

# Syntheses and structures of mononuclear lutetium imido complexes with very short Lu–N bonds†

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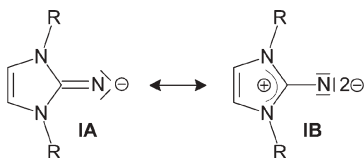
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The reaction of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine ( $\text{Im}^{\text{Dipp}}\text{NH}$ ) with trimethylsilylmethyl lithium and anhydrous lutetium trichloride affords the imido complex  $[\text{LuCl}_2(\text{ImN}^{\text{Dipp}})(\text{THF})_3]$  (**1**), which, on further reaction with dipotassium cyclooctatetraenide,  $\text{K}_2(\text{C}_8\text{H}_8)$ , leads to the half-sandwich cyclooctatetraenyl complex  $[(\eta^8\text{-C}_8\text{H}_8)\text{Lu}(\text{ImN}^{\text{Dipp}})(\text{THF})_2]$  (**2**); both complexes contain very short Lu–N bond lengths, which are shorter than any previously reported Lu–N distances.

Organoimido complexes of the transition metals have been extensively studied in the past because of their important role in a number of biological, industrial and catalytic processes.<sup>1</sup> On the one hand, this interest is stimulated by the ability of the metal–imido group ( $\text{M}=\text{NR}$ ) to undergo a wide range of metathesis, cycloaddition, C–H bond activation and hydroamination reactions.<sup>2</sup> On the other hand, imido ligands are also widely used as ancillary ligands in organotransition metal chemistry, *e.g.* in important catalysts for olefin metathesis and polymerization.<sup>3,4</sup> In stark contrast to the rich chemistry of imido complexes containing d-block elements, lanthanide imido complexes are largely unexplored,<sup>5</sup> and reports on well-defined imido complexes containing 4f-elements are scarce.<sup>6</sup> More specifically, structurally characterized lanthanide complexes containing terminal imido groups are unknown to date, since the imido group is generally found to bind in a capping or bridging fashion.

As a terminal ligand, the formally dianionic imido ligand  $(\text{NR})^{2-}$  coordinates with a metal–nitrogen multiple bond consisting of one  $\sigma$  and either one or two  $\pi$  interactions.<sup>7</sup> This resembles the bonding in transition metal complexes containing monoanionic imidazolin-2-iminato ligands of type **I**, which can be described by the two limiting resonance structures **IA** and **IB** (Scheme 1), indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands<sup>8</sup> with a strong electron



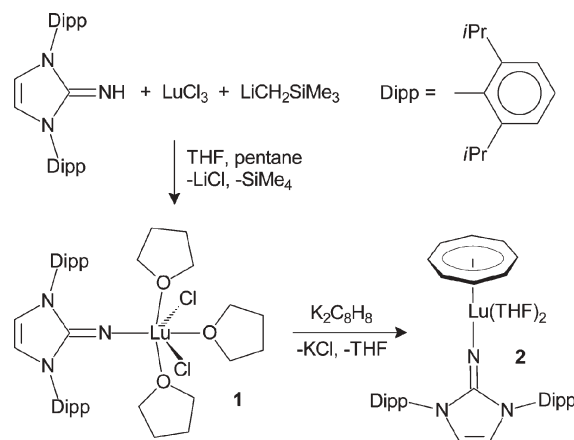
Scheme 1

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donating capacity towards early transition metals.<sup>9,10</sup> Due to their ability to act as  $2\sigma,4\pi$ -electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyls,  $\text{C}_5\text{R}_5$ , and also as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands.<sup>11</sup> Therefore, lanthanide complexes with terminal imidazolin-2-iminato ligands, as presented in this communication, can serve as accurate models for elusive mononuclear lanthanide imido complexes, and their structural investigation could lead to a better understanding of lanthanide–nitrogen multiple bonding.<sup>5,12</sup>

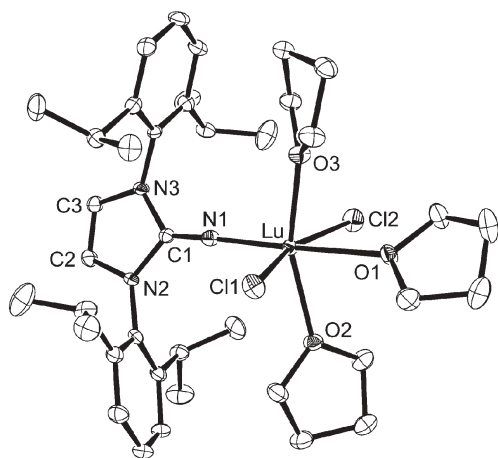
The starting material 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine ( $\text{Im}^{\text{Dipp}}\text{NH}$ ) was synthesized, according to the published procedure, from the corresponding Arduengo-carbene 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene<sup>13</sup> by reaction with trimethylsilyl azide, followed by desilylation of the  $\text{Im}^{\text{Dipp}}\text{N}-\text{SiMe}_3$  intermediate in methanol.<sup>8</sup> Reaction of the resulting imine  $\text{Im}^{\text{Dipp}}\text{NH}$  with trimethylsilylmethyl lithium and anhydrous lutetium trichloride in THF solution affords the lutetium complex  $[\text{LuCl}_2(\text{NIm}^{\text{Dipp}})(\text{THF})_3]$  (**1**) as a colourless crystalline solid in good yield after extraction with pentane (Scheme 2). Treatment of **1** with a THF solution of the dipotassium cyclooctatetraenide salt  $\text{K}_2(\text{C}_8\text{H}_8)$  leads to the formation of the cyclooctatetraenyl lutetium complex  $[(\eta^8\text{-C}_8\text{H}_8)\text{Lu}(\text{NIm}^{\text{Dipp}})(\text{THF})_2]$  (**2**). Both compounds **1** and **2** could be fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, elemental analysis and X-ray crystal structure determination.‡ It should be noted that coordination to the lutetium atom does not have a significant impact on the resonances observed for the hydrogen and carbon atoms of the heterocyclic imidazolin moiety.<sup>8</sup> The  $^1\text{H}$  NMR spectra of both complexes at room temperature exhibit two doublet resonances as expected for one set of diastereotopic isopropyl  $\text{CH}_3$  groups, indicating the



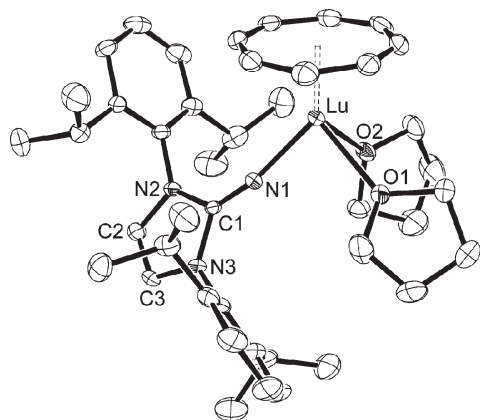
Scheme 2

presence of magnetically equivalent 2,6-diisopropylphenyl groups. The complexes **1** and **2** crystallize as THF solvates, and their molecular structures are shown in Fig. 1 and Fig. 2.

In compound **1**, the metal is hexacoordinated in a meridional fashion with the chlorine atoms and two of the three THF ligands adopting a *trans*-arrangement. The Cl1–Lu–Cl2 and O2–Lu–O3 angles of 161.66(3)° and 157.54(8)° deviate significantly from 180°, whereas the N1–Lu–O1 axis is almost linear [177.86(9)°]. Thus, the coordination geometry about lutetium can be described as a distorted octahedron. Since the Lu–O1 bond is considerably longer than the other two Lu–O bonds [2.459(2) Å vs. 2.303(2) and 2.287(2) Å], this THF ligand can also be regarded as being *trans*-coordinated to a square-pyramid with the imido N1 atom at the apex. Presumably, the elongation of the Lu–O1 bond is a result of the strong N1–Lu interaction, revealed by a very short Lu–N bond length of 2.091(3) Å, the shortest ever observed for lutetium–nitrogen systems, together with an almost linear Lu–N1–C1 angle



**Fig. 1** ORTEP diagram of **1** in 1-THF with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Lu–N1 2.091(3), Lu–O1 2.459(2), Lu–O2 2.303(2), Lu–O3 2.287(2), Lu–Cl1 2.5589(8), Lu–Cl2 2.5668(9), N1–C1 1.251(4); Lu–N1–C1 174.2(2), N1–Lu–O1 177.86(9), Cl1–Lu–Cl2 161.66(3), O2–Lu–O3 157.54(8), N2–C1–N3 101.5(2).



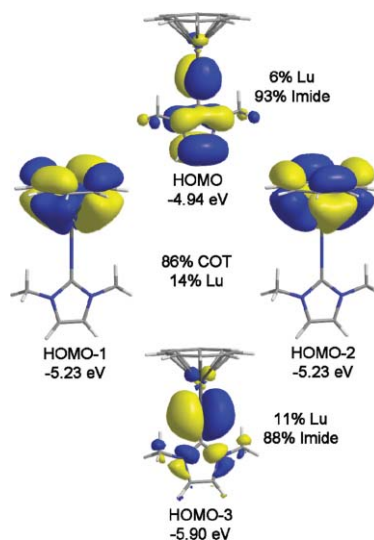
**Fig. 2** ORTEP diagram of **2** in 2-THF with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Lu–N1 2.122(2), Lu–O1 2.380(2), Lu–O2 2.380(2), Lu–C(COT) 2.544(3)–2.643(3); Lu–N1–C1 166.7(2), N1–Lu–O1 89.76(8), N1–Lu–O2 84.90(8), O1–Lu–O2 74.47(8), N2–C1–N3 101.5(2).

of 174.2(2)°. The previous shortest Lu–N distances of 2.145(2) and 2.149(4) Å were found in amido and benzamidate complexes, respectively.<sup>15,16</sup>

The Lu–N1 bond length of 2.122(2) Å in **2** also falls below these values, although it is slightly longer than in **1**. This is accompanied by a greater deviation from linearity at N1, and the Lu–N1–C1 angle is 166.7(2)°. The cyclooctatetraenyl ligand is essentially  $\eta^8$ -bound, but in a slightly distorted fashion with the Lu–C and C–C distances ranging from 2.544(3) to 2.643(3) Å and 1.395(5) to 1.422(5) Å, respectively. The coordination sphere at lutetium is completed by two THF ligands to give a three-legged piano-stool geometry. The imidazole ring subtends an angle of 55.3° with the plane containing the COT centroid, Lu and N1, indicating an intermediate position between a horizontal (90°) and perpendicular (0°) orientation.

To elucidate the nature of the metal–nitrogen bond in imidazolin-2-iminato lutetium complexes and to address the question of lanthanide–nitrogen multiple bonding,<sup>3,12</sup> we performed a DFT (density functional theory) calculation on the model complex  $[(\eta^8\text{-C}_8\text{H}_8)\text{Lu}(\text{NIm}^{\text{Me}})]$  (**3**) ( $\text{Im}^{\text{Me}}\text{N} = 1,3$ -dimethylimidazolin-2-imide), assuming  $C_{2v}$  symmetry. This pseudo-two coordinate system was chosen since it allows an estimate of the full potential of this interaction without lowering of the symmetry by THF coordination. All computations were performed using the hybrid density functional method B3PW91 implemented in the Gaussian03 program.<sup>17</sup> For all main-group elements (C, H, N) the all-electron triple- $\zeta$  basis set (6-311G\*\*) was used, whereas for the Lu atom the Stuttgart relativistic, small core ANO/ECP basis set was employed.<sup>18</sup> The Lu–N bond in the model complex **3** is 2.040 Å, indicating an increase in the bond strength in comparison with the THF complex **2**.

An analysis of the canonical molecular orbitals in **3** reveals several low lying orbitals, which contribute to Lu–N  $\sigma$ -bonding. Fig. 3 shows the isosurfaces for the four highest occupied molecular orbitals. The HOMO and HOMO-3 point towards the presence of two additional  $\pi$ -bonds between the imido ligand and the lutetium atom, whereas the degenerate set of HOMO-1



**Fig. 3** Isosurfaces for the four highest occupied molecular orbitals of the model complex  $[(\eta^8\text{-C}_8\text{H}_8)\text{Lu}(\text{NIm}^{\text{Me}})]$  (**3**) ( $\text{Im}^{\text{Me}}\text{N} = 1,3$ -dimethylimidazolin-2-imide).

and HOMO-2 represent COT–metal  $\delta$ -bonds. A bonding analysis<sup>19</sup> of the  $\pi$ -orbitals HOMO and HOMO-3 reveals 6 and 11% orbital contribution from the metal center, respectively. Although this composition is in agreement with the expected predominantly ionic character of the Lu–N bond, it demonstrates that the imidazolin-2-iminato ligand can be regarded as a  $2\sigma,4\pi$ -electron donor and forms a highly polarized triple bond with the metal atom.<sup>20</sup> In that respect, the bonding situation is similar to that calculated for isostructural “pogo-stick” titanium imido complexes of the type  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\text{NR})_2]$ ,<sup>21</sup> although, as expected for a 3d-metal, a significantly higher degree of covalency is found in these systems.

Future work on imidazolin-2-iminato lanthanide complexes will exploit the reactivity along the highly polarized Ln–N bond, and preliminary studies reveal that complexes of the type  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ln}(\text{ImN})(\text{THF})_x]$  (Ln = Sc, Y, La, Lu) are highly active in the catalytic ring-opening polymerization of lactones.<sup>22</sup>

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## Notes and references

† Preparation of **1** and **2**: **1**: to a mixture of  $\text{LuCl}_3$  (140.7 mg, 0.5 mmol) and  $\text{LiCH}_2\text{SiMe}_3$  (47 mg, 0.5 mmol), THF (10 mL) was added. After 2 h, the imidazolin-2-imine  $\text{Im}^{\text{Dipp}}\text{NH}$  (201.6 mg, 0.5 mmol) was added. The solvent was removed, and the residue was subsequently extracted with pentane. Complex **1** was crystallised from THF–pentane. Yield: 300 mg, 69%.  $[\text{C}_{39}\text{H}_{60}\text{Cl}_2\text{LuN}_3\text{O}_3]$ : calcd C 54.16, H 6.99, N 4.85; found C 54.81, H 6.95, N 4.70%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ , 25 °C, 200 MHz): 7.18 (br, 6H, Ph), 5.91 (s, 2H, NCH), 3.70 (br, 4H, THF), 3.52 (sept., 4H, CHMe), 1.53 (d, 12H, CH<sub>3</sub>), 1.37 (br, 4H, THF), 1.26 (d, 12H, CH<sub>3</sub>) ppm;  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ , 25 °C, 50.3 MHz): 159, 154, 148, 128, 123, 113, 28, 25, 23 ppm. **2**:  $\text{K}_2\text{C}_8\text{H}_8$  (0.5 mmol), freshly prepared from potassium (39 mg) and  $\text{C}_8\text{H}_8$  (0.055 mL), was added to a solution of **1** (432.4 mg, 0.5 mmol) in THF (10 mL), and the reaction mixture was stirred for 12 h. The solvent was removed, and the residue was subsequently extracted with pentane. Complex **2** was crystallised from THF–pentane. Yield: 210 mg, 51%.  $[\text{C}_{47}\text{H}_{68}\text{LuN}_3\text{O}_3]$ : calcd C 62.86, H 7.63, N 4.67; found C 62.15, H 7.04, N 4.12%.  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ , 25 °C, 200 MHz): 7.27–7.20 (m, 4H, *m*-H), 7.11–7.10 (m, 2H, *p*-H), 6.28 (s, 8H, C<sub>8</sub>H<sub>8</sub>), 5.86 (s, 2H, NCH), 3.25–3.18 (m, 4H, THF), 3.09 (sept., 4H, CHMe), 1.30 (d, 12H, CH<sub>3</sub>), 1.24–1.19 (m, 4H, THF), 1.16 (d, 12H, CH<sub>3</sub>) ppm;  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ , 25 °C, 50.3 MHz): 158, 153, 148, 128, 123, 113, 93, 69, 28, 24, 23 ppm.

Crystal data: **1**:  $\text{C}_{43}\text{H}_{68}\text{Cl}_2\text{LuN}_3\text{O}_4$ ,  $M = 936.87$ , monoclinic,  $a = 18.1126(10)$ ,  $b = 12.3042(7)$ ,  $c = 19.9567(11)$  Å,  $\beta = 96.113(10)^\circ$ ,  $V = 4422.3(4)$  Å<sup>3</sup>,  $T = 133$  K, space group  $P2_1/n$  (no. 14),  $Z = 4$ ,  $D_c = 1.407$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 2.395$  mm<sup>-1</sup>. 92 021 reflections measured, 13 523 unique ( $R_{\text{int}} = 0.0768$ ) which were used in all calculations. Final  $R1 = 0.0699$  and  $wR2 = 0.0840$  (all data). CCDC 656208. **2**:  $\text{C}_{47}\text{H}_{68}\text{LuN}_3\text{O}_3$ ,  $M = 898.01$ , orthorhombic,  $a = 12.2567(10)$ ,  $b = 12.5050(10)$ ,  $c = 31.988(3)$  Å,  $V = 4902.8(7)$  Å<sup>3</sup>,  $T = 133$  K, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.217$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 2.051$  mm<sup>-1</sup>. 101 213 reflections measured, 14 992 unique ( $R_{\text{int}} = 0.0515$ ) which were used in all calculations. Final  $R1 = 0.0354$  and  $wR2 = 0.0748$  (all data). CCDC 656209. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b711669a

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