

Organometallic compounds of the lanthanides XCVII[☆]. Synthesis and crystal structures of monomeric bis(ethyltetramethylcyclopentadienyl) amide and alkyl derivatives of the lanthanides

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Abstract

The trichlorides of yttrium, neodymium, samarium and lutetium react with 2 equiv. of Na[C₅Me₄Et] in THF to form [(C₅Me₄Et)₂LnCl(THF)] (Ln = Y, **1**; Nd, **2**; Sm, **3**; Lu, **4**). Metathesis of **1–4** with NaN(SiMe₃)₂ and LiCH(SiMe₃)₂ in toluene gives [(C₅Me₄Et)₂Ln{E(SiMe₃)₂}] (E = N, Ln = Y, **5**; Nd, **6**; Sm, **7**; Lu, **8**; E = CH, Ln = Y, **9**; Nd, **10**; Sm, **11**). The new compounds were characterized by elemental analysis and mass and NMR spectrometry. Additionally, X-ray structural analysis of **5** and **11** was performed. The silylamide **5** crystallized in the monoclinic space group *C2/c* with *a* = 9.169(2), *b* = 21.166(8), *c* = 15.625(3) Å, β = 94.15(2)°, *V* = 3025(2) Å³ and *Z* = 4. The final refinement resulted in *R*₁ = 2.86% (*I* > 4σ(*I*)). Compound **11** crystallized in the orthorhombic space group *Pbca* with *a* = 18.499(6), *b* = 14.181(6), *c* = 23.290(5) Å, *V* = 6110(3) Å³, *Z* = 8, and *R*₁ = 3.04% (*I* > 4σ(*I*)).

Keywords: Yttrium; Neodymium; Samarium; Lutetium; Amides; Crystal structure

1. Introduction

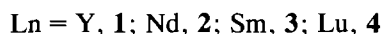
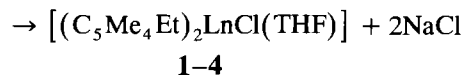
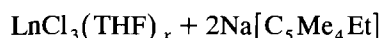
Insertion, σ-bond metathesis and hydrocarbyl protonolysis enable organolanthanide centers to promote efficiently and selectively the following reactions of alkenes and alkynes: hydrogenation [2–6], hydroamination [6–11], hydroboration [12], hydrophosphination [13], hydrosilylation [14–16] and oligomerization/polymerization/cyclization [17–24]. Bis(pentamethylcyclopentadienyl)lanthanide hydrides, analogous complexes containing bridged permethylated bis(cyclopentadienyl) systems as well as bis(cyclopentadienyl)lanthanide amides and carbyls, have been shown to be effective catalysts for such transformations. The advantage of coordination with such bulky cyclopentadienyl ligands is the stabilization of the electron-deficient metal center with simultaneously high reactivity of the com-

plex. Similar properties should be expected for the corresponding ethyltetramethylcyclopentadienyl lanthanide complexes. We therefore initiated a study in this field. The synthesis and characterization of a series of these derivatives are presented here.

2. Results and Discussion

2.1. Synthesis of amide and alkyl complexes

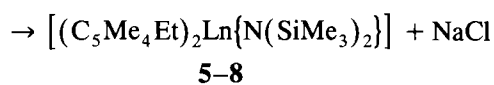
The lanthanide trichloride tetrahydrofuran (THF) adducts of yttrium, neodymium, samarium and lutetium react in THF with 2 equiv. of ethyltetramethylcyclopentadienylsodium to give [(C₅Me₄Et)₂LnCl(THF)] (**1–4**).



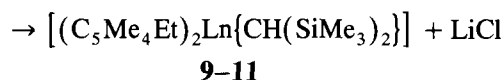
[☆] For Part XCVI, see Ref. [1]. Dedicated to Prof. Dr. B. Sarry on the occasion of her 75th birthday.

* Corresponding author.

The four compounds are extremely soluble in polar solvents (e.g. THF or diethyl ether), in aromatic solvents (e.g. benzene) and in hydrocarbons. Crystals of **1–4** are obtained by slowly cooling a saturated *n*-hexane solution from room temperature to $-25\text{ }^{\circ}\text{C}$. The presence of one molecule of THF per lanthanide atom in **1–4** is confirmed by elemental analysis and signal intensities in the ^1H NMR spectra. The bis(ethyltetramethylcyclopentadienyl)lanthanide chlorides **1–4** are conveniently converted into the monomeric $(\text{C}_5\text{Me}_4\text{Et})_2\text{-Ln}$ amides or alkyls by reaction with equimolar amounts of either $\text{NaN}(\text{SiMe}_3)_2$ or $\text{LiCH}(\text{SiMe}_3)_2$ in toluene at $0\text{ }^{\circ}\text{C}$.



$\text{Ln} = \text{Y}, \mathbf{5}; \text{Nd}, \mathbf{6}; \text{Sm}, \mathbf{7}; \text{Lu}, \mathbf{8}$



$\text{Ln} = \text{Y}, \mathbf{9}; \text{Nd}, \mathbf{10}; \text{Sm}, \mathbf{11}$

The extremely air- and moisture-sensitive complexes **5–11** are obtained in a crystalline form from *n*-hexane and in good yields. Enclosed in evaporated glass capillaries, **5–8** decompose at temperatures higher than $290\text{ }^{\circ}\text{C}$, whereas **9–11** are stable up to $200\text{ }^{\circ}\text{C}$.

The elemental analyses and ^1H and ^{13}C NMR and mass spectra obtained are in agreement with the molecular formulae. The NMR spectra in benzene- d_6 of the diamagnetic complexes **5**, **8** and **9** show the expected signals for the ethyltetramethylcyclopentadienyl rings and the amide and alkyl groups. The ^1H NMR spectra of the paramagnetic compounds **6**, **7**, **10** and **11** show partially broadened signals. The ^1H NMR chemical shifts ranged from δ 9.05 to -19.5 ppm for **6**, δ 2.15 to -6.37 ppm for **7**, δ 60.3 to -16.39 ppm for **10** and δ 20.4 to -4.72 ppm for **11**. Similar values have been reported for $[(\text{C}_5\text{Me}_5)_2\text{Ln}\{\text{E}(\text{SiMe}_3)_2\}]$ ($\text{E} = \text{N}, \text{CH}; \text{Ln} = \text{Nd}, \text{Sm}$) [19,25,26]. In case of the bis(ethyltetramethylcyclopentadienyl)lanthanide alkyl complexes **9–11**, the cyclopentadienyl resonances are observed as eight signals indicating non-equivalent cyclopentadienyl rings. This would be expected for a fixed non-planar α -carbon geometry of the alkyl group. In the case of the yttrium compounds **5** and **9**, clear coupling is observed in the ^{13}C NMR between the metal and several carbons. The largest $^1J(^{89}\text{Y}, ^{13}\text{C})$ coupling constant, 35 Hz, was observed for the α -methyl carbon of the bis(trimethylsilyl)methyl ligand in **9**. The mass spectra of **5–11**, recorded at $100\text{--}140\text{ }^{\circ}\text{C}$, show the molecular ion for

5–8, whereas for **9–11** there is no peak. Because of the high stability of the Ln–N bond, the base peak for **5–8** is $[(\text{C}_5\text{Me}_4\text{Et})\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}]^+$. In contrast, complexes **9–11** show as their base peak $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Ln}]^+$, which can be explained by the loss of the bis(trimethylsilyl)methyl ligand.

2.2. Molecular structure of **5** and **11**

Crystals suitable for X-ray analysis of **5** and **11** were obtained by crystallization from *n*-hexane at $-78\text{ }^{\circ}\text{C}$. The molecular structures, numbering schemes, selected bond distances and bond angles are shown in Figs. 1 and 2.

In **5**, the yttrium ion is coordinated by two ethyltetramethylcyclopentadienyl ligands and one bis(trimethylsilyl)amide ligand. Assuming that the centroids of the η^5 -bound cyclopentadienyl units are the center of these ligands, it can be considered that the yttrium ion is pseudo-trigonal planar coordinated. The average Y–C(η^5) distance (2.678(2) Å) and the Y–N bond length (2.276(3) Å) are in good agreement with the corresponding bond lengths in $[(\text{C}_5\text{Me}_5)_2\text{Y}\{\text{N}(\text{SiMe}_3)_2\}]$ ($d(\text{Y}-\text{C}(\eta^5)) = 2.682(4)$ Å (molecule 1) and 2.678(4) Å (molecule 2); $d(\text{Y}-\text{N}) = 2.274(5)$ Å (molecule 1) and 2.253 Å (molecule 2)) [28]. The ring slippage in **5** has a value of 0.038 Å. Noteworthy is the conformation of the amide ligand. The N1–Si1–C7 angle is more than 7.5° smaller than the N1–Si1–C6 and N1–Si1–C8 bond angles. These distortions are presumably due to γ -agostic bonds between the methyl groups of the amide ligand and the Lewis acidic lanthanide center. The interaction is best seen at C7 with $\text{Y} \cdots \text{H7A} = 2.945$ Å. Similar interactions have been observed in $[(\text{C}_5\text{Me}_5)_2\text{Y}\{\text{N}(\text{SiMe}_3)_2\}]$ [28] and $[(\text{C}_5\text{Me}_5)_2\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}]$ [25].

Like the yttrium ion in **5**, the samarium ion in **11** has a pseudo-trigonal planar coordination sphere consisting of two η^5 -interactions with the ethyltetramethylcyclopentadienyl rings and one σ -bond to the bis(trimethylsilyl)methyl ligand. The average Sm–C(η^5) distances (2.732(3) Å and 2.740(3) Å) correlate with the corresponding distances in the complex $[(\text{C}_5\text{Me}_5)_2\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}]$ (2.754(6) Å and 2.745(6) Å) [25]. The two ethyltetramethylcyclopentadienyl ligands in **11** are slipped 0.38 and 0.24 Å from the centroid of the ring. The Sm–C σ -bond length (2.502(3) Å) is in good agreement with the corresponding bond length in $[(\text{C}_5\text{Me}_5)_2\text{Nd}\{\text{CH}(\text{SiMe}_3)_2\}]$ (2.517(7) Å) [19] when the different ionic radii of the lanthanide centers are taken in consideration. Remarkably, in the crystal structure of **11**, one methyl carbon atom (C17) of the bis(trimethylsilyl)methyl ligand is found very close to the samarium center; the $\text{Sm} \cdots \text{C17}$ distance is 2.953 Å. Because of the close γ -agostic contact of the methyl group to the

C_5Me_5H [35] and converted into the sodium salt with $NaNH_2$ in THF. $LiCH(SiMe_3)_2$ [36,37] and $NaN(SiMe_3)_2$ [38] were synthesized using the literature procedures. The NMR spectra were recorded on a Bruker ARX 200 or a Bruker AM 400 spectrometer. All 1H and ^{13}C NMR chemical shifts are reported in ppm relative to the 1H and ^{13}C residue in benzene- d_6 set at δ 7.15 and 120. Mass spectra were obtained at 70 eV on a Varian MAT 311A spectrometer. Elemental analyses were carried out on a Perkin-Elmer Series II CHNS/O Analyser 2400.

3.2. Chlorobis(ethyltetramethylcyclopentadienyl)(tetrahydrofuran)yttrium(III) (I)

A 0.87 g (1.92 mmol) amount of $YCl_3(THF)_{3,6}$ [39] was suspended in 75 ml of THF and 0.66 g (3.83 mmol) of $Na[C_5Me_4Et]$ was added at room temperature. The

reaction was stirred under reflux for 12 h. After the solvent had been removed under vacuum, the residue was treated with 80 ml of *n*-hexane, stirred, allowed to settle and the solution was decanted off. Concentration to 30 ml and cooling to $-25^\circ C$ gave the product in a crystalline form; yield 0.57 g (60%) of yellow crystals. M.p. $102^\circ C$ (decomp.). Anal. Found: C, 62.77, H, 8.30. $C_{26}H_{42}ClOY$ Calc.: C, 63.09, H, 8.55%. 1H NMR (benzene- d_6 , 200 MHz): δ 3.50 (m, 4H, THF), 2.52 (q, $^3J(^1H, ^1H) = 7$ Hz, 4H, CH_2CH_3), 2.07 (s, 12H, C_5Me), 2.01 (s, 12H, C_5Me), 1.19 (m, 4H, THF), 1.03 (t, $^3J(^1H, ^1H) = 7$ Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (benzene- d_6 , 50.32 MHz): δ 124.43 (C_5Et), 118.20 (C_5Me), 117.26 (C_5Me), 72.14 (THF), 25.30 (THF), 19.98 (CH_2CH_3), 15.65 (CH_2CH_3), 11.70 (C_5Me), 11.46 (C_5Me). MS ($180^\circ C$): m/z (%) 422 (36) $[M - THF]^+$, 387 (8) $[M - THF - Cl]^+$, 273 (100) $[(C_5Me_4Et)YCl]^+$, 238 (1) $[(C_5Me_4Et)Y]^+$.

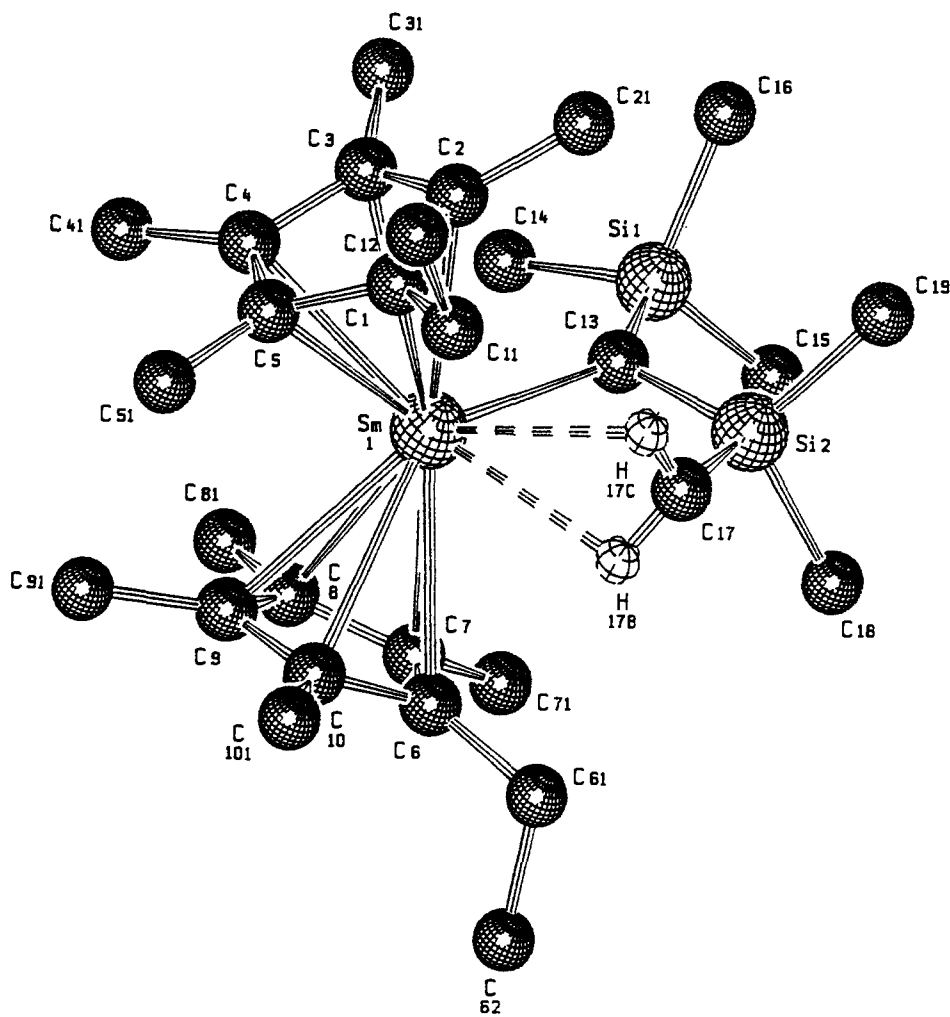


Fig. 2. Crystal structure of **11** (SCHAKAL [27]). Selected distances (Å) and angles ($^\circ$): Sm1–Cp1 2.452, Sm1–Cp2 2.459, Sm1–C1 2.741(3), Sm1–C2 2.746(3), Sm1–C3 2.724(3), Sm1–C4 2.713(3), Sm1–C5 2.738(3), Sm1–C6 2.745(3), Sm1–C7 2.742(3), Sm1–C8 2.718(3), Sm1–C9 2.751(3), Sm1–C10 2.746(3), Sm1–C13 2.502(3); Sm1–C13–Si1 140.3(2), Sm1–C13–Si2 99.91(12), C13–Si1–C14 111.7(2), C13–Si1–C15 113.1(2), C13–Si1–C16 113.3(2), C13–Si2–C17 108.43(13), C13–Si2–C18 115.7(2), C13–Si2–C19 115.9(2).

3.3. Chlorobis(ethyltetramethylcyclopentadienyl)(tetrahydrofuran)neodymium(III) (2)

Following the procedure described for **1**, 0.59 g (1.55 mmol) of $\text{NdCl}_3(\text{THF})_{1.8}$ [39] was treated with 0.45 g (3.12 mmol) of $\text{Na}[\text{C}_5\text{Me}_4\text{Et}]$; yield 0.41 g (48%) of blue crystals. M.p. 122 °C (decomp.). Anal. Found: C, 56.10, H, 7.60. $\text{C}_{26}\text{H}_{42}\text{ClNdO}$ Calc.: C, 56.75, H, 7.69%. ^1H NMR (benzene- d_6 , 400 MHz): δ 10.59 (s, 12H, C_5Me , $1w = 15$ Hz), 9.40 (s, 12H, C_5Me , $1w = 15$ Hz), 6.55 (“q”, 4H, CH_2CH_3), 1.75 (“t”, 6H, CH_2CH_3), -12.6 (“m”, 4H, THF), -39.0 (“m”, 4H, THF). MS (180 °C): m/z (%) 477 (10) $[\text{M} - \text{THF}]^+$, 442 (30) $[\text{M} - \text{THF} - \text{Cl}]^+$, 328 (100) $[(\text{C}_5\text{Me}_4\text{Et})\text{NdCl}]^+$, 293 (10) $[(\text{C}_5\text{Me}_4\text{Et})\text{Nd}]^+$.

3.4. Chlorobis(ethyltetramethylcyclopentadienyl)(tetrahydrofuran)samarium(III) (3)

Following the procedure described for **1**, 0.96 g (2.80 mmol) of $\text{SmCl}_3(\text{THF})_{1.2}$ [39] was treated with 0.96 g (5.57 mmol) of $\text{Na}[\text{C}_5\text{Me}_4\text{Et}]$; yield 1.03 g (66%) of orange crystals. M.p. 130 °C (decomp.). Anal. Found: C, 55.49, H, 7.39. $\text{C}_{26}\text{H}_{42}\text{ClOSm}$ Calc.: C, 56.12, H, 7.61%. ^1H NMR (benzene- d_6 , 200 MHz): δ 1.87 (t, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 6H, CH_2CH_3), 1.63 (q, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 4H, CH_2CH_3), 1.23 (s, 12H, C_5Me), 1.15 (s, 12H, C_5Me), -1.0 (“m”, 4H, THF), -2.0 (“m”, 4H, THF); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 50.32 MHz): δ 122.61 (C_5Et), 116.74 (C_5Me), 115.88 (C_5Me), 65.32 (THF), 25.78 (CH_2CH_3), 21.57 (THF), 17.84 (C_5Me), 17.62 (C_5Me), 11.25 (CH_2CH_3). MS (240 °C, ^{152}Sm): m/z (%) 485 (22) $[\text{M} - \text{THF}]^+$, 450 (10) $[\text{M} - \text{THF} - \text{Cl}]^+$, 336 (100) $[(\text{C}_5\text{Me}_4\text{Et})\text{SmCl}]^+$, 301 (34) $[(\text{C}_5\text{Me}_4\text{Et})\text{Sm}]^+$.

3.5. Chlorobis(ethyltetramethylcyclopentadienyl)(tetrahydrofuran)lutetium(III) (4)

Following the procedure described for **1**, 0.74 g (1.49 mmol) of $\text{LuCl}_3(\text{THF})_3$ [39] was treated with 0.52 g (2.89 mmol) of $\text{Na}[\text{C}_5\text{Me}_4\text{Et}]$; yield 0.50 g (57%) of yellow crystals. M.p. 121 °C (decomp.). Anal. Found: C, 53.11, H, 7.11. $\text{C}_{26}\text{H}_{42}\text{ClLuO}$ Calc.: C, 53.75, H, 7.28%. ^1H NMR (benzene- d_6 , 200 MHz): δ 3.49 (m, 4H, THF), 2.53 (q, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 4H, CH_2CH_3), 2.07 (s, 12H, C_5Me), 2.01 (s, 12H, C_5Me), 1.19 (m, 4H, THF), 1.02 (t, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 6H, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 50.32 MHz): δ 123.75 (C_5Et), 117.52 (C_5Me), 116.62 (C_5Me), 72.46 (THF), 25.45 (THF), 20.11 (CH_2CH_3), 15.56 (CH_2CH_3), 11.89 (C_5Me), 11.67 (C_5Me). MS (180 °C, ^{175}Lu): m/z (%) 508 (30) $[\text{M} - \text{THF}]^+$, 473 (9) $[\text{M} - \text{THF} - \text{Cl}]^+$, 359 (100) $[(\text{C}_5\text{Me}_4\text{Et})\text{LuCl}]^+$, 324 (2) $[(\text{C}_5\text{Me}_4\text{Et})\text{Lu}]^+$.

3.6. [Bis(trimethylsilyl)amido]bis(ethyltetramethylcyclopentadienyl)yttrium(III) (5)

A 0.22 g (1.23 mmol) amount of $\text{NaN}(\text{SiMe}_3)_2$ was added to a solution of 0.61 g (1.23 mmol) of **1** in 80 ml of toluene at 0 °C. The mixture was continually stirred and allowed to warm to room temperature over 1 h. After removal of the volatiles under vacuum, the residue was extracted with 80 ml of *n*-hexane. The clear solution was concentrated to 10 ml and cooled to -78 °C providing the product in a crystalline form; yield 0.50 g (75%) of colorless crystals. M.p. 321 °C (decomp.). Anal. Found: C, 60.98, H, 9.30, N, 2.55. $\text{C}_{28}\text{H}_{52}\text{NSi}_2\text{Y}$ Calc.: C, 61.39, H, 8.57, N, 2.56%. ^1H NMR (benzene- d_6 , 200 MHz): δ 2.49 (q, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, 4H, CH_2CH_3), 2.01 (s, 12H, C_5Me), 1.94 (s, 12H, C_5Me), 0.92 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, 6H, CH_2CH_3), 0.19 (s, 18H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 50.32 MHz): δ 125.88 (d, $^1J(^{89}\text{Y}, ^{13}\text{C}) = 1.3$ Hz, C_5Et), 119.80 (d, $^1J(^{89}\text{Y}, ^{13}\text{C}) = 1.2$ Hz, C_5Me), 118.98 (d, $^1J(^{89}\text{Y}, ^{13}\text{C}) = 1.2$ Hz, C_5Me), 20.42 (CH_2CH_3), 15.27 (CH_2CH_3), 12.21 (C_5Me), 11.96 (C_5Me), 5.39 (SiMe_3). MS (115 °C): m/z (%) 547 (5) $[\text{M}]^+$, 398 (100) $[\text{M} - \text{C}_5\text{Me}_4\text{Et}]^+$, 387 (6) $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Y}]^+$.

3.7. [Bis(trimethylsilyl)amido]bis(ethyltetramethylcyclopentadienyl)neodymium(III) (6)

Following the procedure described for **5**, 0.40 g (0.73 mmol) of **2** was treated with 0.13 g (0.71 mmol) of $\text{NaN}(\text{SiMe}_3)_2$; yield 0.38 g (87%) of blue crystals. M.p. 315 °C (decomp.). Anal. Found: C, 55.01, H, 8.50, N, 2.41. $\text{C}_{28}\text{H}_{52}\text{NNDiSi}_2$ Calc.: C, 55.76, H, 8.69, N, 2.32%. ^1H NMR (benzene- d_6 , 400 MHz): δ 9.05 (s, 12H, C_5Me , $1w = 15$ Hz), 8.15 (s, 12H, C_5Me , $1w = 15$ Hz), 7.08 (“t”, 6H, CH_2CH_3), 1.41 (“q”, 4H, CH_2CH_3), -19.5 (s, 18H, SiMe_3 , $1w = 614$ Hz). MS (110 °C, ^{144}Nd): m/z (%) 602 (7) $[\text{M}]^+$, 453 (100) $[\text{M} - \text{C}_5\text{Me}_4\text{Et}]^+$, 442 (3) $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Nd}]^+$.

3.8. [Bis(trimethylsilyl)amido]bis(ethyltetramethylcyclopentadienyl)samarium(III) (7)

Following the procedure described for **5**, 0.49 g (0.88 mmol) of **3** was treated with 0.16 g (0.88 mmol) of $\text{NaN}(\text{SiMe}_3)_2$; yield 0.41 g (76%) of orange crystals. M.p. 296 °C (decomp.). Anal. Found: C, 55.43, H, 8.33, N, 2.59. $\text{C}_{28}\text{H}_{52}\text{NSi}_2\text{Sm}$ Calc.: C, 55.20, H, 8.60, N, 2.30%. ^1H NMR (benzene- d_6 , 200 MHz): δ 2.15 (t, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 6H, CH_2CH_3), 1.41 (q, $^3J(^1\text{H}, ^1\text{H}) = 7$ Hz, 4H, CH_2CH_3), 0.95 (s, 12H, C_5Me), 0.65 (s, 12H, C_5Me), -6.37 (s, 18H, SiMe_3 , $1w = 80$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 50.32 MHz): δ 125.86 (C_5Et), 120.03 (C_5Me), 119.72 (C_5Me), 29.72 (CH_2CH_3), 21.88 (C_5Me), 8.09 (CH_2CH_3), -2.60

(SiMe₃). MS (140 °C, ¹⁵²Sm): *m/z* (%) 610 (4) [M]⁺, 461 (100) [M – C₅Me₄Et]⁺, 450 (4) [(C₅Me₄Et)₂Sm]⁺.

3.9. [Bis(trimethylsilyl)amido]bis(ethyltetramethylcyclopentadienyl)lutetium(III) (8)

Following the procedure described for **5**, 0.41 g (0.71 mmol) of **4** was treated with 0.13 g (0.71 mmol) of NaN(SiMe₃)₂; yield 0.18 g (40%) of colorless crystals. M.p. 302 °C (decomp.). Anal. Found: C, 52.99, H, 7.98, N, 2.30. C₂₈H₅₂LuNSi₂ Calc.: C, 53.06, H, 8.27, N, 2.21%. ¹H-NMR (benzene-d₆, 200 MHz): δ 2.51 (q, ³J(¹H, ¹H) = 7.4 Hz, 4H, CH₂CH₃), 2.03 (s, 12H, C₅Me), 1.96 (s, 12H, C₅Me), 0.90 (t, ³J(¹H, ¹H) = 7.4 Hz, 6H, CH₂CH₃), 0.21 (s, 18H, SiMe₃); ¹³C{¹H} NMR (benzene-d₆, 50.32 MHz): δ 125.48 (C₅Et), 119.53 (C₅Me), 118.72 (C₅Me), 20.52 (CH₂CH₃), 15.22 (CH₂CH₃), 12.40 (C₅Me), 12.27 (C₅Me), 6.01

Table 1
Crystallographic data for **5** and **11**

| Parameter | 5 | 11 |
|---|--|--|
| <i>Crystal data</i> | | |
| Empirical formula | C ₂₈ H ₅₂ NSi ₂ Y | C ₂₉ H ₅₃ Si ₂ Sm |
| Mol. wt. | 547.80 | 608.25 |
| Crystallized from | <i>n</i> -Hexane | <i>n</i> -Hexane |
| Cryst. system | Monoclinic | Orthorhombic |
| Space group | C2/c (No. 15) | Pbca (No. 61) |
| <i>a</i> (Å) | 9.169(2) | 18.499(6) |
| <i>b</i> (Å) | 21.166(8) | 14.181(6) |
| <i>c</i> (Å) | 15.625(3) | 23.290(5) |
| β (°) | 94.15(2) | |
| <i>V</i> (Å ³) | 3025(2) | 6110(3) |
| <i>Z</i> | 4 | 8 |
| <i>D</i> (calcd) (g cm ⁻³) | 1.203 | 1.323 |
| <i>F</i> (000) (electrons) | 1176 | 2536 |
| μ(Mo Kα) (mm ⁻¹) | 2.023 | 1.930 |
| Crystal size (mm) | 0.3 × 0.2 × 0.25 | 0.5 × 0.35 × 0.9 |
| <i>Data collection</i> | | |
| Temp. (K) | 163(2) | 163(2) |
| Radiation (Å) | 0.71069 | 0.71069 |
| θ range (min, max) (°) | 2.33, 24.99 | 1.75, 30.99 |
| X-ray exposure time (h) | 43 | 131.8 |
| Decay (%) | –0.6 | –0.5 |
| Total data | 2533 | 10592 |
| Total unique | 2464 | 8097 |
| Obsd. data (<i>I</i> > 4σ(<i>I</i>)) | 2257 | 7820 |
| | <i>R</i> (int) = 0.0213 | <i>R</i> (int) = 0.0213 |
| <i>Refinement</i> | | |
| No. of reflections | 2250 | 7768 |
| No. of refined parameters | 250 | 473 |
| DIFABS min, max abs. | 0.875, 1.144 | 0.881, 1.311 |
| corr. factor | | |
| Min, max density (e Å ⁻³) | –0.234, 0.264 | –0.820, 1.235 |
| <i>R</i> ₁ = Σ <i>F</i> _o – <i>F</i> _c / Σ <i>F</i> _o | 0.0286 | 0.0304 |
| <i>wR</i> ₂ = { Σ[w(<i>F</i> _o ² – <i>F</i> _c ²) ²] / Σ[w(<i>F</i> _o ²) ²]} ^{1/2} | 0.0586 | 0.0782 |
| GOF | 1.051 | 1.077 |

(SiMe₃). MS (120 °C, ¹⁷⁵Lu): *m/z* (%) 633 (5) [M]⁺, 484 (100) [M – C₅Me₄Et]⁺, 473 (4) [(C₅Me₄Et)₂Lu]⁺.

3.10. [Bis(trimethylsilyl)methyl]bis(ethyltetramethylcyclopentadienyl)yttrium(III) (9)

Following the procedure described for **5**, 0.55 g (1.11 mmol) of **1** was treated with 0.18 g (1.11 mmol) of LiCH(SiMe₃)₂; yield 0.28 g (46%) of colorless crystals. M.p. 200 °C (decomp.). Anal. Found: C, 63.45, H, 9.67. C₂₉H₅₃Si₂Y Calc.: C, 63.70, H, 9.77%. ¹H NMR (benzene-d₆, 200 MHz): δ 2.51 (q, ³J(¹H, ¹H) = 7 Hz, 2H, CH₂CH₃), 2.43 (q, ³J(¹H, ¹H) = 7 Hz, 2H, CH₂CH₃), 2.00 (s, 6H, C₅Me), 1.95 (s, 6H, C₅Me), 1.94 (s, 6H, C₅Me), 1.88 (s, 6H, C₅Me), 0.91 (“t”, 6H, CH₂CH₃), 0.20 (s, 18H, SiMe₃), –0.09 (d, ²J(⁸⁹Y, ¹H) = 2 Hz, 1H, CH); ¹³C{¹H} NMR (benzene-d₆, 50.32 MHz): δ 126.09 (C₅Et), 125.47 (C₅Et), 119.98 (C₅Me), 119.23 (C₅Me), 119.02 (C₅Me), 118.39 (d, ¹J(⁸⁹Y, ¹³C) = 1.0 Hz, C₅Me) 24.94 (d, ¹J(⁸⁹Y, ¹³C) = 35 Hz, CH), 20.35 (CH₂CH₃), 15.38 (CH₂CH₃), 15.33 (CH₂CH₃), 12.18 (C₅Me), 11.89 (C₅Me), 11.83 (C₅Me), 11.63 (C₅Me), 5.11 (SiMe₃). MS (115 °C): *m/z* (%) 387 (100) [(C₅Me₄Et)₂Y]⁺.

3.11. [Bis(trimethylsilyl)methyl]bis(ethyltetramethylcyclopentadienyl)neodymium(III) (10)

Following the procedure described for **5**, 0.53 g (0.96 mmol) of **2** was treated with 0.16 g (0.96 mmol) of LiCH(SiMe₃)₂; yield 0.42 g (72%) of green crystals. M.p. 196 °C (decomp.). Anal. Found: C, 57.21, H, 8.77. C₂₉H₅₃NdSi₂ Calc.: C, 57.85, H, 8.87%. ¹H NMR (benzene-d₆, 400 MHz): δ 60.3 (s, 1H, CH, lw = 191 Hz), 9.06 (s, 12H, C₅Me, lw = 23 Hz), 7.96 (s, 6H, C₅Me, lw = 19 Hz), 7.74 (s, 6H, C₅Me, lw = 19 Hz), 0.91 (“t”, 6H, CH₂CH₃), 3.84 (“q”, 2H, CH₂CH₃), 3.64 (“q”, 2H, CH₂CH₃), –16.39 (s, 18H, SiMe₃, lw = 23 Hz). MS (120 °C, ¹⁴⁴Nd): *m/z* (%) 442 (100) [(C₅Me₄Et)₂Nd]⁺.

3.12. [Bis(trimethylsilyl)methyl]bis(ethyltetramethylcyclopentadienyl)samarium(III) (11)

Following the procedure described for **5**, 0.79 g (1.42 mmol) of **3** was treated with 0.24 g (1.42 mmol) of LiCH(SiMe₃)₂; yield 0.61 g (71%) of red crystals. M.p. 175 °C (decomp.). Anal. Found: C, 57.30, H, 8.80. C₂₉H₅₃Si₂Sm Calc.: C, 57.26, H, 8.78%. ¹H NMR (benzene-d₆, 200 MHz): δ 20.4 (s, 1H, CH, lw = 70 Hz), 1.8 (m, 8H, CH₂CH₃), 1.5 (m, 2H, CH₂CH₃), 1.00 (s, 6H, C₅Me), 0.90 (s, 6H, C₅Me), 0.79 (s, 6H, C₅Me), 0.70 (s, 6H, C₅Me), –4.72 (s, 18H, SiMe₃); ¹³C{¹H} NMR (benzene-d₆, 50.32 MHz): δ 126.38 (C₅Et), 126.14 (C₅Et), 119.9–119.2 (C₅Me), 27.96

(CH₂CH₃), 27.58 (CH₂CH₃), 19.71 (C₅Me), 19.18 (C₅Me), 10.07 (CH₂CH₃), 9.94 (CH₂CH₃), -2.78 (SiMe₃), CH not found. MS (100 °C, ¹⁵²Sm): *m/z* (%) 450 (100) [(C₅Me₄Et)₂Sm]⁺, 301 (26) [(C₅Me₄Et)Sm]⁺.

3.13. X-ray data collection, structure determination and refinement for **5** and **7**

Crystal data and other details of the structure determination are collected in Table 1. The crystals were selected using a modified device, similar to that of Veith and Bärninghausen [40]. The crystals were mounted on a glass fiber and transferred to an Enraf-Nonius CAD 4 diffractometer equipped with a low-temperature device. Unit cell parameters from 25 reflections in the range of 16.84° ≤ 2θ ≤ 27.38° for **5** and 15.76° ≤ 2θ ≤ 24.12° for **11** were obtained. Data were collected with ω - 2θ scans. Every 200 reflections intensity data were monitored through the measurement of three standard reflections. All data were corrected for Lorentz and polarization effects and absorption effects, (DIFABS) [41]. Systematic absence of reflections *hkl* for *h + k = odd* and *h0l* for *h, l = odd* indicated the centrosymmetric space group *C2/c* for **5**. Systematic extinctions of reflections *00l*, *0k0*, *h00*, *hk0* (*k = odd*), *h0l* (*h = odd*), and *0kl* (*l = odd*) for **11** indicated the centrosymmetric space group *Pcab*, which was transferred via matrix into the standard space group *Pbca*. The position of the heavy atom was determined using Patterson (SHELXS-86) [42] and the rest of the molecule using difference-Fourier methods (SHELXL-93) [43]. The molecules were refined against *F_o²* by full-matrix least-squares techniques. Owing to some disorder of the

Table 2
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **5**

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) ^a |
|-------|----------|----------|----------|----------------------------|
| Y(1) | 0 | 1126(1) | 2500 | 19(1) |
| C(1) | 246(3) | 167(1) | 1381(2) | 23(1) |
| C(11) | -323(4) | -498(1) | 1425(2) | 33(1) |
| C(2) | 1693(3) | 374(1) | 1603(2) | 24(1) |
| C(21) | 2937(3) | -14(2) | 2009(2) | 35(1) |
| C(3) | 1836(3) | 991(1) | 1262(1) | 23(1) |
| C(31) | 3281(3) | 1322(1) | 1178(2) | 33(1) |
| C(32) | 3943(3) | 1126(2) | 349(2) | 47(1) |
| C(4) | 490(2) | 1167(1) | 838(1) | 21(1) |
| C(41) | 219(3) | 1758(1) | 319(2) | 29(1) |
| C(5) | 503(3) | 660(1) | 4077(1) | 22(1) |
| C(51) | 2007(3) | 587(2) | 4520(2) | 32(1) |
| N(1) | 0 | 2202(1) | 2500 | 22(1) |
| Si(1) | -1600(1) | 2573(1) | 2198(1) | 25(1) |
| C(6) | -2458(4) | 3013(2) | 3074(2) | 38(1) |
| C(7) | -2924(4) | 1952(2) | 1764(2) | 44(1) |
| C(8) | -1486(4) | 3176(2) | 1331(2) | 41(2) |

^a *U*(eq) is defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

Table 3
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **11**

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) ^a |
|--------|----------|----------|----------|----------------------------|
| Sm(1) | 95(1) | 2231(1) | 1060(1) | 14(1) |
| Si(1) | 1920(1) | 1972(1) | 2017(1) | 27(1) |
| Si(2) | 1424(1) | 631(1) | 1013(1) | 23(1) |
| C(1) | -1095(1) | 1175(2) | 1341(1) | 21(1) |
| C(11) | -1371(2) | 399(2) | 958(2) | 34(1) |
| C(12) | -2061(2) | -60(3) | 1184(2) | 44(1) |
| C(2) | -623(1) | 1073(2) | 1813(1) | 24(1) |
| C(21) | -323(2) | 160(3) | 2038(2) | 45(1) |
| C(3) | -567(1) | 1960(2) | 2092(1) | 26(1) |
| C(31) | -181(2) | 2154(4) | 2645(1) | 50(1) |
| C(4) | -1011(1) | 2610(2) | 1790(1) | 23(1) |
| C(41) | -1178(2) | 3601(2) | 1988(2) | 39(1) |
| C(5) | -1342(1) | 2119(2) | 1333(1) | 21(1) |
| C(51) | -1948(2) | 2486(3) | 963(2) | 34(1) |
| C(6) | 511(1) | 2820(2) | -12(1) | 21(1) |
| C(61) | 805(2) | 2202(2) | -483(1) | 28(1) |
| C(62) | 958(2) | 2762(3) | -1028(1) | 37(1) |
| C(7) | 920(1) | 3380(2) | 377(1) | 20(1) |
| C(71) | 1726(2) | 3444(2) | 402(2) | 36(1) |
| C(8) | 430(2) | 3983(2) | 670(1) | 22(1) |
| C(81) | 632(2) | 4753(2) | 1080(2) | 37(1) |
| C(9) | -272(1) | 3821(2) | 450(1) | 23(1) |
| C(91) | -902(2) | 4476(2) | 547(2) | 34(1) |
| C(10) | -232(1) | 3091(2) | 36(1) | 22(1) |
| C(101) | -831(2) | 2716(2) | -333(2) | 34(1) |
| C(13) | 1257(2) | 1650(3) | 1480(1) | 40(1) |
| C(14) | 1769(2) | 3198(3) | 2293(2) | 45(1) |
| C(15) | 2870(2) | 1917(4) | 1743(3) | 90(2) |
| C(16) | 1909(4) | 1189(4) | 2656(2) | 95(2) |
| C(17) | 580(2) | 410(2) | 565(1) | 24(1) |
| C(18) | 2189(2) | 762(2) | 489(1) | 30(1) |
| C(19) | 1578(2) | -519(3) | 1386(2) | 43(1) |

U(eq) is defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

methyl groups C15 and C16 in **11**, which showed large thermal parameters, hydrogen atoms for those were placed on calculated positions with *d_{CH}* = 0.98 Å. The hydrogen atom for C13 (H13) in **11** was also placed on a calculated position owing to an unusually short bond distance of *d_{CH}* = 0.3 Å. The final values of the refined positional parameters are presented in Tables 2 and 3. Details of the crystal structure investigations of **5** and **11** may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-58916.

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