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Anionic Lanthanide Complexes Bearing a Bis(phenoxy)-Functionalized N-Heterocyclic Carbene Ligand: Syntheses and Molecular Structures

Haisheng Yao,[a] Yong Zhang,[a] Hongmei Sun,[a] and Qi Shen*[a]

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A series of anionic lanthanide complexes supported by bis(phenoxy)-functionalized N-heterocyclic carbene (NHC) ligand L, where L = 1,3-bis[*O*-4,6-di-*t*Bu-C_6H_2-2-CH_2][C{N(CHCH)N}], were synthesized by the amine-elimination reaction. The in situ reaction of LH_3Cl with Li(thf)Ln(N*i*Pr_2)$_4$ and *n*BuLi in a 2:1:2 molar ratio in thf afforded the discrete ion-pair complexes [L_2Ln][Li(dme)$_3$] (Ln = Sm **1**, Er **2**, Yb **3**) upon crystallization from dme/toluene (10 mL:15 mL). The reaction of LH_3Cl with Li(thf)Sm(N*i*Pr_2)$_4$ and *n*BuLi in a 2:1:2 molar ratio proceeded in thf, followed by crystallization from thf/toluene (2 mL:15 mL), to yield an "ate" complex [(thf)Li(μ-L)SmL] (**4**). The analogous "ate" complex with sodium metal [(Et_2O)Na(μ-L)SmL] (**5**) was also prepared by the in situ treatment of LH_3Cl with Sm[N($SiMe_3$)$_2$]$_3$ and NaN($SiMe_3$)$_2$ in a 2:1:3 molar ratio. Single-crystal X-ray structural analyses of **1**–**5** revealed that complexes **1**–**3** have ion-pair structure consisting of an anion [L_2Ln]$^-$ and a cation [Li(dme)$_3$]$^+$, in which the coordination geometries about each lanthanide metal ion can be best described as a distorted octahedron, while the samarium ion and the alkali metal ion in complexes **4** and **5** are connected together by two phenoxide oxygen bridges, and each alkali metal ion is bound to an additional oxygen atom of one thf (for **4**) and one Et_2O (for **5**).

Introduction

N-heterocyclic carbene (NHC) ligands with a pendant anionic group have attracted increasing attention in the organometallic chemistry of lanthanide metals, as the anionic group in the ligands acts as an anchor leading to enhanced binding of the NHC ligand to electropositive lanthanide metals, which provides the opportunity to isolate discrete NHC lanthanide complexes.[1–4]

Tridentate anionic functionalized NHCs including bis(carbene)s and monocarbenes, have been known to be more rigid ligands. Complexes of transition metals with this class of NHCs have a constrained geometry with a stronger metal–NHC binding by the chelating effect, which has potential in the area of homogeneous catalysis.[5] However, the application of these NHCs in organolanthanide chemistry has been quite limited. To date, only two complexes have been reported. The first yttrium complex supported by an aminodicarbene was synthesized by treatment of the aminodicarbene with a stoichiometric amount of Y[N($SiMe_3$)$_2$]$_3$ in thf[6] by the Arnold group. Very recently, lanthanide dibromides ligated by a tridentate CCC-pincer bis(carbene) have been successfully prepared by the in situ treatment of a xylene-bridged bis(imidazolium) salt with $LnCl_3$ (Ln = Sm, Lu, Sc) and *n*BuLi.[7]

[a] Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Dushu Lake Campus, Suzhou University,
Suzhou, 215123, P. R. China
Fax: +86-512-65880305
E-mail: qshen@suda.edu.cn

We are interested in understanding the chemistry of lanthanide complexes with phenoxy-functionalized NHCs,[4,8] as lanthanide complexes supported by phenoxy groups have been widely used in homogeneous catalysis.[9] The tridentate architecture of bis(phenolate) ligands with a central carbene group provides a suitable backbone for single-site lanthanide catalysts, as a chelating effect with a strongly electron-donating carbene carbon should make the complex more stable and tunable. Of this class of ligands, only the titanium and zirconium complexes have been prepared and found to be the active precatalysts for alkene polymerization.[10] No lanthanide-metal-based counterparts have yet been reported. Moreover, anionic lanthanide complexes containing alkali metals are popular in the family of lanthanide complexes and of interest in homogeneous catalysis, as there is a cooperation effect between lanthanide and alkali metals.[9c,9d,9e] However, no such complex with NHCs has been ever found. Here we describe the syntheses and molecular structures of a series of anionic complexes of lanthanides and alkali metals with a bis(phenoxy)-functionalized NHC ligand L, where L = 1,3-bis[*O*-4,6-di-*t*Bu-C_6H_2-2-CH_2][C{N(CHCH)N}].

Results and Discussion

Syntheses and Crystal Structures of Complexes 1–3

Bis(phenoxy)-functionalized N-heterocyclic carbene proligand LH_3Cl was prepared in high yield through stepwise

alkylation on the nitrogen atoms of the imidazole group by using 2-chloromethyl-4,6-di-*tert*-butylphenol according to the procedures reported previously.[10]

Anionic lanthanide amides have been known to be convenient precursors for the synthesis of NHC derivatives of lanthanides by the amine-elimination reaction.[2] Thus, the amine-elimination reaction was tried in synthesizing anionic complexes. The reaction of LH_3Cl with Li(thf)Sm($Ni Pr_2$)$_4$ and *n*BuLi in a molar ratio of 2:1:2 works cleanly in thf when the reaction mixture is kept first at –50 °C for 10 h and then at room temperature for 10 h. After workup, light yellow crystals were isolated in 62% yield upon crystallization from dme/toluene (10 mL:15 mL). Elemental analysis and low-temperature single-crystal X-ray structure determination revealed the crystals to be a discrete ion-pair complex, [SmL_2][Li(dme)$_3$] (**1**), in which the metal ion is ligated by two ligands (Scheme 1). The same reaction with anionic Er and Yb amides Li(thf)Ln($Ni Pr_2$)$_4$ (Ln = Er or Yb) afforded the analogous complexes [ErL_2][Li(dme)$_3$] (**2**) and [YbL_2][Li(dme)$_3$] (**3**) in yields of 55% and 60%, respectively (Scheme 1).

Complexes **1**–**3** are very sensitive to air and moisture. The paramagnetism of these complexes precludes ^{13}C NMR spectroscopic identification of the carbene carbon. The same situation is also observed for the related NHC complexes of Sm,[1a,8] Er,[8] and Yb.[2b]

Single crystals of **1**–**3** suitable for structural determination were obtained by recrystallization from dme/toluene (10 mL:15 mL) at 0 °C. Complexes **1**–**3** are isostructural, and each complex is composed of an anion [LnL_2]$^-$ and a cation [Li(dme)$_3$]$^+$. The perspective view of the anion is shown in Figure 1 for clarity. Selected bond lengths and angles are listed in Table 1.

Each dianionic ligand in the anion coordinates to the central lanthanide metal ion in a tridentate mode, adopting a meridional conformation. The coordination geometry around the lanthanide metal can be described as a distorted

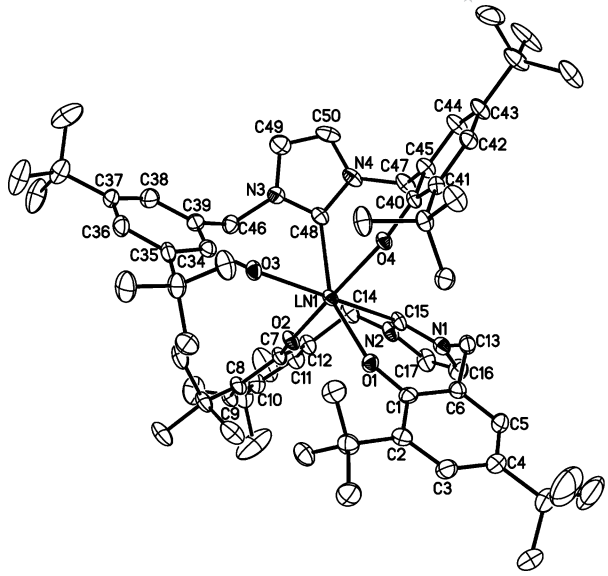
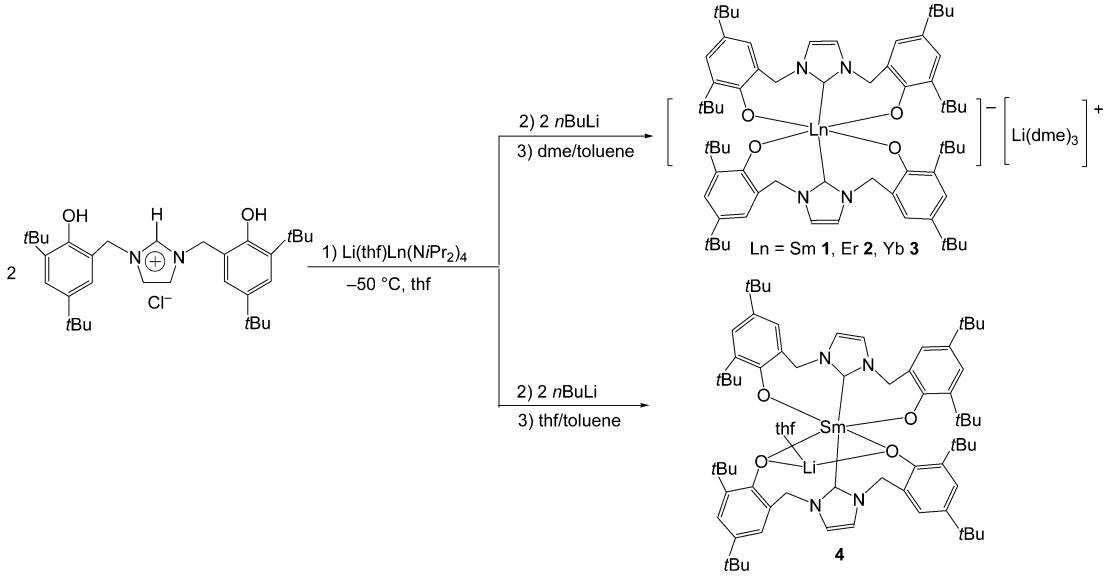


Figure 1. ORTEP diagram of the anion in complexes **1**, **2**, **3** (Ln = Sm **1**, Er **2**, Yb **3**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

octahedron in which the phenoxy donors (O2 and O4) from two ligands occupy axial positions. The O–Ln–O angles are 161.14(17) (Sm), 163.38(17) (Er), and 163.84(19)° (Yb), which deviate greatly from linearity. Two tridentate ligands are located on the same side with C15–Ln1–C48 angles of 86.6(2) (for **1**), 87.1(2) (for **2**), and 86.9(3)° (for **3**). The bis-(aryloxide)-NHC ligand assumes a U-shaped conformation. The phenyl moieties of the two benzyl groups are strongly bent toward the NHC moiety, the dihedral angle between the phenyl ring and the NHC ring ranging from 58.1–65.8° in one ligand to 109.1–118.2° in the other ligand, because of the steric demand caused by the two *tert*-butyl groups of ligand L, and this twist in the ligand is necessary for meridi-



Scheme 1.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**, **2**, **3**.

	1 (Ln = Sm)	**2** (Ln = Er)	**3** (Ln = Yb)
Ln1–O1	2.249(5)	2.189(5)	2.165(5)
Ln1–O2	2.259(4)	2.210(4)	2.180(5)
Ln1–O3	2.246(5)	2.191(4)	2.163(5)
Ln1–O4	2.255(4)	2.214(4)	2.182(5)
Ln1–C15	2.610(7)	2.504(7)	2.492(8)
Ln1–C48	2.606(7)	2.525(7)	2.515(8)
O2–Ln1–O4	161.14(17)	163.38(17)	163.84(19)
O3–Ln1–O1	118.49(17)	114.57(18)	113.4(2)
C48–Ln1–C15	86.6(2)	87.1(2)	86.9(3)
O1–Ln1–C15	78.3(2)	80.0(2)	81.1(2)
O3–Ln1–C48	79.8(2)	81.2(2)	81.5(2)

onal coordination. The dihedral angles between two NHC rings are 76.8 (for **1**), 82.6 (for **2**), and 95.3° (for **3**). The average Ln–$C_{carbene}$ bond lengths, 2.608(7) (for Sm), 2.515(7) (for Er), and 2.504(8) Å (for Yb), are comparable with each other and with the values reported for related NHC–lanthanide bonds.[1,2,7,8] The average lengths of Ln–O bonds, 2.252 (for Sm), 2.201 (for Er), and 2.173 Å (for Yb), also fall in the range published in the literature.[11] The structure of the cation is normal.[11d]

Syntheses and Molecular Structures of [(sol)M(μ-L)SmL] (M = Li, Sol = thf 4; M = Na, Sol = Et_2O 5)

It was found that solvent has an effect on the solid-state structure of the anionic complex. When the reaction of LH_3Cl with Li(thf)Sm(N*i*$Pr_2)_4$ and *n*BuLi proceeded in thf, followed by crystallization from thf/toluene, but not from dme/toluene, an "ate" complex [(thf)Li(μ-L)SmL] (**4**), which was characterized by X-ray analysis, was isolated as light yellow crystals in 38% yield (Scheme 1).

A similar "ate" complex with sodium metal can also be synthesized by a similar procedure. Treatment of LH_3Cl with $Sm[N(SiMe_3)_2]_3$ and $NaN(SiMe_3)_2$ in a 2:1:3 molar ratio at –50 °C for 10 h, then at room temperature for 15 h afforded a light yellow suspension. The extract with Et_2O was crystallized at 0 °C, affording the "ate" complex [(Et_2O)Na(μ-L)SmL] (**5**) as light yellow crystals in 20% yield (Scheme 2).

Complexes **4** and **5** are very soluble in donor solvents, so it is difficult to isolate them as crystals. This may be the reason for their rather low isolated yields. The difference in molecular structures among **1**–**3** and **4** and **5** may be the result of the known ability of a tris(dme) environment to effectively separate a lithium cation from an anionic complex.[11c,12]

The molecular structures of **4** and **5** are depicted in Figures 2 and 3, respectively, and the selected bond lengths and angles are listed in Table 2. The molecular structure of **4** is similar to that of **5**. The only differences in structure between the two complexes are that the cation in **4** is lithium, while it is sodium in **5**, and the coordination donor is thf in **4** but Et_2O in **5**. The coordination geometry about the samarium ion for each complex approximates a distorted octahedron. The central metal atom is coordinated to the phenoxide oxygen atoms (O1 and O4 for **4**, O1 and O3 for **5**) from two ligands occupying axial positions, the samarium atom being directly bound to four oxygen atoms and two carbene carbon atoms from the ligands. The alkali metal ion (lithium for **4** and sodium for **5**) displays a planar, three-coordinate geometry, being bound to two phenoxide

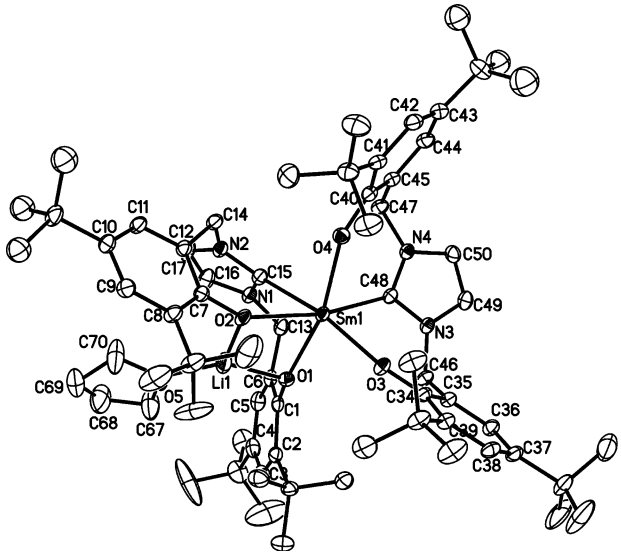
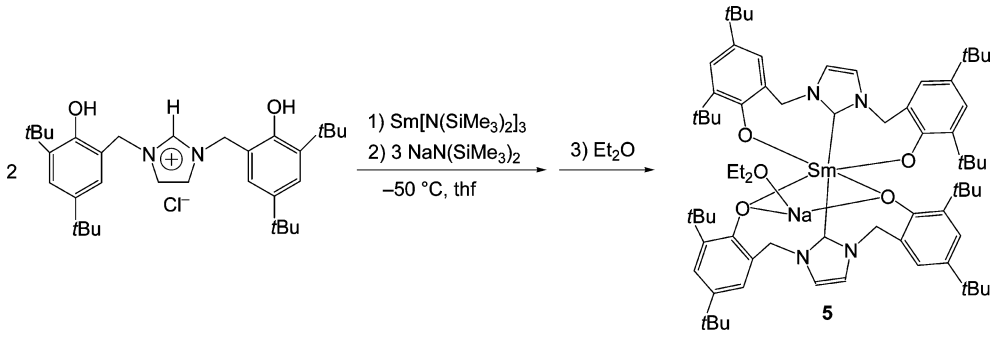


Figure 2. ORTEP diagram of the complex **4** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.



Scheme 2.

oxygen atoms [with Li–O 1.932(8) and 1.927(8) Å for **4** and Na–O 2.342(2) and 2.347(3) Å for **5**] and one oxygen from a thf for **4** and from a Et_2O for **5** [Li–O 1.866(8) and Na–O 2.259(3) Å]. Each samarium ion in complexes **4** and **5** is connected to the alkali metal atoms by two oxygen bridges from one ligand. The average $Sm–C_{carbene}$ distances, 2.611(4) (for **4**) and 2.628(3) Å (for **5**) are comparable to those found in complex **1**. The Sm–μ-O bond lengths of 2.342(2) (for **4**) and 2.317(2) Å (for **5**), which are longer than those for $Sm–O_{terminal}$, are comparable to those found in the related phenoxide Sm complexes.[11] The Li–C_{ortho}-(C1, C7) distances for **4** are 2.678(9) and 2.720(9) Å, which are considerably longer than 2.557 Å,[13] the sum of the van der Waals radii of the Li and carbon atoms.

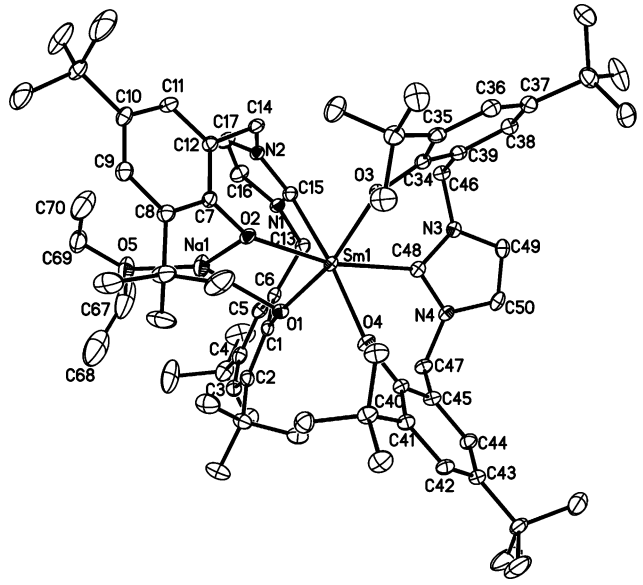


Figure 3. ORTEP diagram of the complex **5** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **4**, **5**.

Complex **4**			
Sm1–O1	2.356(2)	O1–Li1	1.932(8)
Sm1–O2	2.328(2)	O2–Li1	1.927(8)
Sm1–O3	2.201(2)	O5–Li1	1.866(8)
Sm1–O4	2.219(3)	Sm1–C48	2.584(4)
Sm1–C15	2.638(4)		
O4–Sm1–O1	160.88(9)	C48–Sm1–C15	89.19(11)
O3–Sm1–O2	118.96(9)	O2–Li1–O1	101.5(4)
O3–Sm1–C15	156.29(11)	O5–Li1–O2	128.4(4)
O2–Sm1–C15	72.58(10)	O5–Li1–O1	129.4(5)
Complex **5**			
Sm1–O1	2.336(2)	Na1–O5	2.259(3)
Sm1–O2	2.2986(19)	Na1–O1	2.342(2)
Sm1–O3	2.244(2)	Na1–O2	2.347(3)
Sm1–O4	2.202(2)	Sm1–C48	2.601(3)
Sm1–C15	2.654(3)		
O3–Sm1–O1	160.55(7)	C48–Sm1–C15	91.31(9)
O4–Sm1–O2	117.39(7)	O1–Na1–O2	84.95(8)
O4–Sm1–C48	78.24(9)	O5–Na1–O2	147.95(10)
O2–Sm1–C15	73.97(8)	O5–Na1–O1	126.88(10)

Conclusions

In this report we provide a contribution to the synthesis and characterization of a series of new tridentate bis-(phenoxy)-functionalized OCO mono(NHC)-stabilized lanthanide complexes. They represent the first examples of anionic NHC complexes of lanthanides. Discrete molecular structures depending on the donor solvent were reported including "ion-pairs" and an "ate" structure. The further study on the synthesis and reactivity of anionic NHC complexes of lanthanides is ongoing.

Experimental Section

General Details: All manipulations of air-sensitive materials were carried out under a dry, oxygen-free argon atmosphere, by using standard Schlenk techniques. All solvents used (toluene, thf, dme, Et_2O) were distilled from sodium benzophenone ketyl prior to use. Anionic amide complexes $Li(thf)Ln(N\mathit{i}Pr_2)_4$ (Ln = Sm, Er, Yb) were prepared according to literature procedures.[14] Lanthanide analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo–Erba EA 1110 instrument. The IR spectra were recorded with a Varian-1000 FT–IR spectrometer by using KBr pellets. The uncorrected melting points were determined in sealed, air-filled capillary tubes.

LH_3Cl: 2-chloromethyl-4,6-di-*tert*-butylphenol (12.74 g, 50 mmol) in thf (50 mL) was slowly added under vigorous stirring to a refluxed solution of *N*-3,5-di-*tert*-butyl-2-hydroxyphenylmetylimidazole (14.32 g, 50 mmol) in thf (50 mL), which was allowed to react for 12 h. After being cooled to room temperature, the solvent was evaporated to leave behind the crude product. Washing the crude product with toluene and then *n*-hexane gave a fine colorless powder of LH_3Cl (82%, 22.19 g, 41 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 18 H, *t*Bu), 1.38 (s, 18 H, *t*Bu), 5.54 (s, 4 H, CH_2), 7.06 (d, J = 1.5 Hz, 2 H, ArH), 7.11 (br. s, 2 H, OH), 7.26 (s, 2 H, CH), 7.35 (d, J = 1.5 Hz, 2 H, ArH), 9.49 (br. s, 1 H, NCHN) ppm. $C_{33}H_{49}ClN_2O_2$ (541.21): calcd. C 73.23, H 9.13, N 5.18; found C 73.63, H 9.40, N 4.94.

Synthesis of $[L_2Sm]^-[Li(dme)_3]^+$ (1): To a stirred slurry of LH_3Cl (2.81 g, 5.2 mmol) in thf (30 mL) was added a solution of $Li(thf)Sm(N\mathit{i}Pr_2)_4$ (1.64 g, 2.6 mmol) in thf (15 mL) dropwise at –50 °C and stirred for 10 h, and then *n*BuLi (1.50 mol/L in hexane, 5.2 mmol) was introduced dropwise at –50 °C. The mixture was stirred for 10 h, during which time it was warmed slowly to room temperature, resulting in a yellow solution. Volatiles were removed in vacuo to give a sticky yellow solid. The solid was extracted with toluene (2 × 15 mL) and centrifuged to remove LiCl. The obtained solution was concentrated in vacuo to 15 mL, and dme (10 mL) was introduced. The mixture was then stored at 0 °C for crystallization. Colorless crystals of **1** were obtained in 62% yield (2.31 g, 1.61 mmol). M.p. 187–189 °C (dec.). $C_{78}H_{122}LiN_4O_{10}Sm$ (1433.13): calcd. C 65.37, H 8.58, N 3.91, Sm 10.49; found C 65.78, H 8.61, N 3.79, Sm 10.28. IR (KBr pellet): $\tilde{\nu}$ = 3154 (m), 2957 (s), 2903 (m), 2865 (m), 1603 (w), 1558 (m), 1476 (s), 1440 (s), 1390 (m), 1361 (s), 1302 (s), 1236 (s), 1131 (s), 733 (m) cm^{-1}.

Table 3. Details of the crystallographic data and refinements for complexes **1**–**5**.

	1·$C_4H_{10}O_2$·C_7H_8	**2**·$C_4H_{10}O_2$·C_7H_8	**3**·2C_7H_8	**4**·C_7H_8	**5**·$C_4H_{10}O$
Empirical formula	$C_{89}H_{140}LiN_4O_{12}Sm$	$C_{89}H_{140}ErLiN_4O_{12}$	$C_{92}H_{138}LiN_4O_{10}Yb$	$C_{77}H_{108}LiN_4O_5Sm$	$C_{74}H_{112}N_4NaO_6Sm$
Formula mass	1615.34	1632.25	1640.04	1326.96	1327.02
Temperature [K]	153(2)	223(2)	223(2)	213(2)	193(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.1254(18)	15.144(3)	15.1575(11)	16.0002(13)	15.937(2)
b [Å]	20.070(2)	20.238(3)	20.2828(13)	16.1488(11)	15.9955(17)
c [Å]	29.982(4)	30.084(5)	29.971(2)	16.5839(8)	16.015(2)
α [°]	90.00	90	90.00	62.173(4)	90.500(2)
β [°]	97.762(4)	97.983(3)	98.064(2)	80.238(5)	115.692(3)
γ [°]	90.00	90	90.00	89.374(5)	90.815(2)
V [Å^3]	9018.4(18)	9131(3)	9122.9(11)	3723.2(4)	3678.1(8)
Z	4	4	4	2	2
Density [Mg m^{-3}]	1.190	1.187	1.194	1.184	1.198
Abs. coeff. [mm^{-1}]	0.709	0.976	1.081	0.838	0.854
No. of reflections	77831	37365	83514	36602	36273
No. of unique reflections	16467	16786	16662	13540	13371
No. of parameters	845	885	877	807	797
$R1$ ($I > 2\sigma I$)	0.0905	0.0862	0.0940	0.0482	0.0394
$wR2$ (all date)	0.2393	0.1892	0.2063	0.1152	0.0864

Synthesis of $[L_2Er]^-[Li(dme)_3]^+$ (2): The procedure was analogous to that for the preparation of **1**, but with the use of LH_3Cl (2.71 g, 5.00 mmol), Li(thf)Er(N*i*Pr$_2$)$_4$ (1.62 g, 2.50 mmol), and *n*BuLi (1.50 mol/L in hexane, 5.00 mmol). Pink crystals of **2** were isolated in 55% yield (2.00 g, 1.38 mmol). M.p. 179–181 °C (dec.). $C_{78}H_{122}ErLiN_4O_{10}$ (1450.02): calcd. C 64.61, H 8.48, Er 11.53, N 3.86; found C 65.02, H 8.51, Er 11.29, N 3.78. IR (KBr pellet): $\tilde{\nu}$ = 3154 (m), 2957 (s), 2903 (w), 2865 (m), 1603 (w), 1558 (m), 1476 (s), 1440 (s), 1391 (m), 1361 (s), 1298 (s), 1236 (s), 1130 (s), 738 (m) cm^{-1}.

Synthesis of $[L_2Yb]^-[Li(dme)_3]^+$ (3): The procedure was analogous to that for the preparation of **1**, but with the use of LH_3Cl (2.60 g, 4.8 mmol), Li(thf)Yb(N*i*Pr$_2$)$_4$ (1.57 g, 2.4 mmol), and *n*BuLi (1.50 mol/L in hexane, 4.8 mmol). Colorless crystals of **3** were isolated in 60% yield (2.09 g, 1.44 mmol). M.p. 205–207 °C (dec.). $C_{78}H_{122}LiN_4O_{10}Yb$ (1455.81): calcd. C 64.35, H 8.45, N 3.85, Yb 11.89; found C 64.77, H 8.49, N 3.68, Yb 11.62. IR (KBr pellet): $\tilde{\nu}$ = 3153 (m), 2953 (s) 2905(m), 2868 (m), 1605 (m), 1558 (m), 1480 (s), 1440 (m), 1390 (m), 1362 (s), 1305 (s), 1237 (s), 1129 (s), 735 (s) cm^{-1}.

Synthesis of $L_2SmLi(thf)$ (4): The procedure was analogous to that for the preparation of **1**, but with the use of LH_3Cl (2.27 g, 4.20 mmol), Li(thf)Sm(N*i*Pr$_2$)$_4$ (1.32 g, 2.1 mmol), and *n*BuLi (1.50 mol/L in hexane, 4.20 mmol), and the solid was extracted with toluene first to remove LiCl then with some thf for crystallization at 0 °C. Yellow crystals of **4** were obtained in 38% yield (0.99 g, 0.80 mmol). M.p. 213–215 °C (dec). $C_{70}H_{100}LiN_4O_5Sm$ (1234.87): calcd. C 68.08, H 8.16, N 4.54, Sm 12.18; found C 68.51, H 8.21, N 4.32, Sm 11.95. IR (KBr pellet): $\tilde{\nu}$ = 3154 (m), 2957 (s), 2906 (w), 2865 (m), 1604 (w), 1559 (m), 1476 (s), 1439 (s), 1386 (m), 1361 (s), 1302 (s), 1236 (s), 1131 (s), 734 (m) cm^{-1}.

Synthesis of $L_2SmNa(Et_2O)$ (5): To a stirred slurry of LH_3Cl (2.16 g, 4.00 mmol) in thf (20 mL) was added a solution of Sm[N(SiMe$_3$)$_2$]$_3$(thf) (1.41 g, 2.00 mmol) in thf (15 mL) dropwise at –50 °C and stirred for 10 h. Then NaN(SiMe$_3$)$_2$ (1.15 mol/L in thf, 6.00 mmol) was introduced dropwise at –50 °C. The mixture was stirred for 15 h, during which time it was warmed slowly to room temperature, giving a yellow suspension, which was centrifuged to remove NaCl. Volatiles were removed in vacuo to give a sticky yellow solid. The solid was extracted with Et_2O (2 × 10 mL), and the obtained solution was stored at 0 °C for crystallization. Colorless crystals of **5** were obtained in 20% yield. (0.50 g, 0.40 mmol). M.p. 259–261 (dec). $C_{70}H_{102}N_4NaO_5Sm$ (1252.93): calcd. C 67.10, H 8.21, N 4.47, Sm 12.00; found C 67.22, H 8.21, N 4.39, Sm 11.87. IR (KBr pellet): $\tilde{\nu}$ = 3153 (m), 2956 (s), 2906 (w), 2867 (m), 1604 (w), 1559 (m), 1476 (s), 1440 (s), 1386 (m), 1362 (s), 1300 (s), 1236 (s), 1127 (s), 734 (m) cm^{-1}.

X-ray Crystallography: Crystals of complexes **1**–**5** suitable for X-ray diffraction analysis were sealed in a thin-walled glass capillary filled under argon for structural analysis. Diffraction data were collected with a Rigaku Mercury CCD area detector. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined by using SHELXS-97 programs. Crystal and refinement data are listed in Table 3. CCDC-708951 (for **1**), -708952 (for **2**), -708953 (for **3**), -708954 (for **4**), and -708955 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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