Preliminary communication

Organometallic compounds of the lanthanides CXV [1]. Donor substituted chiral *ansa*-lanthanidocenes: synthesis of dimethyl(dimethylaminoethylcyclopentadienyl)(tetramethylcyclopentadienyl)silane dipotassium and of some chiral *ansa*-metallocene derivatives of Y, Sm, Ho, Er and Lu [2]

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Abstract

Reaction of Me_2SiCl_2 with $[C_5HMe_4]Na$ in tetrahydrofuran (THF) followed by treatment with $[C_5H_4CH_2CH_2NMe_2]Na$ gives $Me_2Si(C_5HMe_4)(C_5H_4CH_2CH_2NMe_2)$, which reacts with KH to yield the dipotassium salt $K_2[Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2NMe_2)]$ (1). The reaction of $YCl_3(THF)_3$ and the lanthanide trichlorides $LnCl_3(THF)_n$ (Ln = Sm, Ho, Er, Lu) with 1 in THF results in the yttrium complex and the lanthanide complexes $[Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2NMe_2)]LnCl$ [Ln = Y (2), Sm (3), Ho (4), Er (5), Lu (6)]. The complexes 2, 4 and 6 react with $Li[CH_3]$ in ether to yield the chiral monomethyl compounds $[Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2NMe_2)]LnMe$ [Ln = Y (7), Ho (8), Lu (9)]. The new complexes were characterized by elemental analysis, MS and NMR spectroscopy as well as 2 and 9 by single crystal X-ray structure analysis. © 1997 Elsevier Science S.A.

Keywords: *ansa*-Lanthanidocene complexes; Yttrium; Samarium; Holmium; Erbium; Lutetium; X-ray structure

1. Introduction

In recent years cyclopentadienyl ligands with an additional donor functionality have attracted increasing interest in the organometallic chemistry of transition metals and of the lanthanides [2–6]. Such bidentate ligands coordinate to the metal with the cyclopentadienyl ring and the intramolecular donor atom, increasing the stability of highly reactive complexes and intermediates like alkyl and hydride derivatives of the lanthanides. Several cyclopentadienyl complexes of the lanthanides bear high potential as catalysts for the polymerization of olefins [7,8]. Within this research area, recent investigations focus mainly on the synthesis of polymers with a high grade of tacticity. In consequence, the interest in synthesizing chiral metallocenes increases [9,10]. Modern catalysts for the polymerization of propylene are based on Group 4 *ansa*-metallocenes in the presence of large amounts of alumoxane (MAO) as cocatalyst. Bercaw and coworkers [11] demonstrated that an *ansa*-yttriocene hydride does the same job without MAO. Therefore, chiral *ansa*-metallocene complexes of the Group 3 metals [12] and of the lanthanides seem to be suitable as polymerization catalysts for α-olefins without the necessity of using MAO.

Chiral metallocenes of the lanthanides have been investigated by Marks and coworkers [12–14] using chiral substituents at the cyclopentadienyl ring. Recently, we presented lanthanidocene complexes with chirality at the side chain [15]. In this paper, we present chiral lanthanidocene complexes containing the lanthanide metal as the center of chirality in a pseudo-tetrahedral environment with four different ligands.

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[1] For Part CXIV, see Ref. [1].
[2] Dedicated to the memory of Professor Yu.T. Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

2. Results and discussion

2.1. Ligand synthesis

Dichlorodimethylsilane reacts via two salt elimination steps, firstly with tetramethylcyclopentadienyl sodium [16] to yield chloro(tetramethylcyclopentadienyl)dimethylsilane, which after treatment with (N,N-dimethylaminoethyl)cyclopentadienyl sodium [17] gives dimethyl(dimethylaminoethylcyclopentadienyl)(tetramethylcyclopentadienyl)silane. This silane is deprotonated twice, using two equivalents of potassium hydride in tetrahydrofuran to form the dipotassium salt 1 containing a tridentate donor functionalized dicyclopentadienyl dianion (Scheme 1).

Dimethyl{(N, N-dimethylaminoethyl)cyclopentadienyl}(tetramethylcyclopentadienyl)-silane dipotassium (1): Me_2SiCl_2 (3.62 g, 28.04 mmol) was added to a solution of $Na[C_5HMe_4]$ (4.04 g, 28.02 mmol) in 50 ml of THF. The pale yellow suspension was stirred for 16 h. Both solvent and $Me_2(C_5HMe_4)SiCl$ were condensed into a new flask. After addition of $Na[C_5H_4CH_2CH_2NMe_2]$ (4.46 g, 28.01 mmol), the reaction mixture was stirred for an additional 12 h. The solvent was removed under vacuum and the product extracted with 50 ml of hexane. After filtration and removal of the solvent, 7.33 g (83%) of $Me_2Si(C_5HMe_4)(C_5H_4CH_2CH_2NMe_2)$ was obtained as a yellow oily liquid. It was slowly given to a suspension of KH (1.86 g, 46.47 mmol) in 50 ml of THF. Stirring for 12 h led to an orange solution. The solvent was removed under vacuum and the residue washed with 50 ml of hexane. After drying under vacuum, 6.74 g (61%) of 1 was obtained as a colorless solid. M.p. 181 °C. Anal. Found: C, 60.91; H, 8.24; N, 3.54. $C_{20}H_{31}K_2NSi_2$ (391.75 g mol^{-1}) Calc.: C, 61.32; H, 7.98; N, 3.58%. MS (80 °C) m/z (%) 315 (4, $[M - 2K + 2H]^+$), 194 (22, $[M - HC_5Me_4 - 2K + 2H]^+$), 58 (100, $[CH_2NMe_2]^+$).

2.2. Organolanthanide chlorides {Me$_2$Si(C$_5$Me$_4$)-(C$_5$H$_3$CH$_2$CH$_2$NMe$_2$)}LnCl

The anhydrous lanthanide trichlorides $HoCl_3$ and $ErCl_3$ as well as the tetrahydrofuran adducts $YCl_3(THF)_3$, $SmCl_3(THF)_{1.77}$ and $LuCl_3(THF)_{2.7}$ react with 1 in THF to form the corresponding metallocenes {Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$CH$_2$CH$_2$NMe$_2$)}LnCl (2-6) in up to 60% yield after washing the crude products with small amounts of hexane. They are soluble in THF and arenes (benzene, toluene) and less soluble in ether (Scheme 2).

Chloro(dimethyl{(N, N-dimethylaminoethyl)cyclopentadienyl}(tetramethylcyclopentadienyl)silane)yttrium (2): a suspension of $YCl_3(THF)_3$ (1.11 g, 2.94 mmol) in 50 ml of THF was treated with 1 (1.31 g, 3.09 mmol).

The mixture was stirred at room temperature for 12 h. The clear pale yellow solution was decanted from the solid. The solvent was removed and the residue washed twice with hexane (5 ml). 2 was dried under vacuum to yield 0.60 g (48%) of a colorless solid. Single crystals were obtained by recrystallization from toluene at −25 °C. M.p. 181 °C. Anal. Found: C, 55.24; H, 7.11; N, 3.88. $C_{20}H_{31}ClNSiY$ (437.92 g mol^{-1}) Calc.: C, 54.86; H, 7.14; N, 3.20%. ^{1}H NMR (200 MHz, C_6D_6): δ (ppm) 6.62 (dd, $^{3,4}J$(H,H) = 2.5 Hz, 1H, C_5H_3), 6.02 (dd, $^{3,4}J$(H,H) = 2.5 Hz, 1H, C_5H_3), 5.35 (dd, $^{3,4}J$(H,H) = 2.5 Hz, 1H, C_5H_3), 2.92 (m, 1H, CH_2CH_2), 2.32 (m, 1H, CH_2CH_2), 2.25 (s, 3H, $C_5(CH_3)_4$), 2.08-2.15 (m, 3H, $N(CH_3)_2$), 2.06 (s, 3H, $C_5(CH_3)_4$), 2.03 (m, 1H, CH_2CH_2), 1.91 (s, 3H, $C_5(CH_3)_4$), 1.65 (s, 3H, $C_5(CH_3)_4$), 1.48-1.57 (m, 4H, $N(CH_3)_2$, CH_2CH_2), 0.81 (s, 3H, $Si(CH_3)_2$), 0.70 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (50.34 MHz, C_6D_6): δ (ppm) 133.74 (qC_5(Cp)), 126.22 (qC_5(Cp)), 125.92 (qC_5(Cp)), 123.55 (qC_5(Cp)), 119.80 (qC_5(Cp)), 116.27 (C_5H_3), 115.92 (C_5H_3), 113.82 (C_5H_3), 111.77 (qC_5(Cp)), 105.21 (qC_5(Cp)), 67.41 (CH_2NMe_2), 45.57 (m, $N(CH_3)_2$), 25.58 (CpCH$_2$), 14.43 ($C_5(CH_3)_4$), 13.89 ($C_5(CH_3)_4$), 11.98 ($C_5(CH_3)_4$), 11.35 ($C_5(CH_3)_4$), 1.05 (Si(CH$_3$)$_2$), −0.28 (Si(CH$_3$)$_2$). MS (25 °C, ^{89}Y) m/z (%) 437 (100, $[M]^+$), 422 (2, $[M - CH_3]^+$), 402 (9, $[M - Ci]^+$), 379 (4, $[M - CH_2NMe_2]^+$), 302 (2, $[M - Me_2NEtC_5H_3]^+$.

3 was prepared analogously to 2 from $SmCl_3(THF)_{1.77}$ (1.52 g, 3.96 mmol), 1 (1.52 g, 3.96 mmol) in 50 ml of THF to yield 0.75 g (38%) of an

Scheme 1.

Ln = Y (**2**, x = 3), Sm (**3**, x = 1.77), Ho (**4**, x = 0), Er (**5**, x = 0), Lu (**6**, x = 2.7)
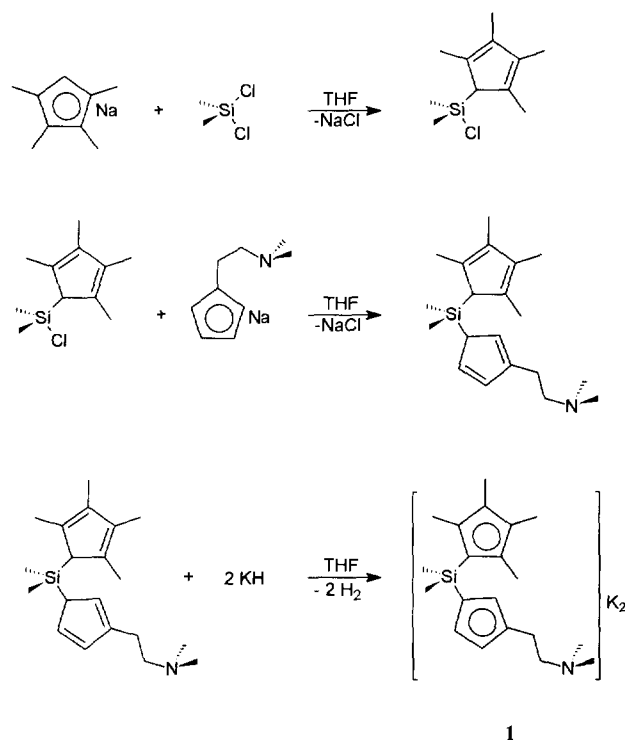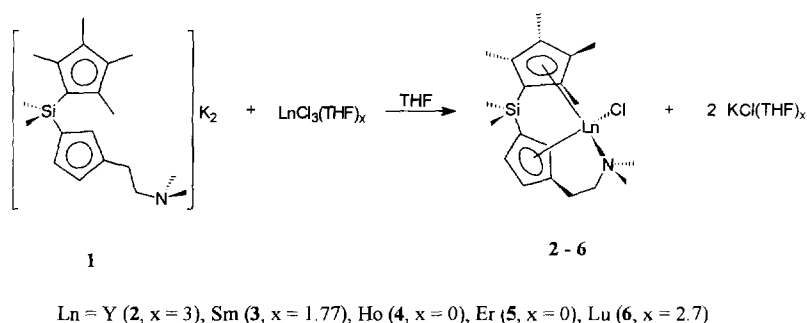
Scheme 2.

orange solid. M.p. 117 °C. Anal. Found: C, 47.77; H, 5.88; N, 2.61. $C_{20}H_{31}ClNSiSm$ (499.37 g mol^{-1}) Calc.: C, 48.10; H, 6.26; N, 2.80%. MS (140 °C, ^{152}Sm) m/z (%) 500 (5, [M]$^+$), 465 (1, [M − Cl]$^+$), 442 (0.3, [M − CH$_3$NMe$_2$]$^+$), 365 (0.4, [M − C$_5$H$_4$C$_2$H$_4$NMe$_2$]$^+$, 58 (100, [CH$_2$NMe$_2$]$^+$).

4 was prepared analogously to **2** from HoCl$_3$ (0.77 g, 2.43 mmol), **1** (0.95 g, 2.43 mmol) in 50 ml of THF to yield 0.61 g (52%) of a pale orange solid. M.p. 168 °C. Anal. Found: C, 46.59; H, 6.23; N, 2.82. $C_{20}H_{31}ClHoNSi$ (513.94 g mol^{-1}) Calc.: C, 46.74; H, 6.08; N, 2.73%. MS (280 °C, ^{168}Ho) m/z (%) 513 (6, [M]$^+$), 478 (1, [M − Cl]$^+$), 255 (1, [M − Me$_2$SiCp^{*H} − HNMe$_2$]$^+$), 58 (100, [Me$_2$NCH$_2$]$^+$).

5 was prepared analogously to **2** from ErCl$_3$ (0.38 g, 1.39 mmol), **1** (0.54 g, 1.39 mmol) in 50 ml of THF to yield 0.52 g (73%) of a pale pink solid. M.p. 140 °C. Anal. Found: C, 46.37; H, 6.12; N, 2.65. $C_{20}H_{31}ClErNSi$ (516.27 g mol^{-1}) Calc.: C, 46.53; H, 6.05; N, 2.71%. MS (220 °C, ^{168}Er) m/z (%) 516 (22, [M]$^+$), 481 (1, [M − Cl]$^+$), 258 (1, [M − Me$_2$SiCp^{*H} − HNMe$_2$]$^+$), 58 (100, [Me$_2$NCH$_2$]$^+$).

6 was prepared analogously to **2** from LuCl$_3$(THF)$_{2.7}$ (0.60 g, 1.25 mmol), **1** (0.49 g, 1.25 mmol) in 50 ml of THF to yield 0.29 g (45%) of a colorless solid. M.p. 136 °C. Anal. Found: C, 45.47; H, 5.45; N, 3.13. $C_{20}H_{31}ClLuNSi$ (523.98 g mol^{-1}) Calc.: C, 45.85; H, 5.96; N, 2.67%. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ (ppm) −6.62 (dd, 1H, C$_5$H$_3$), 5.98 (dd, 1H, C$_5$H$_3$), 5.32 (dd, C$_5$H$_3$), 2.9–3.1 (m, 1H, CH$_2$CH$_2$), 2.2–2.3 (m, 1H, CH$_2$CH$_2$), 2.24 (s, 3H, C$_5$(CH$_3$)$_4$), 2.06 (s, 3H, N(CH$_3$)$_2$), 1.96 (s, 3H, C$_5$(CH$_3$)$_4$), 1.93 (s, 3H, N(CH$_3$)$_2$), 1.66 (s, 3H, C$_5$(CH$_3$)$_4$), 1.47 (s, 3H, C$_5$(CH$_3$)$_4$), 0.81 (s, 3H, Si(CH$_3$)$_2$), 0.70 (s, 3H, Si(CH$_3$)2). ^{13}C NMR (C$_6$D$_6$, 50.34 MHz): δ (ppm) 132.36 (qC(Cp)), 125.92 (qC(Cp)), 124.40 (qC(Cp)), 122.76 (q(C(Cp)), 118.29 (qC(Cp)), 116.85 (C$_5$H$_3$), 114.38 (C$_5$H$_3$), 111.80 (C$_5$H$_3$), 111.56 (qC(Cp)), 105.24 (qC(Cp)), 68.34 (Me$_2$NCH$_2$CH$_2$), 48.59 (N(CH$_3$)$_2$), 42.44 (N(CH$_3$)$_2$), 25.29 (Me$_2$NCH$_2$CH$_2$), 14.51 (C$_5$(CH$_3$)$_4$), 14.04 (C$_5$(CH$_3$)$_4$), 12.12 (C$_5$(CH$_3$)$_4$), 11.70 (C$_5$(CH$_3$)$_4$), 0.95 (Si(CH$_3$)$_2$),

−0.34 (Si(CH$_3$)$_2$). MS (140 °C, ^{175}Lu) m/z (%) 523 (100, [M]$^+$), 508 (0.6, [M − CH$_3$]$^+$), 487 (0.8, [M − Cl − H]$^+$), 58 (100, [CH$_2$NMe$_2$]$^+$).

In comparison with unbridged, unfunctionalized metallocenes of the lanthanides, **2** to **6** are more inert against air and moisture because of their tridentate ligand system. It takes some minutes before decomposition in air becomes noticeable. Elemental analyses and NMR spectra show that there is neither additional coordination by solvent molecules nor a chlorine-bridged lithium chloride adduct present. Mass spectra show the extreme stability at high temperatures under EI conditions; there is no tendency to extensive fragmentation. The molecular ion peak shows intensities up to 100%. A second fragment with high intensity corresponds to [CH$_2$NMe$_2$]$^+$, a typical fragment in (*N*,*N*-dimethylaminoethyl)cyclopentadienyl ligands. The lack of fragments with masses higher than the molecular ion is consistent with a monomeric formulation. Because of the nature of the ligand, the metallocene chlorides **2** to **6** are chiral. They are isolated as racemic mixtures of the enantiomers.

The X-ray structure determination of **2** shows four well-separated monomers in the unit cell, a racemic mixture of the two enantiomers. The structure of one molecule is shown in Fig. 1. This X-ray structure is in agreement with the NMR spectroscopic results. 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 yttrium atom is 8. The bond angles around the metal center are larger than in the related monomeric (C$_5$H$_4$CH$_2$CH$_2$OMe)$_2$YI [19] (O−Y−I 76.3°, 78.1(5)°; O−Y−Cp′ 92.7°, 92.6°). A comparison of the angle Cp1−Y−Cp2 of **2** (123.26(10)°) and [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$CH$_2$CH$_2$P^{t}Bu$_2$)Sc[CH(SiMe$_3$)$_2$] (128.1°), in which one cyclopentadienyl ring is substituted with a non-donating phosphorous atom [20], shows that the coordination of the donor atom induces a reduction of this angle. In the almost planar cyclopenta-
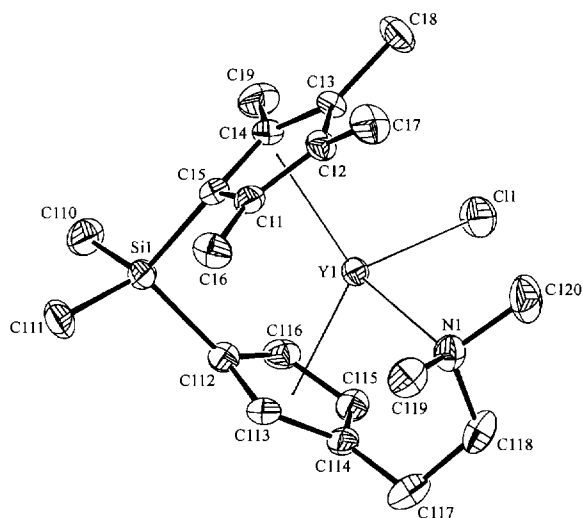
Fig. 1. ORTEP [18] plot of **2**. Selected bond lengths [Å] and angles [°]: Y–N 2.502(5), Y–Cl 2.572(2), Y–Cp1 2.347(3), Y–Cp2 2.319(3); N–Y–Cl 94.40(12), N–Y–Cp1 118.71(13), N–Y–Cp2 95.19(13), Cl–Y–Cp1 110.30(8), Cl–Y–Cp2 110.59(8), Cp1–Y–Cp2 123.26(10), C15–Si–C112 99.1(2). Cp1 and Cp2 define the centroid positions of the Cp rings C11–C15 and C112–C115 respectively.

dienyl ligands, the individual deviations of the silicon atoms out of their planes are $-0.547(9)$ Å (C_5H_4–Si) and $0.616(8)$ Å (Si–$C_5H_3CH_2CH_2NMe_2$).

2.3. Organolanthanide alkyls {Me₂Si(C₅Me₄)-(C₅H₃CH₂CH₂NMe₂)}LnMe

The monomeric organolanthanide chlorides **2**, **4** and **6** react with methyl lithium in diethyl ether to form the monomeric methyl derivatives **7**, **8** and **9**, which are some of the very few examples of monomeric cyclopentadienyllanthanide methyl complexes with terminal methyl groups bonded to the lanthanide metal containing no stabilizing ether ligands [21,22] (Scheme 3).

(Dimethyl{(N,N-dimethylaminoethyl)cyclopentadienyl}(tetramethylcyclopentadienyl)silane)(methyl)yttrium (**7**): to a stirred suspension of **2** (0.57 g, 1.30 mmol) in 30 ml of Et₂O was dropped slowly 0.80 ml (1.30 mmol) of MeLi (1.48 M in Et₂O). The mixture
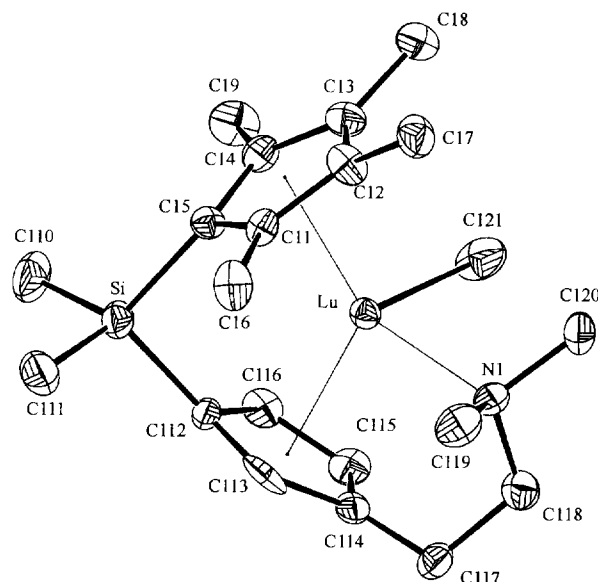

Fig. 2. ORTEP [18] plot of **9**. Selected bond lengths [Å] and angles [°]: Lu–C21 2.370(9), Lu–N 2.445(8), Lu–Cp1 2.321(4), Lu–Cp2 2.297(4); C121–Lu–N 92.9(3), N–Lu–Cp1 118.4(3), N–Lu–Cp2 97.2(3), C121–Lu–Cp1 110.7(3), C121–Lu–Cp2 108.6(3), Cp1–Lu–Cp2 124.2(2), C15–Si–C112 99.0(4). Cp1 and Cp2 define the centroid positions of the Cp rings C11–C15 and C112–C115 respectively.

was stirred at room temperature for an additional 12 h. The clear solution was decanted, the solvent removed in vacuum, and the remaining **7** washed with 2 ml of hexane. Drying under vacuum yielded 0.49 g (90%) of a colorless solid. M.p. 177 °C. Anal. Found: C, 60.16; H, 8.19; N, 3.25. $C_{21}H_{34}NSiY$ (417.50 g mol^{-1}) Calc.: C, 60.41; H, 8.21; N, 3.35%. ¹H NMR (200 MHz, C_6D_6): δ (ppm) 6.62 (dd, ^3J(H,H) = 2.5 Hz, 1H, C_5H_3), 6.02 (dd, ^3J(H,H) = 2.5 Hz, 1H, C_5H_3), 5.34 (dd, $^{3,4}J$(H,H) = 2.5 Hz, 1H, C_5H_3), 2.90 (m, 1H, CH_2CH_2), 2.45 (m, 1H, CH_2CH_2), 2.25 (s, 3H, N(CH_3)₂), 2.05 (s, 3H, $C_5(CH_3)_4$)), 2.01 (m, 1H, CH_2CH_2)), 2.04 (s, 3H, N(CH_3)₂), 1.91 (s, 3H, $C_5(CH_3)_4$)), 1.82 (s, 3H, $C_5(CH)_4$)), 1.45 (m, 1H, CH_2CH_2)), 1.65 (s, 3H, $C_5(CH_3)_4$), 0.81 (s, 3H, Si(CH_3)₂), 0.70 (s, 3H, Si(CH_3)₂), -0.72 (d, ^2J(H,Y) = 2.5 Hz, 3H, YCH_3).

2, 4, 6　　　　　　　**7, 8, 9**

Ln = Y (**2, 7**), Ho (**4, 8**), Lu (**6, 9**)
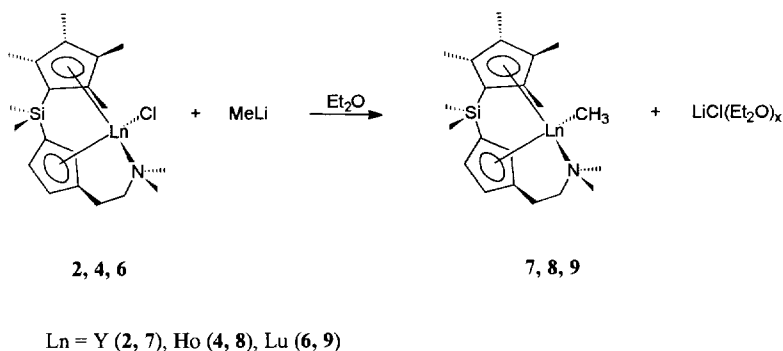
Scheme 3.

^{13}C NMR (pyridine-d_5, 50.34 MHz): δ (ppm) 131.24 (qC(Cp)), 123.47 (qC(Cp)), 121.39 (qC(Cp)), 120.27 (qC(Cp)), 118.62 (qC(Cp)), 114.51 (C_5H_3), 113.74 (C_5H_3), 113.37 (C_5H_3), 109.93 (q(CCp)), 102.06 (qC(Cp)), 65.43 (Me$_2$NCH$_2$$CH_2$), 45.52 (N(CH$_3$)$_2$), 44.45 (N($CH_3$)$_2$), 26.67 (Me$_2NCH_2CH_2$), 14.62 (Y$CH_3$, [1]$J$(Y,C) = 9.6 Hz), 13.96 (C$_5$(CH$_3$)$_4$), 13.77 (C$_5$(CH$_3$)$_4$), 11.15 (C$_5$(CH$_3$)$_4$), 10.96 (C$_5$(CH$_3$)$_4$), 0.64 (Si(CH$_3$)$_2$), 0.10 (Si(CH$_3$)$_2$). MS (240 °C, [89]Y) m/z (%) 417 (1, [M]$^+$), 402 (100, [M − CH$_3$]$^+$), 359 (48, [M − EtNMe$_2$]$^+$), 344 (14, [M − EtNMe$_2$ − CH$_3$]$^+$), 58 (100, [CH$_2$NMe$_2$]$^+$).

8 was prepared analogously to **7** from **4** (0.47 g, 1.25 mmol) and MeLi (0.7 ml, 1.04 mmol, 1.48 M in Et$_2$O) in 30 ml of Et$_2$O to yield 0.29 g (45%) of a light orange solid. M.p. 127 °C. Anal. Found: C, 50.89; H, 6.99; N, 2.86. C$_{20}$H$_{31}$ClHoNSi (493.52 g mol^{-1}) Calc.: C, 51.11; H, 6.94; N, 2.84%. MS (240 °C, [165]Ho) m/z

(%) 493 (1, [M]$^+$), 478 (100, [M − CH$_3$]$^+$), 435 (2, [M − EtNMe$_2$]$^+$), 420 (1, [M − EtNMe$_2$CH$_3$]$^+$), 58 (100, [CH$_2$NMe$_2$]$^+$).

9 was prepared analogously to **7** from **6** (0.62 g, 1.18 mmol) and MeLi (0.77 ml, 1.18 mmol, 1.48 M in Et$_2$O) in 30 ml of Et$_2$O to yield 0.43 g (73%) of a colorless solid. M.p. 164 °C. Anal. Found: C, 49.89; H, 6.32; N, 2.75. C$_{20}$H$_{31}$ClLuNSi (503.56 g mol^{-1}) Calc.: C, 50.09; H, 6.81; N, 2.78%. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ (ppm) 6.57 (dd, [3]J(H,H) = 2.5 Hz, 1H, C$_5$H$_3$), 5.82 (dd, [3]J(H,H) = 2.5 Hz, 1H, C$_5$H$_3$), 5.50 (dd, [3]J(H,H) = 2.5 Hz, 1H, C$_5$H$_3$), 2.64 (m, 1H, CH_2CH_2), 2.24 (m, 1H, CH_2CH_2), 2.17 (s, 3H, N(CH_3)$_2$), 2.02 (s, 3H, C$_5$(CH_3)$_4$), 2.01 (m, 1H, CH_2CH_2), 1.98 (s, 3H, N(CH_3)$_2$), 1.68 (s, 3H, C$_5$(CH_3)$_4$), 1.61 (s, 3H, C$_5$(CH_3)$_4$), 1.55 (m, 1H, CH_2CH_2), 1.40 (s, 3H, C$_5$(CH_3)$_4$), 0.85 (s, 3H, Si(CH_3)$_2$), 0.70 (s, 3H, Si(CH_3)$_2$), −0.67 (LuCH_3). ^{13}C NMR (C$_6$D$_6$,

Table 1
Crystal data and structure refinement for **2** and **9**

	2	9
Empirical formula	C$_{20}$H$_{31}$ClNSiY	C$_{21}$H$_{34}$LuNSi(C$_7$H$_8$)$_{0.5}$
Formula weight (g mol^{-1})	875.82	549.62
Crystal size (mm^3)	0.20 × 0.23 × 0.35	0.18 × 0.24 × 0.36
Temperature (K)	163(2)	163(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	8.6832(11)	13.459(3)
b (Å)	15.514(5)	8.423(2)
c (Å)	15.961(3)	21.469(5)
α (°)	77.06(2)	—
β (°)	88.86(2)	99.3(2)
γ (°)	88.54(2)	—
V (Å^3)	2094.6(8)	2402.0(9)
Z	2	4
Diffractometer	Enraf–Nonius CAD-4	
Radiation	Mo Kα 0.71069	
Density calc. (g cm^{-3})	1.389	1.520
Absorption coefficient (cm^{-1})	2.971	4.169
F(000)	912	1108
Theta range for data (°)	$1 < 2\theta < 48$	$3 < 2\theta < 48$
Index range	$0 \leq h \leq 9, -17 \leq k \leq 17, -18 \leq l \leq 18$	$-15 \leq h \leq 15, 0 \leq k \leq 9, 0 \leq l \leq 24$
Scan type	ω–2θ	ω–2θ
Scan angle (°)	$(0.83 + 0.35 \tan \theta)$	$(0.75 + 0.35 \tan \theta)$
Aperture (mm)	2.4	2.3
Intensity variation	none	none
Reflections collected	7199	3888
Independent reflections	5983 (R(int) = 0.0309)	3619 (R(int) = 0.1121)
Refinement method	Full-matrix least-squares on F^2	
Absorption correction empirical (DIFABS [30])	(min. 0.873, max. 1.623 correction)	(min. 0.825, max. 1.206 correction)
Data/restraints/parameters	5929/0/433	3607/1/27
Goodness-of-fit on F$c^{2\,c}$	0.610	1.091
R indices (all data)	$R_1 = 0.0719$, $wR_2 = 0.1509$	$R_1 = 0.0551$, $wR_2 = 0.1659$
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0424$ [a], $wR_2 = 0.1044$ [b]	$R_1 = 0.0492$, $wR_2 = 0.1497$
Largest difference peak and hole (e Å^{-3})	max. 0.941, min. −0.800	max. 2.870, min. −1.745

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

50.34 MHz): δ (ppm) 130.18 (qC(Cp)), 125.64 (qC(Cp)), 123.17 (qC(Cp)), 119.93 (qC(Cp)), 118.62 (qC(Cp)), 114.42 (C_5H_3), 114.09 (C_5H_3), 112.02 (C_5H_3), 109.99 (qC(Cp)), 103.71 (qC(Cp)), 67.86 ($Me_2NCH_2CH_2$), 46.37 (N(CH_3)$_2$), 41.60 (N(CH_3)$_2$), 25.41 ($Me_2NCH_2CH_2$), 19.32 (LuCH_3), 14.58 ($C_5(CH_3)_4$), 14.00 ($C_5(CH_3)_4$), 11.87 ($C_5(CH_3)_4$), 11.55 ($C_5(CH_3)_4$), 1.09 (Si(CH_3)$_2$), -0.08 (Si(CH_3)$_2$). MS (160 °C, ^{175}Lu) m/z (%) 503 (3, [M]$^+$), 488 (95, [M − CH$_3$]$^+$), 445 (12, [M − EtNMe$_2$]$^+$), 430 (6, [M − EtNMe$_2$ − CH$_3$]$^+$), 58 (100, [CH$_2$NMe$_2$]$^+$).

The X-ray structure of **9** also shows a unit cell containing four molecules in a racemic mixture of the enantiomers. In addition, there are two disordered toluene molecules in the unit cell. The structure of one molecule is shown in Fig. 2.

The geometry around the lutetium center is very similar to that around yttrium in **2**. The Lu–N distance (2.445(8) Å) corresponds to that in related lutetium compounds, e.g. in Cp$_2$Lu(CH$_2$)$_3$NMe$_2$ (2.37 Å) [23], (COT)Lu(C$_6$H$_4$CH$_2$NMe$_2$) (THF) (2.479(6) Å) [24], (C$_6$H$_4$CH$_2$NMe$_2$)$_3$Lu (2.468(6), 2.478(5) and 2.588(5) Å) [25] and [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$Lu(CH$_2$SiMe$_3$)Cl]$_2$ (2.60(2) and 2.541(19) Å [26]. The Lu–C distance is 2.370(9) Å, nearly the same as in Cp$_2^*$Lu(CH$_3$)(μ-CH$_3$)LuCp$_2^*$ (2.344(12) Å for the non-bridging methyl group [7]). Metal–carbon distances in compounds with bridged methyl groups are significantly longer, e.g. in Cp$_2$Lu(μ-CH$_3$)$_2$Li(tmed) 2.461(12) Å [27], in [Li(DME)]$_3$[Lu(CH$_3$)$_6$] 2.53(2) Å [28], and in [Li(tmed)$_2$][Cp*Lu(CH$_3$)$_3$] 2.56(2) and 2.59(2) Å [29].

3. X-ray structure determination of 2 and 9

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 $19.0° < 2\theta <$ $27.6°$ (**2**) and $13.2° < 2\theta < 27.1°$ (**9**). Data were collected at 163(2) K. Both sets of raw data were corrected for Lorentz, polarisation and absorption effects [31]. The structures were solved with three-dimensional Patterson synthesis (SHELXS-86) [32] and refined by full-matrix least-squares on F^2 using (SHELXL-93) [33]. The asymmetric unit of **2** contains two different molecules, and in the case of **9** two toluene solvent molecules per unit cell which showed disorder and were restrained by fixing the C–C distances. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in idealized positions (C–H 0.96 Å, $U_{iso} = 0.08$ Å^2).

Scattering factors were taken from Refs. [34–36]. All calculations were performed on an IBM Risk 6000 computer. All refinements were done with the SHELXL-93 [33] program system. Full details of the crystal structure determination have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and can be obtained on quoting the depository numbers CSD-405549 (**2**) and CSD-405550 (**9**) respectively.

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