Unusual alkyl group activation and cationic complex formation from a novel lutetium dialkyl complex supported by a tridentate monoanionic ligand[†]

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We report herein the synthesis and characterization of a lutetium dialkyl complex supported by a multidentate, anilido-pyridine-imine ligand and its subsequent transformation into an unprecedented cationic monoalkyl derivative.

The cyclopentadienyl (Cp) family of ligands is ubiquitous in trivalent organometallic lanthanide (Ln) chemistry, and examples of bis-and mono-Cp Ln derivatives are known and are the subject of recent reviews.1 These complexes are synthetically important and have found use in catalytic hydroamination² and polymerization.3 In contrast, non-Cp systems based on multidentate mono and diamido ligands remain a relatively unexplored area of research.⁴ Recent developments in this area involve the synthesis of yttrium complexes stabilized by pyrrolyl ligand type I,⁵ chelating anilido-imine donors related to type II,⁶ deprotonated aza-18-crown-6,⁷ and a linked 1,4,7,-triazacyclononane-amide ligand.8 Related reports of organoscandium species stabilized by monoanionic β -diketiminato ligands have been well-documented,9 and the generation of a variety of alkyl (bis)amido Ln complexes reported by Anwander et al. has recently appeared.¹⁰ We have focused our initial efforts in this area on $[2-{(2,6-Pr_2C_6H_3)N=CMe} 6-\{(2,6-Pr_{2}C_{6}H_{3})NHCMe_{2}\}C_{5}H_{3}N]$ (1),¹¹ a sterically demanding precursor to an asymmetric, multidentate, monoanionic, anilido-pyridine-imine ligand (Scheme 1). We herein report the synthesis and structural characterization of [2- $\{(2,6-Pr_{2}C_{6}H_{3})N=CMe\}-6-\{(2,6-Pr_{2}C_{6}H_{3})NCMe_{2}C_{5}H_{3}N\} Lu(CH_2SiMe_3)_2$ (2), the first Ln dialkyl complex stabilized by this ligand class. We also report the synthesis and structure of a $[2-{(2,6-Pr_{2}C_{6}H_{3})N=CMe}$ unique cationic complex $6-{(2,6-Pr_{2}C_{6}H_{3})NCMe_{2}}C_{5}H_{3}N$ Lu(CH2SiMe2CH2Si-Me₃)(THF)][MeB(C₆F₅)₃] (3), generated by an unusual activation pathway.

Treatment of a toluene solution of Lu(CH₂SiMe₃)₃(THF)₂¹² with **1** resulted in the generation of **2** (Scheme 1).[†] Concentration of the reaction solution, under reduced pressure, followed by cooling to -30 °C, gave microcrystalline **2** in 35% yield



[†] Electronic supplementary information (ESI) available: details of the synthesis of **2** and **3** and the hydrolysis of **3**. See http://www.rsc.org/suppdata/cc/b3/b306889g/



after filtration and washing with hexanes. Complex 2 is insoluble in hexanes, slightly soluble in benzene, and soluble in dichloromethane. X-Ray quality crystals of 2 were grown from a concentrated benzene solution, and the thermal ellipsoid plot of 2 is shown in Fig. 1.

Complex **2** crystallized with a monoclinic unit cell with one molecule of benzene per molecule of **2**.[‡] The geometry about the metal center in **2** is best described as distorted square pyramidal. The base of the pyramid is defined by N(1), N(2), N(3), and C(5), and Lu(1) lies 0.6629 Å above the plane defined by these atoms. The Lu(1)–C(1) and Lu(1)–C(5) bond lengths of 2.329(6) Å and 2.349(6) Å, respectively, fall within the expected range for Lu–C bonds in complexes containing a Lu–CH₂SiMe₃ functionality.¹³ The Lu(1)–N(1) amide bond length of 2.188(4) Å is within the range expected and consistent with a monoanionic ligand in **2**.¹² Of particular interest in **2** are the short C(1)–H(1A) and H(1B) α -proton–Lu(1) contacts of 2.62(7) Å and 2.52(7) Å respectively. These distances support Lu– α_{CH} agostic interactions in the solid-state.¹⁴

The ¹H NMR spectrum of **2** is fluxional at 25 °C but does approximate the solid-state structure at low temperature (-50 °C). For example, at -50 °C two Si(CH₃)₃ resonances are observed at -0.75 and -0.45 ppm as well as four α -CH resonances at -1.81, -1.66, -1.24, and -0.75 ppm. The



Fig. 1 Thermal ellipsoid plot of 2 (35% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Lu(1)-C(1) 2.329(6), Lu(1)-C(5) 2.349(6), Lu(1)-N(1) 2.188(4), Lu(1)-N(2) 2.376(4), Lu(1)-N(3) 2.510(4), N(3)-C(29) 1.291(6), N(1)-Lu(1)-N(2) 69.03(13), N(2)-Lu(1)-N(3) 65.75(12), N(3)-Lu(1)-C(5) 96.6(2), C(5)-Lu(1)-N(1) 109.3(2), C(1)-Lu(1)-N(1) 111.09(16), C(1)-Lu(1)-C(5) 107.8(2), C(1)-Lu(1)-N(3) 99.69(16), C(1)-Lu(1)-N(2) 104.73(17).

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 ${}^1J_{C\alpha \cdot H}$ of 99 Hz supports the above discussed agostic interaction in solution at $-50~{}^\circ C.{}^{15,16}$

Treatment of a CD₂Cl₂ solution of **2** with B(C₆F₅)₃ in the presence of THF resulted in the formation of $[2-\{(2,6-Pr_{2}C_{6}H_{3})N=CMe\}-6-\{(2,6-Pr_{2}C_{6}H_{3})NCMe_{2}\}C_{5}H_{3}N$ Lu(CH₂SiMe₂CH₂SiMe₃)(THF)][MeB(C₆F₅)₃] (**3**) (Scheme 1).† Cationic **3** is stable for weeks in solution and has been fully characterized by multinuclear NMR spectroscopy (including two-dimensional experiments).^{16,17} A graphical representation of **3** including selected chemical shifts is shown in Fig. 2.

Complex **3** possesses an asymmetric environment around the metal center, resulting in diastereotopic protons H_a through H_h as well as the inequivalent (non-isopropyl) methyl groups. At room temperature four isopropyl methine resonances and eight isopropyl methyl group resonances are observed by NMR techniques.¹⁶ There are therefore four inequivalent isopropyl groups, implying restricted rotation about the N–Ar bonds on the NMR time-scale and a sterically congested metal center. The ${}^{1}J_{C\alpha-H}$ of 96 Hz in **3** supports a Lu– α_{CH} agostic interaction in solution¹⁵ and the $\Delta \delta_{m,p}$ value of 2.6 in the ¹⁹F NMR spectrum of **3** supports a non-contacting cation–anion pair.⁶

Alkyl group abstraction from Y, Sc, and Lu species, generating cationic complexes is a known process.^{6,7,9,13b} The generation of **3** from treatment of **2** with $B(C_6F_5)_3$ in the presence of THF in lieu of alkyl group (CH₂SiMe₃) abstraction was thus unexpected. A possible mechanism for the transformation of **2** to **3** may involve concerted silyl methyl group extraction by $B(C_6F_5)_3$, accompanied by alkyl migration (Scheme 2). To our knowledge this is the first reported instance of a lanthanide mediated rearrangement of this kind.¹⁸ Steric crowding around the lutetium center in **2** may render the alkyl group α -carbons inaccessible to the boron reagent, redirecting reactivity to the silyl methyl groups.

In summary complexes 2 and 3 represent the first wellcharacterized Ln complexes employing ligand 1. While examples of Sc- and Y-alkyl cations have been reported,^{6–9} only one



Fig. 2 Graphical representation of 3 including selected chemical shifts assigned by multinuclear NMR spectroscopy. The $MeB(C_6F_5)_3$ anion has been omitted for clarity (ov = overlapping, carbon resonances are underlined, Ar = 2,6-Prⁱ₂C₆H₃).



Scheme 2

well-characterized example of a cationic, Ln dialkyl complex has appeared in the literature.^{13b} To the best of our knowledge **3** is the first reported example of a stable, non-Cp-based, cationic, monoalkyl complex of an 4f-element.¹⁹ We are currently in the process of studying the mechanism concerned with the transformation of **2** to **3** and exploring the reactivity of both complexes with other small molecules.

Notes and references

‡ *Crystal data*: for **2**: C₄₂H₆₈N₃Si₂Lu·C₆H₆, M = 924.25, a = 18.450(5), b = 14.220(4), c = 19.167(5) Å, V = 4863(2) Å³, monoclinic, space group $P_{2_1/c}$, Z = 4, μ (Mo-Kα) = 2.112 mm⁻¹, T = 203 K, final *R*1 ($I > 2\sigma$) = 0.0533, *wR*2 ($I > 2\sigma$) = 0.0998, GOF (on F^2) = 2.115. Hydrogen atom positions H(1A) and H(1B) were found on the difference map and refined with isotropic temperature factors set to 0.08 Å². CCDC 213144. See http: //www.rsc.org/suppdata/cc/b3/b306889g/ for crystallographic data in .cif format.

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- 16 See the ESI for full details on the NMR characterization of 2 and 3.
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