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# Cyclopentadienyl yttrium complexes with the $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ metalloligand

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*Dedication:* Dedicated to the late Prof. Dr. Pascual Royo for introducing us to the organometallic chemistry field.

## Abstract:

The reactivity of the yttrium trichloride complex [$Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**2**) with a variety of main-group metal cyclopentadienyl reagents [$M(C_5H_3R^1R^2)$] (M = Li, Na, K, Tl) or [$Mg(C_5H_5)_2$] has been investigated. Treatment of **2** with one equivalent of [$Na(C_5H_5)$] or [$K(C_5H_4SiMe_3)$] gives the monocyclopentadienyl derivatives [$(\eta^5\text{-}C_5H_4R)Cl_2Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (R = H (**3**), $SiMe_3$ (**4**)). Analogous reaction of **2** with lithium [$Li(C_5H_3R^1R^2)$] or thallium [$Tl(C_5H_5)$] reagents (1 or 2 equivalents) leads to complexes [$(\eta^5\text{-}C_5H_3R^1R^2)_2Y(\mu\text{-}Cl)_2M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (M = Li, $R^1$ = $R^2$ = H (**5**), $R^1$ = H, $R^2$ = $SiMe_3$ (**6**), $R^1$ = $R^2$ = $SiMe_3$ (**7**); M = Tl, $R^1$ = $R^2$ = H (**8**)). Complex **2** reacts with [$Mg(C_5H_5)_2$] to yield the ionic compound [$(\mu\text{-}Cl)_3Mg_2\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$][$\{Y(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}Cl)$] (**9**). In contrast to the metathesis of chloride ligands, the reaction of **2** with the lithium indenyl derivative [$Li(C_9H_7)$] at room temperature produces $C_9H_8$ and the precipitation of [$Li(\mu\text{-}Cl)_3Y\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**10**). Crystallization of **10** in pyridine affords the lithium-free [$Cl_2(py)_2Y\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**11**) complex. The X-ray crystal structures of **6** and **11** have been determined.

**Keywords:** Titanium · Yttrium · Cyclopentadienyl · Coordination Compounds · Nitride · Imide

## 1. Introduction

Over the last decades we have been involved in the study of the reactivity of the trimetallic imido-nitrido titanium(IV) derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) [1,2]. The structure of **1** shows a six-membered $[Ti_3(\mu\text{-}NH)_3]$ ring with three NH electron-donor imido groups and one $\mu_3$-N nitrido group bridging the three metal centers. Complex **1** is capable of acting as a Lewis base through the imido NH groups toward many transition and main-group metal derivatives to give cubane-type adducts $[L_nM\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [3]. In particular, we have reported the synthesis of a series of titanium-Group 3/lanthanide metal cubane-type adducts $[X_3M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (X = Cl, M = Sc, Y, La, Sm, Er, Lu; X = OTf, M = Y, Sm, Er) by reaction of **1** with metal halide complexes $[MCl_3(thf)_n]$ or metal trifluoromethanesulfonate derivatives $[M(O_3SCF_3)_3]$ [4]. In those complexes, **1** acts as a facially coordinating ligand to the rare-earth centers and resembles other six-electron donors as the anionic tris(pyrazolyl)borates [5], the neutral analogous tris(pyrazolyl)methanes and tris(pyrazolyl)silanes [6,7], and cyclic triamines such as 1,4,7-triazacyclononanes [7,8] and 1,3,5-triazacyclohexanes [7b,9]. However, the existence of the $\mu_3$-N nitrido apical group confers a more rigid conformation to **1** when compared with those systems.

Since the yttrium trichloride complex $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**) was easily prepared in good yield, we decided to investigate the possibility of preparing its cyclopentadienyl derivatives via salt metathesis. While cyclopentadienyl complexes of the Group 3/lanthanide metals are well-documented [10], mixed-ligand rare-earth species containing cyclopentadienyl ligands and tridentate nitrogen-based systems are scarce in the literature. For instance, Bercaw and co-workers failed to prepare cyclopentandienyl derivatives by salt metathesis of the 1,4,7-triazacylononane scandium and yttrium complexes [M($Me_3$[9]ane$N_3$)$Cl_3$] (M = Sc, Y) [8a]. Unintentionally, an amido-functionalized 1,3,5-triazacyclohexane ligand bonded to a bis(cyclopentadienyl)yttrium(III) unit was obtained by Mitzel [9b]. For the lanthanides, Takats and co-workers have reported a series of samarium(III) complexes supported by hydrotris(pyrazolyl)borate and cyclopentadienyl ligands [11]. Similarly, Zhou and co-workers have described mixed cyclopentadienyl/hydrotris(pyrazolyl)borate frameworks in ytterbium, erbium, dysprosium and yttrium complexes [12]. In this vein, we have previously communicated that the treatment of [$Cl_3Y\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$] (**2**) with one equivalent of [Na($C_5H_5$)] afforded the monocyclopentadienyl derivative [$(\eta^5\text{-}C_5H_5)Cl_2Y\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$] (**3**) [13]. Surprisingly, the analogous reaction of **2** with [K($C_5Me_5$)] led to the paramagnetic green complex [$K(\mu\text{-Cl})_3Y\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$] via one-electron reduction of the titanium metalloligand [14]. Herein we report a systematic study of the reactivity of the yttrium trichloride complex [$Cl_3Y\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$] (**2**) with a variety of main-group metal cyclopentadienyl derivatives.

## 2. Experimental

### *2.1. General Considerations.*

All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene and hexane were distilled from Na/K alloy just before use. Tetrahydrofuran was distilled from purple solutions of sodium benzophenone just prior to use. Pyridine was distilled from $CaH_2$ just before use. NMR solvents were dried with Na/K alloy ($C_6D_6$) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. $1 \times 10^{-3}$ Torr) and subsequently filled with inert gas. $[Tl(C_5H_5)]$ was purchased from Aldrich and used as received. $[M(C_5H_5)]$ (M = Li, Na) [15], $[M(C_5H_4SiMe_3)]$ (M = Li [16], K [17]), $[Li\{C_5H_3(SiMe_3)_2\}]$ [18], $[Mg(C_5H_5)_2]$ [19], and $[Li(C_9H_7)]$ [20] were prepared according to published procedures. The synthesis and characterization of complexes $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**) and $[(\eta^5\text{-}C_5H_5)Cl_2Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**3**) have been reported previously [13].

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using an FT-IR Perkin Elmer SPECTRUM 2000 spectrophotometer. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 and/or Mercury-300 spectrometers. Chemical shifts ($\delta$, ppm) in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to carbon of the solvent. Microanalyses (C, H, N) were performed in a Leco CHNSO-932 microanalyzer.

### *2.2. Synthesis*

*$[(\eta^5\text{-}C_5H_4SiMe_3)Cl_2Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**4**).* A 100 mL Schlenk tube was charged with **2** (0.30 g, 0.37 mmol), $[K(C_5H_4SiMe_3)]$ (0.059 g, 0.34 mmol), toluene

(20 mL) and tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature for 20 h to give an orange solution and a white powder. After filtration, the volatile components of the solution were removed under reduced pressure, and the resultant solid was washed with hexane (10 mL) to afford **4** as an orange solid (0.090 g, 29%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3319 (m), 3085 (w), 2945 (s), 2910 (vs), 1491 (w), 1429 (s), 1377 (vs), 1242 (s), 1183 (m), 1065 (w), 1039 (s), 1023 (m), 908 (s), 839 (vs), 738 (vs), 691 (vs), 653 (vs), 578 (m), 473 (w), 440 (w), 419 (m). $^1$H NMR ($\mathrm{C_6D_6}$, 20 ºC): $\delta$ 11.91 (s br., 3H; NH), 6.69 (m, 2H; $\mathrm{C_5\mathit{H}_4SiMe_3}$), 6.17 (m, 2H; $\mathrm{C_5\mathit{H}_4SiMe_3}$), 1.94 (s, 45H; $\mathrm{C_5Me_5}$), 0.65 (s, 9H, $\mathrm{C_5H_4Si\mathit{Me}_3}$). $^{13}$C{$^1$H} NMR ($\mathrm{C_6D_6}$, 20 ºC): $\delta$ 123.0 ($\mathrm{\mathit{C}_5H_4SiMe_3}$), 122.5 ($\mathrm{\mathit{C}_5Me_5}$), 120.0 ($\mathrm{\mathit{C}_5H_4SiMe_3}$), 112.7 ($\mathrm{\mathit{C}_5H_4SiMe_3}$), 12.7 ($\mathrm{C_5\mathit{Me}_5}$), 1.2 ($\mathrm{C_5H_4Si\mathit{Me}_3}$). Anal. Calcd for $\mathrm{C_{38}H_{61}Cl_2N_4SiTi_3Y}$ ($M_\mathrm{w}$ = 905.43): C 50.41, H 6.79, N 6.19. Found: C 50.36, H 6.90, N 5.94.

*$[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Y}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li}\{(\mu_3\text{-}\mathrm{NH})_3\mathrm{Ti}_3(\eta^5\text{-}\mathrm{C_5Me_5})_3(\mu_3\text{-}\mathrm{N})\}]$ (**5**).* A 100 mL Schlenk tube was charged with **2** (0.20 g, 0.25 mmol), [Li($\mathrm{C_5H_5}$)] (0.036 g, 0.50 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 20 h to give a yellow solution and a white powder. After filtration, the volatile components of the solution were removed under reduced pressure, and the resultant solid was washed with hexane (20 mL) to afford **5** as a yellow solid (0.18 g, 78%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3351 (m), 3088 (w), 2911 (vs), 2858 (s), 1492 (w), 1432 (m), 1377 (s), 1261 (w), 1067 (w), 1013 (s), 781 (vs), 732 (s), 657 (vs), 625 (s), 602 (m), 480 (w), 433 (m). $^1$H NMR ($\mathrm{CDCl_3}$, 20 ºC): $\delta$ 12.69 (s br., 3H; NH), 6.05 (s, 10H; $\mathrm{C_5H_5}$), 2.07 (s, 45H; $\mathrm{C_5Me_5}$). $^{13}$C{$^1$H} NMR ($\mathrm{CDCl_3}$, 20 ºC): $\delta$ 119.8 ($\mathrm{\mathit{C}_5Me_5}$), 111.5 ($\mathrm{\mathit{C}_5H_5}$), 11.7 ($\mathrm{C_5\mathit{Me}_5}$). Anal. Calcd for $\mathrm{C_{40}H_{58}Cl_2LiN_4Ti_3Y}$ ($M_\mathrm{w}$ = 905.28): C 53.07, H 6.46, N 6.19. Found: C 52.46, H 6.33, N 5.63.

*$[(\eta^5\text{-}C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)_2Li\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**6**).* In a fashion similar to the preparation of **5**, the treatment of **2** (0.30 g, 0.37 mmol) with $[Li(C_5H_4SiMe_3)]$ (0.11 g, 0.75 mmol) in toluene (25 mL) afforded **6** as a yellow solid (0.33 g, 85%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3353 (m), 3080 (w), 2950 (s), 2912 (s), 1490 (w), 1444 (m), 1378 (s), 1364 (m), 1243 (s), 1179 (m), 1064 (w), 1043 (s), 952 (w), 907 (m), 837 (vs), 775 (vs), 754 (vs), 659 (vs), 644 (s), 629 (s), 605 (m), 480 (w), 434 (m), 421 (m). $^1$H NMR ($CDCl_3$, 20 ºC): $\delta$ 12.68 (s br., 3H; NH), 6.25 (m, 4H; $C_5H_4SiMe_3$), 6.17 (m, 4H; $C_5H_4SiMe_3$), 2.06 (s, 45H; $C_5Me_5$), 0.18 (s, 18H; $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 120.6 ($C_5H_4SiMe_3$), 119.7 ($C_5Me_5$), 119.0 ($C_5H_4SiMe_3$), 114.4 ($C_5H_4SiMe_3$), 11.8 ($C_5Me_5$), 0.3 ($C_5H_4SiMe_3$). Anal. Calcd for $C_{46}H_{74}Cl_2LiN_4Si_2Ti_3Y$ ($M_w$ = 1049.64): C 52.64, H 7.10, N 5.34. Found: C 52.68, H 7.11, N 5.29.

*$[\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Y(\mu\text{-}Cl)_2Li\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**7**).* In a fashion similar to the preparation of **5**, the treatment of **2** (0.20 g, 0.25 mmol) with $[Li\{C_5H_3(SiMe_3)_2\}]$ (0.10 g, 0.50 mmol) in toluene (25 mL) afforded **7** as a yellow solid (0.14 g, 47%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3356 (s), 3051 (w), 2950 (vs), 2910 (vs), 1490 (w), 1440 (s), 1378 (s), 1317 (w), 1241 (s), 1212 (w), 1080 (s), 1026 (w), 926 (s), 835 (vs), 781 (s), 754 (vs), 660 (vs), 644 (s), 626 (m), 604 (m), 478 (s), 434 (s). $^1$H NMR ($CDCl_3$, 20 ºC): $\delta$ 12.73 (s br., 3H; NH), 6.34 (m, 4H; $C_5H_3(SiMe_3)_2$), 6.22 (m, 2H; $C_5H_3(SiMe_3)_2$), 2.06 (s, 45H; $C_5Me_5$), 0.18 (s, 36H; $C_5H_3(SiMe_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 128.0 ($C_5H_3(SiMe_3)_2$), 125.4 ($C_5H_3(SiMe_3)_2$), 119.9 ($C_5Me_5$), 119.4 ($C_5H_3(SiMe_3)_2$), 11.8 ($C_5Me_5$), 0.8 ($C_5H_3(SiMe_3)_2$). Anal. Calcd for $C_{52}H_{90}Cl_2LiN_4Si_4Ti_3Y$ ($M_w$ = 1194.01): C 52.31, H 7.60, N 4.69. Found: C 52.20, H 7.37, N 3.99.

*$[(C_5H_5)_2Y(\mu\text{-}Cl)_2Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**8**).* In a fashion similar to the preparation of **5**, the treatment of **2** (0.30 g, 0.37 mmol) with $[Tl(C_5H_5)]$ (0.20 g, 0.75 mmol) in toluene (30 mL) afforded **8** as a yellow solid (0.30 g, 73%). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ 3323 (w), 3072 (w), 2909 (s), 2857 (m), 1493 (w), 1429 (m), 1377 (s), 1066 (w), 1013 (m), 765 (vs), 734 (vs), 663 (vs), 528 (w), 476 (w), 427 (m). $^1H$ NMR ($CDCl_3$, 20 ºC): $\delta$ 13.01 (s br., 3H; NH), 6.11 (s, 10H; $C_5H_5$), 2.06 (s, 45H; $C_5Me_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 120.3 ($\mathit{C}_5Me_5$), 111.2 ($\mathit{C}_5H_5$), 11.9 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{40}H_{58}Cl_2N_4Ti_3TlY$ ($M_w$ = 1102.72): C 43.57, H 5.30, N 5.08. Found: C 43.70, H 5.36, N 4.44.

*$[(\mu\text{-}Cl)_3Mg_2\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2][\{Y(C_5H_5)_2Cl\}_2(\mu\text{-}Cl)]$* (**9**). A 100 mL Schlenk tube was charged with **2** (0.20 g, 0.25 mmol), $[Mg(C_5H_5)_2]$ (0.038 g, 0.25 mmol), and toluene (15 mL). The reaction mixture was stirred at room temperature for 3 min to give an orange solution and a white powder. After filtration, the solution was allowed to stand at ambient temperature without any stirring for 24 h to afford yellow crystals of **9**$\cdot C_7H_8$ (0.12 g, 48%). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ 3345 (m), 3091 (w), 2910 (s), 2858 (m), 1604 (w), 1488 (w), 1426 (m), 1378 (m), 1066 (w), 1013 (s), 771 (vs), 686 (vs), 655 (vs), 480 (w), 440 (w), 408 (w). $^1H$ NMR ($CDCl_3$, 20 ºC): $\delta$ 11.56 (s br., 6H; NH), 6.23 (s, 20H; $C_5H_5$), 2.07 (s, 90H; $C_5Me_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 122.9 ($\mathit{C}_5Me_5$), 111.7 ($\mathit{C}_5H_5$), 12.1 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{87}H_{124}Cl_6Mg_2N_8Ti_6Y_2$ ($M_w$ = 2008.33): C 52.03, H 6.22, N 5.58. Found: C 51.63, H 6.04, N 5.05.

*$[Li(\mu\text{-}Cl)_3Y\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**).* A 100 mL Schlenk tube was charged with **2** (0.30 g, 0.37 mmol), $[Li(C_9H_7)]$ (0.046 g, 0.37 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 2 days to give a red solid and a red solution. The solid was isolated by filtration onto a glass frit and washed with toluene

(10 mL) to afford **10** as a red solid (0.19 g, 63%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3324 (m), 3307 (m), 2908 (vs), 2858 (s), 2725 (w), 1491 (m), 1429 (s), 1377 (s), 1066 (w), 1025 (m), 745 (vs), 723 (vs), 694 (vs), 655 (vs), 616 (vs), 536 (m), 475 (m), 449 (m), 424 (m). $^1$H NMR ($CDCl_3$, 20 ºC): $\delta$ 12.37 (s br., 2H; NH), 2.07 (s, 30H; $C_5Me_5$), 2.06 (s, 15H; $C_5Me_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 121.4 ($\mathit{C}_5Me_5$), 120.1 ($\mathit{C}_5Me_5$), 12.1 ($C_5\mathit{Me}_5$), 11.9 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{30}H_{47}Cl_3LiN_4Ti_3Y$ ($M_w$ = 809.54): C 44.51, H 5.85, N 6.92. Found: C 43.67, H 6.02, N 6.98.

*[$Cl_2(py)_2Y\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**11**).* A 100 mL Schlenk tube was charged with **10** (0.20 g, 0.25 mmol) and 5 mL of pyridine. The resultant red solution was concentrated under vacuum to the half of the volume and filtered. After cooling at –35 ºC for 2 days, deep red crystals of **11**·$C_5H_5N$ suitable for a single crystal X-ray diffraction determination were grown. The crystals were dried under dynamic vacuum for 6 h and characterized as **11** (0.11 g, 48%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3339 (m), 2906 (vs), 2856 (s), 1601 (m), 1487 (m), 1443 (s), 1375 (m), 1221 (w), 1149 (w), 1073 (w), 1036 (m), 1005 (w), 772 (s), 725 (vs), 699 (vs), 662 (vs), 616 (s), 532 (w), 477 (w), 447 (w), 426 (m). $^1$H NMR ($CDCl_3$, 20 ºC): $\delta$ 12.55 (s br., 2H; NH), 8.75 (m, 4H; *o*-$C_5H_5N$), 7.73 (m, 2H; *p*-$C_5H_5N$), 7.32 (m, 4H; *m*-$C_5H_5N$), 2.10 (s, 15H; $C_5Me_5$), 1.99 (s, 30H; $C_5Me_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): $\delta$ 150.3 (*o*-$\mathit{C}_5H_5N$), 137.0 (*p*-$\mathit{C}_5H_5N$), 123.9 (*m*-$\mathit{C}_5H_5N$), 121.0 ($\mathit{C}_5Me_5$), 119.2 ($\mathit{C}_5Me_5$), 12.0 ($C_5\mathit{Me}_5$), 11.7 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{40}H_{57}Cl_2N_6Ti_3Y$ ($M_w$ = 925.33): C 51.92, H 6.21, N 9.08. Found: C 51.84, H 5.86, N 8.38.

### *2.3. X-ray crystallography*

Yellow crystals of complex **6** were obtained from a hexane solution at –35 ºC. Yellow crystals of **9**·$C_7H_8$ were obtained from toluene solutions at room temperature as described above in several independent experiments. Deep red crystals of **11**·$C_5H_5N$ were grown in pyridine at –35 ºC as described above. The crystals were removed from the Schlenk tubes and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, attached to a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for complexes **6** and **11** are presented in Table S1 of the Supplementary Material.

The structures were solved, using the WINGX package [21], by intrinsic phasing methods (SHELXT) [22], and refined by least-squares against $F^2$ (SHELXL-97) [23]. Compound **11** crystallized with a molecule of pyridine. In the crystallographic studies of **6** and **11**, all non-hydrogen atoms were anisotropically refined. All the hydrogen atoms were positioned geometrically and refined by using a riding model, except those of the imido groups (H(12), H(13) and H(23) in **6**; H(12) and H(23) in **11**), which were located in the difference Fourier map and refined isotropically. Moreover, DFIX constraints were employed for the lengths N(12)-H(12) in both compounds. Additionally, the atoms of crystallization pyridine molecule in **11** (N(100), C(101), C(102), C(103), C(104) and C(105)) were restrained with DELU instructions.

Compound **9** crystallized with a molecule of toluene in the *Pn* space group with cell parameters of $a$ = 11.451(1) Å, $b$ = 18.564(4) Å, $c$ = 23.236(6) Å and $\beta$ = 95.13(1)º. The poor quality of the crystals precluded a complete X-ray structure determination. Chloride groups bridging the magnesium atoms presented disorder in different sites, so it is not possible to describe the geometry about these atoms. Simultaneously, some carbon atoms of the pentamethylcyclopentadienyl and cyclopentadienyl ligands showed severe disorder. Attempts to model these rings failed, since the thermal parameters of the carbon atoms do not refine properly.

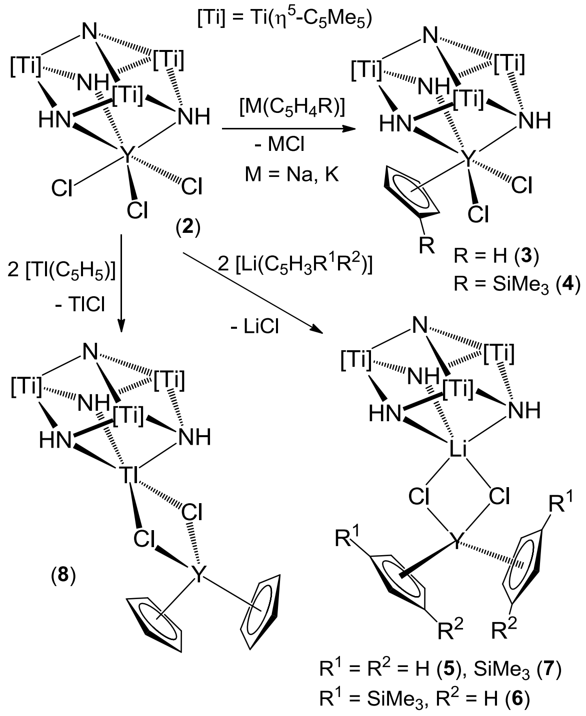
CCDC 1907451-1907452 contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

## 3. Results and discussion

Treatment of [$Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**2**) with one equivalent of sodium or potassium cyclopentadienide reagents [$M(C_5H_4R)$] (M = Na, R = H; M = K, R = $SiMe_3$) in a 4:1 toluene-tetrahydrofuran mixture at room temperature afforded the monocyclopentadienyl complexes [$(\eta^5\text{-}C_5H_4R)Cl_2Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (R = H (**3**), $SiMe_3$ (**4**)) (Scheme 1). Compounds **3** and **4** were isolated as air-sensitive orange or yellow solids in 48 and 29% yield, respectively, which are slightly soluble in hexane but exhibit a good solubility in toluene and chloroform. We have previously reported the synthesis of complex **3** by this route or through the treatment of **1** with [$Y(\eta^5\text{-}C_5H_5)Cl_2(thf)_3$] [13]. The reaction of **2** with two equivalents of [$Na(C_5H_5)$] leads to a mixture of complex [$\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**1**) and the adduct [$(\eta^5\text{-}C_5H_5)_3Y(\mu\text{-}Cl)(\eta^5\text{-}C_5H_5)ClY\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$]. The latter compound was isolated as an orange solid in 18% yield in the treatment of **1** with [$\{Y(\eta^5\text{-}C_5H_5)_2Cl\}_2$] [13]. It appears that a putative bis(cyclopentadienyl) derivative [$(\eta^5\text{-}C_5H_5)_2ClY\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] could be too crowded and decomposes in solution.

Noteworthy, the reaction of compound **2** with lithium [$Li(C_5H_3R^1R^2)$] or thallium [$Tl(C_5H_5)$] reagents in a 1:1 ratio does not produce the expected monocyclopentadienyl derivatives [$(\eta^5\text{-}C_5H_3R^1R^2)Cl_2Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$]. Instead, complexes [$(\eta^5\text{-}C_5H_3R^1R^2)_2Y(\mu\text{-}Cl)_2M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (M = Li, $R^1 = R^2$ = H (**5**), $R^1$ = $SiMe_3$, $R^2$ = H (**6**), $R^1 = R^2$ = $SiMe_3$ (**7**); M = Tl, $R^1 = R^2$ = H (**8**)) were isolated in those reactions (Scheme 1). Compounds **5-8** were obtained as yellow solids in good yields (47-85%) in the treatment of **2** with two equivalents of [$M(C_5H_3R^1R^2)$] (M = Li, Tl) reagents in toluene at room temperature. Most likely, the reaction of **2** with one equivalent of

$[M(C_5H_3R^1R^2)]$ leads to MCl and $[(\eta^5\text{-}C_5H_3R^1R^2)Cl_2Y\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$. However, the second metathesis process on these monocyclopentadienyl intermediates with one equivalent of $[M(C_5H_3R^1R^2)]$ (M = Li, Tl) produces the displacement of the bulky $[Y(\eta^5\text{-}C_5H_3R^1R^2)_2Cl]$ moieties bonded to the titanium metalloligand by the MCl generated in this step. Indeed, treatment of complex **3** with $[Li(C_5H_5)]$ (1 equiv) leads to the clean formation of compound **5**. Remarkable, the $[Y(\eta^5\text{-}C_5H_3R^1R^2)_2Cl]$ fragments of complexes **5-8** remain bonded to the $[MTi_3N_4]$ cubane-type cores through bridging-chloride groups, which are well-documented for these elements [24].



**Scheme 1.** Reactions of **2** with $[M(C_5H_3R^1R^2)]$ reagents.

Complexes **3-8** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for **6**. IR spectra (KBr) of cyclopentadienyl derivatives **3-8** show one $\nu_{NH}$ vibration, between 3356 and 3319 $cm^{-1}$, in a similar range to the value determined for **1** (3352 $cm^{-1}$) [2]. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra in chloroform-$d_1$ at room temperature of complexes **3-8** reveal resonance signals for equivalent NH, $\eta^5$-$C_5Me_5$, and $\eta^5$-$C_5H_3R^1R^2$ groups in the expected proportions. The NH resonance signals in the $^1$H NMR spectra ($\delta$ = 13.01–11.92) are shifted to higher field than that found in **1** ($\delta$ = 13.40), whereas the resonance for the *ipso* carbon of the $\eta^5$-$C_5Me_5$ groups ($\delta$ = 124.0–119.7) in the $^{13}$C NMR spectra are slightly shifted downfield with respect to that found in **1** ($\delta$ = 117.1) [2]. We have noted analogous shifts in many adducts of **1** with a tridentate chelate coordination of the NH groups to the metal centers [3]. The equivalence of the three $\eta^5$-$C_5Me_5$ and NH ligands in complexes **3-8** is consistent with the existence of low-energy exchange processes in solution, similar to those studied in detail for other adducts of **1** such as $[(Me_3C_6H_2N)Cl_2Ti\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [25].

The X-ray crystal structure of **6** is presented in Figure 1, and selected distances and angles are given in Table 1. The molecular structure shows a distorted $[LiTi_3N_4]$ cubane-type core with an $[Y(\eta^5\text{-}C_5H_4SiMe_3)_2]$ fragment linked to lithium via two $\mu$-Cl ligands. Thus, lithium is bonded to two chlorine atoms and three imido groups of the titanium metalloligand. The five-coordinate geometry about the lithium atom may be described as intermediate between square pyramidal and trigonal bipyramidal ($\tau_5$ = 0.52) [26]. The Li–N (averaged 2.302(9) Å) and Li–Cl (2.474(10) and 2.556(10) Å) bond lengths in complex **6** compare well with those determined in the crystal structures of other complexes with $[Li(\mu\text{-}Cl)_2M]$ moieties bonded to other tridentate nitrogen-based ligands [27]. The $[Li(\mu\text{-}Cl)_2Y]$ unit in **6** is planar and exhibits angles close to 90º. If centroids ($Cp'_{ct}$) of the $\eta^5$-$C_5H_4SiMe_3$ ligands are considered, the coordination sphere about the yttrium atom may be described as distorted tetrahedral. The Y–Cl and Y–$Cp'_{ct}$ distances of averaged 2.633(8) and 2.390(1) Å in compound **6** are also comparable to those found in other yttrium bis(cyclopentadienyl) complexes with [Li($\mu$-Cl)$_2$Y] moieties [28]. Within the tridentate titanium metalloligand, the titanium-nitrogen bond lengths and the titanium-nitrogen-titanium angles in complex **6** compare well with those determined for **1** [1].

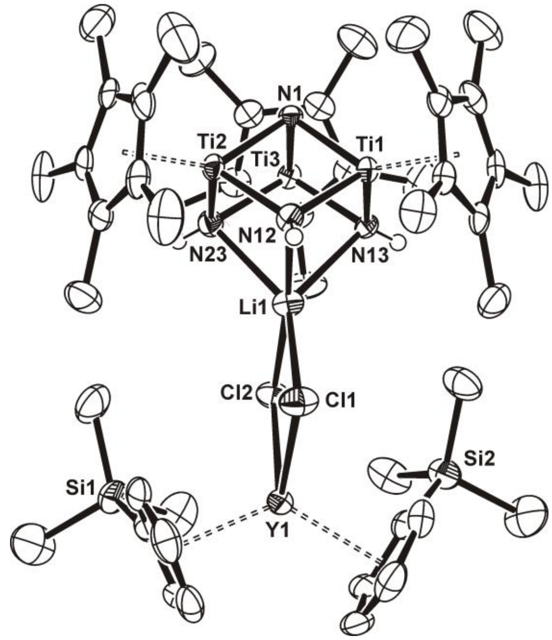


**Figure 1**. Perspective view of complex **6** with thermal ellipsoids at the 50% probability level. Hydrogen atoms in $C_5Me_5$ and $C_5H_4SiMe_3$ ligands are omitted for clarity.

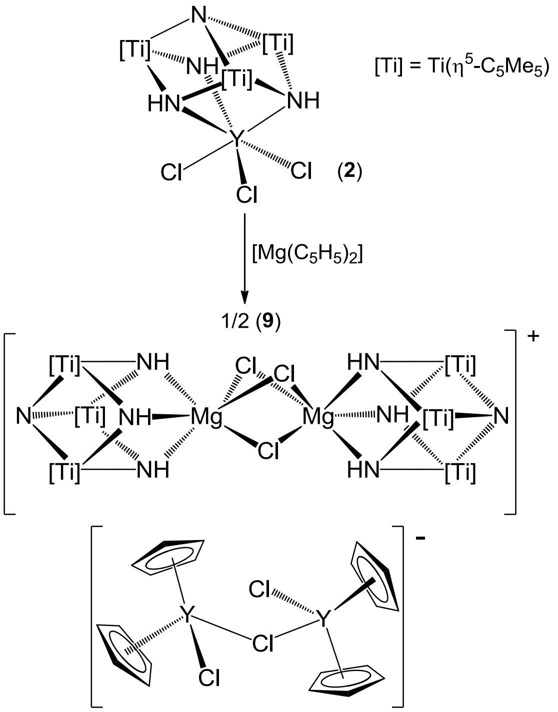
**Table 1.** Selected lengths (Å) and angles (º) for **6**.

| | | | |
|---|---|---|---|
| Li(1)–N(12) | 2.306(11) | Li(1)–N(13) | 2.292(11) |
| Li(1)–N(23) | 2.308(11) | Li(1)–Cl(1) | 2.556(10) |
| Li(1)–Cl(2) | 2.474(10) | Y(1)–Cl(1) | 2.639(2) |
| Y(1)–Cl(2) | 2.627(2) | Y(1)–Cp´$_{ct}$[a] | 2.390(1) |
| Ti–N(1)[a] | 1.941(3) | Ti–N$_{imido}$[a] | 1.946(8) |
| Ti···Ti[a] | 2.846(4) | Ti···Li(1)[a] | 2.986(5) |
| N(12)–Li(1)–N(13) | 81.1(3) | N(12)–Li(1)–N(23) | 80.9(4) |
| N(13)–Li(1)–N(23) | 81.1(4) | N(12)–Li(1)–Cl(1) | 86.6(4) |
| N(12)–Li(1)–Cl(2) | 172.6(5) | N(13)–Li(1)–Cl(1) | 132.7(5) |
| N(13)–Li(1)–Cl(2) | 106.2(4) | N(23)–Li(1)–Cl(1) | 141.5(5) |
| N(23)–Li(1)–Cl(2) | 98.6(4) | Cl(1)–Li(1)–Cl(2) | 89.3(3) |
| Li(1)–Cl(1)–Y(1) | 92.1(2) | Li(1)–Cl(2)–Y(1) | 94.3(2) |
| Cl(1)–Y(1)–Cl(2) | 84.3(1) | Cp´$_{ct}$–Y(1)–Cp´$_{ct}$ | 126.2 |
| Cl–Y(1)–Cp´$_{ct}$[a] | 109(2) | N$_{imido}$–Ti–N(1)[a] | 85.8(3) |
| N$_{imido}$–Ti–N$_{imido}$[a] | 100.5(3) | Ti–N(1)–Ti[a] | 94.3(2) |
| Ti–N$_{imido}$–Ti[a] | 94.0(6) | Ti–N$_{imido}$–Li(1)[a] | 88.9(3) |

[a] Averaged values. Cp´$_{ct}$ = centroid of the $\eta^5$-$C_5H_4SiMe_3$ ring

While presumably the lithium atoms in complexes **5** and **7** exhibit a five-coordinate geometry analogous to that determined for compound **6**, the thallium atom in complex **8** has an additional lone pair of electrons in the coordination sphere. Most likely, this lone pair is stereochemically active, in a fashion similar to that found in the crystal structure of compounds $[(\eta^5\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ and $[(\eta^5\text{-}C_5H_5)Tl(\mu\text{-}C_5H_5)Tl\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ [29], and therefore we propose a square pyramidal geometry for the thallium atom in complex **8** (Scheme 1).

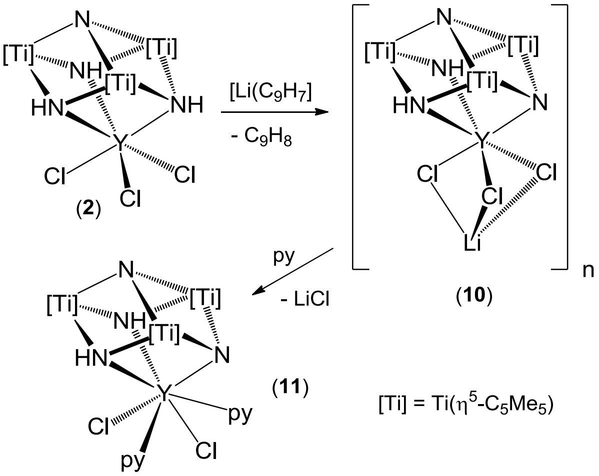
The treatment of **2** with the magnesium bis(cyclopentadienyl) derivative $[Mg(C_5H_5)_2]$ (1 equivalent) in toluene at room temperature led to the precipitation of the ionic compound $[(\mu\text{-}Cl)_3Mg_2\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2][\{Y(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}Cl)]$ (**9**) (Scheme 2). Complex **9** was also obtained in the reaction of **3** with $[Mg(C_5H_5)_2]$ in a 2:1 ratio, suggesting that formation of **3** is the first step in the reaction of **2** and the magnesium reagent. Compound **9**$\cdot C_7H_8$ was isolated in 48% yield as yellow crystals which are only soluble in chloroform. The $^1H$ NMR spectrum of **9** in chloroform-$d_1$ at room temperature reveal singlet resonances for equivalent NH and $\eta^5\text{-}C_5Me_5$ ligands in the double-cubane cation. Similarly, the $\eta^5\text{-}C_5H_5$ ligands of the $[\{Y(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}Cl)]^-$ anionic fragment are also equivalents and give rise to single resonances at $\delta = 6.23$ and $\delta = 111.7$ in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra, respectively.



**Scheme 2**. Reaction of **2** with [Mg($C_5H_5$)$_2$] to give compound **9**.

The crystallographic analysis of several independent samples of **9**·$C_7H_8$ showed well-separated double-cubane magnesium-titanium cations [(μ-Cl)$_3$Mg$_2${(μ$_3$-NH)$_3$Ti$_3$(η$^5$-C$_5$Me$_5$)$_3$(μ$_3$-N)}$_2$]$^+$ and bis(cyclopentadienyl)yttrium anions [{Y(η$^5$-C$_5$H$_5$)$_2$Cl}$_2$(μ-Cl)]$^-$. However, the poor quality of the crystals precluded a complete X-ray structure determination. The cation contains two [MgTi$_3$N$_4$] cubane-type units connected through three bridging chloride ligands between the magnesium atoms (Figure S1 of the Supplementary Material). The [Mg(μ-Cl)$_3$Mg] moiety between the two cubane-type cores of **9** is similar to those found in complexes containing the cation [(thf)$_3$Mg(μ-Cl)$_3$Mg(thf)$_3$]$^+$ [30]. In addition, each magnesium atom is bonded to three NH imido ligands of the metalloligand to give a six-coordinate geometry. On the other hand, the anionic fragment of **9** shows two [Y(η$^5$-C$_5$H$_5$)$_2$Cl] moieties linked by a bridging chloride ligand (Figure S2). We have found no reference in the literature for this anionic yttrium anion, but an analogous samarium complex [{Sm($\eta^5$-$C_5Me_5$)$_2$Cl}$_2$($\mu$-Cl)]$^-$ has been reported [31].

In contrast to the metathesis reaction of chloride ligands observed with main-group cyclopentadienyl reagents, the treatment of the yttrium trichloride complex **2** with one equivalent of the lithium indenyl reagent [Li($C_9H_7$)] in toluene at room temperature afforded the precipitation of [Li($\mu$-Cl)$_3$Y{($\mu_3$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**10**) as a deep red solid (Scheme 3). The reaction in benzene-$d_6$ was monitored by $^1$H NMR spectroscopy and the spectra of the resultant red solution showed resonance signals for indene $C_9H_8$. The deprotonation of a NH ligand in complex **2** could be related with the increased steric bulk and lower acidity (p$K_a$ = 20.1) of indene when compared with cyclopentadiene (p$K_a$ = 18.0) [32].



**Scheme 3**. Reactions of **1** with [Li($C_9H_7$)].

Compound **10** was isolated in 63% yield as a red solid which is not soluble in hydrocarbon solvents suggesting a polymeric structure. However, compound **10** readily dissolves in pyridine to give a red solution from which, upon cooling at –35 ºC, deep red crystals of the lithium-free derivative [Cl$_2$(py)$_2$Y{($\mu_3$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}]

(**11**) were grown in 48% yield (Scheme 3). Most likely, the lithium chloride retained in the structure of **10** could forms an adduct [LiCl(py)$_n$] soluble in the pyridine solvent [33]. Deep red crystals of **11** bear one pyridine solvent molecule per cubane-type unit according to an X-ray crystal structure determination, but these crystallization molecules are easily lost under dynamic vacuum according to $^1$H NMR spectroscopy and elemental analyses. The molecular structure of **11** shows an [$YTi_3N_4$] cubane-type core with the three basal nitrogen atoms of the metalloligand coordinated to the yttrium atom (Figure 2 and Table 2). The coordination sphere of yttrium is completed by two chloride and two pyridine ligands to give a seven-coordinate geometry about yttrium which is best described as distorted capped trigonal prismatic (Figure 3). Thus, one of the triangular face of the prism contains the three nitrogen atoms of the metalloligand, the second one includes the Cl(2) atom and the nitrogen atoms of the pyridine ligands, and the Cl(1) atom is capping one rectangular face of the prism. In that arrangement, the pyridine molecules minimize the steric repulsion with the bulky pentamethylcyclopentadienyl ligands. The Y(1)–N(13) bond length of 2.402(3) Å is shorter than those with the other nitrogen atoms (Y(1)–N(12) and Y(1)-N(23) of 2.522(4) and 2.518(4) Å, respectively) in accord with the deprotonation of one of the NH groups in the metalloligand. The Ti–N(13) bond lengths (1.886(3) and 1.890(3) Å) are also shorter than those for Ti–N(23) and Ti–N(12) (1.946(4)–1.973(4) Å) which is consistent with a higher bond order between the deprotonated nitrogen atom N(13) and the contiguous titanium centers. The Y–Cl and Y–N(py) bond lengths in **11** of averaged 2.62(1) and 2.614(6) Å, respectively, are slightly longer than found in the yttrium tris(pyrazolyl)borate derivative [$YCl_2\{HB(3,5\text{-}Me_2pz)_3\}$(phen)] (averaged Y–Cl and Y–N(phen) are 2.600(2) and 2.544(6) Å, respectively) [34], and the adduct [$YCl_3(py)_4$] (averaged Y–Cl and Y–N(py) are 2.61(2) and 2.55(3) Å) [35].

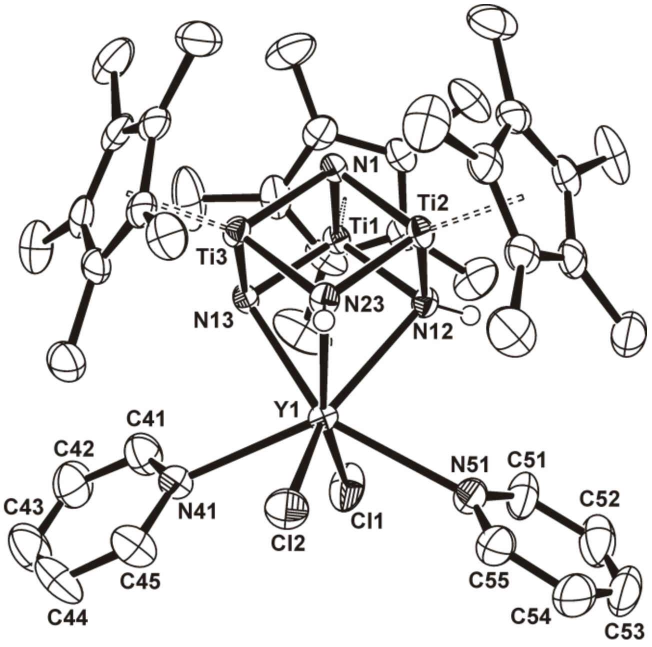


**Figure 2.** Perspective view of complex **11** with thermal ellipsoids at the 50% probability level. Methyl and aromatic hydrogen atoms are omitted for clarity.

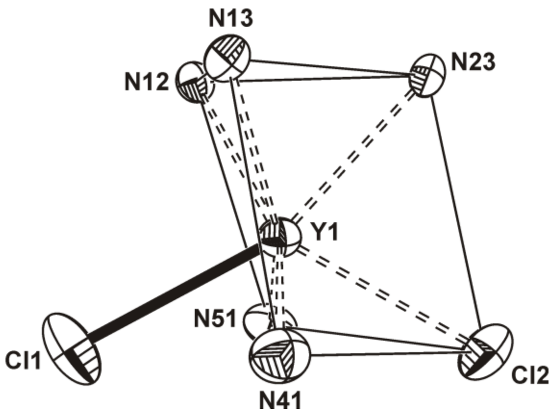


**Figure 3.** Schematic representation of the seven-coordinate geometry about the yttrium center in **11**.

**Table 2.** Selected lengths (Å) and angles (º) for **11**.

| | | | |
|---|---:|---|---:|
| Y(1)–N(12) | 2.522(4) | Y(1)–N(13) | 2.402(3) |
| Y(1)–N(23) | 2.518(4) | Y(1)–Cl(1) | 2.614(1) |
| Y(1)–Cl(2) | 2.631(1) | Y(1)–N(41) | 2.619(4) |
| Y(1)–N(51) | 2.610(4) | Ti(1)–N(12) | 1.955(3) |
| Ti(1)–N(13) | 1.890(3) | Ti(2)–N(12) | 1.946(4) |
| Ti(2)–N(23) | 1.948(4) | Ti(3)–N(13) | 1.886(3) |
| Ti(3)–N(23) | 1.973(4) | Ti–N(1)[a] | 1.92(3) |
| Ti(1)···Ti(2) | 2.819(1) | Ti(1)···Ti(3) | 2.769(1) |
| Ti(2)···Ti(3) | 2.824(1) | Ti···Y(1)[a] | 3.29(7) |
| N(12)–Y(1)–N(13) | 71.2(1) | N(12)–Y(1)–N(23) | 69.7(1) |
| N(13)–Y(1)–N(23) | 71.3(1) | Cl(1)–Y(1)–Cl(2) | 122.8(1) |
| Cl(1)–Y(1)–N(41) | 76.4(1) | Cl(1)–Y(1)–N(51) | 78.0(1) |
| Cl(2)–Y(1)–N(41) | 78.6(1) | Cl(2)–Y(1)–N(51) | 79.5(1) |
| N–Ti–N(1)[a] | 86.7(9) | N–Ti–N[a] | 95.9(5) |
| Ti–N(1)–Ti[a] | 94(2) | Ti–N–Ti[a] | 93(1) |
| Ti–N–Y(1)[a] | 96(3) | | |

[a] Averaged values.

The crystal structure of **11** is very similar to that of the paramagnetic green complex [Cl$_2$(py)$_2$Y{(μ$_3$-NH)$_3$Ti$_3$(η$^5$-C$_5$Me$_5$)$_3$(μ$_3$-N)}] [14]. The latter compound contains one electron delocalized among the three titanium atoms according to density functional theory (DFT) calculations and its $^1$H NMR spectrum in pyridine-d$_5$ reveals one broad resonance at $\delta = 10.2$ for the C$_5$Me$_5$ groups. In contrast, diamagnetic complexes **10** and **11** are very soluble in chloroform-d$_1$, although they react very slowly with this solvent to regenerate compound **2**, and could be characterized by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy. The $^1$H NMR spectra of **10** and **11** display one broad resonance signal for the NH ligands and two sharp singlet resonances for the η$^5$-C$_5$Me$_5$ groups in 2:1 or 1:2 ratio, respectively. In addition, the $^1$H NMR spectrum of **11** shows resonance signals for two equivalents pyridine ligands, suggesting the existence of an exchange process similar to that reported for complexes [Y{HB(pz)$_3$}(thf)$_2$X$_2$] (X = Cl, Br) [36].

## 4. Conclusions

In this work, we have presented a study of the reactivity of yttrium trichloride complex $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**2**) with a variety of main-group metal cyclopentadienyl reagents. While simple metathesis of one chloride ligand in **2** by one $\eta^5$-$C_5H_4R$ group is feasible with $[Na(C_5H_5)]$ or $[K(C_5H_4SiMe_3)]$, the steric congestion of a second cyclopentadienyl group bonded to yttrium causes a significant structural reorganization in the resultant compound. Thus, treatment of **2** with two equivalents of sodium cyclopentadienide leads to the release of the azametalloligand $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) and precipitation of the adduct $[(\eta^5\text{-}C_5H_5)_3Y(\mu\text{-}Cl)(\eta^5\text{-}C_5H_5)ClY\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$. Similarly, the treatment of **2** with lithium and thallium cyclopentadienyl reagents affords derivatives $[(\eta^5\text{-}C_5H_5)_2Y(\mu\text{-}Cl)_2M\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Li, Tl) via displacement of the $[Y(\eta^5\text{-}C_5H_5)_2Cl]$ fragment by the metal chloride generated *in situ*. The analogous reaction of **2** with bis(cyclopentadienyl)magnesium leads to a compound with well-separated yttrium anions $[\{Y(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}Cl)]^-$ and double-cubane magnesium-titanium cations $[(\mu\text{-}Cl)_3Mg_2\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]^+$. In contrast, the more sterically demanding and basic lithium indenyl reacts with **2** via deprotonation of one NH group to give indene and a lithium-containing derivative $[Li(\mu\text{-}Cl)_3Y\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.

## Conflict of interest

The authors declare no competing financial interest.

## Acknowledgments

We are also grateful to the Spanish MINECO (CTQ2013-44625-R) and Universidad de Alcalá (CCG2018/EXP-008) for financial support of this research. J.C. thanks the MEC for a doctoral fellowship.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.jorganchem.2019.xx.xx. These data include experimental crystallographic data of compounds **6** and **11**, simplified views of the ionic fragments of complex **9**, and $^1$H and $^{13}$C{$^1$H} NMR spectra of compounds **4-11**.

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