whereas the rest of the hydrogen atoms in the mole-

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

| | **3** | **5** | **8**·2C$_7$H$_8$ |
|---|---|---|---|
| Empirical formula | $C_{30}H_{48}CdI_2N_4Ti_3$ | $C_{35}H_{56}CdN_4SiTi_3$ | $C_{74}H_{110}CdN_8Ti_6$ |
| *M* | 974.62 | 817.03 | 1511.50 |
| *T* [K] | 200(2) | 200(2) | 200(2) |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | triclinic | orthorhombic |
| Space group | $P2_1/c$ | $P\bar{1}$ | *Pnnm* |
| *a* [Å]; $\alpha$ [°] | 11.051(3); 90 | 11.521(1); 91.60(1) | 14.727(3); 90 |
| *b* [Å]; $\beta$ [°] | 18.824(4); 100.6(1) | 12.134(2); 108.67(1) | 15.504(3); 90 |
| *c* [Å]; $\gamma$ [°] | 17.851(3); 90 | 15.259(3); 91.28(1) | 16.716(3); 90 |
| *V* [Å$^3$] | 3650(1) | 2019.0(5) | 3816(1) |
| Z | 4 | 2 | 2 |
| $\rho_{\text{calcd.}}$ [g cm$^{-3}$] | 1.774 | 1.344 | 1.315 |
| $\mu$(Mo-$K_\alpha$) [mm$^{-1}$] | 2.923 | 1.148 | 0.913 |
| *F*(000) | 1904 | 844 | 1580 |
| Crystal size [mm] | 0.18 × 0.17 × 0.16 | 0.24 × 0.19 × 0.10 | 0.45 × 0.37 × 0.20 |
| $\theta$ range [°] | 3.17–27.51 | 3.10–27.50 | 3.06–27.51 |
| Index ranges | –14 to 14,<br>–23 to 24,<br>–23 to 23 | –14 to 14,<br>–15 to 15,<br>–19 to 19 | –16 to 19,<br>–19 to 20,<br>–21 to 21 |
| Refl. collected | 68936 | 48031 | 47187 |
| Unique data | 8376 | 9134 | 4533 |
| $R_{\text{int}}$ | 0.156 | 0.086 | 0.071 |
| Reflections [$I > 2\sigma(I)$] | 5555 | 6328 | 2997 |
| Goodness-of-fit on $F^2$ | 1.073 | 1.019 | 1.030 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.056<br>$wR_2$ = 0.104 | $R_1$ = 0.044<br>$wR_2$ = 0.103 | $R_1$ = 0.080<br>$wR_2$ = 0.238 |
| *R* indices (all data) | $R_1$ = 0.117<br>$wR_2$ = 0.145 | $R_1$ = 0.077<br>$wR_2$ = 0.114 | $R_1$ = 0.115<br>$wR_2$ = 0.238 |
| Largest diff. peak/hole [e Å$^{-3}$] | 1.331/–1.712 | 0.766/–0.990 | 1.386/–0.709 |

[a] $R_1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

cule were positioned geometrically and refined by using a riding model. Compound **8** crystallised with two molecules of toluene, which were found in the difference Fourier map, but it was not possible to obtain a chemically sensible model for them, so the 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 occupancies of 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 atom (50% final occupancy), whereas 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.

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