



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 665 (2003) 33–42

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorgchem

Synthesis and structural study of a lithium complex of 6-methyl-2-(trimethylsilylamino)pyridine and its use in the formation of some lanthanoid complexes

Jens Baldamus^{a,1}, Marcus L. Cole^a, Ulrike Helmstedt^b, Eva-Marie Hey-Hawkins^b,
Cameron Jones^c, Peter C. Junk^{a,*}, Franziska Lange^a, Neil A. Smithies^c

^a School of Chemistry, Box 23 Monash University, Clayton, Vic., 3800, Australia

^b Institut für Anorganische Chemie der Universität Leipzig, D-04103 Leipzig, Germany

^c Department of Chemistry, University of Wales, Cardiff, P.O. Box 912, Park Place, Cardiff CF10 3TB, UK

Received 9 August 2002; received in revised form 28 October 2002; accepted 28 October 2002

Abstract

Lithiation of 6-methyl-2-(trimethylsilylamino)pyridine (APyTMSH) occurs smoothly in tetrahydrofuran (thf) affording $[\text{Li}(\text{APyTMS})(\text{thf})]_2$ (**1**). Treatment of anhydrous lanthanoid chlorides (LnCl_3 , $\text{Ln} = \text{Gd}, \text{Er}$) with 1.5 equivalents of (**1**) yields the solvent-free homoleptic tris-amido complexes $[\text{Ln}(\text{APyTMS})_3]$, ($\text{Ln} = \text{Gd}$ (**2**); $\text{Ln} = \text{Er}$ (**3**)). Similar treatment of LnCl_3 ($\text{Ln} = \text{Gd}, \text{Er}$) with one equivalents of **1** putatively generates the heteroleptic species $[\text{Ln}(\text{APyTMS})_2\text{Cl}]$, ($\text{Ln} = \text{Gd}$ (**4**); $\text{Ln} = \text{Er}$ (**5**)) in situ, however, these compounds undergo redistribution in hexane to yield homoleptic **2** and **3** and the anhydrous lanthanoid halides ($\text{Ln} = \text{Gd}$, (**6**), $\text{Ln} = \text{Er}$ (**7**)) and were therefore not fully characterised. These lanthanoid reagents are extremely moisture sensitive as exemplified by the low yield isolation of $[\text{APyH}_2 \cdot \text{H}]_2[\text{ErCl}_5(\text{thf})]$ during one preparation of **3**. The structures of compounds **1**, **2**, **3** and **8** were characterised by X-ray crystallographic methods. The X-ray structure of **1** is a centrosymmetric dimer similar to its diethyl ether analogue. Compounds **2** and **3** are six-coordinate homoleptic mononuclear species and compound **8** comprises the unprecedented $[\text{ErCl}_5(\text{thf})]^-$ anion within an intricate hydrogen-bonded ionic system.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium complexes; Lanthanoid complexes; Synthesis and structural study

1. Introduction

Metal amides have attracted considerable attention over the past 30 years [1]. The focus on lithium amides has centred around their utility in inorganic and organic synthesis [2]. The structures of these complexes, both in the solid state and solution, are of great importance since they can significantly affect the outcome of syntheses or transformations. The high polarity of the Li–N bond [3] generally leads to association unless sterically demanding ligands are employed [4]. Further-

more, the binding of solvent molecules, or indeed intramolecular solvation by heteroatoms can also inhibit the aggregation of these complexes.

In this paper we report the synthesis, reactivity and structural study of an *N*-functionalised amido-lithium compound based on 6-methyl-2-(trimethylsilylamino)pyridine (APyTMSH). This material is related to work we have previously published on this sterically hindered ligand [5] and its less hindered unsilylated partner, 6-methyl-2-aminopyridine [6], as well as some studies of the 8-amidoquinoline ligand and its trimethylsilylated analogue [7]. In terms of structure, given the centrosymmetric diethyl ether adducted dimer formed upon lithium metallation of APyTMSH in Et_2O , it was of interest to determine how the etherated dilithium–dinitrogen core changes when tetrahydrofuran (thf) is used as the coordinating solvent. These changes can be

* Corresponding author. Fax: +61-3-9905-4597

E-mail address: peter.junk@sci.monash.edu.au (P.C. Junk).

¹ Both this author and Franziska Lange are on leave from the Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany.

significant, as demonstrated by the similarly anionic-dinitrogen ligand $[(p\text{-CH}_3\text{C}_6\text{H}_4)\text{NC}(\text{H})\text{N}(p\text{-CH}_3\text{C}_6\text{H}_4)]^-$, which modifies from a diethyl ether adducted $\mu\text{-}\eta^2\text{:}\eta^1$ -bound dimer [8a] to an ionic system bearing $\mu\text{-}\eta^1\text{:}\eta^1$ -bound $[\text{Li}_2\{(p\text{-CH}_3\text{C}_6\text{H}_4)\text{NC}(\text{H})\text{N}(p\text{-CH}_3\text{C}_6\text{H}_4)\}_3(\mu\text{-thf})(\text{thf})_2]$ anions upon preparation in thf [8b]. Furthermore, due to increased solubility, thf is often the solvent of choice for the metathetical preparation of organolanthanoid compounds using their parent halides. Accordingly, the structural composition of this intermediate was considered relevant to its utility as an inorganic synthon.

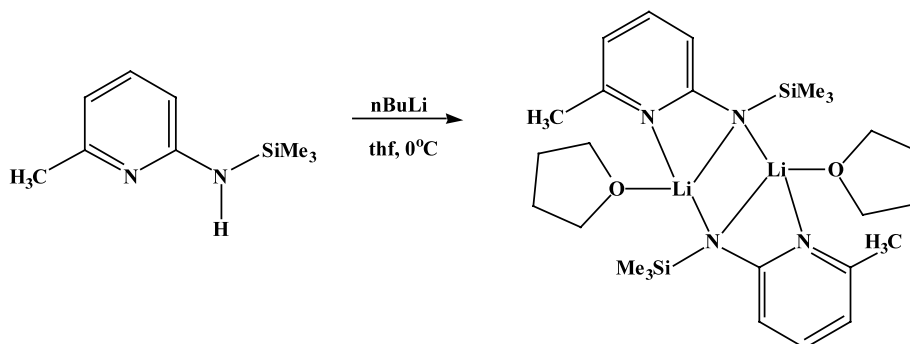
Organometallic complexes of the lanthanoid elements have attracted great interest due to their potential application in hydrogenation, polymerisation, hydroboration and oligomerisation catalytic processes [9–12]. More recently organoamido- and alkoxo-lanthanoid complexes have been studied for their uses in similar roles as well as potential MOCVD and ceramics precursors [13,14]. These compounds are considered alternatives to the ubiquitous cyclopentadienyl (Cp^-) lanthanoid complexes and have scope for considerable chemistry using Cp^- compounds as comparisons. The use of sterically hindered ligands such as $[\text{N}(\text{SiMe}_3)_2]^-$ in $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [15] generates low lanthanoid coordination numbers (i.e. 3) and bidentate anionic species, such as $[\text{APyTMS}]^-$, also lead to the formation of low-coordinate (ca. 6) organoamidolanthanoid complexes. This is illustrated by $[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{NMe}_2]^-$, which forms homoleptic tris-bidentate organoamido complexes within an isostructural series of the lanthanoids [16]. We now extend this lanthanoid work to the smaller bite $[\text{APyTMS}]^-$ species. Herein, we report the synthesis of $[\text{Li}(\text{APyTMS})(\text{thf})_2]$ (**1**) and its use in the formation of homoleptic tris-amido complexes $[\text{Ln}(\text{APyTMS})_3]$ ($\text{Ln} = \text{Gd}$ (**2**); $\text{Ln} = \text{Er}$ (**3**)) and heteroleptic $[\text{Ln}(\text{APyTMS})_2\text{Cl}]$ ($\text{Ln} = \text{Gd}$ (**4**); $\text{Ln} = \text{Er}$ (**5**)). The latter are unstable in hexane and undergo redistribution yielding the homoleptic tris-amido complexes **2** and **3** and the anhydrous unsolvated lanthanoid halides ($\text{Ln} = \text{Gd}$, (**6**); $\text{Ln} = \text{Er}$ (**7**)). We also report the synthesis of a novel by-product $[\text{APyH}_2 \cdot \text{H}]_2[\text{ErCl}_5(\text{thf})]$

(**8**), formed by adventitious inclusion of moisture in a reaction mixture involving ErCl_3 and $[\text{Li}(\text{APyTMS})(\text{thf})_2]$.

2. Results and discussion

Lithiation of 6-methyl-2-(trimethylsilylamino)pyridine (APyTMSH) with one equivalent of *n*-BuLi in thf at 0 °C rapidly formed a light yellow-coloured solution containing $[\text{Li}(\text{APyTMS})(\text{thf})_2]$ (**1**), in good yield (Scheme 1). The $^1\text{H-NMR}$ spectrum of **1** displays resonances for the $-\text{Si}(\text{CH}_3)_3$ protons at 0.30 ppm, resonances at 1.21 and 3.47 ppm for thf, and a singlet at 2.19 ppm for the methyl group, whilst the aromatic protons resonate between 6.15 and 8.11 ppm. The resonances for the thf protons occur slightly upfield compared with those of unbound thf (ca. 1.78 and 3.57 ppm). The absence of an N–H resonance at 4.14 ppm indicates complete metallation [5]. The $^{13}\text{C-NMR}$ spectrum is unexceptional containing aromatic resonances between 108.3 and 171.0 ppm, thf resonances at 28.08 and 68.35 ppm while the methyl and trimethylsilyl resonances occur at 24.56 and 2.62 ppm, respectively. The infrared spectrum shows strong absorbance bands at 1257 and 831 cm^{-1} , attributable to $\nu(\text{C-H}$ deformation) and $\nu(\text{Si-C}$ stretch) of the trimethylsilyl group, and sharp stretches at 1014 and 863 cm^{-1} , attributable to asymmetric and symmetric C–O–C stretches of thf. The absence of any N–H stretching in the infrared is also noteworthy.

Crystals suitable for X-ray diffraction studies of compound **1** were grown from a cooled thf solution. $[\text{Li}(\text{APyTMS})(\text{thf})_2]$ crystallises in the triclinic space group $P\bar{1}$ with two independent halves of the compound in the asymmetric unit. In both, centrosymmetric dimer resides on an inversion centre with distorted tetrahedral Li atoms chelated by one amidopyridine and bridged to another $\text{N}_{(\text{amido})}$ thf molecule completes the lithium coordination number of four (Fig. 1). Compound **1** is isomorphous to the diethyl etherate published previously [5], and bond lengths and angles are unsurpris-



Scheme 1.

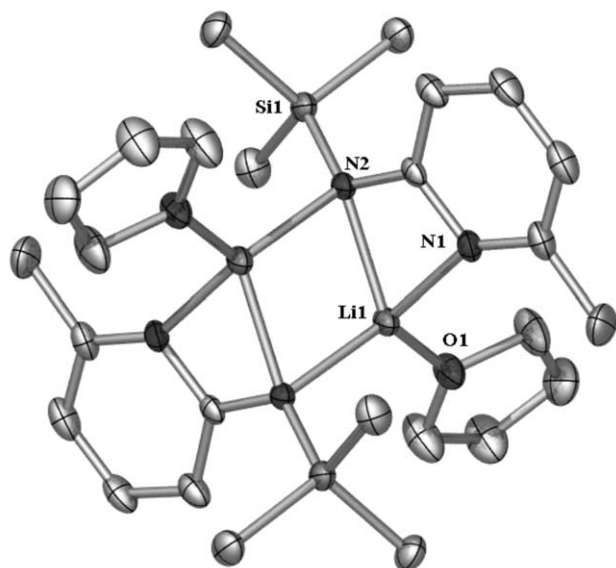


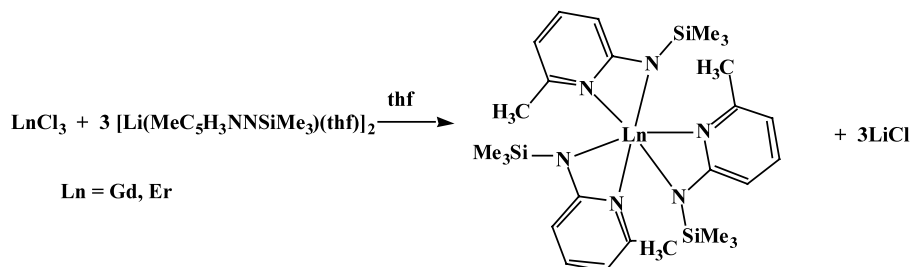
Fig. 1. Molecular structure of the centrosymmetric dinuclear $\{[Li(APySiMe_3)](thf)\}_2$ (**1**). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids.

ingly consistent (Li–N; 2.029(7) to 2.103(7) Å in compound **1**, 2.08(2) Å in $[Li(APyTMS)(Et_2O)]_2$, Li–O; 1.919(7) and 1.933(7) Å in compound **1**, 1.98(1) Å in $[Li(APyTMS)(thf)]_2$). As in $[Li(APyTMS)(Et_2O)]_2$, the small bite of chelating $APyTMS^-$ ($N(1)–Li(1)–N(2) = 67.4(2)^\circ$) contributes to the distortion from tetrahedral about the Li centre.

Compound **1** was found to be a suitable transfer reagent in the formation of homoleptic and, albeit less so, heteroleptic lanthanoid complexes. In the formation of homoleptic complexes, treatment of **1** with 2/3 of a molar equivalent of anhydrous $LnCl_3$ ($Ln = Gd, Er$) in thf affords $[Ln(APyTMS)_3]$ ($Ln = Gd$, (**2**); $Ln = Er$, (**3**)), in good yield, after workup (Scheme 2). These highly hydrocarbon soluble complexes are extremely robust showing no evidence of melting or thermal decomposition up to 360 °C. Due to the paramagnetic nature of the lanthanoid metals involved, the nuclear magnetic spectra of compounds **2** and **3** were severely broadened and no fine structure was discerned (indeed, no signals were observed in the ^{13}C -NMR spectra). Also, as expected, the inclusion of erbium(III) in compound **3** gives rise to a large paramagnetic shift in its 1H -NMR

spectrum (external C_6D_6 standard). With respect to **2**, for which the Gd(III) singlet ground state is not expected to induce paramagnetic shifting, the comparable resonances of **3** are ca. 3.5 ppm downfield (see Experimental Section). However, as hoped, the 1H -NMR spectra of both compounds indicate the absence of thf in the product and display the expected ligand resonances in the correct ratio. Furthermore, the infrared spectra exhibit only absorbances emanating from the deprotonated ligand (with no absorbances attributable to thf or N–H), thus to fully identify complexes **2** and **3** X-ray crystal structures.

Compounds **2** and **3** are essentially isostructural, according to their structures are described together as follows. Compound **2** crystallises in the triclinic space group $P\bar{1}$ and compound **3** in the monoclinic space group $P2_1/c$, with one whole molecule in the asymmetric unit. In both, the six-coordinate Ln centre is bound by three chelating amidopyridine ligands resulting in distorted octahedral geometry (Fig. 2). This distortion arises due to the small bite afforded by the four-membered chelate ring of the ligand ($N'–Ln–N''$ ave = 56.6 and 57.8° for compounds **2** and **3**, respectively). The ligands arrange themselves in a meridional fashion about the metal centre. The binding by the ligand is asymmetric about the metal centre with $Ln–N_{(amido)}$ distances (ranging from 2.334(7) to 2.357(7) and 2.279(4) to 2.319(4) Å for compounds **2** and **3**, respectively) significantly shorter than $Ln–N_{(pyridyl)}$ distances by ca. 0.1 Å (range 2.440(7) to 2.460(7) and 2.378(4) to 2.387(4) Å for compounds **2** and **3**, respectively). The decrease in $Ln–N$ bond distances in moving from **2** to **3** reflects the contraction in ionic radii between six-coordinate Gd^{3+} and Er^{3+} (Table 3). The erbium complex can be compared with some related six-coordinate homoleptic lanthanoid amido complexes where the bite of the ligand is appreciably larger, viz five-membered chelate rings of $[Ln(N(SiMe_3)CH_2CH_2NMe_2)_3]$ [16] (cf. four-membered chelates in the present examples). In $[Ln(N(SiMe_3)CH_2CH_2NMe_2)_3]$, the *fac*-octahedral complex has mean $Er–N$ distances of 2.24(1) and 2.72 Å for $N_{(amido)}$ and $N_{(donor)}$ bonds, which are significantly different to those in **3**. It is noteworthy that there are no solvent thf molecules bound to the metal centres of compounds **2** and **3**.



Scheme 2.

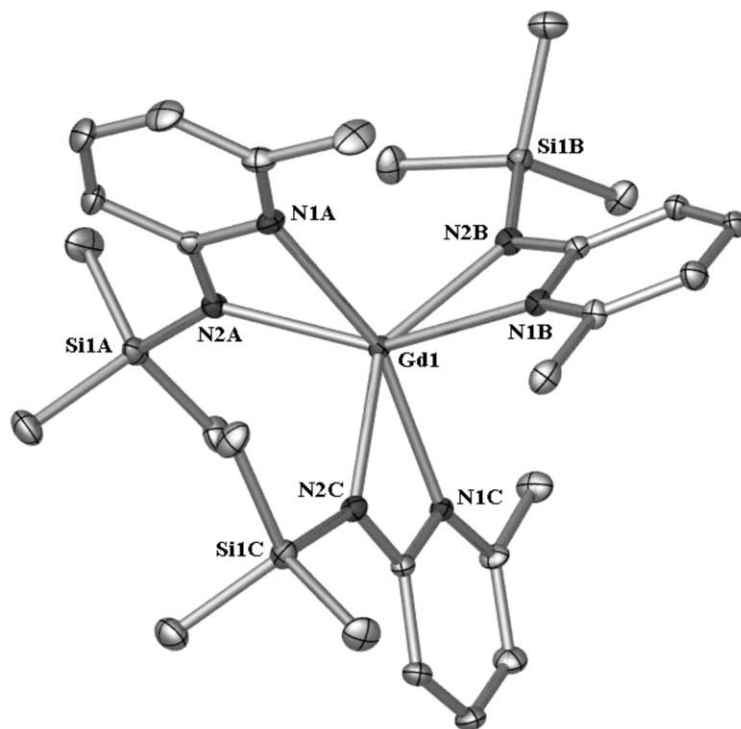
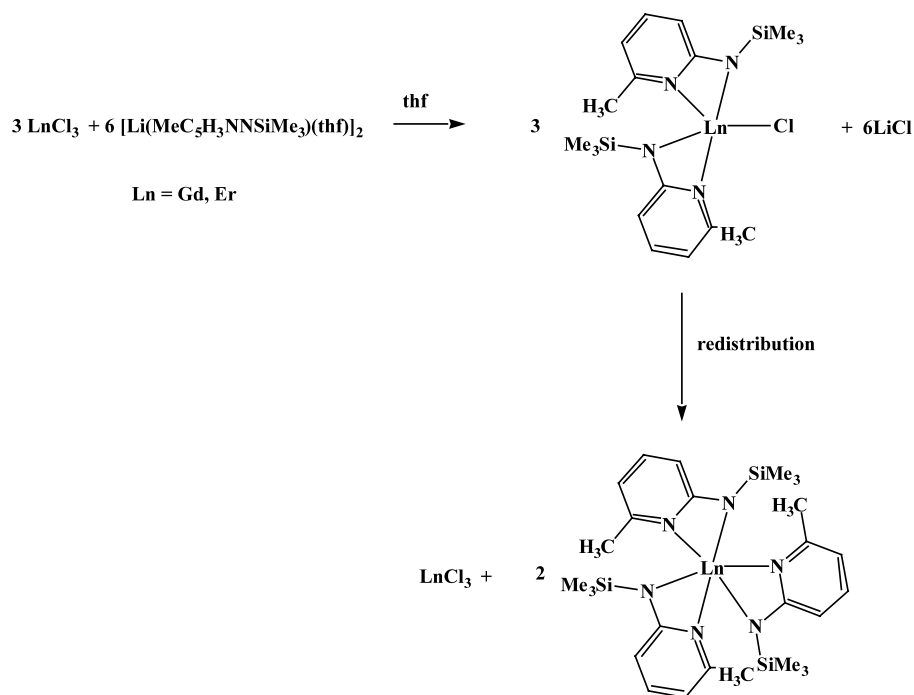


Fig. 2. Molecular structure of mononuclear, *mer*-octahedral [Gd(APyTMS)₃] (2) (Ln = Er, (3) is isostructural). Hydrogen atoms are omitted for clarity; 50% thermal ellipsoids.

This presumably results courtesy of the steric buttressing inherent of trimethylsilylated amido ligands.

In attempting to isolate some heteroleptic complexes of the lanthanoids, anhydrous LnCl₃ (Ln = Gd, Er) was treated with one equivalent of compound 1 in thf

(Scheme 3). In the case of Ln = Er, after extraction of the heteroleptic complex into hexane (in order to remove the thf-soluble LiCl by-product), pink crystals of two morphologies were identified. These compounds were readily identified by X-ray crystallographic and spectro-



Scheme 3.

scopic methods as homoleptic compound **3** and anhydrous unsolvated ErCl_3 (**8**) [17]. In the case of $\text{Ln} = \text{Gd}$, (**2**), again two products were obtained; large colourless crystals of **2** and a microcrystalline powder that was identified by infrared spectroscopy as anhydrous unsolvated GdCl_3 (**7**). The formation of tris-homoleptic compounds and LnCl_3 from this reaction can be explained by the initial formation of the heteroleptic complex $[\text{Ln}(\text{APyTMS})_2\text{Cl}]$ ($\text{Ln} = \text{Gd}$, (**4**); Er (**5**)), followed by slow redistribution in hexane (Scheme 3). Were the redistribution of compounds **4** and **5** to occur prior to extraction in hexane, there would be no possibility of isolating anhydrous unsolvated LnCl_3 from the reaction mixture because of its insolubility in hexane. Also, the affinity of anhydrous LnCl_3 towards oxygen-containing polar solvents is well-documented [18] if any LnCl_3 was carried over from the reaction mixture it would be isolated in minimal yield and presumably be thf-coordinated. Thus, while compounds **4** and **5** were not isolated and characterised, we believe their formation is irrefutable and implied in thf [19].

During the course of one preparation of **3** we identified a by-product in low yield (ca. 5%). This compound was identified by spectroscopic and X-ray crystallographic methods as $[\text{APyH}_2 \cdot \text{H}]_2[\text{ErCl}_5(\text{thf})]$ (**8**), highlighting the extreme moisture sensitivity of this class of compounds. The formation of compound **8** presumably results due to the inadvertent inclusion of a small amount of moisture. Small quantities of water can cleave the hydrolysable N–Si bond while HCl can be formed during the hydrolysis of ErCl_3 . Hence, protonation of the pyridyl ligand conceivably occurs with concomitant formation of the novel $[\text{ErCl}_5(\text{thf})]^{2-}$ anion. $^1\text{H-NMR}$ and infrared spectroscopies support the formation of compound **8**. $^1\text{H-NMR}$ resonances for **8** were observed at 1.75 and 3.60 ppm (thf), a single resonance at 2.33 (6- CH_3), and aromatic multiplets situated between 6.54 and 7.59 ppm. The amino and

pyridinium resonances were observed at 3.31 (NH_2) and 7.16 ppm (C_5NH). Strong absorbances were evident in the infrared spectrum of **8**. These were attributed to N–H stretching (3376 and 3319 cm^{-1}) and thf C–O–C stretching (1019 and 804 cm^{-1}).

The X-ray crystal structure of compound **8** was refined in the orthorhombic space group $Pnma$ with one $[\text{APyH}_2 \cdot \text{H}]$ cation and half an $[\text{ErCl}_5(\text{thf})]^{2-}$ anion comprising the asymmetric unit. The overall structure consists of protonated pyridyl functionalities rendering the cations and an octahedral Er atom bound to five chloride ligands and one thf ligand as the dianion. All partake in an extended hydrogen bonded array (Fig. 3). Structurally, the anion is similar to a recently reported dysprosium ions, $[\text{DyCl}_5(\text{ethanol})]^{2-}$ in $[\text{3-methylpyridinium}]_2[\text{DyCl}_5(\text{ethanol})]$ [20] where the Ln centre is distorted from true octahedral due to the *trans* influence of the solvent ligand (see Table 4). This also affects shortening of the axial Er–Cl distance relative to the Er–Cl equatorial distances in **8** (Er–Cl_(axial) = 2.554(2) Å and Er–Cl_(equatorial) = 2.61 Å (ave)). The Er–Cl and Er–O distances are slightly longer, as expected by ionic radii considerations, than the corresponding Dy–Cl and Dy–O distances in $[\text{3-methylpyridinium}]_2[\text{DyCl}_5(\text{ethanol})]$ [20]. The identification of the $[\text{ErCl}_5(\text{thf})]^{2-}$ anion in the current work is encouraging since there have been a plethora of structural types identified within thf-solvated anhydrous LnCl_3 structures [18], however, this is the first reported dianionic lanthanoid halide to contain thf. Based on far infrared data, we suspect several other structural motifs are present in bulk microcrystalline samples of the aforementioned $[\text{LnCl}_3(\text{thf})_n]$ compounds [18a]. In light of complex **8**, it may therefore be possible to isolate further samples of this anion type and others by treatment of $[\text{LnCl}_3(\text{thf})_n]$ with ethereal HCl. This is supported by the intentional quantitative synthesis of **8** via the stoichiometric addition of HCl to tetrahydrofuran solutions of 6-methyl-2-

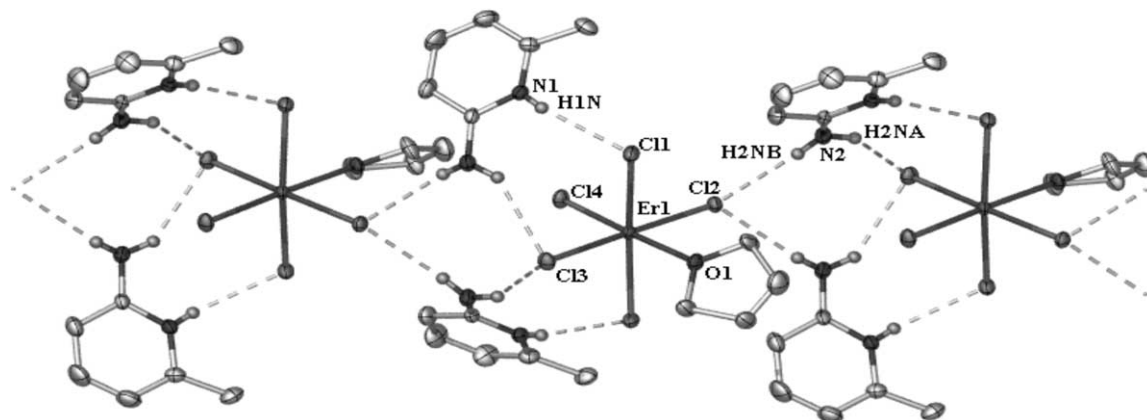


Fig. 3. Molecular structure of the hydrogen bonded network in $[\text{APyH}_2 \cdot \text{H}^+]_2[\text{ErCl}_5(\text{thf})]$ (**8**).

aminopyridine and ErCl_3 (2:1 molar equivalents), whilst, addition of $[\text{APyH}_2 \cdot \text{H}][\text{Cl}^-]$ to ErCl_3 in thf fails to yield **8** due to the low solubility of the pyridinium salt. Within **8**, the anion is hydrogen bonded to the cation through $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonds, forming a stranded polymer where the anion is hydrogen bonded to four separate cations (see Fig. 3 and Table 5). This differs from $[\text{3-methylpyridinium}]_2[\text{DyCl}_5(\text{ethanol})]$ where the anion is hydrogen bonded to three protonated cations and involved in stranded polymers [20].

3. Conclusions

This work has shown that the thf etherate of 6-methyl-2-(trimethylsilylamino)pyridine is a useful transfer reagent in the formation of homoleptic $[\text{Ln}(\text{APyTMS})_3]$ and heteroleptic $[(\text{APyTMS})\text{LnCl}]$ lanthanoid ($\text{Ln} = \text{Gd}, \text{Er}$) complexes. Unfortunately, in the case of the latter, these complexes are involved in redistribution reactions when extracted into hexane, forming $[\text{Ln}(\text{APyTMS})_3]$ and anhydrous unsolvated LnCl_3 . A new thf-solvated anion was identified in $[\text{APyH}_2 \cdot \text{H}]_2[\text{ErCl}_5(\text{thf})]$ and work is under way to isolate more ionic lanthanoid halide structural types.

4. Experimental

2-Amino-6-methylpyridine, *n*-BuLi (1.6 M solution in hexane), HCl (1.0 M in Et_2O) and anhydrous lanthanoid chlorides were purchased from Aldrich and used as received. 2-(Trimethylsilylamino)-6-methylpyridine was prepared according to the literature procedure [5a]. Hexane, diethyl ether and thf were dried over sodium and freshly distilled from sodium/benzophenone and all manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high-purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded as nujol mulls in sodium chloride plates on a Perkin–Elmer 1600 series FTIR spectrophotometer. ^1H -NMR spectra were recorded at 300.13 MHz and ^{13}C -NMR spectra were recorded at 75.46 MHz using a Bruker BZH 300/52 spectrometer with a Varian console and chemical shifts were referenced to an external C_6D_6 standard. Mass spectra were recorded on a VG platform II mass spectrometer using atmospheric pressure chemical ionisation conditions and a CH_2Cl_2 matrix. Melting points were determined in sealed glass capillaries under argon. Ln metal contents were determined using a Na_2EDTA titrimetric method [21].

4.1. Preparation of $\{[\text{Li}(\text{APySiMe}_3)](\text{thf})\}_2$, (**1**)

n-BuLi (3.6 ml, 2.5 M, 9.0 mmol) was added in a dropwise fashion to a solution of 6-methyl-2-(trimethylsilylamino)pyridine (1.62 g, 9.0 mmol) in thf (30 cm^3) at 0 °C, forming a colourless solution. The solution was reduced in volume in vacuo to the point of crystallisation, and placed at –35 °C overnight, yielding large colourless crystals. Yield 1.75 g, 78%; m.p. 101 °C. ^1H -NMR (300 MHz, C_6D_6 , 298 K): δ 0.30 (s, 18H, $\text{Si}(\text{CH}_3)_3$), 1.21 (m, 8H, CH_2), 2.19 (s, 6H, CH_3), 3.47 (m, 8H, CH_2), 6.15–7.11 (m, 6H, aromatics). ^{13}C -NMR (75.46 MHz, C_6D_6 , 298 K): δ 2.62 ($\text{Si}(\text{CH}_3)_3$), 24.56 (CH_3), 28.08 (OCH_2CH_2), 68.35 (OCH_2), 108.31, 112.36, 137.36, 155.47, 171.03 (aromatics); APCI mass spectrum (m/z) 181 (APySiMe_3^+) (100%); IR (nujol, ν): 1583m, 1336w, 1257m, 1237s, 1048m, 1014s, 992w, 951m, 863s, 831s, 743m, 669w, 621w cm^{-1} .

4.2. Preparation of $[\text{Ln}(\text{APySiMe}_3)_3]$, ($\text{Ln} = \text{Gd}$, **2**; $\text{Ln} = \text{Er}$, **3**)

In the case of erbium, 6-methyl-2-(trimethylsilylamino)pyridine (0.81 g, 4.5 mmol) was dissolved in tetrahydrofuran (ca. 30 cm^3). The solution was cooled to 0 °C and *n*-butyllithium (3.00 cm^3 , 4.8 mmol) was slowly added. The resulting yellow solution was transferred into a suspension of anhydrous ErCl_3 (0.41 g, 1.50 mmol) in tetrahydrofuran (ca. 25 cm^3) at room temperature (r.t.). The suspension immediately dissolved and the reaction mixture was stirred for overnight at r.t. The tetrahydrofuran was removed under reduced pressure and the solid material was extracted with hexane (ca. 40 cm^3). The resulting solution was filtered from the white residue (LiCl) and concentration of the mother liquor afforded small light pink crystals. Yield 0.84 g, 80%, m.p. > 360 °C. ^1H -NMR (300 MHz, C_6D_6 , 298 K): δ 3.90 (27H, br s, $\text{Si}(\text{CH}_3)_3$); 5.91 (9H, br s, $\text{C}(\text{CH}_3)$); 9.46, 9.88 (9H, br s, Ar–H). IR (KBr, nujol, ν): 1599sh s, 1552w, 1349m, 1305m, 1246m, 1153w, 1073w, 947w, 870s, 842s, 782m, 762m cm^{-1} . $\text{C}_{27}\text{H}_{45}\text{N}_6\text{Si}_3\text{Er}$ requires Er 23.7%; found Er 23.2%.

The gadolinium complex (**2**) was formed in an identical manner using anhydrous GdCl_3 in place of ErCl_3 yielding large colourless crystals. Yield 72%, m.p. > 360 °C. ^1H -NMR (300 MHz, C_6D_6 , 298 K): δ 0.1 (27H, br s, $\text{Si}(\text{CH}_3)_3$); 2.5 (9H, br s, $\text{C}(\text{CH}_3)$); 5.6 (3H, br s, 2-*CH*); 6.4 (3H, br s, 4-*CH*), 7.4 (3H, br s, 3-*CH*). IR (KBr, nujol, ν): 1597sh s, 1350m, 1308m, 1248m, 1151w, 1072w, 946w, 870s, 842s, 780m, 763m cm^{-1} . $\text{C}_{27}\text{H}_{45}\text{N}_6\text{Si}_3\text{Gd}$ requires Gd 22.6%; found Gd 21.9%.

Table 1
Crystal data and summary of data collection for complexes 1–3 and 8

| Compound | [Li(APySiMe ₃)(thf)] ₂ (1) | [Gd(APySiMe ₃) ₃] (2) | [Er(APySiMe ₃) ₃] (3) | [APyH ₂ ·H] ₂ [ErCl ₅ (thf)] (8) |
|--|--|--|--|--|
| Formula | C ₁₃ H ₂₀ LiN ₂ OSi | C ₂₇ H ₄₅ GdN ₆ Si ₃ | C ₂₇ H ₄₅ ErN ₆ Si ₃ | C ₁₆ H ₂₆ Cl ₅ ErN ₄ O |
| Formula weight | 255.3 | 695.21 | 705.2 | 634.92 |
| F(000) | 548 | 710 | 1436 | 1244 |
| Space group | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>Pnma</i> (no. 62) |
| Unit cell dimensions | | | | |
| <i>a</i> (Å) | 10.921(1) | 9.912(2) | 10.0379(7) | 16.794(2) |
| <i>b</i> (Å) | 11.054(1) | 10.572(2) | 20.784(1) | 16.305(2) |
| <i>c</i> (Å) | 14.636(1) | 17.226(4) | 17.692(1) | 8.915(1) |
| α (°) | 79.57(1) | 79.579(4) | 90 | 90 |
| β (°) | 77.03(1) | 73.851(4) | 104.739(1) | 90 |
| γ (°) | 70.21(1) | 89.527(4) | 90 | 90 |
| <i>V</i> (Å ³) | 1609.5(1) | 1703.6(6) | 3569.6(4) | 2441.3(6) |
| <i>Z</i> | 4 (2 dimers) | 2 | 4 | 4 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.054 | 1.355 | 1.312 | 1.727 |
| μ (mm ⁻¹) | 0.136 | 2.076 | 2.475 | 3.998 |
| <i>T</i> (max, min) | 0.9579, 0.9353 | 0.6815, 0.6815 | 0.5239, 0.4376 | 0.3801, 0.2977 |
| Crystal size (mm ³) | 0.50 × 0.44 × 0.32 | 0.20 × 0.20 × 0.20 | 0.40 × 0.30 × 0.30 | 0.40 × 0.30 × 0.30 |
| Colour | Colourless | Colourless | Pink | Pink |
| Diffractometer | Enraf–Nonius CAD4 | Enraf–Nonius CCD | Bruker AXS CCD | Bruker AXS CCD |
| Reflections collected | 5943 | 10949 | 16234 | 10531 |
| Unique reflections | 5619 (<i>R</i> _{int} = 0.0379) | 7560 (<i>R</i> _{int} = 0.0595) | 5121 (<i>R</i> _{int} = 0.0441) | 1828 (<i>R</i> _{int} = 0.058) |
| Parameters | 328 | 346 | 340 | 160 |
| Temperature (K) | 296 | 123 | 296 | 296 |
| <i>R</i> | 0.0757 | 0.0682 | 0.0324 | 0.0334 |
| <i>wR</i> ₂ | 0.1932 | 0.1502 | 0.0684 | 0.0845 |

4.3. Attempted preparation of [Ln(APySiMe₃)₂Cl], (Ln = Gd, 4; Ln = Er, 5)

In the case of erbium 6-methyl-2-(trimethylsilylamino)pyridine (0.54 g, 3.0 mmol) was dissolved in tetrahydrofuran (ca. 30 cm³). The solution was cooled to 0 °C and *n*-butyllithium (2.00 cm³, 3.2 mmol) was slowly added. The yellow solution was transferred into a suspension of anhydrous ErCl₃ (0.41 g, 1.5 mmol) in tetrahydrofuran (ca 30 cm³) at r.t. The solution went clear pink and the reaction mixture was stirred for 2 h at r.t. The tetrahydrofuran was removed under reduced pressure leaving a pink solid which was extracted with hexane, filtered to remove LiCl and then concentrated in vacuo. Pink crystals formed overnight, and two crystal morphologies were identified. Spectroscopic and X-ray analysis of both samples identified these two compounds as compound 3 and anhydrous unsolvated ErCl₃ (6), m.p. > 360 °C for (3). ¹H-NMR (300 MHz, C₆D₆, 298K): δ 3.88 (9H, br s, Si(CH₃)₃); 5.91 (3H, br s, C(CH₃)); 9.32; 9.98 (9H, br s, Ar–H). IR (KBr, nujol, ν): 1597s, 1552w, 1354s, 1259s, 1246, 1072s, 1032s, 948w, 867s, 842s, 782m, 763m cm⁻¹.

In a similar experiment using gadolinium, identical results were obtained yielding 2 and anhydrous GdCl₃ (6). M.p. > 360 °C for (2). ¹H-NMR (300 MHz, C₆D₆, 298 K): δ 0.3 (27H, br s, Si(CH₃)₃); 2.3 (9H, br s, C(CH₃)); 5.9 (3H, br s, 2-CH); 6.4 (3H, br s, 4-CH), 7.1 (3H, br s, 3-CH). IR (KBr, nujol, ν): 1597s, 1552w,

1354s, 1259s, 1247s, 1072s, +1032s, 948w, 867s, 842s, 782m, 763m cm⁻¹.

4.4. Preparation of [APyH₂·H]₂[ErCl₅(thf)] (8)

4.4.1. Method 1

[6-Methyl-2-(trimethylsilylamino)pyridine] (0.27 g, 1.50 mmol) was dissolved in tetrahydrofuran (ca 30 cm³) and the solution cooled to 0 °C and butyllithium (0.94 cm³, 1.50 mmol) of was slowly added. The yellow solution was transferred into a suspension of anhydrous ErCl₃ (0.41g, 1.50 mmol) in tetrahydrofuran (40 cm³). A clear orange solution formed immediately which was stirred at r.t. for 2 h and then tetrahydrofuran was removed in vacuo. The orange solid was extracted with diethylether and filtered to remove the LiCl. Concentration and cooling to 0 °C afforded small pink crystals in low yield. Recrystallisation from thf yielded pink crystals. Yield 0.05 g, 5%, m.p. 152–75 °C (dec.).

4.4.2. Method 2

Hydrogen chloride in diethyl ether (1.0 M, 1.60 cm³, 1.60 mmol) was added dropwise to a fully dissolved solution of 6-methyl-2-aminopyridine (0.17 g, 1.57 mmol) and anhydrous ErCl₃ (0.22 g, 0.80 mmol) in thf (ca. 70 cm³). This occurred without precipitation of 8, however, after standing for 24 h a significant quantity of pink powder had deposited. This was collected by

Table 2
Selected bond lengths (Å) and bond angles (°) for [Li(APySiMe₃)(thf)₂] (1)

| Bond lengths | | | |
|-------------------|-----------|---------------------|-----------|
| O(1)–Li(1) | 1.919(7) | O(2)–Li(2) | 1.933(7) |
| N(1)–Li(1) | 2.042(7) | Li(2)–N(4) | 2.072(7) |
| Li(1)–N(2)#1 | 2.063(7) | Li(2)–N(4)#2 | 2.103(7) |
| Li(1)–N(2) | 2.097(7) | N(3)–Li(2)#2 | 2.029(7) |
| Li(1)–Li(1)#1 | 2.548(12) | Li(2)–Li(2)#2 | 2.487(13) |
| Bond angles | | | |
| O(1)–Li(1)–N(1) | 112.2(3) | O(2)–Li(2)–N(3)#2 | 115.6(4) |
| O(1)–Li(1)–N(2)#1 | 118.4(3) | O(2)–Li(2)–N(4) | 117.1(3) |
| O(1)–Li(1)–N(2) | 125.2(4) | O(2)–Li(2)–N(4)#2 | 118.9(4) |
| N(1)–Li(1)–N(2)#1 | 119.7(4) | N(3)#2–Li(2)–N(4) | 120.7(3) |
| N(1)–Li(1)–N(2) | 67.4(2) | N(3)#2–Li(2)–N(4)#2 | 67.4(2) |
| N(2)#1–Li(1)–N(2) | 104.5(3) | N(4)–Li(2)–N(4)#2 | 106.9(3) |

Symmetry transformations used to generate equivalent atoms: #1 – $x+1, -y+2, -z+1$; #2 – $-x+2, -y+1, -z$.

filtration and washed with hexane ($3 \times 10 \text{ cm}^3$), followed by drying in vacuo, rendering material that characterised as **8** (see ¹H-NMR, IR and m.p. below). Attempts to obtain single crystals via method 2 failed due to pronounced insolubility in thf. Yield 0.58 g, 93%, m.p. 151–54 °C (decomp.).

¹H-NMR (300 MHz, dms-*d*₆, 298 K): δ 1.75 (br s, 2H, β -CH₂ THF); 2.33 (br s, 3H, CCH₃); 3.31 (br s, 2H, NH₂), 3.60 (br s, 2H, α -CH₂ THF); 6.54 (br d, 1H, 2-CH); 6.59 (br d, 1H, 4-CH); 7.16 (br s, 1H, –NH⁺); 7.59 (br m, 1H, 3-CH). IR: (KBr, nujol, ν) 3376m (br), 3319m (br), 3199m (br), 2726m, 1656m, 1637m, 1301m, 1260s, 1094m (br), 1019m (br), 804m cm^{-1} .

4.5. Collection of X-ray diffraction data, and solution and refinement of the structures

For compound **1** a r.t. data sets was acquired on an Enraf–Nonius CAD4 diffractometer on capillary mounted specimen ($2\theta_{\text{max}} 50^\circ$, 2θ – θ scan mode; monochromatic Mo–K α radiation, $\lambda = 0.71073 \text{ \AA}$; $T \sim 295 \text{ K}$) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered ‘observed’ and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})_H were included constrained at estimated values. Conventional residuals on $|F|$, R , R_w (statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$) are quoted. Neutral atom complex scattering factors were employed, computation using the XTAL-3.4 program system implemented by Hall et al. [22].

A crystalline sample of compound **2** was mounted on a glass fibre, in viscous hydrocarbon oil. Crystal data were obtained using an Enraf–Nonius Kappa CCD at –150 °C (123 K). Structural solution and refinement was carried out using the SHELX suite of programs [23]

Table 3
Selected bond lengths (Å) and bond angles (°) for [Ln(APySiMe₃)₃] (Ln = Gd, (2); Ln = Er, (3))

| Compound 2 | | Compound 3 | |
|-------------------|----------|-------------------|------------|
| Bond lengths | | | |
| Gd(1)–N(1A) | 2.440(7) | Er(1)–N(1A) | 2.386(3) |
| Gd(1)–N(2A) | 2.334(7) | Er(1)–N(2A) | 2.279(4) |
| Gd(1)–N(1C) | 2.440(7) | Er(1)–N(1C) | 2.387(4) |
| Gd(1)–N(1B) | 2.460(7) | Er(1)–N(1B) | 2.378(4) |
| Gd(1)–N(2B) | 2.348(7) | Er(1)–N(2B) | 2.319(4) |
| Gd(1)–N(2C) | 2.357(7) | Er(1)–N(2C) | 2.312(4) |
| Bond angles | | | |
| N(1A)–Gd(1)–N(1B) | 95.3(2) | N(1A)–Er(1)–N(1B) | 161.36(14) |
| N(1A)–Gd(1)–N(1C) | 161.1(2) | N(1A)–Er(1)–N(1C) | 95.06(13) |
| N(1A)–Gd(1)–N(2A) | 56.8(2) | N(1A)–Er(1)–N(2A) | 58.08(12) |
| N(1A)–Gd(1)–N(2B) | 101.5(3) | N(1A)–Er(1)–N(2B) | 107.09(14) |
| N(1A)–Gd(1)–N(2C) | 107.8(2) | N(1A)–Er(1)–N(2C) | 96.43(13) |
| N(1B)–Gd(1)–N(1C) | 96.9(2) | N(1B)–Er(1)–N(1C) | 97.59(13) |
| N(1B)–Gd(1)–N(2A) | 150.1(2) | N(1B)–Er(1)–N(2A) | 111.28(13) |
| N(1B)–Gd(1)–N(2B) | 56.6(2) | N(1B)–Er(1)–N(2B) | 57.47(16) |
| N(1B)–Gd(1)–N(2C) | 96.3(2) | N(1B)–Er(1)–N(2C) | 101.89(15) |
| N(1C)–Gd(1)–N(2A) | 112.8(2) | N(1C)–Er(1)–N(2A) | 150.87(12) |
| N(1C)–Gd(1)–N(2B) | 97.3(2) | N(1C)–Er(1)–N(2B) | 98.67(14) |
| N(1C)–Gd(1)–N(2C) | 56.5(2) | N(1C)–Er(1)–N(2C) | 57.85(14) |
| N(2A)–Gd(1)–N(2B) | 114.1(2) | N(2A)–Er(1)–N(2B) | 100.04(13) |
| N(2A)–Gd(1)–N(2C) | 102.2(2) | N(2A)–Er(1)–N(2C) | 110.18(12) |
| N(2B)–Gd(1)–N(2C) | 141.9(2) | N(2B)–Er(1)–N(2C) | 148.54(14) |

with the graphical interface X-SEED [24]. All hydrogen atoms were placed in calculated positions using the riding model.

For compounds **3** and **8** a hemisphere of data were collected at r.t. on a Bruker SMART CCD diffractometer using the omega scan mode yielding a total of N reflections which reduced to N_o unique data with $F_o > 4\sigma(F_o)$ being considered observed. Data were corrected for absorption using the program SADABS [25]. The structures were solved using direct methods in SHELXS and refined using SHELXL-97-2 [23,24]. All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions (riding model) and were not refined. The thf molecule in compound **8** was disordered over two sites and this was successfully modelled.

Crystal data and a summary of data collection appear in Table 1 and pertinent results are shown in Tables 2–5 and the Figures.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 191403–191406 for compounds **1**, **2**, **3** and **8**, respectively. Copies of this

Table 4
Selected bond lengths (Å) and bond angles (°) for [APyH₂-H]₂[ErCl₅(thf)] (3)

| Bond lengths | | | |
|---------------------|-----------|-------------------|----------|
| Er(1)–O(1) | 2.347(5) | Er(1)–Cl(1) | 2.621(2) |
| Er(1)–Cl(2) | 2.630(2) | Er(1)–Cl(3) | 2.588(2) |
| Er(1)–Cl(4) | 2.544(2) | | |
| Bond angles | | | |
| O(1)–Er(1)–Cl(1) | 84.98(4) | O(1)–Er(1)–Cl(2) | 86.1(1) |
| O(1)–Er(1)–Cl(3) | 92.0(1) | O(1)–Er(1)–Cl(4) | 177.0(1) |
| Cl(1)–Er(1)–Cl(1)#1 | 168.25(8) | Cl(1)–Er(1)–Cl(2) | 92.69(3) |
| Cl(1)–Er(1)–Cl(3) | 87.15(4) | Cl(1)–Er(1)–Cl(4) | 95.18(4) |
| Cl(2)–Er(1)–Cl(3) | 178.19(6) | Cl(2)–Er(1)–Cl(4) | 90.89(7) |
| Cl(3)–Er(1)–Cl(4) | 90.92(7) | | |

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1/2, z$.

Table 5
Hydrogen bonds (Å, °) for [APyH₂-H]₂[ErCl₅(thf)] (8)

| D–H...A | <i>d</i> (D–H) | <i>d</i> (H...A) | <i>d</i> (D...A) | ∠(DHA) |
|-----------------------|----------------|------------------|------------------|--------|
| N(1)–H(1N)...Cl(1) | 0.72(5) | 2.51(5) | 3.203(5) | 162(5) |
| N(2)–H(2NA)...Cl(3) | 0.85(6) | 2.62(6) | 3.358(7) | 146(5) |
| N(2)–H(2NB)...Cl(2)#1 | 0.79(8) | 2.57(8) | 3.344(7) | 166(7) |

Symmetry transformations used to generate equivalent atoms: #1 $x-1/2, y, -z+1/2$.

information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the ARC Small Grants Scheme for support of this work. Studienstiftung des Deutschen Volkes is acknowledged for financial support for J.B. and U.H. and Universitaet Leipzig for F.L. M.L.C. would like to acknowledge the Royal Society for the provision of a postdoctoral fellowship.

References

- (a) For a recent review see: R. Kempe, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 468;
(b) But also see: M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, UK, 1980.
- (a) M. Majewski, D.M. Gleave, *J. Organomet. Chem.* 470 (1994) 1 (and references therein);
(b) B.J. Wakefield, *Organolithium Methods*, Academic Press, New York, 1988;
(c) A.M. Sapsa, P.v.R. Schleyer (Eds.), *Lithium Chemistry: a Theoretical and Experimental Overview*, Wiley-Interscience, New York, 1995.;
(d) M. Gray, M. Tinkl, V. Snieckus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry*, Ch. 1, vol. 11, 2nd ed., Pergamon, Oxford, 1995, p. 1;
(e) C.H. Heathcock, in: E. Buncl, T. Durst (Eds.), *Comprehensive Carbanion Chemistry*, Ch. 4, vol. B, Elsevier, New York, 1980.
- W.N. Setzer, P.v.R. Schleyer, *Adv. Organomet. Chem.* 24 (1985) 353.
- (a) K. Gregory, P.v.R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* 37 (1991) 47;
(b) R.E. Mulvey, *Chem. Soc. Rev.* 20 (1991) 176;
(c) D.S. Wright, M.A. Beswick, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry*, Ch. 1, vol. 1, 2nd Edition, Pergamon, Oxford, 1995, p. 1;
(d) D. Seebach, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1624;
(e) D.R. Armstrong, D. Barr, W. Clegg, R.E. Mulvey, D. Reed, R. Snaith, K. Wade, *J. Chem. Soc. Chem. Commun.* (1986) 869.;
(f) T. Fjeldberg, P.B. Hitchcock, M.F. Lappert, A.J. Thorne, *J. Chem. Soc. Chem. Commun.* (1984) 822.
- (a) L.M. Engelhardt, G.E. Jacobsen, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, *J. Chem. Soc. Dalton Trans.* (1988) 1011.;
(b) L.M. Engelhardt, G.E. Jacobsen, P.C. Junk, C.L. Raston, A.H. White, *J. Chem. Soc. Chem. Commun.* (1990) 89;
(c) C. Jones, P.C. Junk, S.G. Leary, N.A. Smithies, *Main Group Metal Chem.* 24 (2001) 383;
(d) C. Jones, P.C. Junk, S.G. Leary, N.A. Smithies, J.W. Steed, *Inorg. Chem. Comm.* 5 (2002) 533.
- (a) C. Jones, P.C. Junk, S.G. Leary, N.A. Smithies, *J. Chem. Soc. Dalton Trans.* (2000) 3186.;
(b) C. Jones, P.C. Junk, N.A. Smithies, *Main Group Metal Chem.* 24 (2001) 801.
- (a) L.M. Engelhardt, P.C. Junk, W.C. Patalinghug, R.E. Sue, C.L. Raston, B.W. Skelton, A.H. White, *J. Chem. Soc. Chem. Commun.* (1991) 930.;
(b) L.M. Engelhardt, M.G. Gardiner, C. Jones, P.C. Junk, C.L. Raston, A.H. White, *J. Chem. Soc. Dalton Trans.* (1996) 3053.;
(c) C. Jones, P.C. Junk, N.A. Smithies, *J. Organomet. Chem.* 607 (2000) 105.
- (a) F.A. Cotton, S.C. Haefner, J.H. Matonic, X. Wang, C.A. Murillo, *Polyhedron* 16 (1997) 541;
(b) M.L. Cole, P.C. Junk, L.M. Louis, *J. Chem. Soc. Dalton Trans.* (2002) 3906.
- (a) W.A. Herrmann (Ed.), *Top. Curr. Chem.* (1996) 179.;
(b) F.T. Edelmann, @in: E.W. Abel, F.G.A. Stone, G. Wilkinson, eds., 'Comprehensive Organometallic Chemistry, Ch. 2', vol. 4, 2nd Edn., Oxford: Pergamon, 1995, p. 11;
(c) H. Schumann, J.A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* 95 (1995) 865;
(d) C.J. Schaverien, *Adv. Organomet. Chem.* 36 (1994) 238.
- E.N. Kirillov, E.A. Fedorova, A.A. Trifonov, M.N. Bochkarev, *Appl. Organomet. Chem.* 15 (2001) 151.
- (a) L. Wang, B. He, *React. Polym.* 12 (1990) 45;
(b) W.J. Evans, S.C. Engerer, P.A. Piliero, A.L. Wayda, *J. Chem. Soc. Chem. Commun.* (1979) 1007.
- K. Takaki, *Kikan Kagaku Sosetsu* 37 (1998) 147.
- (a) A.C. Greenwald, W.S. Rees, U.W. Lay, *Mater. Res. Soc. Symp. Proc.* 301 (1993) 21;
(b) W.S. Rees, U.W. Lay, A.C. Greenwald, *Mater. Res. Soc. Symp. Proc.* 334 (1994) 207.
- R.L. LaDuca, P.T. Wolczanski, *Inorg. Chem.* 31 (1992) 1311.
- D.C. Bradley, J.S. Ghotra, F.A. Hart, *J. Chem. Soc. Dalton Trans.* (1973) 1021.
- G.B. Deacon, C.M. Forsyth, P.C. Junk, B.W. Skelton, A.H. White, *J. Chem. Soc. Dalton Trans.* (1998) 1381.
- The X-ray crystal structure of the anhydrous unsolvated ErCl₃ was determined and will be reported elsewhere. Unit cell parameters being: hexagonal space group, $P6_3/m$, $a = 7.390(3)$, $c = 4.244(2)$ Å. The infrared spectra of both GdCl₃ and ErCl₃ showed

- no obvious absorbances in the region 4000–500 cm^{-1} , which is similar to that of authentic LnCl_3 samples ($\text{Ln} = \text{Gd}, \text{Er}$).
- [18] (a) See for example: G.B. Deacon, T. Feng, P.C. Junk, B.W. Skelton, A.N. Sobolev, A.H. White, *Aust. J. Chem.* 51 (1998) 75 (and references therein);
(b) G.B. Deacon, T. Feng, P.C. Junk, G. Meyer, N.M. Scott, B.W. Skelton, A.H. White, *Aust. J. Chem.* 53 (2000) 853 (and references therein).
- [19] Subsequent to this work, heteroleptic bis(6-methyl-2-(trimethylsilyl)amidopyridine) lanthanoid chlorides have been prepared quantitatively employing heavier group 1 metathesis reagents. Data from these agree with lithium chloride contaminated samples of **4** and **5** obtained using the paths described in this article, and thereby subscribe to their formation. M.L. Cole, P.C. Junk, Unpublished material.
- [20] J. Hallfeldt, W. Urland, *Z. Anorg. Allg. Chem.* 627 (2001) 545.
- [21] (a) G.B. Deacon, T. Feng, B.W. Skelton, A.H. White, *Aust. J. Chem.* 48 (1995) 741;
(b) G.B. Deacon, A.J. Koplick, T.D. Tuong, *Aust. J. Chem.* 37 (1984) 517;
(c) G.B. Deacon, A.J. Koplick, W.D. Raverty, D.G. Vince, *J. Organomet. Chem.* 182 (1979) 121;
(d) G.B. Deacon, W.D. Raverty, D.G. Vince, *J. Organomet. Chem.* 135 (1977) 103;
(e) G.B. Deacon, R.H. Newnham, *Aust. J. Chem.* 38 (1985) 1757;
(f) G.B. Deacon, C.M. Forsyth, R.H. Newnham, T.D. Tuong, *Aust. J. Chem.* 40 (1987) 895.
- [22] S.R. Hall, G.S.D. King, J.M. Stewart, *XTAL-3.4 User's Manual*, University of Western Australia, 1995.
- [23] G.M. Sheldrick, *SHELX-97*, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, 1998.
- [24] L. Barbour, 'X-SEED', University of Missouri–Columbia, 1999.
- [25] R.H. Blessing, *Acta Crystallogr. Sect. A* 51 (1995) 33.