Organometallic Compounds of the Lanthanides. 128.[1] Donor-Functionalized Chiral Nonracemic Cyclopentadienyl Complexes of Yttrium, Samarium(III), and Lutetium†

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Optically active metallocene complexes of Y, Sm(III), and Lu containing cyclopentadienyl ligands with chiral nonracemic *N*- or *O*-substituted side chains as ligands are described. Specifically, the ligand systems reported are (*S*)-(2-methoxypropyl)cyclopentadienyl [(*S*)-$C_5H_4CH_2CH(Me)OMe$)], (*S*)-[2-(dimethylamino)propyl]cyclopentadienyl [(*S*)-$C_5H_4CH_2CH(Me)NMe_2$)], and (*S*)-[2-(dimethylamino)-1-(phenylethyl)]cyclopentadienyl [(*S*)-$C_5H_4CH(Ph)CH_2NMe_2$)]. Reaction of the potassium salts of these cyclopentadienyl systems with the trichlorides of Y, Sm, and Lu in a 2:1 molar ratio yielded the complexes [Ln{(*S*)-η^5:η^1-$C_5H_4(CH_2CH(Me)OMe)\}_2$Cl] (Ln = Y **1a**, Sm **1b**), [Ln{(*S*)-η^5:η^1-$C_5H_4[CH_2CH(Me)NMe_2]\}_2$Cl] (Ln = Y **2a**, Sm **2b**), and [Ln{(*S*)-η^5:η^1-$C_5H_4[CH(Ph)CH_2NMe_2]\}_2$Cl] (Ln = Y **3a**, Sm **3b**, Lu **3c**). Alternatively, **2b** was synthesized by oxidation of the corresponding divalent complex [Sm{(*S*)-η^5:η^1-$C_5H_4[CH_2CH(Me)NMe_2]\}_2$] with *tert*-butyl chloride. The mixed chiral sandwich complexes [(η^5-C_5Me_5)Ln{(*S*)-η^5:η^1-$C_5H_4[CH_2CH(Me)NMe_2]\}$Cl] (Ln = Y **4a**, Lu **4c**) and [(η^5-C_5Me_5)Ln{(*S*)-η^5:η^1-$C_5H_4[CH(Ph)CH_2NMe_2]\}$Cl] (Ln = Y **5a**, Lu **5c**) were prepared by successive reaction of the lanthanide trichlorides with 1 equiv of the potassium salt of the chiral nonracemic cyclopentadienyl ligand and 1 equiv of Na(C_5Me_5). Methylation of **5c** with LiMe produced [(η^5-C_5Me_5)Ln{(*S*)-η^5:η^1-$C_5H_4[CH(Ph)CH_2NMe_2]\}$Me] (**6c**). X-ray structural analyses of **1b**, **3b**, **3c**, **5a**, and **6c** were performed.

Introduction

Cyclopentadienyl ligands with donor-functionalized side chains have attracted great interest in lanthanide chemistry[2] because of their ability to stabilize π-complexes by additional intramolecular lanthanide coordination, thus allowing the synthesis of both monocyclopentadienyl and mixed sandwich complexes. Alkylbis(cyclopentadienyl)lanthanide complexes have been shown to be active catalysts for special organic reactions.[3] Since sidearm participation may also play an important role in catalytic processes, it seemed desirable to synthesize complexes that combine both properties in the same molecule. Therefore, we initiated a program to prepare trivalent lanthanide complexes with asymmetric cyclopentadienyl ligands incorporating a donor function by using our previous experiences with donor-functionalized divalent lanthanide sandwich complexes.[4]

Experimental Section

All operations involving organometallics were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured on a hot-stage microscope under vacuum (0.01 mbar) in sealed capillaries and are uncorrected. Optical rotations were determined on a Schmidt + Haensch Polar-

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† Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

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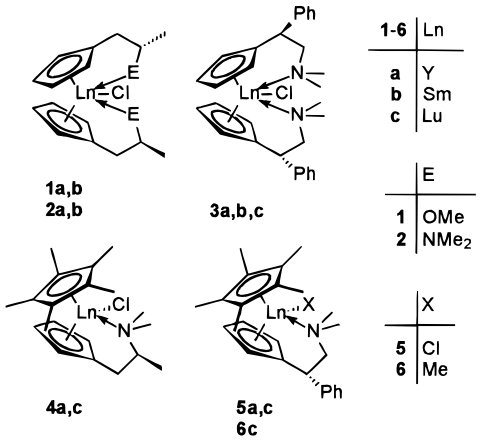
Chart 1



tronic−D polarimeter. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz) spectrometer at ambient temperatures. All chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Mass spectra (EI, 70 eV) were obtained using a Varian MAT 311 A instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities in percent are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. $LnCl_3(THF)_x$ (Ln = Y, Sm, Lu),[5] [(*S*)-(2-methoxypropyl)-cyclopentadienyl]potassium (**7**),[4] {(*S*)-[2-(dimethylamino)-propyl]cyclopentadienyl}potassium (**8**),[4] {(*R*)-[2-(dimethylamino)-2-(phenylethyl)]cyclopentadienyl}potassium (**9**),[4] and bis{η^5:η^1-(*S*)-[2-(dimethylamino)propyl]cyclopentadienyl}samarium-(II)[4] (**10**) were prepared according to published procedures.

Chlorobis[η^5:η^1-(*S*)-(2-methoxypropyl)cyclopentadienyl]yttrium (1a). To a suspension of 0.66 g (1.6 mmol) of $YCl_3(THF)_3$ in THF (60 mL) was added 0.56 g (3.2 mmol) of **7**. The mixture was stirred for 12 h at 25 °C. The clear solution was decanted from precipitated KCl, and the solvent was removed in a vacuum (10^{-2} mbar), leaving a solid which was washed twice with *n*-hexane (10 mL) and was recrystallized from toluene (5 mL) at −28 °C; 0.38 g (60%) of colorless **1a**; mp 168 °C dec; $[\alpha]^{25}_D$ −18.5° (*c* 0.33, THF). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.19 (m, 2H, C_5H_4), 6.06 (m, 4H, C_5H_4), 5.81 (m, 2H, C_5H_4), 3.73−3.63 (m, 2H, C*H*), 3.24 (s, 6H, O−CH_3), 2.56 (dd, J = 14.5, 5.1 Hz, 2H, CH_2), 2.17 (dd, J = 14.5, 8.4 Hz, 2H, CH_2) 0.83 (d, J = 6.2 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 50.32 MHz): δ 123.35 (d, ^1J(YC) = 1.2 Hz, C_5−C), 113.69 (d, ^1J(YC) = 0.9 Hz, C_5H_4), 110.68 (d, ^1J(YC) = 0.8 Hz, C_5H_4), 110.01 (d, ^1J(YC) = 0.9 Hz, C_5H_4), 107.73 (d, ^1J(YC) = 0.8 Hz, C_5H_4), 82.89 (*C*H), 59.02 (O−*C*H$_3$), 36.43 (*C*H$_2$), 18.12 (C−*C*H$_3$). MS (120 °C): *m*/*z* 398 (25) [M]$^+$, 363 (13) [M − Cl]$^+$, 261 (100) [Y{$C_5H_4CH_2CH$(Me)OMe}Cl]$^+$, 229 (65) [Y{$C_5H_4CH_2$-CH(Me)OMe}Cl − CH_4O]$^+$. Anal. Calcd for $C_{18}H_{26}ClO_2Y$ (398.76 g/mol): C, 54.22; H, 6.57. Found: C, 54.62; H, 6.32.

Chlorobis[η^5:η^1-(*S*)-(2-methoxypropyl)cyclopentadienyl]samarium(III) (1b). In analogy with the synthesis of **1a**, 0.50 g (1.3 mmol) of $SmCl_3(THF)_2$ was treated with 0.44 g (2.5 mmol) of **7** in 60 mL of THF; 0.29 g (51%) of yellow crystalline **1b**; mp 178 °C dec; $[\alpha]^{25}_D$ −23.8° (*c* 1.51, THF). ^{1}H NMR (toluene-d_8, 200 MHz): δ 13.24 (s_{br}, 2H, C_5H_4), 9.64 (s_{br}, 2H, C_5H_4), 6.65 (s_{br}, 2H, C_5H_4), 6.29 (s_{br}, 2H, C_5H_4), 4.07 (s_{br}, 2H, C*H*), 3.28 (dd, J = 14.5, 4.4 Hz, 2H, CH_2), 2.20 (dd, J = 14.5, 8.1 Hz, 2H, CH_2), −0.04 (d, J = 5.7 Hz, 6H, C−CH_3), −0.18 (s, 6H, O−CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, 50.32 MHz): δ 137.44 (C_5−C), 107.99 (C_5H_4), 106.78 (C_5H_4), 103.38 (C_5H_4), 98.79 (C_5H_4), 83.19 (*C*H), 57.01 (O−*C*H$_3$), 42.55 (*C*H$_2$), 17.59 (C−*C*H$_3$). MS (^{152}Sm, 142 °C): *m*/*z* 461 (58) [M]$^+$, 426 (25) [M − Cl]$^+$, 324 (100) [Sm{$C_5H_4CH_2CH$(Me)OMe}Cl]$^+$, 292 (46) [Sm{$C_5H_4CH_2CH$(Me)OMe}Cl − CH_4O]$^+$. Anal. Calcd for $C_{18}H_{26}ClO_2Sm$ (460.22 g/mol): C, 46.98; H, 5.69. Found: C, 46.61; H, 5.49.

Chlorobis[η^5:η^1-(*S*)-(2-dimethylaminopropyl)cyclopentadienyl]yttrium (2a). To a suspension of 0.98 g (2.3 mmol) of $YCl_3(THF)_3$ in THF (70 mL) was added 0.87 g (4.6 mmol) of **8** at 25 °C. The mixture was heated at reflux for 12 h. The solvent was removed in a vacuum (10^{-2} mbar), and the residue was washed twice with *n*-hexane (10 mL) and was then extracted with 60 mL of the same solvent. On concentrating the clear solution to 20 mL and cooling it to 0 °C, 0.55 g (57%) of colorless crystalline **2c** was obtained as a mixture of diastereomers; mp 134 °C dec; $[\alpha]^{25}_D$ −6.0° (*c* 1, THF). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.21−6.03 (m, 16H, C_5H_4), 3.63 (m, 2H, C*H*), 3.24 (m, 2H, CH_2), 2.90−2.72 (m, 2H, C*H*), 2.50 (m, 2H, CH_2), 2.42 (m, 2H, CH_2), 2.40 (s, 6H, N−CH_3), 2.34 (s, 6H, N−CH_3), 1.93 (m, 2H, CH_2), 1.10 (d, J = 6.8 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 134.44, (C_5−C), 127.74 (d, ^1J(YC) = 1.0 Hz, C_5−C), 115.02 (d, ^1J(YC) = 1.1 Hz, C_5H_4), 114.71 (d, ^1J(YC) = 1.1 Hz, C_5H_4), 110.27 (d, ^1J(YC) = 0.7 Hz, C_5H_4), 107.70 (d, ^1J(YC) = 0.7 Hz, C_5H_4), 106.93 (d, ^1J(YC) = 0.9 Hz, C_5H_4), 106.74 (d, ^1J(YC) = 0.8 Hz, C_5H_4), 106.21 (d, ^1J(YC) = 0.7 Hz, C_5H_4), 104.86 (d, ^1J(YC) = 1.0 Hz, C_5H_4), 71.68 (*C*H$_2$), 62.50 (*C*H), 47.67 (N−*C*H$_3$), 40.79 (N−*C*H$_3$), 34.08 (*C*H$_2$), 30.81 (*C*H), 18.91 (C−*C*H$_3$), 10.10 (C−*C*H$_3$). MS (80 °C): *m*/*z* 424 (3) [M]$^+$, 389 (2) [M − Cl]$^+$, 366 (2) [M − C_3H_8N]$^+$, 274 (37) [Y{$C_5H_4CH_2CH$(Me)-NMe_2}Cl]$^+$, 72 (100) [$C_4H_{10}N$]$^+$. Anal. Calcd for $C_{20}H_{32}ClN_2Y$ (424.85 g/mol): C, 56.54; H, 7.59; N, 6.59. Found: C, 56.58; H, 7.92; N, 6.44.

Chlorobis[η^5:η^1-(*S*)-(2-dimethylaminopropyl)cyclopentadienyl]samarium(III) (2b). Method A. To a solution of 0.19 g (0.4 mmol) of **10** in THF (40 mL) was added dropwise 0.04 g (0.4 mmol) of *tert*-butyl chloride in toluene (10 mL) while the color of the solution changed from dark green to yellow. The reaction mixture was stirred for 12 h at 25 °C. The solvent was removed in a vacuum (10^{-2} mbar), and the residue was extracted with 20 mL of *n*-hexane. Concentration of the clear solution to 5 mL at 10^{-2} mbar and cooling to 0 °C caused crystallization of 0.11 g (54%) of yellow **2b** as a 1:1 mixture of diastereomers.

Method B. In analogy with the synthesis of **2a**, 0.43 g (1.1 mmol) of $SmCl_3(THF)_2$ in THF (60 mL) was reacted with 0.41 g (2.2 mmol) of **8**. Yellow crystalline **2b**, 0.23 g (44%), was obtained as a 1:1 mixture of diastereomers; mp 157 °C dec; $[\alpha]^{25}_D$ −9.7° (*c* 2.69, THF). ^{1}H NMR (THF-d_8, 200 MHz): δ

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11.92 (s_{br}, 2H, C_5H_4), 11.85 (s_{br}, 2H, C_5H_4), 9.09 (s_{br}, 2H, C_5H_4), 8.24 (s_{br}, 2H, C_5H_4), 7.61 (s_{br}, 2H, C_5H_4), 7.23 (s_{br}, 2H, C_5H_4), 7.15 (s_{br}, 2H, C_5H_4), 5.77 (s_{br}, 2H, C_5H_4), 4.29 (s_{br}, 2H, C*H*), 3.72−3.58 (m, 2H, CH_2), 3.36−3.17 (m, 2H, C*H*), 3.14−3.00 (m, 2H, CH_2), 2.03 (d, J = 6.5 Hz, 6H, C−CH_3), 1.77 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 0.55 (d, J = 6.2 Hz, 6H, C−CH_3), 0.16 (s_{br}, 12H, N−CH_3), −0.44 (s, 12H, N−CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 50.32 MHz): δ 135.33 (C_5−C), 129.63 (C_5−C), 110.21 (C_5H_4), 108.98 (C_5H_4), 108.13 (C_5H_4), 104.54 (C_5H_4), 102.65 (C_5H_4), 101.17 (C_5H_4), 97.95 (C_5H_4), 96.48 (C_5H_4), 75.85 (CH_2), 66.11 (*C*H), 40.77 (N−*C*H_3), 40.52 (CH_2), 36.53 (*C*H), 18.20 (C−*C*H_3), 9.79 (C−*C*H_3). MS (^{152}Sm, 140 °C): *m*/*z* 487 (2) $[M]^+$, 456 (1) $[M - Cl]^+$, 429 (1) $[M - C_3H_8N]^+$, 337 (5) $[Sm\{C_5H_4CH_2$-$CH(Me)NMe_2\}Cl]^+$, 304 (1) $[Sm\{C_5H_4CH_2CH(Me)NMe_2\}]^+$, 72 (100) $[C_4H_{10}N]^+$. Anal. Calcd for $C_{20}H_{32}ClN_2Sm$ (486.30 g/mol): C, 49.40; H, 6.63; N, 5.76. Found: C, 48.98; H, 6.42; N, 6.06.

Chlorobis{η^5:η^1-(*S*)-[2-(dimethylamino)-1-(phenylethyl)]-cyclopentadienyl}yttrium (3a). A 1.16 g (4.6 mmol) sample of **9** was added to 0.96 g (2.3 mmol) of $YCl_3(THF)_3$ in THF (70 mL), and the mixture was heated at reflux for 12 h. The solvent was removed in a vacuum (10^{-2} mbar), and the remaining solid was washed twice with *n*-hexane (10 mL) and was then extracted with toluene (70 mL). Cooling of the concentrated toluene solution (40 mL) to −28 °C yielded 0.73 g (57%) of colorless crystalline **3a**; mp 236 °C dec; $[\alpha]^{25}_D$ −66.5° (*c* 1.24, THF). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.46−7.22 (m, 10H, C_6H_5), 6.29−6.24 (m, 4H, C_5H_4), 6.19−6.12 (m, 4H, C_5H_4), 4.17 (dd, J = 10.5, 3.9 Hz, 2H, CH_2), 4.00 (dd, J = 10.6, 10.5 Hz, 2H, C*H*), 2.50 (s, 12H, N−CH_3), 2.29 (dd, J = 10.6, 3.9 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 142.90, (C_6−C), 132.92 (C_5−C), 128.42 (C_6H_5), 127.92 (C_6H_5), 126.38 (C_6H_5), 115.49 (C_5H_4), 108.21 (C_5H_4), 107.67 (C_5H_4), 105.07 (C_5H_4), 68.87 (CH_2), 47.87 (N−*C*H_3), 42.17 (*C*H). MS (240 °C): *m*/*z* 548 (1) $[M]^+$, 513 (1) $[M - Cl]^+$, 490 (1) $[M - C_3H_8N]^+$, 336 (13) $[Y\{C_5H_4CH(Ph)CH_2NMe_2\}Cl]^+$, 58 (100) $[C_3H_8N]^+$. Anal. Calcd for $C_{30}H_{36}ClN_2Y$ (548.99 g/mol): C, 65.64; H, 6.61; N, 5.10. Found: C, 65.28; H, 6.35; N, 5.19.

Chlorobis{η^5:η^1-(*S*)-[2-(dimethylamino)-1-(phenylethyl)]-cyclopentadienyl}samarium(III) (3b). In analogy with the preparation of **3a**, 1.20 g (3.0 mmol) of $SmCl_3(THF)_2$ reacted with 1.51 g (6.0 mmol) of **9** in 120 mL of THF to give 0.74 g (40%) of yellow crystalline **3b**; mp 288 °C dec; $[\alpha]^{25}_D$ −82.8° (*c* 4.25, THF). ^{1}H NMR (THF-d_8, 200 MHz): δ 11.99 (s_{br}, 2H, C_5H_4), 8.53 (s_{br}, 2H, C_5H_4), 8.03 (m, 4H, C_6H_5), 7.55 (m, 4H, C_6H_5), 7.36 (m, 2H, C_6H_5), 7.34 (s_{br}, 2H, C_5H_4), 7.21 (s_{br}, 2H, C_5H_4), 4.38 (dd, J = 12.8, 3.6 Hz, 2H, CH_2), 4.02 (m, 2H, C*H*), 1.72 (dd, J = 11.4, 3.6 Hz, 2H, CH_2), 0.19 (s, 12H, N−CH_3). ^{1}H NMR (toluene-d_8, 400 MHz): δ 12.06 (s_{br}, 2H, C_5H_4), 8.29 (s_{br}, 2H, C_5H_4), 7.95 (d, J = 7.4 Hz, 4H, C_6H_5), 7.43 (dd, J = 7.5, 7.4 Hz, 4H, C_6H_5), 7.30 (m, 2H, C_6H_5), 7.24 (s_{br}, 2H, C_5H_4), 6.89 (s_{br}, 2H, C_5H_4), 4.09 (s_{br}, 2H, CH_2), 2.08 (m, 2H, C*H*), 1.42 (m, 2H, CH_2), 0.94 (s, 6H, N−CH_3), −0.55 (s, 6H, N−CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 50.32 MHz): δ 142.74, (C_6−C), 133.81 (C_5−C), 129.34 (C_6H_5), 129.23 (C_6H_5), 127.23 (C_6H_5), 110.74 (C_5H_4), 106.81 (C_5H_4), 102.24 (C_5H_4), 96.61 (C_5H_4), 72.90 (CH_2), 48.15 (N−*C*H_3), 47.85 (*C*H). MS (^{152}Sm, 280 °C): *m*/*z* 611 (2) $[M]^+$, 576 (1) $[M - Cl]^+$, 553 (1) $[M - C_3H_8N]^+$, 399 (5) $[Sm\{C_5H_4CH(Ph)CH_2NMe_2\}Cl]^+$, 364 (1) $[Sm\{C_5H_4CH(Ph)$-$CH_2NMe_2\}]^+$, 58 (100) $[C_3H_8N]^+$. Anal. Calcd for $C_{30}H_{36}ClN_2Sm$ (610.44 g/mol): C, 59.03; H, 5.94; N, 4.59. Found: C, 59.45; H, 6.00; N, 4.23.

Chlorobis{η^5:η^1-(*S*)-[2-(dimethylamino)-1-(phenylethyl)]-cyclopentadienyl}lutetium (3c). In analogy with the preparation of **3a**, 1.01 g (2.0 mmol) of $LuCl_3(THF)_3$ was treated with 1.01 g (4.0 mmol) of **9** in 60 mL of THF. Colorless crystalline **3c**, 0.85 g (67%), was obtained from 20 mL of toluene at −28 °C; mp 178 °C dec; $[\alpha]^{25}_D$ −32.5° (*c* 1.66, THF). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.48−7.43 (m, 4H, C_6H_5), 7.37−7.23 (m, 6H, C_6H_5), 6.31 (m, 2H, C_5H_4), 6.21−6.16 (m, 4H, C_5H_4), 6.05 (m, 2H, C_5H_4), 4.24 (dd, J = 11.6, 5.1 Hz, 2H, CH_2), 3.83 (dd, J = 11.6, 11.6 Hz, 2H, C*H*), 2.47 (s, 12H, N−CH_3), 2.46 (dd, J = 11.6, 5.1 Hz, 2H, CH_2). ^{1}H NMR (toluene-d_8, 400 MHz): δ 7.25 (m, 4H, C_6H_5), 7.12 (m, 4H, C_6H_5), 7.04 (m, 2H, C_6H_5), 6.11 (m, 2H, C_5H_4), 5.86 (m, 2H, C_5H_4), 5.79 (m, 2H, C_5H_4), 5.67 (m, 2H, C_5H_4), 3.84−3.82 (m, 4H, CH_2 + C*H*), 2.13 (s, 12H, N−CH_3), 2.09 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 142.97 (C_6−C), 131.66 (C_5−C), 128.37 (C_6H_5), 128.09 (C_6H_5), 126.37 (C_6H_5), 113.57 (C_5H_4), 108.94 (C_5H_4), 107.44 (C_5H_4), 105.77 (C_5H_4), 68.90 (CH_2), 47.50 (N−*C*H_3), 42.35 (*C*H). $^{13}C\{^1H\}$ NMR (toluene-d_8, 100.64 MHz): δ 143.00 (C_6−C), 131.79 (C_5−C), 128.60 (C_6H_5), 128.57 (C_6H_5), 126.56 (C_6H_5), 113.94 (C_5H_4), 109.13 (C_5H_4), 106.85 (C_5H_4), 105.21 (C_5H_4), 68.90 (CH_2), 47.86 (N−*C*H_3), 42.65 (*C*H). MS (^{175}Lu, 140 °C): *m*/*z* 634 (2) $[M]^+$, 599 (1) $[M - Cl]^+$, 576 (2) $[M - C_3H_8N]^+$, 422 (18) $[Lu\{C_5H_4CH$-$(Ph)CH_2NMe_2\}Cl]^+$, 58 (100) $[C_3H_8N]^+$. Anal. Calcd for $C_{30}H_{36}ClLuN_2$ (635.05 g/mol): C, 56.74; H, 5.71; N, 4.41. Found: C, 56.34; H, 5.66; N, 4.65.

Chloro[η^5:η^1-(*S*)-(2-(dimethylamino)propyl)cyclopentadienyl](pentamethylcyclopentadienyl)yttrium (4a). To a mixture of 1.85 g (4.5 mmol) of $YCl_3(THF)_3$ and 0.85 g (4.5 mmol) of **8** in 80 mL of THF, which was stirred for 12 h at 25 °C, was added 0.71 g (4.5 mmol) of $Na(C_5Me_5)$, and the mixture was stirred for a further 12 h at room temperature. The solvent was removed, and the residue was washed twice with *n*-pentane (20 mL). The remaining pale solid was extracted with diethyl ether (80 mL). The clear extraction solution was concentrated to 10 mL and then cooled to −28 °C. Colorless crystalline **4a**, 0.64 g (35%), precipitated; mp 195 °C dec; $[\alpha]^{25}_D$ −11.8° (*c* 1.185, toluene). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.60 (m, 1H, C_5H_4), 6.20 (m, 1H, C_5H_4), 5.85 (m, 1H, C_5H_4), 5.37 (m, 1H, C_5H_4), 3.31 (m, 1H, C*H*), 2.34 (dd, J = 14.6, 4.7 Hz, 1H, CH_2), 2.01 (s_{br}, 18H, C_5CH_3 + N−CH_3), 1.95 (m, 1H, CH_2), 1.81 (s, 3H, N−CH_3), 0.35 (d, J = 6.3 Hz, 3H, C−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.32 MHz): δ 124.52 (C_5−CH_2), 117.73 (C_5CH_3), 114.88 (C_5H_4), 112.48 (C_5H_4), 109.26 (C_5H_4), 108.10 (C_5H_4), 64.68 (*C*H), 39.63 (N−*C*H_3), 32.81 (CH_2), 29.73 (N−*C*H_3), 11.02 (C_5CH_3), 8.36 (CH*C*H_3). MS (163 °C): *m*/*z* 409 (22) $[M]^+$, 374 (4) $[M - Cl]^+$, 274 (69) $[M - C_5Me_5]^+$, 259 (5) $[(C_5Me_5)YCl]^+$, 72 (100) $[C_4H_{10}N]^+$. Anal. Calcd for $C_{20}H_{31}ClNY$ (409.83 g/mol): C, 58.61; H, 7.62; N, 3.42. Found: C, 58.49; H, 7.93; N, 3.30.

Chloro[η^5:η^1-(*S*)-(2-(dimethylamino)propyl)cyclopentadienyl](pentamethylcyclopentadienyl)lutetium (4c). In analogy with the preparation of **4a**, 1.74 g (3.5 mmol) of $LuCl_3(THF)_3$ in 80 mL of THF was reacted with 0.66 g (3.5 mmol) of **8** followed by 0.55 g (3.5 mmol) of $Na(C_5Me_5)$. Instead of ether, toluene was used as extracting agent. Concentration of the extraction solution to 10 mL and cooling it to −28 °C afforded 0.71 g (41%) of colorless crystalline **4c**; mp 199 °C dec; $[\alpha]^{25}_D$ −1.6° (*c* 3.65, toluene). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.15 (m, 2H, C_5H_4), 6.09 (m, 1H, C_5H_4), 6.03 (m, 1H, C_5H_4), 2.80−2.72 (2 m, 2H, C*H* + CH_2), 2.41 (m, 1H, CH_2), 2.17 (s, 6H, N−CH_3), 1.00 (s, 15H, C_5CH_3), 0.86 (d, J = 6.3 Hz, 3H, CH_3). ^{1}H NMR (toluene-d_8, 200 MHz): δ 6.46 (m, 2H, C_5H_4), 6.18 (m, 1H, C_5H_4), 5.64 (m, 1H, C_5H_4), 5.25 (m, 1H, C_5H_4), 3.36 (m, 1H, C*H*), 2.36 (dd, J = 14.6, 4.9 Hz, 2H, CH_2), 2.10 (s_{br}, 3H, N−CH_3), 1.99 (s, 15H, C_5CH_3), 1.97 (m, 2H, CH_2), 1.53 (s_{br}, 3H, N−CH_3), 0.39 (d, J = 6.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 125.60 (C_5−CH_2), 116.83 (C_5CH_3), 113.17 (C_5H_4), 112.85 (C_5H_4), 109.98 (C_5H_4), 109.66 (C_5H_4), 62.04 (*C*H), 40.42 (N−*C*H_3), 33.40 (CH_2), 13.09 (CH*C*H_3), 11.48 (C_5CH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, 50.32 MHz): δ 123.50 (C_5−CH_2), 117.84 (C_5CH_3), 116.30 (C_5H_4), 113.40 (C_5H_4), 108.21 (C_5H_4), 107.54 (C_5H_4), 65.91 (*C*H), 44.67 (N−*C*H_3), 33.60 (CH_2), 33.45 (N−*C*H_3), 12.10 (C_5CH_3), 9.50 (CH*C*H_3). MS (^{175}Lu, 140 °C): *m*/*z* 495 (19) $[M]^+$, 460 (2) $[M - Cl]^+$, 360 (57) $[M - C_5Me_5]^+$, 345 (2) $[(C_5Me_5)LuCl]^+$, 72 (100) $[C_4H_{10}N]^+$. Anal. Calcd for $C_{20}H_{31}ClLuN$ (495.89 g/mol): C, 48.44; H, 6.30; N, 2.82. Found: C, 48.40; H, 6.10; N, 2.84.

Chloro{η^5:η^1-(*S*)-[2-(dimethylamino)-1-(phenylethyl)]-

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cyclopentadienyl}(pentamethylcyclopentadienyl)-yttrium (5a). In analogy with the preparation of **4a**, 1.42 g (3.5 mmol) of $YCl_3(THF)_3$ in 80 mL of THF was treated with 0.87 g (3.5 mmol) of **9** followed by 0.55 g (3.5 mmol) of $Na(C_5Me_5)$. Instead of ether, toluene was used as extracting agent. From the extraction solution concentrated to 30 mL and cooled to −28 °C, 0.58 g (36%) of colorless crystalline **5a** was isolated; mp 294 °C; $[\alpha]^{25}_D$ −54.7° (*c* 1.5, toluene). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.42−7.15 (several m, 5H, C_6H_5), 6.52 (m, 1H, C_5H_4), 6.21 (m, 1H, C_5H_4), 6.11 (m, 1H, C_5H_4), 5.89 (m, 1H, C_5H_4), 4.46 (dd, J = 8.2, 8.1 Hz, 1H, C*H*), 3.27 (dd, J = 11.7, 8.2 Hz, 1H, CH_2), 2.74 (dd, J = 11.7, 8.1 Hz, 1H, CH_2), 2.26 (s, 6H, N−CH_3), 2.02 (s, 15H, C_5CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 143.98 (C_6−C), 132.10 (C_5−CH_2), 128.27 (C_6H_5), 128.16 (C_6H_5), 126.03 (C_6H_5), 118.12 (d, ^1J(YC) = 1.1 Hz, C_5CH_3), 111.96 (C_5H_4), 111.56 (C_5H_4), 111.41 (C_5H_4), 110.59 (C_5H_4), 68.08 (CH_2), 45.67 (N−*C*H_3), 43.01 (*C*H), 11.43 (C_5CH_3). MS (211 °C): *m*/*z* 471 (8) $[M]^+$, 436 (1) $[M - Cl]^+$, 336 (20) $[M - C_5Me_5]^+$, 259 (2) $[(C_5Me_5)YCl]^+$, 58 (100) $[C_3H_8N]^+$. Anal. Calcd for $C_{25}H_{33}ClNY$ (471.90 g/mol): C, 63.63; H, 7.05; N, 2.97. Found: C, 63.44; H, 6.84; N, 2.83.

Chloro{η^5:η^1-(*S*)-[2-(dimethylamino)-1-(phenylethyl)]-cyclopentadienyl}(pentamethylcyclopentadienyl)-lutetium (5c). In analogy with **4a**, 1.69 g (3.4 mmol) of $LuCl_3(THF)_3$ in 80 mL of THF was treated with 0.80 g (3.4 mmol) of **9** followed by 0.54 g (3.4 mmol) of $Na(C_5Me_5)$. Instead of ether, toluene was used as an extracting agent. Colorless **5c**, 1.15 g (61%), crystallized on cooling the concentrated extraction solution (20 mL) to −28 °C; mp 297 °C; $[\alpha]^{25}_D$ −49.6° (*c* 3.87, toluene). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.39−7.13 (several m, 5H, C_6H_5), 6.45 (m, 1H, C_5H_4), 6.20 (m, 1H, C_5H_4), 6.07 (m, 1H, C_5H_4), 5.78 (m, 1H, C_5H_4), 4.47 (dd, J = 8.6, 8.5 Hz, 1H, C*H*), 3.28 (dd, J = 11.7, 8.5 Hz, 1H, CH_2), 2.81 (dd, J = 11.7, 8.6 Hz, 1H, CH_2), 2.23 (s, 6H, N−CH_3), 1.99 (s, 15H, C_5CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 144.43 (C_6−C), 130.73 (C_5−CH_2), 128.39 (C_6H_5), 128.06 (C_6H_5), 125.90 (C_6H_5), 117.11 (C_5CH_3), 111.84 (C_5H_4), 111.07 (C_5H_4), 110.57 (C_5H_4), 108.96 (C_5H_4), 67.50 (CH_2), 45.72 (N−*C*H_3), 43.05 (*C*H), 11.48 (C_5CH_3). MS (^{175}Lu, 208 °C): *m*/*z* 557 (15) $[M]^+$, 522 (1) $[M - Cl]^+$, 422 (27) $[M - C_5Me_5]^+$, 345 (1) $[(C_5Me_5)LuCl]^+$, 58 (100) $[C_3H_8N]^+$. Anal. Calcd for $C_{25}H_{33}ClLuN$ (557.96 g/mol): C, 53.82; H, 5.96; N, 2.51. Found: C, 53.90; H, 5.91; N, 2.37.

{η^5:η^1-(*S*)-[2-(Dimethylamino)-1-(phenylethyl)]cyclopentadienyl}(methyl)(pentamethylcyclopentadienyl)-lutetium (6c). To a solution of 1.45 g (2.6 mmol) of **5c** in 70 mL of toluene was added 1.7 mL (2.7 mmol) of a 1.6 M solution of methyllithium in diethyl ether at −78 °C. The reaction mixture was stirred for 3 days at 25 °C, during which time LiCl precipitated. The solid was filtered off, and the clear, colorless solution was reduced in volume to 15 mL. Cooling of the solution to −28 °C resulted in the precipitation of 0.38 g (27%) of colorless crystalline **6c**; mp 179 °C dec; $[\alpha]^{25}_D$ −12.0° (*c* 1.17, toluene). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.36−7.15 (several m, 5H, C_6H_5), 6.43 (m, 1H, C_5H_4), 5.99 (m, 1H, C_5H_4), 5.85 (m, 2H, C_5H_4), 4.11 (dd, J = 8.6, 8.2 Hz, 1H, C*H*), 2.73 (m, 1H, CH_2), 2.18 (m, 1H, CH_2), 2.12 (s, 6H, N−CH_3), 1.98 (s, 15H, C_5CH_3), −0.51 (s, 3H, Lu−CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 128.16 (C_6−C), 127.12 (C_6H_5), 126.06 (C_6H_5), 117.11 (C_5−CH_2), 115.18 (C_5CH_3), 109.93 (C_5H_4), 109.09 (C_5H_4), 108.54 (C_5H_4), 68.57 (CH_2), 45.80 (N−*C*H_3), 42.69 (*C*H), 21.48 (Lu−*C*H_3), 11.40 (C_5CH_3). MS (^{175}Lu, 196 °C): *m*/*z* 522 (100) $[M - CH_3]^+$, 402 (1) $[M - C_5Me_5]^+$. Anal. Calcd for $C_{26}H_{36}LuN$ (537.55 g/mol): C, 58.09; H, 6.75; N, 2.61. Found: C, 58.48; H, 7.07; N, 2.90.

X-ray Structure Determination. Crystals were selected by using a device similar to that reported by Veith and Bärninghausen,[6] glued with grease on the top of a glass fiber, and transferred directly into the cold nitrogen stream of the low-temperature unit mounted to an Enraf-Nonius CAD-4 automatic diffractometer (graphite crystal monochromator, Mo Kα radiation = 0.710 69 Å), controlled by a Compaq Deskpro 386s. The cell parameters were obtained from the angles of 25 reflections (scan type ω−2θ). Reflections were scanned with variable scan time, depending on intensities, with two-thirds of the time used for scanning the peak and each one-sixth measuring the left and right background. The raw data were corrected for Lorentz, polarization, and absorption effects.[7] The positions of the metal atoms were determined by direct methods (SHELXS86).[8] The calculated difference Fourier map (SHELXL93)[9] revealed all other missing non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The C−H hydrogen atoms were calculated in idealized positions (C−H 0.96 Å, U_{iso} = 0.08 Å^2). Scattering factors were taken from the literature.[10] Data reduction was performed using a IBM RISC System/6000, 340.[11] All other calculations were undertaken with SHELXL93.[9] Absolute structure parameters were determined using the Flack parameters[12] with SHELXL93.[9] In all chiral compounds the Flack parameter is 0 within estimated standard deviations. The geometrical aspects of the structure were analyzed by using the PLUTON program.[13] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-410142 (**1b**), CSD-410157 (**3b**), CSD-410140 (**3c**), CSD-410141 (**5a**), CSD-410139 (**6c**), the authors, and the full citation of the journal.

Results and Discussion

Chiral Nonracemic Bis(cyclopentadienyl) Lanthanide(III) Complexes. The metathetic reactions of 2 equiv of the potassium salts **7**−**9** with yttrium, samarium, or lutetium trichloride cleanly gave the metallocenes **1**−**3** (Scheme 1). Crystallization from toluene (**1a,b**; **3a,b,c**) or hexane (**2a,b**) afforded the complexes in 40−69% isolated yields. Only the yttrium and samarium(III) compounds **2a** and **2b** containing the (*S*)-[2-(dimethylamino)propyl]cyclopentadienyl ligand were obtained as mixtures of diastereomers.

In a previous publication we reported the synthesis of divalent lanthanide complexes using the same chiral, nonracemic cyclopentadienyl ligands.[4] These complexes can be oxidized to the corresponding trivalent sandwich complexes by alkyl- or arylhalides.[14] In this way, the oxidative addition of *tert*-butyl chloride to **10** produced **2b** with 54% yield (Scheme 2) as a mixture of diastereomers, the composition of which is identical to that obtained by the metathetical route. Thus, the synthetic pathway does not influence the composition of the diastereomeric mixture.

As expected, the colorless yttrium and lutetium derivatives as well as the yellow samarium(III) com-

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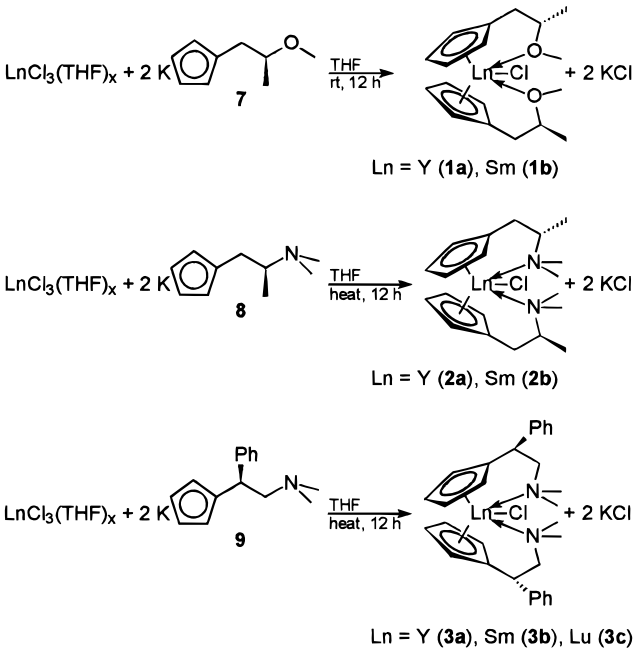
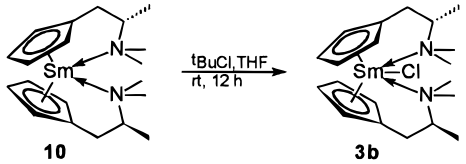
Scheme 1



Scheme 2



pounds obtained are more stable against air and moisture than non-donor-functionalized lanthanide sandwich complexes. It requires a several hour exposure to open air until decomposition can be recognized by discoloration of the complexes. The complexes **1**, **2**, and **3** are soluble in polar solvents such as THF and pyridine as well as in aromatic solvents such as toluene. **1** and **2** are also moderately soluble in *n*-hexane. The melting points range from 134 to 288 °C and are highest for the derivatives **3**, bearing the phenyl-substituted ligand **9**. All new compounds were characterized by elemental analyses, NMR spectroscopy, mass spectrometry, and their rotation angle.

The ^{1}H and ^{13}C NMR spectra of **1** and **3** show only one set of the expected signals, whereas the spectra of **2** show twice as many signals, indicating the existence of two diastereomers. Collin et al. also observed only one set of signals in the spectra of bis(cyclopentadienyl)-lanthanide iodides which contain chiral benzyl ether functionalized cyclopentadienyl ligands.[15] Three scenarios could account for the appearance of only one set of signals. (1) The minor isomer is present in an amount too small to be detected, (2) only the best crystallizing isomer has been isolated, or (3) a rapid exchange occurs between the two diastereomeric forms. In the case of **2**, the $^{1}H,^{1}H$ and $^{1}H,^{13}C$ COSY NMR spectra permitted a clear assignment of the signals, but did not determine to which of the diastereomers the respective signals

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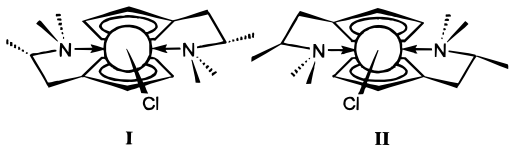

Figure 1. Diastereomers of the complexes **2**.

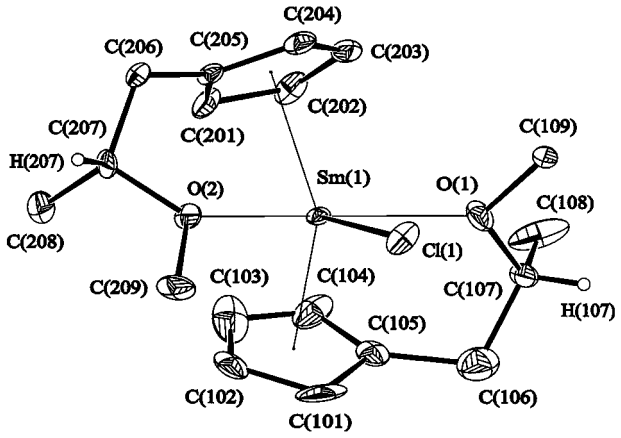

Figure 2. ORTEP plot[20] of the molecular structure and numbering scheme of **1b**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except on the stereocenter are removed.

belonged. The two sets of proton signals, as well as their intensities, did not change either at temperatures up to 100 °C or after standing at ambient temperature for several days.

Depending on the kind of solvent and on the temperature, the nitrogen-containing complexes **2** and **3** differ in their NMR spectra, indicating fluctional behavior in solution. All proton and carbon spectra recorded in coordinating solvents show only a single peak for the *N*-methyl groups and, in the case of **2**, a single peak for each diastereomer. However, in noncoordinating solvents such as deuterated toluene, **3b** exhibits at room temperature two broad proton resonances at 0.94 and −0.55 ppm for the dimethylamino group, whereas the spectra of **3c** shows only one narrow signal at 2.14 ppm. As the temperature was lowered to −83 °C, the half width of the signals of **3b** decreased and the signal of **3c** split into two broad signals at 2.25 and 1.66 ppm. On the other hand, the two signals of **3b** appearing at room temperature already merge at +37 °C into one broad signal located at −0.22 ppm. These observations provide insight into not only the strength dependence of the coordinative nitrogen−metal bond upon the central metal characteristics, but also the temperature dependence of the abstraction rate of the donating nitrogen from the metal atom.

All the mass spectra, recorded between 80 and 280 °C, show the molecular ion as the peak of highest mass and a fragment formed by loss of the chlorine atom and of one of the cyclopentadienyl ligands. The spectra show the expected isotopic pattern for the elements.

Molecular Structures of 1b, 3b, and 3c. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from toluene. One of the two non-superimposable molecules in the unit cell of **1b** is shown in Figure 2. The unit cells of **3b** and **3c** contain two identical, well-separated molecules. Except for the difference in the ionic radii of samarium and lutetium,

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Table 1. Crystal Data and Structure Refinement for 1b, 3b, and 3c

compd	**1b**	**3b**	**3c**
empirical formula	$C_{18}H_{26}ClO_2Sm$	$C_{30}H_{36}ClN_2Sm$	$C_{30}H_{36}ClLuN_2$
fw	460.19	610.41	635.03
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1$
Z	4	2	2
a, b, c (Å)	12.670(2), 9.449(5), 16.332(4)	12.8078(14), 8.326(2), 13.325(5)	12.627(4), 8.369(3), 13.204(7)
α, β, γ (deg)	90.0, 111.09(2), 90.0	90.0, 110.66(2), 90.0	90.0, 110.21(2), 90.0
volume (10^{-30}m^3)	1824.3(11)	1329.6(6)	1309.4(9)
D_{calcd} (g/cm^{-3})	1.676	1.525	1.611
μ (Mo Kα) (cm^{-1})	0.3369	0.2329	0.3892
abs struct param	0.01(3)	0.02(2)	−0.01(2)
cryst size (mm)	0.36 × 0.18 × 0.09	0.3 × 0.3 × 0.24	0.45 × 0.36 × 0.18
temp (K)	193(2)	163(2)	163(2)
θ range (deg)	$2.68 < 2\theta < 51.94$	$3.26 < 2\theta < 47.88$	$3.28 < 2\theta < 57.96$
cell measurement θ range (deg)	$13.16 < 2\theta < 27.58$	$12.84 < 2\theta < 24.9$	$12.7 < 2\theta < 29.6$
scan (deg)	$0.70 + 0.35 \tan\theta$	$0.75 + 0.35 \tan\theta$	$1.05 + 0.35 \tan\theta$
data set: h^{min}, h^{max}	0, 15	0, 14	−14, 0
k^{min}, k^{max}	0, 11	−1, 9	−9, 9
l^{min}, l^{max}	−20, 18	−15, 14	−14, 15
no. of total/unique reflns	3969/3796 [$R_{(int)} = 0.1988$]	2403/2235 [$R_{(int)} = 0.0321$]	4309/4103 [$R_{(int)} = 0.0500$]
goodness-of-fit on F^2	1.061	1.047	1.079
intensity variation	none	none	none
N_{ref}, N_{par}	3784, 405	2226, 311	4097, 301
R1, wR2 [$I > 2\sigma(I)$]	0.0554, 0.1419	0.0305, 0.0743	0.0639, 0.1548
R1, wR2 (all data)	0.0575, 0.1563	0.0333, 0.0799	0.0648, 0.1601
residual density (e Å^{-3})	max. 4.850	max. 1.394	max. 3.532
	min. −5.029	min. −1.898	min. −4.460

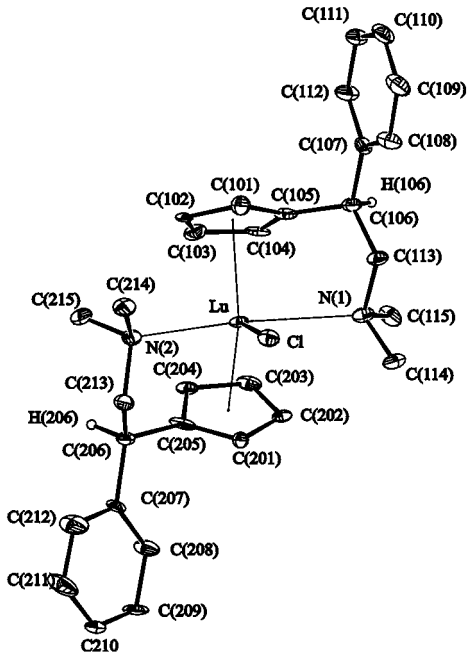

Figure 3. ORTEP plot[20] of the molecular structure and numbering scheme of **3c**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except on the stereocenter are removed.

the complexes are isostructural. Figure 3 shows the structure of **3c**. The crystallographic data are listed in Table 1, and selected structural data are given in Table 3.

All three complexes are monomeric, free of solvent, and *S*-configurated at the stereocenter. In each case both donor atoms are intramolecularly coordinated to the samarium or lutetium atom, respectively, and only one diastereomer (Figure 2) is present. Overall, the structures closely resemble the distorted trigonal bipyramidal geometry of other donor-functionalized bis(cyclopentadienyl) lanthanide(III) halides possessing the formal coordination number of 9.[15b,16] The ring centers and the chlorine atom occupy the equatorial positions, and the donor atoms the apical positions, forming donor−metal−donor angles of approximately 160°.

The cyclopentadienyl rings in **3b** are planar within the estimated standard deviations, whereas the rings in **1b** and **3c** deviate from the ring plane by a maximum of 0.022(7) and 0.21(6) Å, respectively. The vertical projection of the metal atom on the ring planes is shifted from the ring center by 0.052 Å (Cp1, Cp3) and 0.075 Å (Cp2, Cp4) in **1b**, by 0.056 Å (Cp1) and 0.03 Å (Cp2) in **3b**, and by 0.06 Å (Cp1) and 0.077 Å (Cp2) in **3c**.

The distance from the lanthanide to the ring center in **1b** [2.428(7), 2.432(5), and 2.444(5) Å] equals that in [Sm{(*S*)-η^5:η^1-$C_5H_4CH_2CH(Me)OCH_2Ph$}$_2$I][15b] (2.43 and 2.45 Å). The corresponding distances for **3b** [2.467(4) and 2.462(4) Å] are only insignificantly longer. The distances of 2.343(6) Å and 2.354(6) Å in **1c** are in the expected range for bis(cyclopentadienyl)lutetium compounds.[17]

The Sm−O distances in **1b** [2.51(1) and 2.547(9) Å, 2.535(8) and 2.58(1) Å] are slightly shorter than those in [Sm{(*S*)-η^5:η^1-$C_5H_4CH_2CH(Me)OCH_2Ph$}$_2$I][15b] [2.56(2) and 2.57(2) Å], but they are in good agreement with the values in other samarium compounds with a formal coordination number of 9, e.g., [(η^5-C_5Me_5)$_2$Sm(N_2Ph_2)-(THF)][18] [2.532(8) and 2.557(9) Å, respectively] and [(η^5-C_5Me_5)$_2$Sm(η^2-PhNHNPh)(THF)][19] [2.548(4) Å].

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Table 2. Crystal Data and Structure Refinement for 5a and 6c

compd	5a	6c
empirical formula	$C_{25}H_{33}ClNY$	$C_{26}H_{36}LuN$
fw	471.88	537.53
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a, b, c (Å)	11.859(2), 12.67(8), 15.814(5)	11.815(2), 12.219(8), 16.003(3)
volume (10^{-30}m^3)	2319(2)	2310(2)
D_{calcd} (g/cm^{-3})	1.351	1.545
μ (Mo Kα) (cm^{-1})	0.2640	0.4284
abs struct param	−0.032(8)	0.00(3)
cryst size (mm)	0.36 × 0.21 × 0.18	0.3 × 0.12 × 0.12
temp (K)	193(2)	162(3)
θ range (deg)	$4.18 < 2\theta < 48.00$	$4.2 < 2\theta < 47.98$
cell measurement θ range (deg)	$10.34 < 2\theta < 24.56$	$10.81 < 2\theta < 22.44$
scan (deg)	$0.61 + 0.35 \tan\theta$	$1.1 + 0.35 \tan\theta$
data set: h^{min}, h^{max}	−1, 13	−1, 13
k^{min}, k^{max}	−2, 14	3, 13
l^{min}, l^{max}	−18, 18	−18, 18
no. of total/unique reflns	4085/3628 [$R_{(int)} = 0.0207$]	4062/3596 [$R_{(int)} = 0.0397$]
goodness-of-fit on F^2	1.000	1.019
N_{ref}, N_{par}	3611, 260	3567, 261
R1, wR2 [$I > 2\sigma(I)$]	0.0369, 0.0837	0.0429, 0.1091
R1, wR2 (all data)	0.0538, 0.0905	0.0511, 0.1202
residual density (e Å^{-3})	max. 0.835, min. −0.430	max. 1.176, min. −0.997

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] for 1b, 3b, and 3c with Estimated Standard Deviations

compd	1b	3b	3c
Ln−E1[a]	2.51(1)/2.547(9)	2.696(7)	2.77(1)
Ln−E2[a]	2.535(8)/2.58(1)	2.795(7)	2.65(1)
Ln−Cl	2.668(3)/2.648(3)	2.657(2)	2.535(3)
Ln−Cp1[b]	2.428(7)/2.432(5)	2.467(4)	2.343(6)
Ln−Cp2[b]	2.444(5)/2.444(5)	2.462(4)	2.354(6)
Cp1−Ln−Cp2[b]	123.5(2)/129.7 (2)	132.2(1)	132.7(2)
E1−Ln−E2[a]	156.9(3)/167.4(3)	158.2(2)	156.4(6)

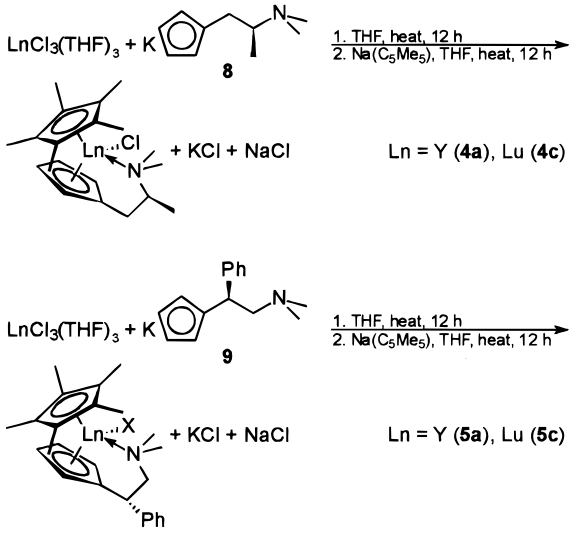
[a] E = O for **1b**, E = N for **3b** and **3c**. [b] Cp defines the centroid of the ring atoms Cp1(C101−C105) and Cp2(C201−C205).

Although the coordinative bonds between the nitrogen atoms and the samarium atom in **3b** [2.696(7) and 2.795(7) Å] or the lutetium atom in **3c** [2.77(1) and 2.65(1) Å] are fairly long compared to other *N*-donating systems,[16c;17d;21] bond lengths of this magnitude were estimated for [(η^5-C_5Me_5)$_2$Sm(η^2-PhNHNPh)(THF)][19] [2.610(5) Å], [(η^5-C_5Me_5)$_2$Sm(η^2-$C_6H_{10}N_4$)][22] [2.81(2) Å], or [(η^5-C_5H_5)$_2$Lu{η^1:η^1-$CH_2CH(Me)CH_2NMe_2$}(Cl)(THF)$_2$] [2.637(8) Å].[23]

To generate precatalysts suitable for selective organic reactions, the complexes **1**−**3** have to be alkylated. Unfortunately, they proved to be inert to ionic metathetical substitution by, for example, methyllithium, trimethylaluminum, or methylpotassium. Since these 18-electron complexes seem to be sterically and coordinatively saturated, a lowering of the coordination number and of the steric demand of the ligands by using only one donor-functionalized cyclopentadienyl ligand may be promising.

Mixed Chiral Lanthanide(III) Sandwich Complexes. In contrast to the difficulties usually arising during the synthesis of mixed lanthanide sandwich complexes,[21,24] the stage of the intermediately formed monocyclopentadienyl complex is obviously stabilized by donor-functionalized cyclopentadienyl ligands.[25] Thus, the mixed sandwich complexes **4** and **5** could be easily prepared in a one-pot reaction by adding to yttrium or lutetium trichloride first the donor-functionalized cyclopentadienyl reagent **8** or **9** followed by Na(C_5Me_5) (Scheme 3). Crystallization from diethyl ether (**4**) or toluene (**5**) afforded the complexes in 35−61% isolated yield.

Scheme 3



The presence of the pentamethylcyclopentadienyl ligand in **4a**, **4c**, **5a**, and **5c** causes a higher solubility in nonpolar solvents compared to **2a**, **2c**, **3a**, and **3c**. They are also more sensitive to oxidation and hydrolysis. The melting points of about 200 °C for **4** and of about

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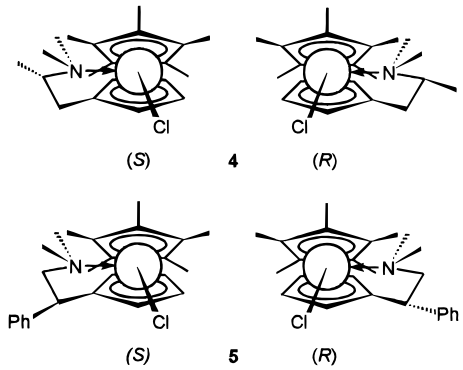

Figure 4. Diastereomers of the complexes **4** and **5**.

300 °C for **5** are comparable to those of **2a**, **2c**, **3a**, and **3c**. The presence of two different cyclopentadienyl ligands in **4** and **5** was confirmed by elemental analyses, NMR spectroscopy, and mass spectrometry. In addition, optical rotation has been measured for all optically active compounds.

The room-temperature ^{1}H and ^{13}C NMR spectra of **4** and **5** show the signals expected for monomeric, solvent-free compounds. Because of the stereocenter in the side chain, four signals are observed in the ^{1}H NMR spectra for each of the donor-functionalized cyclopentadienyl rings. They appear in the typical range from 6.60 to 5.25 ppm. The lack of one peak in the spectra of solutions of **4** in deuterated pyridine must be due to an accidental equivalence. Independent of the solvent, pyridine or toluene, all ^{13}C NMR spectra show four signals between 114.88 and 107.54 ppm for the tertiary carbons of the donor-substituted rings. As in the spectra of the chiral complexes described above, the *N*-methyl groups are inequivalent in noncoordinating solvents, thus indicating $Me_2N \rightarrow Ln$ coordination, but are equivalent and give rise to only one NMR signal in coordinating solvents such as pyridine or THF. Two signals are observed for the diastereotopic protons of the methylene group, and one is observed for the single protons at the stereocenter of the side chain. In the spectra of **4**, additionally a doublet is observed at high field, which is assigned to the protons of the methyl group adjacent to the stereocenter of the functionalized ligand. The signals for the aryl protons of the phenyl-containing compounds **5** appear at low field. The observation of one signal for the methyl protons of the pentamethylcyclopentadienyl ring in the ^{1}H NMR and two signals in the ^{13}C NMR spectra, and one for the methyl groups and one for the quaternary carbons in the ring, indicates free rotation of this ligand system. Because of the two stereocenters in the molecules, one in the donating side chain and one at the metal center, and because of the stereorigidity of the side chain, two diastereomers of each complex should be expected, but again all spectra show only one set of signals. The designation of the diastereomers used in Figure 4 is based on the expanded *Cahn Ingold Prelog* sequence rule for inorganic and organometallic complexes.[26] It remains unclear at this point whether selectively one diastereomer is formed or if there is fast exchange between the two diastereomers on the NMR time scale.

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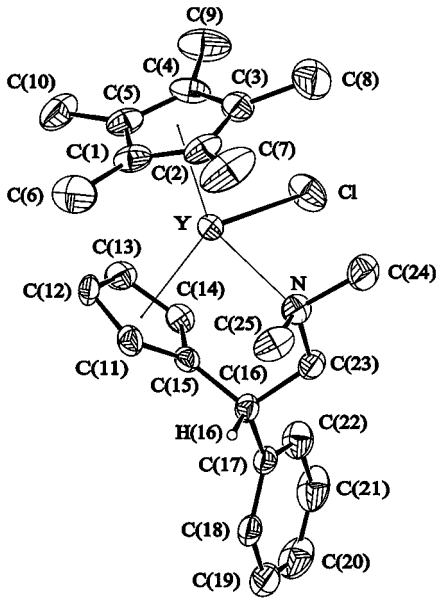

Figure 5. ORTEP plot[20] of the molecular structure and numbering scheme of **5a**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except on the stereocenter are removed.

Table 4. Selected Bond Lengths [Å] and Bond Angles [deg] for 5a and 6c with Estimated Standard Deviations

compd	5a	6c
Ln−N	2.501(4)	2.454(9)
Y−Cl/Lu−C26	2.571(2)	2.35(1)
Ln−Cp1[a]	2.358(3)	2.325(2)
Ln−Cp2[a]	2.357(3)	2.323(2)
Cp1−Ln−Cp2[a]	130.81(8)	132.30(2)
N−Ln−Cp1[a]	118.1(1)	117.8(2)
N−Ln−Cp2[a]	94.9(1)	96.1(2)
Cl−Y−Cp1/C26−Lu−Cp1[a]	107.83(6)	106.4(3)
Cl−Y−Cp2/C26−Lu−Cp2[a]	108.60(6)	105.3(3)
Cl−Y−N/C26−Lu−N	88.2(1)	91.3(5)

[a] Cp defines the centroid of the ring atoms Cp1(C1−C5) and Cp2(C11−C15).

The mass spectra of **4** and **5** were recorded between 140 and 211 °C and show the molecular ion peaks as the peaks of highest mass. The fragments formed by loss of the pentamethylcyclopentadienyl ring are the metal-containing fragments of highest relative intensity, thus indicating stronger bonding of the donor-functionalized ligand to the metals. Fragments formed by loss of the dimethylamino-substituted ligand have only very low intensities.

Molecular Structure of 5a. Crystals of **5a** suitable for single-crystal X-ray analysis were obtained from toluene. Figure 5 shows the structure of one of the four well-separated identical molecules found in the unit cell. It is the diastereomer with *R* configuration at the yttrium atom and *S* configuration in the side chain. The experimental data and selected bond parameters are presented in Tables 2 and 4. The geometry around the yttrium atom is that of a distorted tetrahedron. The formal coordination number of the metal is 8. The Cp1−Y−Cp2 angle of 130.81(8)° and the N−Y−Cl angle of 88.2(1)° are those with the largest deviation from the ideal angle for a tetrahedron, but they may be compared to those found in $[(\eta^5\text{-}C_5H_5)_2Y(\eta^1{:}\eta^1\text{-}C_6H_4\text{-}2\text{-}CH_2NMe_2)]$[27]

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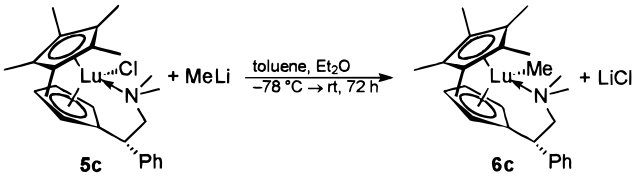
Scheme 4



(Cp−Y−Cp 129°) and $[(\eta^5\text{-}C_5Me_5)_2YCl(THF)]$[28] (Cl−Y−O 89.6° and 90.5°, respectively).

The cyclopentadienyl rings in **5a** are approximately planar, with a maximum deviation from the ring plane of 0.007(3) Å for the donor-substituted (Cp2) and 0.004(3) Å for the permethylated ligand (Cp1). The methyl groups of the pentamethylcyclopentadienyl ring (Cp1) are bent from of the ring plane by up to 0.216(9) Å away from the yttrium atom. The ring slippage is nearly the same for both rings [0.034 Å (Cp1), 0.036 Å (Cp2)]. Both the Cp rings are equidistant from the Y center [2.358(3) and 2.357(3) Å]. Similar distances were determined for each of the two different molecules in the unit cell of $[(\eta^5\text{-}C_5H_5)_2Y(\eta^1{:}\eta^1\text{-}C_6H_4\text{-}2\text{-}CH_2NMe_2)]$[27] (2.35/2.39 and 2.36/2.38 Å) and $[(\eta^5\text{-}C_5Me_5)_2YCl(THF)]$[28] (2.382/2.379 and 2.373/2.388 Å).

The Y−Cl bond length of 2.571(2) Å is almost identical with the Y−Cl distances in $[(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2]$[29] [2.579(6) Å], $[(\eta^5\text{-}C_5Me_5)_2YCl(THF)]$[28] [2.579(3) and 2.577(3) Å for the two molecules in the unit cell, respectively], and in the bridged donor-functionalized $[Y\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5{:}\eta^1\text{-}C_5H_3CH_2CH_2NMe_2)\}Cl]$[30] [2.572(2) Å]. Also the Y−N distance of the last complex [2.502(5) Å] equals that of **5a** [2.501(4) Å].

Whereas the complexes **1**−**3** in which the central lanthanide metal possesses the formal coordination number 9 could not be alkylated by metathetical procedures to give the desired precatalysts, the complexes **4** and **5**, in which the formal coordination number of the metal is lowered to 8, do react with alkylating agents. Thus, treatment of the lutetium complex **5c** with methyllithium in toluene (Scheme 4) resulted in the formation of the methylated compound **6c** with 27% yield.

Compared to the chloro complex **5c**, the colorless crystalline **6c** is highly sensitive to air and moisture. It decomposes at 179 °C and is thus also thermally less stable than **5c**, which melts at 297 °C. Allowing solutions of the sample to stand at room temperature for several days caused discoloration of the previously pale solution into dark brown. The solubility of **6c** in aliphatic and aromatic solvents is only somewhat higher than for **5c**. Elemental analysis, NMR spectroscopy, and mass spectrometry confirm the formation of a lutetium methyl carbon bond.

The ^{1}H and ^{13}C NMR signals of **6c** appear at higher fields than the comparable signals of **5c**, except those for the methylene and the dimethylamino carbon atoms. The resonance of the methyl group bonded to lutetium appears at −0.51 ppm in the ^{1}H NMR spectrum and at 21.48 ppm in the ^{13}C NMR spectrum. Both values are in good agreement with those of $[(\eta^5\text{-}C_5H_5)_2LuMe(THF)]$[31] (^{1}H δ −0.62 ppm) and $[(\eta^5\text{-}C_5Me_4{}^i\text{Pr})_2LuMe(THF)]$[32] (^{1}H δ −0.57 ppm, ^{13}C {^{1}H} δ 25.51 ppm).

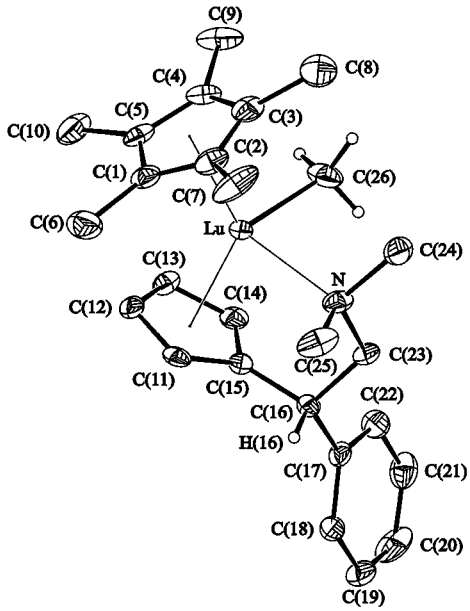


Figure 6. ORTEP plot[20] of the molecular structure and numbering scheme of **6c**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except on the stereocenter are removed.

No molecular ion peak appears in the mass spectrum of **6c** recorded at 140 °C. Under the conditions of electron ionization the fragment that is formed by loss of the methyl group marks the base peak, thus proving the weakness of the Lu−C bond.

Molecular Structure of 6c. Crystals suitable for single-crystal X-ray structure analysis were obtained from toluene. Figure 6 shows the structure of one of the four well-separated identical molecules found in the unit cell. The experimental data and selected bond parameters are listed in Tables 2 and 4. **6c** is the first structurally characterized monomeric and solvent-free lutetium methyl sandwich complex with nonbridged cyclopentadienyl ligands. The geometry around the lutetium atom, which has the formal coordination number 8, very closely resembles the distorted-tetrahedral geometry around the yttrium atom in **5a**. According to the expanded *CIP* rule,[26] the configuration at the chiral lutetium center is *S* because of the lower priority of the methyl group compared to Cl in **5a**.

The angle of 91.3(5)° between the methyl group at the Lu^{3+} ion and the nitrogen atom in the side chain (C26−Lu−N) is larger than the corresponding N−Y−Cl angle of 88.2(1)° in **5a**. The Cp1-Lu−Cp2 angle [132.30(2)°] is in the same range as those of other bent lutetium sandwich complexes such as $[(\eta^5\text{-}C_5H_5)_2LuCl(THF)]$[17a] (129°) or $[(\eta^5\text{-}C_5H_5)_2LuCH_2SiMe_3]$[31b] (130.2°).

In contrast to **5a** the ring slippage in **6c** is not identical for both rings, but is significantly larger (0.065

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Å) for the pentamethylcyclopentadienyl ring Cp1 than for the donor-substituted Cp2 ligand (0.039 Å). The distances between the lutetium atom and the ring centers [2.325(2) Å for Cp1, 2.323(2) Å for Cp2] are typical for formally eight-coordinate bis(cyclopentadienyl)lutetium compounds.[17] Cp2 is planar within the estimated standard deviations, whereas Cp1 shows a maximum deviation from the ring plane of 0.013 Å. The Lu−C(methyl) distance in **6c** [2.35(1) Å] is shorter than the corresponding distance in $[(\eta^5\text{-}C_5Me_4{}^iPr)_2LuMe(THF)]$[32] [2.390(5) Å] or $[Lu\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5{:}\eta^1\text{-}C_5H_3CH_2CH_2NMe_2)\}Cl]$[30] [2.370(9) Å]. Considering the 1 Å larger effective ionic radius of the Yb^{3+} ion compared to the Lu^{3+} ion,[33] the Lu−C(methyl) distance in **6c** matches that in $[(\eta^5\text{-}C_5H_5)_2YbMe(THF)]$[34] [2.36(1) Å]. Values comparable to the Lu−N bond length of 2.454(9) Å were found in bridged, donor-functionalized lutetium derivatives.[21]

Conclusion

We prepared novel chiral nonracemic metallocenes of yttrium(III), samarium(III), and lutetium(III) with chiral, nonracemic donor-functionalized cyclopentadienyl ligands by metathetic reactions and, in one case, also by oxidation of the corresponding divalent compound. The enantiomeric purity of the stereogenic centers in the ligands as well as the intramolecular coordination of the donor atom in the side chain was confirmed by structure determination of the complexes **1b**, **3b**, and **3c**. Using the stabilizing influence of the donor-substituted ligands, we were able to isolate lanthanide sandwich complexes with two different cyclopentadienyl ligands, systems that are otherwise only very difficult to synthesize. X-ray structural analyses of **5a** and **6c** show the presence of only one diastereomer in the solid state. Preliminary results of our experiments employing the alkyl complex **6c** as a precatalyst in organic chemistry showed that the compound was unsuitable for the polymerization of α-olefins at low pressures, but has a certain potential in hydrosilylation reactions. These studies are still under investigation.

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Supporting Information Available: Full details of the X-ray structures of complexes **1b**, **3b**, **3c**, **5a**, and **6c**, including complete tables of crystal data, atomic coordinates, bond length and angles, and positional and anisotropic thermal parameters (41 pages). Ordering information is given on any current masthead page.

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