



LANTHANIDE ALKOXIDES—III.* FOUR-COORDINATE ANIONIC NEODYMIUM(III) ALKOXIDES AND AMIDES

FRANK T. EDELMANN,† ALEXANDER STEINER and DIETMAR STALKE

Institut für Anorganische Chemie der Universität Göttingen, Tammannstr. 4,
 D-37077 Göttingen, F. R. G.

and

JOHN W. GILJE

Department of Chemistry, University of Hawaii at Manoa, 2545 The Mall, Honolulu,
 HI 96822, U.S.A.

and

SUSAN JAGNER and MIKAEL HÅKANSSON

Department of Inorganic Chemistry, Chalmers University of Technology and University
 of Göteborg, S-41296 Göteborg, Sweden

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Abstract—Tetracoordinate anionic neodymium(III) alkoxides and amides are obtained by adduct formation of $\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (1) and $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (2) with either LiCl or LiOSiMe_3 . The compounds $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (3), $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (4) and $[\text{Li}(\text{THF})_4][\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Nd}(\text{OSiMe}_3)]$ (5) have been characterized by single-crystal X-ray analyses.

There is a growing interest in lanthanide alkoxide and amide chemistry. In part this is motivated by their potential use as precursors for oxide materials, which include high temperature superconductors and optical materials.^{2–4} The most common preparation of these alkoxides and amides involves the metathesis reaction of a lanthanide halide with an alkali metal amide or alkoxide.^{5–8} In recent years, however, it has become apparent that the partial retention of halide occurs in many cases.^{9–12} This has led to the isolation of many new and interesting compounds, but it is also a pernicious problem since halide-free precursors are often required for oxide preparations.¹³ These preparations are also commonly complicated by the formation of “ate” salts which retain some of the alkali metal, usually but not always coordinated through a bridging ligand to the lanthanide.^{14–19} Typical examples of such “ate” complexes are $[\text{Li}(\text{THF})_4][\text{Ln}$

$(\text{CH}_2\text{SiMe}_3)_4]_3$,¹⁶ $[\text{Li}(\text{THF})_4][\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3\text{Cl}]$,¹⁶ $[\text{Li}(\text{THF})_4][\text{Ln}(2,6\text{-Me}_2\text{C}_6\text{H}_3)_4]$,¹⁷ $(\text{pmdeta})\text{Li}(\mu\text{-Cl})\text{Ln}[\text{CH}(\text{SiMe}_3)_2]_3$ ($\text{pmdeta} = N,N,N',N'',N'''$ -pentamethyldiethylenetriamine)¹⁸ and $\text{K}[\text{Nd}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_4]$.¹⁹ Formally, the well-investigated bis(pentamethylcyclopentadienyl)lanthanide halide derivatives $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{LiL}_2$ ($\text{L} = \text{THF}$, Et_2O , $1/2\text{DME}$) can also be regarded as “ate” complexes.^{20–22}

EXPERIMENTAL

All manipulations were routinely performed under N_2 using dry box and Schlenk techniques. LiOSiMe_3 ,²³ $\text{LiOC}(\text{tBu})_3$,^{24,25} NdCl_3 ,²⁶ $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ ^{27,28} and $\text{Nd}[\text{OC}(\text{tBu})_3]_3(\text{THF})$ ²⁹ were obtained according to the literature. ^1H NMR and IR spectra were run on Bruker WP 80 SY and Bruker AM 250 spectrometers, respectively. Mass spectra were performed on a Varian MAT CH5 instrument. Analytical data were obtained from the analytical laboratory at the Department of Inorganic Chemistry at Göttingen.

*For part II, see Ref. 1.

†Author to whom correspondence should be addressed.

Synthesis of $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (3)

Compound **3** was obtained during an attempted preparation of $\text{Li}[\text{Nd}\{\text{OC}(\text{tBu})_3\}_4]$. Anhydrous NdCl_3 (1.25 g, 5.0 mmol) was added to a solution of four equivalents of $\text{LiOC}(\text{tBu})_3$ (4.13 g, 20.0 mmol) in THF (60 cm³) at 0°C. After stirring at room temperature for 16 h, the mixture was filtered, the solution concentrated and cooled to -25°C. After 48 h, light blue crystals (1.30 g, 26%) had formed. M.p. 138°C. Found: C, 60.1; H, 10.1; Cl, 3.5. Calc. for $\text{C}_{51}\text{H}_{105}\text{ClLiO}_6\text{Nd}$ (1001.0): C, 61.2; H, 10.6; Cl, 3.5%. IR (Nujol, cm⁻¹): 3631 m, 3509 m, 1304 m, 1261 s, 1183 m, 1060 vs, 1038 vs, 1000 vs, 922 m, 884 s, 801 s, 673 s, 466 m, 395 m. ¹H NMR (80 MHz, C₆D₆/TMS ext., 23°C): δ 6.48 (s br, $\nu_{1/2}$ = 14 Hz, 81H, tBu), 3.22 (s br, $\nu_{1/2}$ = 16 Hz, 24H, THF) ppm. MS m/z : 999 (M^+ , 2%), 719 [(tritox)₃NdCl⁺ - CMe₃, 2%], 57 (CMe₃⁺, 100%).

Synthesis of $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (4)

Compound **4** was isolated in very small amounts (<10 mg) as a less soluble by-product during a preparation of $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ according to the literature procedure. Blue crystals, m.p. 86°C. Found: C, 39.5; H, 8.6; Cl, 4.2; N, 4.5. Calc. for $\text{C}_{30}\text{H}_{78}\text{ClLiN}_3\text{NdO}_3\text{Si}_6$ (884.1): C, 40.8; H, 8.9; Cl, 4.0; N, 4.8%. IR (Nujol, cm⁻¹): 1243 vs, 1178 m, 1091 s, 1047 s, 1017 s, 977 vs, 890 s, 828 vs, 769 s, 684 m, 664 s, 609 m, 599 s, 380 s. ¹H NMR (80 MHz, C₆D₆/TMS ext., 23°C): δ -0.73 (s br, $\nu_{1/2}$ = 37 Hz, 12H, THF), -1.48 (s br, $\nu_{1/2}$ = 69 Hz, 12H, THF), -5.5 (br, $\nu_{1/2}$ = 308 Hz, 54H, SiMe₃) ppm. MS m/z : 884 (M^+ , 25%), 812 (M^+ - THF, 13%), 740 (M^+ - 2THF, 12%), 281 (NdNSiMe₃⁺, 35%), 207 (NdNSi⁺, 100%), 73 (SiMe₃⁺, 41%).

Synthesis of $[\text{Li}(\text{THF})_4]\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Nd}(\text{OSiMe}_3)\}$ (5)

A solution of LiOSiMe₃ (6.8 mmol) in 30 cm³ THF was freshly prepared from 1.10 g (6.8 mmol) Me₃SiOSiMe₃ and a stoichiometric amount of methyl lithium. This solution was slowly added to 4.26 g (6.8 mmol) Nd[N(SiMe₃)₂]₃, dissolved in 20 cm³ THF. After 16 h the THF was evaporated, the residue washed with 40 cm³ hexane and extracted with 30 cm³ toluene. The toluene extract was reduced to about 10 cm³ and cooled to -25°C. After 24 h the resulting pale blue crystals (1.75 g, 25%) were isolated by filtration and dried *in vacuo*. M.p. ca 100°C (dec.). Found: C, 42.8; H, 9.3; N,

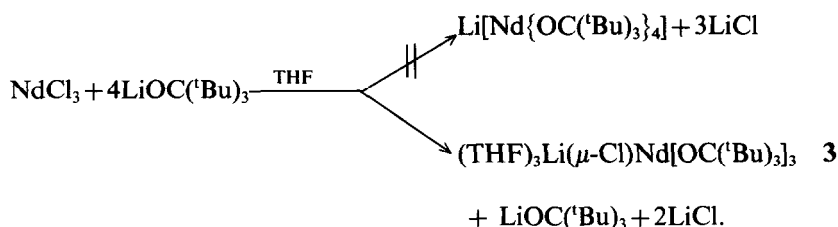
3.7. Calc. for $\text{C}_{37}\text{H}_{95}\text{LiN}_3\text{NdO}_5\text{Si}_7$ (1010.0): C, 44.0; H, 9.5; N, 4.2%. IR (Nujol, cm⁻¹): 1270 s, 1065 m, 1040 s, 1020 s, 930 m, 885 s, 850 s. ¹H NMR (80 MHz, C₆D₆/TMS ext., 32°C): 3.73 (br, $\nu_{1/2}$ = 48 Hz, 16H, THF), 1.22 (br, $\nu_{1/2}$ = 24 Hz, 16H, THF), -3.48 (br, $\nu_{1/2}$ = 21 Hz, 54H, NSiMe₃), -5.36 (s br, $\nu_{1/2}$ = 9 Hz, 9H, OSiMe₃) ppm. MS m/z : 713 (Me₃SiOND[N(SiMe₃)₂]₃⁺, 2%), 553 (Me₃SiOND[N(SiMe₃)₂]₂⁺, 7%), 464 (Nd[N(SiMe₃)₂]₂⁺, 6%), 146 (Si₂Me₆⁺, 100%), 73 (SiMe₃⁺, 5%).

RESULTS AND DISCUSSION

We have become interested in the formation of such "ate" complexes and in the factors which govern their formation. In this paper we would like to describe three neodymium "ate" compounds: $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (**3**), $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**) and $[\text{Li}(\text{THF})_4]\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Nd}(\text{OSiMe}_3)\}$ (**5**). Formally, they are complexes of the homoleptic Nd[OC(tBu)₃]₃ (**1**) and/or Nd[N(SiMe₃)₂]₃ (**2**) with a halide, chlorine, to which an alkali metal, lithium, is also coordinated or with an oxygen donor, OSiMe₃, to which the counter cation is unable to complex. Together, they begin to establish some of the structural trends which can be expected in the lanthanide "ate" complexes.

The compounds described here contain the bulky alkoxide and amido ligands (tBu)₃CO⁻ (= "tritox") and (Me₃Si)₂N⁻. Both ligands have frequently been used to stabilize very low coordination numbers (three or four) around lanthanide atoms.

The sterically demanding tritox ligand has been shown to effectively stabilize monomeric and dimeric lanthanide alkoxides.²⁹⁻³¹ The mononuclear neodymium derivatives Nd[OC(tBu)₃]₃(THF)²⁹ and Nd[OC(tBu)₃]₃(MeCN)₂³¹ have been structurally characterized by single-crystal X-ray analyses. Unsolvated Ce(tritox)₃³⁰ and Nd(tritox)₃ (**1**)³¹ have been mentioned but not fully characterized. Presumably these molecules are dimers and contain bridging tritox ligands. Four-coordinate Nd[OC(tBu)₃]₃(THF) was prepared by treatment of Nd[N(SiMe₃)₂]₃(THF)₂ with (tBu)₃COH (molar ratio 1:3) in hexane solution.²⁹ A different neodymium tritox derivative was isolated during an attempted preparation of the "ate" complex Li[Nd{OC(tBu)₃}]₄. Treatment of anhydrous NdCl₃ with four equivalents of LiOC(tBu)₃ in THF resulted in the formation of a blue solution, from which light blue crystals were isolated. This material was shown by X-ray diffraction to be the chloride-bridged "ate" complex $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (**3**):

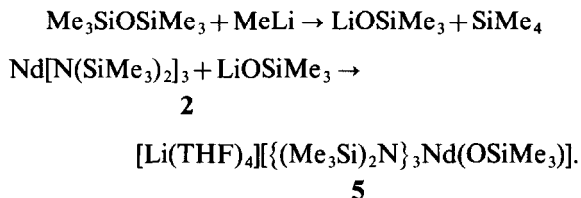


compound **3** was obtained in 26% yield. The pale blue crystals of **3** are very sensitive to hydrolysis.

Tricoordination in lanthanide chemistry was first observed in the silylamide derivatives $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ which were reported by Bradley *et al.* in 1973.²⁷ The original preparation of these silylamides involves treatment of anhydrous LnCl_3 with three equivalents of $\text{LiN}(\text{SiMe}_3)_2$ in THF solution.²⁷ This reaction appears to be somewhat temperamental.^{31,32} The isolation of pure unsolvated $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ species requires careful sublimation of the initially formed THF adducts. In some cases the sublimed materials have been found to be contaminated with either $\text{LiN}(\text{SiMe}_3)_2$ or $[\text{LiN}(\text{SiMe}_3)_2(\text{THF})]_2$. Simple recrystallization of the crude products from hexane yields the THF solvates and in this case too the retention of LiCl can cause additional problems. Small amounts (<10 mg) of a chloride-bridged “ate” complex derived from $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (**2**) were isolated as a less soluble by-product during a large-scale preparation of **2**. The blue crystals obtained from hexane were found to be suitable for X-ray diffraction and were subsequently shown to be $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**). Formally, compound **4** can be regarded as a solvated adduct of **2** and LiCl. In a separate experiment, however, it was found that pure **2** did not react with anhydrous LiCl in THF solution. The blue crystals of **4** are very sensitive towards air and moisture. Crystals of **4** rapidly disintegrate upon contact with trace amounts of air.

The third “ate” complex described in this work was also first observed serendipitously as a minor by-product in the preparation of **2**. A small amount of well-formed pale blue crystals was obtained which were found to be suitable for X-ray diffraction. The X-ray analysis revealed that this material had to be formulated as $[\text{Li}(\text{THF})_4][\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Nd}(\text{OSiMe}_3)]$ (**5**).

The formation of this product is easily rationalized by assuming that a small amount of LiOSiMe_3 was present in the starting material $\text{LiN}(\text{SiMe}_3)_2$. The oxophilic character of the lanthanide ions should be responsible for the facile formation of an “ate” complex containing the Me_3SiO^- ligand. In contrast to the unsuccessful large-scale preparation of **4**, a more rational synthesis of compound **5** was achieved by addition of LiOSiMe_3 ²³ to **2** in THF solution. This method gave pure **5** as a pale blue crystalline solid in 25% yield:



These three examples illustrate the ease of formation of lanthanide “ate” complexes. Low-coordinate “ate” complexes now appear to be quite common even for the early lanthanide ions if the ligands are sufficiently bulky to prevent aggregation and formation of polymeric species.

STRUCTURAL INVESTIGATIONS (TABLE 1)*

$(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (**3**) (Fig. 1, Table 2)

Light blue single crystals of **3** were obtained by slow cooling of a saturated solution in THF to -25°C . The central neodymium atom is coordinated by three oxygen atoms of the tritox ligands and a chlorine atom bridging neodymium and lithium. This results in a slightly distorted tetrahedral coordination geometry around neodymium. The angles at neodymium range from $100.7(1)^\circ$ to $115.7(1)^\circ$. The Nd—O distances (2.150, 2.171 and 2.158 Å) are in good agreement with values found in previously characterized neodymium tritox derivatives {average values: 2.150(3)–2.153(5) Å in $(\text{tritox})_3\text{Nd}(\text{THF})$,²⁹ 2.106(3) Å in $[(\text{tritox})_2\text{Nd}(\mu\text{-Cl})\text{THF}]_2$ ²⁹ and 2.149(5)–2.171(5) Å in $(\text{tritox})_3\text{Nd}(\text{MeCN})_2$.³¹ All these distances can be

* Further details of the crystal structure determinations are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-55750, the authors and the journal citation.

Table 1. Crystallographic data for (THF)₃Li(μ-Cl)Nd[OC(^tBu)₃]₃ (**3**), (THF)₃Li(μ-Cl)Nd[N(SiMe₃)₂]₃ (**4**) and [Li(THF)₄][{(Me₃Si)₂N}₃NdOSiMe₃]₃ (**5**)

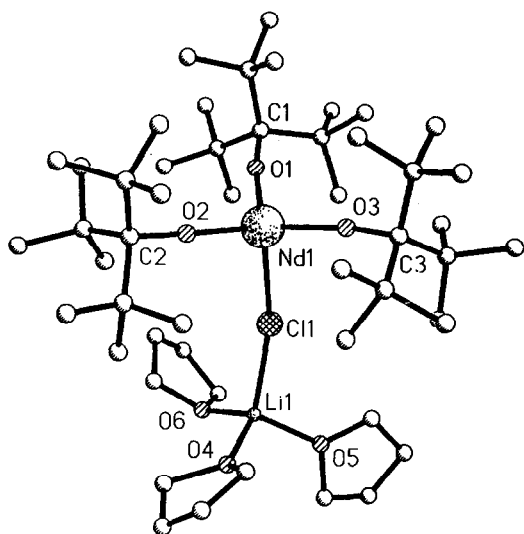
Compound	3	4	5
Empirical formula	C ₅₁ H ₁₀₅ ClLiO ₆ Nd	C ₃₀ H ₇₈ ClLiN ₃ NdO ₃ Si ₆ · C ₃ O _{1.5}	C ₃₇ H ₆₃ LiN ₃ NdO ₅ Si ₇
Colour	Light blue	Blue	Light blue
Crystal size (mm)	0.5 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.1
Molecular weight	1001.0	944.1	977.7
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.507(1)	36.244(9)	36.451(6)
<i>b</i> (Å)	19.639(2)	16.226(4)	21.927(3)
<i>c</i> (Å)	22.834(3)	26.822(6)	23.036(3)
α (°)	90	90	90
β (°)	97.440(10)	136.299(7)	107.118(8)
γ (°)	90	90	90
<i>V</i> (Å ³)	5561.4(10)	10898(9)	17640(4)
<i>Z</i>	4	8	12
<i>D</i> _{calc} (g cm ⁻³)	1.195	1.151	1.104
<i>F</i> (000) (e ⁻)	2156	3976	6084
Diffractometer	Siemens-Stoe	Rigaku AFC6R	Siemens-Stoe
Radiation	Mo- <i>K</i> _α	Mo- <i>K</i> _α	Mo- <i>K</i> _α
λ (Å)	0.71073	0.71069	0.71073
Temperature (°C)	-120	-140	-120
Linear absorption coefficient (mm ⁻¹)	1.023	1.165	1.058
Scan type	ω-2θ	ω-2θ	ω-2θ
2θ range (°)	8.0-48.0	3.5-50.0	8.0-45.0
Reflections collected	9236	10,192	26,053
Independent reflections	8673	9895	22,887
Observed refl. [<i>I</i> > 3.0σ(<i>I</i>)]	7024	4950	12,085
Number of parameters refined	596	445	1190
<i>R</i>	0.043	0.057	0.097
<i>R</i> _w	0.044	0.067	0.097
Residual density			
min (e Å ⁻³)	-0.64	-0.89	-0.92
max (e Å ⁻³)	0.77	1.21	1.07

considered as very short Nd—O bonds, as the shortest Nd—O distance reported so far is 2.03 Å found in the hexanuclear alkoxide derivative Nd₆(O^{*i*}Pr)₁₇Cl.³³ The values for the O—Nd—O angles (between 113.8° and 115.7°) agree well with those found in other tritox derivatives of neodymium. The Nd—Cl—Li unit (157.7°) shows a significant deviation from linearity, whereas in **4** the Nd—Cl—Li unit is approximately linear [175.4(6)°]. In previous studies it was demonstrated that the cone angle of tritox approaches that of cyclopentadienyl. Thus, despite its different chemical nature, this bulky alkoxide ligand can be regarded as a “steric cyclopentadienyl equivalent”.^{24,29} For example, well-known cyclopentadienyl complexes of neodymium such as Cp₃Nd(THF),³⁴ [Cp₂Nd(μ-Cl)THF]₂^{35,36} and Cp₃Nd(MeCN)₂³⁷ have parallels in tritox chemistry {e.g. (tritox)₃Nd(THF),²⁹ [(tritox)₂Nd(μ-Cl)THF]₂²⁹ and (tritox)₃Nd(MeCN)₂}.³¹ Thus a proposed³¹

stereochemical difference between Cp and tritox cannot be substantiated.

(THF)₃Li(μ-Cl)Nd[N(SiMe₃)₂]₃ (**4**) (Fig 2, Table 3)

Blue rectangular prisms of **4** were obtained by slow cooling of a concentrated THF solution. The overall structure of **4** is very similar to that of the chloro-bridged tritox derivative **3**. With the angles at neodymium ranging from 97.8(2)° to 120.2(3)°, compound **4** displays a similar distortion of the tetrahedral coordination environment around the central neodymium atom. The three Nd—N distances are almost equal and the Nd—Cl [2.701(3) Å] and Li—Cl [2.33(2) Å] bond lengths agree well with the corresponding distances found for **3** [Nd—Cl: 2.742(1) Å, Li—Cl 2.310(10) Å]. The only major difference is that the Nd—Cl—Li unit in **4** is almost linear [175.4(6)°], whereas in **3** this part of the molecule is significantly bent (157.7°). Apart



[Li(THF)₄][{(Me₃Si)₂N}₃Nd(OSiMe₃)] (5) (Fig. 3, Table 4)

CONCLUSIONS

Three new four-coordinate anionic neodymium compounds have been prepared and structurally

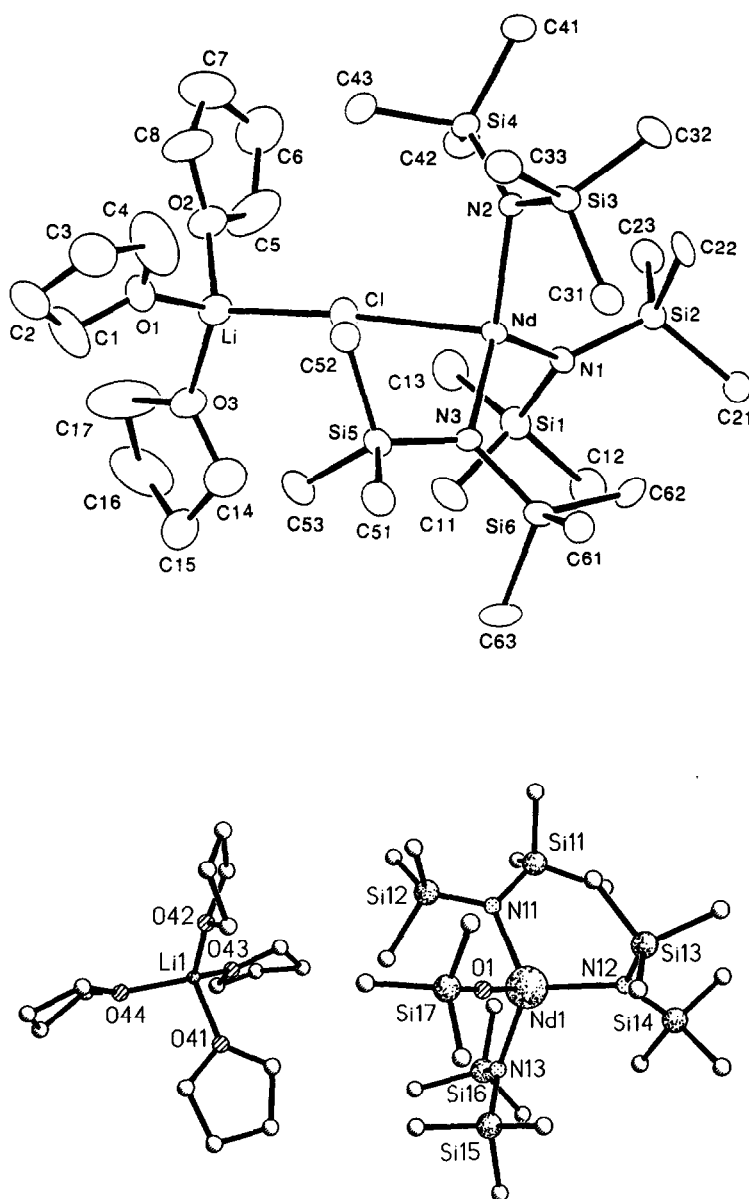
Nd(1)—O(1)	2.150(3)	Cl(1)—Li(1)	2.310(10)
Nd(1)—O(2)	2.171(3)	Li(1)—O(4)	1.886(11)
Nd(1)—O(3)	2.158(3)	Li(1)—O(5)	1.931(12)
Nd(1)—Cl(1)	2.742(1)	Li(1)—O(6)	1.908(11)
O(1)—C(1)	1.403(5)		
O(2)—C(2)	1.389(6)		
O(3)—C(3)	1.396(6)		
O(1)—Nd(1)—O(2)	115.4(1)	Cl(1)—Li(1)—O(4)	114.6(5)
O(1)—Nd(1)—O(3)	115.7(1)	Cl(1)—Li(1)—O(5)	109.7(5)
O(1)—Nd(1)—Cl(1)	101.9(1)	Cl(1)—Li(1)—O(6)	106.2(5)
O(2)—Nd(1)—O(3)	113.8(1)	O(4)—Li(1)—O(5)	108.5(5)
O(2)—Nd(1)—Cl(1)	107.0(1)	O(4)—Li(1)—O(6)	108.4(5)
O(3)—Nd(1)—Cl(1)	100.7(1)	O(5)—Li(1)—O(6)	109.5(5)
Nd(1)—O(1)—C(1)	170.2(3)		
Nd(1)—O(2)—C(2)	170.0(3)		
Nd(1)—O(3)—C(3)	170.4(3)		
Nd(1)—Cl(1)—Li(1)	157.7(3)		

Table 3. Selected bond lengths (Å) and angles (°) for (THF)₃Li(μ-Cl)Nd[N(SiMe₃)₂]₃ (4)

Nd—N(1)	2.324(8)	N(1)—Si(1)	1.712(9)
Nd—N(2)	2.335(8)	N(1)—Si(2)	1.724(8)
Nd—N(3)	2.348(8)	N(2)—Si(3)	1.710(8)
Nd—Cl	2.701(3)	N(2)—Si(4)	1.700(8)
Cl—Li	2.33(2)	N(3)—Si(5)	1.704(9)
Li—O(1)	1.94(2)	N(3)—Si(6)	1.712(9)
Li—O(2)	1.88(2)		
Li—O(3)	1.91(2)		
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N(1)—Nd—N(2)	115.8(3)	Cl—Li—O(1)	107(1)
N(1)—Nd—N(3)	117.9(3)	Cl—Li—O(2)	109(1)
N(1)—Nd—Cl	98.8(2)	Cl—Li—O(3)	114(1)
N(2)—Nd—N(3)	120.2(3)	O(1)—Li—O(2)	108(1)
N(2)—Nd—Cl	98.4(2)	O(1)—Li—O(3)	110(1)
N(3)—Nd—Cl	97.8(2)	O(2)—Li—O(3)	109(1)
Nd—N(1)—Si(1)	116.6(4)	Si(1)—N(1)—Si(2)	121.3(5)
Nd—N(1)—Si(2)	122.1(4)	Si(3)—N(2)—Si(4)	123.6(5)
Nd—N(2)—Si(3)	115.8(4)	Si(5)—N(3)—Si(6)	122.2(5)
Nd—N(2)—Si(4)	120.5(4)		
Nd—N(3)—Si(5)	118.3(4)		
Nd—N(3)—Si(6)	119.4(4)		
Nd—Cl—Li	175.4(6)		

Table 4. Selected bond lengths (Å) and angles (°) for [Li(THF)₄][{(Me₃Si)₂N}₃Nd(OSiMe₃)] (5)

Nd(1)—O(1)	2.173(11)	O(1)—Si(17)	1.618(13)
Nd(1)—N(11)	2.402(10)	N(11)—Si(11)	1.707(12)
Nd(1)—N(12)	2.364(11)	N(11)—Si(12)	1.691(12)
Nd(1)—N(13)	2.382(13)	N(12)—Si(13)	1.741(15)
		N(12)—Si(14)	1.702(13)
Li(1)—O(41)	1.92(3)		
Li(1)—O(42)	1.83(4)		
Li(1)—O(43)	1.93(4)		
Li(1)—O(44)	1.86(3)		
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N(11)—Nd(1)—N(12)	114.6(4)	Nd(1)—N(11)—Si(11)	121.7(5)
N(11)—Nd(1)—N(13)	115.0(4)	Nd(1)—N(11)—Si(12)	114.4(6)
N(11)—Nd(1)—O(1)	102.9(4)	Nd(1)—N(12)—Si(13)	114.0(6)
N(12)—Nd(1)—N(13)	114.4(4)	Nd(1)—N(12)—Si(14)	125.3(7)
N(12)—Nd(1)—O(1)	104.2(4)	Nd(1)—N(13)—Si(15)	112.6(7)
N(13)—Nd(1)—O(1)	103.7(4)	Nd(1)—N(13)—Si(16)	123.8(6)
		Nd(1)—O(1)—Si(17)	177.1(6)
O(41)—Li(1)—O(42)	109(2)	Si(11)—N(11)—Si(12)	123.6(7)
O(41)—Li(1)—O(43)	104(2)	Si(13)—N(12)—Si(14)	120.4(7)
O(41)—Li(1)—O(44)	102(2)	Si(15)—N(13)—Si(16)	123.3(8)
O(42)—Li(1)—O(43)	114(2)		
O(42)—Li(1)—O(44)	113(2)		
O(43)—Li(1)—O(44)	114(2)		



characterized in this study: $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{OC}(\text{tBu})_3]_3$ (**3**), $(\text{THF})_3\text{Li}(\mu\text{-Cl})\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (**4**) and $[\text{Li}(\text{THF})_4][\{(\text{Me}_3\text{Si})_2\text{N}\}_3\text{Nd}(\text{OSiMe}_3)]$ (**5**). All three compounds are monomeric alkoxide or amide derivatives of an early lanthanide metal. Together they demonstrate that very low coordination numbers are becoming a familiar sight in lanthanide coordination chemistry, provided that the ancillary ligands are sufficiently bulky. Using the sterically highly demanding alkoxide and amide ligands tBu_3CO^- and $(\text{Me}_3\text{Si})_2\text{N}^-$, four-coordinate derivatives are available even for the early lanthanides, i.e. the largest ions in the series.

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