



# Synthesis and characterization of homoleptic imidazolin-2-iminato rare earth metal complexes

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## ABSTRACT

The reactions of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine ( $\text{Im}^{\text{ipr}}\text{NH}$ ) with the trimethylsilylmethyl (neosilyl) complexes  $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  ( $\text{M} = \text{Sc}, \text{Y}, \text{Lu}$ ) in a 3:1 ratio afforded tetramethylsilane (TMS) and the dinuclear imidazolin-2-iminato complexes  $[\text{M}_2(\text{Im}^{\text{ipr}}\text{N})_6(\text{THF})_n]$  (**1a**,  $\text{M} = \text{Sc}$ ,  $n = 0$ ; **1b**,  $\text{M} = \text{Y}$ ,  $n = 1$ ; **1c**,  $\text{M} = \text{Lu}$ ,  $n = 1$ ), in which the metal atoms are bridged by two  $\mu_2$ - $\text{Im}^{\text{ipr}}\text{N}$  ligands. **1a** crystallized from THF/pentane solution to afford a solvent-free, centrosymmetric, dimeric complex, in which both scandium atoms attain a coordination number of four; three uncoordinated THF per dimer are observed. In contrast, the X-ray crystal structures of **1b**·2THF and **1c**·2THF reveal the formation of unsymmetric THF solvate complexes that contain one THF ligand and therefore both four- and five-coordinated rare earth metal atoms; other THF molecules are non-coordinating. The reaction of  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  with three equivalents of the sterically more demanding 1,3-di-*tert*-butylimidazolin-2-imine ( $\text{Im}^{\text{tBu}}\text{NH}$ ) afforded the mononuclear complex  $[\text{Y}(\text{Im}^{\text{tBu}}\text{N})_3(\text{THF})_2]$  (**2**) with a five-coordinated yttrium atom, as indicated by X-ray diffraction analysis of **2**·2THF.

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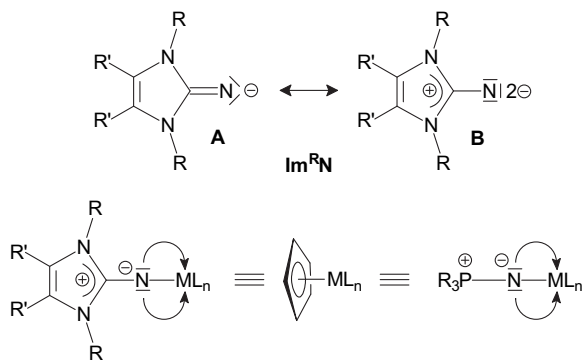
## 1. Introduction

Ever since the preparation of the first tris(cyclopentadienyl) rare earth metal complexes,  $[(\eta\text{-C}_5\text{H}_5)_3\text{M}]$ , by Wilkinson and Birmingham in 1954 [1], the organometallic chemistry of the rare earth elements has been dominated by cyclopentadienyl ligands (Cp) or related aromatic ligands [2]. In recent years, however, cyclopentadienyl-free complexes have been playing an increasingly important role in organolanthanide and organo rare earth metal chemistry [3], and a number of monodentate and monoanionic ancillary ligands such as alkoxides, siloxides, aryloxides [4], amides [5], and phosphoraneiminates [6] have been used to replace of the Cp ligand and to prepare homoleptic complexes of the type  $\text{ML}_3$  ( $\text{L} = \text{OR}, \text{OSiR}_3, \text{NR}_2, \text{NPR}_3$ ). For the latter ligands, *Dehnicke* has proposed a pseudo-isolobal relationship with the cyclopentadienyl system because of their ability to act as  $2\sigma, 4\pi$ -electron donors [6–9]. Similar considerations apply to related imidazolin-2-iminato ligands ( $\text{Im}^{\text{R}}\text{N}$ ) [10,11], which can be described by the two limiting resonance structures **A** and **B** (Scheme 1), indicating that the ability of the imidazolium ring to efficiently stabilize a positive charge

affords highly basic ligands with a strong electron-donating capacity toward early transition metals or metals in a higher oxidation state [12,13]. In our hands, these ligands proved to be viable systems for the preparation of catalytically active transition metal complexes [14] and also for the stabilization of mononuclear rare earth metal complexes, in which the terminal imidazolin-2-iminato ligands exhibit exceptionally short metal–nitrogen bonds [15].

In the course of these studies, a number of mono- and bis(imidazolin-2-iminato) scandium, yttrium, gadolinium and lutetium complexes of the types  $[(\text{Im}^{\text{Dipp}}\text{N})\text{MCl}_2(\text{THF})_3]$  [15] and  $[(\text{Im}^{\text{Dipp}}\text{N})_2\text{MCl}(\text{THF})_2]$  [16] containing the  $\text{Im}^{\text{Dipp}}\text{N}$  ligand ( $\text{R} = \text{Dipp} = 1,3$ -diisopropylphenyl,  $\text{R}' = \text{H}$ , Scheme 1) were prepared, which proved to be versatile starting materials for the preparation of cyclooctatetraenyl, cyclopentadienyl, amido and alkyl complexes by chloride substitution [15]. In continuation of this work, we aimed at the synthesis of tris(imidazolin-2-iminato) rare earth metal complexes, which might be regarded as isolobal to tris(cyclopentadienyl) complexes  $[(\text{Cp})_3\text{M}]$  [2] and to homoleptic tris(phosphoraneiminato) complexes  $[\text{M}(\text{NPR}_3)_3]$  [6]. For the latter, however, only dinuclear species such as  $[\text{M}(\text{NPPH}_3)_3]_2$  ( $\text{M} = \text{Y}, \text{La}$ ) were reported, which can be used as initiators for the ring-opening polymerization of lactones [9]. Herein, we wish to present the preparation and structural characterization of analogous homoleptic imidazolin-2-iminato complexes containing the

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**Scheme 1.** Mesomeric structures for imidazolin-2-iminato complexes and isobal relationship between imidazolin-2-iminato, cyclopentadienyl and phosphoraneiminato complexes.

ligands 1,3-diisopropyl-4,5-dimethylimidazolin-2-imide ( $Im^{iPr}N$ ,  $R = iPr$ ,  $R' = Me$ ) and 1,3-di-*tert*-butylimidazolin-2-imide ( $Im^{tBu}N$ ,  $R = tBu$ ,  $R' = H$ ), which have a different steric demand and might therefore lead to rare earth metal complexes of variable nuclearity.

## 2. Experimental

### 2.1. General information

All air-sensitive materials were manipulated with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum ( $10^{-4}$  torr) line, or in an argon-filled glove box (MBraun 200B). All solvents were purified using an MBraun system and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all  $\geq 99$  atom % D) and were degassed, dried, and stored in the argon-filled glove box. NMR spectra were recorded on a Bruker DPX 200 spectrometer. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard. Elemental analyses (C, H, N) were carried out by combustion and gas chromatographical analysis with an Elementar vario MICRO. 1,3-Diisopropyl-

4,5-dimethylimidazolin-2-imine ( $Im^{iPr}NH$ ) [11], 1,3-di-*tert*-butylimidazolin-2-imine ( $Im^{tBu}NH$ ) [11], and  $[Ln(CH_2SiMe_3)_3(THF)_2]$  ( $Ln = Sc, Y, Lu$ ) [17] were prepared according to literature procedures.

### 2.2. General procedure for the preparation of $[M_2(Im^{iPr}N)_6(THF)_n]$ (**1a**, $M = Sc$ , $n = 0$ ; **1b**, $M = Y$ , $n = 1$ ; **1c**, $M = Lu$ , $n = 1$ ) and $[Y(Im^{tBu}N)_3(THF)_2]$ (**2**)

100 mg of  $[M(CH_2SiMe_3)_3(THF)_2]$  were dissolved in hexane (5 mL) and added dropwise to a hexane solution (5 mL) containing three equivalents of  $Im^{iPr}NH$  or  $Im^{tBu}N$ , respectively. In all cases, a white suspension formed instantaneously, which gradually re-dissolved. After stirring the reaction mixture for 12 h at room temperature, the solvent was evaporated. The yellowish residues were re-crystallized from THF/pentane solutions to isolate the complexes **1** and **2** as a colourless crystalline materials.

### 2.3. Characterization of $[Sc_2(Im^{iPr}N)_6]$ (**1a**)

From  $[Sc(CH_2SiMe_3)_3(THF)_2]$  (100.0 mg, 0.22 mmol) and  $Im^{iPr}NH$  (130.1 mg, 0.66 mmol), 115 mg of **1a** were obtained. Yield: 83%.  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C):  $\delta$  5.83 (sept., 4H, CH,  $^3J_{H,H}$  6.8 Hz), 5.21 (sept., 8H, CH,  $^3J_{H,H}$  6.8 Hz), 1.92 (s, 24H,  $CH_3$ ), 1.86 (s, 12H,  $CH_3$ ), 1.52 (d, 24H,  $CH_3$ ,  $^3J_{H,H}$  7.2 Hz), 1.32 (d, 48H,  $CH_3$ ,  $^3J_{H,H}$  7.2 Hz).  $^{13}C\{H\}$  NMR ( $C_6D_6$ , 50.32 MHz, 25 °C):  $\delta$  113.3 (NCMe), 44.7 (CHMe), 22.9 (CHCH<sub>3</sub>), 10.6 (NCCH<sub>3</sub>); the resonance for the CN carbon atom was not observed. Anal. Calc. for  $C_{66}H_{120}N_{18}Sc_2$  (1255.72): C, 63.13; H, 9.63; N, 20.07. Found: C, 62.94; H 9.28; N, 19.89.

### 2.4. Characterization of $[Y_2(Im^{iPr}N)_6(THF)]$ (**1b**)

From  $[Y(CH_2SiMe_3)_3(THF)_2]$  (100 mg, 0.20 mmol) and  $Im^{iPr}NH$  (119 mg, 0.60 mmol) 140 mg of **1b** were obtained. Yield: 91%.  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C):  $\delta$  5.18 (br, 12H, CH), 3.56–3.50 (br, 4H, THF), 1.86 (s, 36H,  $CH_3$ ) 1.67–1.42 (m, 4H, THF), 1.33 (d, 72H,  $CH_3$ ,  $^3J_{H,H}$  5.8 Hz).  $^{13}C\{H\}$  NMR ( $C_6D_6$ , 50.32 MHz, 25 °C):  $\delta$  113.1 (NCMe), 44.3 (CHMe), 22.5 (CHCH<sub>3</sub>), 10.5 (NCCH<sub>3</sub>); the resonance for the CN carbon atom was not observed.  $^1H$  NMR (THF-*d*<sub>8</sub>, 300 MHz,

**Table 1**  
Crystallographic data for complexes **1a**·3THF, **1c**·2THF, and **2**·2THF.

	<b>1a</b> ·3THF	<b>1b</b> ·2THF	<b>1c</b> ·2THF	<b>2</b> ·2THF
Empirical formula	$C_{78}H_{144}N_{18}O_3Sc_2$	$C_{78}H_{144}N_{18}O_3Y_2$	$C_{78}H_{144}Lu_2N_{18}O_3$	$C_{49}H_{92}N_9O_4Y$
$M_r$ [ $g\ mol^{-1}$ ]	1472.03	1559.93	1732.05	960.23
$T$ [K]	133(2)	133(2)	100(2)	100(2)
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
$a$ [Å]	20.9793(15)	13.0964(14)	13.0315(8)	24.2650(7)
$b$ [Å]	13.9545(10)	14.3019(14)	25.9173(15)	9.5954(3)
$c$ [Å]	28.989(2)	24.788(2)	25.3648(15)	23.2667(7)
$\alpha$ , °	90	80.713(3)	90	90
$\beta$ , °	98.109(2)	84.841(3)	91.442(3)	105.1140(1)
$\gamma$ , °	90	72.241(3)	90	90
$V$ [Å <sup>3</sup> ]	8401.8(10)	4359.6(8)	8564.0(9)	5229.9(3)
$Z$	4	2	4	4
$\rho_{calcd.}$ [ $Mg/m^3$ ]	1.164	1.188	1.343	1.220
$\mu$ [ $mm^{-1}$ ]	0.217	1.378	2.346	1.165
$F(000)$	3216	1680	3616	2080
Reflections collected	66,574	66,129	282,997	116,189
Independent reflections	8599	17,784	32,619	13,052
$R(int)$	0.0853	0.0856	0.0455	0.0952
GOF	1.136	1.011	1.062	1.023
$R1$ [ $I > 2\sigma(I)$ ]	0.0610	0.0545	0.0278	0.0441
wR2	0.1880	0.1496	0.0585	0.0932

25 °C):  $\delta$  5.09 (br, 12H, CH), 3.70–3.61 (m, 4H, THF), 2.01 (s, 36H, CH<sub>3</sub>) 1.88–1.72 (m, 4H, THF), 1.21 (d, 72H, CH<sub>3</sub>,  $^3J_{\text{H,H}}$  7.2 Hz).  $^{13}\text{C}\{\text{H}\}$  NMR (THF-*d*<sub>8</sub>, 75.47 MHz, 25 °C):  $\delta$  112.8 (NCMe), 44.3 (CHMe), 22.8 (CHCH<sub>3</sub>), 10.9 (NCCH<sub>3</sub>); the resonance for the NCN carbon atom was not observed. Anal. Calc. for C<sub>78</sub>H<sub>122</sub>N<sub>18</sub>O<sub>3</sub>Y<sub>2</sub> (1537.76): C, 60.92; H, 7.99; N, 16.39. Found: C, 60.62; H, 7.85; N, 16.10.

### 2.5. Characterization of [Lu<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)] (1c)

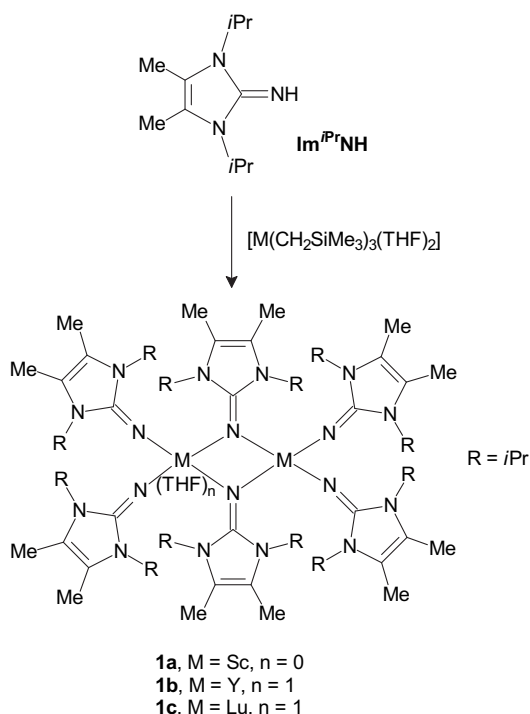
From [Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (100.0 mg, 0.17 mmol) and Im<sup>iPr</sup>NH (100.0 mg, 0.51 mmol) 120 mg of **1c** were obtained. Yield: 89%.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C):  $\delta$  5.20 (br, 12H, CH), 3.53–3.49 (br, 4H, THF), 1.89 (s, 36H, CH<sub>3</sub>) 1.65–1.42 (m, 4H, THF), 1.31 (d, 72H, CH<sub>3</sub>,  $^3J_{\text{H,H}}$  5.8 Hz).  $^{13}\text{C}\{\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 50.32 MHz, 25 °C):  $\delta$  113.3 (NCMe), 44.6 (CHMe), 22.5 (CHCH<sub>3</sub>), 10.4 (NCCH<sub>3</sub>); the resonance for the NCN carbon atom was not observed. Anal. Calc. for C<sub>70</sub>H<sub>128</sub>Lu<sub>2</sub>N<sub>18</sub>O (1587.84): C, 52.95; H, 8.12; N, 15.87. Found: C, 52.47; H, 7.91; N, 15.68.

### 2.6. Characterization of [Y(Im<sup>tBu</sup>N)<sub>3</sub>(THF)<sub>2</sub>] (2)

From [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (100.0 mg, 0.20 mmol) and Im<sup>tBu</sup>NH (119.0 mg, 0.60 mmol) 150 mg of **2** were obtained. Yield: 92%.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 25 °C):  $\delta$  6.20 (s, 6H, CH=CH), 3.88–3.85 (m, 8H, THF), 1.69 (s, 54H, CCH<sub>3</sub>), 1.43–1.37 (m, 8H, THF).  $^{13}\text{C}\{\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz, 25 °C):  $\delta$  105.7 (NCH), 69.3 (THF), 53.6 (NCMe<sub>3</sub>), 29.4 (CCH<sub>3</sub>), 25.6 (THF); the resonance for the NCN carbon atom was not observed. Anal. Calc. for C<sub>41</sub>H<sub>76</sub>N<sub>9</sub>O<sub>2</sub>Y (816.02): C, 60.34; H, 9.38; N, 15.44. Found: C, 59.99; H, 9.11; N, 15.22.

### 2.7. Single-crystal X-ray structure determinations

CCDC-775522 (for **1a**), CCDC-775523 (for **1b**), CCDC-775524 (for **1c**) and CCDC-775525 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of



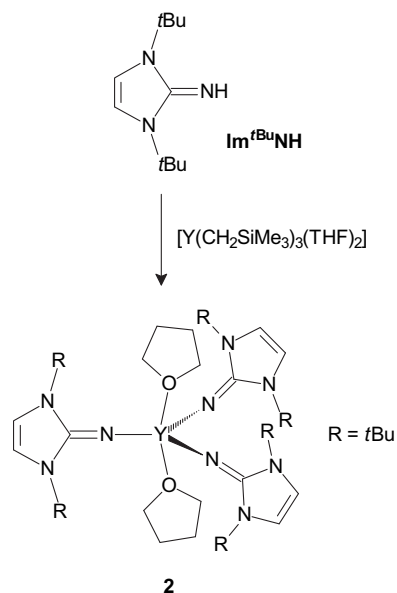
**Scheme 2.** Synthesis of dincuclear imidazolin-2-iminato rare earth metal complexes.

charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The hydrogen atoms were included in the model at geometrically calculated positions and refined using either a riding model or with rigid methyl groups. *Special features:* The structures all suffer to varying extents from problems of disorder, especially of the THF. In **1a** two distorted sites of uncoordinated THF (one around a special position) were removed using the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands). In **1b** the two uncoordinated molecules of THF are distorted over two positions and were refined isotropically. Two distorted molecules of uncoordinated THF were removed from **1c** and **2** as above. In **2** one CH<sub>2</sub> group of the coordinated THF molecule is disordered over two positions. The CH<sub>3</sub> groups of **1c** at C26 are disordered over two positions. Diffractometers: Bruker SMART and APEX2. Program system: SHELXL-97 (G. M. Sheldrick, University of Göttingen) (Table 1).

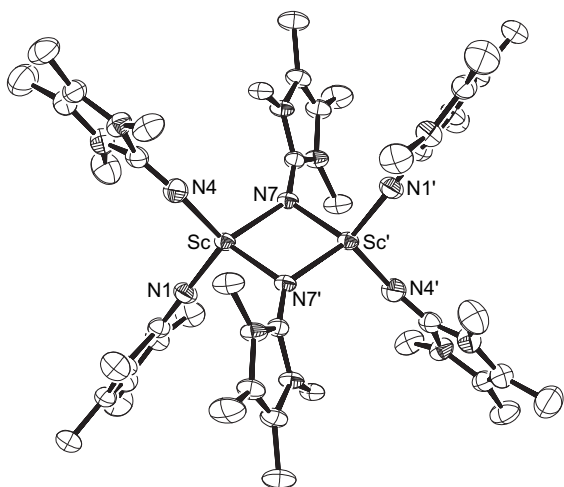
## 3. Results and discussion

The acid–base reaction between the rare earth metal tris(neosilyl) complexes [M(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (M = Sc, Y, Lu) and three equivalents of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine (Im<sup>iPr</sup>NH) in hexane cleanly afforded the tris(imidazolin-2-iminato) complexes **1** with release of tetramethylsilane (Scheme 1). After recrystallization from THF/pentane solution, the complexes **1a** (M = Sc), **1b** (M = Y), and **1c** (M = Lu) were isolated as colourless crystalline materials in excellent yield. The molecular structures of **1a–1c** were established by X-ray diffraction analyses, revealing the presence of dimeric complexes of the type [M<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)<sub>n</sub>] in the solid state. The scandium complex **1a** crystallizes with n = 0 but with uncoordinated THF (**1a**·3THF) in the space group C2/c, whereas the corresponding yttrium and lutetium complexes crystallize as THF solvates of THF complexes, [Y<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)]·2THF (**1b**·2THF) and [Lu<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)]·2THF (**1c**·2THF) in the space groups P and P2<sub>1</sub>/c, respectively (Schemes 2 and 3).

The molecular structure of **1a** is shown in Fig. 1, revealing the formation of a centrosymmetric dimer of [Sc<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>] with the two scandium atoms connected by two bridging  $\mu_2$ -Im<sup>iPr</sup>N groups to generate a Sc<sub>2</sub>N<sub>2</sub> square with Sc–N distances of 2.122(2) and 2.143(2) Å together with Sc–N7–Sc' and N7–Sc–N7' angles of



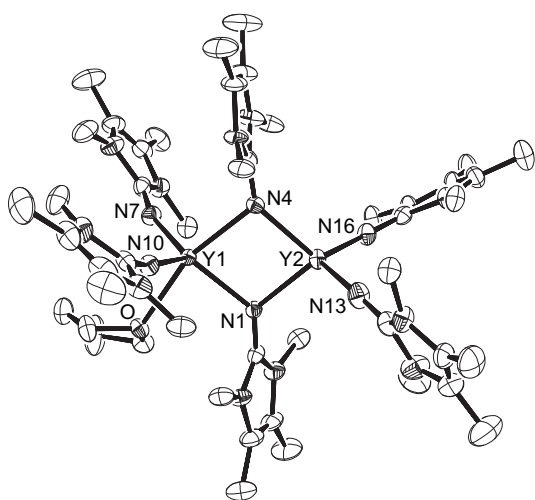
**Scheme 3.** Synthesis of a mononuclear imidazolin-2-iminato yttrium complex.



**Fig. 1.** ORTEP diagram of **1a** in **1a**·3THF with thermal displacement parameters drawn at the 50% probability level; hydrogen atoms and isopropyl CH<sub>3</sub> groups were omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc–N1 1.984(2), Sc–N4 2.004(2), Sc–N7 2.122(2), Sc–N7A 2.143(2); Sc–N7–Sc' 94.21(14), N7–Sc–N7' 85.79(7), Sc–N1–C1 172.41(2), Sc–N4–C12 155.5(2).

94.21(14)° and 85.79(7)°, respectively. The coordination sphere of each Sc atom is completed by two terminal Im<sup>iPr</sup>N groups, affording a distorted tetrahedral geometry. The terminal metal–nitrogen distances are shorter [Sc–N1 = 1.984(2) Å, Sc–N4 = 2.004(2) Å] than those to the bridging nitrogen atoms; however, they are longer than previously observed for complexes such as [(Im<sup>DipP</sup>N)ScCl<sub>2</sub>(THF)<sub>3</sub>] [1.963(2) Å] and [(Im<sup>DipP</sup>N)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)] [1.9520(18) Å] [15b,15c]. It should also be noted that a related centrosymmetric dimeric molecular structure was reported for the homoleptic phosphoraneiminato complex [Yb<sub>2</sub>(NPPH<sub>3</sub>)<sub>2</sub>] [9], confirming the similarity between imidazolin-2-iminato and phosphoraneiminato ligands.

In contrast to **1a**, the dimeric complex units in [Y<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)] (**1b**) and [Lu<sub>2</sub>(Im<sup>iPr</sup>N)<sub>6</sub>(THF)] (**1c**) contain two metal atoms each,

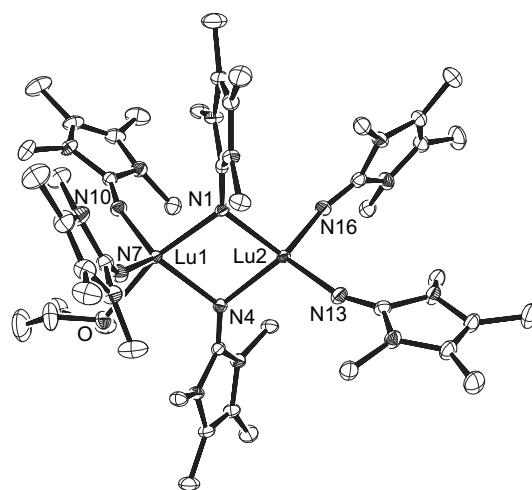


**Fig. 2.** ORTEP diagram of **1b** in **1b**·2THF with thermal displacement parameters drawn at the 50% probability level; hydrogen atoms and isopropyl CH<sub>3</sub> groups were omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N7 2.167(3), Y1–N10 2.164(3), Y2–N13 2.167(4), Y2–N16 2.161(4), Y1–N1 2.355(3), Y1–N4 2.335(3), Y2–N1 2.282(3), Y2–N4 2.255(3), Y1–O1 2.463(3); Y1–N1–Y2 97.04(1), Y1–N4–Y2 98.36(1), N1–Y1–N4 80.50(1), N1–Y2–N4 83.80(1), Y1–N7–C23 163.6(3), Y1–N10–C34 169.4(3), Y2–N13–C45 165.3(4), Y2–N16–C56 160.2(3).

which display different coordination geometries, since one metal atom (Y1, Lu1) coordinates an additional THF molecule to acquire a coordination number of five, whereas the other atom (Y2, Lu2) remains in a distorted tetrahedral environment (Figs. 2 and 3). The geometries at the five-coordinate metal atoms are in both cases best described as distorted trigonal–bipyramidal with the THF oxygen atom and one of the bridging nitrogen atoms adopting the axial positions, albeit with a considerable deviation from a perfectly linear arrangement [O–Y1–N4 = 162.06(10)°, O–Lu1–N1 = 165.62(4)°]. Similarly to **1a**, both complexes feature M<sub>2</sub>N<sub>2</sub> rectangles with the Y–N distances ranging from 2.255(3) to 2.355(3) Å and the Lu–N distances ranging from 2.1946(12) to 2.2921(12) Å. Again, the terminal metal–nitrogen distances are considerably shorter with Y–N = 2.161(4)–2.167(4) Å and Lu–N = 2.1102(14)–2.1380(14) Å. Interestingly, the closely related phosphoraneiminato complex [La<sub>2</sub>(NPPH<sub>3</sub>)<sub>2</sub>(THF)] exhibits a bridging μ<sub>2</sub>-THF ligand, which results in trigonal–bipyramidal coordination around both lanthanum atoms [9].

In agreement with a dimeric structure, the <sup>1</sup>H NMR spectrum (in C<sub>6</sub>D<sub>6</sub>) of the scandium complex **1a** shows separate resonances for the terminal and bridging Im<sup>iPr</sup>N groups, and two septets, two doublets and two singlets are observed in the expected 8:4, 48:24 and 24:12 ratios, which can be assigned to the isopropyl and methyl hydrogen atoms of the imidazole backbone. In contrast, dynamic behaviour is observed for the yttrium and lutetium congeners **1b** and **1c** in solution at room temperature, and broad, averaged resonances are observed for the terminal and bridging ligands. Therefore, <sup>1</sup>H NMR spectra of **1b** were recorded in THF-*d*<sub>8</sub> at variable temperature (Fig. 4), revealing fully resolved signals at about –40 °C. As expected, THF coordination is still fluxional at low temperature, and the low temperature spectra are in agreement with time-averaged D<sub>2h</sub>-symmetry.

To investigate whether the introduction of a more sterically demanding imidazolin-2-iminato ligand would affect the nuclearity of the resulting rare earth metal complexes, a hexane solution of [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] was treated with three equivalents of 1,3-di-*tert*-butylimidazolin-2-imine (Im<sup>tBu</sup>NH), and re-crystallization of the resulting yellowish residue from THF/pentane solution



**Fig. 3.** ORTEP diagram of **1c** in **1c**·2THF with thermal displacement parameters drawn at the 50% probability level; hydrogen atoms and isopropyl CH<sub>3</sub> groups were omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1–N7 2.1247(14), Lu1–N10 2.1380(14), Lu2–N13 2.1211(13), Lu2–N16 2.1102(14), Lu1–N1 2.2519(13), Lu1–N4 2.2921(12), Lu2–N1 2.1946(12), Lu2–N4 2.2407(13), Lu1–O 2.3868(11); Lu1–N1–Lu2 98.52(5), Lu1–N4–Lu2 96.02(5), N1–Lu1–N4 81.48(4), N1–Lu2–N4 83.92(5), Lu1–N7–C23 153.67(13), Lu1–N10–C34 163.91(12), Lu2–N13–C45 160.88(13), Lu2–N16–C56 153.36(12).

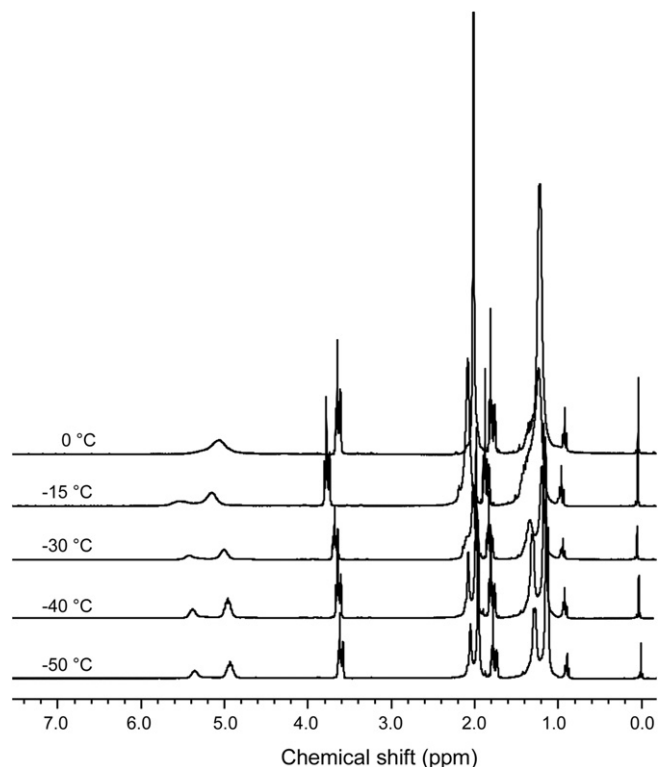


Fig. 4.  $^1\text{H}$  NMR spectra (THF- $d_8$ , 300 MHz) of **1b** at variable temperature.

afforded  $[\text{Y}(\text{Im}^{t\text{Bu}}\text{N})_3(\text{THF})_2]$  (**2**) as a colourless, crystalline solid in almost quantitative yield. The  $^1\text{H}$  NMR spectrum of **2** shows one set of resonances each for the imidazolin-2-iminato and THF ligands, and their relative intensities are in agreement with a  $\text{Im}^{t\text{Bu}}\text{N}/\text{THF}$  ratio of 3:2. Single crystals of the THF solvate **2**·2THF were subjected to an X-ray diffraction analysis; it crystallizes in the space group  $P2_1/c$  with one molecule of  $[\text{Y}(\text{Im}^{t\text{Bu}}\text{N})_3(\text{THF})_2]$  (**2**) in the asymmetric unit. The molecular structure of **2** is shown in Fig. 5, revealing that a monomeric complex has formed, in which the yttrium atom attains a coordination number of five by formation of three Y–N and two Y–O bonds.

The geometry about the yttrium atom can be described as either distorted trigonal–bipyramidal with the oxygen atoms O1 and O2

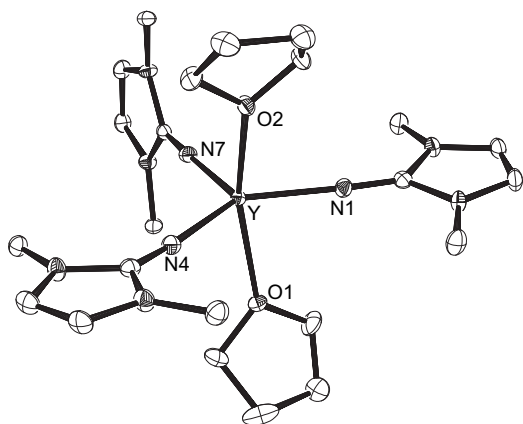


Fig. 5. ORTEP diagram of **2** in **2**·2THF with thermal displacement parameters drawn at the 50% probability level; hydrogen atoms and isopropyl  $\text{CH}_3$  groups were omitted for clarity. Selected bond lengths [Å] and angles [ $^\circ$ ]: Y–N1 2.2066(16), Y–N4 2.2122(17), Y–N7 2.1625(16), Y–O1 2.4179(13), Y–O2 2.4043(13); Y–N1–C1 176.80(15), Y–N4–C12 174.43(14), Y–N7–C23 174.88(14).

in axial positions, or as square–pyramidal with the nitrogen atom N7 adopting the apical position. For structures that are intermediate between the idealized square–pyramidal and trigonal–bipyramidal extremes, Addison and Reedijk have introduced the structural index parameter  $\tau = (\alpha - \beta)/60$ , in which  $\alpha$  and  $\beta$  represent the two largest angles around the metal atom [18]. Accordingly, a  $\tau$  value of zero is obtained for perfect tetragonal geometry, while it becomes unity for a perfect trigonal bipyramid [18]. The largest angles in **2** are  $\text{O1–Y–O2} = 157.17(5)^\circ$  and  $\text{N1–Y–N4} = 133.45(6)^\circ$ , and the resulting  $\tau$  value of 0.40 thus indicates an intermediate position between the two limiting structures. The yttrium–nitrogen distances are Y–N1 = 2.2066(16) Å, Y–N4 = 2.2122(17) Å and Y–N7 = 2.1625(16) Å and fall among the shortest Y–N bond lengths ever observed. Even shorter bonds have been reported for the imidazolin-2-iminato complexes  $[(\text{Im}^{\text{RN}})\text{YCl}_2(\text{THF})_3]$  [R = Dipp, Y–N = 2.1278(18) Å; R = *t*Bu, Y–N = 2.115(2) Å] [15,19] and  $[(\text{Im}^{\text{DippN}})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2]$  [Y–N = 2.1255(13) Å] and also for a tetranuclear cyclopentadienyl–yttrium complex containing  $\mu_3$ -ethylimido ligands, which features the previously shortest yttrium–nitrogen bond of 2.116(6) Å [20]. To accommodate the three bulky di-*tert*-butylimidazole moieties, the heterocycle that is attached via the “apical” nitrogen atom N7 adopts a perpendicular orientation with respect to the other two rings with dihedral angles of  $82.2^\circ$  and  $88.3^\circ$ , and all Y–N–C angles are close to linearity [Y–N1–C1 =  $176.80(15)^\circ$ , Y–N4–C12 =  $174.43(14)^\circ$ , Y–N7–C23 =  $174.88(14)^\circ$ ].

#### 4. Conclusion

We have presented the syntheses and structures of the dinuclear homoleptic rare earth metal complexes  $[\text{M}_2(\text{Im}^{\text{Pr}}\text{N})_6(\text{THF})_n]$  (**1**) containing the 1,3-diisopropyl-4,5-dimethylimidazolin-2-iminato ligand ( $\text{Im}^{\text{Pr}}\text{N}$ ). For M = Sc, the solvent-free ( $n = 0$ ), centrosymmetric complex **1a** was obtained, whereas the larger ionic radii of yttrium and lutetium allow for coordination of one additional THF ligand ( $n = 1$ ), affording asymmetric complexes **1b** and **1c** with two different metal coordination spheres. Employing the more sterically demanding 1,3-di-*tert*-butylimidazolin-2-iminato ligand ( $\text{Im}^{t\text{Bu}}\text{N}$ ) leads to the mononuclear complex  $[\text{Y}(\text{Im}^{t\text{Bu}}\text{N})_3(\text{THF})_2]$  (**2**) with a coordination geometry that can be described as being 40% along the pathway of distortion from square–pyramidal toward trigonal–bipyramidal ( $\tau = 0.40$ ) [18]. As a future perspective, the application complexes of **1** and **2** as initiators for ring-opening polymerization of lactones and lactides can be envisaged in view of the results obtained for related phosphoraneiminato complexes [9].

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