Group 13 and 14 Alkyl Derivatives of the Imido−Nitrido Metalloligand [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)]

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The reactivity of the imido−nitrido trinuclear complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) toward alkyl derivatives of group 13 and 14 elements has been investigated. Treatment of **1** with trialkyl derivatives of aluminum, gallium, or indium at room temperature afforded the adducts [R_3M{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (R = CH_2SiMe_3, M = Al (**3**), Ga (**4**), In (**5**); R = $CH_2C_6H_5$, M = Ga (**6**), In (**7**)). The analogous reaction of **1** with [$AlMe_3$] at 90 °C gave the methylaluminum derivative [MeAl{(μ_3-N)$_2$(μ_3-NH)Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (**8**) via methane elimination. Complexes **3** and **6** at this temperature gave also monoalkyl complexes [RM{(μ_3-N)$_2$(μ_3-NH)Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (M = Al, R = CH_2SiMe_3 (**9**); M = Ga, R = $CH_2C_6H_5$ (**11**)), whereas the indium derivative **7** led to the indium(I) complex [In{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (**12**) and bibenzyl. Analogous chloromethylaluminum adducts [Me_n-Cl_{3-n}Al{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (n = 1 (**13**), 2 (**14**)) were obtained by treatment of **1** with [$AlCl_{3-n}Me_n$]. Reaction of the lithium reagent [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}]$_2$ with tin, germanium, and silicon chloroalkyl derivatives [$MClMe_3$] gave the group 14 alkyl complexes [Me_3M-{(μ_3-N)Ti$_3$(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (M = Sn (**15**), Ge (**16**), Si (**17**)). The X-ray crystal structures of **6**, **7**, **9**, **13**, **15**, and **16** have been determined.

Introduction

The reactions of trialkyl derivatives of group 13 elements (M = Al, Ga, In) with amines have been studied for decades.[1] Trialkylmetal−amine adducts [$R_3M(NR'_3)$] are formed in the first step of the reaction.[2] In many cases, adducts with secondary or primary amines [$R_3M(NHR'_2)$] decompose at moderate temperatures via alkane RH elimination to give amido complexes [{$R_2M(NR'_2)$}$_n$], the most common in the literature being the dimeric structures containing a four-membered ring with alternating metal and nitrogen atoms.[3] Further heating at higher temperatures of the amido derivatives obtained from primary amines [{$R_2M(NHR')$}$_n$] may result in an additional alkane elimination with formation of more condensed imido species [{$RM(NR')$}$_n$].[4,5]

The chemistry of trialkyl derivatives of group 13 with macrocyclic amines is comparatively scarcer. Several examples show the formation of adducts with macrocyclic amines,[6] but at high temperatures the derivatives containing macrocyclic secondary amines release alkanes.[7] As an exception, the 1:1 adduct [$AlMe_3${(tacn)H}] ((tacn)H = 1,4-diisopropyl-1,4,7-triazacyclononane) is surprisingly thermally stable and does not release methane in refluxing toluene.[8] Most of those examples

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show the coordination of the macrocyclic nitrogen donors to several alkylmetal fragments, while their link as chelate to a single alkyl group 13 metal center remains rare. Early work by Ito and co-workers demonstrated the formation of the complex [AlEtL] by reaction of [$AlEt_3$] in hexane solution with the macrocyclic H_2L (L = [$C_{22}H_{24}N_4$]) via a two-step ethane elimination sequence.[9] Similar complexes [MRL] and [MR_2L] were characterized later from the reactions of aluminum, gallium, and indium trialkyl derivatives with analogous polydentate amines.[10]

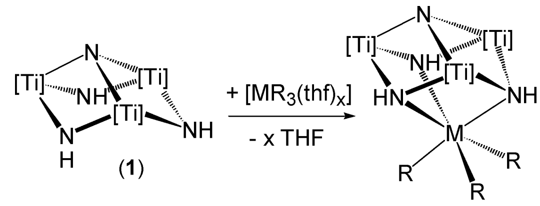
In the last few years, we have been studying the coordination chemistry of the trinuclear titanium imido−nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)][11,12] (**1**). Compound **1** shows a cyclic [Ti_3(μ-NH)$_3$] system with three NH electron-donor imido groups similar to the macrocyclic secondary triamines. Our previous work with transition metal derivatives has shown that **1** is capable of acting as a neutral tridentate 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.[13,14] More recently, we have also demonstrated the ability of **1** to coordinate main-group metal cyclopentadienides and halides to give the adducts [X_nM{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}].[15] Additionally in this similarity with amines, **1** can be deprotonated by treatment with lithium bis(trimethylsilyl)amido to give the lithium complex [Li(μ_4-N)(μ_3-NH)$_2${Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}]$_2$ (**2**),[16,17] which has shown to be an efficient reagent to prepare new heterometallic nitrido complexes through the reaction with chloride derivatives.[14,16]

Herein, we report the synthesis, structure, and thermal behavior of adducts of **1** with group 13 alkyl derivatives. The analogous reactions of **1** with group 14 alkyl derivatives were not successful, but several compounds were obtained through the metathesis reaction of **2** with group 14 cloroalkyl derivatives.

Results and Discussion

Reactions with Group 13 Trialkyl Derivatives. The synthetic chemistry is outlined in Scheme 1. Treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) with 1 equiv of tris(trimethylsilylmethyl) derivatives [M(CH_2SiMe_3)$_3$] of aluminum,[18] gallium,[19] or indium[20] in hexane at room temperature led to the precipitation of the group 13 adducts [(Me_3SiCH_2)$_3$M{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (M = Al (**3**), Ga (**4**), In (**5**)) as yellow or orange solids in 43−63% yields. Analogous reactions of **1** with tribenzyl derivatives of gallium and indium [M($CH_2C_6H_5$)$_3$(thf)$_x$] (M = Ga,[21] x = 1; M = In,[22] x = 0) in toluene afforded the adducts [($C_6H_5CH_2$)$_3$M{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (M = Ga (**6**), In (**7**)) as orange crystals in 51−59% yield.

Scheme 1. Reactions of 1 with [MR_3] ([Ti] = Ti(η^5-C_5Me_5))



R = CH_2SiMe_3; M = Al (**3**), Ga (**4**), In (**5**); x = 0
R = $CH_2C_6H_5$; M = Ga (**6**) x = 1, In (**7**) x = 0

The trimethylsilylmethyl derivatives **3**−**5** are light sensitive in solution, giving unknown greenish products, and therefore their preparations and manipulations in solution were carried out in amber-colored flasks. Solutions of the benzyl derivatives **6** and **7** were not altered under ambient light during weeks in an argon atmosphere. Compounds **3**−**7** were characterized by spectral and analytical methods, as well as by X-ray crystal structure determinations for **6** and **7**. The mass spectra of complexes **3**−**7** (EI, 70 eV) do not show the expected molecular peaks for the adducts, but those found of higher mass/charge correspond to the elimination of alkyl groups from the molecules. IR spectra (KBr) of complexes **3**−**7** reveal one ν_{NH} vibration in the range 3361−3343 cm^{-1} similar to the value determined for **1**, 3352 cm^{-1}, and other adducts of **1** with metal cyclopentadienides and halides.[15] The ^1H and ^{13}C NMR spectra in benzene-d_6 or chloroform-d_1 at room temperature of complexes **3**, **6**, and **7** show resonances for equivalent NH, C_5Me_5, and alkyl groups, suggesting a highly symmetrical structure or the existence of dynamic exchange processes with a low-energy barrier in solution, in a similar fashion to those found in the analogous compounds [I_3In{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] and [$Cl_2$Sn{($\mu_3$-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}].[15b] The NH resonance signals in these spectra (δ = 12.7−12.4) are shifted to a higher field than that found for **1** (δ = 13.8). We have noted an analogous shift in other adducts of **1**[15] and used those data to propose the coordination of the NH groups to the incorporated elements. ^{13}C NMR spectra revealed a singlet for the *ipso*-carbon resonance of the C_5Me_5 ligands (δ = 120.3−120.0), which is slightly shifted downfield with respect to that found for **1** (δ = 117.1).[12]

Surprisingly, the trimethylsilylmethyl derivatives of gallium **4** and indium **5** are not soluble in benzene-d_6 and decompose in chloroform-d_1, precluding their characterization by NMR spectroscopy. However, NMR analysis of the dilute resultant solutions in benzene-d_6 reveals resonance signals almost identi-

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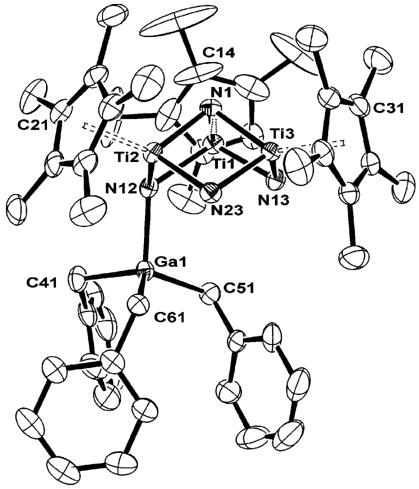

Figure 1. Perspective view of **6** with thermal ellipsoids at the 50% probability level.

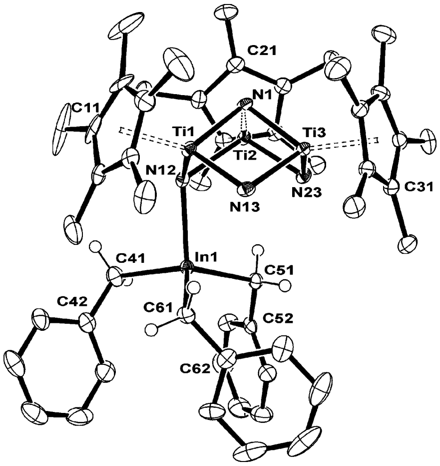

Figure 2. Perspective view of **7** with thermal ellipsoids at the 50% probability level.

Table 1. Selected Lengths (Å) and Angles (deg) for Complexes 6 and 7

	M = Ga (**6**)	M = In (**7**)
M−N(12)	2.094(2)	2.296(2)
M−C[a]	2.036(3)	2.248(3)
Ti⋯Ti[a]	2.826(7)	2.821(1)
Ti−N(1)[a]	1.920(2)	1.923(2)
Ti−N(12)[a]	2.022(2)	2.004(3)
Ti−(μ_2-NH)[a]	1.917(2)	1.919(3)
N(12)−M−C[a]	105.9(1)	105.9(1)
C−M−C[a]	112.8(1)	112.7(2)
M−N(12)−Ti(1)	123.3(1)	119.6(1)
M−N(12)−Ti(2)	118.9(1)	116.9(1)
Ti(1)−N(12)−Ti(2)	89.5(1)	90.3(1)
Ti−(μ_2-NH)−Ti[a]	94.5(1)	94.1(1)
Ti−N(1)−Ti[a]	94.8(1)	94.4(1)
N(1)−Ti−N_{imido}[a]	85.9(1)	86.1(1)
N_{imido}−Ti−N_{imido}[a]	106.9(1)	106.4(1)

[a] Averaged values

cal to those determined for **1** and uncomplexed [$M(CH_2SiMe_3)_3$] reagents, suggesting the dissociation of complexes **4** and **5** in solution. Partial dissociation in solution has been reported for the complexes [$(Me_3SiCH_2)_3Ga\{N(Me)_2C_2H_4(Me)_2N\}Ga(CH_2SiMe_3)_3$][23] and [$(Me_3SiCH_2)_3Ga(PHPh_2)$].[24] The higher stability of group 13 tribenzyl adducts [$M(CH_2C_6H_5)_3(L)$] (M = Ga, In) when compared with the analogous trimethylsilylmethyl derivatives [$M(CH_2SiMe_3)_3(L)$] has been observed previously and attributed to the decreased steric bulk of the benzyl ligand.[22]

The molecular structures of complexes **6** and **7** are presented in Figures 1 and 2, and selected distances and angles for both compounds are given in Table 1. The solid-state structures show a distorted tetrahedral geometry for the gallium and indium centers, comprising three methylene carbon atoms of the benzyl groups and one nitrogen atom of the metalloligand **1**. The benzyl groups stay in a propeller-like disposition like that shown by the starting reagent [$Ga(CH_2C_6H_5)_3(thf)$].[21] The gallium−nitrogen, 2.094(2) Å, and gallium−carbon, average 2.036(3) Å, bond lengths in **6** compare well with those found in other trialkylgallium amine adducts.[25,26] The indium−nitrogen, 2.296(2) Å, and indium−carbon bond lengths in **7**, average 2.248(3) Å, are similar to other trialkylindium amine adducts.[26,27]

The overall structure of **7** resembles that of the indium(III) iodide adduct [$I_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] reported by us.[15b] However, the higher electronic deficiency of indium in the InI_3 fragment makes shorter the In−N bond length (0.1 Å) and forces it to occupy the cavity formed in the inner part of the metalloligand **1** to permit some interaction with the other two imido groups, showing a value for the angle formed by the In(1)−N(12) bond and the Ti(1)−Ti(2)−Ti(3) plane of 71.0(3)°, while a value of 87.2(1)° is obtained for **7**.

As can be seen in Table 1, the indium−nitrogen and indium−carbon bond lengths in **7** are 0.202 and 0.212 Å longer than the respective gallium bond lengths in **6**, which correspond mainly to the difference in covalent radii from gallium to indium (0.18 Å).[28] The geometry about N(12) in both structures, sum of angles M−N(12)−M = 331.7° (**6**) and 326.8° (**7**), is close to that expected for the ideal tetrahedral 328.5°. Within the organometallic ligand the coordination of one NH group to gallium or indium atoms does not affect significantly the average bond distances and angles, presenting values close to those found for the parent compound **1**,[11] except those related with the nitrogen atom N(12) coordinated to the metal, which presents longer Ti−N bonds (0.1 Å) and a narrower Ti−N(12)−Ti angle (4°).

In a procedure similar to the preparation of complexes **3**−**7**, the reaction of **1** with trimethylaluminum in toluene at room temperature gave an orange solution. Analysis by NMR spectroscopy of the solution components revealed a mixture of compounds containing Al−Me fragments. The reaction in benzene-d_6 was monitored by ^{1}H NMR spectroscopy using an amber-colored NMR tube. The spectra at room temperature and different reaction intervals showed resonances for several organometallic species and methane. After heating at 90 °C for 4 days the spectra showed complete transformation of the mixture to give resonance signals assigned to the complex [$MeAl\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**8**) and methane as the sole diamagnetic species in solution. In a preparative experiment using amber-colored glassware, the reaction of **1** with [$AlMe_3$] in hexane at 90 °C for 4 days afforded a red solid. Analysis of this solid by NMR spectroscopy showed

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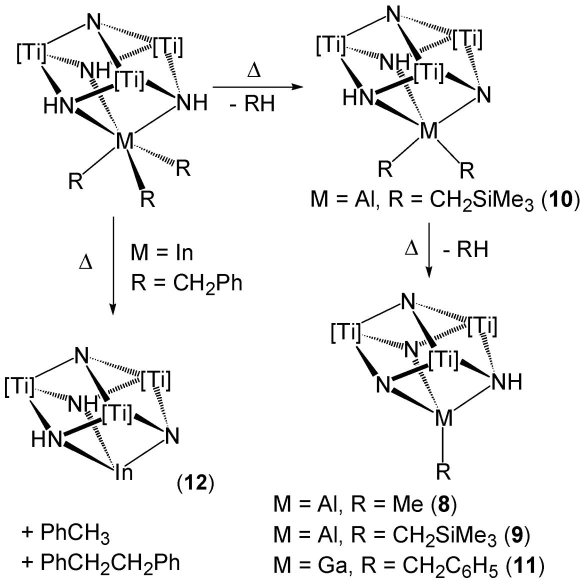
Scheme 2. Thermal Behavior of Adducts [$R_3M\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$] ([Ti] = Ti($\eta^5$-$C_5Me_5$))



resonance signals for **8** as the major product along with minor broad resonances that could be due to paramagnetic species. Despite many attempts **8** could not be obtained in a pure form and was only characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.[29]

In contrast, the heating of the trimethylsilylmethyl aluminum adduct **3** in toluene at 90 °C in the absence of light progressed cleanly to give the analogous complex [(Me$_3$SiCH$_2$)Al{(μ_3-N)$_2$-(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**9**) as a red solid in 82% yield (Scheme 2). The thermal decomposition of **3** in benzene-d_6 solution was monitored by NMR spectroscopy. Spectra taken after heating at 50 °C showed new resonances assigned to the dialkylaluminum compound [(Me$_3$SiCH$_2$)$_2$Al{(μ_3-N)(μ_3-NH)$_2$-Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**10**) and tetramethylsilane. After 3 days at that temperature, the ^{1}H NMR spectrum revealed a mixture of **10** (ca. 70%) and complexes **3** and **9**. After heating at 90 °C for 20 h, the spectra revealed complete consumption of **3** and **10** to give complex **9** and the corresponding 2 equiv of tetramethylsilane. It is noteworthy that although one NH group remains in complexes **8** and **9**, no further alkane elimination occurs on heating those compounds in benzene-d_6 solutions at 180 °C.

Compound **9** was characterized by spectroscopic and analytic methods as well as by an X-ray crystal structure determination. ^{1}H NMR spectra of complexes **8** and **9** in benzene-d_6 reveal resonance signals for two η^5-C$_5$Me$_5$ groups in a 1:2 ratio, those due to one alkyl ligand and broad signals for the NH imido ligand. These data are consistent with C_s-symmetry in solution. The molecular structure of the azaheterometallocubane **9** is presented in Figure 3, while selected lengths and angles are given in Table 2. Complex **9** shows an almost perfect [AlTi$_3$N$_4$] cube core with angles M−N−M, N−Al−N, and N−Ti−N all close to 90°. The coordination environment of aluminum is best described as distorted tetrahedral with angles spanning 90.2-(2)−127.9(4)°. The bond lengths Al−C, 1.946(8) Å, and Al−N, average 1.981(6) Å, are similar to those found in the aluminum macrocyclic complexes [AlEt(C$_{22}$H$_{22}$N$_4$)],[9] [(AlMe)$_2$-[C$_{10}$H$_{20}$N$_4$](AlMe$_3$)$_2$],[7a] and [AlMe(OEP)][30] (OEP = 2,3,7,8,-12,13,17,18-octaethylporphinato).

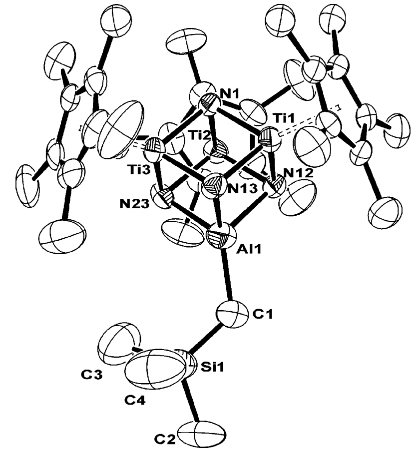


Figure 3. Perspective view of **9** with thermal ellipsoids at the 50% probability level.

Table 2. Selected Lengths (Å) and Angles (deg) for 9

Al(1)−C(1)	1.946(8)	Al(1)−N(12)	1.977(6)
Al(1)−N(13)	1.981(6)	Al(1)−N(23)	1.984(6)
Ti−N[a]	1.929(5)	Ti⋯Ti[a]	2.804(2)
Ti⋯Al[a]	2.714(3)		
N(12)−Al(1)−N(13)	90.6(2)	N(12)−Al(1)−N(23)	90.3(2)
N(13)−Al(1)−N(23)	90.2(2)	C(1)−Al(1)−N(12)	121.2(3)
C(1)−Al(1)−N(13)	127.9(4)	C(1)−Al(1)−N(23)	125.7(3)
N(1)−Ti−N$_{imido}$[a]	86.8(2)	N$_{imido}$−Ti−N$_{imido}$[a]	93.6(2)
Ti−N−Ti[a]	93.2(2)	Ti−N−Al[a]	88.0(2)

[a] Averaged values

The thermal behavior of the benzyl gallium (**6**) and indium (**7**) adducts in benzene-d_6 was also investigated by NMR spectroscopy. Both complexes decompose, slowly at room temperature and rapidly at higher temperatures, giving different products. Upon heating **6** at 110 °C for 1 day the monobenzyl gallium(III) derivative [(C$_6$H$_5$CH$_2$)Ga{(μ_3-N)$_2$(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}][31] (**11**) and toluene (1:2 ratio) were observed. However, the data for the decomposition studies of the indium adduct **7** at that temperature indicated the formation of toluene, bibenzyl, and the indium(I) complex [In{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**12**) in a 1:1:1 ratio.

In preparative scale experiments, complex **11** could not be isolated in a pure form due to the presence of small impurities of **1**, which shows similar solubility in common solvents. The thermal decomposition of the benzyl indium derivative **7** in toluene at 130 °C for 3 days afforded a mixture of **12** and bibenzyl. Alternatively, heating of complex **7** in the solid state under dynamic vacuum at 200 °C for 12 h afforded complex **12** in quantitative yield. We had previously published the synthesis and characterization of **12** through the reaction of the lithium derivative [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (**2**) with InCl in toluene.[16]

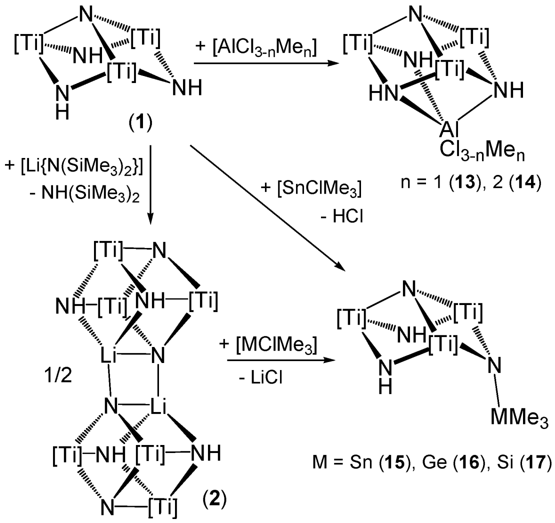
In view of these results, the thermal decomposition of adducts of **1** with group 13 trialkyl derivatives appears to proceed in a first step via elimination of an alkane molecule to give dialkyl intermediates [R$_2$M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}], unambiguously identified in the bis(trimethylsilylmethyl)aluminum

(29) NMR data for **8**: ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 8.47 (s br, 1H; NH), 2.20 (s, 15H; C$_5$Me$_5$), 2.01 (s, 30H; C$_5$Me$_5$), −0.37 (s, 3H; AlMe). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 118.7, 118.2 (*C*$_5$Me$_5$), 12.0, 11.9 (C$_5$*Me*$_5$), −17.0 (AlMe).

(30) Guilard, R.; Zrineh, A.; Tabard, A.; Endo, A.; Han, B. C.; Lecomte, C.; Souhassou, M.; Habbou, A.; Ferhat, M.; Kadish, K. M. *Inorg. Chem.* **1990**, *29*, 4476−4482.

(31) NMR data for **11**: ^{1}H NMR (C$_6$D$_6$, 20 °C, δ): 8.26 (s br, 1H; NH), 7.20−6.90 (m, 5H; C$_6$H$_5$), 2.34 (s, 2H; CH$_2$), 2.20 (s, 15H; C$_5$Me$_5$), 1.98 (s, 30H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C, δ): 141.5, 128.7, 128.1, 124.3 (C$_6$H$_5$), 118.5, 117.9 (*C*$_5$Me$_5$), 16.3 (Ga-CH$_2$), 12.1, 12.0 (C$_5$*Me*$_5$).

Scheme 3. Reactions with Chloromethyl Complexes [$AlCl_{3-n}Me_n$] and [$MClMe_3$] ([Ti] = Ti(η^5-C_5Me_5))



derivative **10**. From those intermediates, an additional alkane elimination affords the aluminum and gallium monoalkyl derivatives **8**, **9**, and **11**. This pathway is comparable to those reported for the chemistry of aluminum, gallium, and indium with macrocyclic secondary amines by Ito[9] and other authors.[10] In contrast, the formation of the indium(I) complex **12**, toluene, and bibenzyl may be explained as a result of the reductive elimination reaction from the undetected intermediate [$(C_6H_5$-$CH_2)_2$In{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}]. An analogous decomposition of indium(III) to indium(I) derivatives in organometallic chemistry has been observed upon heating [In(η^1-C_5H_5)$_3$], in the solid state or solution, to give [In(η^5-C_5H_5)].[32]

Reactions with Group 13 and 14 Chloromethyl Derivatives. Treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) with 1 equiv of dichloromethylaluminum [$AlCl_2Me$] or chlorodimethylaluminum [$AlClMe_2$] derivatives at room temperature led to the adducts [Me_nCl_{3-n}Al{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (n = 1 (**13**), 2 (**14**)) (Scheme 3). Whereas the reaction of **1** with [$AlCl_2Me$] in toluene afforded compound **13**·C_7H_8 in high purity as an orange precipitate in 41% yield, the analogous treatment of **1** with [$AlClMe_2$] gave a dark green precipitate. This green solid is not soluble in benzene-d_6 and produced orange solutions in chloroform-d_1, where complex **14** was identified by NMR spectroscopy. Complex **14** was obtained as an orange solid (83% yield) in higher purity by using chloroform-d_1 as reaction solvent and amber-colored glassware in all the manipulations.

Complexes **13** and **14** were characterized by spectral and analytical techniques, as well as by an X-ray crystal structure determination for **13**·C_7H_8. ^{1}H and ^{13}C{^{1}H} NMR spectra in chloroform-d_1 at room temperature show resonances for equivalent η^5-C_5Me_5, Al−CH_3, and NH groups, suggesting rapid exchange processes in solution. Upon cooling at −50 °C, the ^{1}H NMR spectrum of **13** still revealed a single sharp resonance for the η^5-C_5Me_5 ligands. The molecular structure of complex **13** is presented in Figure 4, while selected bond lengths and angles are given in Table 3. Crystals of **13** bear one toluene molecule per aluminum adduct. The solid-state structure presents a distorted tetrahedral geometry for the aluminum center, comprising two chlorine atoms, one carbon atom of a methyl group, and one NH ligand, with angles spanning 101.8(1)−117.5(1)°. The Al−N distance of 1.902(2) Å is shorter than those found in **9** (average 1.981(6) Å) but similar to that found in [$MeCl_2$Al{N($SnMe_3$)$_3$}], 1.919(8) Å.[33] The Al−N, Al−C (1.977(3) Å), and Al−Cl (average 2.174(1) Å) bond lengths in **13** compare well with those recently reported for [$MeCl_2$Al-($NH_2{}^tBu$)].[34] The sum of angles M−N(23)−M (329.8°) is very close to an ideal tetrahedral geometry. Within the organometallic ligand the coordination of one NH group to aluminum gives a 0.1 Å lengthening of the Ti−N(23) bonds and a Ti(2)−N(23)−Ti(3) angle 4° narrower than that of **1**,[11] in a similar disposition to that of **6** and **7**.

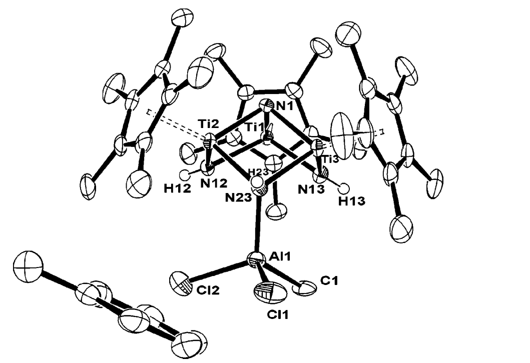


Figure 4. Perspective view of **13**·C_7H_8 with thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 13·C_7H_8

Al(1)−N(23)	1.902(2)	Al(1)−C(1)	1.977(3)
Al(1)−Cl(1)	2.185(1)	Al(1)−Cl(2)	2.163(1)
Ti···Ti[a]	2.833(1)	Ti−N(1)[a]	1.919(2)
Ti(2)−N(23)	2.055(2)	Ti(2)−N(12)	1.887(3)
Ti(3)−N(23)	2.049(2)	Ti(3)−N(13)	1.878(2)
Ti(1)−N(12)	1.958(2)	Ti(1)−N(13)	1.958(2)
N(23)−Al(1)−C(1)	117.5(1)	N(23)−Al(1)−Cl(1)	101.8(1)
N(23)−Al(1)−Cl(2)	111.6(1)	C(1)−Al(1)−Cl(1)	110.2(1)
C(1)−Al(1)−Cl(2)	109.3(1)	Cl(1)−Al(1)−Cl(2)	105.6(1)
Al(1)−N(23)−Ti(2)	121.1(1)	Al(1)−N(23)−Ti(3)	119.8(1)
Ti(2)−N(23)−Ti(3)	88.9(1)	Ti−(μ_2-NH)−Ti[a]	94.2(1)
Ti−N(1)−Ti[a]	95.2(1)	N(1)−Ti−N_{imido}[a]	85.9(1)
N_{imido}−Ti−N_{imido}[a]	105.9(1)		

[a] Averaged values

Thermal decomposition of complexes **13** and **14** in benzene-d_6 solutions was examined by NMR spectroscopy. After heating at 50 °C for 1 day, the spectra showed a complicated mixture of unknown products. The thermal processes presumably involve activation of aluminum−chlorine bonds with generation of reactive HCl and were not further investigated.

We have also examined the reaction of **1** with alkyl derivatives of group 14 elements. Compound **1** did not react with silicon or tin [MMe_4] derivatives even after prolonged heating at 200 °C in benzene-d_6 solutions. The reaction of **1** with chlorotrimethyltin in benzene-d_6 was monitored by NMR spectroscopy. After heating at 50 °C for 1 day the spectra showed resonances for the compound [Me_3Sn{(μ_3-N)Ti$_3$(η^5-C_5-Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (**15**) presumably via generation of HCl. The formation of **15** at 50 °C is very slow, and at higher temperatures the spectra show resonances for complexes **15**, **1**, [$SnMe_4$], and several unidentified species. Complex **15** and the analogous silicon derivative [Me_3Si{(μ_3-N)Ti$_3$(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (**17**) have been previously obtained as orange

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(33) Cheng, Q. M.; Stark, O.; Merz, K.; Winter, M.; Fischer, R. A. *J. Chem. Soc., Dalton Trans.* **2002**, 2933−2936.

(34) Carmalt, C. J.; King, S. J.; Mileham, J. D.; Sabir, E.; Tocher, D. A. *Organometallics* **2004**, *23*, 2939−2943.

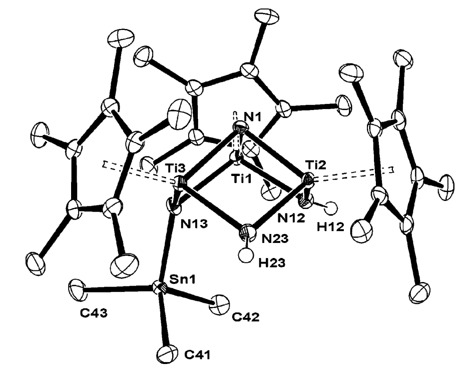

Figure 5. Perspective view of **15** with thermal ellipsoids at the 50% probability level.

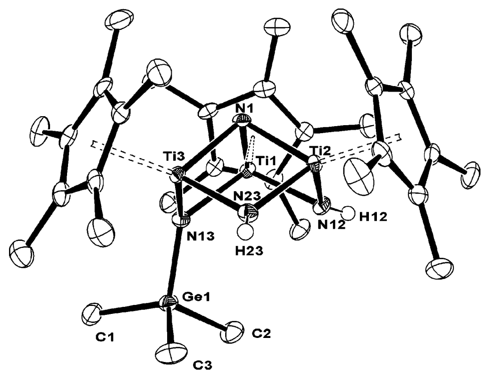

Figure 6. Perspective view of **16** with thermal ellipsoids at the 50% probability level.

Table 4. Selected Lengths (Å) and Angles (deg) for Complexes 15 and 16

	M = Sn (**15**)	M = Ge (**16**)^b
M−N(13)	2.060(4)	1.861(4)
M−C^a	2.150(5)	1.954(5)
Ti−N^a	1.928(4)	1.930(4)
Ti···Ti^a	2.806(1)	2.808(1)
N(13)−M−C^a	109.5(2)	110.1(2)
C−M−C^a	109.5(2)	108.9(2)
M−N(13)−Ti(1)	125.9(2)	127.5(2)
M−N(13)−Ti(3)	124.2(2)	126.1(2)
Ti(1)−N(13)−Ti(3)	93.0(2)	92.6(2)
Ti−N−Ti^a	93.5(2)	93.4(2)
N(1)−Ti−N$_{imido}$^{a}	86.2(2)	86.2(2)
N$_{imido}$−Ti−N$_{imido}$^{a}	105.9(2)	106.0(2)

^{a} Averaged values ^{b} Averaged values for the two independent molecules in the asymmetric unit.

crystals by treatment of [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (**2**) with [MClMe$_3$] in toluene at room temperature (Scheme 3).[16] The reaction of **2** with chlorotrimethylgermanium afforded the new complex [Me$_3$Ge{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] (**16**) in 88% yield. Compounds **15**−**17** are very soluble in hexane or toluene, and their solutions in benzene-d_6 remain unaltered at high temperatures. Complex **16** features similar spectroscopic data to those reported for **15** and **17**.[16] In addition, from saturated pentane solutions of **15** and **16** at −40 °C it was possible to grow suitable single crystals for X-ray diffraction. The molecular structures of **15** and **16** are shown in Figures 5 and 6, while selected bond lengths and angles for both complexes are given in Table 4. Complex **16** crystallizes with two independent molecules in the asymmetric unit. The solid-state structures of **15** and **16** reveal the coordination of the metalloligand by one μ_3-N nitrido group to the tin and germanium centers, respectively. The coordination sphere of the group 14 elements contains three methyl groups and the nitrido group in an almost perfect tetrahedral geometry. The tin−nitrogen, 2.060(4) Å, and tin−carbon, average 2.150(5) Å, bond lengths in **15** are similar to those found in other trimethyltin amido complexes.[35] The germanium−nitrogen, 1.861(4) Å, and germanium−carbon, average 1.954(5) Å, bond lengths in **16** compare well with reported values in the literature for trimethylgermanium amides.[36] As can be seen in Table 4, the tin−nitrogen and tin−carbon bond lengths in **15** are 0.199 and 0.196 Å longer than the respective germanium bond lengths in **16**, which correspond to the difference in covalent radii of germanium and tin (0.18 Å).[28]

The sum of angles M−N−M about N(13) in **15**, 343.1°, and **16**, 346.2°, are slightly smaller than that expected for a trigonal planar geometry (360°) but bigger than the analogous sum for the bridging nitrogen atom in the structures determined for adducts **6**, **7**, and **13**. Within the metalloligand the titanium−nitrogen bond lengths (average 1.928(4) Å in **15** and 1.930(4) Å in **16**) and the Ti−N−Ti (average ≈ 93°) and N−Ti−N (average 106°) angles are very similar to those found in **1**.[11]

^{1}H NMR spectra of complexes **15**−**17** in benzene-d_6 at room temperature show resonance signals for two η^5-C$_5$Me$_5$ groups in a 2:1 ratio, singlets for the M*Me*$_3$ fragments, and broad signals for equivalent NH ligands. These data are consistent with C_s-symmetric structures in solution. The NH resonance signals in these spectra (δ = 14.2−14.1) are shifted to lower field than those found in **1** (δ = 13.8). We have not observed this shift to lower field in any other derivatives of **1**, and we suggest that these data are indicative of the absence of coordination of the NH ligands to the silicon, germanium, or tin centers in solution. The NMR data of **15**−**17** are therefore in agreement with the solid-state structures and rule out the existence of six-coordinate metal centers in solution. Thus, we propose that complexes **15**−**17** both in solution and in the solid state show an incomplete cube structure similar to the organometallic ligand **1**.

Conclusion

The reaction of the organometallic ligand [{Ti(η^5-C$_5$Me$_5$)(μ-NH)}$_3$(μ_3-N)] (**1**) with alkyl group 13 derivatives affords adducts [R$_3$M{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] and [Me$_n$Cl$_{3-n}$Al{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] in the first step. Adducts of trialkyl derivatives of aluminum and gallium further react at moderate temperatures to form monoalkyl derivatives [RM{(μ_3-N)$_2$(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] via elimination of 2 equiv of alkane. In contrast, the indium tribenzyl adduct of **1** releases toluene in the first step and later a reductive elimination reaction takes place, affording the indium(I) complex [In{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] and bibenzyl. On the other hand, highly stable trimethyl derivatives of group 14 elements [Me$_3$M-{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] with incomplete cube structure can be obtained through the reaction of the lithium reagent [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$ (**2**) with [MClMe$_3$].

(35) For some examples, see: (a) Dilworth, J. R.; Hanich, J.; Krestel, M.; Beck, J.; Strähle, J. *J. Organomet. Chem.* **1986**, *315*, C9−C12. (b) Stalke, D.; Klingebiel, U.; Sheldrick, G. M. *J. Organomet. Chem.* **1988**, *341*, 119−124. (c) Bai, Y.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Z. Naturforsch.* **1992**, *B47*, 603−608. (d) Hillwig, R.; Harms, K.; Dehnicke, K. *J. Organomet. Chem.* **1995**, *501*, 327−332.

(36) For some examples, see: (a) Halder, T.; Schwarz, W.; Weidlein, J.; Fischer, P. *J. Organomet. Chem.* **1983**, *246*, 29−48. (b) Hausen, H. D.; Mundt, O.; Kaim, W. *J. Organomet. Chem.* **1985**, *296*, 321−337. (c) Miller, G. A.; Lee, S. W.; Trogler, W. C. *Organometallics* **1989**, *8*, 738−744. (d) Trapp, M.; Hausen, H. D.; Weckler, G.; Weidlein, J. *J. Organomet. Chem.* **1993**, *450*, 53−61.

Table 5. Experimental Data for the X-ray Diffraction Studies on 6, 7, 9, 13·C_7H_8, 15, and 16

formula	$C_{51}H_{69}GaN_4Ti_3$ (**6**)	$C_{51}H_{69}InN_4Ti_3$ (**7**)	$C_{34}H_{57}AlN_4SiTi_3$ (**9**)	$C_{38}H_{59}AlCl_2N_4Ti_3$ (**13**·C_7H_8)	$C_{33}H_{56}N_4SnTi_3$ (**15**)	$C_{33}H_{56}GeN_4Ti_3$ (**16**)
M_r	951.52	996.62	720.61	813.47	771.21	725.11
T [K]	200(2)	100(2)	200(2)	150(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71069	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2(1)/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]; α [deg]	11.848(2)	11.841(2)	11.135(1)	18.467(5)	11.512(1); 95.60(1)	11.029(2); 111.66(1)
b [Å]; β [deg]	17.045(3); 91.38(1)	17.002(2); 91.44(1)	23.600(3); 101.56(1)	11.320(5); 103.73(1)	12.096(1); 100.52(1)	17.912(2); 90.19(1)
c [Å]; γ [deg]	24.126(5)	24.252(3)	15.116(1)	20.250(5)	13.315(2); 98.43(1)	19.780(1); 102.22(1)
V [Å^3]	4871.0(15)	4881(1)	3891.5(7)	4112(2)	1788.3(3)	3535.1(8)
Z	4	4	4	4	2	4
ρ_{calcd} [g cm^{-3}]	1.298	1.356	1.230	1.314	1.432	1.362
$\mu_{MoK\alpha}$ [mm^{-1}]	1.058	0.977	0.681	0.751	1.362	1.522
F(000)	2000	2072	1528	1712	796	1520
cryst size [mm]	0.15 × 0.15 × 0.15	0.52 × 0.33 × 0.33	0.20 × 0.15 × 0.13	0.67 × 0.42 × 0.19	0.69 × 0.43 × 0.09	0.55 × 0.32 × 0.21
θ range [deg]	3.05 to 27.50	5.02 to 27.50	5.06 to 20.00	3.15 to 27.52	5.10 to 27.50	5.01 to 27.00
index ranges	−15 to 15, −22 to 21, −31 to 31	−15 to 15, −22 to 22, −31 to 31	−10 to 10, −22 to 22, −14 to 14	−23 to 23, −14 to 14, −26 to 26	−14 to 14, −15 to 15, −17 to 17	−14 to 14, −22 to 22, −25 to 25
no. of reflns collected	39 326	38 873	13 850	82 307	67 791	104 445
no. of unique data	11 173 [R_{int} = 0.101]	11 138 [R_{int} = 0.074]	3572 [R_{int} = 0.089]	9442 [R_{int} = 0.151]	8166 [R_{int} = 0.188]	15 301 [R_{int} = 0.145]
no. of obsd data [$I > 2\sigma(I)$]	7970	8070	2472	7084	6444	11 405
goodness-of-fit on F^2	0.912	0.944	1.041	1.056	1.093	1.125
final R indices [$I > 2\sigma(I)$]	R1 = 0.044, wR2 = 0.097	R1 = 0.040, wR2 = 0.079	R1 = 0.054, wR2 = 0.126	R1 = 0.048, wR2 = 0.108	R1 = 0.052, wR2 = 0.126	R1 = 0.056, wR2 = 0.140
R indices (all data)	R1 = 0.075, wR2 = 0.111	R1 = 0.071, wR2 = 0.090	R1 = 0.092, wR2 = 0.149	R1 = 0.076, wR2 = 0.124	R1 = 0.072, wR2 = 0.139	R1 = 0.087, wR2 = 0.168
largest diff peak/hole [e Å^{-3}]	0.533/−0.495	0.802/−0.582	0.341/−0.386	0.499/−0.615	1.544/−1.988	1.732/−0.985

[a] $R1 = \sum||F_o| - |F_c||/[\sum|F_o|]$ $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

Experimental Section

General Comments. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Thermolyses in solution at high temperatures were carried out by heating flame-sealed NMR or Carius tubes in a Roth autoclave model III. [$AlMe_3$] (2 M in toluene), [$AlCl_2Me$] (1 M in hexane), [$AlClMe_2$] (1 M in hexane), and bibenzyl were purchased from Aldrich and used as received. [$GeClMe_3$] was purchased from ABCR and used as received. [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**),[11,12] [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}]$_2$·C_7H_8 (**2**·C_7H_8),[16] [M(CH_2SiMe_3)$_3$] (M = Al,[37] Ga,[19] In[38]), [Ga($CH_2C_6H_5$)$_3$(thf)],[21] and [In($CH_2C_6H_5$)$_3$][22] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts (δ) are given relative to residual protons or to carbon of the solvent. Electron impact mass spectra were obtained at 70 eV on a Hewlett-Packard 5988A mass spectrometer. Microanalyses (C, H, N) were performed in a Heraeus CHN-O-Rapid or a Leco CHNS-932 microanalyzer.

Synthesis of [(Me_3SiCH_2)$_3$Al{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (3). All manipulations were carried out in the absence of light by using amber-colored glassware. A 100 mL amber-colored Schlenk flask was charged with **1** (0.50 g, 0.82 mmol), [Al(CH_2SiMe_3)$_3$] (0.24 g, 0.83 mmol), and hexane (20 mL). The reaction mixture was stirred at room temperature for 2 h with precipitation of a solid. This solid was isolated by filtration onto a glass frit, washed with hexane (15 mL), and vacuum-dried to afford **3** as a yellow powder (0.47 g, 63%). IR (KBr, cm^{-1}): 3361 (w), 2946 (vs), 2910 (vs), 1493 (w), 1431 (m), 1377 (s), 1322 (w), 1238 (vs), 1025 (w), 961 (s), 858 (vs), 824 (vs), 788 (w), 754 (vs), 735 (vs), 675 (w), 657 (s), 589 (m), 542 (w), 510 (w), 462 (w), 419 (w). NMR spectra were obtained from solutions of **3** in amber-colored NMR tubes. ^{1}H NMR (C_6D_6, 20 °C, δ): 12.44 (s br, 3H; NH), 1.94 (s, 45H; C_5Me_5), 0.38 (s, 27H; $SiMe_3$), −1.04 (s, 6H; CH_2). ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ): 120.3 (*C*$_5$Me$_5$), 12.4 (C$_5$*Me*$_5$), 4.4 ($SiMe_3$), not observed Al*C*H$_2$. MS (EI, 70 eV): *m/z* (%) 722 (18) [M − 2($SiMe_4$)]$^+$, 608 (15) [M − Al(CH_2SiMe_3)$_3$]$^+$, 202 (13) [Al(CH_2SiMe_3)$_2$]$^+$, 115 (7) [Al(CH_2SiMe_3)]$^+$, 73 (100) [$SiMe_3$]$^+$. Anal. Calcd for $C_{42}H_{81}AlN_4Si_3Ti_3$ (M_w = 896.97): C 56.24, H 9.10, N 6.25. Found: C 56.06, H 9.29, N 5.96.

Synthesis of [(Me_3SiCH_2)$_3$Ga{(μ_3-NH)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (4). In a fashion similar to the preparation of **3**, treatment of **1** (0.50 g, 0.82 mmol) with [Ga(CH_2SiMe_3)$_3$] (0.30 g, 0.90 mmol) in hexane (20 mL) for 9 h afforded **4** as an orange solid (0.33 g, 43%). IR (KBr, cm^{-1}): 3343 (w), 2942 (vs), 2913 (vs), 2858 (m), 1590 (w), 1489 (m), 1434 (m), 1377 (m), 1233 (s), 1161 (w), 1024 (w), 911 (s), 855 (s), 822 (vs), 756 (m), 720 (vs), 676 (w), 648 (s), 621 (w), 529 (w), 496 (w), 474 (w), 428 (w). MS (EI, 70 eV): *m/z* (%) 678 (1) [M − 3(CH_2SiMe_3)]$^+$, 608 (1) [M − Ga(CH_2SiMe_3)$_3$]$^+$, 243 (35) [Ga(CH_2SiMe_3)$_2$]$^+$, 157 (2) [Ga(CH_2SiMe_3)]$^+$, 73 (49) [$SiMe_3$]$^+$.

(37) Tessier-Youngs, C.; Beachley, O. T., Jr. *Inorg. Synth.* **1986**, *24*, 92−93.

(38) Kopasz, J. P.; Hallock, R. B.; Beachley, O. T., Jr. *Inorg. Synth.* **1986**, *24*, 89−91.

Anal. Calcd for $C_{42}H_{81}GaN_4Si_3Ti_3$ (M_w = 939.71): C 53.68, H 8.69, N 5.96. Found: C 54.06, H 8.58, N 6.40.

Synthesis of $[(Me_3SiCH_2)_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (5). In a fashion similar to the preparation of **3**, treatment of **1** (0.50 g, 0.82 mmol) with $[In(CH_2SiMe_3)_3]$ (0.31 g, 0.82 mmol) in hexane (25 mL) for 5 h afforded **5** as an orange solid (0.36 g, 44%). IR (KBr, cm^{-1}): 3344 (m), 2941 (vs), 2915 (vs), 1492 (w), 1436 (m), 1378 (m), 1233 (s), 1164 (w), 1102 (w), 1068 (w), 1023 (w), 879 (s), 853 (vs), 821 (s), 720 (vs), 646 (vs), 548 (w), 473 (w), 427 (m). MS (EI, 70 eV): *m/z* (%) 723 (1) $[M - 3(CH_2SiMe_3)_3]^+$, 608 (2) $[M - In(CH_2SiMe_3)_3]^+$, 289 (46) $[In(CH_2SiMe_3)_2]^+$, 115 (100) $[In]^+$, 73 (51) $[SiMe_3]^+$. Anal. Calcd for $C_{42}H_{81}InN_4Si_3Ti_3$ (M_w = 984.81): C 51.22, H 8.29, N 5.69. Found: C 51.18, H 7.98, N 5.80.

Synthesis of $[(C_6H_5CH_2)_3Ga\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (6). A solution of $[Ga(CH_2C_6H_5)_3(thf)]$ (0.34 g, 0.49 mmol) in toluene (10 mL) was carefully added to **1** (0.30 g, 0.49 mmol) in toluene (20 mL). The system was allowed to react without any stirring for 2 days. After decantation, **6** was obtained as orange crystals (0.24 g, 51%). IR (KBr, cm^{-1}): 3349 (m), 3047 (w), 3014 (w), 2909 (vs), 2860 (w), 1595 (s), 1488 (s), 1448 (m), 1430 (m), 1376 (s), 1309 (w), 1204 (s), 1178 (w), 1067 (vs), 1026 (m), 996 (m), 894 (w), 839 (m), 798 (s), 751 (vs), 731 (vs), 697 (vs), 651 (vs), 591 (s), 539 (w), 517 (w), 462 (m), 447 (m), 420 (w). ^1H NMR (C_6D_6, 20 °C, δ): 12.50 (s br, 3H; NH), 7.13 (m, 6H; *m*-C_6H_5), 6.93 (m, 3H; *p*-C_6H_5), 6.64 (m, 6H; *o*-C_6H_5), 1.86 (s, 45H; C_5Me_5), 1.74 (s, 6H; CH_2). ^{13}C NMR ($CDCl_3$, 20 °C, δ): 148.1 (m, ipso-C_6H_5), 127.5 (m, $^1J_{C-H}$ = 156 Hz; *o*-C_6H_5), 127.1 (m, $^1J_{C-H}$ = 155 Hz; *m*-C_6H_5), 120.5 (m, $^1J_{C-H}$ = 159 Hz; *p*-C_6H_5), 120.3 (s, C_5Me_5), 27.3 (t, $^1J_{C-H}$ = 129 Hz; CH_2), 12.2 (q, $^1J_{C-H}$ = 126 Hz; C_5Me_5). MS (EI, 70 eV): *m/z* (%) 768 (1) $[M - 2(CH_2Ph)]^+$, 676 (7) $[M - 3(CH_2Ph)]^+$, 609 (29) $[M - Ga(CH_2Ph)_3]^+$, 541 (8) $[M - 3(CH_2Ph) - C_5Me_5]^+$, 474 (6) $[M - Ga(CH_2Ph)_3 - C_5Me_5]^+$, 405 (10) $[M - 3(CH_2Ph) - 2C_5Me_5]^+$, 251 (41) $[Ga(CH_2Ph)_2]^+$, 160 (15) $[Ga(CH_2Ph)]^+$, 91 (86) $[CH_2Ph]^+$, 69 (100) $[Ga]^+$. Anal. Calcd for $C_{51}H_{69}GaN_4Ti_3$ (M_w = 951.46): C 64.38, H 7.31, N 5.89. Found: C 64.48, H 7.42, N 5.72.

Synthesis of $[(C_6H_5CH_2)_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (7). In a fashion similar to the preparation of **6**, treatment of **1** (0.30 g, 0.49 mmol) with $[In(CH_2C_6H_5)_3]$ (0.19 g, 0.49 mmol) in toluene (30 mL) for 2 days afforded **7** as orange crystals (0.29 g, 59%). IR (KBr, cm^{-1}): 3349 (m), 3048 (w), 3014 (w), 2908 (vs), 2857 (w), 1595 (s), 1486 (s), 1448 (m), 1430 (m), 1376 (s), 1304 (w), 1261 (w), 1205 (vs), 1178 (w), 1029 (s), 1016 (s), 990 (s), 890 (w), 839 (m), 796 (s), 749 (vs), 731 (vs), 696 (vs), 652 (vs), 628 (w), 596 (s), 538 (w), 465 (m), 422 (m). ^1H NMR (C_6D_6, 20 °C, δ): 12.69 (s br, 3H; NH), 7.18 (m, 6H; *m*-C_6H_5), 6.91 (m, 3H; *p*-C_6H_5), 6.76 (m, 6H; *o*-C_6H_5), 1.91 (s, 45H; C_5Me_5), 1.89 (s, 6H; CH_2). ^{13}C NMR ($CDCl_3$, 20 °C, δ): 148.8 (m, ipso-C_6H_5), 127.8 (m, $^1J_{C-H}$ = 155 Hz; *o*-C_6H_5), 126.2 (m, $^1J_{C-H}$ = 152 Hz; *m*-C_6H_5), 120.0 (m, $^1J_{C-H}$ = 164 Hz; *p*-C_6H_5), 120.0 (s, C_5Me_5), 26.9 (t, $^1J_{C-H}$ = 127 Hz; CH_2), 12.1 (q, $^1J_{C-H}$ = 125 Hz; C_5Me_5). MS (EI, 70 eV): *m/z* (%) 722 (6) $[M - 3(CH_2Ph)]^+$, 608 (2) $[M - In(CH_2Ph)_3]^+$, 588 (5) $[M - 3(CH_2Ph) - C_5Me_5]^+$, 451 (9) $[M - 3(CH_2Ph) - 2C_5Me_5]^+$, 315 (22) $[M - 3(CH_2Ph) - 3C_5Me_5]^+$, 115 (100) $[In]^+$. Anal. Calcd for $C_{51}H_{69}InN_4Ti_3$ (M_w = 996.55): C 61.47, H 6.98, N 5.62. Found: C 61.07, H 7.01, N 4.96.

Synthesis of $[(Me_3SiCH_2)Al\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)Ti(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (9). A 100 mL amber-colored ampule (Teflon stopcock) was charged with **3** (0.50 g, 0.56 mmol) and toluene (40 mL). After stirring at 90 °C for 4 days, the volatile components were removed under reduced pressure to afford **9** as a red solid (0.33 g, 82%). IR (KBr, cm^{-1}): 3377 (w), 3352 (w), 2948 (s), 2910 (vs), 2854 (s), 2721 (w), 1435 (m), 1375 (s), 1243 (s), 1024 (w), 971 (s), 827 (vs), 726 (vs), 699 (vs), 674 (vs), 652 (vs), 625 (m), 592 (w), 456 (m), 441 (m). ^1H NMR (C_6D_6, 20 °C, δ): 9.18 (s br, 1H; NH), 2.20 (s, 15H; C_5Me_5), 2.02 (s, 30H; C_5Me_5), 0.16 (s, 9H; $SiMe_3$), −0.69 (s, 2H; $AlCH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 118.7, 118.3 (C_5Me_5), 12.0, 11.9 (C_5Me_5), 2.5 ($SiMe_3$), not observed $AlCH_2$. MS (EI, 70 eV): *m/z* (%) 722 (42) $[M]^+$, 609 (18) $[M - Al(CH_2SiMe_3)]^+$, 73 (100) $[SiMe_3]^+$. Anal. Calcd for $C_{34}H_{57}AlN_4SiTi_3$ (M_w = 720.52). C 56.68, H 7.97, N 7.78. Found: C 56.50, H 8.24, N 7.13.

Thermal Decomposition of 3 in a NMR Tube Scale Experiment. A 5 mm amber-colored valved-NMR tube was charged with $[(Me_3SiCH_2)_3Al\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**) (0.020 g, 0.016 mmol) and benzene-d_6 (1.00 mL). The reaction course was monitored by NMR spectroscopy at different temperatures. After heating at 50 °C in an oil bath for 4 h, the spectra revealed new resonances assigned to the dialkylaluminum compound $[(Me_3SiCH_2)_2Al\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**) and tetramethylsilane. Upon leaving the tube at this temperature for 3 days, the ^1H NMR spectrum showed **10** as the major product (ca. 70%) of a mixture of this complex with **3** and **9**. After heating at 90 °C for 20 h, the spectra revealed complete consumption of **3** and **10** to give complex **9** and the corresponding 2 equiv of $SiMe_4$.

NMR data for $[(Me_3SiCH_2)_2Al\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**): ^1H NMR (C_6D_6, 20 °C, δ): 10.23 (s br, 2H; NH), 2.05 (s, 30H; C_5Me_5), 1.90 (s, 15H; C_5Me_5), 0.33 (s, 18H; $SiMe_3$), −0.90 (s, 4H; $AlCH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 120.1, 119.2 (C_5Me_5), 12.3, 11.9 (C_5Me_5), 4.1 ($SiMe_3$), not observed $AlCH_2$.

Thermal Decomposition of $[C_6H_5CH_2)_3In\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (7). In Solution. A 100 mL Carius tube was charged with **7** (0.20 g, 0.20 mmol) and toluene (30 mL). The tube was flame-sealed and heated at 130 °C for 3 days. The tube was opened in the glovebox and the solution filtered. The volatile components of the solution were removed under reduced pressure to give a sticky, orange solid. Analysis of the solid by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy showed resonances for complex $[In\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**12**),[16] along with those due to bibenzyl, assigned by comparison with spectra obtained from a commercially available bibenzyl sample.

In the Solid State. Complex **7** (0.15 g, 0.15 mmol) was heated in a horizontal tube furnace at 200 °C under dynamic vacuum (ca. 0.1 mmHg) for 12 h. Examination of the orange residue (0.11 g, 100%) by NMR spectroscopy revealed complete consumption of **7** and resonances for pure **12**.

NMR data for $[In\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**12**): ^1H NMR (C_6D_6, 20 °C, δ): 11.61 (s br, 2H; NH), 2.09 (s, 30H; C_5Me_5), 1.86 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 117.9, 117.2 (C_5Me_5), 12.0, 11.9 (C_5Me_5).

NMR data for bibenzyl: ^1H NMR (C_6D_6, 20 °C, δ): 7.15−6.97 (m, 10H; C_6H_5), 2.73 (s, 4H; CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 142.0 (ipso-C_6H_5), 128.8 (*o*-C_6H_5), 128.6 (*m*-C_6H_5), 126.2 (*p*-C_6H_5), 38.2 (CH_2).

Synthesis of $[MeCl_2Al\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (13). A solution of $[AlCl_2Me]$ (1 M in hexane) (1.00 mL, 1.00 mmol) in toluene (10 mL) was added dropwise to **1** (0.60 g, 0.99 mmol) in toluene (20 mL) in an amber-colored Schlenk flask. The reaction mixture was stirred at room temperature for 1 h to give the precipitation of an orange solid. This solid was isolated by filtration onto a glass frit and vacuum-dried to afford **13**·C_7H_8 as an orange powder (0.33 g, 41%). IR (KBr, cm^{-1}): 3359 (m), 3345 (w), 3271 (w), 2912 (vs), 2857 (m), 1605 (w), 1494 (w), 1428 (m), 1377 (s), 1261 (w), 1176 (m), 1067 (w), 1024 (m), 894 (s), 738 (vs), 713 (s), 659 (vs), 619 (vs), 557 (w), 487 (w), 466 (s), 424 (s). ^1H NMR ($CDCl_3$, 20 °C, δ): 11.75 (s br, 3H; NH), 2.07 (s, 45H; C_5Me_5), −1.14 (s, 3H; AlMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C, δ): 121.6 (C_5Me_5), 12.2 (C_5Me_5), −4.34 (br AlMe). Anal. Calcd for $C_{38}H_{59}AlCl_2N_4Ti_3$ (M_w = 813.40): C 56.11, H 7.31, N 6.89. Found: C 56.00, H 7.22, N 6.72.

Synthesis of $[Me_2ClAl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (14). A solution of $[AlClMe_2]$ (1 M in hexane) (0.50 mL, 0.50 mmol) in chloroform-d_1 (10 mL) was added dropwise to a solution of **1** (0.30 g, 0.49 mmol) in chloroform-d_1 (20 mL) in an amber-colored Schlenk flask. The reaction mixture was stirred at room temperature for 15 min to give an orange solution. The volatile components were removed under reduced pressure to give **14** as an orange solid (0.29 g, 83%). IR (KBr, cm^{-1}): 3361 (m), 3267 (m), 2913 (vs), 1488 (w), 1428 (m), 1378 (s), 1261 (w), 1174 (m), 1067 (m), 1023 (m), 867 (m), 735 (vs), 663 (vs), 618 (vs), 524 (w), 460 (m). ^{1}H NMR ($CDCl_3$, 20 °C, δ): 11.66 (s br, 3H; NH), 1.98 (s, 45H; C_5Me_5), −1.33 (s, 6H; AlMe). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, δ): 122.8 (*C*$_5$Me$_5$), 12.3 (C$_5$*Me*$_5$), not observed Al*C*H$_3$. MS (EI, 70 eV): *m*/*z* (%) 669 (1) [M − 2MeH]$^+$, 648 (14) [M − MeH − Cl]$^+$, 513 (14) [M − MeH − Cl − C_5Me_5]$^+$, 377 (29) [M − MeH − Cl − 2C_5Me_5]$^+$, 91 (50) [$AlClMe_2$]$^+$. Anal. Calcd for $C_{32}H_{54}AlClN_4Ti_3$ (M_w = 700.85): C 54.84, H 7.77, N 7.99. Found: C 54.27, H 7.52, N 6.47.

Synthesis of [Me$_3$Ge{(μ_3-N)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)$_2$(μ_3-N)}] (16). A 100 mL Schlenk flask was charged with [Li(μ_4-N)(μ_3-NH)$_2${Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}]$_2$·C$_7$H$_8$ (0.30 g, 0.23 mmol), [GeClMe$_3$] (0.07 g, 0.46 mmol), and toluene (40 mL). After stirring at room temperature for 24 h the solution was filtered and the volatile components were removed under reduced pressure to afford **16** as an orange solid (0.29 g, 88%). IR (KBr, cm^{-1}): 3348 (w), 2907 (vs), 2855 (s), 2719 (w), 1490 (w), 1433 (m), 1374 (s), 1261 (w), 1225 (m), 1065 (w), 1024 (m), 878 (m), 795 (vs), 758 (s), 710 (vs), 672 (vs), 645 (vs), 620 (s), 592 (m), 566 (m), 524 (s), 475 (w), 451 (m), 413 (m). ^{1}H NMR (C_6D_6, 20 °C, δ): 14.19 (s br, 2H; NH), 2.09 (s, 30H; C_5Me_5), 1.91 (s, 15H; C_5Me_5), 0.31 (s, 9H; $GeMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, δ): 117.5, 117.3 (*C*$_5$Me$_5$), 12.2, 11.8 (C$_5$*Me*$_5$), 7.5 (Ge*Me*$_3$). MS (EI, 70 eV): *m*/*z* (%): 726 (3) [M]$^+$, 609 (21) [M − $GeMe_3$]$^+$, 592 (3) [M − C_5Me_5]$^+$, 458 (10) [M − 2C_5Me_5]$^+$, 320 (22) [M − 3C_5Me_5]$^+$, 119 (100) [$GeMe_3$]$^+$. Anal. Calcd for $C_{33}H_{56}GeN_4Ti_3$ (M_w = 725.04): C 54.67, H 7.79, N 7.73. Found: C 54.69, H 7.72, N 6.87.

X-ray Structure Determination of 6, 7, 9, 13, 15, and 16. Orange crystals of **6** and **7** were grown in toluene at room temperature as described in the Experimental Section. Red crystals of complex **9** and orange crystals of **13**, which crystallized with one molecule of toluene, were obtained from toluene solutions at −40 °C. Finally, orange crystals of **15** and **16** were grown from a pentane solution at −40 °C. Crystals were removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (FomblinY). 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 on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. The molybdenum radiation was used in all cases, graphite monochromated, and enhanced with a MIRACOL collimator. Crystallographic data for all the complexes are presented in Table 5.

Multiscan[39] (**6**, **7**, and **9**) or analytical[40] (**13**, **15**, and **16**) absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[41] by direct methods (SHELXS-97[42] for **6**, **7**, **9**, and **16**, SIR97[43] for **13**) or Patterson techniques (SHELXS-97 for **15**)[42] and refined by least-squares against F^2 (SHELXL-97).[42]

All non-hydrogen atoms of **6** were anisotropically refined. All the hydrogen atoms of the imido and benzyl groups were located in the difference Fourier map and refined isotropically. The hydrogen atoms of the pentamethylcyclopentadienyl rings were positioned geometrically and refined by using a riding model.

In a similar treatment to that of **6**, all non-hydrogen atoms of **7** were anisotropically refined. All the hydrogen atoms of the imido and methylene benzyl groups were located in the difference Fourier map and refined isotropically. The hydrogen atoms of the pentamethylcyclopentadienyl and phenyl rings were positioned geometrically and refined by using a riding model.

In the case of **9**, all non-hydrogen atoms were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model.

All the non-hydrogen atoms of **13**, **15**, and **16** were anisotropically refined. The hydrogen atoms of the imido groups were located in the difference Fourier map and refined isotropically, while the rest were positioned geometrically and refined by using a riding model.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **6**, **7**, **9**, **13**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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