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Synthesis and structure of the first non 'ate' heteroleptic lanthanoid complexes bearing monoanionic 2-amidopyridine ligands

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The synthetic utility of the polymeric alkali metal *N*-silylated-2-amidopyridine species [{Na(AMPTMS)(THF)$_{0.5}$}$_n$] (AMPTMS = 2-(trimethylsilylamido)-6-methylpyridine) toward the first non 'ate' heteroleptic lanthanoid complexes bearing monoanionic 2-amidopyridine ligands has been investigated. The preliminary results of this study are presented herein. These comprise the preparation and structural characterisation of dimeric [{Nd(AMPTMS)$_2$(THF)(μ-Cl)}$_2$] and monomeric [TbCp*$_2$-(AMPTMS)] (Cp* = C$_5$Me$_5$), the latter being the first terbium Cp* compound structurally characterised.

In recent times the development of non-cyclopentadienyl (Cp) lanthanoid chemistry has increasingly lain with bulky amide species that,[1–3] owing to their commensurate ionic charge and steric coordination, have assumed the position of Cp mimics when bound to electropositive metals.[4–7] Within this arena the seminal bis(trimethylsilyl)amide studies of Bradley *et al.*,[8] and subsequent developments thereof,[9–13] have paved the way toward the study of several functionalised mono-silylated amido species that have potential utility in hydrogenation, polymerisation, hydroboration and oligomerisation catalytic processes[14–19] as-well-as displaying promise as MOCVD and ceramics precursors.[20–22] From these it appears that, in terms of both materials chemistry and synthetic discovery, *N*-silylated 2-amidopyridine lanthanoid complexes have infinite scope using Cp compounds as comparisons.[23,24]

Our significant contribution to the field of metallated 2-amidopyridine chemistry,[25–31] which has been keenly studied within the above,[23,24,32–37] gave us a particular interest in related lanthanoid studies. Until now, perhaps the most novel aspect of this sub field has been the exciting bimetallic species of Kempe[34,35] and, more recently, Hill,[36] using tethered dianionic functionalised 2-amidopyridine derivatives, while studies concerning related monoanionic systems have been hampered by a failure to isolate non 'ate' lanthanoid halide species[23,37] capable of acting as precursors to further heteroleptic derivatives *via* metathetical exchange. To address this we have undertaken preliminary studies that culminated in an earlier report detailing the attempted preparation of AMPTMS lanthanoid chlorides utilising lithium AMPTMS reagents, wherein, hexane extraction of intended "[Ln(AMPTMS)$_2$Cl]" species, in order to remove unwanted lithium chloride by-product, induced redistribution yielding the homoleptic 6-coordinate tris(amide) and anhydrous unsolvated lanthanoid chloride.[38] Further to these developments, our assertion that these heteroleptic species form in ethereal solution (THF) with high solubility has been questioned by recent studies from Lee *et al.*, suggesting related "[LnL$_2$Cl]" species incorporating a minor AMPTMS derivative; 2-(*tert*-butyldimethylsilylamido)-6-methylpyridine, are insoluble in common organic solvents.[39] Accordingly, we herein present preliminary results detailing the formation of [{Nd(AMPTMS)$_2$(THF)(μ-Cl)}$_2$] and [TbCp*$_2$-(AMPTMS)] utilising the new sodium AMPTMS reagent; [{Na(AMPTMS)(THF)$_{0.5}$}$_n$], which, in contrast to 22 archival homometallic alkali metal *N*-substituted-2-amidopyridine species (all dimeric, cluster or cation-anion),[40] exhibits a polymeric composition with three sodium coordination motifs.

To circumvent the removal of lithium chloride, and thus the hexane extraction step that has prohibited the isolation of "[LnL$_2$Cl]" species (L = 2-amidopyridine ligand),[38] a 'new' metathesis reagent; [{Na(AMPTMS)(THF)$_{0.5}$}$_n$] (**1**), was prepared *via* the stoichiometric addition of sodium bis(trimethylsilylamide) to 2-(trimethylsilylamino)-6-methylpyridine (AMPTMS.H) in tetrahydrofuran (see Scheme 1). Further to washing with cold hexane and extraction into fresh THF, this gave colourless needles of (**1**) in high yield (74%), which provided NMR (^{1}H and ^{13}C), FTIR and microanalytical data consistent with the suggested empirical formulation. Our extensive background in group 1 metallated anionic β-dinitrogen ligands[25–31,38,41] gave us a particular interest in elucidating the structure of this sodium reagent for comparison with its lithium analogue.[25,38] We also felt it necessary to determine the structure to eliminate the likelihood of suppressed reactivity like that observed using bulky potassium *N,N′*-di(aryl)formamidinate compounds during related lanthanoid syntheses.[42,43] Accordingly, the X-ray structure determination of **1** was undertaken (see Fig. 1).[44–47]

Unlike the lithium analogue, which crystallises as a bis-THF coordinated μ_2:η^2:η^1-AMPTMS bound dimer;[38] **1** crystallises with five crystallographically unique sodium coordination environments that participate in a 1-dimensional polymeric array (space group *C*2/*c*). Two of these environments, those of Na(2) and Na(4), can be thought of as square-based pyramidal (deviation of Na(2) from N(1A)–N(2A)–N(1B)–N(2B) plane; 0.394(3) Å, Na(4) from N(1C)–N(2C)–N(1D)–N(2D) plane; 0.453(3) Å), whilst Na(1) and Na(5) reside in a distorted octahedral pocket (*cis* N–Na–N intra- and interligand angles, Na(1); 53.51(13)° and 126.49(13)°, Na(5); 54.71(13)° and mean 126.65°) and Na(3) sits in a heavily distended four coordinate square planar site (deviation of Na(3) from N(1B)–N(2B)–N(1C)–N(2C) plane; 0.016(3) Å, mean inter- and intraligand N–Na–N angles; 124.67° and 55.42°). The disparate bond lengths and angles described (see Fig. 1 caption) indicate significant steric buttressing within the extended frame of **1** that is not similarly observed in the dimeric/cation–anion composition of other structurally authenticated sodium *N*-alkyl/aryl/silyl-2-amidopyridine species.[48–50] Perhaps the best illustration of this is the irregular nature of the Na–N$_{Amide}$ and

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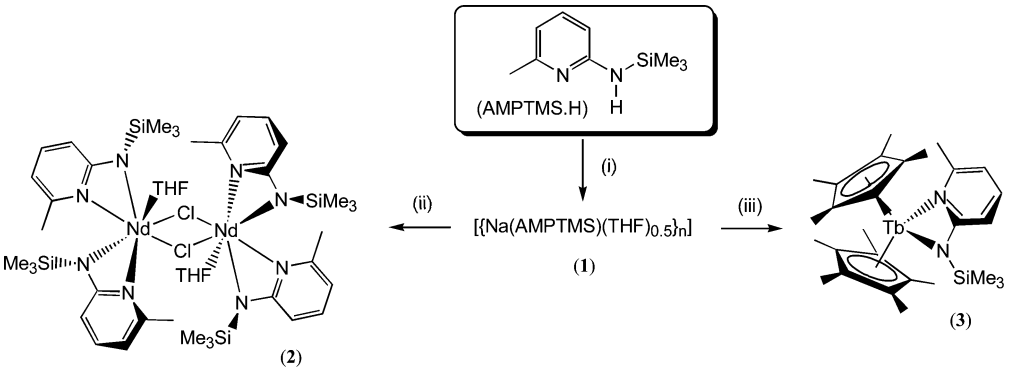

Scheme 1 *Reagents and conditions:* (i) 1.0 Eq. [Na{N(SiMe$_3$)$_2$}], THF, 25 °C, −HN(SiMe$_3$)$_2$. (ii) 0.5 Eq. anhydrous NdCl$_3$, THF, *ca.* 40 °C, 3 h, −NaCl. (iii) 1.0 Eq. [TbCp*$_2$(μ-Cl)$_2$Li(OEt$_2$)$_2$] (**4**), THF, 25 °C, 2 h, −NaCl, −LiCl.

Na–N$_{Pyridine}$ bonds. These range from 2.408(5) Å (Na(2)–N(2B)) to 2.605(4) Å (Na(1)–N(2A)/N(2A)#^{a})† and 2.494(4) Å (Na(5)–N(1D)/N(1D)#^{b})† to 2.624(5) Å (Na(4)–N(1C)) respectively, and possess mean values (2.478 Å and 2.545 Å resp.) that, particularly in the case of the latter, are smaller than the analogous mean bonds observed for related dimeric species (2.48 Å and 2.63 Å resp.).[48,49] Surprisingly, this increased sodium–ligand contact leads to a mean N$_{Pyrdine}$–Na–N$_{Amido}$ angle that is appreciably acute with respect to the analogous angles of the anion in [Na(12-crown-4)$_2$][Na{2-(NSiMe$_3$)C$_5$H$_4$N}$_2$(THF)] (**1**; 54.47°, anion; 55.42(4)° and 56.45(4)°).[50] This almost certainly results from the high degree of η^2:η^2-ligand–metal bridging in **1**. Meanwhile, the bridging Na–O bond lengths of 2.505(3) Å (Na(1)–O(1)) and 2.692(4) Å (Na(5)–O(2)) are extended relative to the mean structurally characterised sodium–oxygen bond (2.450 Å),[40] while those of Na(2)–O(1) (2.345(4) Å) and Na(4)–O(2) (2.335(4) Å) are diminished.

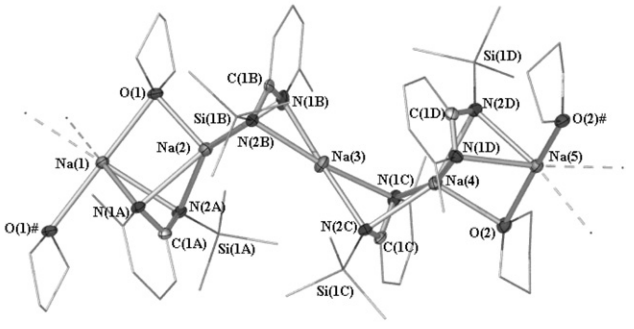

Fig. 1 Molecular structure of [{Na(AMPTMS)(THF)$_{0.5}$}$_n$], **1**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Na(1)–O(1) 2.505(3), Na(1)–N(1A) 2.520(4), Na(1)–N(2A) 2.605(4), Na(2)–O(1) 2.345(4), Na(2)–N(1A) 2.578(5), Na(2)–N(2A) 2.436(5), Na(2)–N(1B) 2.607(5), Na(2)–N(2B) 2.408(5), Na(3)–N(1B) 2.523(5), Na(3)–N(2B) 2.443(4), Na(3)–N(1C) 2.499(4), Na(3)–N(2C) 2.421(4), Na(4)–O(2) 2.335(4), Na(4)–N(1C) 2.624(5), Na(4)–N(2C) 2.417(5), Na(4)–N(1D) 2.592(5), Na(4)–N(2D) 2.437(5), Na(5)–O(2) 2.692(5), Na(5)–N(1D) 2.494(4), Na(5)–N(2D) 2.505(4), N(1A)–Na(1)–N(2A) 53.51(13), N(1A)–Na(1)–N(2A)#^{a} 126.49(13), Na(1)–O(1)–Na(2) 85.26(12), N(1A)–Na(2)–N(2A) 54.74(14), N(1B)–Na(2)–N(2B) 118.55(16), O(1)–Na(2)–N(1A) 93.19(4), O(1)–Na(2)–N(2A) 92.84(15), O(1)–Na(2)–N(1B) 96.77(15), O(1)–Na(2)–N(2B) 115.11(16), N(1A)–Na(2)–N(2B) 118.55(16), N(1B)–Na(1)–N(2A) 126.79(19), N(1B)–Na(3)–N(2B) 55.32(16), N(1C)–Na(3)–N(2C) 55.51(15), N(1C)–Na(4)–N(2C) 53.90(14), N(1D)–Na(4)–N(2D) 54.24(14), O(2)–Na(4)–N(1C) 96.96(15), O(2)–Na(4)–N(2C) 112.35(15), O(2)–Na(4)–N(1D) 97.66(14), O(2)–Na(4)–N(2D) 95.50(15), N(1C)–Na(4)–N(2D) 124.59(17), N(1D)–Na(4)–N(2C) 119.03(16)), Na(4)–O(2)–Na(5) 80.39(12), N(1D)–Na(5)–N(2D) 54.71(13), N(1D)–Na(5)–N(2D)#^{b} 168.51(14). Symmetry transformations used to generate # atoms: ^{a} 12 − *x*, 12 − *y*, 1 − *z*. ^{b} 1 − *x*, *y*, 12 − *z*.

† See the appropriate figure caption for the symmetry transformations employed to generate # atoms

The structure of **1** marks the first incidence of a sodium 2-amidopyridine species that does not include a bi/multidentate donor (*e.g.* 12-crown-4, TMEDA) or hexamethylphosphoramide.[48–50] This may countenance the bonding exhibited as the lessened steric and electronic donor characteristics of THF, *vis-à-vis* poly N- or O-donors, presumably lead to increased dependence upon supplementary ligand donation. This increases the steric crowding experienced within the framework and promotes extended 1-dimensional binding instead of supplementary ether donation, thereby limiting THF inclusion to 0.5 equivalents. When one considers the increase in ionic radius from lithium to sodium (0.60 Å and 1.00 Å resp.)[51] this is a marked difference from the lithium analogue (one equivalent of THF).[38] However, the absence of strong chelate donors can be viewed as synthetically advantageous, permitting metathetical syntheses without the robust coordination of bulky, high-boiling chelate donors that potentially frustrate high nuclearity and novel binding modes for the ligands of interest.

The preparative utility of compound **1** was demonstrated *via* the treatment of anhydrous NdCl$_3$ in THF solution with two molar equivalents under relatively mild conditions (see Scheme 1). This frustrated the adverse inclusion of alkali metal halide allowing near quantitative formation of a material analysing as [Nd(AMPTMS)$_2$(Cl)(THF)] (**2**) as a clean light blue/green solution which, further to filtration to remove sodium chloride, could be crystallised directly following concentration *in vacuo* in near quantitative yield (93%). As per the related tris-AMPTMS species,[38] **2** is acutely sensitive to both air and moisture decomposing immediately under aerobic conditions. However, using **2** and lithium AMPTMS derived species as our basis for comparison, contrary to the findings of Lee *et al.*[39] species of the form "[LnL$_2$Cl]" (L = *N*-silylated-2-amidopyridine ligand) are extremely soluble in THF, diethyl ether and DME, but do redistribute upon dissolution in hexane or toluene. In addition, **2** appears less thermally robust than the related tris-AMPTMS lanthanoid species, undergoing solvent loss at 178 °C and the onset of full decomposition above 250 °C. This compares to decomposition at temperatures greater than 360 °C for the homoleptic AMPTMS species (no melting)[38] and 132–139 °C for related homoleptic tris{2-(*tert*-butyldimethylsilylamido)pyridine} compounds.[39]

Further to characterisation by C,H,N microanalyses, neodymium content[52] and FTIR, the molecular structure of **2** was deduced by single crystal X-ray structure determination.[44–47] A POV-RAY illustration can be seen in Fig. 2 (40% thermal ellipsoids), wherein the centrosymmetric nature of the bis(chloro) bridged dimer can be seen. The geometric parameters of the AMPTMS interaction with the Nd metal centre are similar to those in both [Gd(AMPTMS)$_3$] and [Er(AMPTMS)$_3$].[38] As

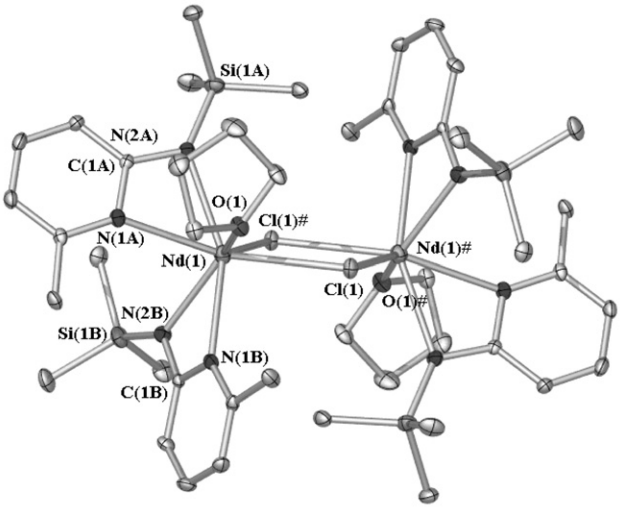

Fig. 2 Molecular structure of $[\{Nd(AMPTMS)_2(Cl)(THF)\}_2]$, **2**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: Nd(1)–N(1A) 2.5373(19), Nd(1)–N(2A) 2.414(2), Nd(1)–N(1B) 2.5419(19), Nd(1)–N(2B) 2.385(2), Nd(1)–O(1) 2.5174(16), Nd(1)–Cl(1) 2.8340(8), Nd(1)–Cl(1)# 2.8309(8), N(1A)–Nd(1)–N(2A) 54.79(6), N(1B)–Nd(1)–N(2B) 54.92(6), N(1A)–Nd(1)–N(1B) 95.26(6), N(2A)–Nd(1)–N(2B) 118.59(7), N(2A)–Nd(1)–N(1B) 149.07(6), N(2B)–Nd(1)–N(1A) 80.65(7), O(1)–Nd(1)–N(1A) 77.92(6), O(1)–Nd(1)–N(2A) 83.26(6), O(1)–Nd(1)–N(1B) 82.76(6), O(1)–Nd(1)–N(2B) 130.01(6), O(1)–Nd(1)–Cl(1) 76.14(4), O(1)–Nd(1)–Cl(1)# 143.26(4), Nd(1)–Cl(1)–Nd(1)# 104.124(19), Cl(1)–Nd(1)–Cl(1)# 75.876(19). Symmetry transformations used to generate # atoms: $1-x, -y, 1-z$.

expected, these indicate a lengthening of the Ln–N_{amido} (mean; 2.346 Å (Gd), 2.303 Å (Er), 2.400 Å (**2**)) and Ln–N_{py} bonds (mean; 2.447 Å (Gd), 2.384 Å (Er), 2.540 Å (**2**)) and narrowing of the intra-ligand N–Ln–N angles (54.79(6)° and 54.92(6)°, mean $[Gd(AMPTMS)_3]$ 56.6°, mean $[Er(AMPTMS)_3]$ 57.8°) due to the increased ionic radius of neodymium (0.98 Å) relative to six-coordinate gadolinium (0.94 Å) and erbium (0.89 Å).[51] The mean Nd–N_{amido} bond length of **2** is significantly longer than that of $[Nd\{N(SiMe_3)_2\}_3]$ (2.29(2) Å)[10] due to increased coordination of the neodymium centre, whilst both the Nd–N_{amido} and Nd–N_{py} bonds are slightly shorter than those in moderately bulkier tris{2-(*tert*-butyldimethylsilylamido)pyridine} $[NdL_3]$ species reported by Lee (mean Nd–N_{amido}2.437 Å, mean Nd–N_{py} 2.573 Å).[39] Furthermore, the decreased congestion of the metal centres, *vis-à-vis* tris-AMPTMS relatives, leads to a decrease in the inter-ligand plane angles of 81.71° and 84.18° (mean for $[Gd(AMPTMS)_3]$ and $[Er(AMPTMS)_3]$ resp.) to 74.11(8)°. This accompanies the orientation of the bulky trimethylsilyl groups away from the THF donor that completes the non-halide coordination of **2** (Nd(1)–O(1) 2.5174(16) Å). The coordination environment that surrounds the central four membered Nd_2Cl_2 metallocycle of **2** bears a resemblance to that of a THF adducted, chloride bridged 1,3-bis{2-(isopropylamino)troponimine}propane neodymium complex recently reported by the group of P. W. Roesky.[53] However, the propyl tether of this ligand and the five-membered chelate rings that accompany coordination lessen the steric strain incited by mononuclear tetradentate coordination. This renders N–Nd–N bite angles of magnitude 63.83° (mean iminotroponamine bite-angle) and 73.22° (mean inter-iminotroponamine bite-angle, mean intraligand N–Nd–N bite angle for **2**; 54.85°).[53] Interestingly, this series of lanthanoid species displays a structural discontinuity whereby heavier lanthanoid species, *e.g.* those of erbium and ytterbium, possess a THF-donor free composition.[53,54] This arises due to contraction of ionic radii as the lanthanoid elements are transcended, and may suggest a similar structural trend for "$[Ln(AMPTMS)_2Cl]$" complexes of the heavier lanthanoids. In the present case, the combination of two moderately bulky ligands about the Nd_2Cl_2 unit renders a central rhombohedral motif dissimilar from the asymmetric geometry observed for the troponimine derivative (Nd(1)–Cl(1)–Nd(1)# 104.124(19)°, Cl(1)–Nd(1)–Cl(1)# 75.876(19)°). This accompanies a shortening of the Nd–Cl bonds due to lessened steric congestion about the bridging chloride linkages, which expectedly exhibit greater symmetry (2.8309(8) Å and 2.8340(8) Å (**2**)). It is interesting to note that analogous yttrium studies by Kempe *et al* using a related 2-amidopyridine ligand, wherein diethyl ether/pyridine solvated YCl_3 was treated with 2, 3 and 4 equivalents of lithiated 2-(trimethylsilylamino)-4-methylpyridine, yielded exclusively lithium yttrate complexes; $[Li(Py)YL_4]$ (Py = pyridine, L = 2-amidopyridine ligand).[23,37] With respect to **2**, it is unlikely that this preference for 'ate' complex formation occurs on the basis of differing ionic radii (Y = 0.90 Å, Nd = 0.98 Å).[51] Instead, it is far more likely that the steric imposition of a 6-methyl (4-methyl for the yttrate examples) substituent frustrates the coordination of greater than three AMPTMS ligands about a rare earth metal centre, while a failure to isolate homoleptic species of yttrium from the 3:1 stoichiometric addition of Li(L) to YCl_3 presumably arises as a solvent effect. Overall, the tractable isolation of **2** suggests greater control of AMPTMS stoichiometry than our original studies of homoleptic erbium and gadolinium complexes had indicated,[38] whereby not only can we control the number of AMPTMS ligands about the lanthanoid centre but we can also successfully isolate "$[LnL_2Cl]$" species with increased metal ionic radii than yttrium. This increase in size presumably invites $[LnL_4]$ type 'ate' formation, and can therefore be considered a significant advance for the rare earth chemistry of these ligands.

Since the pioneering lanthanoid pentamethylcyclopentadienyl work of Watson,[55] Marks[56,57] and Evans[58] during the early eighties, including the ground breaking isolation of $[SmCp^*_2(THF)_2]$ ($Cp^* = [C_5Me_5]^-$),[58] the area of lanthanoid organometallic study has blossomed, in-part, due to the impressive number of catalysts derived upon the decamethyllanthanocene frame and its derivatives.[59–70] Indeed, the isolation of the first tris(pentamethylcyclopentadienyl) metal complex; $[SmCp^*_3]$,[71] and subsequent studies thereof,[72–74] has exposed ligand based redox chemistry with no requirement for redox active metal centres. These exciting ventures have vitalised organolanthanoid chemistry. As such, it is perhaps surprising that the preparation of related terbium species, *i.e.* derivatives of the decamethylterbocene fragment, have been neglected. This may be due to the prohibitive cost of terbium metal and its anhydrous halides, however, our interest in the optophysical properties of organoeuropium(III) and organoterbium(III) compounds,[75] and the overt absence of a structurally characterised Cp* derivative of terbium, invited our use of **1** in the formation of an AMPTMS derivative of $[TbCp^*_2L]$.

As can be seen in Scheme 1, treatment of the terbium bis(pentamethylcyclopentadienide) precursor; $[TbCp^*_2(\mu\text{-}Cl)_2Li(Et_2O)_2]$ (**4**), prepared using a known synthetic procedure,[76] with a stoichiometric amount of **1**, in THF, rendered a colourless solution of the intended product (**3**) rich in precipitate (full precipitation of NaCl by mass) that, further to filtration and concentration *in vacuo*, yielded colourless impressively thermally robust (no melting or decomposition $< 370\,°C$, the limit of the instrument used) crystalline blocks analysing as $[TbCp^*_2(AMPTMS)]$, **3**,[52] in high yield (88%). A single crystal structure determination of **3**[44–47] (see Fig. 3, 40% thermal ellipsoids) confirms the monomeric composition and indicates that the expected extension of Tb–N bonds, due to the bulk of the AMPTMS ligand within the cleft between the two Cp* rings, does not manifest. This renders Tb–N bonds that roughly approximate those expected on the basis of lanthanoid ionic radii when compared to **2** (Tb; 0.92 Å,[51] Tb(1)–N(1) 2.4206(19) Å, Tb(1)–N(2) 2.3601(18) Å Nd ionic radius 0.98

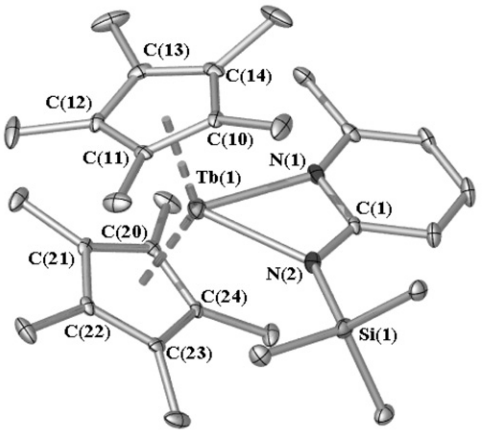

Fig. 3 Molecular structure of $[Tb(C_5Me_5)_2(AMPTMS)]$, **3**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **3** {centroid C(10)–C(14) = (1), centroid C(20)–C(24) = (2)}: Tb(1)–N(1) 2.4206(19), Tb(1)–N(2) 2.3601(18), Tb(1)–(1) 2.4206(19), Tb(1)–(2) 2.385(9) N(1)–Tb(1)–N(2) 57.27(6), N(1)–Tb(1)–(1) 106.94(26), N(1)–Tb(1)–(2) 106.07(25), N(2)–Tb(1)–(1) 110.98(26), N(2)–Tb(1)–(2) 109.38(25), Cp*:Cp* interplanar angle 42.65(17), (1)–Tb(1)–(2) 137.33(34).

Å,[51] Nd(1)–N(1A) in **2**; 2.5373(19) Å, Nd(1)–N(2A) in **2**; 2.414(2) Å). Instead, the central placement of the AMPTMS causes an increase in the Cp*:Cp* interplanar angle (42.65(17)°, mean Tb(1)–C; 2.692 Å, mean Tb(1)–$Cp^*_{centroid}$; 2.403 Å) relative to the analogous angles of a related bis-Cp* ytterbium species; $[YbCp^*_2(N,N'\text{-7-azaindolate})]$ (39.50°), which contains a discrete NCN 'planar' donor.[77] This transpires due to increased buttressing of the amide ligand within the decamethyllanthanocene core in spite of longer Ln–N bonds (Yb–N lengths in above example; 2.279(8) Å and 2.362(8) Å).[77] This interaction appears diminished relative to similar samarocene derived species, *e.g.* $[SmCp^*_2\{(N\text{-benzylidene-}\alpha\text{(trimethylsilyl)amino)benzylamine}\}]$,[69] which exhibit accentuated Cp*:Cp* interplanar angles (45.57° for this example)[69] consistent with increased steric bulk orthogonal to the plane of the anionic NCN donor ligand. However, without exception, these species bear geometries that suggest less structural perturbation than those derived from the ligation of *ortho*-methoxy and -phenoxy substituted trimethylsilylated anilides about decamethylytterbocene[78] (respective Cp*:Cp* angles 46.2(1)° and 47.3(1)°), wherein the larger N,O bite-angle of the five-membered metallocyclic species facilitates increased metal–ligand proximity (Yb–N; OMe 2.275(1) Å, OPh 2.270(3) Å **3**). Finally, it is noteworthy that compound **3** represents the first structurally authenticated decamethyllanthanocene complex incorporating a 2-amidopyridine ligand system.

Studies concerning the synthesis, structural characterisation and applications potential of substituted 2-amidopyridine and related ligand system complexes of the lanthanoids are ongoing in our laboratory.

Experimental

$[\{Na(AMPTMS)(THF)_{0.5}\}_n]$, 1

Sodium bis(trimethylsilyl)amide (1.7 cm^3, 1.70 mmol) was added dropwise to a solution of 2-(trimethylsilylamino)-6-methylpyridine (0.31 g, 1.72 mmol) in THF (25 cm^3). The resulting clear colourless solution was stirred overnight prior to removal of all volatiles *in vacuo*. This yielded an oily white solid that upon washing with cold (*ca.* 0 °C) hexane (2 × 5 cm^3) yielded a light colourless powder. Extraction into fresh THF (< 10 cm^3), and placement at −10 °C gave the title compound as fine colourless needles suitable for X-ray study and microanalysis (0.30 g, 74%), m.p. (no decomp.) 93 °C. ^{1}H NMR (C_6D_6, 300 K): δ 0.40 (s, 9H, $Si(CH_3)_3$), 1.48 (m, 2H, thf), 2.30 (s, 3H, 6-CH_3), 3.64 (s, 2H, thf), 6.16 (m, 1H, Py–H), 6.32 (m, 1H, Py–H), 7.14 (m, 1H, Py–H). ^{13}C NMR (C_6D_6, 300 K): δ 2.9 (s, $Si(CH_3)_3$), 25.8 (s, 6-CH_3), 26.2 (s, thf), 68.2 (s, thf), 110.3, 118.4, 137.4, 150.6, 156.8 (s, Py–C). IR (Nujol) ν/cm^{-1}: 614 m sh, 669 m, 708 w sh, 742 m, 784 m, 866 m br, 941 w sh, 988 m, 1037 m, 1066 m, 1163 w, 1206 w sh, 1244 s, 1360 m br, 1547 m, 1587 s br. Anal. Calc. for $C_{11}H_{19}N_2O_{0.5}Si_1Na_1$: C, 55.43; H, 8.03; N, 11.75. Found: C, 55.01; H, 7.78; N, 11.83.

$[\{Nd(AMPTMS)_2(Cl)(THF)\}_2]$, 2

A solution of **1** (0.57 g, 2.39 mmol) in THF (30 cm^3) was added dropwise to a stirred slurry of anhydrous $NdCl_3$ (0.30 g, 1.20 mmol) in THF (75 cm^3). The resulting opaque light blue solution was heated (*ca.* 40 °C) for 3 hours and cooled to ambient temperature, whereupon subsequent stirring overnight followed by filtration rendered a light blue/green solution that was concentrated *in vacuo* (*ca.* 5 cm^3). Placement of this solution at room temperature for several days yielded large blue-green prisms of **2** that were washed with cold (−40 °C) hexane (3 × 2 cm^3) (0.68 g, 93%), m.p. 178 °C (solvent loss, no decomp. < 250 °C). IR (Nujol) ν/cm^{-1}: 620 w, 675 w, 712 w, 732 w, 764 w, 782 m sh, 782 m sh, 859 m br, 948 w, 998 w, 1034 m, 1071 m sh, 1162 w, 1240 m, 1377 m, 1552 m sh, 1593 s sh. Anal. Calc. for $C_{44}H_{76}N_8O_2Si_4Cl_2Nd_2$: C, 43.29; H, 6.27; N, 9.18; Nd, 23.63. Found: C, 43.02; H, 6.57; N, 9.36; Nd, 23.71.[52]

$[Tb(\eta^5\text{-}C_5Me_5)_2(AMPTMS)]$, 3

A solution of **1** (0.057 g, 0.24 mmol) in THF (10 cm^3) was added dropwise to a stirred solution of $[TbCp^*_2(\mu\text{-}Cl)_2Li(OEt_2)_2]$ (0.154 g, 0.23 mmol), also in THF (10 cm^3), yielding a colourless slurry of precipitated sodium chloride and dissolved **3**. Filtration followed by concentration *in vacuo* (*ca.* 1 cm^3) gave large rectangular prisms of **3** in near quantitative yield that were microanalytically pure, devoid of lithium halide contaminant and luminesced strongly upon irradiation under a 380 nm ultraviolet lamp (0.116 g, 81%), no melting or decomposition below 370 °C (limit of instrument used). IR (Nujol) ν/cm^{-1}: 590 s sh, 675 m, 732 m sh, 778 m, 842 m, 872 m, 950 m, 1022 m, 1067 m, 1167 w, 1211 w sh, 1258 s, 1556 m, 1599 s sh. Anal. Calc. for $C_{29}H_{45}N_2Si_1Tb_1$: C, 57.38; H, 7.47; N, 4.61; Tb, 26.18. Found: C, 57.47; H, 7.62; N, 4.31; Tb, 26.57.[52]

Crystal data:[44–47] $[\{Na_4(AMPTMS)_4(THF)_2\}_n]$, **1**: $C_{44}H_{76}N_8Na_4O_2Si_4$, M = 953.45, monoclinic, a = 33.348(7), b = 11.020(2), c = 32.188(6) Å, β = 110.03(3)°, V = 11 113(4) $Å^3$, T = 123(2) K, space group $C2/c$ (No. 15), Z = 8, μ(MoKα) = 0.178 mm^{-1}, 52 435 reflections collected, 12 887 unique (R_{int} = 0.2635). Final $GooF$ = 0.939, $R1$ = 0.0972, $wR2$ = 0.1909, R indices based on 4164 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 578 parameters, 0 restraints. Note: Data were weak owing to consistent twinning of **1**. CCDC 209443.‡

Crystal data:[44–47] $[\{Nd(AMPTMS)_2(Cl)(THF)\}_2]$, **2**: $C_{22}H_{38}Cl_1N_4Nd_1O_1Si_2$, M = 610.43, orthorhombic, a = 16.194(3), b = 17.076(3), c = 20.335(4) Å, V = 5623.4(19) $Å^3$, T = 123(2) K, space group $Pbca$ (No. 61), Z = 8, μ(MoKα) = 2.047 mm^{-1}, 58 793 reflections collected, 6990 unique (R_{int} = 0.0504). Final $GooF$ = 1.031, $R1$ = 0.0271, $wR2$ = 0.0581, R indices based on 5391 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 288 parameters, 0 restraints. CCDC 209444.

‡ CCDC reference numbers 209443–209445. See http://www.rsc.org/suppdata/nj/b3/b304197b/ for crystallographic data in .cif or other electronic format.

Crystal data:[44–47] [Tb(C_5Me_5)$_2$(AMPTMS)], **3**: $C_{29}H_{45}N_2Tb_1Si_1$, $M = 608.68$, trigonal, $a = b = 17.207(2)$, $c = 50.082(10)$ Å, $V = 12841(4)$ Å^3, $T = 123(2)$ K, space group R-3 (No. 148), $Z = 18$, $\mu(\mathrm{MoK}\alpha) = 2.539$ mm^{-1}, 20 174 reflections collected, 7058 unique ($R_{int} = 0.0292$). Final $GooF = 1.056$, $R1 = 0.0258$, $wR2 = 0.0564$, R indices based on 5938 reflections with $I > 2\mathrm{sigma}(I)$ (refinement on F^2), 312 parameters, 0 restraints. CCDC 209445.

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References

1 F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2466.
2 F. T. Edelmann, D. M. M. Freckman and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851.
3 W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233**, 131.
4 R. Duchateau, T. Tuinstra, E. A. C. Brusee, A. Meetsma, P. T. van Duijnen and J. H. Teuben, *Organometallics*, 1997, **16**, 3511.
5 R. Duchateau, E. A. C. Brussee, A. Meetsma and J. H Teuben, *Organometallics*, 1997, **16**, 5506.
6 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
7 F. Estler, G. Eickerling, E. Herdtweck and R. Anwander, *Organometallics*, 2003, **22**, 1212.
8 D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
9 P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24**, 1.
10 R. A. Anderson, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 2317.
11 J. A. Ghotra, M. B. Hursthouse and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669.
12 W. S. Rees, O. Just and D. S. V. Derveer, *J. Mater. Chem.*, 1999, **9**, 249.
13 O. Eisenstein, P. B. Hitchcock, A. G. Hulkes, M. F. Lappert and L. Maron, *Chem. Commun.*, 2001, 1560.
14 *Organolanthanoid Chemistry: Synthesis, Structure, Catalysis*, ed. W. A. Herrman, *Top. Curr. Chem.*, 1996, 179.
15 F. T. Edelmann, in *Comprehensive Organometallic Chemistry*, vol. 4, 2nd edn., eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, UK, 1995.
16 H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.
17 C. J. Schaverien, *Adv. Organomet. Chem.*, 1994, **36**, 238.
18 E. N. Kirillov, E. A. Fedorova, A. A. Trifonov and M. N. Bochkarev, *Applied Organometallic Chemistry*, 2001, **15**, 151.
19 W. J. Evans, S. C. Engerer, P. A. Piliero and A. L. Wayda, *J. Chem. Soc., Chem. Commun.*, 1979, 1007.
20 A. C Greenwald, W. S. Rees and U. W. Lay, *Mater. Res. Soc. Symp. Proc.*, 1993, **301**, 21.
21 W. S. Rees, U. W. Lay and A. C. Greenwald, *Mater. Res. Soc. Symp. Proc.*, 1994, **334**, 207.
22 R. L. LaDuca and P. T. Wolczanski, *Inorg. Chem.*, 1992, **31**, 1311.
23 R. Kempe, *Eur. J. Inorg. Chem.*, 2003, 791.
24 R. Kempe, *Angew. Chem., Int. Ed.*, 2000, **39**, 468.
25 L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 1011.
26 L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1990, 89.
27 C. Jones, P. C. Junk, S. G. Leary and N. A. Smithies, *Main Group Met. Chem.*, 2001, **24**, 383.
28 C. Jones, P. C. Junk, S. G. Leary, N. A. Smithies and J. W. Steed, *Inorg. Chem. Commun.*, 2002, **5**, 533.
29 C. Jones, P. C. Junk, S. G. Leary and N. A. Smithies, *J. Chem. Soc., Dalton Trans.*, 2000, 3186.
30 C. Jones, P. C. Junk and N. A. Smithies, *Main Group Met. Chem.*, 2001, **24**, 801.
31 M. L. Cole and P. C. Junk, *Dalton Trans.*, 2003, 2109.
32 W.-Y. Yang, L. Chen and S. Wang, *Inorg. Chem.*, 2001, **40**, 507.
33 H. Noss, M. Oberthür, C. Fischer, W. P. Kretschmer and R. Kempe, *Eur. J. Inorg. Chem.*, 1999, 2283.
34 A. Spannenberg, M. Oberthür, H. Noss, A. Tillack, P. Arndt and R. Kempe, *Angew. Chem. Int. Ed.*, 1998, **37**, 2079.
35 R. Kempe, H. Noss and H. Fuhrmann, *Chem. Eur. J.*, 2001, **7**, 1630.
36 M. S. Hill and P. B. Hitchcock, *Angew. Chem., Int. Ed.*, 2001, **40**, 4089.
37 A. Spannenberg, P. Arndt and R. Kempe, *Angew. Chem., Int. Ed.*, 1998, **37**, 832.
38 J. Baldamus, M. L. Cole, U. Helmstedt, E. Hey-Hawkins, C. Jones, P. C. Junk, F. Lange and N. A. Smithies, *J. Organomet. Chem.*, 2003, **665**, 33.
39 S. C. F. Kui, H.-W. Li and H. K. Lee, *Inorg. Chem.*, 2003, **42**, 2824.
40 From a survey of the Cambridge Crystallographic Structural Database (CCSD).
41 M. L. Cole, D. J. Evans, P. C. Junk and M. K. Smith, *Chem. Eur. J.*, 2003, **9**, 415.
42 J. Baldamus, C. Berghof, M. L. Cole, D. J. Evans, E. Hey-Hawkins and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 2002, 2802.
43 M. L. Cole and P. C. Junk, *J. Organomet. Chem.*, 2003, **666**, 55.
44 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, 276: Macromolecular Crystallography, Part A*, 1997, 307, eds. C. W. Cater and R. M. Sweet, Academic Press, New York.
45 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
46 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
47 L. J. Barbour, X- Seed, *Crystallographic Interface*, University of Missouri-Columbia, MO, USA, 1999.
48 P. C. Andrews, W. Clegg and R. E. Mulvey, *Angew. Chem. Int. Ed.*, 1990, **29**, 1440.
49 P. C. Andrews, D. R. Baker, R. E. Mulvey, W. Clegg and P. A. O'Neil, *Polyhedron*, 1991, **10**, 1839.
50 S. T. Liddle and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 2001, 402.
51 E. Fluck, K. G. Heumann, *Periodic Table of the Elements*, VCH, Weinheim, Germany, 1991.
52 J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, *Inorg. Chem.*, 1981, **20**, 4115.
53 P. W. Roesky and M. R. Bürgstein, *Inorg. Chem.*, 1999, **38**, 5629.
54 P. W. Roesky, *Inorg. Chem.*, 1998, **37**, 4507.
55 P. L. Watson, J. F. Whitney and R. L. Harlow, *Inorg. Chem.*, 1981, **20**, 3271.
56 G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8091.
57 G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8111.
58 W. J. Evans, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 6507.
59 *Applied Homogeneous Catalysis with Organometallic Compounds*, eds. B. Corniels and W. A. Herrman, VCH, Weinheim, Germany, 1996.
60 *Metallocenes*, eds. A. Togni and R. L. Halterman, Wiley-VCH, Weinheim, Germany, 1998.
61 C. M. Haar, C. L. Stern and T. J. Marks, *Organometallics*, 1996, **15**, 1765.
62 M. A. Giardello, V. P. Conticello, L. Brard, M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10 241.
63 H. J. Heeres, J. Renkema, M. Booij, A. Meetsma and J. H. Teuben, *Organometallics*, 1988, **7**, 2495.
64 P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51.
65 G. A. Molander and P. J. Nichols, *J. Am. Chem. Soc.*, 1995, **117**, 4415.
66 K. N. Harrison and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 9220.
67 X. Yang, A. M. Seyam, P.-F. Fu and T. J. Marks, *Macromolecules*, 1994, **27**, 4625.
68 M. R. Gagne, S. P. Nolan and T. J. Marks, *Organometallics*, 1990, **9**, 1716.
69 Y. Obora, T. Ohta, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1997, **119**, 3745.
70 H. Schumann, A. Helm, J. Demtschuk and S. H. Mühle, *Organometallics*, 2003, **22**, 118.
71 W. J. Evans, S. L. Gonzales and J. W. Ziller, *J. Am. Chem. Soc.*, 1991, **113**, 7423.

72 W. J. Evans, J. M. Perotti, R. J. Doedens and J. W. Ziller, *Chem. Commun.*, 2001, 2326.
73 W. J. Evans, G. W. Nyce and J. W. Ziller, *Angew. Chem., Int. Ed.*, 2000, **39**, 240.
74 W. J. Evans, C. A. Seibel, J. W. Ziller and R. J. Doedens, *Organometallics*, 1998, **17**, 2103.
75 D. Sendor, M. Hilder, P. C. Junk, T. Jüstel and U. H. Kynast, *New J. Chem.*, 2003 in press (DOI: 10.1039/b302499g).
76 H. Schumann, K. Zietzke and R. Weimann, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 121.
77 G. B. Deacon, E. E. Delbridge, G. D. Fallon, C. Jones, D. E. Hibbs, M. B. Hursthouse, B. W. Skelton and A. H. White, *Organometallics*, 2000, **19**, 1713.
78 G. B. Deacon, C. M. Forsyth, N. M. Scott, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 2001, **54**, 439.