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Organometallic compounds of the lanthanides[1]. CXXI. Donor-substituted lanthanidocenes. Synthesis of mixed unbridged lanthanidocene chloride and alkyl derivatives

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Abstract

Stepwise reaction of $ScCl_3(THF)_3$ and the lanthanide trichlorides $LnCl_3(THF)_n$ (Ln = Nd, Sm, Ho, Lu) first with (dimethylaminoethyl)cyclopentadienyl potassium (KCp^{Do}) and then with tetramethylcyclopentadienyl sodium ($NaCp^{*H}$) or with pentamethylcyclopentadienyl sodium (NaCp*), respectively, yields the mixed sandwich complexes $Cp^{Do}Cp^{*H}ScCl$ (**1**), $Cp^{Do}Cp^{*H}LnCl$ {Ln = Nd (**2**), Sm (**3**), Ho (**4**), Lu (**5**)} and $Cp^{Do}Cp^{*}LuCl$ (**6**), respectively. Treatment of **1**–**5** with methyl lithium in Et_2O afforded the chiral alkyl derivatives $Cp^{Do}Cp^{*H}ScMe$ (**7**) and $Cp^{Do}Cp^{*H}LnMe$ {Ln = Nd (**8**), Sm (**9**), Ho (**10**), Lu (**11**)}, respectively. Reaction of **6** with $LiCH_2SiMe_3$ yields the corresponding alkyl derivative $Cp^{Do}Cp^{*}LuCH_2SiMe_3$ (**12**). The new complexes were characterized by elemental analysis, MS and NMR spectroscopy, as well as by single crystal X-ray structure analysis (**1** and **7**).

Keywords: Chiral lanthanidocene complexes; Scandium; Neodymium; Samarium; Holmium; Lutetium; X-ray structure

1. Introduction

The use of donor-functionalized cyclopentadienyl ligands for the synthesis of organometallic compounds created a large variety of new metallocene derivatives of transition elements and the lanthanides [2,3]. Recently, we presented our first results in the area of chiral chloro- and methyl *ansa*-dicyclopentadienyl derivatives of the lanthanides [4], demonstrating that dimethylsilyl-bridged bis(cyclopentadienyl) dianions $[CpSiMe_2Cp]^{2-}$ allow the isolation of racemic mixtures of lanthanidocene derivatives with two different cyclopentadienyl ligands. In contrast, the synthesis of mixed dicyclopentadienyl complexes CpCp′LnX without a bridge is difficult, because of the tendency of monocyclopentadienyl lanthanide dihalides to redistribute [5]. Monocyclopentadienyl lanthanide dihalides are required as the starting material for such complexes. They can be found in the literature mostly with the bulky pentamethylcyclopentadienyl ligand [6,7] as well as donor-functionalized cyclopentadienyl derivatives like $(C_5H_4CH_2CH_2OMe)LnI_2(THF)_2$ (Ln = Sm, Yb) [8]. In the latter case, the intramolecular Lewis basic methoxy group increases the stability against hydrolysis of these highly reactive complexes. Therefore, only very few group III and lanthanide sandwich complexes with two different ring systems are known, e.g. bridged dicyclopentadienyl derivatives [9], cyclooctatetraenyl cyclopentadienyl lanthanide complexes [10] and mixed dicyclopentadienyl scandium alkyl compounds [11]. In this paper we describe the synthesis of some new chiral unbridged lanthanidocene complexes containing the lanthanide metal as the center of chirality in a pseudo-tetrahedral environment with four different ligands, as well as the molecular structure of two of them.

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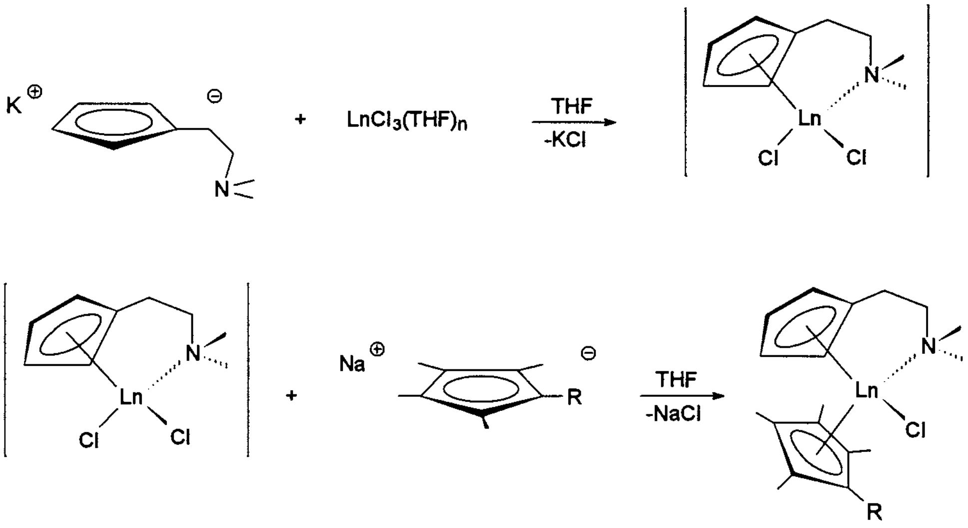


R = H **Ln = Sc (1, n = 3), Nd (2, n = 0), Sm (3, n = 1.77), Ho (4, n = 0), Lu (5, n = 2.84)**

R = Me **Ln = Lu (6, n = 3)**

Scheme 1.

2. Results and discussion

2.1. Organolanthanide chlorides $(C_5RMe_4)(C_5H_4CH_2CH_2NMe_2)LnCl$ (R = H, Me)

Stepwise reaction of the rare earth trichlorides $LnCl_3(THF)_n$ {Ln = Sc ($n = 3$), Nd ($n = 0$), Sm ($n = 1.77$), Ho ($n = 0$) and Lu ($n = 2.84$)} with dimethylaminoethylcyclopentadienyl potassium (KCp^{Do}) and in the second step, without isolation of the cyclopentadienyl metal dichlorides formed, with tetramethylcyclopentadienyl sodium ($NaCp^{*H}$) or with pentamethylcyclopentadienyl sodium (NaCp*), respectively, in THF yields racemic mixtures of chiral complexes of the type $Cp^{Do}Cp^{*H}LnCl$ {Ln = Sc (**1**), Nd (**2**), Sm (**3**), Ho (**4**), Lu (**5**)} and $Cp^{Do}Cp^{*}LuCl$ (**6**) in up to 89% yield (Scheme 1).

The complexes **1**–**6** are soluble in THF and arenes (toluene, benzene). However, in arenes they are less soluble than the corresponding dimethylsilyl-bridged compounds [4]. Compared with the bridged complexes of the similar type [4], **1**–**6** are more sensitive to moisture and air, presumably due to an increased intramolecular mobility of the ligands. Neither comproportionation nor ligand exchange could be detected by NMR investigations in solution after several days. Elemental analyses as well as MS spectra show the complexes monomeric, solvent free and salt free. The ^1H- and ^{13}C-NMR spectra of the diamagnetic lutetium derivatives **5** and **6** in C_6D_6 show a diversity of proton and carbon signals in the expected chemical shift ranges in accordance with the presence of a chiral center at the metal. The racemic mixture of the chiral molecules could not be resolved. The ^1H-NMR spectrum of **5** shows four resonances at 6.55, 6.12, 5.79 and 5.31 ppm, respectively, which can be assigned to the ring protons of the donor-substituted cyclopentadienyl ring. The methyl groups of the tetramethylcyclopentadienyl ring give rise to four distinct resonances as well, appearing at 2.25, 2.053, 2.047 and 2.04 ppm, respectively. The chiral nature of the molecule is also evident from the ethylene bridge resonances, which appear at 3.09, 2.20, 2.00 and 1.55 ppm, respectively. The methyl groups of the dimethylamino functionality appear as a broad singlet at 1.80 ppm in the ^1H-NMR spectrum (bonded to the nitrogen atom of the non-coordinating amino group). In contrast, two distinct resonances are observed for the dimethylamino group in the ^{13}C-NMR spectrum at 49.55 and 43.41 ppm. Thus, it seems that we are in the vicinity of the coalescence region for the dimethylamino group. This process does not appear to involve loss of chirality at the metal. This can be rationalized by invoking rapid coordination, decoordination of the dimethylamino group from the metal without simultaneous inversion of configuration at the metal. All assignments were confirmed by ^{13}C-DEPT and C, H-COSY spectra. Recording the NMR spectra of **5** in pyridine-d_5 reduces the total number of resonance lines in both spectra because of the replacement of the coordinating dimethylaminoethyl group at the lutetium center by the stronger Lewis base pyridine, and the fast exchange of free and coordinated pyridine leading to the introduction of a time-averaged plane of symmetry. The ^1H-NMR spectrum now shows two

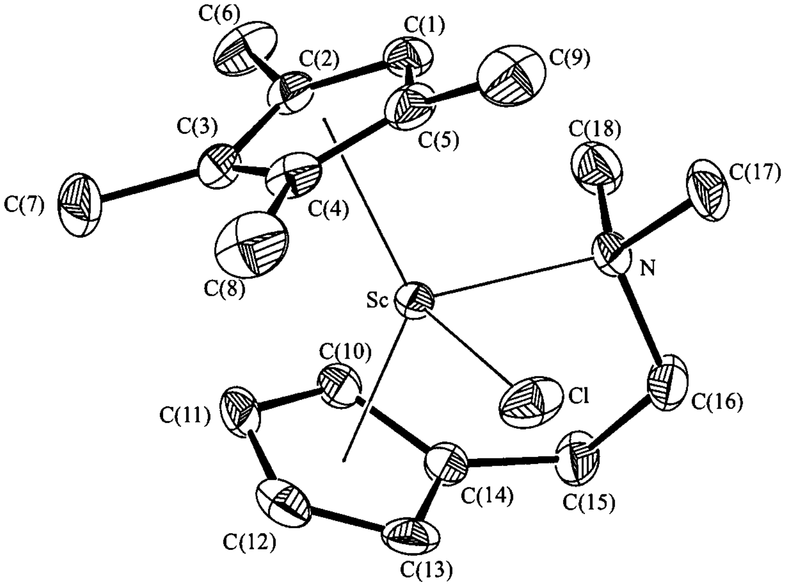


Fig. 1. ORTEP [12] plot of the molecular structure of **1**. Selected bond lengths (Å) and angles [°] with estimated S.D. in parentheses: Sc–N 2.396(3), Sc–Cl 2.4574(12), Sc–Cp(1) 2.193(2), Sc–Cp(2) 2.199(2), N–Sc–Cl 90.98(8), N–Sc–Cp(1) 111.36(10), N–Sc–Cp(2) 98.67(10), Cl–Sc–Cp(1) 108.12(6), Cl–Sc–Cp(2) 107.30(6), Cp(1)–Sc–Cp(2) 132.43(7). Cp(1) and Cp(2) define the centroid position of the Cp rings C(1)–C(5) and C(10)–C(14), respectively.

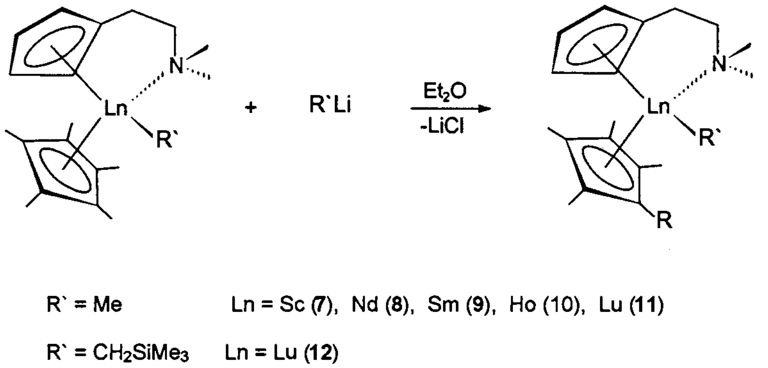
sharp singlets for the methyl groups of the tetramethylcyclopentadienyl ligand and one singlet for the two methyl groups bound to the nitrogen atom of the non-coordinating amino group.

The X-ray structure determination of **1** shows four well-separated monomers in the unit cell, two pairs of enantiomers. The structure of one molecule is shown in Fig. 1. It shows the four coordinating units of the ligands surrounding the metal center in a distorted tetrahedral geometry. The solid-state structure is the same as in solution, separated monomers without additional coordinating solvent molecules. The formal coordination number of the scandium atom is 8. The Sc–N distance is with 2.396(3) Å, as long as in $N_2H_5[Sc(N_2H_3COO)_4](H_2O)_3$ (2.409(6) and 2.402 Å) [13] but significantly longer than in $[\{(C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}(PMe_3)Sc]_2(\mu\text{-}CH_2CH_2)$ (2.071(6) Å) or in $[\{C_5Me_4SiMe_2NCMe_3)Sc]_2(\mu\text{-}CH_2CH_2CH_3)_2$ (2.083(5) Å) [14], respectively, in which the donor group is bound as an anion to the metal center. The distance of the cyclopentadienyl center to the scandium atom is not influenced by the steric surrounding in the molecule. The values of 2.193(2) and 2.199(2) Å, respectively, are comparable with the distances in $(C_5Me_4SiMe_2C_5H_3CH_2CH_2P(CMe_3)_2)ScCH(SiMe_3)_2$ (2.200 and 2.203 Å), respectively [15]. Compound **1** is one of the very few examples of a dicyclopentadienyl scandium chloride without bridging chlorine atoms. This terminal Sc–Cl distance is 2.4574(12) Å shorter than in $[(C_5H_3(SiMe_3)_2)_2Sc(\mu\text{-}Cl)]_2$ (2 58 Å) [16] but longer than in $ScCl_3(THF)_3$ (2.406(4), 2.420(4) and 2.415(4) Å) [17]. The Cp–Sc–Cp′ angle is with 132.43(7)°, similar to that in $[(C_5H_3(SiMe_3)_2)_2Sc(\mu\text{-}Cl)]_2$ (131°) [16] but larger than that in $(C_5Me_4SiMe_2C_5H_3CH_2CH_2P(CMe_3)_2)ScCH(SiMe_3)_2$ (128.1°) [15] and smaller than that in Cp^*_2ScMe (144.65(7)°) [18]. All other angles around the metal center are comparable with those in the related Me_2Si-bridged yttrium compound $[(Cp^{*H})(Cp^{Do})SiMe_2]YCl$ [Cl–Y–Cp 110.30(8)° and 110.59(8)°, N–Y–Cl 94.40(12)°, N–Y–Cp 118.71(13)° and 95.19(13)°] [4].

2.2. Organolanthanide alkyls $(C_5RMe_4)(C_5H_4CH_2CH_2NMe_2)LnR'$ ($R = H$, $R' = Me$; $R = Me$, $R' = CH_2SiMe_3$)

The monomeric rare earth chlorides **1**–**5** react with methyl lithium in diethylether to give the monomeric methyl derivatives **7**–**11**; the pentamethylcyclopentadienyl derivative **6** reacts with $LiCH_2SiMe_3$ to yield $Cp^{Do}Cp^*LuCH_2SiMe_3$ (**12**) (Scheme 2).

Apart from the mixed sandwich compounds of scandium presented by Bercaw et al. [11], **7**–**12** are the only other examples of unbridged mixed sandwich alkyl complexes of the rare earth elements. Neither coordinating solvent molecules nor additional methyl lithium complete the coordination sphere of the rare earth metal, because of the strong chelating coordination of the dimethylaminoethylcyclopentadienyl ligand, which agrees with the situation in the *ansa*-metallocene derivatives described previously [4]. The mass spectra of **7**–**12** show the molecular ions in each case with low intensity. Relative masses with intensities up to 80% show the loss of the alkyl ligand. No fragments could



Scheme 2.

be detected for dicyclopentadienyl metal complexes containing only one type of ligand, confirming that no redistribution rearrangements take place. The NMR spectra are similar to those of the chloride complexes **1**–**6**. The coordinating dimethylamino group is replaced by the stronger Lewis base pyridine in pyridine solution. The ^{1}H-NMR spectrum of **12** in C_6D_6 solution gives rise to the expected two doublets with a geminal coupling of 10.3 Hz, corresponding to the CH_2 group of the Me_3SiCH_2 moiety in **12** at r.t.

The X-ray structure of **7** (Fig. 2) shows the same geometry around scandium like **1**. The bond angles around the metal differ only slightly from those in **1**. The Sc–N distance (2.414(2) Å) and the Cp–Sc distances (2.2054(14) and 2.2212(15) Å) are only slightly longer and correspond to those in **1**. The Sc–C distance (2.346(2) Å) is as long as in μ-alkyl compounds like $[\{(C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}(PMe_3)Sc]_2(\mu\text{-}CH_2\text{-}CH_2)$ (2.320(9) and 2.257(9) Å) or $[\{C_{M}e_4Si\text{-}Me_2NCMe_3)Sc]_2(\mu\text{-}CH_2CH_2CH_3)_2$ (2.334(7) and 2.372(7) Å) [14] but it is significantly longer than in unbridged alkyl derivatives such as $[C_5Me_4SiMe_2C_5H_3CH_2CH_2P(CMe_3)_2]ScCH(SiMe_3)_2$ (2.253(6) Å) [15] or Cp^*_2ScMe (2.24(1) Å) [19]. The coordinating dimethylamino group decreases the Lewis acidity of the scandium atom resulting in a weakening of the bond strength between scandium and the carbon atom of the methyl group.

3. Experimental

3.1. General

All experiments were carried out in an atmosphere of dried, oxygen-free nitrogen by using standard Schlenk techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl prior to use. Melting points and thermal decomposition temperatures were determined in sealed capillaries under vacuum (0.01 mbar) and are uncorrected. MS spectra (EI, 70 eV) were recorded on a Varian MAT 311A spectrometer. Only characteristic fragments and isotopes of the highest abundance are listed. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyser 2400. NMR spectra were obtained by using a Bruker ARX 200 (^{1}H-NMR: 200 MHz, ^{13}C-NMR: 50.32 MHz) and are referenced to the ^{1}H and ^{13}C residue of the deuterated solvents. (Dimethylaminoethyl)cyclopentadienyl potassium [20], tetramethylcyclopentadienyl sodium [21] and pentamethylcyclopentadienyl sodium [22] were prepared according to published methods.

3.2. *Organolanthanide chlorides* $(C_5RMe_4)(C_5H_4CH_2CH_2NMe_2)LnCl$ *(R = H, Me)*

3.2.1. *Chloro{(dimethylaminoethyl)cyclopentadienyl}tetramethylcyclopentadienyl scandium (**1**)*

To a suspension of $ScCl_3(THF)_3$ (1.08 g, 2.94 mmol) in 50 ml of THF (dimethylaminoethyl)cyclopentadienyl potassium (0.52 g, 2.94 mmol) was added. The resulting mixture was stirred at r.t. for 4 h. Subsequent addition of tetramethylcyclopentadienyl sodium (0.42 g, 2.94 mmol) led to a pale-yellow suspension, which was stirred at r.t. for 12 h. Then the volatile materials were removed under reduced pressure. The resulting solid was washed with hexane (3 × 30 ml). After extraction with toluene (50 ml), the volume of the toluene extract was reduced to ca. 20 ml. Cooling to -30°C yielded colourless crystals that were filtered off and dried under reduced pressure. Yield 0.60 g (61%). Single crystals were obtained by recrystallization from THF at 0°C. M.p. 220°C. Anal. Calc. for $C_{18}H_{27}ClNSc$ (337.83 g mol^{-1}): C, 64.00; H, 8.06; N, 4.15. Found: C, 63.78; H, 7.72; N, 4.08. ^{1}H-NMR (200 MHz, C_6D_6) δ (ppm) 6.74 (m, 1H, C_5H_4), 6.24 (m, 1H, C_5H_4), 5.60 (m, 1H, C_5H_4), 5.18 (m, 1H, C_5H_4), 4.88 (s, 1H, C_5Me_4H), 3.43 (m, 1H, $CH_2CH_2N(CH_3)_2$), 2.26 (s, 3H, $C_5(CH_3)_4H$), 2.19 (m, 1H, $CH_2CH_2N(CH_3)_2$), 2.14 (s, 3H, $N(CH_3)_2$), 2.02 (m, 1H, $CH_2CH_2N(CH_3)_2$), 2.00 (s, 3H,

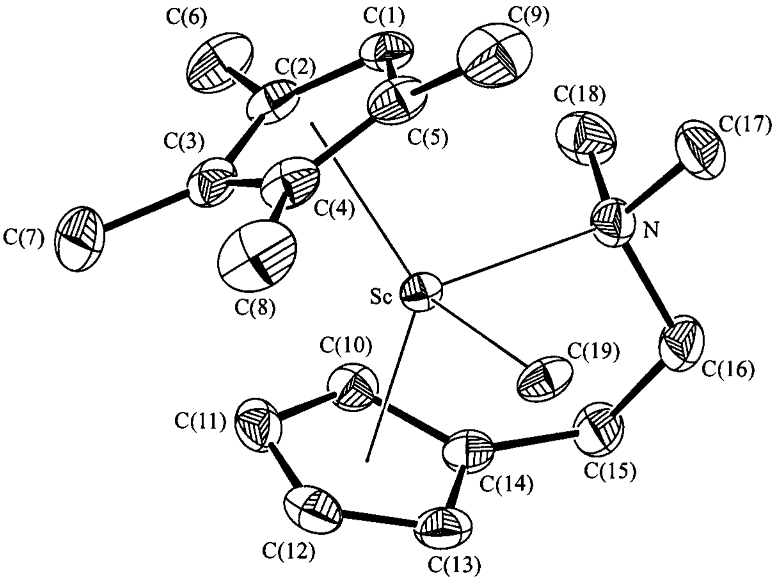


Fig. 2. ORTEP [12] plot of the molecular structure of **7**. Selected bond lengths (Å) and angles (°) with estimated S.D. in parentheses: Sc–C(19) 2.346(2), Sc–N 2.4174(2), Sc–Cp(1) 2.2054(14), Sc–Cp(2) 2.2212(14), N–Sc–C(19) 91.54(8), N–Sc–Cp(1) 112.13(7), N– Sc–Cp(2) 98.44(7), C(19)–Sc–Cp(1) 108.20(8), C(19)–Sc–Cp(2) 106.16(8), Cp(1)–Sc–Cp(2) 132.60(5). Cp(1) and Cp(2) define the centroid position of the Cp rings C(1)–C(5) and C(10)–C(14), respectively.

$C_5(CH_3)_4H$), 1.98 (s, 3H, $C_5(CH_3)_4H$), 1.96 (s, 3H, $C_5(CH_3)_4H$), 1.53 (s, 3H, $C_5(CH_3)_4H$), 1.42 (m, 1H, $CH_2CH_2N(CH_3)_2$). ^{13}C-NMR (50.32 MHz, C_6D_6) δ (ppm) 127.07 (^{q}C), 123.92 (^{q}C), 123.43 (^{q}C), 120.89 (^{q}C), 119.84 (C_5H), 116.95 (^{q}C), 114.61 (C_5H), 113.81 (CH of $C_5(CH_3)_4$), 108.83 (C_5H), 108.82 (C_5H), 66.23 (Me_2NCH_2), 50.81 ($N(CH_3)_2$), 43.61 ($N(CH_3)_2$), 25.49 (CH_2Cp), 14.59 ($C_5(CH_3)_4$), 13.67 ($C_5(CH_3)_4$), 13.36 ($C_5(CH_3)_4$), 12.29 ($C_5(CH_3)_4$). MS (25°C, ^{45}Sc) *m*/*z*(%) 337 (18) $[M]^+$, 302 (4) $[M\text{-}Cl]^+$, 216 (100) $[M\text{-}C_5HMe_4]^+$, 201 (4) $[M\text{-}C_5H_4C_2H_4NMe_2]^+$, 58 (38) $[CH_2NMe_2]^+$.

3.2.2. Chloro{(dimethylaminoethyl)cyclopentadienyl}tetramethylcyclopentadienyl neodymium (2)

Compound **2** was prepared analogously to **1** from $NdCl_3$ (0.50 g, 2.00 mmol), (dimethylaminoethyl)cyclopentadienyl potassium (0.35 g, 2.00 mmol) and tetramethylcyclopentadienyl sodium (0.29 g, 2.00 mmol) to yield 0.50 g (57%) of a light-blue solid. M.p. 181°C. Anal. Calc. for $C_{18}H_{27}ClNNd$ (437.11 g mol^{-1}): C, 49.46; H, 6.23; N, 3.20. Found: C, 49.98; H, 5.85; N, 3.69. MS (120°C, ^{144}Nd) *m*/*z*(%) 436 (5) $[M]^+$, 315 (20) $[M\text{-}C_5HMe_4]^+$, 300 (2) $[M\text{-}C_5H_4C_2H_4NMe_2]^+$, 58 (100) $[CH_2NMe_2]^+$.

3.2.3. Chloro{(dimethylaminoethyl)cyclopentadienyl}tetramethylcyclopentadienyl samarium (3)

Compound **3** was prepared analogously to **1** from $SmCl_3(THF)_{1.77}$ (0.75 g, 1.95 mmol), (dimethylaminoethyl)cyclopentadienyl potassium (0.34 g, 1.95 mmol) and tetramethylcyclopentadienyl sodium (0.28 g, 1.95 mmol) to yield 0.64 g (74%) of an orange solid. M.p. 174°C. Anal. Calc. for $C_{18}H_{27}ClNSm$ (443.23 g mol^{-1}): C, 48.78; H, 6.14; N, 3.16. Found: C, 49.13; H, 6.07; N, 3.43. MS (260°C, ^{152}Sm) *m*/*z*(%) 444 (5) $[M]^+$, 323 (22) $[M\text{-}C_5HMe_4]^+$, 308 (11) $[M\text{-}C_5H_4C_2H_4NMe_2]^+$, 58 (100) $[CH_2NMe_2]^+$.

3.2.4. Chloro{(dimethylaminoethyl)cyclopentadienyl}tetramethylcyclopentadienyl holmium (4)

Compound **4** was prepared analogously to **1** from $HoCl_3$ (0.74 g, 2.73 mmol), (dimethylaminoethyl)cyclopentadienyl potassium (0.51 g 2.91 mmol) and tetramethylcyclopentadienyl sodium (0.44 g, 3.08 mmol) to yield 0.74 g (59%) of a pale-orange solid. M.p. 140°C. Anal. Calc. for $C_{18}H_{27}ClNHo$ (457.80 g mol^{-1}): C, 47.23; H, 5.94; N, 3.06. Found: C, 46.88; H, 6.16; N, 2.97. MS (260°C, ^{165}Ho) *m*/*z*(%) 457 (30) $[M]^+$, 336 (100) $[M\text{-}C_5HMe_4]^+$, 321 (5) $[M\text{-}C_5H_4C_2H_4NMe_2]^+$, 58 (99) $[CH_2NMe_2]^+$.

3.2.5. Chloro{(dimethylaminoethyl)cyclopentadienyl}tetramethylcyclopentadienyl lutetium (5)

Compound **5** was prepared analogously to **1** from $LuCl_3(THF)_3$ (0.88 g, 1.77 mmol), (dimethylaminoethyl)cyclopentadienyl potassium (0.31 g, 1.77

mmol) and tetramethylcyclopentadienyl sodium (0.25 g, 1.77 mmol) to yield 0.47 g (57%) of a light-yellow solid. M.p. 210°C. Anal. Calc. for $\mathrm{C_{18}H_{27}ClNLu}$ (467.84 g mol^{-1}): C, 46.21; H, 5.82; N, 2.99. Found: C, 46.45; H, 6.03; N, 2.84. ^{1}H-NMR (200 MHz, $\mathrm{C_6D_6}$) δ (ppm) 6.55 (m, 1H, $\mathrm{C_5}H_4$), 6.12 (m, 1H, $\mathrm{C_5}H_4$), 5.79 (m, 1H, $\mathrm{C_5}H_4$), 5.31 (m, 1H, $\mathrm{C_5}H_4$), 4.97 (s, 1H, $\mathrm{C_5Me_4}H$), 3.09 (m, 1H, $\mathrm{CH_2C}H_2\mathrm{N(CH_3)_2}$), 2.25 (s, 3H, $\mathrm{C_5(C}H_3\mathrm{)_4H}$), 2.20 (m, 1H, $\mathrm{C}H_2\mathrm{CH_2N(CH_3)_2}$) 2.053 (s, 3H, $\mathrm{C_5(C}H_3\mathrm{)_4H}$), 2.047, (s, 3H, $\mathrm{C_5(C}H_3\mathrm{)_4H}$), 2.04 (s, 3H, $\mathrm{C_5(C}H_3\mathrm{)_4H}$), 2.00 (m, 1H, $\mathrm{C}H_2\mathrm{CH_2N(CH_3)_2}$), 1.80 ($\mathrm{s_{br}}$, 6H, $\mathrm{N(CH_3)_2}$), 1.55 (m, 1H, $\mathrm{CH_2C}H_2\mathrm{N(CH_3)_2}$). ^{13}C-NMR (50.32 MHz, $\mathrm{C_6D_6}$) δ (ppm) 126.16 (^{q}C), 121.26 (^{q}C), 120.40 (^{q}C), 118.27 (^{q}C), 116.02 (^{q}C), 115.28 ($C_5\mathrm{H}$), 112.21 ($C_5\mathrm{H}$), 110.65 ($C_5\mathrm{H}$), 108.80 ($C_5\mathrm{H}$), 108.12 ($C_5\mathrm{H}$), 66.52 ($\mathrm{Me_2N}C\mathrm{H_2}$), 49.55 ($\mathrm{N(}C\mathrm{H_3)_2}$), 43.41 ($\mathrm{N(}C\mathrm{H_3)_2}$), 25.32 ($C\mathrm{H_2Cp}$), 13.46 ($\mathrm{C_5(}C\mathrm{H_3)_4}$), 13.46 ($\mathrm{C_5(}C\mathrm{H_3)_4}$), 12.61 ($\mathrm{C_5(}C\mathrm{H_3)_4}$), 11.71 ($\mathrm{C_5(}C\mathrm{H_3)_4}$). MS (140°C, ^{175}Lu) *m*/*z*(%) 467 (28) [M]$^+$, 346 (100) [M-$\mathrm{C_5HMe_4}$]$^+$, 331 (5) [M-$\mathrm{C_5H_4C_2H_4NMe_2}$]$^+$, 58 (84) [$\mathrm{CH_2NMe_2}$]$^+$.

3.2.6. *Chloro{(dimethylaminoethyl)cyclopentadienyl}pentamethylcyclopentadienyl lutetium (**6**)*

A suspension of $\mathrm{LuCl_3}$ (0.57 g, 2.03 mmol) in 30 ml THF was treated first with (dimethylaminoethyl)cyclopentadienyl potassium (0.36 g, 2.03 mmol) and after 5 min with pentamethylcyclopentadienyl sodium (0.32 g, 2.03 mmol). The reaction mixture was stirred for 30 min. After removal of the solvent under vacuum, the residue was treated with 30 ml of $\mathrm{Et_2O}$. Filtration followed by removal of the solvent under vacuum yielded in 0.61 g (63%) of colourless crystals. M.p. 228°C. Anal. Calc. for $\mathrm{C_{19}H_9ClLuN}$ (481.87 g mol^{-1}): C, 47.36; H, 6.07; N, 2.91. Found: C, 46.97; H, 6.17; N, 2.82. ^{1}H-NMR (200 MHz, $\mathrm{C_6D_6}$) δ (ppm) 6.56 (m, 1H, $\mathrm{C_5}H_4$), 6.19 (m, 1H, $\mathrm{C_5}H_4$), 5.74 (m, 1H, $\mathrm{C_5}H_4$), 5.26 (m, 1H, $\mathrm{C_5}H_4$), 3.24 (m, 1H, $\mathrm{C}H_2\mathrm{CH_2}$), 2.24 (m, 1H, $\mathrm{CH_2C}H_2$), 2.08 (s, 3H, $\mathrm{N(C}H_3\mathrm{)_2}$), 2.00 (s, 15H, $\mathrm{C_5(C}H_3\mathrm{)_5}$), 1.99 (m, 1H, $\mathrm{C}H_2\mathrm{CH_2}$), 1.62 (m, 1H, $\mathrm{CH_2C}H_2$), 1.54 (s, 3H, $\mathrm{N(C}H_3\mathrm{)_2}$). ^{13}C-NMR (50.32 MHz, $\mathrm{C_6D_6}$) δ (ppm) 125.76 (^{q}C), 117.85 (^{q}C), 115.85 ($C_5\mathrm{H_4}$), 112.74 ($C_5\mathrm{H_4}$), 108.56 ($C_5\mathrm{H_4}$), 107.58 ($C_5\mathrm{H_4}$), 66.84 ($\mathrm{Me_2N}C\mathrm{H_2}$), 49.02 ($\mathrm{N(}C\mathrm{H_3)_2}$), 42.06 ($\mathrm{N(}C\mathrm{H_3)_2}$), 25.31 ($\mathrm{Cp}C\mathrm{H_2}$), 12.06 ($\mathrm{C_5(}C\mathrm{H_3)_5}$). MS (140°C, ^{175}Lu) *m*/*z*(%) 481 (29) [M]$^+$, 446 (3) [MCl]$^+$, 346 (100) [M-Cp*]$^+$, 58 (50) [$\mathrm{CH_2NMe_2}$]$^+$.

3.3. *Organolanthanide alkyls (C_5RMe_4)($C_5H_4CH_2CH_2NMe_2$)LnR′ (R = H, R′ = Me; R = Me, R′ = CH_2SiMe_3, $CH(SiMe_3)_2$)*

*{(Dimethylaminoethyl)cyclopentadienyl}(methyl)tetramethylcyclopentadienyl scandium (**7**)*

A stirred suspension of **1** (0.43 g, 1.27 mmol) in 30 ml of $\mathrm{Et_2O}$ was treated dropwise with 0.80 ml (1.27 mmol) of methyl lithium (1.60 M in $\mathrm{Et_2O}$). The mixture was stirred at r.t. for 12 h. The clear solution was decantated and the solvent was removed under vacuum. The remaining **7** was washed with 5 ml of hexane. Drying under vacuum yielded 0.36 g (89%) of a colourless solid. Single crystals were obtained by recrystallization from $\mathrm{Et_2O}$ at 0°C. M.p. 127°C. Anal. Calc. for $\mathrm{C_{19}H_{30}NSc}$ (317.41 g mol^{-1}): C, 71.90; H, 9.53; N, 4.41. Found: C, 71.62; H, 9.30; N, 4.74. ^{1}H-NMR (200 MHz, $\mathrm{C_6D_6}$) δ (ppm) 6.31 (m, 1H, $\mathrm{C_5}H$), 6.26 (m, 1H, $\mathrm{C_5}H$), 6.18 (m, 1H, $\mathrm{C_5}H$), 6.13 (m, 1H, $\mathrm{C_5}H$), 5.28 (m, 1H, $\mathrm{C_5}H$), 3.20 (m, 1H, $\mathrm{C}H_2\mathrm{C}H_2$), 2.90 (m, 1H, $\mathrm{C}H_2\mathrm{C}H_2$), 2.40 (s, 3H, $\mathrm{C}H_3$), 2.33 (s, 3H, $\mathrm{C}H_3$), 2.31 (s, 3H, $\mathrm{C}H_3$), 2.25 (m, 3H, $\mathrm{C}H_3$), 2.18 (s, 3H, $\mathrm{C}H_3$), 2.12 (m, 1H, $\mathrm{C}H_2\mathrm{C}H_2$), 2.02 (s, 3H, $\mathrm{C}H_3$), 1.84 (m, 1H, $\mathrm{C}H_2\mathrm{C}H_2$), −0.49 (s, 3H, $\mathrm{ScC}H_3$). MS (25°C, ^{45}Sc) *m*/*z*(%) 317 (1) [M]$^+$, 302 (100) [M-$\mathrm{CH_3}$]$^+$, 58 (43) [$\mathrm{CH_2NMe_2}$]$^+$.

3.3.2. *{(Dimethylaminoethyl)cyclopentadienyl}(methyl)tetramethylcyclopentadienyl neodymium (**8**)*

Compound **8** was prepared analogously to **7** from **2** (0.79 g, 1.78 mmol) and 0.99 ml (1.79 mmol) of methyl lithium (1.81 M in $\mathrm{Et_2O}$) to yield 0.75 g (99%) of a blue solid. M.p. 95°C. Anal. Calc. for $\mathrm{C_{19}H_{30}NNd}$ (416.69 g mol^{-1}): C, 54.77; H, 7.26; N, 3.36. Found: C, 55.03; H, 7.33; N, 3.24. MS (180°C, ^{142}Nd) *m*/*z*(%) 414 (50) [M]$^+$, 399 (7) [M-$\mathrm{CH_3}$]$^+$, 278 (4) [M-$\mathrm{CH_3}$–$\mathrm{C_5HMe_4}$]$^+$, 263 (6) [M-$\mathrm{CH_3}$–$\mathrm{C_5H_4CH_2CH_2NMe_2}$]$^+$, 58 (100) [$\mathrm{CH_2NMe_2}$]$^+$.

3.3.3. *{(Dimethylaminoethyl)cyclopentadienyl}(methyl)tetramethylcyclopentadienyl samarium (**9**)*

Compound **9** was prepared analogously to **7** from **3** (0.30 g, 0.68 mmol) and 0.89 ml (0.68 mmol) of methyl lithium (0.76 M in $\mathrm{Et_2O}$) to yield 0.21 g (74%) of a yellow solid. M.p. 125°C. Anal. Calc. for $\mathrm{C_{19}H_{30}NSm}$ (422.81 g mol^{-1}): C, 53.97; H, 7.15; N, 3.31. Found: C, 53.54; H, 7.35; N, 3.62. MS (260°C, ^{152}Sm) *m*/*z*(%) 424 (10) [M]$^+$, 409 (2) [M-$\mathrm{CH_3}$]$^+$, 288 (6) [M-$\mathrm{CH_3}$–$\mathrm{C_5HMe_4}$]$^+$, 273 (2) [M-$\mathrm{CH_3}$–$\mathrm{C_5H_4CH_2CH_2NMe_2}$]$^+$, 58 (100) [$\mathrm{CH_2NMe_2}$]$^+$.

3.3.4. *{(Dimethylaminoethyl)cyclopentadienyl}(methyl)tetramethylcyclopentadienyl holmium (**10**)*

Compound **10** was prepared analogously to **7** from **4** (0.30 g, 0.68 mmol) and 0.89 ml (0.68 mmol) of methyllithium (0.76 M in $\mathrm{Et_2O}$) to yield 0.15 g (55%) of a yellow solid. M.p. 90°C. Anal. Calc. for $\mathrm{C_{19}H_{30}NHo}$ (437.38 g mol^{-1}): C, 52.18; H, 6.91; N, 3.20. Found: C, 53.54; H, 7.35; N, 3.62. MS (90°C, ^{165}Ho) *m*/*z*(%) 437 (2) [M]$^+$, 422 (2) [M-$\mathrm{CH_3}$]$^+$, 301 286 (2) [M-$\mathrm{CH_3}$–$\mathrm{C_5H_4CH_2CH_2NMe_2}$]$^+$, 58 (100) [$\mathrm{CH_2\ NMe_2}$]$^+$.

3.3.5. {(Dimethylaminoethyl)cyclopentadienyl}(methyl)tetramethylcyclopentadienyl lutetium (**11**)

Compound **11** was prepared analogously to **7** from **5** (1.16 g, 2.45 mmol) and 1.35 ml (2.44 mmol) of methyl lithium (1.81 M in Et_2O) to yield 0.93 g (84%) of a colourless solid. M.p. 112°C. Anal. Calc. for $C_{19}H_{30}NLu$ (447.42 g mol^{-1}): C, 51.00; H, 6.76; N, 3.13. Found: C, 53.54; H, 7.35; N, 3.62. ^{1}H-NMR (200 MHz, C_5D_5N) δ (ppm) 6.11 (dd, 2H $^{3,4}J$(H, H) = 2.6 Hz, C_5H_4), 5.89 (dd, 2H, $^{3,4}J$(H, H) = 2.6 Hz, C_5H_4), 5.34 (s, 1H, C_5Me_4H), 2.53 (m, 2H, CH_2CH_2), 2.19 (m, 2H, CH_2CH_2), 2.17 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 1.95 (s, 6H, CH_3), −0.61 (s, 3H, $LuCH_3$). ^{13}C-NMR (50.32 MHz, C_5D_5N) δ (ppm) 124.71 (^qC), 116.95 (^qC), 116.02 (^qC), 109.98 (C_5H), 108.77 (C_5H), 108.56 (C_5H), 65.04 (Me_2NCH_2), 44.98 ($N(CH_3)_2$), 25.90 ($CpCH_2$), 20.10 ($LuCH_3$), 13.28 ($C_5(CH_3)_4$), 11.38 ($C_5(CH_3)_4$). MS (40°C, ^{175}Lu) m/z(%) 447 (3) $[M]^+$, 432 (81) $[M\text{-}CH_3]^+$, 311 (1) $[M\text{-}CH_3\text{–}C_5HMe_4]^+$, 296 (2) $[M\text{-}CH_3\text{–}C_5H_4CH_2CH_2NMe_2]^+$, 58 (100) $[CH_2NMe_2]^+$.

3.3.6. {(Dimethylaminoethyl)cyclopentadienyl}pentamethylcyclopentadienyl(trimethylsilylmethyl) lutetium (**12**)

At r.t. a solution of trimethylsilylmethyl lithium (0.12 g, 1.25 mmol) in 30 ml of toluene was treated with **6** (0.60 g, 1.25 mmol). The reaction mixture was stirred for 12 h. Then the volatile materials were removed under reduced pressure. The resulting solid was extracted with hexane (30 ml). After filtration the volume of the hexane extract was reduced to ca. 15 ml. Cooling to −30°C yielded colorless crystals which were filtered off and dried under reduced pressure. Yield: 0.36 g (54%). M.p. 251°C, Anal. Calc. for $C_{23}H_{40}LuNSi$ (533.63 g mol^{-1}): C, 51.77; H, 7.55; N, 2.62. Found: C, 51.55; H, 8.08; N, 2.41. ^{1}H-NMR (200 MHz, C_6D_6) δ (ppm) 6.60 (m, 1H, C_5H_4), 5.93 (m, 1H, C_5H_4), 5.85(m, 1H, C_5H_4), 5.45 (m, 1H, C_5H_4), 2.72 (m, 1H, CH_2CH_2), 2.25 (m, 1H, CH_2CH_2),), 2.03 (m, 1H, CH_2CH_2), 1.95 (s, 15H, C_5CH_3), 1.65 (s, 3H, $N(CH_3)_2$), 1.51 (m, 1H, CH_2CH_2), 1.47 (s, 3H, $N(CH_3)_2$), 0.45 (s, 18H, $CH_2(Si(CH_3)_3)$, −0.73 (d, 1H, ^{2}J(H, H) = 10.3 Hz, $LuCH_2Si(CH_3)_3$), −1.55 (d, 1H, ^2J(H, H) = 10.3 Hz, $LuCH_2Si(CH_3)_3$). ^{13}C-NMR (50.32 MHz, C_6D_6) δ (ppm) 125.05 (^qC), 116.35 (^qC), 110.40 (C_5H), 119.98 (C_5H), 109.93 (C_5H), 107.29 (C_5H), 67.25 (Me_2NCH_2), 48.14 ($N(CH_3)_2$), 42 79 ($N(CH_3)_2$), 27.88 ($CH_2Si(CH_3)_3$), 25.37 ($CpCH_2$), 12.33 ($C_5(CH_3)_5$), 5.60 ($CH_2Si(CH_3)_3$). MS (240°C, ^{175}Lu) m/z(%) 460 (< 1) $[M\text{-}SiMe_3]^+$, 446 (100) $[M\text{-}CH_2Si(CH_3)_3]^+$, 58 (20) $[CH_2NMe_2]^+$.

4. X-ray structure determination of 1 and 7

Crystal data and other details of the structural determination are collected in Table 1. Data collections were carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a PC fitted with a low-temperature equipment. The cell parameters were obtained from a least-squares treatment of the SET4 setting angles of 25 reflections in the range of $18.4° < 2\theta < 27.6°$ (**1**) and $19.1° < 2\theta < 30.0°$ (**7**). Data were collected at 240(2) K. Both raw data were corrected for Lorentz, polarization and absorption effects [23]. The structures were solved with three-dimensional Patterson

Table 1
Crystal data and structure refinement for **1** and **7**

	1	**7**
Empirical formula	$C_{18}H_{27}ClNSc$	$C_{19}H_{30}NSc$
Formula weight (g mol^{-1})	337.82	317.40
Temperature (K)	240(2)	240(2)
Radiation (Mo–K$_\alpha$) (Å)	0.71069	0.71069
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)
a (Å)	14.740(2)	14.787(3)
b (Å)	8.517(2)	8.5719(10)
c (Å)	15.702(3)	15.826(4)
β (°)	117.99(2)	117.95(2)
V (Å^3)	1740.7(6)	1772.1(6)
Z	4	4
D_{calc} (g cm^{-3})	1.289	1.190
Diffractometer	Enraf-Nonius CAD-4	Enraf- Nonius CAD-4
Absorption coefficient (mm^{-1})	0.553	0.393
F(000)	708	676
Crystal size (mm^3)	$0.13 \times 0.36 \times 0.43$	$0.23 \times 0.36 \times 0.53$
Theta range for data collection	$1° < 2\theta < 50°$	$1° < 2\theta < 50°$
Index ranges	$0 \le h \le 17$, $0 \le k \le 10$, $-18 \le l \le 18$	$0 \le h \le 17$, $0 \le k \le 10$, $-18 \le l \le 18$
Scan technique	ω-2θ	ω-2θ
Scan angle	(0.78 + 0.35 tan θ)°	$(0.74 + 0.35 \tan \theta)°$
Aperture (mm)	2.1	2.1
Intensity variation	none	none
Reflections collected	3245	3308
Independent reflections	3036 [R_{int} = 0.0190]	3100 [R_{int} = 0.0230]
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2985/0/190	3045/0/190
Final R indices [$I > 2\sigma(I)$]	R_1 ^{a} = 0.0535 wR_2 ^{b} = 0.1591	R_1 ^{a} = 0.0443 wR_2 ^{b} = 0.1272
R indices (all data)	R_1 = 0.0892 wR_2 = 0.2470	R_1 = 0.0635 wR_2 = 0.188
Goodness-of-fit on F^2 ^{c}	1.361	1.093
Largest diff. peak and hole (eÅ^{-3})	max. 0.706, min. −0.480	max. 0.561, min. −0.379

^{a} $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(1|F_o|)$; ^{b} $wR_2 = [\Sigma\, w(|F_o| - |F_c|^2/\Sigma\, w|F_o|^2]^{1/2}$.
^{c} GOOF $= [\Sigma\, w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$.

synthesis (SHELXS-86) [24] and refined by full-matrix least-squares using (SHELXL-93) [25], which minimizes R_{w2} (based on F^2). All non-hydrogen atoms were refined anisotropicaly. Hydrogen atoms were calculated in idealized positions (C–H 0.96 Å, $U_{iso} = 0.08$ Å^2). Scattering factors were taken from [26–28]. All calculations were performed on an IBM Risk 6000 computer. All refinements were done with the SHELXL-93 [25] program system. Full details of the crystal structure determination have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-408330 (1) and CSD408331 (7), respectively.

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