Articles

Coordination of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ to Metal Cyclopentadienides: Cyclopentadienyl Azaheterometallocubanes†

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Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with lithium and sodium cyclopentadienide complexes $[M(C_5H_5)]$ in toluene gives cube-type adducts $[(\eta^5\text{-}C_5H_5)M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$. The reaction with thallium(I) cyclopentadienide in toluene affords the analogous $[(\eta^5\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot C_7H_8$, whereas in hexane it gives $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.

Introduction

The trinuclear imido-nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**)[1,2] shows an incomplete-cube structure with three NH electron-donor imido groups in the base. From the structural point of view, **1** shows a resemblance to other trinitrogen ligands such as 1,4,7-triazacyclononanes[3] and trispirazolylborates[4] and other tripodal amido ligands,[5] whose extensive coordination chemistry is known. Our project devoted to explore the utility of **1** as a preorganized tridentate ligand toward inorganic derivatives containing labile ligands has given to date a variety of cube-type complexes among the transition[6] and main group metals.[7,8] In those examples, **1** is capable of acting as a neutral ligand through the basal NH groups, but later those imido groups can also be deprotonated to give monoanionic, dianionic, and even trianionic forms of **1** depending on the metal and the other ligands present in the coordination sphere.

In particular, we have recently shown that **1** is deprotonated by group 1 bis(trimethylsilyl)amido derivatives $[MN(SiMe_3)_2]$ (M = Li, Na, K) in toluene to give bis(trimethylsilyl)amine and the alkali metal complexes $[M\{(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$.[7] No intermediates were detected in those processes, although coordination of **1** to the alkali metal center presumably could be the first step; this suggested that this possibility should be explored. Herein we report the synthesis, structure, and properties of adducts of **1** with group 1 and 13 metal cyclopentadienides. The new complexes $[(\eta^5\text{-}C_5H_5)M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ show cube-type structures where **1** is coordinated as a neutral ligand to lithium, sodium, and thallium(I) centers. The thallium compound decomposes in hexane to give **1** and the dithallium complex $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.

Results and Discussion

Treatment of **1** with lithium and sodium cyclopentadienide complexes (1 equiv) in toluene at room temperature gave red solutions from which the adducts $[(\eta^5\text{-}C_5H_5)M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [M = Li (**2**) 76%, Na (**3**) 65%] were isolated as brown and orange solids after workup (Scheme 1). Interestingly, the analogous treatment of **1** with potassium cyclopentadienide gave the initial products unaltered. This behavior might be due to the different solid-state structure[9] and solubility in the reaction solvent of KCp when compared with those of the lithium and sodium derivatives.

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† In memory of Professor Moisés Morán, deceased on December 30, 2002.

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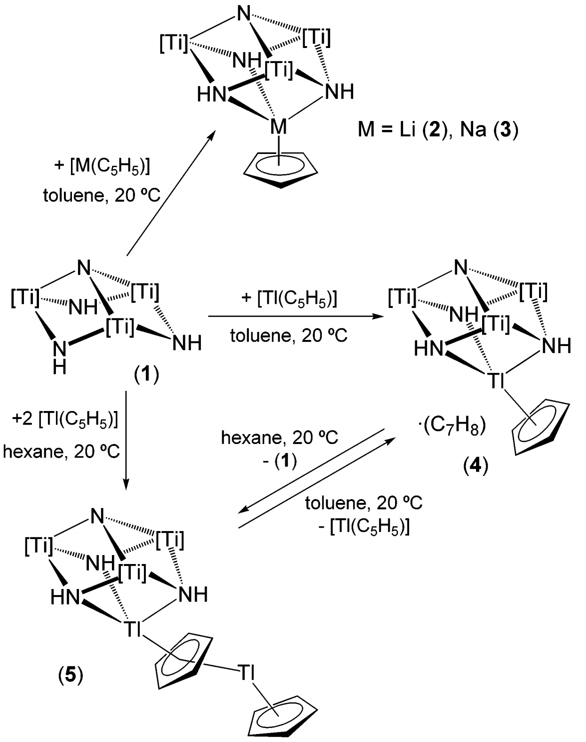
10.1021/om030554l CCC: $27.50

Scheme 1. Coordination of 1 to Metal Cyclopentadienides[a]



[a] [Ti] = Ti(η^5-C_5Me_5).

Complexes **2** and **3** are soluble in toluene or benzene but scarcely in *n*-hexane. Solutions of **2** remain unaltered in benzene-d_6 even after heating at 150 °C for several days. Complexes **2** and **3** were characterized by spectral and analytical techniques, as well as by an X-ray crystal structure determination for **3**. IR spectra (KBr) of the compounds showed two ν_{NH} vibrations, between 3356 and 3312 cm^{-1}, in a range similar to that determined for **1** (3352 cm^{-1}).[2] The ^1H NMR spectra in benzene-d_6 at room temperature revealed singlets due to equivalent NH, η^5-C_5Me_5, and η^5-C_5H_5 groups in the expected proportions 3:45:5. The NH resonance signals in those spectra ($\delta = 12.33$ and 12.87, respectively) are shifted to higher field with respect to that found in **1** ($\delta = 13.80$). We have noted an analogous shift in several transition and main group azaheterometallocubane derivatives and used those data to propose the coordination of the NH imido groups to the incorporated elements.[7] The $^{13}C\{^1H\}$ NMR spectra of **2** and **3** in benzene-d_6 at room temperature are very similar and show a chemical shift for the C_5Me_5 ipso carbon resonance ($\delta = 118.9$ and 119.0, respectively) slightly shifted downfield with respect to that found for **1** ($\delta = 117.1$). The NMR data suggest a highly symmetrical structure in solution and are consistent with the solid-state structure determined for **3**.

The drawing of the molecular structure of **3** is represented in Scheme 1. The crystal structure shows a $[NaTi_3N_4]$ cube-type core with a mirror plane bearing the sodium, one titanium, and two nitrogen core atoms. The sodium atom exhibits a distorted tetrahedral geometry if the centroid of the cyclopentadienyl ligand is considered. The neutral ligand $[(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)]$ coordinates in a tripodal fashion with nitrogen−sodium−nitrogen angles of 70.6(3)° and 71.2(4)°, whereas the nitrogen−sodium−centroid angles are 133.6° and 146.2°. The sodium−centroid distance (2.350 Å) is similar to those found in the polymeric chain of $[Na(C_5H_5)]$ (2.357 Å)[9] and the sodocene anion of $[PPh_4][Na(C_5H_5)_2]$ (2.366 Å)[10] and shorter than those reported in the literature for other nitrogen−ligand adducts of sodium cylopentadienides.[11] In addition, the sodium−nitrogen distances in **3** (2.597(10) and 2.630(14) Å) are also longer than in those examples and suggest a weaker coordination of the tripodal ligand. Accordingly, the distortions in bond distances and angles within the tridentate ligand are small when compared with **1**.[1]

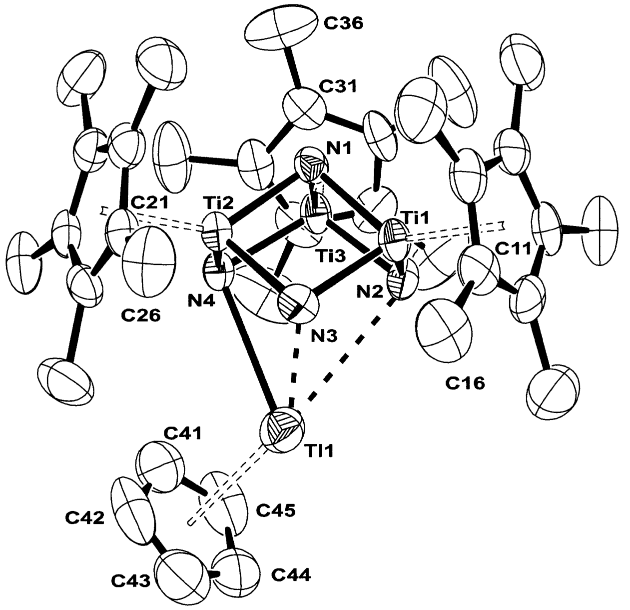


Figure 1. Molecular structure of **4**. The C_7H_8 solvent molecule is omitted for clarity. Selected lengths [Å] and angles [deg]: Tl(1)−N(4) 2.868(1), Tl(1)−N(3) 3.152(1), Tl(1)−N(2) 3.190(1), Tl(1)−Cp 2.687, N(2)−Tl(1)−N(3) 57.8(1), N(2)−Tl(1)−N(4) 60.4(1), N(3)−Tl(1)−N(4) 60.9(1), N(4)−Tl(1)−Cp 107.1, N(3)−Tl(1)−Cp 145.9, N(2)−Tl(1)−Cp 148.2.

Analogous treatment of **1** with thallium(I) cyclopentadienide (1 equiv) in toluene affords $[(\eta^5\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot C_7H_8$ (**4**) as an orange solid in 77% yield (Scheme 1). Complex **4** was characterized by spectral and analytical techniques, as well as by an X-ray crystal structure determination.

Crystals of **4** bear one toluene solvent molecule per thallium compound. The molecular structure of **4** consists of a distorted $[TlTi_3N_4]$ cube-type core (Figure 1). Thallium is bonded to one η^5-cyclopentadienyl ligand and three imido groups of the incomplete cube core $[Ti_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$. If the centroid (Cp) of the cyclopentadienyl ligand is considered, the coordination sphere about

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Table 1. Crystallographic Data for Complexes 3, 4, and 5

	3	**4**	**5**
empirical formula	$C_{35}H_{53}N_4NaTi_3$	$C_{35}H_{53}N_4Ti_3Tl\cdot C_7H_8$	$C_{40}H_{58}N_4Ti_3Tl_2$
fw	696.50	970.02	1147.34
temperature (K)	293(2)		
λMo Kα (Å)	0.71069		
cryst syst	monoclinic	triclinic	monoclinic
space group	*C*2/*m*	$P\bar{1}$	*P*2(1)/*c*
a (Å); α (deg)	18.382(5)	11.225(4); 96.03(1)	14.445(3)
b (Å); β (deg)	18.604(5); 103.69(1)	11.820(3); 92.12(2)	12.943(3); 105.08(3)
c (Å); γ (deg)	11.582(5)	17.235(5); 105.45(1)	24.060(5)
volume (Å^3)	3848(2)	2187(1)	4343(2)
Z	4	2	4
D_{calc} (g cm^{-3})	1.202	1.473	1.755
μ (mm^{-1})	0.645	4.233	7.953
F(000)	1472	976	2216
cryst size (mm^3)	0.23 × 0.18 × 0.13	0.25 × 0.20 × 0.18	0.25 × 0.20 × 0.15
θ range for data collection (deg)	1.58 to 24.95	1.80 to 22.97	1.46 to 22.99
index ranges	$0 \le h \le 21, 0 \le k \le 22, -13 \le l \le 13$	$0 \le h \le 12, -12 \le k \le 12, -18 \le l \le 18$	$-15 \le h \le 15, 0 \le k \le 14, -26 \le l \le 0$
scan mode	$\omega - 2\theta$		
no. of reflns collected	3602	6422	6210
no. of indep reflns	3485 [*R*(int) = 0.090]	6055 [*R*(int) = 0.030]	6039 [*R*(int) = 0.102]
completeness to θ	100.0%	100.0%	100.0%
abs corr	psi scan		
refinement method	full-matrix least-squares on F^2		
goodness-of-fit on F^2	1.074	1.019	0.953
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.110, wR2 = 0.293	R1 = 0.043, wR2 = 0.097	R1 = 0.086, wR2 = 0.167
R indices (all data)	R1 = 0.233, wR2 = 0.355	R1 = 0.076, wR2 = 0.108	R1 = 0.332, wR2 = 0.229
largest diff peak and hole (e Å^{-3})	0.668 and −0.537	1.258 and −0.485	1.207 and −0.797

the thallium atom may be described as distorted trigonal bypiramidal with a "missing vertex" which corresponds to the lone pair on the thallium(I) center. In this geometry, the neutral ligand [(μ-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] coordinates in a tripodal fashion, occupying one axial, N(4), and two equatorial coordination sites, whereas the η^5-C$_5$H$_5$ ligand and the lone pair are in the remaining equatorial and axial positions, respectively. Therefore, the sum of angles subtended at the thallium center in the equatorial plane that contains N(2), N(3), and Cp is 351.9°. The thallium−nitrogen(4) distance (2.868(1) Å) is shorter than those found for Tl−N(2), 3.190(1) Å, and Tl−N(3), 3.152(1) Å, which are in front of the cyclopentadienyl ligand. The thallium−nitrogen bond lengths compare well with those found in the literature for other structures bearing weak Tl−N interactions[12] and are within the sum (3.47 Å) of the van der Waals radii of thallium and nitrogen.[13] The cyclopentadienyl ligand is bonded in an η^5 fashion to thallium with a Tl(1)−Cp(centroid) distance of 2.687 Å, in the range observed for other crystalline cyclopentadienyl-containing Tl complexes.[14,15] Within the neutral ligand [(μ-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)] there is not any important distortion in bond lengths and angles when compared with **1**.

The mass spectrum (EI, 70 eV) of **4** does not show the molecular ion, but the peak of highest mass corresponds to the elimination of one C$_5$H$_5$ fragment and the base peak is [Tl]$^+$. The IR spectrum (KBr) of **4** reveals only one ν_{NH} absorption at 3345 cm^{-1}. ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** in benzene-*d*$_6$ at room temperature are consistent with the tridentate coordination of **1** to one Tl(η^5-C$_5$H$_5$) fragment. The ^{1}H NMR spectrum shows single resonances due to the NH and η^5-C$_5$Me$_5$ groups, suggesting the existence of low-energy exchange processes in solution. Furthermore, it does not show ^{1}H−^{203,205}Tl couplings for the imido NH groups (δ = 13.37) in contrast to those reported by us in the thallium(I) cube-type derivative [Tl{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] ($^2J_{H,Tl}$ = 78 Hz), where **1** acts as a tridentate monoanionic ligand.[7] No ^{1}H−^{203,205}Tl and ^{13}C−^{203,205}Tl couplings for the Tl(η^5-C$_5$H$_5$) fragment were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The absence of coupling to thallium has been attributed in the literature to either predominantly ionic interactions or fast intermolecular exchange processes.[14]

Complex **4** is soluble in toluene or benzene-*d*$_6$, and those solutions are stable at 150 °C for several days. In contrast, **4** is only slightly soluble in *n*-hexane, and the resultant orange suspension changes within hours at room temperature to give a yellow solid and an orange solution. NMR spectra of this solution revealed **1** as the only soluble species. The yellow solid shows two ν_{NH} absorptions at 3345 and 3313 cm^{-1} in the IR spectrum (KBr) and was unambiguously identified as [(η^5-C$_5$H$_5$)Tl(μ-C$_5$H$_5$)Tl{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**5**) by C,H,N microanalysis and an X-ray crystal structure determination. Interestingly, ^{1}H and ^{13}C{^{1}H} NMR spectra obtained from a solution of **5** in benzene-*d*$_6$ are very similar to those found for pure **4**. Indeed, complex **5** decomposes in toluene to give an orange solution of **4** and a fine white precipitate of [Tl(C$_5$H$_5$)]$_\infty$. The preparation of complex **5** is achieved in higher yield (68%) by the reaction of **1** with 2 equiv of thallium cyclopentadienide in hexane at room temperature for 7 days. If toluene is used as solvent in this treatment, only **4** and unreacted [Tl(C$_5$H$_5$)]$_\infty$ are isolated.

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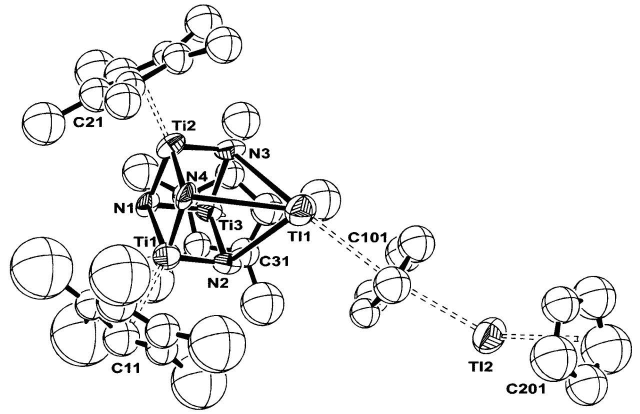

Figure 2. Molecular structure of **5**. Selected lengths [Å] and angles [deg]: Tl(1)−N(2) 2.776(18), Tl(1)−N(4) 2.959 (18), Tl(1)−N(3) 3.011(21), Tl(1)−Cp(1) 2.835, Tl(2)−Cp1-(1) 2.875, Tl(2)−Cp(2) 2.585, N(3)−Tl(1)−N(4) 59.8(5), N(2)−Tl(1)−N(3) 62.1(5), N(2)−Tl(1)−N(4) 62.2(6), N(2)−Tl(1)−Cp1 102.8, N(3)−Tl(1)−Cp(1) 141.7, N(4)−Tl(1)−Cp1 147.5, Cp1−Tl(2)−Cp2 133.36.

The molecular structure of **5** is presented in Figure 2. The overall structure resembles that described for **4**, but with a [Tl(η^5-C_5H_5)] fragment linked to thallium via a μ-C_5H_5 ligand. The coordination of this additional fragment does not produce significant distortions about the thallium(1) center (sum of angles in the equatorial plane = 349.0°) when compared with **4**. The donation of electron density from the μ-C_5H_5 to thallium(2) results in a lengthening of the Tl(1)−Cp1 (centroid of the μ-C_5H_5 ligand) bond distance and a shortening of the thallium(1)−nitrogen distances of approximately 0.1−0.2 Å with respect to those found in **4**. The μ-C_5H_5 group is bridging almost symmetrically to the thallium atoms (Tl(1)−Cp1 2.835 Å and Tl(2)−Cp1 2.875 Å), whereas the terminal C_5H_5−Tl(2) bond distance is shorter (2.585 Å). On the other hand, the angle subtended by the centroids of the C_5H_5 rings at the Tl(2) atom is rather acute (Cp1−Tl(2)−Cp2 = 133.36°) and compares well with other complexes containing the moiety (η^5-C_5H_5)-Tl(μ-C_5H_5)Tl as [Li(12-crown-4)$_2$]$^+$[(η^5-C_5H_5)Tl(μ-C_5H_5)-Tl(η^5-C_5H_5)]$^-$·THF (av 134.2°)[16] and the polymeric structure of [Tl(η^5-C_5H_5)]$_\infty$ (137°[17] or 130°[18]), and it is quite different from those determined for the ion-separated complex [(η^5-C_5H_5)Mg{($Me_2NCH_2CH_2)_2NMe$}]$^+$[(η^5-C_5H_5)-Tl(η^5-C_5H_5)]$^-$ (av 156.7°)[19] and the ion-contacted complex [(η^5-C_5H_5)Tl(μ-C_5H_5)Li($Me_2NCH_2CH_2)_2NMe$}] (av 153.3°).[19]

In summary, the metalloligand **1** is able to break the polymeric chain structure of cyclopentadienide complexes of lithium, sodium, and thallium in arene solvents to give adducts **2**−**4** by its coordination as a neutral trinitrogen ligand to monomeric units [M(C_5H_5)]. In accordance with the obtained data, the thallium complex **4** decomposes in hexane to give **1** and the adduct of the dimeric unit [M(C_5H_5)]$_2$.

Experimental Section

General Comments. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K amalgam just prior to use. Toluene was freshly distilled from sodium. NMR solvent (C_6D_6) was dried with Na/K amalgam and vacuum-distilled. Oven-dried (70−80 °C) glassware was repeatedly evacuated with a pumping system (ca. 1 × 10^{-3} Torr) and subsequently filled with inert gas. [Tl(C_5H_5)] was purchased from Aldrich and used as received. [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**)[1,2] and [M(C_5H_5)] (M = Li, Na)[9] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts are given in ppm (δ) downfield from TMS (δ = 0.0), using the residual protons or carbons of the solvent as an internal reference. Electron impact mass spectra were obtained at 70 eV. Microanalyses (C, H, N) were performed in a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of [(η^5-C_5H_5)Li{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (2). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Li(C_5H_5)] (0.035 g, 0.49 mmol), and toluene (40 mL). The reaction mixture was stirred for 20 h at room temperature to give a red solution. After filtration, the volatile components were removed under reduced pressure. The resultant solid was washed with hexane (20 mL) to give **2** as a brown solid (0.25 g, 76%). IR (KBr, cm^{-1}): 3356 (m), 3316 (m), 3068 (m), 2911 (s), 2859 (m), 2724 (w), 1540 (w), 1490 (m), 1429 (m), 1376 (s), 1119 (w), 1066 (w), 1024 (m), 1006 (m), 735 (vs), 663 (vs), 642 (s), 599 (m), 570 (m), 477 (w), 430 (m). ^{1}H NMR (C_6D_6, 20 °C, δ): 12.33 (s br, 3H, NH), 6.01 (s, 5H, C_5H_5), 1.90 (s, 45H, C_5Me_5). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ): 118.9 (*C*$_5$Me$_5$), 104.4 (*C*$_5$H$_5$), 11.7 (C$_5$*Me*$_5$). Anal. Calcd for $C_{35}H_{53}LiN_4Ti_3$: C 61.79, H 7.85, N 8.23. Found: C 62.16, H 8.14, N 7.73.

Synthesis of [(η^5-C_5H_5)Na{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (3). In a fashion similar to the preparation of **2**, treatment of **1** (0.30 g, 0.49 mmol) with [Na(C_5H_5)] (0.043 g, 0.49 mmol) in toluene (40 mL) afforded **3** as an orange solid (0.22 g, 65%). IR (KBr, cm^{-1}): 3346 (m), 3312 (m), 3070 (m), 2909 (s), 2856 (m), 1490 (w), 1429 (s), 1377 (s), 1025 (m), 1005 (s), 783 (s), 736 (vs), 658 (vs), 641 (s), 605 (m), 527 (m), 474 (m), 423 (m). ^{1}H NMR (C_6D_6, 20 °C, δ): 12.87 (s br, 3H, NH), 6.40 (s, 5H, C_5H_5), 1.85 (s, 45H, C_5Me_5). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ): 119.0 (*C*$_5$Me$_5$), 104.3 (*C*$_5$H$_5$), 11.6 (C$_5$*Me*$_5$). Anal. Calcd for $C_{35}H_{53}N_4NaTi_3$: C 60.36, H 7.67, N 8.04. Found: C 60.50, H 7.82, N 6.92.

Synthesis of [(η^5-C_5H_5)Tl{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}]·C_7H_8 (4). In a fashion similar to the preparation of **2**, treatment of **1** (0.30 g, 0.49 mmol) with [Tl(C_5H_5)] (0.13 g, 0.49 mmol) in toluene (40 mL) afforded **4** as a red solid (0.37 g, 77%). IR (KBr, cm^{-1}): 3345 (s), 3068 (m), 3016 (w), 2909 (s), 1603 (w), 1494 (m), 1429 (m), 1375 (s), 1024 (w), 1005 (m), 732(vs) 719 (vs), 669 (vs), 655 (vs), 640 (s), 585 (m), 471 (m), 425 (m). ^{1}H NMR (C_6D_6, 20 °C, δ): 13.37 (s br, 3H, NH), 6.32 (s, 5H, C_5H_5), 1.92 (s, 45H, C_5Me_5). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ): 118.1 (*C*$_5$Me$_5$), 107.7 (*C*$_5$H$_5$), 11.8 (C$_5$*Me*$_5$). MS (EI, 70 eV): *m/z* (%) 813 (3) [M − C_5H_5]$^+$, 608 (34) [M − C_5H_5 − Tl]$^+$, 473 (18) [M − C_5H_5 − Tl − C_5Me_5]$^+$, 205 (100) [Tl]$^+$. Anal. Calcd for $C_{42}H_{61}N_4Ti_3Tl$: C 52.01, H 6.34, N 5.78. Found: C 52.29, H 6.50, N 5.09.

Synthesis of [(η^5-C_5H_5)Tl(μ-C_5H_5)Tl{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (5). A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Tl(C_5H_5)] (0.26 g, 0.96 mmol), and hexane (25 mL). The reaction mixture was stirred for 7 days at room temperature to give a yellow precipitate and a brown solution. The yellow solid was isolated and washed with hexane (15 mL) to yield **5** (0.39 g, 68%). IR (KBr, cm^{-1}): 3345 (m), 3313 (m), 3069 (m), 2909 (s), 2853 (s), 1558 (w), 1490 (w), 1429 (m), 1377 (s), 1261 (w), 1117 (w), 1025 (w), 1005 (m), 789

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(s), 736 (vs), 658 (vs), 641 (s), 603 (m), 525 (w), 474 (m), 423 (m). Anal. Calcd for $C_{40}H_{58}N_4Ti_3Tl_2$: C 41.88, H 5.10, N 4.88. Found: C 42.70, H 5.14, N 3.71 (small amounts of polymeric $[Tl(C_5H_5)]$ may be the responsible for the discrepancies in the C and N percentage). NMR data of a solution of **5** in benzene-*d*$_6$: ^1H NMR (C_6D_6, 20 °C, δ): 13.24 (s br, 3H, NH), 6.31 (s br, 5H, C_5H_5), 1.89 (s, 45H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 118.1 (C_5Me$_5$), 107.6 (br, C_5H$_5$), 11.8 (C$_5$*Me*$_5$).

X-ray Crystal Structure Determination of Complexes 3, 4, and 5. Orange crystals of compounds **3** and **4** were obtained from toluene solutions at −40 °C. Yellow crystals of **5** were grown from a recently prepared hexane solution of **4** at −40 °C. Crystals 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. Crystallographic data for all of these complexes are presented in Table 1. The structures were solved, using the WINGX package,[20] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[21]

Complex **3** presented severe disorder both in the Cp linked to the sodium atom (two positions for C31, see Supporting Information, refined with 50% occupancy) and in the pentamethylcyclopentadienyl ligand joined to Ti(1) (two positions for every carbon atom, refined with 50% occupancy). All nonhydrogen atoms except those of the disordered units were anisotropically refined. Hydrogen atoms were geometrically added only to the imido bridging groups and to the nondisordered pentamethylcyclopentadienyl rings, and they were refined using a riding model. Refinement converged at R1 = 0.109 and wR2 = 0.292 for 1671 unique reflections with $I > 2\sigma(I)$. R1 and wR2 are defined as $R1 = \sum||F_o| - |F_c||/[\sum|F_o|]$ and $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

Complex **4** crystallized with one molecule of toluene. All nonhydrogen atoms were anisotropically refined while the hydrogen atoms were refined using a riding model. Refinement converged at R1 = 0.043 and wR2 = 0.097 for 4569 unique reflections with $I > 2\sigma(I)$.

Complex **5** diffracted very weakly (average $\sigma(I)/I = 0.472$), and this prevented a very accurate solution. However, the determination of the core of the molecule was unambiguous. Only the non-hydrogen or carbon atoms were anisotropically refined. The hydrogen atoms were refined using a riding model. Refinement converged at R1 = 0.086 and wR2 = 0.167 for 2060 unique reflections with $I > 2\sigma(I)$.

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Supporting Information Available: X-ray structural information for **3**, **4**, and **5** and the IR spectra of **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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