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Iodine Attack on the Metalloligand [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)]: Surprising Formation of the [Ti_3(η^5-C_5Me_5)$_3$$I_2$($\mu$-NH)$_3$($NH_3$)]$^+$ Cation

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The reactivity of the trinuclear imido-nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) and derivatives thereof with iodine has been investigated. Treatment of the indium(I) adduct [IIn{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**2**) with I_2 (1 equiv.) in benzene afforded the indium(III) complex [I_3In{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**3**), but with excess of iodine the precipitation of orange crystals of the ionic complex [Ti_3(η^5-C_5Me_5)$_3$$I_2$($\mu$-NH)$_3$($NH_3$)][$InI_4$] (**4**) takes place. Analogous treatment of the metalloligand **1** with I_2 in toluene gave initially the iodine(I) derivative [I{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}][$I_3$] (**5**). Surprisingly, toluene solutions of **5** at room temperature produced crystals of the ionic complex [Ti_3(η^5-C_5Me_5)$_3$$I_2$($\mu$-NH)$_3$($NH_3$)][$I_3$]·$C_7H_8$ (**6**·C_7H_8). The trinuclear titanium cation [Ti_3(η^5-C_5Me_5)$_3$$I_2$($\mu$-NH)$_3$($NH_3$)]$^+$ of complexes **4** and **6** has been structurally characterized by a combination of X-ray and DFT studies.

Introduction

Transition metal nitrido complexes have received considerable attention over the last decades.[1,2] Compounds of group 6–8 metals usually bear the nitrido ligand as a terminal functionality [M]≡N and the study of its reactivity is an area of increasing activity.[1,3] The analogous early transition metal derivatives have not received the same treatment due to their difficult characterization and, perhaps more importantly, the lack of a systematic method of synthesis. This could be related with the tendency of the nitrido ligand to bridge two or more early-transition metal centers, which produces singular and very often unpredictable polynuclear structures.[2,4]

The imido-nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**)[5,6] shows a cyclic [Ti_3(μ-NH)$_3$] system, which resembles that of other triazamacrocycles such as 1,4,7-triazacyclononanes,[7] and especially 1,3,5-triazacyclohexanes,[8] whose extensive coordination chemistry is known. In fact, we have recently shown the capacity of **1** to act as a preorganized tridentate ligand with transition,[4,9,10] and main group metals.[11] The great versatility of **1** is also confirmed by the possibility of preparing complexes with metals in low [e.g. Mo^0, Ir^I] or high oxidation states [e.g. Ti^{IV}, Ta^V]. Although the main driving force in the coordination of **1** is the electron donation of the nitrogen atom lone pair to the incorporated metals, theoretical calculations performed on adducts of **1** with transition metals in low oxidation states have shown that the presence of Ti^{IV} centers in the metalloligand produces an additional stabilization through metal–metal coupling.[9]

We have recently shown the formation of indium(I) and indium(III) iodide adducts [I_xIn{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] [$x$ = 1 (**2**), x = 3 (**3**)] through the reaction of **1** with the corresponding metal halides,[12] and were interested in performing the oxidation reactions directly on the metallocubane system, for example preparing **3** from the indium(I) complex **2**. Here we present the results obtained in this reaction, including the opening of the metalloligand **1** in the presence of excess iodine to give ionic complexes containing the singular unprecedented cation [Ti_3(η^5-C_5Me_5)$_3$$I_2$($\mu$-NH)$_3$($NH_3$)]$^+$, which has been structurally characterized by X-ray and DFT studies.

Results and Discussion

The objective of this work was to evaluate the possibility of performing oxidation processes on inorganic fragments incorporated into the preorganized metallocubane ligand [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**). In this way, we tried to obtain the indium(III) iodide adduct [I_3In{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**3**) from the indium(I) analogue [IIn{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**2**) via oxidation with iodine. In a NMR experiment, complex **3** was quanti-

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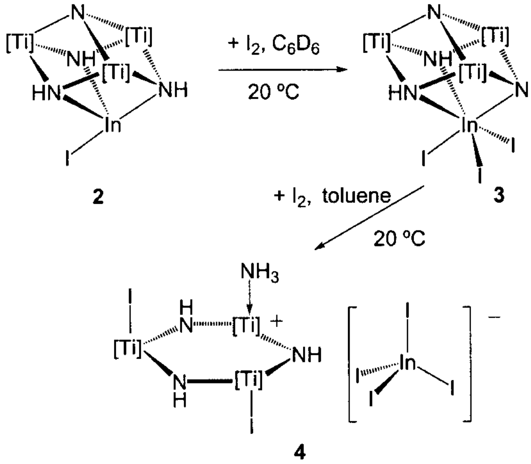
tatively formed within minutes by oxidation of **2** using a solution of I_2 in [D$_6$]benzene (Scheme 1). However, an excess of iodine in the reaction produced the consumption of **3**.



Scheme 1. Reaction of **2** with iodine. [Ti] = Ti(η^5-C_5Me_5).

In a preparative scale reaction, a toluene solution of **3** was layered with a solution containing an excess of iodine (3 equiv.) in toluene to afford orange crystals of the ionic complex [$Ti_3(\eta^5$-$C_5Me_5)_3I_2(\mu$-$NH)_3(NH_3)$][InI_4] (**4**) in 49% yield. The X-ray analysis of **4** confirms the structure proposed in Scheme 1, containing a tetraiodoindiate(III) anion and a trinuclear titanium cation (see Figure 1). The InI_4^- moiety found in **4** shows an average bond length for In–I of 2.703(2) Å and bond angles I–In–I of 109.5(6)°, typical for this tetrahedral fragment[13] (vide infra discussion about the cation structure). Complex **4** is not soluble in benzene or toluene and decomposes immediately in [D$_8$]tetrahydrofuran, [D$_5$]pyridine, [D$_1$]chloroform, or [D$_2$]dichloromethane, precluding its characterization by NMR spectroscopy. The IR (KBr) spectrum shows several bands in the range 3304–2942 cm^{-1} and one at 1587 cm^{-1} that are similar to those found for the Ti–NH_3-containing complex [{$Ti_2(\eta^5$-$C_5Me_5)_2Cl_3(NH_3)$}(μ-N)].[6] The latter absorption is assigned to the NH_3 bending mode.[14]

Since the metalloligand **1** coordinated to indium was affected in the reaction with I_2, we have also investigated the reaction of "free" **1** with iodine in toluene (Scheme 2). Treatment of **1** with excess of iodine leads to precipitation of a dark brown solid in 64% yield. Spectroscopic and analytical data are consistent with the iodine(I) derivative [I{(μ_3-$NH)_3Ti_3(\eta^5$-$C_5Me_5)_3(\mu_3$-N)}][I_3] (**5**). This complex is slightly soluble in [D$_6$]benzene and soluble in [D$_2$]dichloromethane. The ^{1}H and ^{13}C{^{1}H} NMR spectra show resonances for equivalent η^5-C_5Me_5 ligands. The *ipso* carbon resonances of the C_5Me_5 ligands are shifted to a lower field with respect to those of **1**, in a similar tendency to that found for our previously reported adducts [X_nM·**1**].[12] Resonances due to the μ-NH ligands were not detected in the ^{1}H NMR spectrum, but the presence of those groups was confirmed in the IR (KBr) spectrum with two ν_{NH} absorptions at 3340 and 3218 cm^{-1}.

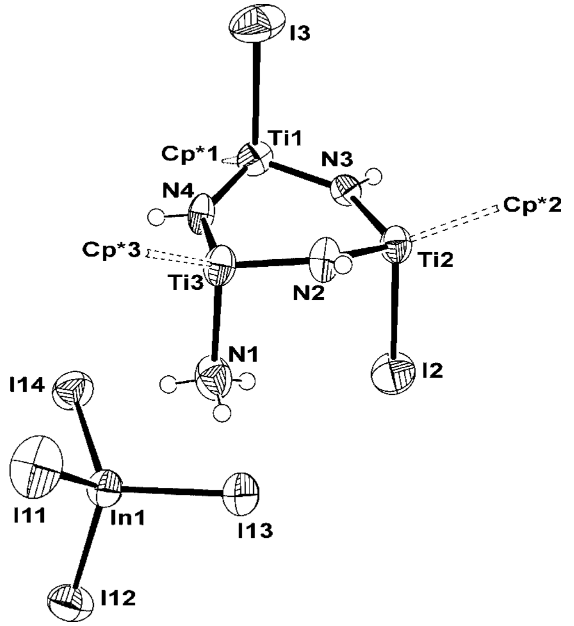
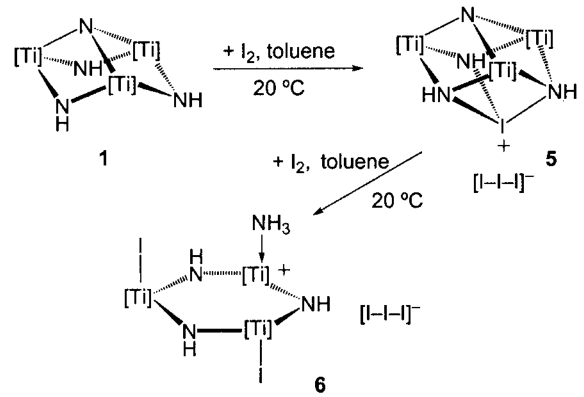


Figure 1. Simplified view of the complex [$Ti_3(\eta^5$-$C_5Me_5)_3I_2(\mu$-$NH)_3$-(NH_3)][InI_4] (**4**) with thermal ellipsoids at the 50% probability level. The pentamethylcyclopentadienyl ligands are not shown for clarity.



Scheme 2. Reaction of **1** with iodine. [Ti] = Ti(η^5-C_5Me_5).

Analogous disproportionation reactions of I_2 in the presence of tetraazamacrocyclic or cryptand ligands to give coordination compounds of iodine(I) have been previously reported.[15] Attempts to grow suitable crystals of **5** for a X-ray crystal structure determination failed, but saturated toluene solutions of **5** at room temperature afforded orange crystals of [$Ti_3(\eta^5$-$C_5Me_5)_3I_2(\mu$-$NH)_3(NH_3)$][I_3]·C_7H_8 (**6**·C_7H_8) in poor yields.[16] Complex **6** is not soluble in unreactive solvents and its IR (KBr) spectrum is essentially identical to that of **4**.

The X-ray crystal structure determination of **6** shows a triiodide anion and the same trinuclear titanium cation [$Ti_3(\eta^5$-$C_5Me_5)_3I_2(\mu$-$NH)_3(NH_3)$]$^+$ found for **4** (see Figure 2). While **4** crystallizes as a solvent-free compound, crystals of **6** bear one toluene solvent molecule per complex. The I_3^- ion in **6** is asymmetric [I–I distances are

Table 1. Selected lengths [Å] and angles [°] for the cation of complexes **4** and **6**.

[$Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)$]$^+$							
	4	**6**	DFT		**4**	**6**	DFT
N(1)–Ti(3)	2.167(11)	2.149(4)	2.191	Ti(3)–N(2)–Ti(2)	127.7(5)	125.8(2)	127.7
N(2)–Ti(3)	1.854(9)	1.891(3)	1.915	Ti(2)–N(3)–Ti(1)	137.4(5)	138.3(2)	133.6
N(2)–Ti(2)	1.904(9)	1.918(3)	1.958	Ti(3)–N(4)–Ti(1)	135.6(5)	131.4(2)	129.8
N(3)–Ti(2)	1.808(9)	1.823(3)	1.919	N(3)–Ti(1)–N(4)	101.6(4)	102.6(1)	105.4
N(3)–Ti(1)	1.810(9)	1.825(3)	1.917	N(3)–Ti(1)–I(3)	102.1(3)	101.4(1)	102.6
N(4)–Ti(3)	1.790(9)	1.850(3)	1.893	N(4)–Ti(1)–I(3)	104.0(3)	103.6(1)	101.7
N(4)–Ti(1)	1.845(10)	1.880(3)	1.962	N(3)–Ti(2)–I(2)	100.6(3)	99.7(1)	101.1
Ti(1)–I(3)	2.664(3)	2.673(1)	2.723	N(2)–Ti(2)–I(2)	102.1(3)	102.1(1)	101.7
Ti(2)–I(2)	2.678(3)	2.695(1)	2.753	N(3)–Ti(2)–N(2)	103.4(4)	103.9(1)	104.3
Ti(1)···Ti(2)	3.370(3)	3.408(1)	3.526	N(4)–Ti(3)–N(2)	105.4(4)	108.1(1)	108.4
Ti(1)···Ti(3)	3.366(3)	3.399(1)	3.490	N(4)–Ti(3)–N(1)	99.2(5)	100.0(1)	99.5
Ti(2)···Ti(3)	3.374(3)	3.391(1)	3.476	N(2)–Ti(3)–N(1)	98.8(4)	98.5(1)	97.9

2.867(1) and 3.000(1) Å, I–I–I 179.0(1)°] as determined in many other crystalline structures with such an anion.[17] Selected distances and angles of the cation structures are shown in Table 1.

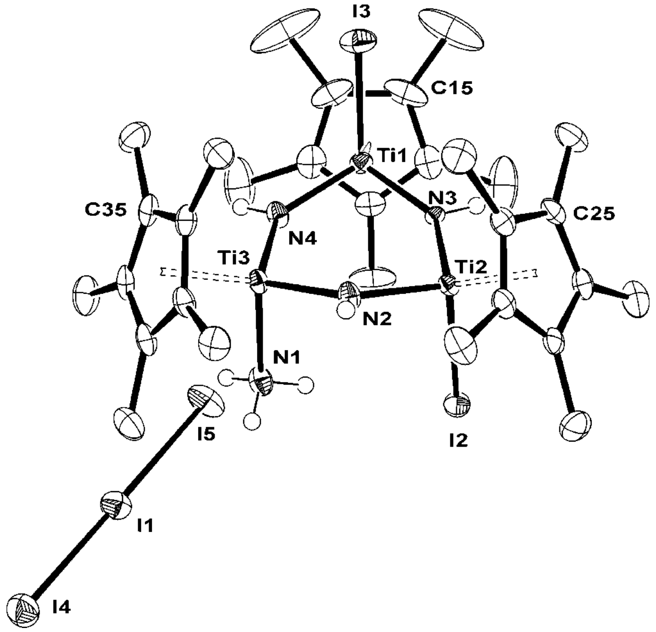


Figure 2. Perspective view of the [$Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)$][$I_3$] (**6**) with thermal ellipsoids at the 50% probability level. Solvent molecule is not shown for clarity.

The cation of both **4** and **6** is a cyclic trinuclear complex, with three Ti(η^5-C_5Me_5)L moieties held together by bridging (μ-NH) imido ligands. Each titanium atom has a classical three-legged piano-stool arrangement, where the legs are occupied by one iodine and two imido groups for Ti(1) and Ti(2), and one ammonia and two imido ligands for Ti(3). With respect to the plane formed by the three titanium atoms, I(3) is located above while I(2) and the ammonia molecule are below the plane. This structural disposition (two below, one above) of the ligands resembles that of the oxotitanium complexes [{Ti(η^5-C_5Me_5)L}$_3$(μ-O)$_3$] (L = Me,[18] Cl,[19] Br,[20] $CH_2CH{=}CH_2$[21]). The titanium–iodine distances of 2.677(av.) Å are in the normal range[22] and the titanium–nitrogen (ammonia) bond lengths [2.167(11) for **4** and 2.149(4) Å for **6**] are very similar to the unique crystallographic documented titanium organometallic complex with ammonia [{$Ti_2(\eta^5\text{-}C_5Me_5)_2Cl_3(NH_3)$}(μ-N)] (2.158 Å).[6] This distance is longer than that found for the Ti–OH_2 bonds in aquotitanium(IV) derivatives.[23] Surprisingly, only seven other examples of metal–ammonia interactions are found for groups 3, 4, and 5 when a search is performed in the CSD.[24] The bridging imido ligands are characterized by titanium–nitrogen bond lengths in the range 1.790(3)–1.918(3) Å [av. 1.85 Å], which are slightly shorter than those found in **1** [av. 1.92 Å], and angles Ti–N–Ti clearly wider 125.8(2)–138.3(2)° than those of complex **1** (93.2° av.) where the μ_3-nitrogen apical atom constrains the geometry. On the other hand, distances from N(1) to I(2) of 3.661(1) in **4** and 3.623(3) Å in **6** could be indicative of the existence of an intramolecular hydrogen bonding interaction between them (sum of the van der Waals' radii 3.650 Å).[25]

DFT calculations were conducted to characterize the trinuclear fragment [$Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)$]$^+$. The optimized geometry coincides quite well with the X-ray ones, as can be seen in Table 1. Calculated distances are slightly longer than the experimental and some of the angles differ by a small number of degrees. Especially significant is the distance Ti(3)–N(1) 2.191 Å, which is only ≈0.02 and ≈0.04 Å longer than those found in complexes **3** and **6**, respectively. The cation [$Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)$]$^+$ displays a relatively large HOMO–LUMO gap of 1.88 eV, a fact that is a signal of its relative stability.

Although all the three metal atoms in the titanium complex are formally in their highest oxidation state, the Mulliken population analysis suggests that the Ti atom bonded to NH_3 carries a larger positive charge (+1.42 e) than the other two titaniums [computed charge for Ti(1) + Ti(2) = +0.92 e]. The LUMO is a nonbonding orbital with a larger participation of Ti(3) (Figure 3). As a matter-of-fact, the monoreduction of [$Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)$]$^+$ hardly induces changes in the geometry of the cluster, the additional metal electron being mainly localized on the Ti bonded to ammonia [spin density on Ti(3) of ≈0.5 e, whereas the other two Ti share ≈0.6 e]. All these results are in concordance with the drawings proposed for the trinuclear titanium cation in Schemes 1 and 2.

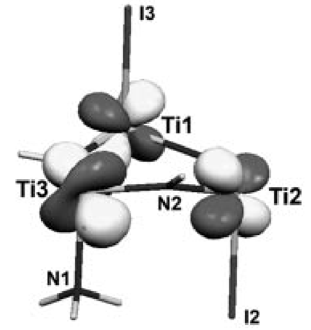


Figure 3. 3D representation of the LUMO for $[Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)]^+$.

In summary, the heterometallocubane $[IIn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**) allows the oxidation with iodine of the supported InI, under mild conditions, to cleanly give the expected indium(III) derivative $[I_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**). However, an excess of iodine in the solution produces the rupture of the preorganized structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) to give the singular cation $[Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)]^+$. This complex is also accessible through the reaction of **1** with an excess of iodine. DFT studies support the cationic nature of the unprecedented ammonia adduct.

Experimental Section

General Considerations and Starting Materials: All manipulations were carried out under argon using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just prior to use. Toluene was freshly distilled from sodium. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride (CD_2Cl_2) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. $1 \cdot 10^{-3}$ Torr) and subsequently filled with inert gas. Iodine was purchased from Aldrich and sublimed under vacuum prior to use. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[6] $[IIn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**),[12] and $[I_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**)[12] were prepared according to published procedures.

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

Oxidation Reaction of 2 with Iodine: A 5-mm valved NMR tube was charged with **2** (10 mg, 0.012 mmol), I_2 (3.0 mg, 0.012 mmol) and [D$_6$]benzene or [D$_8$]toluene (1.00 mL). The course of the reaction was monitored by ^1H NMR spectroscopy. After 5 min at room temperature the spectrum shows the complete consumption of **2** along with resonances due to complex **3**.[12]

$[IIn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (2): ^1H NMR (300 MHz, C_6D_6, 20 °C): δ = 12.87 (br. s, 3 H, NH), 2.01 (s, 45 H, C_5Me_5) ppm.

$[I_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (3): ^1H NMR (300 MHz, C_6D_6, 20 °C): δ = 11.58 (br. s, 3 H, NH), 1.95 (s, 45 H, C_5Me_5) ppm.

Synthesis of $[Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)][InI_4]$ (4): A solution of I_2 (0.062 g, 0.24 mmol) in toluene (10 mL) was carefully added to $[I_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**) (0.090 g, 0.08 mmol) in toluene (30 mL). The system was allowed to react without any stirring for 5 days to yield **4** as orange crystals suitable for X-ray analysis. The resultant red solution was concentrated in volume under vacuum until ca. 15 mL and allowed to stand at room temperature to give a second crop of crystals. The combined yield of **4** was 0.059 g (49%). IR (KBr) $\tilde{\nu}$ = 3304 (m), 3261 (m), 3192 (w),

Table 2. Experimental data for the X-ray diffraction studies on compounds **4** and **6**.

Formula	$C_{30}H_{51}I_6InN_4Ti_3$ (**4**)	$C_{37}H_{59}I_5N_4Ti_3$ (**6**$\cdot C_7H_8$)
M_r	1487.67	1338.08
T [K]	293(2)	150(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]; α [°]	12.063(2); 91.85(2)	11.823(1); 79.10(1)
b [Å]; β [°]	13.031(5); 99.36(4)	13.086(1); 87.60(1)
c [Å]; γ [°]	14.769(4); 90.39(2)	15.886(1); 78.14(1)
V [Å^3]	2289.3(11)	2362.0(3)
Z	2	2
$\rho_{calcd.}$ [g cm^{-3}]	2.158	1.881
$\mu_{Mo\text{-}K\alpha}$ [mm^{-1}]	5.071	3.791
$F(000)$	1384	1280
Crystal size [mm]	0.25 × 0.20 × 0.18	0.34 × 0.33 × 0.22
θ range	1.40 to 24.97°	3.06 to 27.50°
Index ranges	–14 to 14, –15 to 15, –17 to 0	–15 to 15, –17 to 17, –20 to 20
Reflections collected	8382	20854
Unique data	8038 [R_{int} = 0.052]	10824 [R_{int} = 0.033]
Observed data [$I > 2\sigma(I)$]	5147	8331
Goodness-of-fit on F^2	1.041	1.033
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.062, wR_2 = 0.164	R_1 = 0.031, wR_2 = 0.069
R indices (all data)	R_1 = 0.122, wR_2 = 0.189	R_1 = 0.051, wR_2 = 0.074
Largest diff. peak/hole [e·Å^{-3}]	1.465/–0.976	1.529/–1.010

[a] $R_1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$ $wR_2 = \{[\Sigma w(F_0^2 - F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$.

3124 (w), 2942 (w), 2910 (m), 2850 (w), 1587 (m), 1485 (m), 1450 (m), 1427 (s), 1377 (s), 1268 (s), 1067 (m), 1019 (m), 790 (vs), 753 (vs), 711 (vs), 622 (m), 548 (w), 536 (w), 494 (w), 435 (m) cm^{-1}. $C_{30}H_{51}I_6InN_4Ti_3$ (1487.67): calcd. C 24.22, H 3.45, N 3.77; found C 24.85, H 3.39, N 2.69.

Synthesis of $[I\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}][I_3]$ (5): A solution of I_2 (0.75 g, 2.96 mmol) in toluene (30 mL) was carefully added to **1** (0.40 g, 0.66 mmol) in toluene (30 mL). The system was allowed to react without any stirring for 3 days. After decantation, the resultant dark brown crystals were vacuum-dried to afford **5** (0.47 g, 64%). IR (KBr) $\tilde{\nu}$ = 3340 (m), 3218 (m), 2911 (s), 1486 (m), 1426 (s), 1376 (s), 1021 (w), 762 (s), 717 (s), 660 (vs), 638 (vs), 594 (s), 467 (m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 1.88 (s, 45 H, C_5Me_5) ppm. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 2.10 (s, 45 H, C_5Me_5) ppm, NH resonance was not detected. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 20 °C): δ = 123.8 (C_5Me$_5$), 12.3 (C$_5$*Me*$_5$) ppm. $C_{30}H_{48}I_4N_4Ti_3$ (1115.94): calcd. C 32.29, H 4.33, N 5.02; found C 31.18, H 4.23, N 4.52.

Synthesis of $[Ti_3(\eta^5\text{-}C_5Me_5)_3I_2(\mu\text{-}NH)_3(NH_3)][I_3]$ (6): A saturated solution of **5** in toluene at room temperature for 5 days gave orange crystals (0.050 g) of **6**·C_7H_8 suitable for X-ray crystallographic studies. IR (KBr) $\tilde{\nu}$ = 3301 (m), 3234 (m), 3116 (m), 2909 (s), 2852 (w), 1587 (m), 1493 (m), 1428 (m), 1377 (s), 1271 (s), 1021 (m), 798 (vs), 753 (s), 729 (s), 710 (vs), 622 (m), 494 (w), 465 (w), 432 (m) cm^{-1}. $C_{37}H_{59}I_5N_4Ti_3$ (1338.08): calcd. C 33.21, H 4.44, N 4.19; found C 32.67, H 4.37, N 3.67.

X-ray Crystal Structure Determination of Complexes 4 and 6: Orange crystals of compounds **4** and **6** were obtained from toluene solutions at room temperature. Crystals of **4** were mounted in a glass capillary in a random orientation and transferred to an Enraf–Nonius CAD4 diffractometer for characterization and data collection at room temperature. Complex **6** crystallized with one molecule of toluene, so the crystals were removed from the Schlenk and covered with a layer of 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 150 K with a Bruker–Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 2. The structures were solved, using the WINGX package,[26] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[27] All non-hydrogen atoms of **4** and **6** were anisotropically refined. All the hydrogen atoms were positioned geometrically and refined by using a riding model except those attached to N(1) and N(2) in complex **6** which were directly located in the difference Fourier map and refined isotropically. The largest residual density peaks are located at 0.88 Å of I(14) in compound **4** and at 0.83 Å of I(4) in compound **6**. The refinement of the crystal structure of complex **6** was also performed substituting the ammonia molecule by water and the result was a decrease of the quality of the study, increased *R* values, poorer temperature factors for the oxygen atom and always the appearance of the third hydrogen atom in the difference Fourier map, excluding the existence of a water molecule.

CCDC-283509 and -283510 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.

Computational Details: All DFT calculations were carried out with the ADF program[28] 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 α = 2/3) together with Vosko–Wilk–Nusair parametrization[29] for correlation. Becke's nonlocal corrections[30] to the exchange energy and Perdew's nonlocal corrections[31] to the correlation energy were added. Quasirelativistic corrections were employed by using the ZORA formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC.[28]

Supporting Information (see footnote on the first page of this article): The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of complex **5** are provided as Supporting Information.

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