

Organometallic Compounds of the Lanthanides 169 [1]. Lanthanidocene Complexes Containing Chiral Nitrogen-Functionalized Cyclopentadienyl Ligands

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SmCl_3 reacts with equimolar amounts of $\text{K}[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2]$ and $\text{Na}[\text{C}_5\text{Me}_5]$ yielding $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{SmCl}$ (**1**). The methylation of complex **1** with LiMe and the reactions of the known analogues of **1**, $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{LnCl}$ ($\text{Ln} = \text{Y}$ (**2**), Lu (**3**)) with $\text{LiCH}_2\text{SiMe}_3$ afford $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{SmMe}$ (**4**) and $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{LnCH}_2\text{SiMe}_3$ ($\text{Ln} = \text{Y}$ (**5**), Lu (**6**)), respectively. The reactions of ScCl_3 and LuCl_3 with 1 equivalent of $\text{K}[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2]$ or $\text{K}[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2]$ followed by 2 equivalents of $\text{Me}_3\text{SiCH}_2\text{Li}$ yield the complexes $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{Ln} = \text{Sc}$ (**7a**), Lu (**7b**)) or $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{Ln} = \text{Sc}$ (**8a**), Lu (**8b**)), respectively.

Key words: Lanthanidocenes, Nitrogen-Functionalized Cyclopentadienyl Ligands, Scandium, Yttrium, Samarium, Lutetium

Introduction

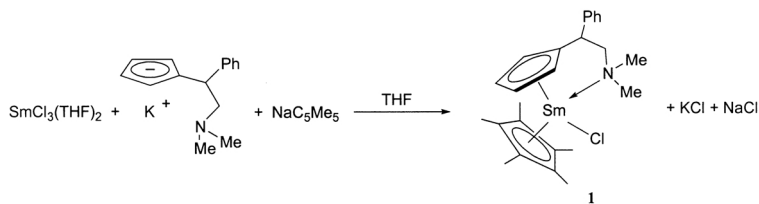
Cyclopentadienyl ligands with oxygen-, nitrogen-, or sulfur-functionalized side chains have attracted great interest in lanthanidocene chemistry since their ability to stabilize such π -complexes by additional intramolecular coordination of the respective lanthanide via their donor atoms allows the synthesis of far more stable compounds [2]. Since the very sensitive dicyclopentadienyl lanthanide alkyl complexes are known to be active catalysts for enantioselective organic reactions [3], it was desirable to synthesize alkyl lanthanidocenes which possess besides their catalytic activity also a higher stability. We already reported on our first results concerning the synthesis of dicyclopentadienyl lanthanide(II) complexes and dicyclopentadienyl lanthanide(III) alkyl complexes with asymmetric cyclopentadienyl ligands incorporating a donor function in the side chain [2b,4]. Here we describe the preparation of new mixed ligand complexes of yttrium, samarium, and lutetium containing the chiral (*S*)-(2-dimethylamino-1-phenylethyl) cyclopentadienyl ligand, as well as of achiral monocyclopentadienyl bis(alkyl) complexes of scandium, yttrium, and lutetium.

Results and Discussion

Chiral bis(cyclopentadienyl)lanthanide chloride and alkyl complexes

In an earlier paper we reported on the synthesis of the chiral, nonracemic bis(cyclopentadienyl)lanthanide complexes $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2]_2\text{LnCl}$ ($\text{Ln} = \text{Y}$, Sm , Lu), $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{LnCl}$ ($\text{Ln} = \text{Y}$ (**2**), Lu (**3**)), and $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{LuCH}_3$ [2b]. Following the procedure for the synthesis of **2** and **3**, the samarium analogue $[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2](\text{C}_5\text{Me}_5)\text{SmCl}$ (**1**) is obtained in a one-pot reaction by addition of $\text{K}[(S)\text{-C}_5\text{H}_4\text{CHPhCH}_2\text{NMe}_2]$ to a solution of $\text{SmCl}_3(\text{THF})_2$ in THF followed by the addition of $\text{Na}[\text{C}_5\text{Me}_5]$ (mole ratio 1:1:1). The crystalline, solvent-free complex **1** was isolated from the reaction mixture with 64% yield (Scheme 1).

The yellow complex melts with decomposition at 167 °C and is soluble in polar solvents such as THF or diethyl ether as well as in aromatic hydrocarbons like benzene or toluene. In contrast to non-donor stabilized bis(cyclopentadienyl)lanthanide halides, **1** is less sensitive towards moisture and oxygen and turns brown only after about 30 min when exposed to air.



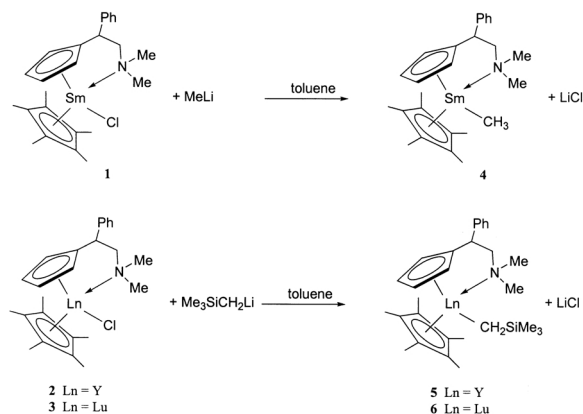
Scheme 1.

By reason of the stereocenter in the side chain of the (*S*)-C₅H₄CHPhCH₂NMe₂ ligand, the ¹H NMR spectrum of **1** shows four signals for the cyclopentadienyl protons, two signals for the diastereotopic protons of the methylene group, and one for the single proton at the stereocenter of the side chain. The N-methyl groups are not equivalent in noncoordinating solvents like C₆D₆, indicating Me₂N→Sm coordination. However, in the coordinating solvent C₅D₅N, the methyl groups are equivalent and give rise to only one NMR signal, demonstrating the replacement of the coordinating dimethylamino nitrogen by the nitrogen atom of the stronger base pyridine. The observation of only one signal for the methyl groups of the C₅Me₅ ligand in the ¹H NMR spectrum and of two signals in the ¹³C NMR spectrum indicates free rotation of this ligand system. Like the NMR spectra of **2** and **3**, the spectrum of **1** shows only one set of signals, although two diastereomers should be expected because of the two stereocenters in the molecule, one in the side chain and the other one at the metal center. Whether this fact is caused by the preferential formation of only one diastereomer or by a rapid exchange between the two possible diastereomers, could not be clarified.

Complex **1** reacts in toluene at −78 °C with an ethereal solution of methyllithium, forming the corresponding methyl derivative [(*S*)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)SmCH₃ (**4**). The reactions of the yttrium and lutetium derivatives **2** and **3** with Me₃SiCH₂Li in toluene at room temperature yield [(*S*)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)YCH₂SiMe₃ (**5**) and [(*S*)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)LuCH₂SiMe₃ (**6**), respectively (Scheme 2).

Compared to the chloro complexes **1**, **2**, and **3**, the yellow (**4**) or colorless (**5**, **6**) crystalline products **4–6** are extremely sensitive against moisture and air, thus rendering their analytical characterization more difficult. Reasonable elemental analysis results could be obtained only for complex **6**.

The ¹H NMR spectrum of **4** shows a broad signal at −79 ppm (half width 51 Hz) for the protons of the methyl group bonded to the samarium atom.



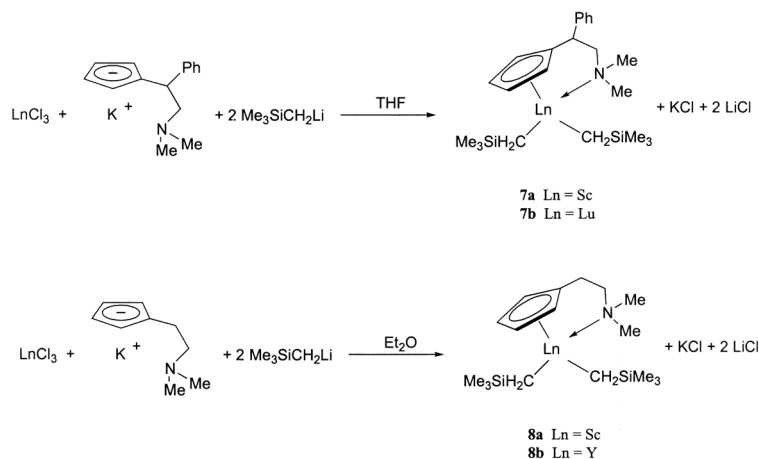
Scheme 2.

The corresponding signal in the ¹³C NMR spectrum was not detected. Whereas in the ¹H NMR spectrum of **5** the diastereotopic protons of the CH₂Si group bonded to the central yttrium atom give rise to two double doublets at −0.87 and −1.61 ppm according to their ¹H-⁸⁹Y and vicinal ¹H-¹H coupling (²*J*(Y,H) = 3.6 Hz, ²*J*(H,H) = 10.2 Hz), the corresponding CH₂Si protons of the lutetium complex **6** give rise to two doublets at −0.66 and −1.46 ppm with ²*J*(H,H) = 10.3 Hz. The same signal pattern as for complex **6** appears in the spectrum of the achiral complex [C₅H₄CH₂CH₂NMe₂](C₅Me₅)LuCH₂SiMe₃ [**2a**], proving that the inequivalence of the CH₂Si protons is not the result of the chirality in the cyclopentadienyl side chain, but of the chirality at the lanthanide atom induced by the coordination of the nitrogen atom of this side chain to the metal center.

The EI mass spectra of **4**, **5**, and **6** show no molecular ion peaks. The fragments formed by the loss of the CH₃ or the CH₂SiMe₃ group, respectively, appear as the peaks of highest mass.

Chiral and prochiral cyclopentadienyllanthanide bis(alkyl) complexes

Mono(cyclopentadienyl)lanthanide complexes with two σ-bonded alkyl ligands are very scarce, ow-



Scheme 3.

ing to the low degree of steric saturation of the lanthanide ion by the unsubstituted cyclopentadienyl group [5,6]. However, the additional chelation of the central lanthanide ion by the N-donor function of the chiral [(*S*)-C₅H₄CHPhCH₂NMe₂] or the achiral [C₅H₄CH₂CH₂NMe₂] substituted cyclopentadienyl ligand, allows the isolation of such bis(alkyl)lanthanidocenes. Thus, the one-pot reactions of scandium, yttrium, or lutetium trichloride with the potassium salt of the respective cyclopentadienyl ligand followed by the addition of trimethylsilylmethyl-lithium (1:1:2 mole ratio) afford the complexes [(*S*)-C₅H₄CHPhCH₂NMe₂]₂Ln(CH₂SiMe₃)₂ (Ln = Sc (**7a**), Lu (**7b**)) and (C₅H₄CH₂CH₂NMe₂)₂Ln(CH₂SiMe₃)₂ (Ln = Sc (**8a**), Y (**8b**)) (Scheme 3).

All four colorless complexes are highly sensitive against air and moisture. They are soluble in polar and nonpolar solvents and separate from hexane at -28°C as colorless crystals in yields of 40 to 45% (**7a,b**) and 80% (**8a,b**), respectively. Their ¹H and ¹³C NMR spectra show the expected signals. The inequivalence of the CH₂Si protons in the ¹H NMR spectra of the compounds is the result of the prochirality of the respective central lanthanide atom.

Experimental Section

All operations involving organometallic compounds were carried out in dry, oxygen-free solvents in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Melting points were measured in sealed capillaries with a Büchi 510 apparatus and are uncorrected. The NMR spectra were recorded on a Bruker ARX 200 (¹H 200 MHz; ¹³C 50.32 MHz) or ARX 400 (¹H 400 MHz; ¹³C 100.64 MHz) spectrometer at 298 K. Chemical shifts

are reported in ppm relative to the residual ¹H and ¹³C resonances of the deuterated solvents. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Na[C₅Me₅] [7], Li(CH₂SiMe₃) [8], K[C₅H₄CH₂CH₂NMe₂] [9], K[(*S*)-C₅H₄CHPhCH₂NMe₂] [4], [(*S*)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)YCl (**2**), and [(*S*)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)LuCl (**3**) [2b] were prepared according to published procedures. Anhydrous ScCl₃, YCl₃, SmCl₃, and LuCl₃ were obtained by reaction of the pure oxides with NH₄Cl followed by Soxhlet extraction with THF [10].

[(*S*)-(2-Dimethylamino-1-phenylethyl)cyclopentadienyl]-(pentamethylcyclopentadienyl)samarium chloride (**1**)

To a stirred suspension of SmCl₃(THF)₂ (1.10 g, 2.74 mmol) in THF (70 ml), K[(*S*)-C₅H₄CHPhCH₂NMe₂] (0.69 g, 2.74 mmol) was added at r. t., followed after 12 h of stirring by Na[C₅Me₅] (0.43 g, 2.74 mmol). The reaction mixture was stirred for further 12 h at r. t.. After removal of the solvent under vacuum, the residue was washed with *n*-hexane (20 ml) and was then extracted with toluene (60 ml). The resulting toluene solution was concentrated under vacuum (10^{-2} mbar) to 50 ml. Cooling of the solution to -28°C provided 0.94 g (64%) of yellow crystals of **1**. M. p. 167°C dec; $[\alpha]_{\text{D}}^{25} = -78.2^{\circ}$ (c 0.56, toluene). ¹H NMR ([D₆]-benzene, 200 MHz): δ 15.89 (s_{br}, 1 H, Cp), 10.88 (s_{br}, 1 H, Cp), 10.45 (m, 1 H, CH₂), 9.27 (m, 2 H, Ph), 8.61 (s_{br}, 1 H, Cp), 7.88 (m, 2 H, Ph), 7.64 (m, 1 H, Ph), 4.91 (m, 1 H, CH), 2.07 (m, 1 H, CH₂), 1.20 (s, 15 H, C₅Me₅), -1.03 (s_{br}, 1 H, Cp), -2.17 (s_{br}, $\nu_{1/2} = 100$ Hz, 3 H, NCH₃), -7.42 (s_{br}, $\nu_{1/2} = 100$ Hz, 3 H, NCH₃); ([D₅]-pyridine; 200 MHz): δ 12.98 (s_{br}, 1 H, Cp), 10.98 (s_{br}, 1 H, Cp), 8.51 (m, 2 H,

Ph), 8.05 (s_{br}, 1 H, Cp), 7.70 (m, 2 H, Ph), 7.48 (m, 1 H, Ph), 5.44 (m, 1 H, CH₂), 4.78 (m, 1 H, CH), 2.35 (m, 1 H, CH₂), 1.24 (s, 15 H, C₅Me₅), 0.16 (s_{br}, 1 H, Cp), −0.85 (s_{br}, Hz, 6 H, NCH₃). – ¹³C{¹H} NMR ([D₆]-benzene, 50.32 MHz): δ 141.43 (C^q_{Ph}), 138.98 (C^q_{Cp}), 129.78 (Ph), 129.27 (Ph), 127.76 (Ph), 117.02 (C₅CH₃), 113.41 (Cp), 111.50 (Cp), 101.54 (Cp), 98.54 (Cp), 77.24 (CH₂Cp), 51.60 (CH), 46.02 (NCH₃), 34.50 (NCH₃), 19.17 (C₅CH₃). – MS (¹⁵²Sm, 174 °C; *m/z* (%)): 534 (8) [M]⁺, 499 (1) [M–Cl]⁺, 399 (12) [M–C₅Me₅]⁺, 58 (100) [C₃H₈N]⁺. – C₂₅H₃₃ClNSm (533.36): calcd. C 56.30, H 6.24, N 2.63; found C 56.01, H 6.11, N 2.89.

Methyl-[(S)-(2-dimethylamino-1-phenylethyl)cyclopentadienyl](pentamethylcyclopentadienyl)samarium (4)

To a solution of [(S)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)SmCl (**1**; 0.71 g, 1.33 mmol) in toluene (50 ml) methylolithium (1.5 M in diethyl ether; 0.89 ml, 1.33 mmol) was added at −78 °C. After stirring for 72 h at r.t., the reaction mixture was filtered and the clear solution was concentrated under vacuum (10^{−2} mbar) to 20 ml and cooled to −28 °C. Yellow crystals of **4** precipitated (0.28 g, 41%). M.p. 198 °C dec; [α]_D²⁵ = −51.6° (c = 1.14 in toluene). – ¹H NMR ([D₆]-benzene, 400 MHz): δ 15.72 (s_{br}, 1 H, Cp), 10.77 (s_{br}, 1 H, Cp), 10.39 (m, 1 H, CH₂), 9.21 (m, 2 H, Ph), 8.54 (s_{br}, 1 H, Cp), 7.76 (m, 2 H, Ph), 7.59 (m, 1 H, Ph), 4.80 (m, 1 H, CH), 2.04 (m, 1 H, CH₂), 1.19 (s, 15 H, C₅Me₅), −0.97 (s_{br}, 1 H, Cp), −2.10 (s_{br}, 3 H, NCH₃), −7.36 (s, 3 H, NCH₃), −7.96 (s_{br}, ν_{1/2} = 51 Hz, 3 H, SmCH₃). – MS (¹⁵²Sm, 151 °C; *m/z* (%)): 499 (100) [M–CH₃]⁺, 379 (5) [M–C₅Me₅]⁺. – C₂₆H₃₆NSm (512.94): calcd. C 60.88, H 7.07, N 2.73; found C 58.67, H 6.54, N 2.61.

Trimethylsilylmethyl-[(S)-(2-dimethylamino-1-phenylethyl)cyclopentadienyl](pentamethylcyclopentadienyl)yttrium (5)

To a solution of [(S)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)YCl (**2**; 0.71 g, 1.50 mmol) in toluene (40 ml) trimethylsilylmethylolithium (0.14 g, 1.50 mmol) was added at r.t.. After stirring of the mixture for 12 h, the solvent was removed under vacuum (10^{−2} mbar) and the residue was extracted with *n*-hexane (40 ml). The clear extract was concentrated under vacuum to 20 ml and was then cooled to −28 °C. Colorless crystals of **5** precipitated (0.36 g, 46%). M.p. 151 °C dec; [α]_D²⁵ = −51.3° (c = 0.89 in toluene). – ¹H NMR ([D₆]-benzene, 200 MHz): δ 7.35–7.17 (m, 5 H, Ph), 6.74 (m, 1 H, Cp), 5.96 (m, 2 H, Cp), 5.68 (m, 1 H, Cp), 3.55 (dd, ³*J* = 13.0/4.2 Hz, 1 H, CH), 3.23 (dd, ^{2,3}*J* = 13.0/11.4 Hz, 1 H, CH₂), 2.03 (m, 1 H, CH₂), 1.98 (s, 15 H, C₅Me₅), 1.77 (s, 3 H, NCH₃), 1.64 (s, 3 H, NCH₃), 0.43 (s, 9 H, SiMe₃), −0.87 (dd, ²*J*(H, H) = 10.2 Hz, ²*J*(⁸⁹Y, H) = 3.6 Hz, 1 H, CH₂SiMe₃), −1.61 (dd, ²*J*(H, H) = 10.2 Hz,

²*J*(⁸⁹Y, H) = 3.6 Hz, 1 H, CH₂SiMe₃). – ¹³C{¹H} NMR ([D₆]-benzene, 50.32 MHz): δ 141.26 (C^q_{Ph}), 128.01 (C^q_{Cp}), 128.78 (Ph), 127.99 (Ph), 127.01 (Ph), 116.93 (C₅CH₃), 111.04 (Cp), 109.92 (Cp), 108.71 (Cp), 107.68 (Cp), 77.98 (CH₂Cp), 48.84 (NCH₃), 43.62 (NCH₃), 41.87 (CH), 28.82 (CH₂SiMe₃), 12.34 (C₅CH₃), 5.41 (CH₂Si(CH₃)₃). – MS (121 °C; *m/z* (%)): 436 (34) [M–CH₂SiMe₃]⁺, 58 (100) [C₃H₈N]⁺. – C₂₉H₄₄NSiY (523.67): calcd. C 66.52, H 8.47, N 2.67; found C 67.14, H 8.91, N 3.06.

Trimethylsilylmethyl-[(S)-(2-dimethylamino-1-phenylethyl)cyclopentadienyl](pentamethylcyclopentadienyl)lutetium (6)

In analogy to the preparation of **5**, [(S)-C₅H₄CHPhCH₂NMe₂](C₅Me₅)LuCl (**3**; 0.78 g, 1.40 mmol) was reacted with trimethylsilylmethylolithium (0.13 g, 1.40 mmol) in toluene (40 ml) to provide 0.44 g (51%) of colorless crystals of **6**. M.p. 154 °C dec; [α]_D²⁵ = −67.4° (c = 1.59 in toluene). – ¹H NMR ([D₆]-benzene, 200 MHz): δ 7.29–7.08 (m, 5 H, Ph), 6.69 (m, 1 H, Cp), 5.92 (m, 2 H, Cp), 5.60 (m, 1 H, Cp), 3.56 (dd, ³*J* = 13.0/4.2 Hz, 1 H, CH), 3.24 (dd, ^{2,3}*J* = 13.0/11.4 Hz, 1 H, CH₂), 2.01 (m, 1 H, CH₂), 1.95 (s, 15 H, C₅Me₅), 1.71 (s, 3 H, NCH₃), 1.59 (s, 3 H, NCH₃), 0.41 (s, 9 H, SiMe₃), −0.66 (d, ²*J* = 10.3 Hz, 1 H, CH₂SiMe₃), −1.46 (d, ²*J* = 10.3 Hz, 1 H, CH₂SiMe₃). – ¹³C{¹H} NMR ([D₆]-benzene, 50.32 MHz): δ 141.59 (C^q_{Ph}), 128.94 (C^q_{Cp}), 128.71 (Ph), 127.87 (Ph), 126.88 (Ph), 116.51 (C₅CH₃), 110.94 (Cp), 109.70 (Cp), 108.53 (Cp), 107.52 (Cp), 72.87 (CH₂Cp), 48.82 (NCH₃), 43.59 (NCH₃), 41.91 (CH), 28.94 (CH₂SiMe₃), 12.37 (C₅CH₃), 5.56 (CH₂Si(CH₃)₃). – MS (¹⁷⁵Lu, 113 °C; *m/z* (%)): 552 (26) [M–CH₂SiMe₃]⁺, 58 (100) [C₃H₈N]⁺. – C₂₉H₄₄LuNSi (609.73): calcd. C 57.13, H 7.27, N 2.30; found C 57.67, H 6.93, N 2.48.

Bis(trimethylsilylmethyl) [(S)-(2-dimethylamino-1-phenylethyl)cyclopentadienyl]scandium (7a)

To a stirred suspension of ScCl₃(THF)₃ (0.96 g, 2.61 mmol) in THF (40 ml) K[(S)-C₅H₄CHPhCH₂NMe₂] (0.66 g, 2.61 mmol) was added in portions at r.t. and after 30 min of stirring the mixture, the solvent was evaporated under vacuum (10^{−2} bar). The residue was suspended in diethyl ether (40 ml) and was then reacted with LiCH₂SiMe₃ (0.49 g, 4.22 mmol). The mixture was stirred for 12 h at r.t.. After removal of the solvent under vacuum, the oily residue was washed with cold *n*-hexane (10 ml), and then extracted with *n*-hexane (50 ml). The resulting hexane solution was concentrated under vacuum (10^{−2} mbar) to 20 ml. Cooling to −28 °C provided 0.51 g (45%) of colorless crystals of **7a**. M.p. 104 °C dec.; [α]_D²⁵ = −44.8° (c = 0.59 in toluene). – ¹H NMR ([D₆]-benzene, 200 MHz): δ 7.20–7.13 (m, 5 H, Ph), 6.67 (m, 1 H, Cp), 6.49 (m, 1 H, Cp), 6.31 (m, 1 H, Cp),

6.13 (m, 1 H, Cp), 3.65 (dd, $^3J = 13.0/4.2$ Hz, 1 H, CH), 2.88 (dd, $^{2,3}J = 13.0/11.4$ Hz, 1 H, CH₂), 2.01 (m, 1 H, CH₂), 1.91 (s, 3 H, NCH₃), 1.78 (s, 3 H, NCH₃), 0.37 (s, 18 H, SiMe₃), –0.21 (s_{br}, 2 H, CH₂SiMe₃), –1.25 (s_{br}, 2 H, CH₂SiMe₃). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]-benzene, 50.32 MHz): δ 140.52 (C_{Ph}^q), 129.17 (C_{Cp}^q), 128.72 (Ph), 127.79 (Ph), 127.05 (Ph), 115.20 (Cp), 114.10 (Cp), 110.49 (Cp), 110.14 (Cp), 71.17 (CH₂Cp), 48.53 (NCH₃), 43.37 (NCH₃), 42.04 (CH), 25.59 (CH₂SiMe₃), 3.98 (CH₂Si(CH₃)₃). – MS (113 °C; m/z (%)): 416 (2) [M–CH₃]⁺, 344 (49) [M–CH₂SiMe₃]⁺, 257 (26) [M–(CH₂SiMe₃)₂]⁺, 256 (89) [M–(CH₂SiMe₃)₂–H]⁺, 73 (100) [SiMe₃]⁺, 58 (100) [C₃H₈N]⁺. – C₂₃H₄₀NScSi₂ (431.70): calcd. C 63.99, H 9.34, N 3.24; found C 62.64, H 8.92, N 2.51.

Bis(trimethylsilylmethyl)[(S)-(2-dimethylamino-1-phenylethyl)cyclopentadienyl]lutetium (7b)

In analogy to the preparation of **7a**, LuCl₃(THF)₃ (1.27 g, 2.55 mmol) in THF (40 ml) was reacted with K[(S)-C₅H₄CHPhCH₂NMe₂] (0.64 g, 2.55 mmol) and trimethylsilylmethylolithium (0.48 g, 5.10 mmol) to provide 0.57 g (40%) of colorless crystals of **7b**. M. p. 108 °C dec; $[\alpha]_{\text{D}}^{25} = -59.1^\circ$ (c = 1.11 in toluene). – ^1H NMR ([D₆]-benzene, 200 MHz): δ 7.24–7.11 (m, 5 H, Ph), 6.57 (m, 1 H, Cp), 6.38 (m, 1 H, Cp), 6.26 (m, 1 H, Cp), 6.04 (m, 1 H, Cp), 3.54 (dd, $^3J = 13.0/4.2$ Hz, 1 H, CH), 2.72 (dd, $^{2,3}J = 13.0/11.4$ Hz, 1 H, CH₂), 1.97 (m, 1 H, CH₂), 1.80 (s, 3 H, NCH₃), 1.63 (s, 3 H, NCH₃), 0.40 (s, 18 H, SiMe₃), –0.54 (s_{br}, 2 H, CH₂SiMe₃), –0.61 (s_{br}, 2 H, CH₂SiMe₃). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]-benzene, 50.32 MHz): δ 140.99 (C_{Ph}^q), 129.94 (C_{Cp}^q), 128.82 (Ph), 127.99 (Ph), 126.91 (Ph), 115.83 (Cp), 114.70 (Cp), 110.92 (Cp), 110.21 (Cp), 71.77 (CH₂Cp), 48.79 (NCH₃), 43.54 (NCH₃), 42.10 (CH), 25.87 (CH₂SiMe₃), 4.06 (CH₂Si(CH₃)₃). – MS (^{175}Lu , 121 °C; m/z (%)): 546 (5) [M–CH₃]⁺, 474 (56) [M–CH₂SiMe₃]⁺, 387 (32) [M–(CH₂SiMe₃)₂]⁺, 386 (71) [M–(CH₂SiMe₃)₂–H]⁺, 73 (100) [SiMe₃]⁺, 58 (41) [C₃H₈N]⁺. – C₂₃H₄₀LuNSi₂ (561.72): calcd. C 49.14, H 7.18, N 2.49; found C 48.34, H 6.80, N 2.05.

Bis(trimethylsilylmethyl)[(2-dimethylaminoethyl)cyclopentadienyl]scandium (8a)

In analogy to the preparation of **7a**, ScCl₃(THF)₃ (1.36 g, 3.70 mmol) in THF (40 ml) was reacted

with K[C₅H₄CH₂CH₂NMe₂] (0.60 g, 3.70 mmol) and trimethylsilylmethylolithium (0.70 g, 7.40 mmol) to provide 1.02 g (78%) of colorless crystals of **8a**. M. p. 82 °C dec. – ^1H NMR ([D₆]-benzene, 200 MHz): δ 6.47 (dd, $^{3,4}J = 2.6$ Hz, 2 H, Cp), 6.03 (dd, $^{3,4}J = 2.6$ Hz, 2 H, Cp), 2.00 (t, $^3J = 5.5$ Hz, 2 H, CH₂N), 1.92 (t, $^3J = 5.5$ Hz, 2 H, CH₂Cp), 1.71 (s, 6 H, NCH₃), 0.30 (s, 18 H, SiMe₃), –0.29 (s, 2 H, CH₂SiMe₃), –0.30 (s, 2 H, CH₂SiMe₃). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]-benzene, 50.32 MHz): δ 125.99 (C_{Cp}^q), 125.18 (Cp), 112.23 (Cp), 67.62 (CH₂SiMe₃), 64.72 (CH₂N), 44.85 (NCH₃), 25.14 (CH₂Cp), 3.59 (Si(CH₃)₃). – MS (^{45}Sc , 100 °C; m/z (%)): 340 (2) [M–CH₃]⁺, 317 (60) [M–(CH₂SiMe₃)₂]⁺, 268 (23) [M–CH₂SiMe₃]⁺, 180 (72) [M–(CH₂SiMe₃)₂–H]⁺, 73 (82) [SiMe₃]⁺, 58 (100) [C₃H₈N]⁺. – C₁₇H₃₆NScSi₂ (355.61): calcd. C 57.42, H 10.20, N 3.94; found C 57.45, H 10.60, N 3.56.

Bis(trimethylsilylmethyl)[(2-dimethylaminoethyl)cyclopentadienyl]yttrium (8b)

In analogy to the preparation of **7a**, YCl₃(THF)₃ (1.00 g, 2.45 mmol) in THF (40 ml) was reacted with K[C₅H₄CH₂CH₂NMe₂] (0.40 g, 2.45 mmol) and trimethylsilylmethylolithium (0.46 g, 4.90 mmol) to provide 0.79 g (81%) of colorless crystals of **8b**. M. p. 66 °C dec. – ^1H NMR ([D₆]-benzene, 200 MHz): δ 6.27 (dd, $^{3,4}J = 2.6$ Hz, 2 H, Cp), 5.94 (dd, $^{3,4}J = 2.6$ Hz, 2 H, Cp), 2.31 (t, $^3J = 5.5$ Hz, 2 H, CH₂N), 2.27 (t, $^3J = 5.5$ Hz, 2 H, CH₂Cp), 1.88 (s, 6 H, NCH₃), 0.38 (s, 18 H, SiMe₃), –1.04 (s, 2 H, CH₂SiMe₃), –1.05 (s, 2 H, CH₂SiMe₃). – $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]-benzene, 50.32 MHz): δ 126.60 (C_{Cp}^q), 110.43 (Cp), 109.86 (Cp), 70.60 (CH₂SiMe₃), 64.60 (CH₂N), 45.74 (NCH₃), 27.51 (CH₂Cp), 4.87 (Si(CH₃)₃). – MS (^{89}Y , 281 °C; m/z (%)): 335 (6) [M–C₅H₄]⁺, 313 (2) [M–CH₂SiMe₃ + H]⁺, 263 (1) [M–C₅H₄CH₂CH₂NMe₂]⁺, 169 (10) [C₅H₅CH₃]⁺, 147 (6) [YCH₂NMe₂]⁺, 58 (100) [CH₂NMe₂]⁺. – C₁₇H₃₆NSi₂Y (399.56): calcd. C 51.10, H 9.08, N 3.51; found C 51.32, H 9.21, N 3.43.

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