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# Studies on the chemical reduction of polynuclear titanium(IV) nitrido complexes†

Jorge Caballo, Adrián Calvo-Molina, Sergio Claramonte, Maider Greño, Adrián Pérez-Redondo and Carlos Yélamos*

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The redox chemistry of cube-type titanium(IV) nitrido complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $\eta^5$-$C_5Me_5$ (**1**), $N(SiMe_3)_2$ (**2**), $\eta^5$-$C_5H_4SiMe_3$ (**3**), and $\eta^5$-$C_5H_5$ (**4**)) was investigated by electrochemical methods and chemical reactions. Cyclic voltammetry studies indicate that **1–4** undergo a reversible one-electron reduction at *ca.* −1.8 V *vs.* ferrocenium/ferrocene. Thus, complex **1** reacts with sodium sand in tetrahydrofuran to produce the highly reactive ionic compound $[Na(thf)_6][\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**5**). The treatment of complexes **1–4** in toluene with one equivalent of $[K(C_5Me_5)]$ in the presence of macrocycles (L) leads to $C_{10}Me_{10}$ and the formation of more stable derivatives $[K(L)][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $\eta^5$-$C_5Me_5$, L = 18-crown-6 (**6**), crypt-222 (**7**); R = $N(SiMe_3)_2$, L = 18-crown-6 (**8**), crypt-222 (**9**); R = $\eta^5$-$C_5H_4SiMe_3$, L = 18-crown-6 (**10**), crypt-222 (**11**); R = $\eta^5$-$C_5H_5$, L = crypt-222 (**12**)). However, the analogous reaction of **4** with $[K(C_5Me_5)]$ and 18-crown-6 affords $[\{(18\text{-crown-6})K\}_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_5)][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}N)_4]$ (**13**) *via* abstraction of one cyclopentadienide group from a putative intermediate $[(18\text{-crown-6})K(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_5)Ti_4(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)_4]$. In contrast to the cube-type nitrido systems **1–4**, the cyclic voltammogram of the trinuclear imido-nitrido titanium(IV) complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**14**) does not reveal any reversible redox event and **14** readily reacts with $[K(C_5Me_5)]$ to afford $C_5Me_5H$ and the diamagnetic derivative $[\{K(\mu_4\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**15**). The treatment of **15** with two equiv. of 18-crown-6 polyethers produces the molecular species $[(L)K\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (L = 18-crown-6 (**16**), dibenzo-18-crown-6 (**17**)). Complex **17** further reacts with one equiv. of dibenzo-18-crown-6 to yield the ion-separated compound $[K(\text{dibenzo-18-crown-6})_2][Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}N)(\mu\text{-}NH)_2]$ (**18**) similar to the ion pair $[K(\text{crypt-222})][Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}N)(\mu\text{-}NH)_2]$ (**19**) obtained in the treatment of **15** with cryptand-222.

## Introduction

Polynuclear transition-metal nitrido complexes are an important type of molecule with a wide structural diversity and singular bonding situations.[1] While the nitrido ligand usually behaves as a terminal functionality (M≡N) in the complexes of mid transition metals (groups 6–8) in high oxidation states,[2] early transition metal (groups 4 and 5) species have a strong tendency to form dinuclear or polynuclear aggregates with nitrido moieties ($\mu_n$-N) shared between two or more metal centers. In addition, the bridging nitrido ligand in these polynuclear species is capable of displaying diverse coordination modes in several structural variations.[1c] Well-defined multimetallic molecular compounds with $\mu_n$-nitrido groups can shed light on the bridging modes of the chemisorbed nitrogen atoms on the metal surfaces of heterogeneous catalytic systems such as the Haber–Bosch process for the synthesis of ammonia.[3]

One of the most common synthetic routes to early transition metal polynuclear nitrido derivatives is the treatment of high-valent organometallic complexes with ammonia.[4–8] The resultant multimetallic species usually contain nitrido ($\mu_n$-N), imido ($\mu_n$-NH), or amido ($\mu_n$-$NH_2$) ligands bridging several metal centers. The presence of bulky ancillary ligands (*e.g.*, cyclopentadienyl, alkoxido) strongly bonded to the metals is crucial to isolating discrete and soluble molecular metal nitrides. These compounds contain metal elements in their highest possible oxidation state held together by strong interactions with the bridging ligands. Several theoretical studies on these complexes indicate that the lowest-lying unoccupied orbitals are metal-based and the compounds are able to

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*Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, 28805 Alcalá de Henares-Madrid, Spain. E-mail: carlos.yelamos@uah.es*

† Electronic supplementary information (ESI) available: Cyclic voltammograms of complexes **1**, **3**, **4**, and **14**. Experimental crystallographic data of complexes **5**, **11**, **13**, and **17**. Perspective view of the crystal structure of compounds **5**, **11**, and **13**. Tables for selected lengths and angles of the crystal structures of **5**, **11**, **13**, and **17**. EPR spectra for complex **7**. Selected $^1H$ and $^{13}C\{^1H\}$ NMR spectra. CCDC 2309190–2309193. For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d3dt04241c**

undergo reduction without sacrificing cluster bonding.[8a,9–12] For instance, density functional theory (DFT) calculations on the model titanium(IV) cubane complex $[\{Ti(\eta^5\text{-}C_5H_5)\}_4(\mu_3\text{-}N)_4]$ show that the LUMOs are bonding combinations of metal d orbitals and the compound has a high value (2.14 eV) of adiabatic electron affinity.[10] Calculations for the isostructural vanadium(IV) model compound $[\{V(\eta^5\text{-}C_5H_5)\}_4(\mu_3\text{-}N)_4]$, analogous to $[\{V(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ isolated by Bottomley and co-workers in the reduction of $[\{V(\eta^5\text{-}C_5Me_5)Cl\}_2(\mu\text{-}N)_2]$ with sodium,[13] indicate that the four metal electrons occupy molecular orbitals which show a certain vanadium–vanadium overlap.[10]

Interestingly, many di- and polynuclear complexes with bridging nitrido ligands have been prepared by dinitrogen fixation *via* splitting of the triple bond by low-valent species.[14] In particular, Hou and co-workers have described the formation of tri- and tetranuclear titanium compounds with $\mu_3$-N nitrido and $\mu_n$-NH imido bridging ligands by cleavage of dinitrogen on multimetallic polyhydride complexes bearing the $\eta^5$-$C_5Me_4SiMe_3$ supporting ligand.[15] The hydride ligands in these complexes serve as electron and proton sources for $N_2$ splitting and partial hydrogenation of the resultant nitrido units with no need for external reductants or proton sources.[16] In a related work, we reported the isolation of a paramagnetic methylidene–methylidyne–nitrido cube-type complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}CH)(\mu_3\text{-}CH_2)(\mu_3\text{-}N)_2]$ by the reaction of $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ with forming gas ($H_2/N_2$ mixture) under ambient conditions.[17] These monocyclopentadienyltitanium nitrido species derived from $N_2$ contain titanium(IV) or titanium(III) centers and their structures resemble those of the trinuclear imido-nitrido $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[4] and the tetranuclear nitrido $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$[5] complexes prepared previously by the reaction of $[Ti(\eta^5\text{-}C_5Me_5)R_3]$ (R = Me, $NMe_2$) with ammonia.

Over two decades, we have been investigating the rational synthesis of a family of heterometallic nitrido complexes by incorporation of diverse metal complex fragments into the incomplete cube-type structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$.[1c] Remarkably, complexes with cube-type $[MTi_3N_4]$ cores where M is an electron-rich metal center (*e.g.*, $Mo^0$, $Ir^I$) are stabilized by sharing of the electrons of the metal with the $Ti_3$ system.[11,18] Within an extensive study of the reactivity of these polynuclear systems, a few examples of reduced heterometallic species have been unexpectedly isolated. For instance, the formation of cube-type species $[(RCC)Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}NCCR)\}]$ is accompanied by a two-electron reduction of the $Ti_3$ core according to DFT calculations.[19] Later, we have described one-electron reduced species by the reaction of trichloride complexes $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ and $[Cl_3Zr\{(\mu_3\text{-}N)(\mu_3\text{-}NH)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ with potassium pentamethylcyclopentadienide $[K(C_5Me_5)]$.[20,21] Theoretical calculations on the electronic structure of yttrium–titanium complexes indicated that the additional electron is delocalized among the three titanium atoms.[20]

Herein we report a systematic study on the electrochemical and chemical reduction of cube-type titanium(IV) nitrido complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $\eta^5$-$C_5Me_5$ (**1**), $N(SiMe_3)_2$ (**2**), $\eta^5$-$C_5H_4SiMe_3$ (**3**), and $\eta^5$-$C_5H_5$ (**4**)). The reduced species $[K(18\text{-crown-}6)][\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**6**) derived from **1** was previously isolated as an intermediate in the preparation of the paramagnetic imido–nitrido derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$.[22] In addition, we have evaluated the possibility of reducing the trinuclear imido–nitrido titanium(IV) complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**14**).

## Results and discussion

### One-electron reduction of cube-type nitrido complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$

The redox chemistry of the cube-type titanium nitrido complexes was initially investigated by electrochemical methods. Cyclic voltammograms of complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $\eta^5$-$C_5Me_5$ (**1**), $\eta^5$-$C_5H_4SiMe_3$ (**3**), and $\eta^5$-$C_5H_5$ (**4**)) were obtained under an argon atmosphere in tetrahydrofuran solutions at 22 °C (see Fig. 1 and S1† for **1**, and Fig. S2 and S3† for **3** and **4** in the ESI,† respectively). The cyclic voltammograms revealed a reversible one-electron redox event at $E_{1/2} = -1.84$ V for **1**, at $E_{1/2} = -1.80$ V for **3**, and at $E_{1/2} = -1.86$ V for **4** *vs.* ferrocenium/ferrocene ($Fc^+/Fc$). No redox waves due to other chemically reversible redox events were observed even at a very low potential of about −3.50 V, where reductive decomposition of tetrahydrofuran began in our setup. For comparison, dinuclear imido titanium(IV) complexes $[\{Ti(\eta^5\text{-}C_5H_5)X\}_2(\mu\text{-}NR)_2]$ (X = Cl, Me; R = *t*Bu, Ph, 3,5-$(CF_3)_2C_6H_3$) exhibited reversible one electron redox waves between −0.72 and −1.42 V *vs.* $Fc^+/Fc$ with no further reduction observable.[23] Likewise, the monopentamethylcyclopentadienyltitanium(IV) analogue $[\{Ti(\eta^5\text{-}C_5Me_5)_3Cl\}_2\{\mu\text{-}NC_6H_3(CF_3)_2\}_2]$ displayed one reversible redox process at $E_{1/2} = -1.07$ V and its reaction with the mild reducing agent $[Co(\eta^5\text{-}C_5H_5)_2]$ ($E \approx -1.3$ V)[24] afforded the mixed-valence Ti(III)–Ti(IV) species $[Co(\eta^5\text{-}C_5H_5)_2][\{Ti(\eta^5\text{-}C_5Me_5)Cl\}_2\{\mu\text{-}NC_6H_3(CF_3)_2\}_2]$.[23b] Similarly, the cyclic voltammogram of the dinuclear tungsten(VI) nitrido complex $[\{W(CH_2tBu)(OAr)_2\}_2(\mu\text{-}N)_2]$ (Ar = 2,6-$i$$Pr_2C_6H_3$) revealed a reversible redox

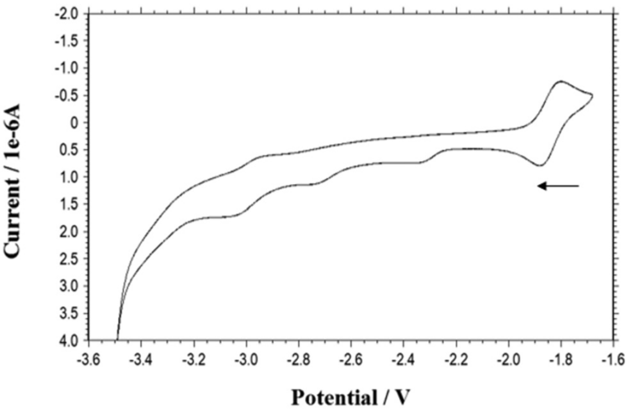
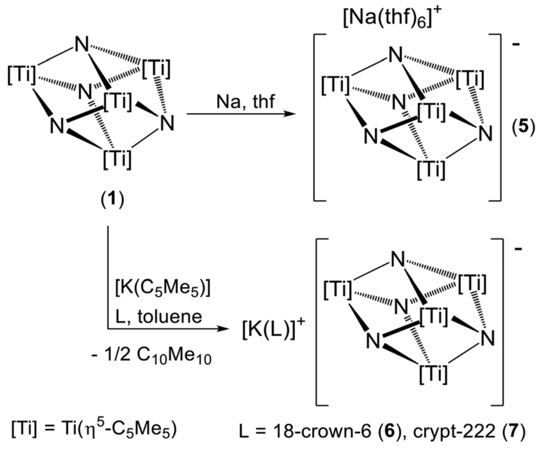


Fig. 1 Cyclic voltammogram of $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**1**) in thf/0.1 M $[N(nBu)_4][PF_6]$ *versus* $Fc^+/Fc$ at 50 mV $s^{-1}$ scan rate at 22 °C.

event at $E_{1/2}$ = −1.08 V and chemical reduction of this complex was accomplished with $[Co(\eta^5\text{-}C_5H_5)_2]$.[25] Furthermore, the trinuclear tantalum(V) nitrido compound $[\{Ta(\eta^5\text{-}C_5Me_5)Me\}_3(\mu\text{-}N)_3]$ showed a reversible reduction wave at $E \approx -2.0$ V and was reduced with a Na/K alloy in diethyl ether to yield $[K(OEt_2)_n][\{Ta(\eta^5\text{-}C_5Me_5)Me\}_3(\mu\text{-}N)_3]$.[8a] Lastly, the tetranuclear nitrido vanadium(IV) complex $[\{V(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ structurally analogous to **1** can be reduced electrochemically with a reversible reduction wave at +0.16 V, although no chemical reduction of the complex was reported.[13]

In agreement with the electrochemical studies, compounds **1–4** did not react with $[Co(\eta^5\text{-}C_5H_5)_2]$ and stronger reductants such as sodium ($E \approx -3.04$ V)[24] and $[K(C_5Me_5)]$ were required to obtain one-electron reduced species. The treatment of complex $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**1**) with an excess of fine sodium sand (10 equiv.) in tetrahydrofuran at ambient temperature led to a dark purple solution (Scheme 1). Slow diffusion of toluene into this solution gave dark purple crystals of $[Na(thf)_6][\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (**5**) in 66% yield. Crystals of **5** exhibited good solubility in tetrahydrofuran-$d_8$ but were insoluble in benzene-$d_6$ and pyridine-$d_5$ solvents, in which the release of tetrahydrofuran molecules took place as observed in the $^1$H NMR spectra. In addition, in the solid state and under vacuum at room temperature, complex **5** lost all tetrahydrofuran molecules to give a dark solid that can be formulated as $Na[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ according to elemental analyses and the absence of absorptions due to coordinated tetrahydrofuran ligands (1052 and 901 cm$^{-1}$) in the IR spectrum (KBr). This solid readily dissolves in tetrahydrofuran-$d_8$ to give a dark purple solution, and the $^1$H NMR spectrum shows a single broad resonance at $\delta$ = 9.2 ($\Delta\nu_{1/2}$ = 67 Hz) similar to that observed in a solution of crystals of **5** in the same solvent. These NMR data are consistent with a $T_d$ symmetry for the $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]^-$ anion in solution. The magnetic moment measurement by the Evans method for solutions of compound **5** in tetrahydrofuran-$d_8$ gave a $\mu_{eff}$ value of $1.68\mu_B$ owing to an unpaired electron in the complex.



**Scheme 1** Reactions of **1** with Na and $[K(C_5Me_5)]$.

The crystal structure of **5** consists of well-separated $[Na(thf)_6]^+$ and $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]^-$ ions (Fig. S6†). The anionic fragment shows an almost perfect $[Ti_4N_4]$ cube core with the Ti–N–Ti and N–Ti–N angles very close to 90° (Fig. 2). The average Ti–N (1.952(4) Å) and Ti–Ti (2.793(4) Å) separation distances in **5** are only slightly longer than those found in the molecular structure of complex **1** (1.938(7) and 2.783(2) Å, respectively).[5] Most likely, the additional electron is delocalized among the titanium atoms in a fashion similar to those determined by DFT calculations in the electronic structures of heterometallic cube-type complexes $[(RCC)Zn\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}NCCR)\}]$[19] and $[Cl_3Y\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]^-$.[20]

The nitrido salt **5** was found to be extremely sensitive to H-atom sources such as moisture and organic solvents, precluding the isolation of the compound in its pure form according to elemental analysis. Furthermore, minor resonance signals for other paramagnetic and diamagnetic species in solution were always detected in the $^1$H NMR spectra of **5**. For instance, broad resonances attributable to the paramagnetic imido–nitrido derivative $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_3(\mu_3\text{-}NH)]$[22] were typically observed in the $^1$H NMR spectra and a weak $\nu_{NH}$ vibration at 3333 cm$^{-1}$ assignable to that compound was identified in the IR spectra. The impurities in the spectra were reduced when the synthesis of **5** was performed in tetrahydrofuran-$d_8$, suggesting that one of the sources of the H atoms is the solvent.

To obtain more stable reduced species from **1**, we turned our attention to potassium pentamethylcyclopentadienide which we had previously used as a one-electron reducing reagent.[20–22] While $[M(C_5Me_5)]$ (M = Li, K) compounds are rare reducing agents in organometallic chemistry,[24] several examples of metal reduction have been reported in attempts to prepare pentamethylcyclopentadienyl metal complexes.[26] The one-electron oxidation of the $C_5Me_5^-$ anion involves the generation of $(C_5Me_5)^{\bullet}$ radicals which are known to dimerize

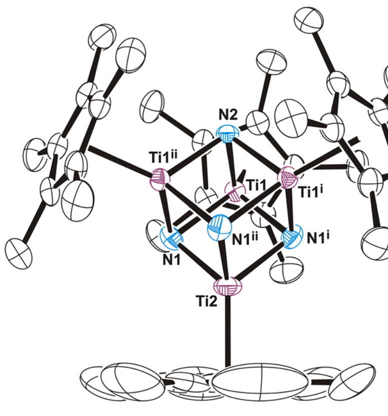
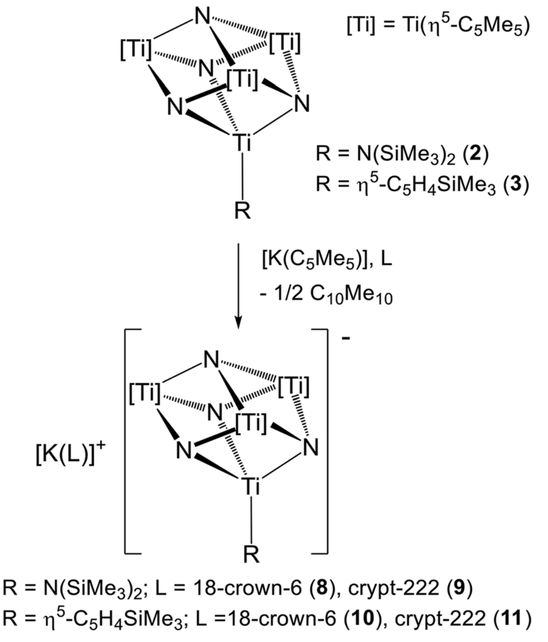


**Fig. 2** Perspective view of the anion of compound **5** (thermal ellipsoids at the 50% probability level). Hydrogen atoms of the $\eta^5\text{-}C_5Me_5$ ligands are omitted for clarity. Selected average lengths (Å) and angles (°): Ti–N 1.952(4), Ti–Ti 2.793(4), Ti–N–Ti 91.3(2), N–Ti–N 88.6(2). Symmetry code: (i) $z, x, y$; (ii) $y, z, x$.

rapidly and irreversibly. The organic $(C_5Me_5)_2$ byproduct is a liquid at room temperature, and it can be easily separated from the poorly soluble reduced inorganic species in hydrocarbon solvents.

The treatment of **1** with one equivalent of $[K(C_5Me_5)]$ in toluene in the presence of one equivalent of 18-crown-6 or cryptand-222 led to the precipitation of the ionic derivatives $[K(L)][\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ (L = 18-crown-6 (**6**),[22] crypt-222 (**7**)) and a solution of $C_{10}Me_{10}$ (Scheme 1).[27] While the reaction was observed at room temperature, the syntheses of complexes **6** and **7** were carried out at 110 °C to ensure complete consumption of **1**, which is nearly insoluble in toluene. It is noteworthy that the presence of the macrocyclic ligand for stabilizing $K^+$ is essential because treatments in toluene or tetrahydrofuran attempted without these polyethers showed no reaction and the starting materials were recovered unaltered. This could be related both to the low solubility of potassium pentamethylcyclopentadienide in those solvents and to the presence of aggregates in solution which are hard to oxidize or solvate.[28] Most likely, the macrocycles break up these oligomers in solution to give more soluble well-separated $C_5Me_5^-$ ions with higher reduction potential.

In a similar fashion, treatment of cube-type nitrido complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $N(SiMe_3)_2$ (**2**) and $\eta^5$-$C_5H_4SiMe_3$ (**3**)) with one equivalent of $[K(C_5Me_5)]$ in the presence of one equivalent of 18-crown-6 or cryptand-222 led to the precipitation of the ionic derivatives $[K(L)][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ (R = $N(SiMe_3)_2$, L = 18-crown-6 (**8**), and crypt-222 (**9**); R = $\eta^5$-$C_5H_4SiMe_3$, L = 18-crown-6 (**10**), and crypt-222 (**11**)) (Scheme 2). Compounds **8–11** were prepared in toluene at room temperature since the titanium precursors **2** and **3** are soluble in aromatic hydrocarbon solvents.



**Scheme 2** Reactions of complexes **2** and **3** with $[K(C_5Me_5)]$.

Complexes **6–11** were isolated in 48–83% yields as dark purple or green solids, which are not soluble in aromatic hydrocarbon solvents but exhibit good solubility in pyridine-$d_5$. Compounds **6–11** readily react with chloroform-$d_1$ to give green solutions of the starting materials **1–3** and the corresponding free macrocycles according to $^1H$ NMR spectroscopy. The IR spectra (KBr) of **6–11** show several absorptions in the range 1359–832 $cm^{-1}$ for the macrocyclic polyethers.[29] The $^1H$ NMR spectra of compounds **6–11** in pyridine-$d_5$ reveal one broad signal at $\delta = 10.7\text{–}9.4$ ($\Delta\nu_{1/2} = 59\text{–}89$ Hz), attributable to the $\eta^5$-$C_5Me_5$ groups and sharp resonances for one 18-crown-6 or cryptand-222 ligand. In addition, the $^1H$ NMR spectra of complexes **8** and **9** display one broad resonance at $\delta = 1.22$, assignable to the $N(SiMe_3)_2$ ligand. Similarly, the spectra of compounds **10** and **11** show a broad signal at $\delta = 0.77$ for the trimethylsilyl group of the $C_5H_4SiMe_3$ ligand but resonances for the $C_5H_4$ protons could not be detected likely because of their broad nature. These NMR data of complexes **8–11** are consistent with a $C_{3v}$ symmetry for the $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]^-$ (R = $N(SiMe_3)_2$, $\eta^5$-$C_5H_4SiMe_3$) anion in solution. Interestingly, $^1H$ NMR spectroscopy analyses of samples containing 1 : 1 mixtures of pairs of complexes **2**/**9** and **3**/**11** in pyridine-$d_5$ at room temperature show one set of signals with averaged chemical shifts. This is consistent with a fast electron exchange between the oxidized and reduced forms of the complexes as those studied in detail for iron heterocubane clusters with $[Fe_4S_4]$ and $[Fe_4N_4]$ cores.[30] The magnetic moment measurements by the Evans method for solutions of compounds **6–11** in pyridine-$d_5$ gave $\mu_{eff}$ values of 1.79–1.99$\mu_B$ in good agreement with the presence of an unpaired electron in the complexes. The EPR spectrum of compound **7** in pyridine solution at room temperature was silent. However, the EPR spectrum in a frozen pyridine solution at 93 K (Fig. S10†) shows a broad signal with a $g$ value of 1.996 similar to those previously reported ($g$ = 1.988 and 1.986) for one-electron reduced dinuclear imido-bridged species $[Co(\eta^5\text{-}C_5H_5)_2][\{Ti(\eta^5\text{-}C_5R_5)Cl\}_2\{\mu\text{-}NAr\}_2]$ (R = H, Me; Ar = 3,5-$(CF_3)_2C_6H_3$).[23b]

Dark purple crystals of **11**·$C_6D_6$ were grown by slow cooling at room temperature of a benzene-$d_6$ solution heated at 80 °C. The X-ray crystal structure shows two independent ion pairs of $[K(crypt\text{-}222)]^+$ cations and $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_4SiMe_3)\}(\mu_3\text{-}N)_4]^-$ anions in the asymmetric unit (Fig. S7 and S8†). There are no substantial differences between the ion pairs of **11**, and the structure of one of the anions is shown in Fig. 3. The potassium atoms are encapsulated by the cryptand-222 ligands in the cationic fragments with K–O and K–N bond distances of 2.785(5)–2.855(5) Å and 3.004(7)–3.030(6) Å, respectively. The anionic fragments contain an almost perfect $[Ti_4N_4]$ cube core with Ti–N–Ti (av. 91.3(9)°) and N–Ti–N (av. 88.6(9)°) angles very close to 90°. The average Ti–N (1.93(2) Å) and Ti–Ti (2.77(1) Å) distances in **11** are similar to those found in the anion of compound **5** and in the molecular structures of complexes **1** and **2**.[5,21] Despite many attempts, we were not able to grow suitable crystals of 18-crown-6 compounds **6**, **8** and **10** for X-ray crystal structure determination but most likely the structures contain $[K(18\text{-}crown\text{-}6)]^+$ cations with the potassium

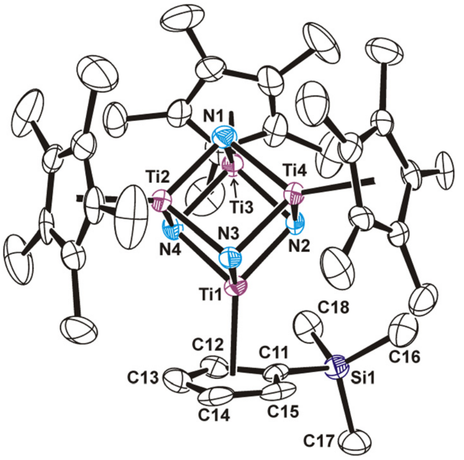
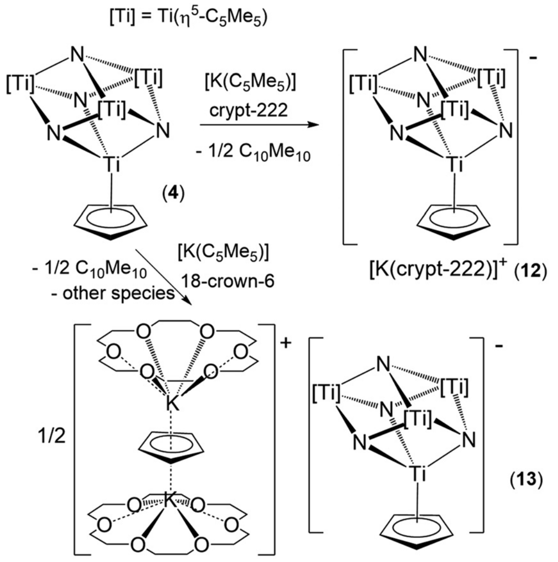


**Fig. 3** Perspective view of one crystallographically independent anion of compound **11** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected average lengths (Å) and angles (°): Ti–N 1.94(2), Ti–Ti 2.77(1), Ti–N–Ti 89.8(2)–93.0(2), N–Ti–N 87.2(2)–90.2(2).



**Scheme 3** Reactions of **4** with $[K(C_5Me_5)]$.

atom oriented toward one of the cyclopentadienyl rings of the $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3R\}(\mu_3\text{-}N)_4]^-$ anions.[31] These K⋯cyclopentadienylp interactions in the solid state can be broken upon dissolving the complexes in pyridine according to a disordered crystal structure of $[K(18\text{-crown-6})(py)_2][\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-}N)_4]$ for dark purple crystals of **6** in pyridine.[22] However, complexes **6**, **8** and **10** in benzene-d$_6$ did not react with an additional equivalent of 18-crown-6 even at high temperatures as determined by $^1$H NMR spectroscopy.

In a fashion similar to the preparation of compounds **6–11**, the reaction of $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}N)_4]$ (**4**) with $[K(C_5Me_5)]$ and cryptand-222 at room temperature gave $[K(\text{crypt-222})][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}N)_4]$ (**12**) in 76% yield (Scheme 3). However, the treatment of **4** with $[K(C_5Me_5)]$ and 18-crown-6 afforded a compound with a cyclopentadienyl inverse sandwich countercation $[\{(18\text{-crown-6})K\}_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_5H_5)][Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)(\mu_3\text{-}N)_4]$ (**13**) in 52% yield. Compounds **12** and **13** were isolated as dark purple solids which are only soluble in pyridine and readily react with chloroform to give the starting material **4** and the free macrocycles. The $^1$H NMR spectra of both compounds in pyridine-d$_5$ showed one broad resonance at $\delta = 10.6$ ($\Delta\nu_{1/2} = 82$ Hz) attributable to the η$^5$-C$_5$Me$_5$ groups but resonance signals for the η$^5$-C$_5$H$_5$ ligand of the anionic fragment were not observed. While the $^1$H NMR spectrum of **12** revealed resonances for one cryptand-222 ligand in the countercation, the spectrum of **13** displayed a singlet at $\delta = 3.43$ for two 18-crown-6 ligands and a sharp singlet at $\delta = 6.50$ for the protons of one cyclopentadienide anion. The paramagnetic nature with an unpaired electron of compounds **12** and **13** was confirmed by the determination of their magnetic effective moments ($\mu_{\text{eff}} = 1.82$ and $1.74\mu_B$, respectively) by the Evans method.

Slow diffusion of a toluene solution of **4** into a toluene solution of $[K(C_5Me_5)]$ and 18-crown-6 at room temperature afforded dark purple crystals of $\mathbf{13}\cdot 2C_7H_8$ suitable for X-ray crystal structure determination. The crystal structure of compound **13** consists of well-separated $[\{(18\text{-crown-6})K\}_2(\mu\text{–}\eta^5\text{:}\eta^5\text{-}C_5H_5)]^+$ and $[Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)(\mu_3\text{-}N)_4]^-$ ions (Fig. S9†). The inverse cyclopentadienyl sandwich cation in **13** contains a C$_5$H$_5$ ring coordinated to two potassium cations which are also bonded to two 18-crown-6 ligands in a fashion similar to other examples in the literature.[31d,32] If a centroid (Ct) is considered for the carbon atoms of the cyclopentadienide ring, the K–Ct (2.846 and 2.856 Å) bond lengths are similar to those found in compounds with $\{K(\eta^5\text{-}C_5H_5)\}$ units such as the polymer $[K(\eta^5\text{-}C_5H_5)]_n$ (K–Ct = 2.816 Å).[33] The anionic fragment of **13** (Fig. 4) contains an almost perfect $[Ti_4N_4]$ cube core with Ti–N (av. 1.935(6) Å) and Ti–Ti (av. 2.770(4) Å) distances essentially identical to those found in the crystal structures of the ionic compounds **5** and **11**. It appears that the structural parameters in

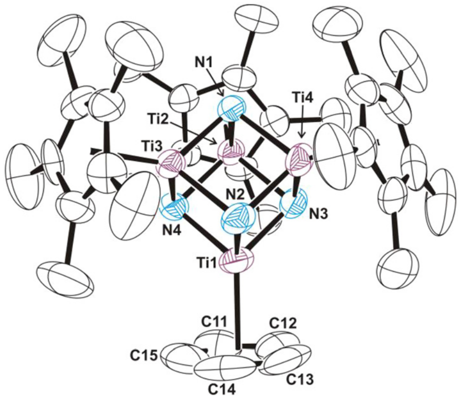


**Fig. 4** Perspective view of the anion of compound **13** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected average lengths (Å) and angles (°): Ti–N 1.935(6), Ti–Ti 2.770(4), Ti–N–Ti 91.4(3), N–Ti–N 88.6(4).

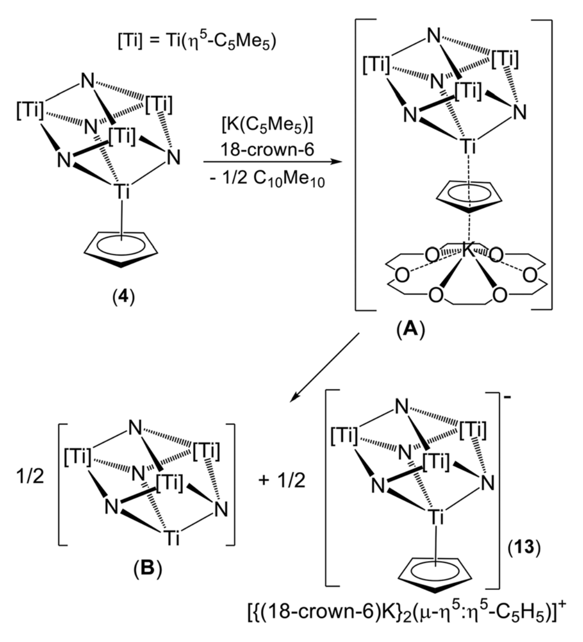
the [$Ti_4N_4$] cores are not significantly affected by the addition of an electron which is delocalized among the titanium atoms.

A plausible proposal for the formation of compound **13** is shown in Scheme 4, which is based on reported studies on the reduction of lanthanide complexes [$Ln(\eta^5$-$C_5H_4SiMe_3)_3$] with potassium in the presence of 18-crown-6 by the Evans group.[31c] The isolation of **13** with the [{(18-crown-6)K}$_2$(μ–$\eta^5$:$\eta^5$-$C_5H_5$)]$^+$ countercation could be related to the instability of the anticipated complex [K(18-crown-6)][{$Ti_4(\eta^5$-$C_5Me_5)_3(\eta^5$-$C_5H_5)$}($\mu_3$-N)$_4$] (**A**) similar to compounds **6–12**. In contrast to cryptand-222, the 18-crown-6 macrocycle is not capable of sequestering the $K^+$ cation, and the [K(18-crown-6)]$^+$ unit may interact with the $\eta^5$-$C_5H_5$ ligand bonded to titanium. Such interaction promotes dissociation of the $C_5H_5^-$ group to generate a neutral [K($\eta^5$-$C_5H_5$)(18-crown-6)] moiety which could react with another equivalent of intermediate **A** to form the ionic compound **13**. Presumably a soluble paramagnetic species [{$Ti_4(\eta^5$-$C_5Me_5)_3$}($\mu_3$-N)$_4$] (**B**) was formed but, despite many attempts, we failed to isolate any derivative from the solution resulting in the formation of **13**. It is noteworthy that compound **13** was isolated in a similar yield when the reaction of **4** with [K($C_5Me_5$)] was performed in the presence of two equivalents of 18-crown-6 polyether.

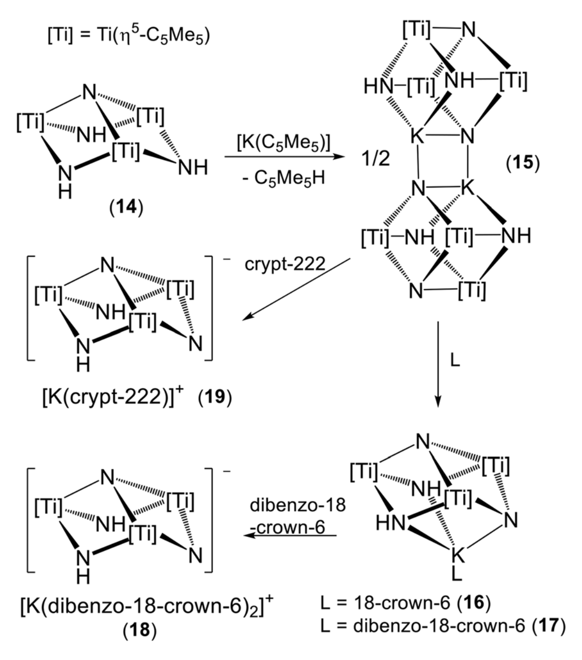
### Attempted reduction of [{Ti($\eta^5$-$C_5Me_5$)(μ-NH)}$_3$($\mu_3$-N)] (14)

The redox chemistry of the imido–nitrido trititanium complex **14** was also investigated by electrochemical methods. The cyclic voltammogram of **14** in a tetrahydrofuran solution at 22 °C did not reveal any reversible redox event but showed two cathodic reduction peaks at −2.86 and −3.00 V *vs.* $Fc^+/Fc$ (Fig. S4 and S5†). When the scan is reversed, a return oxidation peak is observed at −2.17 V. With these results in hand, the chemical reaction of **14** with one equiv. of [K($C_5Me_5$)] in benzene-$d_6$ at room temperature was monitored by NMR spectroscopy (Scheme 5). Immediately, an abundant yellow solid was deposited at the bottom of the NMR tube. Analysis of the supernatant yellow solution by $^1H$ NMR spectroscopy only showed the formation of $C_5Me_5H$ while resonances due to $C_{10}Me_{10}$ were not detected.[27] The yellow solid was isolated by filtration, dissolved in pyridine-$d_5$ and characterized by $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy as the diamagnetic derivative [{K($\mu_4$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$_2$] (**15**). This edge-linked double-cube nitrido complex has been previously synthesized in 57% yield through the reaction of **14** with one equiv. of [K{N(SiMe$_3$)$_2$}].[34]

Treatment of **15** with two equiv. of 18-crown-6 polyethers (L) in toluene at room temperature afforded complexes [(L)K{($\mu_3$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (L = 18-crown-6 (**16**), dibenzo-18-crown-6 (**17**)) (Scheme 5). Compounds **16** and **17** were isolated in good yields (78 and 87%) as yellow solids which are soluble in toluene or benzene, suggesting a molecular structure. While complex **16** did not react with an additional equivalent of 18-crown-6, the treatment of **17** with dibenzo-18-crown-6 (one equiv.) in toluene at room temperature led to the precipitation of the ion-separated compound [K(dibenzo-18-crown-6)$_2$][Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)(μ-N)(μ-NH)$_2$] (**18**) as a yellow solid in 62% isolated yield. An analogous ionic compound [K(crypt-222)][Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)(μ-N)(μ-NH)$_2$] (**19**) was obtained in 70% yield through the treatment of **15** with crypt-222 in toluene at 120 °C. Compounds **18** and **19** are not soluble in hydrocarbon aromatic solvents but exhibit good solubility in polar solvents such as pyridine or tetrahydrofuran. This is in good agreement with the ability of two 18-crown-6 units and the cryptand-222 ligand to encapsulate the potassium cation and produce well-separated ion pairs. Compounds



**Scheme 4** Proposed pathway for the formation of **13**.



**Scheme 5** Reaction of [{Ti($\eta^5$-$C_5Me_5$)(μ-NH)}$_3$($\mu_3$-N)] with [K($C_5Me_5$)].

**16–19** immediately react with chloroform-$d_1$ to give orange solutions of complex **14** and the corresponding free macrocyclic polyether according to NMR spectroscopy.

Compounds **16–19** were characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure of **17** on single crystals grown from a benzene-$d_6$ solution at room temperature. The molecular structure of **17** shows a distorted [$KTi_3N_4$] cube core (Fig. 5). The potassium atom is bonded to three nitrogen atoms with K(1)–N distances of 2.904(3)–3.034(3) Å and N–K(1)–N angles of average 60.7(8)°. While the K(1) atom is also bound to five oxygen atoms of the 18-crown-6 ligand with K(1)–O bond lengths between 2.862(2) and 3.085(3) Å, the sixth oxygen of the macrocycle is clearly not coordinated to the potassium center (distance K(1)···O(43) 3.407(3) Å). Bond distances and angles involving the titanium and nitrogen atoms of the cube do not differ significantly with respect to those found in complex **14**.[4] Thus, most of the Ti–N distances are in the range 1.909(3)–1.951(3) Å with the exception of those associated with the nitrido ligand N(13), which are slightly shorter (Ti(1)–N(13) 1.886(3) Å and Ti(3)–N(13) 1.882(3) Å).

The IR spectra (KBr) of **16–19** show one $\nu_{NH}$ vibration between 3350 and 3327 $cm^{-1}$ and several absorptions in the range 1360–830 $cm^{-1}$ for the macrocyclic polyethers.[29] The $^1H$ NMR spectra of compounds **16** and **17** in benzene-$d_6$ at room temperature show one broad resonance for the NH imido groups at 13.01 and 12.86 ppm, respectively, and two sharp singlets in a 2 : 1 ratio for the $\eta^5$-$C_5Me_5$ ligands in accordance with $C_s$ symmetric structures in solution. In addition, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **16** and **17** reveal typical resonances for one 18-crown-6 or dibenzo-18-crown-6 ligand. These resonances are broad indicating a slow exchange between the free and coordinated oxygen atoms of the 18-crown-6 macrocyclic polyethers on the NMR timescale. The $^1H$ NMR spectra of **18** and **19** in pyridine-$d_5$ at room temperature show one resonance for the NH imido groups at 12.96 ppm, two singlets in a 2 : 1 ratio for the $\eta^5$-$C_5Me_5$ ligands, and one set of resonance signals for two equivalent dibenzo-18-crown-6 or one cryptand-222 ligands. In contrast to those observed for complexes **16** and **17**, the resonance signals for the macrocyclic polyethers are sharp in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **18** and **19**. However, while the resonances for the $\eta^5$-$C_5Me_5$ ligands in complex **19** are sharp in the NMR spectra, those for complex **18** are broad, suggesting some kind of interaction between the $[K(\text{dibenzo-18-crown-6})_2]^+$ and $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)(\mu\text{-}N)(\mu\text{-}NH)_2]^-$ ions in solution. The $^{13}C\{^1H\}$ NMR spectra of complexes **16–19** show two resonances for the *ipso*-carbons of the $\eta^5$-$C_5Me_5$ ligands in the narrow ranges of 114.6–114.5 and 113.4–113.1 ppm. These resonances are slightly shifted upfield with respect to that found for **14** ($\delta$ = 117.3 ppm) and are similar to those reported for a solution of **15** in pyridine-$d_5$ ($\delta$ = 114.9 and 113.5).[34b] Most likely, the structure of compound **15** in this donor solvent contains a cube-type [$KTi_3N_4$] core with solvent molecules coordinated to the potassium atom as a result of the rupture of the edge-linked double-cube structure in the solid state.

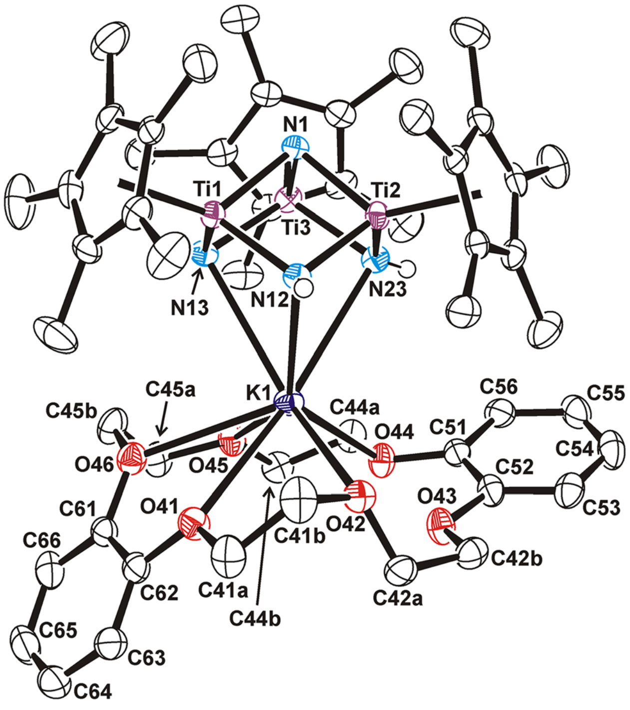


Fig. 5 Perspective view of compound **17** (thermal ellipsoids at the 50% probability level). Hydrogen atoms bound to carbon are omitted for clarity. Selected lengths (Å) and angles (°): K(1)–N 2.904(3)–3.034(3), K(1)–O 2.862(2)–3.085(3), K(1)···O(43) 3.407(3), Ti–N(1) 1.922(3)–1.951(3), Ti(1)–N(13) 1.886(3), Ti(3)–N(13) 1.882(3), Ti(1)–N(12) 1.918(3), Ti(2)–N(12) 1.909(3), Ti(2)–N(23) 1.934(3), Ti(3)–N(23) 1.941(3), Ti···Ti 2.768(1)–2.800(1), K(1)···Ti 3.657(1)–3.762(1), N–K(1)–N 59.8(1)–61.2(1), N–Ti–N 102.9(1)–105.0(1), N(1)–Ti–N 86.4(1)–87.4(1), Ti–N–Ti 92.5(1)–94.5(1), Ti–N(1)–Ti 91.1(1)–93.3(1), K(1)–N–Ti 93.1(1)–98.0(1).

## Conclusion

The cyclic voltammograms of cube-type titanium(IV) nitrido complexes $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]$ show a reversible one-electron redox wave at *ca.* −1.8 V *vs.* ferrocenium/ferrocene, and chemically reduced titanium complexes are successfully prepared using sodium sand in tetrahydrofuran or $[K(C_5Me_5)]$ in the presence of macrocycles capable of stabilizing the $K^+$ cation. The anionic fragments $[\{Ti_4(\eta^5\text{-}C_5Me_5)_3(R)\}(\mu_3\text{-}N)_4]^-$ of the resultant ionic species contain one electron delocalized among the titanium atoms and essentially maintain the same structural parameters as the parent neutral cube-type compounds. While cryptand-222 is capable of sequestering the potassium ion in the reduced species to give well-separated ion pairs, the 18-crown-6 polyether appears to allow some interaction between the $K^+$ cation and the cyclopentadienyl ligands of the anion. Such interaction may be responsible for the formation of compound $[\{(\text{18-crown-6})K\}_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_5)][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}N)_4]$ *via* abstraction of one cyclopentadienide group of an unstable intermediate $[K(\text{18-crown-6})][\{Ti_4(\eta^5\text{-}C_5Me_5)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}N)_4]$.

While [K($C_5Me_5$)] is an efficient one-electron reductant to the tetranuclear nitrido complexes, its reaction with the imido–nitrido trinuclear complex [{Ti($\eta^5$-$C_5Me_5$)(μ-NH)}$_3$($\mu_3$-N)] leads to the deprotonation of one NH imido group and the formation of the double-cube compound [{K($\mu_4$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$_2$]. The treatment of this potassium complex with 18-crown-6 polyethers or cryptand-222 affords molecular complexes with [$KTi_3N_4$] cube cores or well-separated ion pairs with [Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)(μ-N)(μ-NH)$_2$]$^-$ anions.

## 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 the Na/K alloy just before use. Tetrahydrofuran was distilled from purple solutions of sodium benzophenone just prior to use. Pyridine was distilled from calcium hydride just prior to use. NMR solvents were dried with the Na/K alloy ($C_6D_6$, $C_4D_8O$) or calcium hydride ($CDCl_3$, $C_5D_5N$) and distilled before use. Oven-dried glassware was repeatedly evacuated with a pumping system (*ca.* $1 \times 10^{-3}$ Torr) and subsequently filled with inert gas. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6) and 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecene (dibenzo-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$_4$($\eta^5$-$C_5Me_5$)$_3$(R)}($\mu_3$-N)$_4$] (R = $\eta^5$-$C_5Me_5$ (**1**),[5] N(SiMe$_3$)$_2$ (**2**),[21] $\eta^5$-$C_5H_4SiMe_3$ (**3**),[6] and $\eta^5$-$C_5H_5$ (**4**)[6,21]), [{Ti($\eta^5$-$C_5Me_5$)(μ-NH)}$_3$($\mu_3$-N)] (**14**),[4] [{K($\mu_4$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$_2$] (**15**),[34] fine sodium sand,[35] and [K($C_5Me_5$)][36] were prepared according to published procedures. The synthesis and characterization of [K(18-crown-6)][{Ti($\eta^5$-$C_5Me_5$)}$_4$($\mu_3$-N)$_4$] (**6**) have been previously reported.[22]

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using an FT-IR PerkinElmer Spectrum 2000 or FT-IR PerkinElmer Frontier spectrophotometer. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Varian Unity-300 spectrometer and/or a Mercury-300 spectrometer. Chemical shifts ($\delta$, ppm) in the $^1$H and $^{13}$C{$^1$H} NMR spectra are given relative to residual protons or to the carbon of the solvent: $C_6D_6$ ($^1$H: $\delta$ = 7.15; $^{13}$C: $\delta$ = 128.0), $C_4D_8O$ ($^1$H: $\delta$ = 3.58; $^{13}$C: $\delta$ = 67.2) or $C_5D_5N$ ($^1$H: $\delta$ = 8.71; $^{13}$C: $\delta$ = 149.9). 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).[37] Microanalyses (C, H, N) were performed in a Leco CHNS-932 microanalyzer. CW-EPR spectra were recorded on a Bruker Magnettech ESR5000 spectrometer.

The cyclic voltammograms were recorded using a potentiostat/galvanostat CH Instruments CHI620E. All experiments were carried out using a conventional three-electrode cell. Platinum was used as the working electrode, a platinum wire as the counter electrode, and a silver wire as the pseudo reference electrode. Potentials were internally referenced to the ferrocenium/ferrocene redox couple at 0 mV. Measurements were made under a purified argon atmosphere in a glovebox using tetrahydrofuran solutions of [N(*n*Bu)$_4$][PF$_6$] (0.1 M).

**Synthesis of [Na(thf)$_6$][{Ti($\eta^5$-$C_5Me_5$)}$_4$($\mu_3$-N)$_4$] (5).** A 100 mL Schlenk tube was charged with **1** (0.20 g, 0.25 mmol), sodium sand (0.058 g, 2.54 mmol), and tetrahydrofuran (30 mL). The reaction mixture was stirred at room temperature for 24 h and a color change from green to dark purple was observed. After filtration, the solution was carefully layered with toluene (30 mL). The system was allowed to equilibrate at room temperature for 5 days to give **5** as dark purple crystals (0.21 g, 66%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2969 (s), 2902 (vs), 2856 (s), 2716 (w), 1491 (w), 1435 (s), 1372 (s), 1052 (s) (thf), 1023 (m), 901 (m) (thf), 789 (m), 623 (s), 529 (s), 426 (s). $^1$H NMR (300 MHz, $C_4D_8O$, 20 °C): $\delta$ 9.2 (s br., $\Delta\nu_{1/2}$ = 75 Hz, 60H; $C_5Me_5$), 3.62 (m, 24H; OC*H*$_2$CH$_2$), 1.77 (m, 24H; OCH$_2$C*H*$_2$). Anal. Calcd (%) for $C_{64}H_{108}N_4NaO_6Ti_4$ ($M_w$ = 1244.02): C 61.79, H 8.75, N 4.50. Found: C 60.78, H 8.44, N 5.00. The effective magnetic moment of **5** was determined to be 1.68$\mu_B$ (based on a unit formula of $C_{64}H_{108}N_4NaO_6Ti_4$) in a $C_4D_8O$ solution.

Crystals of compound **5** (0.10 g, 0.080 mmol) were ground with a mortar and pestle to give a fine dark purple powder. This powder was dried under dynamic vacuum for 1 h to afford Na[{Ti($\eta^5$-$C_5Me_5$)}$_4$($\mu_3$-N)$_4$] (0.063 g, 97%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2961 (m), 2909 (vs), 2855 (s), 2719 (w), 1494 (w), 1438 (m), 1374 (m), 1021 (m), 789 (m), 650 (m), 627 (m), 531 (s), 427 (s). $^1$H NMR (300 MHz, $C_4D_8O$, 20 °C): $\delta$ 9.2 (s br., $\Delta\nu_{1/2}$ = 67 Hz, 60H; $C_5Me_5$). Anal. Calcd (%) for $C_{40}H_{60}N_4NaTi_4$ ($M_w$ = 811.39): C 59.20, H 7.45, N 6.91. Found: C 59.23, H 7.34, N 6.37.

**Synthesis of [K(crypt-222)][{Ti($\eta^5$-$C_5Me_5$)}$_4$($\mu_3$-N)$_4$] (7).** A 100 mL ampule (Teflon stopcock) was charged with **1** (0.30 g, 0.38 mmol), [K($C_5Me_5$)] (0.066 g, 0.38 mmol), crypt-222 (0.14 g, 0.38 mmol), and toluene (40 mL). The reaction mixture was stirred at 110 °C for 24 h to give a dark purple solution and a fine dark purple solid. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **7** as a dark purple powder (0.38 g, 83%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2962 (s), 2890 (vs), 1477 (m), 1445 (m), 1372 (m), 1354 (s), 1297 (m), 1260 (m), 1134 (s), 1107 (vs), 1078 (s), 951 (s), 933 (m), 832 (w), 792 (m), 752 (m), 623 (m), 543 (s), 425 (s). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 9.5 (s br., $\Delta\nu_{1/2}$ = 77 Hz, 60H; $C_5Me_5$), 3.40 (s, 12H; OCH$_2$CH$_2$O), 3.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; OC*H*$_2$CH$_2$N), 2.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; OCH$_2$C*H*$_2$N). Anal. Calcd (%) for $C_{58}H_{96}KN_6O_6Ti_4$ ($M_w$ = 1204.00): C 57.86, H 8.03, N 6.98. Found: C 57.56, H 7.45, N 6.83. The effective magnetic moment of **7** was determined to be 1.79$\mu_B$ (based on a unit formula of $C_{58}H_{96}KN_6O_6Ti_4$) in a $C_5D_5N$ solution.

**Synthesis of [K(18-crown-6)][(Ti$_4$($\eta^5$-$C_5Me_5$)$_3${N(SiMe$_3$)$_2$})($\mu_3$-N)$_4$] (8).** A 100 mL Schlenk tube was charged with **2** (0.20 g, 0.25 mmol), [K($C_5Me_5$)] (0.043 g, 0.25 mmol), 18-crown-6 (0.065 g, 0.25 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a green solution and a green solid. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **8** as a green powder (0.15 g, 54%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2902 (vs), 1452 (w), 1373 (w), 1352 (m), 1286 (w), 1248 (m), 1108 (vs), 979 (s), 962 (s), 877 (m), 836 (s), 790 (vs), 753 (m), 688 (s), 624 (w), 591 (w), 529 (w), 431 (w). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 10.6 (s br., $\Delta\nu_{1/2}$ = 59 Hz, 45H; $C_5Me_5$), 3.43 (s, 24H; $OCH_2CH_2O$), 1.22 (s br., $\Delta\nu_{1/2}$ = 26 Hz, 18H; $N(SiMe_3)_2$). Anal. Calcd (%) for $C_{48}H_{87}KN_5O_6Si_2Ti_4$ ($M_w$ = 1116.98): C 51.61, H 7.85, N 6.27. Found: C 51.53, H 7.64, N 6.86. The effective magnetic moment of **8** was determined to be 1.99$\mu_B$ (based on a unit formula of $C_{48}H_{87}KN_5O_6Si_2Ti_4$) in a $C_5D_5N$ solution.

**Synthesis of [K(crypt-222)][(Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3${N(SiMe$_3$)$_2$})($\mu_3$-N)$_4$] (9).** In a fashion similar to the preparation of **8**, the treatment of **2** (0.15 g, 0.18 mmol) with a mixture of $[K(C_5Me_5)]$ (0.032 g, 0.18 mmol) and crypt-222 (0.069 g, 0.18 mmol) in toluene (30 mL) at room temperature for 24 h afforded **9** as a green powder (0.18 g, 82%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2952 (s), 2892 (vs), 2716 (w), 1477 (m), 1444 (m), 1357 (s), 1298 (m), 1239 (m), 1134 (s), 1107 (vs), 978 (s), 951 (s), 876 (s), 846 (s), 783 (m), 753 (m), 706 (w), 672 (m), 627 (m), 591 (m), 525 (m), 432 (m). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 10.7 (s br., $\Delta\nu_{1/2}$ = 60 Hz, 45H; $C_5Me_5$), 3.40 (s, 12H; $OCH_2CH_2O$), 3.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; $OCH_2CH_2N$), 2.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; $OCH_2CH_2N$), 1.22 (s br., $\Delta\nu_{1/2}$ = 36 Hz, 18H; $N(SiMe_3)_2$). Anal. Calcd (%) for $C_{54}H_{99}KN_7O_6Si_2Ti_4$ ($M_w$ = 1229.16): C 52.77, H 8.12, N 7.97. Found: C 52.68, H 7.50, N 7.94. The effective magnetic moment of **9** was determined to be 1.83$\mu_B$ (based on a unit formula of $C_{54}H_{99}KN_7O_6Si_2Ti_4$) in a $C_5D_5N$ solution.

**Synthesis of [K(18-crown-6)][{Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3$($\eta^5$-C$_5$H$_4$SiMe$_3$)}($\mu_3$-N)$_4$] (10).** In a fashion similar to the preparation of **8**, the treatment of **3** (0.20 g, 0.25 mmol) with a mixture of $[K(C_5Me_5)]$ (0.044 g, 0.25 mmol) and 18-crown-6 (0.067 g, 0.25 mmol) in toluene (40 mL) at room temperature for 4 h afforded **10** as a dark purple powder (0.13 g, 47%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2902 (vs), 1471 (m), 1442 (m), 1373 (m), 1353 (s), 1286 (w), 1248 (s), 1180 (w), 1107 (vs), 1042 (m), 961 (s), 908 (m), 837 (vs), 790 (s), 774 (s), 692 (w), 625 (m), 548 (m), 420 (m). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 10.3 (s br., $\Delta\nu_{1/2}$ = 89 Hz, 45H; $C_5Me_5$), 3.42 (s, 24H; $OCH_2CH_2O$), 0.77 (s br., $\Delta\nu_{1/2}$ = 32 Hz, 9H; $C_5Me_4SiMe_3$). Anal. Calcd (%) for $C_{50}H_{82}KN_4O_6SiTi_4$ ($M_w$ = 1093.86): C 54.90, H 7.56, N 5.12. Found: C 54.51, H 7.25, N 5.29. The effective magnetic moment of **10** was determined to be 1.92$\mu_B$ (based on a unit formula of $C_{50}H_{82}KN_4O_6SiTi_4$) in a $C_5D_5N$ solution.

**Synthesis of [K(crypt-222)][{Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3$($\eta^5$-C$_5$H$_4$SiMe$_3$)}($\mu_3$-N)$_4$] (11).** In a fashion similar to the preparation of **8**, the treatment of **2** (0.20 g, 0.25 mmol) with a mixture of $[K(C_5Me_5)]$ (0.044 g, 0.25 mmol) and crypt-222 (0.095 g, 0.25 mmol) in toluene (30 mL) at room temperature for 4 h afforded **11** as a dark purple powder (0.22 g, 73%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2961 (s), 2889 (vs), 2815 (s), 1477 (m), 1444 (m), 1359 (s), 1355 (s), 1297 (m), 1260 (m), 1242 (m), 1177 (w), 1133 (s), 1106 (vs), 1079 (s), 1040 (w), 951 (s), 933 (m), 907 (w), 833 (s), 796 (vs), 753 (m), 682 (m), 627 (w), 547 (w), 525 (w), 417 (w). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 10.3 (s br., $\Delta\nu_{1/2}$ = 89 Hz, 45H; $C_5Me_5$), 3.40 (s, 12H; $OCH_2CH_2O$), 3.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; $OCH_2CH_2N$), 2.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; $OCH_2CH_2N$), 0.77 (s br., $\Delta\nu_{1/2}$ = 30 Hz, 18H; $C_5Me_4SiMe_3$). Anal. Calcd (%) for $C_{56}H_{94}KN_6O_6SiTi_4$ ($M_w$ = 1206.03): C 55.77, H 7.86, N 6.97. Found: C 56.01, H 7.51, N 7.38. The effective magnetic moment of **11** was determined to be 1.92$\mu_B$ (based on a unit formula of $C_{56}H_{94}KN_6O_6SiTi_4$) in a $C_5D_5N$ solution.

**Synthesis of [K(crypt-222)][{Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3$($\eta^5$-C$_5$H$_5$)}($\mu_3$-N)$_4$] (12).** In a fashion similar to the preparation of **8**, the treatment of **4** (0.25 g, 0.35 mmol) with a mixture of $[K(C_5Me_5)]$ (0.060 g, 0.34 mmol) and crypt-222 (0.13 g, 0.35 mmol) in toluene (30 mL) for 24 h afforded **12** as a dark purple powder (0.30 g, 76%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 2952 (s), 2891 (vs), 1478 (m), 1446 (m), 1354 (s), 1297 (m), 1261 (m), 1133 (s), 1105 (vs), 1075 (s), 953 (s), 931 (m), 790 (s), 681 (m), 625 (w), 549 (m), 426 (m). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 10.6 (s br., $\Delta\nu_{1/2}$ = 82 Hz, 45H; $C_5Me_5$), 3.39 (s, 12H; $OCH_2CH_2O$), 3.34 (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 $C_{53}H_{86}KN_6O_6Ti_4$ ($M_w$ = 1133.86): C 56.14, H 7.64, N 7.41. Found: C 56.31, H 7.47, N 7.14. The effective magnetic moment of **12** was determined to be 1.82$\mu_B$ (based on a unit formula of $C_{53}H_{86}KN_6O_6Ti_4$) in a $C_5D_5N$ solution.

**Synthesis of [{(18-crown-6)K}$_2$($\mu$–$\eta^5$:$\eta^5$-C$_5$H$_5$)][{Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3$($\eta^5$-C$_5$H$_5$)}($\mu_3$-N)$_4$] (13).** A 100 mL Schlenk tube was charged with **4** (0.20 g, 0.28 mmol), $[K(C_5Me_5)]$ (0.050 g, 0.29 mmol), 18-crown-6 (0.074 g, 0.28 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a dark purple solution and a dark purple solid. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **13** as a dark purple powder (0.10 g, 52% yield based on the formation of a half equivalent (theoretical yield of 0.14 mmol, 0.19 g) of compound **13** from one equivalent of complex **4**). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3057 (w), 2897 (vs), 2855 (s), 1471 (m), 1452 (m), 1434 (m), 1373 (w), 1351 (s), 1284 (m), 1249 (m), 1115 (vs), 1007 (w), 963 (m), 839 (m), 789 (s), 763 (m), 714 (m), 626 (w), 547 (m), 430 (w). $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ 10.6 (s br., $\Delta\nu_{1/2}$ = 82 Hz, 45H; $C_5Me_5$), 6.50 (s, 5H; $C_5H_5$), 3.43 (s, 48H; $OCH_2CH_2O$). $^{13}$C{$^1$H} NMR ($C_5D_5N$, 20 °C): $\delta$ 104.8 ($\mu$-$C_5H_5$), 70.3 ($OCH_2CH_2O$). Anal. Calcd (%) for $C_{64}H_{103}K_2N_4O_{12}Ti_4$ ($M_w$ = 1390.19): C 55.29, H 7.47, N 4.03. Found: C 54.91, H 7.30, N 3.93. The effective magnetic moment of **13** was determined to be 1.74$\mu_B$ (based on a unit formula of $C_{64}H_{103}K_2N_4O_{12}Ti_4$) in a $C_5D_5N$ solution.

**Synthesis of [(18-crown-6)K{($\mu_3$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu_3$-N)}] (16).** Compound **15** (0.20 g, 0.15 mmol) was slowly added in small portions to a toluene solution (30 mL) of 18-crown-6 (0.082 g, 0.31 mmol) under vigorous stirring. The reaction mixture was stirred at room temperature for 1 h to give an orange solution. After filtration, the volatile components of the solution were removed under reduced pressure to afford **16** as a yellow powder (0.21 g, 78%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3348 (w) (NH), 2896 (s), 1472 (w), 1452 (w), 1374 (w), 1351 (m), 1286 (w), 1250 (w), 1117 (vs), 964 (m), 842 (w), 769 (m), 735 (s), 697 (s), 633 (m), 530 (w), 467 (w). $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ 13.01 (s br., 2H; NH), 3.18 (s br., 24H; $OCH_2CH_2O$), 2.29 (s, 30H; $C_5Me_5$), 2.16 (s, 15H; $C_5Me_5$). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ 114.6, 113.4 ($C_5Me_5$), 69.8 (br., $OCH_2CH_2O$), 12.4, 12.3 ($\mathrm{C_5}\mathit{Me}_5$). Anal. Calcd for $C_{42}H_{71}KN_4O_6Ti_3$ ($M_w$ = 910.75): C 55.39, H 7.86, N 6.15. Found: C 55.18, H 7.80, N 5.70.

**Synthesis of [(dibenzo-18-crown-6)K{($\mu_3$-N)($\mu_3$-NH)$_2$Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu_3$-N)}] (17).** In a fashion similar to the preparation of **16**, slow addition of **15** (0.20 g, 0.15 mmol) to a stirred toluene solution (25 mL) of dibenzo-18-crown-6 (0.11 g, 0.31 mmol) at room temperature afforded **17** as a yellow powder (0.26 g, 87%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3329 (w) (NH), 3070 (w), 2898 (m), 2873 (m), 1596 (m), 1505 (s), 1454 (m), 1374 (w), 1327 (w), 1252 (s), 1217 (m), 1128 (s), 1063 (m), 942 (m), 783 (m), 735 (s), 700 (m), 623 (m), 468 (w). $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta$ 12.86 (s br., 2H; NH), 6.85 (m br., 4H; $\mathrm{C_6}\mathit{H}_2\mathrm{H_2}$), 6.57 (m br., 4H; $\mathrm{C_6H_2}\mathit{H}_2$), 3.75 (m br., 8H; $\mathrm{O}\mathit{CH}_2\mathrm{CH_2O}$), 3.36 (m br., 8H; $\mathrm{OCH_2}\mathit{CH}_2\mathrm{O}$), 2.24 (s, 30H; $C_5Me_5$), 2.08 (s, 15H; $C_5Me_5$). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 20 °C): $\delta$ 148.4 (br., $C_6H_4$), 121.3 ($C_6H_4$), 114.6, 113.4 ($\mathit{C}_5\mathrm{Me_5}$), 112.5 (br., $C_6H_4$), 68.6 (br., $OCH_2CH_2O$), 12.2 ($\mathrm{C_5}\mathit{Me}_5$); one $OCH_2CH_2O$ resonance signal and one $\mathrm{C_5}\mathit{Me}_5$ resonance signal were not found due to coincidence with those at 68.6 and 12.2 ppm, respectively. Anal. Calcd for $C_{50}H_{71}KN_4O_6Ti_3$ ($M_w$ = 1006.84): C 59.65, H 7.11, N 5.56. Found: C 59.64, H 6.71, N 4.43.

**Synthesis of [K(dibenzo-18-crown-6)$_2$][Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu_3$-N)($\mu$-N)($\mu$-NH)$_2$] (18).** Compound **17** (0.16 g, 0.16 mmol) was slowly added in small portions to a toluene solution (25 mL) of dibenzo-18-crown-6 (0.058 g, 0.16 mmol) under vigorous stirring. The reaction mixture was stirred at room temperature for 3 days to give a yellow solution and a yellow solid. The solid was isolated by filtration onto a glass frit and was washed with toluene (5 mL) to afford **18** as a yellow powder (0.26 g, 62%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3327 (w) (NH), 3069 (w), 2950 (m), 2896 (s), 2874 (m), 1596 (m), 1505 (s), 1454 (m), 1375 (w), 1329 (m), 1291 (w), 1254 (s), 1232 (m), 1218 (m), 1129 (s), 1063 (m), 1049 (w), 996 (w), 934 (m), 777 (m), 736 (s), 701 (m), 624 (m), 595 (w), 533 (w), 469 (w). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 12.96 (s br., 2H; NH), 6.93 (m, 16H; $C_6H_4$), 4.12 (m, 16H; $\mathrm{O}\mathit{CH}_2\mathrm{CH_2O}$), 3.75 (m, 16H; $\mathrm{OCH_2}\mathit{CH}_2\mathrm{O}$), 2.24 (s br., 30H; $C_5Me_5$), 2.15 (s br., 15H; $C_5Me_5$). $^{13}$C{$^1$H} NMR (75 MHz, $C_5D_5N$, 20 °C): $\delta$ 148.9, 121.3 ($C_6H_4$), 114.5, 113.2 ($\mathit{C}_5\mathrm{Me_5}$), 112.7 ($C_6H_4$), 69.5 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_2O}$), 68.1 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2O}$), 12.2 ($\mathrm{C_5}\mathit{Me}_5$); one $\mathrm{C_5}\mathit{Me}_5$ resonance signal was not found due to coincidence with that at 12.2 ppm. Anal. Calcd for $C_{70}H_{95}KN_4O_{12}Ti_3$ ($M_w$ = 1367.24): C 61.49, H 7.00, N 4.10. Found: C 61.87, H 6.88, N 4.15.

**Synthesis of [K(crypt-222)][Ti$_3$($\eta^5$-C$_5$Me$_5$)$_3$($\mu_3$-N)($\mu$-N)($\mu$-NH)$_2$] (19).** A 100 mL ampule (Teflon stopcock) was charged with **15** (0.19 g, 0.15 mmol), crypt-222 (0.11 g, 0.30 mmol), and toluene (40 mL). The reaction mixture was stirred at 120 °C for 2 days to give a yellow solid and an orange solution. The solid was isolated by filtration onto a glass frit and washed with toluene (5 mL) to afford **19** as a yellow powder (0.21 g, 70%). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3350 (w) (NH), 2896 (vs), 1477 (m), 1444 (m), 1373 (m), 1354 (s), 1297 (w), 1260 (w), 1133 (s), 1106 (vs), 1079 (s), 1028 (w), 951 (s), 933 (s), 884 (w), 741 (vs), 705 (s), 625 (s), 586 (w), 529 (w), 506 (w), 468 (w), 408 (m). $^1$H NMR (300 MHz, $C_5D_5N$, 20 °C): $\delta$ 12.96 (s br., 2H; NH), 3.40 (s, 12H; $OCH_2CH_2O$), 3.35 (t, $^3J$(H,H) = 4.8 Hz, 12H; $\mathrm{O}\mathit{CH}_2\mathrm{CH_2N}$), 2.35 (t, $^3J$(H,H) = 4.5 Hz, 12H; $\mathrm{OCH_2}\mathit{CH}_2\mathrm{N}$), 2.31 (s, 30H; $C_5Me_5$), 2.21 (s, 15H; $C_5Me_5$). $^{13}$C{$^1$H} NMR (75 MHz, $C_5D_5N$, 20 °C): $\delta$ 114.5, 113.1 ($\mathit{C}_5\mathrm{Me_5}$), 70.5, 67.7, 53.9 (crypt-222), 12.3, 12.2 ($\mathrm{C_5}\mathit{Me}_5$). Anal. Calcd for $C_{48}H_{83}KN_6O_6Ti_3$ ($M_w$ = 1022.93): C 56.36, H 8.18, N 8.22. Found: C 56.71, H 7.78, N 8.08.

### X-ray structure determination of 5, 11, 13, and 17

Dark purple crystals of **5**, **11**·$C_6D_6$ and **13**·2$C_7H_8$, and yellow crystals of **17** were obtained as described in the Results and discussion section. The crystals were removed from the NMR tubes or Schlenk tubes and covered with a layer of viscous perfluoropolyether (FomblinY). 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 a diffractometer. The intensity data sets were collected at 200 K (compound **13**) or 150 K (the rest) on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table S1.†

The structures were solved using the WINGX package,[38] by intrinsic phasing methods (SHELXT),[39] and refined by least-squares against $F^2$ (SHELXL-2014/7).[40] Compound **5** crystallized in the cubic space group $I2_13$ ($Z$ = 8), and the asymmetric unit is composed of a third of the cation and a third of the anion. The pentamethylcyclopentadienyl ligand linked to Ti(2) is located on a three-fold axis, so it was not possible to define a proper geometry for this $C_5Me_5$ group. This disorder was modelled by refining each atom of this fragment with an occupancy of 0.8333, which is the result of the 10/12 quotient. Moreover **5** was treated as a two-component inversion twin using TWIN and BASF instructions. The final value of the BASF parameter was 0.011. All non-hydrogen atoms were anisotropically refined, whereas the hydrogen atoms were positioned geometrically by using a riding model. DELU and SIMU restraints were used for the carbon atoms of the disordered $C_5Me_5$ ring (C(21), C(22), C(26) and C(27)) and the atoms of one tetrahydrofuran ligand (O(2), C(5), C(6), C(7) and C(8)).

In the case of **11**, several crystalline samples were obtained, and the best possible single crystal was employed for data collection. Compound **11** crystallized with a molecule of benzene in the $P2_12_12$ space group. The asymmetric unit was constituted by two molecules of benzene, two anions [{Ti$_4$($\eta^5$-C$_5$Me$_5$)$_3$($\eta^5$-C$_5$H$_4$SiMe$_3$)}($\mu_3$-N)$_4$]$^-$, an entire cation [K(crypt-222)]$^+$, and two halves of two crystallographically independent cations [K(crypt-222)]$^+$. One molecule of benzene and one half of the cation [K(crypt-222)]$^+$ lie on the same crystallographic 2-fold axis, so it was not possible to obtain a sensible chemical model for them. Thus, the PLATON[41] squeeze procedure was used to remove their contribution to the structural factors. Crystals of **11** also show disorder for the carbon atoms C(81)–C(90) of the pentamethylcyclopentadienyl group linked to Ti(8). This disorder was treated conventionally by using the PART tool of the SHELXL program and allowing free refinement of the occupancy factor with the FVAR command. The final values of occupancy were 51 and 49%. Simultaneously, the data were refined as a two-component inversion twin using

TWIN and BASF instructions, with a final value for the BASF parameter of 0.42. All non-hydrogen atoms were anisotropically refined, except those carbon atoms of the disordered $C_5Me_5$ ring (C(81)–C(90) and C(81)′–C(90)′), which were refined isotropically. All the hydrogen atoms were positioned geometrically and refined by using a riding model. DELU and SIMU restraints were applied for the carbon atoms C(61)–C(70) of the pentamethylcyclopentadienyl ligand bound to Ti(6). The carbon atoms C(21)–C(30), C(31)–C(40), C(71)–C(80), C(15)a and C(15)b were also restrained with DELU instructions. Additionally, a DFIX constraint was employed for a carbon–carbon distance in a crypt-222 moiety.

Compound **13** crystallized with two molecules of toluene, which were found in the difference Fourier map, but it was not possible to obtain a chemically sensible model for them, so the PLATON[41] squeeze procedure was used to remove their contribution to the structural factors. Crystals of **13** showed disorder for the carbon atoms C(31)–C(40) and C(41)–C(50) of the pentamethylcyclopentadienyl rings linked to Ti(3) and Ti(4) respectively. Moreover the 18-crown-6 connected to the potassium atom K(2) presented disorder as well. These disorders were also treated by using the PART tool. The final values of occupancy were 66 and 34% for the $C_5Me_5$ group bound to Ti(3), 66 and 34% for the ring linked to Ti(4), and 78.7 and 21.3% for the macrocyclic ligand. All non-hydrogen atoms were anisotropically refined, except those atoms for the disordered crown ether with minor occupancy (C(71)c, C(71)d, C(72)c, C(72)d, C(73)c, C(73)d, C(74)c, C(74)d, C(75)c, C(75)d, C(76)c, C(76)d and O(71)′–O(76)′), which could be only refined isotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. DELU and SIMU restraints were employed for the disordered pentamethylcyclopentadienyl groups, whereas the disordered macrocyclic ether was treated with SIMU and SADI instructions.

Finally, in the crystallographic study of **17**, all non-hydrogen atoms were anisotropically refined. All hydrogen atoms were positioned geometrically and refined by using a riding model, except those linked to nitrogen atoms (H(12) and H(23)), which were located in the difference Fourier map and refined isotropically.

## Author contributions

Conceptualization: C. Y.; investigation: J. C., A. C.-M., S. C., M. G. and A. P.-R.; validation: A. C.-M. and C. Y.; supervision: C. Y. and A. P.-R.; visualization: A. C.-M., A. P.-R. and C. Y.; writing – original draft: C. Y.; writing – review & editing: A. C.-M., A. P.-R. and C. Y.; funding acquisition and project administration: C. Y. and A. P.-R. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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