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Homo and heteropolymetallic Group 4 molecular nitrides

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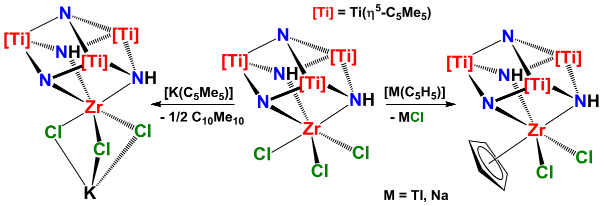
Table of Contents Entry:

The trichloride zirconium complex reacts with $[M(C_5H_5)_x]$ via metathesis of chloride ligands while $[K(C_5Me_5)]$ produces the one-electron reduction of the titanium nitrido metalloligand.



Abstract:

Treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**) with zirconium or hafnium tetrachloride adducts [MCl_4(thf)$_2$] affords complexes [Cl_3M{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (M = Zr (**2**), Hf (**3**)). Titanium chloride complexes [Cl_2Ti{(μ_3-N)$_2$(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (**4**) and [(Me_2NH)ClTi{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**5**) are obtained by reaction of **1** with [$TiCl_{4-x}$(NMe_2)$_x$] (x = 2, 3). The dimethylamine ligand in **5** is displaced by pyridine to give the analogue complex [(py)$_2$ClTi{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**6**). Treatment of the titanium chloride complexes **4** and **5** with sodium cyclopentadienide or lithium bis(trimethylsilyl)amide reagents leads to the cube-type nitrido derivatives [RTi{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (R = η^5-C_5H_5 (**7**), N($SiMe_3$)$_2$ (**8**)). The reaction of the zirconium trichloride complex **2** with [Tl(C_5H_5)] yields exclusively the dichloride-monocyclopentadienyl derivative [(η^5-C_5H_5)Cl_2Zr{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**9**). However, the treatment of **2** with excess [Na(C_5H_5)] produces further chloride replacement in **9** and subsequent cyclopentadiene elimination to give [(η^5-C_5H_5)Zr{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**10**) via intermediates [(η^5-C_5H_5)$_2$ClZr{(μ_3-N)Ti_3(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (**11**) and [(η^5-C_5H_5)ClZr{(μ_3-N)$_2$(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (**12**). Treatment of **2** or **9** with [Mg(C_5H_5)$_2$] leads to the magnesium derivative [(η^5-C_5H_5)Mg(μ-Cl)$_2$(η^5-C_5H_5)Zr{(μ_4-N)(μ_3-N)(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (**13**), which can be visualized as the result of the incorporation of one [Mg(η^5-C_5H_5)Cl] moiety to complex **12**. In contrast to the metathesis process with [M(C_5H_5)$_x$] derivatives and subsequent C_5H_6 eliminations, the reaction of **2** with potassium pentamethylcyclopentadienide in toluene produces the paramagnetic derivative [K(μ-Cl)$_3$Zr{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**14**) and $C_{10}Me_{10}$. Complex **14** reacts with one equivalent of 18-crown-6 or cryptand-222 to give the molecular complex $[(18\text{-crown-6})\mathrm{K}(\mu\text{-Cl})_3\mathrm{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\mathrm{Ti}_3(\eta^5\text{-C}_5\mathrm{Me}_5)_3(\mu_3\text{-N})\}]$ (**15**) or the ion pair $[\mathrm{K}(\text{crypt-222})][\mathrm{Cl}_3\mathrm{Zr}\{(\mu_3\text{-N})(\mu_3\text{-NH})_2\mathrm{Ti}_3(\eta^5\text{-C}_5\mathrm{Me}_5)_3(\mu_3\text{-N})\}]$ (**16**). The X-ray crystal structures of **2**, **8**, **13** and **15** have been determined.

Introduction

Transition-metal nitrido complexes constitute a large family of coordination compounds with a wide structural variety and diverse reactivity patterns.[1,2] By far the most studied are complexes of the mid transition-metals (Groups 6, 7 and 8) in high oxidation states, which are typically mononuclear and exhibit a terminal nitrido functionality [M]≡N.[1,3] In early transition-metal (Groups 4 and 5) systems, structurally documented mononuclear nitrido complexes are limited to a few Group 5 complexes, specifically vanadium[4] and niobium[5] derivatives, whereas neutral mononuclear Group 4 nitrido complexes are unknown although a number of ionic titanium compounds containing the Ti≡N moiety have been recently developed. Lancaster and co-workers have prepared a series of anionic titanium complexes with the terminal nitrido functionality protected by a borane group [Ti≡N-B(C_6F_5)$_3$].[6] Mindiola and co-workers have described that deprotonation of the parent titanium imido derivative [Ti(^{tBu}nacnac)(Ntolyl$_2$)(=NH)] (^{tBu}nacnac$^-$ = [ArNC*t*Bu]$_2$CH) with [K(CH_2Ph)] gave a dinuclear nitrido salt [{Ti(^{tBu}nacnac)(Ntolyl$_2$)(μ_3-N)K}$_2$].[7] Finally, by using more robust amido-phosphane PN$^-$ ancillary ligands, the latter research group have reported that treatment of the analogous dinuclear salt [{Ti(PN)$_2$(μ_3-N)K(OEt$_2$)}$_2$] with 18-crown-6 or crypt-222 yielded mononuclear titanium nitrido complexes, including the first discrete salt of titanium having a terminally bound nitrido ligand [K(crypt-222)][Ti(PN)$_2$(≡N)].[8]

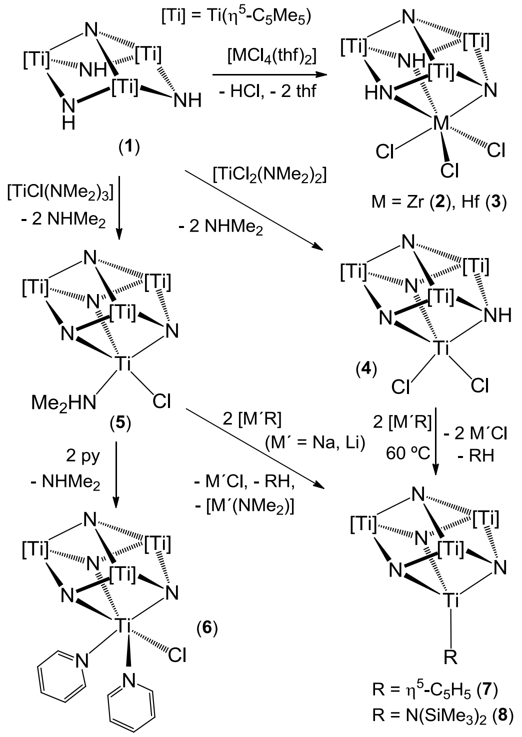
In contrast to those rare examples, the majority of early transition-metal complexes are polynuclear with the nitrido ligands bridging two or more metal centers.[2] Molecular species with μ_n-nitrido groups are relevant to the bridging modes of the nitrides in heterogeneous catalytic ammonia synthesis.[9] Despite several examples in Group 5 metals,[10] only a few dinuclear Group 4 complexes with μ-N ligands have been isolated by reaction of reduced species with dinitrogen.[11] Notably, Hou and co-workers have recently characterized a trinuclear titanium hydride complex that cleaves molecular nitrogen to form μ_3-N and μ-NH ligands bound to the metal centers.[12] Structurally related Group 4 and 5 polynuclear nitrido complexes, usually containing additional imido (NH) or amido (NH_2) bridging ligands, are synthesized using excess ammonia as the N-atom source.[13,14] However, this methodology precludes the desired control in the composition and structure of the resulting polynuclear aggregates. For instance, Roesky and co-workers described the preparation of the trinuclear imido-nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) by ammonolysis of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$,[15] whereas the analogous treatment of $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ with NH_3 gave the cube-type tetranuclear nitrido derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$.[16] Interestingly, the latter compound could also be obtained by the reaction of **1** with $[Ti(\eta^5\text{-}C_5Me_5)(NMe_2)_3]$ at high temperatures which can be viewed as the incorporation of the missed fourth metal vertex into the incomplete cube structure of **1**.[17]

By using similar protocols, our group has extensively reported about the incorporation of early[18] and late[19] transition, main-group,[20] or lanthanide[21] metals as a rational entry to well-defined heteropolymetallic nitrido complexes with $[MTi_3N_4]$ cores. Those studies have established that the trinuclear titanium complex **1** acts as a neutral tridentate donor through the three NH imido groups to Lewis acidic metal centers, but the N-H bonds can also be subsequently activated to give monoanionic, dianionic or even trianionic systems coordinated to the heterometals. Further indication of the versatility of the titanium metalloligand is the capacity of **1** to accept one electron delocalized among the three titanium atoms to form a radical anion as observed in the reaction of $[Cl_3Y\{(\mu_3\text{-}$

$NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ with $[K(C_5Me_5)]$.[22] As part of this program, we sought to prepare chloride complexes of the early transition-metals stabilized by metalloligands derived from **1** and to explore their use as starting materials for new organometallic derivatives. Herein we report the synthesis, structure, and properties of a series of Group 4 chloride complexes $[Cl_{4-x}M\{(\mu_3-N)_x(\mu_3-NH)_{3-x}Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$ (M = Ti, Zr, Hf). The metathesis reaction of these derivatives with main-group reagents $[M'(C_5H_5)_x]$ afford Group 4 cyclopentadienyl complexes supported by deprotonated trinitrogen systems. In contrast, the treatment of the trichloride zirconium complex with potassium pentamethylcylopentadienide leads to new examples of paramagnetic species with the titanium metalloligand acting in a reduced form.

Results and discussion

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with one equivalent of zirconium or hafnium tetrachloride tetrahydrofuran adducts $[MCl_4(thf)_2]$ in a 2:1 toluene-thf mixture at room temperature afforded the precipitation of the trichloride complexes $[Cl_3M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Zr (**2**), Hf (**3**)) (Scheme 1). Compounds **2** and **3** were isolated in moderate yields (68 and 48%, respectively) as air-sensitive brown-green solids, which are not soluble in hydrocarbon solvents. The analogous reaction of **1** with the titanium $[TiCl_4(thf)_2]$ or Group 5 $[MCl_5(thf)]$ (M = Nb, Ta) adducts led to complicated mixture of products, where only $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$[23] was unambiguously identified by NMR spectroscopy. Most likely, the lack of solubility of compounds **2** and **3** in the toluene-thf mixture precludes the subsequent attack of generated HCl which leads to extensive decomposition of analogous titanium or Group 5 derivatives.



Scheme 1 Synthesis of Group 4 nitrido complexes **2-8**.

Complexes **2** and **3** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination for the zirconium derivative **2**. IR spectra (KBr) of **2** and **3** show one ν_{NH} vibration at 3327 and 3330 cm^{-1}, respectively, in a similar range to the value determined for **1** (3352 cm^{-1}).[17] The ^1H NMR spectra in chloroform-d_1 at room temperature reveal one resonance signal for two equivalent NH groups and two resonances in a 1:2 ratio for the η^5-C_5Me_5 ligands. The NMR data are consistent with C_s symmetric structures in solution. The solid-state structure of compound **2** is shown in Fig. 1, while selected distances and angles are given in Table 1. The crystal structure shows a $[ZrTi_3N_4]$ cube-type core with the metalloligand $\{(\mu_3\text{-N})(\mu_3\text{-NH})_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$ coordinating in a tripodal fashion to the zirconium atom. The zirconium center is six-coordinate and its geometry is best described as distorted trigonal antiprismatic with one tighter triangle defined by the nitrogen atoms and with a more open one defined by the chloride ligands. This is clearly seen by comparing the N–Zr–N [76.6(4)°] and Cl–Zr–Cl [96(2)°] averaged angles. The coordination environment about the zirconium atom in complex **2** is analogous to those reported for zirconium trichloride complexes containing *fac*–coordinating trinitrogen ligands such as $[Zr\{HB(3,5\text{-}Me_2pz)_3\}Cl_3]$[24] and $[Zr\{HB(3\text{-}Mespz)_3\}Cl_3]$[25] complexes. The Zr–Cl and Zr–N distances in **2** (average 2.444(5) and range 2.289(3)–2.324(3) Å, respectively) compare well with those found in the tris(pyrazolyl)borate derivatives (ranges Zr–Cl 2.370(1)–2.399(2) Å and Zr–N 2.280(4)–2.353(3) Å). The three zirconium–nitrogen bond lengths are similar, and range between the Zr–N(amido) (2.002(5) Å) and Zr–N(amino) (2.46(4) Å) distances determined in the triazacyclononane complex $[Zr(iPr_2tacn)Cl_3]$.[26] The distortions in bond distances and angles within the {(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)} fragment are small when compared to those of **1**.[15]

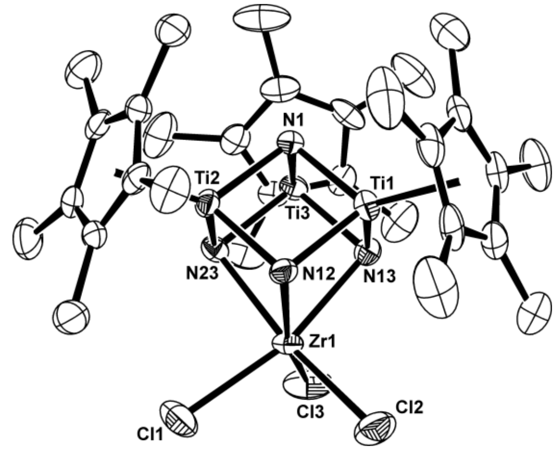


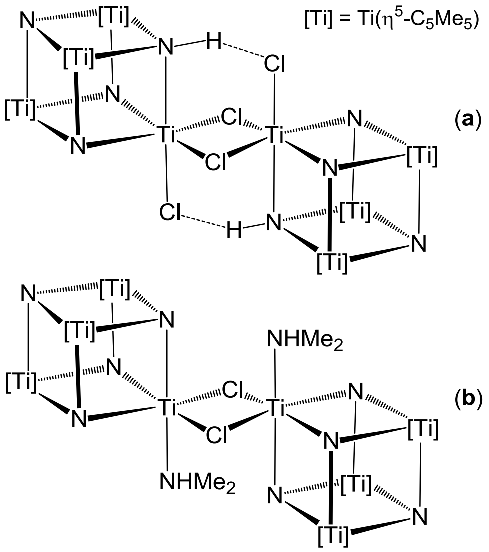
Fig. 1 Perspective view of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Selected lengths (Å) and angles (º) for **2**.

Zr(1)–N(12)	2.324(3)	Zr(1)–Cl(1)	2.449(2)
Zr(1)–N(13)	2.298(3)	Zr(1)–Cl(2)	2.444(1)
Zr(1)–N(23)	2.289(3)	Zr(1)–Cl(3)	2.440(1)
Ti–N(1) av	1.935(9)	Ti–N av	1.966(5)
Ti···Ti av	2.841(7)	Ti···Zr(1) av	3.148(13)
N(12)–Zr(1)–N(13)	76.4(1)	Cl(1)–Zr(1)–Cl(2)	94.6(1)
N(13)–Zr(1)–N(23)	77.0(1)	Cl(1)–Zr(1)–Cl(3)	97.6(1)
N(12)–Zr(1)–N(23)	76.3(1)	Cl(2)–Zr(1)–Cl(3)	97.0(1)
N(12)–Zr(1)–Cl(1)	96.4(1)	N(12)–Zr(1)–Cl(2)	88.4(1)
N(12)–Zr(1)–Cl(3)	164.5(1)	N(13)–Zr(1)–Cl(1)	166.0(1)
N(13)–Zr(1)–Cl(2)	97.3(1)	N(13)–Zr(1)–Cl(3)	88.5(1)
N(23)–Zr(1)–Cl(1)	89.7(1)	N(23)–Zr(1)–Cl(2)	164.5(1)
N(23)–Zr(1)–Cl(3)	97.3(1)	N–Ti–N(1) av	86.5(3)
N–Ti–N av	93.1(1)	Ti–N–Zr(1) av	94.7(6)
Ti–N(1)–Ti av	94.5(6)	Ti–N–Ti av	92.6(1)

To obtain titanium chloride complexes, the reaction of **1** with amido-chloride species [$TiCl_{4-x}(NMe_2)_x$] (x =1, 2, 3) was examined (Scheme 1). Despite many attempts, a titanium trichloride complex similar to **2** and **3** could not be isolated in the treatment of **1** with [$TiCl_3(NMe_2)$]. However, compound **1** cleanly reacted with one equivalent of [$TiCl_2(NMe_2)_2$] in toluene at room temperature to give the titanium dichloride complex [$Cl_2Ti\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]\cdot C_7H_8$ (**4**$\cdot C_7H_8$) in 60% yield. Compound **4** have been previously obtained in the treatment of **1** with the *tert*-butylimido derivative [$TiCl_2(N$*t*$Bu)(py)_3$].[18a] The analogous reaction of **1** with [$TiCl(NMe_2)_3$] afforded the monochloride complex [$(Me_2NH)ClTi\{(\mu_3\text{-}N)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**5**) in 72% yield. Compounds **4** and **5** were isolated as green solids, which are not soluble in hydrocarbon solvents but exhibit a good solubility in chloroform-d_1. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** at room temperature showed sharp resonances for equivalent $\eta^5\text{-}C_5Me_5$ ligands and broad singlets for the methyl groups of the $NHMe_2$ ligand. Although the resonance for the N-H proton of the dimethylamine ligand was not observed in the ^1H NMR spectrum, the N-H stretch was identified in the IR spectrum (KBr) at 3232 cm^{-1}.

Complex **5** decomposes completely in chlorinated solvents after 24 h at room temperature to give an intractable mixture of products. The lack of solubility of **5** in apolar solvents suggests a dimeric structure similar to that calculated by DFT methods for complex **4** (Scheme 2).[18b] In those structures, two azatitanocubanes are connected by symmetrical chloro bridges leading to octahedral geometries for the incorporated titanium atoms. Indeed, the dissociation energy for the dimeric structure of **4** to give the monomeric units was computed to be 74 $kJ\cdot mol^{-1}$.[18b] The dimethylamine ligand in **5** is strongly bonded to the titanium center and the compound remains unaltered upon dissolving the compound in tetrahydrofuran and subsequent elimination of the solvent under dynamic vacuum. However, treatment of **5** with excess pyridine (≥ two equivalents) in dichloromethane for 30 min at room temperature leads to the adduct $[(py)_2ClTi\{(\mu_3\text{-}N)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**6**) via $NHMe_2$ elimination. Complex **6** was isolated in 97% yield as a green solid, which is stable for weeks in chloroform-d_1 at room temperature. The presence of two pyridine ligands in **6** would result in a single-cube structure with a distorted octahedral geometry for the incorporated titanium atom (Scheme 1).



Scheme 2 Computed structure for **4** (**a**) and proposed structure for **5** (**b**).

Attempts to alkylate complexes **4** and **5** with conventional organolithium reagents (*e.g.*, [LiMe], $[Li(CH_2SiMe_3)]$) provided complicated mixtures of products which could not be characterized. However, the treatment of the titanium dichloride complex **4** with two equivalents of sodium cyclopentadienide in toluene at 60 ºC led to the known derivative $[(\eta^5\text{-}C_5H_5)Ti\{(\mu_3\text{-}N)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**7**) in 84% yield.[17] Similarly, the amido complex $[\{(Me_3Si)_2N\}Ti\{(\mu_3\text{-}N)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**8**) was obtained in 86% yield by treatment of **4** with two equivalents of lithium bis(trimethylsilyl)amide. Green compounds

7 and **8** are very soluble in toluene and hexane and consequently are easily separated from the NaCl or LiCl salts and the volatile C_5H_6 or $NH(SiMe_3)_2$ byproducts. The synthesis of complexes **7** and **8** by reaction of **5** with $[Na(C_5H_5)]$ or $[Li\{N(SiMe_3)_2\}]$ is more complicated because those reagents deprotonate the NH group of the coordinated dimethylamine ligand. However, reaction of **5** with two equivalents of those alkali metal derivatives in toluene at room temperature afforded complexes **7** and **8** in 83 and 43% isolated yield, respectively.

^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **7** and **8** in benzene-d_6 reveal resonance signals for three equivalents η^5-C_5Me_5 groups and one η^5-C_5H_5 or $N(SiMe_3)_2$ ligand. The NMR data are consistent with C_{3v} symmetric structures in solution. The solid-state structure of **8** was determined by X-ray crystallography (Fig. 2 and Table 2). The molecular structure shows an almost perfect $[Ti_4N_4]$ cube core with the Ti–N–Ti and N–Ti–N angles very close to 90º. Three of the titanium atoms [Ti(1), Ti(2) and Ti(3)] have classical three-legged piano-stool arrangements, whereas Ti(4) exhibits a distorted tetrahedral geometry. The average Ti–N [1.933(18) Å] and Ti–Ti [2.777(9) Å] separations within the cube-type core of **8** are essentially identical to those found in $[\{Ti(\eta^5\text{-}C_5Me_5\}_4(\mu_3\text{-}N)_4]$, 1.938(7) and 2.783(2) Å respectively.[16] The longer Ti(4)–N(2) distance of 1.998(2) Å is typical for bis(trimethylsilyl)amido ligands bonded to titanium(IV) centers.[27]

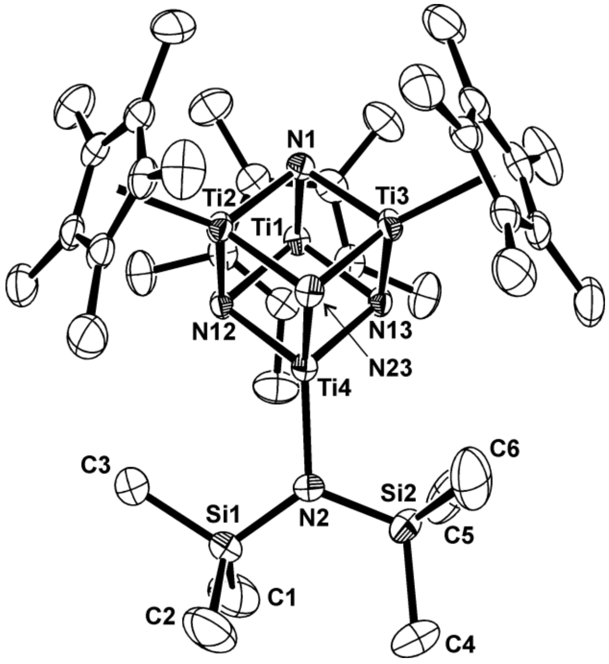
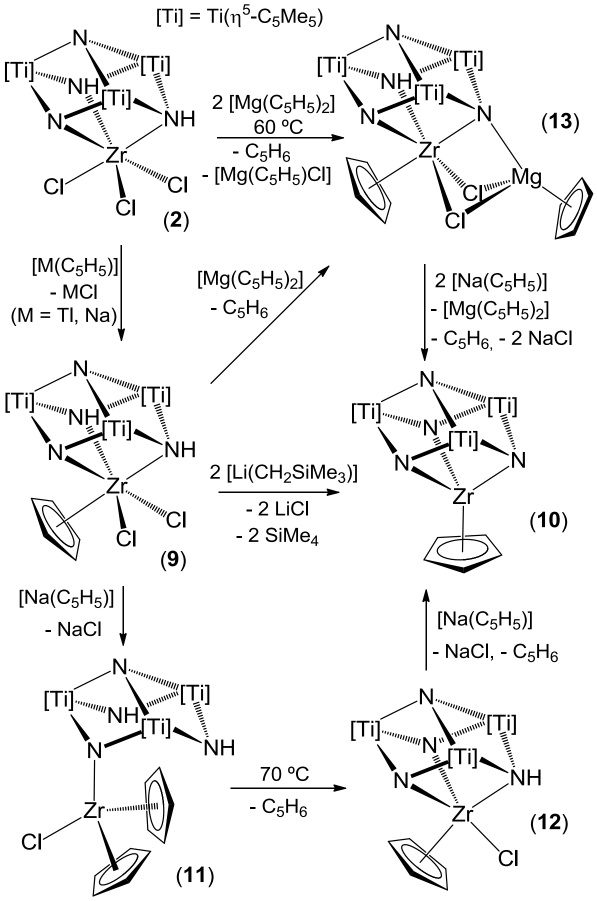


Fig. 2 Perspective view of **8** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected lengths (Å) and angles (º) for **8**.

Ti–N av	1.933(18)	Ti(4)–N(2)	1.998(2)
N(2)–Si av	1.723(1)	Ti···Ti av	2.777(9)
N–Ti–N av	88.1(8)	Ti–N–Ti av	91.8(5)
Si(1)–N(2)–Si(2)	121.5(1)	Si(1)–N(2)–Ti(4)	123.8(1)
Si(2)–N(2)–Ti(4)	114.1(1)		

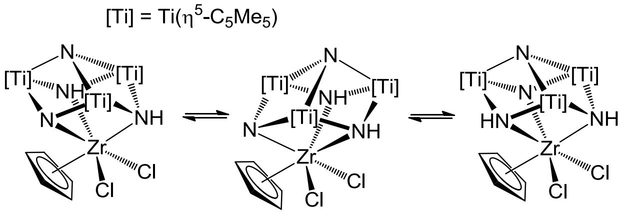
The reaction of the zirconium trichloride complex **2** with main-group metal cyclopentadienyl reagents [$M(C_5H_5)_x$] was also examined (Scheme 3). Treatment of **2** with thallium cyclopentadienide (≥ one equivalent) in toluene at room temperature gave exclusively the dichloride-monocyclopentadienyl derivative [$(\eta^5\text{-}C_5H_5)Cl_2Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (**9**). Compound **9** was isolated in 85% yield as a deep red solid which contains half molecule of toluene per cube-type complex according to analytical and spectral data.



Scheme 3 Reactions of **2** with [$M(C_5H_5)_x$].

The ^1H NMR spectra of **9** in benzene-d_6 or chloroform-d_1 at room temperature revealed two resonance signals for the η^5-C_5Me_5 ligands in a 2:1 ratio, one resonance for two equivalent NH imido groups and a singlet for one η^5-C_5H_5 ligand. Those NMR data are consistent with a C_s symmetry in solution, but the singlet resonance integrating for two η^5-C_5Me_5 ligands and that for the NH groups are very broad. Upon cooling to –40 ºC the ^1H NMR spectrum of a solution of **9** in chloroform-d_1 revealed three sharp resonances for the η^5-C_5Me_5 ligands and two well-defined singlets for the NH groups in accord with a C_1

symmetry. This experiment suggests the existence of a dynamic exchange process in solution similar to those reported for the niobium and tantalum imido complexes $[Cl_2(RN)M\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Nb, Ta; R = *t*Bu, 2,4,6-$C_6H_2Me_3$).[18b] The kinetic parameters of the dynamic process in compound **9** were calculated on the basis of ^{1}H DNMR data with line shape analysis of the η^5-C_5Me_5 resonances using the gNMR program (see Table S1 and Figures S1-S2 in the ESI†).[28] The results are consistent with an intramolecular nondissociative mechanism (log A = 12.5(1.6) and $\Delta S^‡ = -3.1(1.4)$ eu) similar to that found for the above mentioned Group 5 imido complexes.[18b] The fluxional process can be visualized as rotation (trigonal antiprism – trigonal prism – trigonal antiprism) of the metalloligand $\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$ around the $[Zr(\eta^5\text{-}C_5H_5)Cl_2]$ fragment (Scheme 4). In this trigonal-twist rearrangement, the nitrido group bonded to zirconium would be exchanged between the sites *trans* to the chloride ligands.



Scheme 4 Proposed trigonal-twist process for complex **9.**

Complex **9** can also be prepared by reaction of **2** with one equivalent of $[Na(C_5H_5)]$ in toluene, but this procedure afforded lower yields of **9** because excess of sodium cyclopentadienide produces further replacement of chloride groups. Thus, the treatment of **2** with excess $[Na(C_5H_5)]$ (≥ three equivalents) in toluene at 70 ºC for 2 days gave complex

$[(\eta^5\text{-}C_5H_5)Zr\{(\mu_3\text{-}N)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**10**) as a green solid very soluble in toluene or hexane. Alternatively, compound **10** was isolated in higher yield (79%) through the reaction of **9** with two equivalents of $[Li(CH_2SiMe_3)]$ in toluene at room temperature (Scheme 3). ^1H and $^{13}C\{^1H\}$ NMR spectra of **10** in benzene-d_6 reveal resonance signals for three equivalents $\eta^5\text{-}C_5Me_5$ groups and one $\eta^5\text{-}C_5H_5$ ligand. The NMR data are consistent with a C_{3v} symmetric structure for this compound similar to those described above for complexes **7** and **8**.

The reaction of **9** with one equivalent of sodium cyclopentadienide in benzene-d_6 was monitored by NMR spectroscopy (Scheme 3). After 4 days at room temperature a white fine solid precipitated at the bottom of the tube, and the NMR spectra of the supernatant orange solution showed complete consumption of **10** along with resonance signals attributable to the chloride-dicyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)_2ClZr\{(\mu_3\text{-}N)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)_2(\mu_3\text{-}N)\}]$ (**11**). The solid was eliminated by filtration and the benzene-d_6 solution was heated at 70 ºC for 3 days. Analysis of the resultant dark red solution by NMR spectroscopy revealed resonance signals for the chloride-monocyclopentadienyl derivative $[(\eta^5\text{-}C_5H_5)ClZr\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**12**) and C_5H_6. In addition to the resonances due to complexes **11** and **12**, the NMR spectra showed resonance signals assignable to **10** in *ca.* 15%. Despite many attempts in preparative scale reactions, complexes **11** and **12** could not be isolated in a pure form for complete characterization, and were only characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR data of **11** and **12** are consistent with C_s symmetry in solution for these compounds. The ^1H NMR spectrum of **11** in benzene-d_6 at room temperature showed two resonance signals for the $\eta^5\text{-}C_5Me_5$ groups in a 2:1 ratio, a singlet assignable to two equivalent $\eta^5\text{-}C_5H_5$ ligands, and a broad signal for two NH groups. Importantly, the NH resonance signal in the spectrum (δ = 14.05) is slightly shifted to lower field than those found in **1** (δ = 13.80).[17] This unusual shift of the NH resonance has been determined in several complexes with $\{(\mu_3\text{-N})Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-NH})_2(\mu_3\text{-N})\}$ trinuclear titanium systems bonded in a monodentate fashion to other metals.[29] Most likely, the steric effects of two η^5-C_5H_5 ligands on the zirconium atom preclude the coordination of the NH groups of the metalloligand. In contrast, the ^1H NMR spectrum of **12** in benzene-d_6 revealed two resonance signals for the η^5-C_5Me_5 groups in a 1:2 ratio, a singlet assignable to one η^5-C_5H_5 ligand, and a broad signal for one NH group at δ = 13.57. These NMR data suggest the coordination of the NH ligand to the zirconium center at the opposite position to the cyclopentadienyl ligand.

To isolate the intermediates observed in the reaction of derivative **9** with $[Na(C_5H_5)]$, we used the magnesium dicyclopentadienyl derivative $[Mg(C_5H_5)_2]$ as reagent. Treatment of **9** with one equivalent of $[Mg(C_5H_5)_2]$ in toluene at room temperature or the reaction of **2** with two equivalents of $[Mg(C_5H_5)_2]$ at 60 ºC afforded the magnesium derivative $[(\eta^5\text{-}C_5H_5)Mg(\mu\text{-Cl})_2(\eta^5\text{-}C_5H_5)Zr\{(\mu_4\text{-N})(\mu_3\text{-N})(\mu_3\text{-NH})Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}]$ (**13**) (Scheme 3), which can be visualized as the result of the incorporation of one $[Mg(\eta^5\text{-}C_5H_5)Cl]$ moiety to complex **12**. Indeed, the treatment of **13** with two equivalents of $[Na(C_5H_5)]$ in benzene-d_6 at room temperature afforded complex **10**, $[Mg(C_5H_5)_2]$, and C_5H_6 as determined by NMR spectroscopy.

Complex **13** was isolated in 91% yield as a deep red solid which is very soluble in toluene or benzene and poorly soluble in hexane. Compound **13** was characterized by spectroscopic and analytical methods, as well as by an X-ray crystallographic determination of crystals of **13**·C_7H_8 obtained in toluene at –30 ºC. Complex **13** crystallized in the space group $P2_1/c$ with two independent molecules in the asymmetric unit and the crystals contain one toluene solvent molecule per cube-type complex. The two independent molecules show somewhat different structural parameters (see Table S2 in the ESI†), but the overall geometry is similar in both cases. The structure of one of them is presented in Fig. 3, while selected distances and angles for this molecule are given in Table 3. Each molecule shows a distorted [$ZrTi_3N_4$] cube-type core with the zirconium atom bonded to two nitrido and one imido groups of the titanium metalloligand. In addition, zirconium is bonded to one η^5-cyclopentadienyl ligand and two chlorine atoms to complete a distorted trigonal antiprismatic geometry about the Group 4 metal center. The magnesium atom is connected to zirconium by two chloride and one nitrido ligands, which along with one η^5-C_5H_5 group lead to a typical three-legged piano-stool arrangement for the Group 2 metal. The magnesium–nitrogen bond lengths (Mg(1)–N(23) 2.131(4) Å and Mg(2)–N(57) 2.094(4) Å) in the two independent molecules are similar to those observed in dimeric amido complexes with Mg_2N_2 cores (2.08–2.15 Å).[30] The binding of those nitrido atoms to magnesium turns Zr(1)–N(23) and Zr(2)–N(57) into pure dative bonds whose lengths (2.447(3) and 2.494(3) Å, respectively) should be compared to the remaining relatively short zirconium–nitrogen distances (2.151(3)–2.232(3) Å).

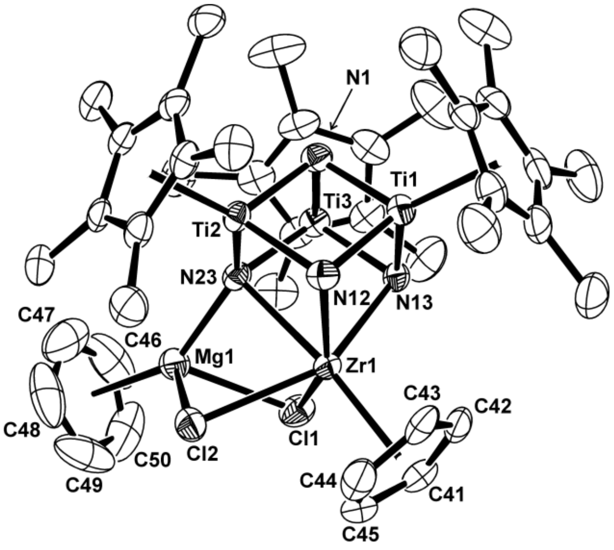


Fig. 3 Perspective view with thermal ellipsoids at the 50% probability level of one of the two crystallographically independent molecules of **13**. Hydrogen atoms and the toluene solvent molecule are omitted for clarity.

Table 3 Selected lengths (Å) and angles (º) for one of the two crystallographycally independent molecules of **13**.

Zr(1)–N(12)	2.194(3)	Zr(1)–N(13)	2.203(3)
Zr(1)–N(23)	2.447(3)	Zr(1)–Cl(1)	2.607(1)
Zr(1)–Cl(2)	2.620(1)	Zr(1)–Cm(1)	2.241(1)
Mg(1)–N(23)	2.131(4)	Mg(1)–Cm(2)	2.114(2)
Mg(1)–Cl(1)	2.512(2)	Mg(1)–Cl(2)	2.469(2)
Ti(1)–N(12)	1.957(3)	Ti(1)–N(13)	1.940(3)
Ti(2)–N(12)	1.972(4)	Ti(2)–N(23)	1.908(3)
Ti(3)–N(13)	1.969(3)	Ti(3)–N(23)	1.906(3)
Ti(1)–N(1)	1.915(4)	Ti(2)–N(1)	1.931(3)
Ti(3)–N(1)	1.939(3)		
N(12)–Zr(1)–N(13)	77.7(1)	N(12)–Zr(1)–N(23)	76.4(1)
N(13)–Zr(1)–N(23)	75.9(1)	Cl(1)–Zr(1)–Cl(2)	82.4(1)
Cl(1)–Zr(1)–Cm(1)	101.8(1)	Cl(2)–Zr(1)–Cm(1)	100.0(1)

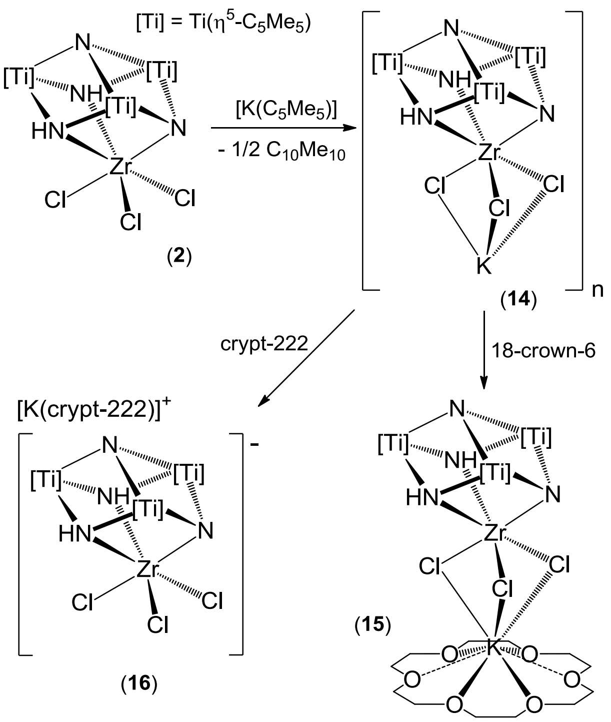
Cl(1)–Mg(1)–Cl(2)	87.5(1)	Cl(1)–Mg(1)–Cm(2)	118.6(1)
Cl(2)–Mg(1)–Cm(2)	118.1(1)	N(23)–Mg(1)–Cl(1)	83.0(1)
N(23)–Mg(1)–Cl(2)	82.9(1)	N(23)–Mg(1)–Cm(2)	148.6(1)
N(12)–Ti(1)–N(13)	90.1(1)	N(12)–Ti(2)–N(23)	95.7(1)
N(13)–Ti(3)–N(23)	95.4(1)	Zr(1)–Cl(1)–Mg(1)	79.1(1)
Zr(1)–Cl(2)–Mg(1)	79.6(1)	Zr(1)–N(23)–Mg(1)	90.5(1)
Ti(2)–N(23)–Mg(1)	136.3(2)	Ti(3)–N(23)–Mg(1)	130.1(2)
Ti(2)–N(23)–Ti(3)	93.6(2)	Ti(1)–N(12)–Ti(2)	92.4(1)
Ti(1)–N(13)–Ti(3)	92.8(1)		

Cm(1) = centroid of the C(41)–C(45) ring; Cm(2) = centroid of the C(46)–C(50) ring.

In accord with the C_1 symmetry determined in the solid-state structure, the ^{1}H NMR spectrum of **13** in benzene-d$_6$ at room temperature reveals three resonance signals for the η^5-C_5Me_5 groups in a 1:1:1 ratio, two singlets for nonequivalent η^5-C_5H_5 ligands and a broad signal for one NH imido group. The singlet at δ = 6.19 is assigned to the cyclopentadienyl group bonded to magnesium by comparison with that of [Mg(C_5H_5)$_2$] (δ = 5.97) and several [{Mg(C_5H_5)(NRR´)}$_2$] (δ = 5.94–6.28) derivatives.[30d] The ^{13}C{^{1}H} NMR spectrum contains one resonance at δ = 107.3 for the Mg(η^5-C_5H_5) fragment, which is again similar to that of [Mg(C_5H_5)$_2$] (δ = 107.7) and [{Mg(C_5H_5)(NRR´)}$_2$] (δ = 106.1–106.5) complexes.

In contrast to the metathesis reaction observed with [M(C_5H_5)$_x$] reagents, the treatment of the zirconium trichloride complex **2** with one equivalent of potassium pentamethylcyclopentadienide afforded the precipitation of [K(μ-Cl)$_3$Zr{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (**14**) as a paramagnetic blue-green solid (Scheme 5). The reaction in benzene-d$_6$ was monitored by ^{1}H NMR spectroscopy and the spectra showed resonance signals for $C_{10}Me_{10}$ and one far-downfield and broad resonance ($\delta = 10.3$, $\Delta\nu_{1/2} =$ 24 Hz) attributable to the η^5-C_5Me_5 ligands of complex **14**. Compound **14** was isolated in 71% yield through the reaction of **2** with one equivalent of $[K(C_5Me_5)]$ in toluene at room temperature in the absence of light. The paramagnetic nature of **14** was confirmed by an Evans method determination of its effective magnetic moment ($\mu_{eff} = 1.97\ \mu_B$, 293 K, C_6D_6 solution),[31] which is in accord with an unpaired electron in the complex. This result, along with the exclusive formation of $C_{10}Me_{10}$ as byproduct, which is formed via coupling of pentamethylcyclopentadienyl radicals,[32] suggests that the reaction pathway for the synthesis of **14** consists in an electron transfer from the $C_5Me_5^-$ anion to the zirconium/titanium cube-type complex **2**. Most likely, the additional electron is delocalized among the three titanium atoms of the metalloligand in a fashion similar to that determined by DFT calculations for the analogue yttrium/titanium anion $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]^-$.[22]

The reduced species **14** retains one potassium cation as part of the structure according to analytical data and presumably has a polymeric structure. Despite considerable efforts we could not grow suitable crystals of **14** for an X-ray crystal structure determination and its reaction with macrocyclic polyethers was examined (Scheme 5). Treatment of compound **14** with one equivalent of 18-crown-6 in toluene at 80 ºC gave a green solution from which the molecular complex $[(18\text{-crown-}6)K(\mu\text{-}Cl)_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**15**) was isolated in 63% yield as a blue-green solid. In contrast, the reaction of **14** with cryptand-222 at room temperature afforded the immediate precipitation of the ionic complex $[K(\text{crypt-}222)][Cl_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (**16**) as a blue-green powder in 72% yield. Whereas compound **15** exhibits an enhanced solubility in benzene and toluene when compared with **14**, complex **16** is poorly soluble in those solvents but exhibits a good solubility in pyridine. Compounds **15** and **16** immediately react with chloroform-d$_1$ to give brown solutions of complex **2** and the corresponding free macrocycle according to NMR spectroscopy.



Scheme 5 Reaction of **2** with [K(C_5Me_5)].

The ^{1}H NMR spectrum of **15** in benzene-d$_6$ shows two broad resonances in a 1:2 ratio at $\delta = 10.6$ ($\Delta\nu_{1/2} = 73$ Hz) and $\delta = 10.2$ ($\Delta\nu_{1/2} = 61$ Hz) attributed to the C_5Me_5 groups and one resonance signal at $\delta = 3.3$ ($\Delta\nu_{1/2} = 9$ Hz) for the crown ether ligand. Similarly, the ^{1}H NMR spectrum of **16** in pyridine-d$_5$ reveals two broad resonances in a 1:2 ratio at $\delta = 10.9$ ($\Delta\nu_{1/2} = 75$ Hz) and $\delta = 10.2$ ($\Delta\nu_{1/2} = 66$ Hz) for the C_5Me_5 groups and three well-defined resonances at $\delta = 3.40$ (s), 3.34 (t, ^3J(H,H) = 4.5 Hz) and 2.34 (t, ^3J(H,H) = 4.5 Hz) for the methylene groups of the cryptand-222 ligand. While the two resonances for the C_5Me_5 ligands in the ^{1}H NMR spectra of **15** and **16** are consistent with a C_s symmetry in solution, the spectrum of **14** showed only one resonance at $\delta = 10.3$ ($\Delta\nu_{1/2} = 24$ Hz) for those ligands, which could be due to the overlapping of two close and broad signals. The far-downfield and broad resonances in the ^{1}H NMR spectra of complexes **14-16** compare well with that found δ = 11.1–10.2 for equivalents η^5-C_5Me_5 ligands in yttrium complexes with the one-electron reduced radical metalloligand $\{(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})\}$.[22] The magnetic moment measurements by the Evans method gave μ_{eff} = 2.01 μ_B for **15** and μ_{eff} = 1.95 μ_B for **16** confirming their paramagnetic nature with an unpaired electron.

Crystals of **15**·$7C_6D_6$ were grown by slow cooling at room temperature of a benzene-d_6 solution heated at 80 ºC. The molecular structure shows a $[ZrTi_3N_4]$ cube-type core linked to the potassium atom by three bridging chloride ligands (Fig. 4 and Table 4). Molecules of **15** present a C_3 axis which crosses the N(1), Zr(1), and K(1) atoms. The zirconium atom exhibits a distorted trigonal antiprismatic geometry similar to that determined in complex **2**. However, the interaction of the chloride ligands with the potassium atom in **15** results in a closing of the Cl–Zr(1)–Cl angles in about 6º and a lengthening of the Zr(1)–Cl bond lengths of approximately 0.09 Å with respect to those found in **2**. On the other hand, the tridentate metalloligand coordinates to zirconium with Zr(1)–N bond lengths of 2.175(2) Å which are significantly shorter than the zirconium–nitrogen distances found in complex **2** (range 2.289(3)-2.324(3) Å). The K(1)–Cl(1) distance of 3.425(1) Å indicates a weak interaction similar to those found in complexes $[(18\text{-crown-}6)K(\mu\text{-Cl})_3Pt(C_4Me_4)]$[33] and $[\{(18\text{-crown-}6)K(\mu\text{-Cl})_3\}_2Se]$[34] (range 3.097–3.482 Å). As observed in those examples, a further indication of this K–Cl interaction is that the potassium atom is 0.85 Å above the plane defined by the six oxygen atoms of the 18-crown-6 ligand.

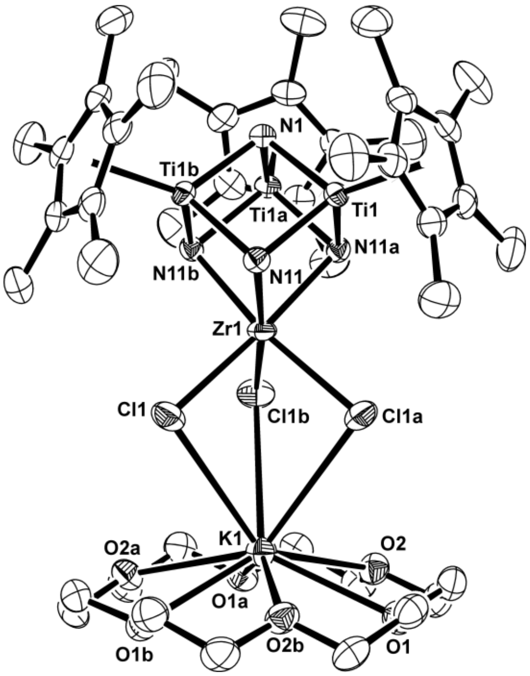


Fig. 4 Perspective view of **15** with thermal ellipsoids at the 50% probability level. Benzene molecules and hydrogen atoms are omitted for clarity. Symmetry transformation: (a) – *x* + *y*, 1 – *x*, *z*; (b) 1 – *y*, 1 + *x* – *y*, *z*.

Table 4 Selected lengths (Å) and angles (º) for **15**.

Zr(1)–N(11)	2.175(2)	Zr(1)–Cl(1)	2.529(1)
Ti(1)–N(11)	1.980(3)	Ti(1)–N(1)	1.923(2)
K(1)–Cl(1)	3.425(1)	K(1)–O(1)	2.947(3)
K(1)–O(2)	2.879(2)	Ti(1)···Ti(1)a	2.810(1)
Ti(1)···Zr(1)	3.073(1)	Zr(1)···K(1)	4.207(2)
N(11)–Zr(1)–N(11)a	79.7(1)	N(11)–Zr(1)–Cl(1)	91.8(1)
N(11)–Zr(1)–Cl(1)a	98.9(1)	N(11)–Zr(1)–Cl(1)b	171.4(1)
Cl(1)–Zr(1)–Cl(1)a	89.6(1)	N(11)–Ti(1)–N(1)	87.8(1)
N(11)–Ti(1)–N(11)a	89.4(2)	O(1)–K(1)–O(2)	57.5(1)
O(1)–K(1)–O(2)b	57.5(1)	O(2)–K(1)–O(1)a	57.5(1)
Cl(1)–K(1)–O(1)	126.9(1)	Cl(1)–K(1)–O(2)	140.2(1)
Cl(1)–K(1)–O(1)a	121.5(1)	Cl(1)–K(1)–O(2)a	81.6(1)

Cl(1)–K(1)–O(1)b	73.8(1)	Cl(1)–K(1)–O(2)b	86.3(1)
Zr(1)–N(11)–Ti(1)	95.3(1)	Ti(1)–N(11)–Ti(1)b	90.4(1)
Ti(1)–N(1)–Ti(1)a	93.9(1)	Zr(1)–Cl(1)–K(1)	88.6(1)

Symmetry transformation: (a) – *x* + *y*, 1 – *x*, *z*; (b) 1 – *y*, 1 + *x* – *y*, *z*.

All the structural data determined for **15** are fully comparable to those found for the yttrium analogue $[(18\text{-crown-6})\text{K}(\mu\text{-Cl})_3\text{Y}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]\cdot 7\text{C}_6\text{D}_6$.[22] Furthermore, inspection of the crystal structure of both complexes revealed that the $[(18\text{-crown-6})\text{K}(\mu\text{-Cl})_3\text{M}\{(\mu_3\text{-N})_n(\mu_3\text{-NH})_{3-n}\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$ moieties are ordered in layers by C-H···π interactions between the pentamethylcyclopentadienyl ligands to give rise hexagons (see Fig. 5 and Fig. S3 in the ESI†). This lattice architecture produces channels in the [001] direction with crystallization benzene molecules occupying the empty space.

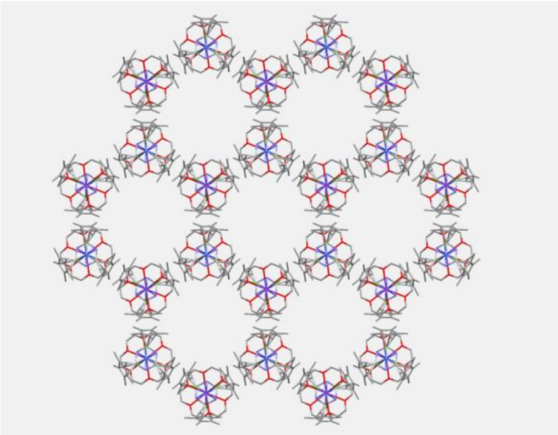


Fig. 5 View along the c axe of the crystal lattice of **15**. Hydrogen atoms and benzene molecules are omitted for clarity.

Conclusion

In this work, we have presented the synthesis of a series of chloride Group 4 complexes $[Cl_{4-x}M\{(\mu_3\text{-}N)_x(\mu_3\text{-}NH)_{3-x}Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (M = Ti, x = 2, 3; M = Zr, Hf, x =1) by treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with $[TiCl_{4-x}(NMe_2)_x]$ or $[MCl_4(thf)_2]$ (M = Zr, Hf) reagents. The titanium compounds react with alkali metal derivatives [M´R] via metathesis of chloride ligands but only by using bulky R groups (C_5H_5 and $N(SiMe_3)_2$) discrete nitrido species with $[Ti_4(\mu_3\text{-}N)_4]$ cores could be isolated. Similar metathesis reaction of the zirconium complex $[Cl_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ with main-group $[M'(C_5H_5)_x]$ reagents and subsequent C_5H_6 elimination afforded cyclopentadienyl zirconium derivatives supported by deprotonated tridentate titanium nitrido metalloligands. In contrast, the analogous treatment of the trichloride zirconium derivative with $[K(C_5Me_5)]$ led to the one-electron reduction of the titanium trinuclear system to give the paramagnetic $[K(\mu\text{-}Cl)_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ derivative and $C_{10}Me_{10}$.

Experimental section

General Considerations. All manipulations were carried out under an argon atmosphere using Schlenk line or glovebox techniques. Toluene and hexane were distilled from Na/K alloy just before use. Tetrahydrofuran was distilled from a purple solution of sodium benzophenone just prior to use. Pyridine was dried with calcium hydride and distilled prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$, C_5D_5N) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (*ca.* 1×10^{-3} Torr) and subsequently filled with inert gas. $[Tl(C_5H_5)]$, $[Li\{N(SiMe_3)_2\}]$, and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) were purchased from Aldrich and used as received. 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacoxane (crypt-222) was purchased from Acros and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**),[17] $[MCl_4(thf)_2]$[35] (M = Zr, Hf), $[TiCl_{4-x}(NMe_2)_x]$ (x = 1,[36] 2, 3[37]),[38] $[Na(C_5H_5)]$,[39] $[Mg(C_5H_5)_2]$,[40] and $[K(C_5Me_5)]$[41] were prepared according to published procedures.

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, Mercury-300, and/or Unity-500 Plus spectrometers. Chemical shifts (δ) in the ^1H and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to the carbon of the solvent. The effective magnetic moments were determined by the Evans NMR method at 293 K (using a 300 MHz instrument with a field strength of 7.05 Tesla).[31] Microanalyses (C, H, N) were performed in a Leco CHNS-932 microanalyzer.

Synthesis of [$Cl_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (2). A 100 mL Schlenk flask was charged with **1** (0.70 g, 1.15 mmol), [$ZrCl_4(thf)_2$] (0.43 g, 1.14 mmol), toluene (10 mL) and tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature for 24 h to give a brown solid and a brown solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **2** as a brown-green powder (0.63 g, 68%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3327 (s), 2911 (s), 2859 (m), 1487 (w), 1426 (s), 1379 (vs), 1164 (w), 1067 (w), 1023 (w), 801 (m), 732 (vs), 714 (vs), 695 (vs), 655 (vs), 509 (m), 468 (m), 450 (m), 432 (m). ^1H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 11.74 (s br., 2H; NH), 2.14 (s, 15H; C_5Me_5), 2.12 (s, 30H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 124.8, 123.8 (C_5Me$_5$), 12.7, 12.2 (C$_5$*Me*$_5$). Anal. Calcd for $C_{30}H_{47}Cl_3N_4Ti_3Zr$ (M_w = 804.90): C 44.77, H 5.89, N 6.96. Found: C 45.39, H 5.50, N 6.91.

Synthesis of [$Cl_3Hf\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (3). In a fashion similar to the preparation of **2**, the treatment of **1** (0.30 g, 0.49 mmol) with [$HfCl_4(thf)_2$] (0.21 g, 0.45 mmol) in toluene (10 mL) and tetrahydrofuran (5 mL) afforded **3** as a brown-green powder (0.19 g, 48%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3330 (s), 2911 (s), 1487 (w), 1426 (m), 1379 (s), 1067 (w), 1023 (w), 801 (m), 734 (vs), 720 (vs), 702 (vs), 659 (vs), 608 (vs), 541 (m), 506 (w), 469 (m), 449 (m), 433 (m). ^1H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 11.24 (s br., 2H; NH), 2.14 (s, 15H; C_5Me_5), 2.12 (s, 30H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 124.8, 123.6 (C_5Me$_5$), 12.7, 12.2 (C$_5$*Me*$_5$). Anal. Calcd for $C_{30}H_{47}Cl_3HfN_4Ti_3$ (M_w = 892.17): C 40.39, H 5.31, N 6.28. Found: C 40.14, H 5.08, N 5.41.

Synthesis of [$Cl_2Ti\{(\mu_3\text{-}N)_2(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (4). A 100 mL Schlenk flask was charged with **1** (1.10 g, 1.81 mmol), [$TiCl_2(NMe_2)_2$] (0.37 g, 1.79 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 2 days to give a green solid and a brown solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **4**·C_7H_8 as a green powder (0.88 g, 60%). ^{1}H NMR ($CDCl_3$, 20 ºC): δ 13.46 (s br., 1H; NH), 2.15 (s, 15H; C_5Me_5), 2.07 (s, 30H; C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC): δ 123.3 (C_5Me_5), 12.3, 12.0 ($C_5\mathit{Me}_5$), one C_5Me_5 resonance signal was not found.[18a]

Synthesis of [(Me_2NH)ClTi{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (5). In a fashion similar to the preparation of **4**, the treatment of **1** (1.00 g, 1.64 mmol) with [TiCl(NMe_2)$_3$] (0.35 g, 1.62 mmol) in toluene (30 mL) for 24 h afforded **5** as a green powder (0.86 g, 72%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3232 (w), 2906 (s), 1488 (w), 1432 (s), 1373 (s), 1244 (w), 1112 (w), 1022 (m), 895 (s), 801 (s), 653 (vs), 611 (vs), 443 (s). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 2.41 (s br., 6H; $NH\mathit{Me}_2$), 2.03 (s, 45H; C_5Me_5), the $N\mathit{H}Me_2$ resonance signal was not found. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ 120.2 (C_5Me_5), 38.4 (br., $NHMe_2$), 11.8 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{32}H_{52}ClN_5Ti_4$ (M_w = 733.71): C 52.38, H 7.14, N 9.55. Found: C 52.55, H 7.55, N 9.41.

Synthesis of [(py)$_2$ClTi{(μ_3-N)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (6). A 100 mL Schlenk flask was charged with **5** (0.60 g, 0.82 mmol), pyridine (0.30 mL, 3.67 mmol), and dichloromethane (40 mL). The reaction mixture was stirred at room temperature for 30 min. After filtration, the volatile components of the solution were removed under reduced pressure to afford **6** as a green solid (0.67 g, 97%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2906 (s), 1599 (m), 1483 (w), 1442 (s), 1374 (m), 1218 (w), 1150 (w), 1071 (m), 1036 (m), 1007 (m), 759 (w), 697 (s), 660 (vs), 445 (s). ^{1}H NMR (300 MHz, $CDCl_3$, 20 ºC): δ 8.82 (m, 4H; *o*-NC_5H_5), 7.73 (m, 2H; *p*-NC_5H_5), 7.33 (m, 4H; *m*-NC_5H_5), 1.93 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 ºC): δ

151.0, 137.2, 123.9 (NC_5H_5), 119.7 (C_5Me_5), 11.7 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{40}H_{55}ClN_6Ti_4$ (M_w = 846.82): C 56.73, H 6.55, N 9.92. Found: C 56.88, H 6.66, N 9.61.

Synthesis of [(C_5H_5)Ti{(μ_3-N)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (7). A 100 mL Schlenk flask was charged with **5** (0.68 g, 0.93 mmol), [Na(C_5H_5)] (0.17 g, 1.93 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 20 h to give a green solution and a fine white solid. After filtration, the volatile components of the solution were removed under reduced pressure to afford **7** as a green solid (0.56 g, 84%). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 6.12 (s, 5H; C_5H_5), 2.03 (s, 45H; C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 ºC): δ 119.7 (C_5Me_5), 110.3 (C_5H_5), 11.9 ($C_5\mathit{Me}_5$).[17]

Synthesis of [{($Me_3Si)_2$N}Ti{(μ_3-N)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (8). *Method A:* A 100 mL ampule (Teflon stopcock) was charged with **4**·C_7H_8 (0.30 g, 0.37 mmol), [Li{N($SiMe_3)_2$}] (0.12 g, 0.72 mmol), and toluene (25 mL). The reaction mixture was stirred at 60 ºC for 2 days to give a green solution and a fine white solid. After filtration, the volatile components of the solution were removed under reduced pressure to afford **8** as a green solid (0.25 g, 86%). *Method B:* A 100 mL Schlenk flask was charged with **5** (0.57 g, 0.78 mmol), [Li{N($SiMe_3)_2$}] (0.26 g, 1.55 mmol) and toluene (30 mL). After stirring at room temperature for 24 h, the volume of the reaction mixture was concentrated to *ca.* 15 mL under reduced pressure. After filtration, crystallization of the resultant green solution at -35 ºC for 2 days afforded green crystals (0.16 g) of **8** which were isolated by filtration. The filtrate was concentrated to about 7 mL and was cooled at -35 ºC to give a second crop (0.11 g) of **8** as green crystals. The combined yield of **8** was 43%. IR (KBr, cm^{-1}): $\tilde{\nu}$ 2908 (s), 1494 (w), 1436 (m), 1376 (m), 1244 (s), 1024 (w), 947 (s), 854 (s), 836 (s), 788 (s), 689 (s), 647 (vs), 618 (s), 452 (s). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 2.06 (s, 45H; C_5Me_5), 0.41 (s, 18H; $SiMe_3$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 120.9 (C_5Me$_5$), 12.2 (C_5*Me*$_5$), 5.9 ($SiMe_3$). Anal. Calcd for $C_{36}H_{63}N_5Si_2Ti_4$ (M_w = 813.56): C 53.15, H 7.80, N 8.61. Found: C 53.59, H 7.63, N 9.08.

Synthesis of [(η^5-C_5H_5)Cl_2Zr{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (9). A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.37 mmol), [Tl(C_5H_5)] (0.12 g, 0.45 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 16 h to give a red solution and a white fine solid. After filtration, the volatile components of the solution were removed under reduced pressure to afford **9**·0.5C_7H_8 as a red solid (0.28 g, 85%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3338 (m), 3022 (w), 2907 (s), 2857 (m), 1604 (w), 1494 (w), 1431 (m), 1376 (s), 1067 (w), 1019 (m), 879 (w), 803 (vs), 702 (vs), 659 (vs), 612 (s), 525 (m), 482 (w), 465 (w), 447 (m), 425 (m). ^1H NMR (300 MHz, C_6D_6, 20 ºC): δ 11.23 (s br., 2H; NH), 6.26 (s, 5H; C_5H_5), 2.02 (s br., 30H; C_5Me_5), 1.98 (s, 15H; C_5Me_5). ^1H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 11.23 (s br., 2H; NH), 6.14 (s, 5H; C_5H_5), 2.09 (s br., 30H; C_5Me_5), 2.07 (s, 15H; C_5Me_5). ^1H NMR (500 MHz, $CDCl_3$, -40 ºC): δ 11.64 (s br., 1H; NH), 10.89 (s br., 1H; NH), 6.14 (s, 5H; C_5H_5), 2.13 (s, 15H; C_5Me_5), 2.05 (s, 15H; C_5Me_5), 2.04 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 122.7 (C_5Me$_5$), 121.0 (br., C_5Me$_5$), 116.0 (C_5H_5), 12.9, 12.4 (C_5*Me*$_5$). Anal. Calcd for $C_{38.5}H_{56}Cl_2N_4Ti_3Zr$ (M_w = 880.61): C 52.51, H 6.41, N 6.36. Found: C 52.28, H 6.03, N 6.37.

Synthesis of [(η^5-C_5H_5)Zr{(μ_3-N)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-N)}] (10). A 100 mL Schlenk flask was charged with **9**·0.5C_7H_8 (0.50 g, 0.57 mmol), [Li(CH_2SiMe_3)] (0.11 g, 1.17 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 30 min to give a green solution and a white fine solid. After filtration, the volatile components of the solution were removed under reduced pressure to afford **10** as a green solid (0.34 g, 79%).

IR (KBr, cm^{-1}): $\tilde{\nu}$ 2908 (s), 2856 (s), 1646 (w), 1494 (w), 1434 (m), 1374 (m), 1259 (w), 1009 (m), 777 (vs), 729 (m), 643 (vs), 607 (vs), 447 (m), 425 (vs). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 6.16 (s, 5H; C_5H_5), 2.06 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 119.2 (C_5Me_5), 111.1 (C_5H_5), 12.1 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{35}H_{50}N_4Ti_3Zr$ (M_w = 761.62): C 55.19, H 6.62, N 7.36. Found: despite numerous attempts, low values for carbon were obtained, *e.g.*, C 52.73, H 6.10, N 7.09.

Reaction of 9 with one equivalent of [Na(C_5H_5)] in an NMR tube scale experiment. A 5 mm valved NMR tube was charged with **9**·0.5C_7H_8 (0.010 g, 0.011 mmol), [Na(C_5H_5)] (0.001 g, 0.011 mmol), and benzene-d_6 (1.00 mL). The reaction course was monitored by NMR spectroscopy. After 4 days at room temperature, the spectra showed complete consumption of **9** and complex [(η^5-C_5H_5)$_2$ClZr{(μ_3-N)Ti_3(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (**11**) was characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, the ^{1}H NMR spectrum of the resultant orange solution revealed minor resonance signals (*ca.* 13%) attributable to complex **10**. The solution was filtered to eliminate a fine white solid, and was heated at 70 ºC for 3 days to give a dark red solution. Analysis of the solution by ^{1}H NMR spectroscopy showed it to be a mixture of [(η^5-C_5H_5)ClZr{(μ_3-N)$_2$(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (**12**), complex **10** (≈ 16%), and C_5H_6.

NMR data for [(η^5-C_5H_5)$_2$ClZr{(μ_3-N)Ti_3(η^5-C_5Me_5)$_3$(μ-NH)$_2$(μ_3-N)}] (**11**): ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 14.05 (s br., 2H; NH), 6.11 (s, 10H; C_5H_5), 2.12 (s, 30H; C_5Me_5), 1.88 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 118.1, 117.2 (C_5Me_5), 113.5 (C_5H_5), 12.9, 12.1 ($C_5\mathit{Me}_5$).

NMR data for [(η^5-C_5H_5)ClZr{(μ_3-N)$_2$(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (**12**): ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 13.57 (s br., 1H; NH), 6.30 (s, 5H; C_5H_5), 2.10 (s, 15H; C_5Me_5), 1.97

(s, 30H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 119.5, 119.0 (C_5Me_5), 114.2 (C_5H_5), 12.1, 11.1 ($C_5\mathit{Me}_5$).

Synthesis of [(η^5-C_5H_5)Mg(μ-Cl)$_2$(η^5-C_5H_5)Zr{(μ_4-N)(μ_3-N)(μ_3-NH)Ti_3(η^5-C_5Me_5)$_3$(μ_3-N)}] (13). A 100 mL ampule (Teflon stopcock) was charged with **2** (0.30 g, 0.37 mmol), [$Mg(C_5H_5)_2$] (0.12 g, 0.78 mmol), and toluene (20 mL). The reaction mixture was stirred at 60 ºC for 20 h. After filtration, the volatile components of the solution were removed under reduced pressure. The resultant deep red solid was washed with hexane (10 mL) and vacuum-dried to afford **13** (0.31 g, 91%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3331 (w), 3091 (w), 2907 (s), 2857 (s), 2723 (w), 1493 (w), 1443 (m), 1376 (s), 1120 (w), 1066 (w), 1011 (s), 803 (vs), 771 (vs), 738 (vs), 712 (vs), 675 (vs), 664 (vs), 632 (vs), 612 (vs), 538 (s), 470 (w), 427 (m). ^1H NMR (300 MHz, C_6D_6, 20 ºC): δ 11.04 (s br., 1H; NH), 6.75 (s, 5H; C_5H_5), 6.19 (s, 5H; C_5H_5), 2.13 (s, 15H; C_5Me_5), 2.02 (s, 15H; C_5Me_5), 1.91 (s, 15H; C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 ºC): δ 120.7, 120.5, 119.7 (C_5Me_5), 114.9 (C_5H_5), 107.3 (C_5H_5), 12.9, 12.85, 12.83 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{40}H_{56}Cl_2MgN_4Ti_3Zr$ (M_w = 922.93): C 52.05, H 6.12, N 6.07. Found: C 52.03, H 6.10, N 6.06.

Synthesis of [K(μ-Cl)$_3$Zr{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (14). A 100 mL amber stained Schlenk flask was charged with **2** (0.40 g, 0.50 mmol), [$K(C_5Me_5)$] (0.087 g, 0.50 mmol), and toluene (20 mL). The reaction mixture was stirred at room temperature for 24 h to give an abundant green solid and a green solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **14** as a blue-green powder (0.30 g, 71%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3333 (m), 2906 (vs), 2857 (vs), 2724 (w), 1494 (m), 1431 (s), 1376 (vs), 1260 (w), 1066 (w), 1025 (m), 915 (w), 800 (s), 729 (vs), 694 (vs), 612 (s), 509 (w), 464 (m), 434 (m). ^1H NMR (300 MHz, C_6D_6, 20 ºC): δ 10.3 (s br., $\Delta\nu_{1/2}$ = 24 Hz; C_5Me_5).

Anal. Calcd (%) for $C_{30}H_{47}Cl_3KN_4Ti_3Zr$ (M_w = 844.00): C 42.69, H 5.61, N 6.64. Found: C 42.06, H 5.75, N 5.99. The effective magnetic moment of **14** was determined to be 1.97 μ_B (based on a unit formula of $C_{30}H_{47}Cl_3KN_4Ti_3Zr$) on a C_6D_6 solution.

Synthesis of [(18-crown-6)K(μ-Cl)$_3$Zr{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (15). A 100 mL ampule (Teflon stopcock) was charged with **14** (0.30 g, 0.36 mmol), 18-crown-6 (0.094 g, 0.36 mmol), and toluene (40 mL). The reaction mixture was stirred at 80 ºC for 2 days to give a green solution and a fine green solid. The solid was eliminated by filtration and the volatile components of the solution were removed under reduced pressure to afford **15** as a blue-green solid (0.25 g, 63%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3338 (w), 3230 (w), 2900 (s), 1495 (w), 1474 (w), 1453 (m), 1376 (m), 1352 (s), 1284 (w), 1251 (m), 1115 (vs), 1028 (w), 964 (s), 841 (m), 800 (m), 732 (m), 696 (m), 675 (m), 619 (w), 467 (w), 431 (w). ^{1}H NMR (300 MHz, C_6D_6, 20 ºC): δ 10.6 (s br., $\Delta\nu_{1/2}$ = 73 Hz, 15H; C_5Me_5), 10.2 (s br., $\Delta\nu_{1/2}$ = 61 Hz, 30H; C_5Me_5), 3.3 (s br., $\Delta\nu_{1/2}$ = 9 Hz, 24H; OCH_2CH_2O). Anal. Calcd (%) for $C_{42}H_{71}Cl_3KN_4O_6Ti_3Zr$ (M_w = 1108.32): C 45.51, H 6.46, N 5.06. Found: C 46.04, H 6.81, N 5.28. The effective magnetic moment of **15** was determined to be 2.01 μ_B (based on a unit formula of $C_{42}H_{71}Cl_3KN_4O_6Ti_3Zr$) on a C_6D_6 solution.

Synthesis of [K(crypt-222)][Cl$_3$Zr{(μ$_3$-N)(μ$_3$-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ$_3$-N)}] (16). A 100 mL Schlenk flask was charged with **14** (0.20 g, 0.24 mmol), crypt-222 (0.099 g, 0.26 mmol), and toluene (20 mL). The reaction mixture was stirred at ambient temperature for 24 h to give a green solid and a green solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **16** as a blue-green powder (0.21 g, 72%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3338 (w), 2966 (m), 2896 (s), 2815 (s), 1478 (m), 1445 (m), 1375 (m), 1359 (s), 1293 (m), 1260 (m), 1131 (s), 1100 (vs), 1028 (w), 950 (s), 932 (m), 830 (w), 800 (m), 751 (w), 695 (w), 665 (w), 621 (w), 561 (w), 524 (w), 428 (w). ^{1}H NMR (300 MHz, C_5D_5N, 20 ºC): δ 10.9 (s br., $\Delta\nu_{1/2}$ = 75 Hz, 15H; C_5Me_5), 10.2 (s br., $\Delta\nu_{1/2}$ = 66 Hz, 30H; C_5Me_5), 3.40 (s, 12H; OCH_2CH_2O), 3.35 (t, ^3J(H,H) = 4.5 Hz, 12H; OCH_2CH_2N), 2.34 (t, ^3J(H,H) = 4.5 Hz, 12H; OCH_2CH_2N). Anal. Calcd (%) for $C_{48}H_{83}Cl_3KN_6O_6Ti_3Zr$ (M_w = 1220.49): C 47.24, H 6.85, N 6.89. Found: C 47.09, H 6.55, N 6.17. The effective magnetic moment of **16** was determined to be 1.95 μ_B (based on a unit formula of $C_{48}H_{83}Cl_3KN_6O_6Ti_3Zr$) on a C_5D_5N solution.

X-ray structure determination of 2, 8, 13 and 15. Crystals of complex **2** were obtained by slow diffusion of a tetrahydrofuran solution of $[ZrCl_4(thf)_2]$ in a toluene solution of **1**. Green crystals of **8** and red crystals of compound **13**·C_7H_8 were grown from toluene solutions at -30 ºC. Green crystals of **15**·7C_6D_6 were obtained by slow cooling at room temperature of a benzene-d_6 solution of the compound heated at 80 ºC in an NMR tube. The crystals were removed from the Schlenk flasks or the NMR tube and covered with a layer of a viscous perfluoropolyether (Fomblin Y). A suitable crystal was selected with the aid of a microscope, mounted on 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. 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 (see page 44).

The structures were solved, using the WINGX package,[42] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[43] In the crystallographic studies of compounds **2** and **8**, all non-hydrogen atoms were anisotropically refined, whereas all the hydrogen atoms were positioned geometrically and refined by using a riding model. In addition, one of the two imido hydrogen atoms in complex **2** was statistically distributed over two nitrogen atoms (N(13) and N(23)) linked to the zirconium atom (50% of occupancy).

Crystals of **13** contained two independent molecules in the asymmetric unit, and they showed some differences on their lengths and angles (see Table S2 in the ESI†). Moreover this compound crystallized with a molecule of toluene per cube. All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were positioned and refined by using a riding model. DFIX and DELU instructions were used for one of the toluene molecules (C(110)-C(116)).

On the other hand, compound **15** crystallized with seven molecules of benzene (two molecules and a third per asymmetric unit), which were found in the difference Fourier map, but it was not possible to obtain a chemically sensible model for one of them, so the Squeeze[44] procedure was used to remove its contribution to the structure factors. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined by using a riding model, with a 2/3 factor of occupancy for the imido hydrogen. Furthermore, the benzene molecules were treated with DFIX constraints.

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Electronic supplementary information (ESI) available: Kinetic data and analyses for the dynamic NMR spectroscopy study for compound **9**, selected lengths and angles for the two independent molecules of compound **13**, and a view along the a axe of the crystal lattice of compound **15**. CCDC 1415001-1415004. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dtxxxxxx.

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Table 5 Experimental data for the X-ray diffraction studies on complexes **2**, **8**, **13** and **15**.

	2	**8**	**13**·C_7H_8	**15**·$7C_6D_6$
Formula	$C_{30}H_{47}Cl_3N_4Ti_3Zr$	$C_{36}H_{63}N_5Si_2Ti_4$	$C_{47}H_{64}Cl_2MgN_4Ti_3Zr$	$C_{84}H_{113}Cl_3KN_4O_6Ti_3Zr$
M_r	804.99	813.69	1015.15	1655.15
T [K]	200(2)	200(2)	200(2)	200(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Cryst syst	Monoclinic	Triclinic	Monoclinic	Trigonal
Space group	$P2_1/n$	P–1	$P2_1/c$	P–3
a [Å]; α [º]	11.065(3)	11.597(1); 81.30(1)	23.940(5)	16.515(2)
b [Å]; β [º]	17.559(4); 93.44(4)	11.772(1); 87.72(1)	18.507(2); 97.63(1)	16.515(2)
c [Å]; γ [º]	18.813(3)	17.319(2); 66.10(1)	21.328(3)	17.886(3)
V [Å^3]	3649(1)	2136.1(3)	9366(3)	4225(1)
Z	4	2	8	2
ρ_{calcd} [g cm^{-3}]	1.466	1.265	1.440	1.301
$\mu_{MoK\alpha}$ [mm^{-1}]	1.155	0.806	0.874	0.589
F(000)	1648	860	4208	1738
Cryst size [mm^3]	0.17 × 0.13 × 0.12	0.36 × 0.36 × 0.16	0.27 × 0.24 × 0.17	0.27 × 0.25 × 0.12
θ range (º)	5.04 to 27.51	3.02 to 27.50	3.00 to 27.51	3.07 to 27.51
Index ranges	–14 to 14, –22 to 22, 0 to 24	–15 to 14,–15 to 15, –22 to 22	0 to 31, –24 to 24, –27 to 27	–21 to 21, –21 to 20, –23 to 21
Reflns collected	80915	44784	198900	51159
Unique data	8322 [R(int) = 0.148]	9792 [R(int) = 0.072]	21487 [R(int) = 0.095]	6488 [R(int) = 0.115]
Obsd data [$I>2\sigma(I)$]	4934	7022	11234	5156
Goodness–of–fit on F^2	0.986	1.036	1.011	1.150
Final R^a indices [I>2σ(I)]	R1 = 0.054, wR2 = 0.114	R1 = 0.049, wR2 = 0.124	R1 = 0.055, wR2 = 0.126	R1 = 0.066, wR2 = 0.119
R^a indices (all data)	R1 = 0.114, wR2 = 0.134	R1 = 0.082, wR2 = 0.139	R1 = 0.140, wR2 = 0.160	R1 = 0.091, wR2 = 0.128
Largest diff. peak/hole [e·Å^{-3}]	0.888 and –0.710	0.702 and –0.525	0.859 and –0.738	0.372 and –0.498

[a] $R1=\Sigma||F_0|-|F_c||/[\Sigma|F_0|]$, $wR2=\{[\Sigma w(F_0^2-F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$.