Organometallic Compounds of the Lanthanides. 110.[1] Donor-Functionalized Chiral Cyclopentadienyl Complexes of Calcium, Samarium(II), and Ytterbium(II). A New Class of Chiral Metallocenes

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Twelve optically active metallocene complexes of Ca, Sm(II), and Yb(II) containing cyclopentadienyl systems with a chiral N- or O-substituted side chain as ligands are described. Specifically, the ligand systems (*S*)-(2-methoxypropyl)cyclopentadienyl ((*S*)-$C_5H_4CH_2CH(Me)OMe$)) and (*S*)-(2-methoxy-2-phenylethyl)cyclopentadienyl ((*S*)-$C_5H_4CH_2CH(Ph)OMe$)) and the novel (*S*)-[2-(dimethylamino)propyl]cyclopentadienyl ((*S*)-$C_5H_4CH_2CH(Me)NMe_2$)) and (*S*)-[2-(dimethylamino)-1-phenylethyl]cyclopentadienyl ((*S*)-$C_5H_4CH(Ph)CH_2NMe_2$)) systems were employed. The starting materials for their synthesis are ethyl (*S*)-(−)-lactate, (*R*)-(−)-2-methoxy-2-phenylethanol, (*S*)-(+)-2-amino-1-propanol, and (*R*)-(−)-2-phenylglycinol, respectively. Each of the cyclopentadienyl systems was converted by a 2:1 reaction of the potassium salt with the metal diiodide into the corresponding metallocene, [M{(*S*)-η^5:η^1-$C_5H_4(CH_2CH(R)OMe)$}$_2$] (R = Me, M = Ca (**1a**), Sm (**1b**), Yb (**1c**); R = Ph, M = Ca (**3a**), Sm (**3b**), Yb (**3c**)), [M{(*S*)-η^5:η^1-$C_5H_4(CH_2CH(Me)NMe_2)$}$_2$] (M = Ca (**2a**), Sm (**2b**), Yb (**2c**)), and [M{(*S*)-η^5:η^1-$C_5H_4(CH(Ph)CH_2NMe_2)$}$_2$] (M = Ca (**4a**), Sm (**4b**), Yb (**4c**)). The novel compounds have been characterized by C, H, N analysis, mass spectrometry, NMR spectroscopy, and optical rotation. Additionally, an X-ray structural analysis of **2c**, **3a**, and **4a** was performed.

Introduction

Over the past several years cyclopentadienyl ligands bearing a donor-functionalized side chain have attracted great interest in lanthanide[2] and alkaline-earth chemistry[2h,3] because the donating ability of the terminal functional group in the side chain can stabilize π-complexes by additional intramolecular coordination and side arm participation may play an important role in catalytic processes. Consequently, an ether-substituted cyclopentadienyl ligand has been used first to stabilize bis(cyclopentadienyl) complexes of early-lanthanide chlorides.[2a] Catalytic activity has been demonstrated by three yttrium complexes that isomerize 1-alkenes in combination with sodium hydride.[2b] Besides a calcium complex,[2h] Grignard compounds containing chelating dimethylamino cyclopentadienyl ligands have been prepared by Jutzi and co-workers[3] as transfer reagents for this kind of ligand.

Although asymmetric chelating cyclopentadienyl systems have been synthesized[2n,4] and used to prepare titanium and zirconium complexes[5] previously, among the lanthanides only a trivalent samarium iodide complex containing two cyclopentadienyl ligands with a chiral benzylic ether in the side chain is known.[2n] To the best of our knowledge, the dimethylsilyl-bridged bis(cyclopentadienyl)lanthanide complexes employing a chiral auxiliary described by Marks et al.[6] remain the only enantiomerically pure organolanthanides and no report has appeared in the literature concerning the crystal structure of chiral metallocenes of calcium or divalent lanthanides.

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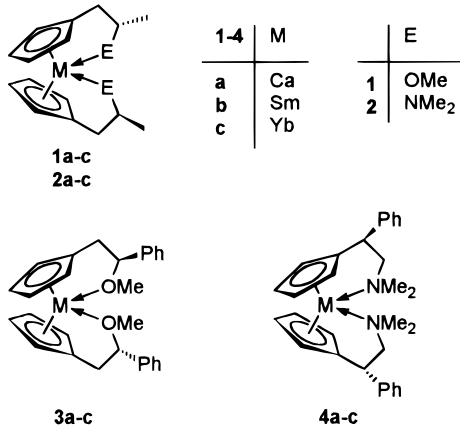
Chart 1



In order to extend the number of optically active cyclopentadienyl ligands useful for coordination to electron-deficient metals and to reveal possible applications of their complexes in stereospecific catalytic reactions, we started to prepare enantiomerically pure calcium, samarium(II), and ytterbium(II) complexes involving four different asymmetric donor-functionalized cyclopentadienyl ligands and present X-ray structure determinations of representative complexes.

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 in vacuum (0.01 mbar)-sealed capillaries and are uncorrected. Optical rotations were determined on a Schmidt + Haensch Polartronic-D polarimeter. The NMR spectra were recorded on Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) and ARX 400 and AM 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz) spectrometers at ambient temperatures. All chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residues of the deuterated solvents. Infrared spectra were run on a Perkin-Elmer 1600 Series FTIR as a neat film. Mass spectra (EI, 70 eV) were obtained by using a VG7070 EQ-HF or a Varian MAT 311 A instrument. Only characteristic fragments and isotopes of the highest abundance are listed. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. (*S*)-2-(Dimethylamino)propyl chloride hydrochloride (**15**),[7] (*R*)-2-(dimethylamino)-2-phenylethyl chloride hydrochloride (**19**),[7] (*S*)-(2-methoxypropyl)cyclopentadiene (**9**),[4] (*S*)-(2-methoxy-2-phenylethyl)cyclopentadiene (**12**),[4] and $LnI_2(THF)_x$ (Ln = Sm, Yb)[8] were prepared according to published procedures. CaI_2 was used as purchased from Alfa.

(*S*)-[2-Dimethylamino)propyl]cyclopentadiene (16). An 8.18 g (51.7 mmol) amount of **15** was stirred in THF (80 mL) and HMPA (30 mL) at 0 °C, and a 1.9 M solution of cyclopentadienylsodium in THF (68 mL, 130.9 mmol) was added dropwise over 30 min. The mixture was heated at reflux for 4 h and concentrated. Water (250 mL) was added and the aqueous layer extracted with ether. After it was dried over magnesium sulfate, the organic layer was concentrated and the residue was fractionally distilled from iron powder under reduced pressure to provide 4.63 g (58%) of **16** as a colorless liquid. Bp: 23 °C/0.1 mbar.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.45 (m, 3H, Cp C*H*), 6.25 (m, 1H, Cp C*H*), 6.20 (m, 1H, Cp C*H*), 6.05 (m, 1H, Cp C*H*), 2.97−2.63 (several m, 10H, CH_2 and C*H*−N), 2.30, 2.27 (2 s, 12H, N−CH_3), 0.96, 0.95 (2 d, J = 6.5 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50.32 MHz): δ 147.25, 144.83 (C_5−C), 134.57, 133.47, 132.22, 130.58, 127.71, 127.30 (C_5H_5), 59.48, 58.81 (*C*H−N), 40.46, 40.39 (N−*C*H$_3$), 45.66, 43.22, 34.17, 33.11 (*C*H$_2$), 13.93, 13.81 (C−*C*H$_3$). MS (25 °C; *m*/*z* (relative intensity, %)): 153 (1) [M]$^+$, 72 (100) [$C_4H_{10}N$]$^+$, 58 (3) [C_3H_8N]$^+$, 42 (4) [C_2H_4N]$^+$. Anal. Calcd for $C_{10}H_{19}N$ (M_r 153.27): C, 78.37; H, 12.49; N, 9.14. Found: C, 78.44; H, 12.41; N, 8.98.

(*S*)-[2-(Dimethylamino)-1-phenylethyl]cyclopentadiene (21). This ligand was prepared from 12.24 g (55.6 mmol) of **19** by the method described above to yield 8.84 g (75%) of **21** as a colorless liquid. Bp: 70 °C/0.03 mbar.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30−7.17 (m, 10H, C_6H_5), 6.42 (m, 3H, Cp C*H*), 6.27 (m, 1H, Cp C*H*), 6.25 (m, 1H, Cp C*H*), 6.11 (m, 1H, Cp C*H*), 3.91 (m, 2H, CH_2−N), 2.97 (m, 2H, Cp CH_2), 2.82−2.71 (several m, 6H, CH_2 and C*H*Ph), 2.24, 2.23 (2 s, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.64 MHz): δ 150.90, 148.52, 143.86, 143.15 (C_6−C and C_5−C), 133.84, 133.64, 132.09, 131.23, 128.35, 128.31, 127.91, 127.71, 126.82, 126.36, 126.21, 126.17 (=*C*H−), 64.81, 64.56 (*4C*H$_2$−N), 45.88, 45.85 (*C*H$_3$), 45.57, 44.75 (*C*HPh), 42.35, 41.11 (Cp *C*H$_2$). IR (cm^{-1}): ν 3061, 3025, 2918, 2850, 2763, 1600, 1493, 1455, 898, 748, 699, 677. LRMS (25 °C; *m*/*z* (relative intensity, %)): 213 (1) [M]$^+$, 134 (11) [$C_9H_{12}N$]$^+$, 58 (100) [C_4H_8N]$^+$, 42 (8) [C_2H_4N]$^+$. HRMS: calcd for $C_{15}H_{19}N$ 213.1517, found 213.1529.

Deprotonation of the Functionalized Cyclopentadienes with Potassium Hydride. In a typical procedure an equimolar amount of potassium hydride is added in portions to a solution of the substituted cyclopentadiene in THF at room temperature. The mixture is stirred for 2 h, the solvent removed under vacuum, and the residue washed with hexanes. After they are dried under vacuum, the potassium compounds are obtained as white solids.

((*S*)-[2-Methoxypropyl]cyclopentadienyl)potassium (22). The reaction of 2.84 g (20.6 mmol) of **9** with 0.82 g (20.6 mmol) of potassium hydride in 80 mL of THF gave 3.44 g (95%) of **22**. Mp: 126 °C dec. $[\alpha]^{25}_D = -12.1°$ (c = 0.33, THF).

^{1}H NMR (THF-d_8, 400 MHz): δ 5.28 (m, 2H, C_5H_4), 5.21 (m, 2H, C_5H_4), 3.37 (m, 1H, C*H*), 3.12 (s, 3H, O−CH_3), 2.62 (dd, J = 14.4, 4.4 Hz, 1H, CH_2), 2.33 (dd, J = 14.4, 6.4 Hz, 1H, CH_2), 1.04 (d, J = 6.1 Hz, 3H, C−CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 100.64 MHz): δ 116.33 (C_5−C), 105.13 (C_5H$_4$), 79.20 (*C*H), 54.96 (O−*C*H$_3$), 37.30 (*C*H$_2$), 19.71 (C−*C*H$_3$). Anal. Calcd for $C_9H_{13}KO$ (M_r = 176.30): C, 61.32; H, 7.43. Found: C, 61.58; H, 7.14.

((*S*)-[2-Methoxy-2-phenylethyl]cyclopentadienyl)potassium (23). The reaction of 1.96 g (9.8 mmol) of **12** with 0.39 g (9.8 mmol) of potassium hydride in 200 mL of THF gave 1.84 g (79%) of **23**. Mp: 232 °C dec. $[\alpha]^{25}_D = -36.1°$ (c = 0.06, THF).

^{1}H NMR (THF-d_8, 400 MHz): δ 7.25 (m, 4H, C_6H_5), 7.15 (m, 1H, C_6H_5), 5.34 (m, 2H, C_5H_4), 5.29 (m, 2H, C_5H_4), 4.37 (dd, J = 10.2, 3.6 Hz, 1H, C*H*$_2$0, 2.97 (s, 6H, CH_3), 2.77 (dd, J = 14.8, 3.6 Hz, 1H, CH_2), 2.63 (dd, J = 14.8, 10.2 Hz, 1H, C*H*). ^{13}C{^{1}H} NMR (THF-d_8, 100.64 MHz): δ 144.98 (C_6−C), 129.06, 127.81, 127.60 (C_6H_5), 117.42 (C_5−C), 104.68, 104.52 (C_5H_4), 87.16 (*C*H), 56.46 (*C*H$_3$), 40.99 (*C*H$_2$). Anal. Calcd for $C_{14}H_{15}KO$ (M_r = 238.37): C, 70.54; H, 6.34. Found: C, 70.93; H, 6.21.

((*S*)-[2-Dimethylamino)propyl]cyclopentadienyl)potassium (24). The reaction of 4.68 g (30.2 mmol) of **16** with 1.21 g (30.2 mmol) of potassium hydride in 200 mL of THF gave 5.19 g (90%) of **24**. Mp: 174 °C dec. $[\alpha]^{25}_D = +13.9°$ (c = 2.16, THF).

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^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.04 (m, 2H, C_5H_4), 5.88 (m, 2H, C_5H_4), 2.90−2.58 (m, 3H, C*H* and CH_2), 2.16 (s, 6H, N−CH_3), 0.92 (d, J = 6.0 Hz, 3H, C−CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 118.29 (C_5−C), 104.48, 103.69 (C_5H_4), 62.19 (*C*H), 45.24 (CH_2), 39.69 (N−CH_3), 11.81 (C−CH_3). Anal. Calcd for $C_{10}H_{18}KN$ (M_r = 191.36): C, 62.77; H, 9.48; N, 7.32. Found: C, 63.16; H, 9.25; N, 7.50.

((*S*)-[2-(Dimethylamino)-1-phenylethyl]cyclopentadienyl)potassium (25). The reaction of 8.84 g (41.4 mmol) of **21** with 1.66 g (41.4 mmol) of potassium hydride in 200 mL of THF gave 8.75 g (85%) of **25**. Mp: 186 °C dec.

^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.73 (d, J = 7.1 Hz, 2H, C_6H_5), 7.30 (dd, J = 7.3, 7.1 Hz, 2H, C_6H_5), 7.14 (t, J = 7.3 Hz, 1H, C_6H_5), 6.31 (m, 2H, C_5H_4), 6.23 (m, 2H, C_5H_4), 4.40 (dd, J = 11.5, 4.6 Hz, 1H, CH_2), 3.35 (m, 1H, C*H*), 2.54 (dd, J = 11.5, 4.6 Hz, 1H, CH_2), 2.21 (s, 6H, CH_3). Anal. Calcd for $C_{15}H_{18}KN$ (M_r = 251.41): C, 71.66; H, 7.22; N 5.56. Found: C, 71.54; H, 7.27; N, 5.79.

Bis(η^5:η^1-(*S*)-[2-methoxypropyl]cyclopentadienyl)-calcium (1a). To a solution of 0.89 g (3.0 mmol) of CaI_2 in THF (50 mL) was added 1.07 g (6.1 mmol) of **22**. The reaction mixture was stirred for 12 h at 25 °C. The clear solution was separated from the solid by decantation. The solvent was removed and the residue washed twice with hexanes (10 mL) and recrystallized from THF/hexanes (1:6; 20 mL) at −20 °C; 0.75 g (79%) of colorless crystals of **1a** was obtained. Mp: 193 °C dec. $[\alpha]^{25}_D$ = −25.9° (C = 0.06, THF).

^{1}H NMR (THF-d_8, 400 MHz): δ 5.66−5.58 (m, 6H, C_5H_4), 5.45 (m, 2H, C_5H_4), 3.67 (m, 2H, C*H*), 3.26 (s, 6H, O−CH_3), 2.68 (dd, J = 14.1, 6.1 Hz, 1H, CH_2), 2.50 (dd, J = 14.1, 5.2 Hz, 2H, CH_2), 1.25 (d, J = 6.2 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 100.64 MHz): δ 119.16 (C_5−C), 107.50−106.96 (m, C_5H_4), 81.68 (C*H*), 56.85 (O−CH_3), 37.76 (CH_2), 19.19 (C−CH_3). MS (100 °C; *m*/*z* (relative intensity, %)): 314 (49) [M]$^+$, 177 (100) [Ca($C_5H_4CH_2CH$(Me)OMe)]$^+$, 145 (37) [Ca($C_5H_4CH_2CH$-(Me)OMe) − CH_4O]$^+$, 59 (50) [C_3H_7O]$^+$. Anal. Calcd for $C_{18}H_{26}CaO_2$ (M_r = 314.48): C, 68.75; H, 8.33. Found: C, 68.54; H, 8.01.

Bis(η^5:η^1-(*S*)-[2-methoxypropyl]cyclopentadienyl)-samarium(II) (1b). Analogously to **1a** 0.61 g (1.1 mmol) of $SmI_2(THF)_{2.0}$ was treated with 0.39 g (2.2 mmol) of **22** in 50 mL of THF. A 0.31 g (66%) amount of red-brown crystals of **1b** was obtained from 20 mL of THF/hexanes (1:6) at −20 °C. Mp: 138 °C dec.

MS (^{152}Sm, 220 °C; *m*/*z* (relative intensity, %)): 426 (56) [M]$^+$, 289 (5) [Sm($C_5H_4CH_2CH$(Me)OMe)]$^+$, 257 (7) [Sm(C_5H_4-CH_2CH(Me)OMe) − CH_4O]$^+$, 59 (100) [C_3H_7O]$^+$. Anal. Calcd for $C_{18}H_{26}O_2Sm$ (M_r = 424.76): C, 50.90; H, 6.17. Found: C, 50.85; H, 6.53.

Bis(η^5:η^1-(*S*)-[2-methoxypropyl]cyclopentadienyl)-ytterbium(II) (1c). Analogously to **1a** 0.71 g (1.2 mmol) of $YbI_2(THF)_{2.3}$ was treated with 0.42 g (2.4 mmol) of **22** in 50 mL of THF. A 0.29 g (54%) amount of dark red crystals of **1c** was obtained from 20 mL of ether/hexanes (1:5) at −20 °C. Mp: 121 °C dec.

^{1}H NMR (C_6D_6, 400 MHz): δ 6.36 (m, 2H, C_5H_4), 6.21 (m, 2H, C_5H_4), 5.91 (m, 2H, C_5H_4), 5.67 (m, 2H, C_5H_4), 3.33 (m, 2H, C*H*), 2.88 (s, 6H, O−CH_3), 2.70 (dd, J = 14.4, 5.6 Hz, 2H, CH_2), 2.30 (dd, J = 14.4, 4.2 Hz, 2H, CH_2), 0.91 (d, J = 6.4 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 100.64 MHz): δ 119.66 (C_5−C), 107.70, 106.88, 106.47, 106.35 (C_5H_4), 84.47 (C*H*), 57.56 (O−CH_3), 35.33 (CH_2), 18.71 (C−CH_3). MS (^{174}Yb, 140 °C; *m*/*z* (relative intensity, %)): 448 (25) [M]$^+$, 311 (13) [Yb-($C_5H_4CH_2CH$(Me)OMe)]$^+$, 279 (6) [Yb($C_5H_4CH_2CH$(Me)OMe) − CH_4O]$^+$, 59 (100) [C_3H_7O]$^+$. Anal. Calcd for $C_{18}H_{26}O_2Yb$ (M_r = 447.44): C, 48.32; H, 5.86. Found: C, 48.13; H, 6.08.

Bis(η^5:η^1-(*S*)-[2-methoxy-2-phenylethyl]cyclopentadienyl)calcium (3a). Analogously to **2a** 0.47 g (1.6 mmol) of CaI_2 was treated with 0.76 g (3.2 mmol) of **23** in 50 mL of THF. A 0.55 g (79%) amount of colorless crystals of **2a** was obtained from 20 mL of toluene at −28 °C. Mp: 159 °C dec. $[\alpha]^{25}_D$ = −61.7° (c = 0.06, THF).

^{1}H NMR (toluene-d_8, 200 MHz): δ 7.18−7.04 (m, 10H, C_6H_5), 6.40 (m, 2H, C_5H_4), 6.28 (m, 2H, C_5H_4), 5.85 (m, 4H, C_5H_4), 4.44 (dd, J = 9.3, 4.9 Hz, 2H, CH_2), 3.09−2.99 (m, 2H, CH_2), 2.91 (s, 6H, O−CH_3), 2.87 (m, 2H, C*H*). ^{13}C{^{1}H} NMR (toluene-d_8, 50.32 MHz): δ 140.38 (C_6−C), 128.97, 126.36, 126.28 (C_6H_5), 119.79 (C_5−C), 109.45, 109.09, 106.81, 105.68 (C_5H_4), 89.38 (*C*H), 57.16 (CH_3), 38.75 (CH_2). MS (60 °C; *m*/*z* (relative intensity, %)): 438 (10) [M]$^+$, 239 (40) [Ca($C_5H_4CH_2CH$(Ph)-OMe)]$^+$, 207 (35) [Ca($C_5H_4CH_2CH$(Ph)OMe) − CH_4O]$^+$, 121 (100) [C_8H_9O]$^+$. Anal. Calcd for $C_{28}H_{30}CaO_2$ (M_r = 438.62): C, 76.67; H, 6.89. Found: C, 76.39; H, 7.15.

Bis(η^5:η^1-(*S*)-[2-methoxy-2-phenylethyl]cyclopentadienyl)samarium(II) (3b). Analogously to **1a** 0.47 g (0.9 mmol) $SmI_2(THF)_{2.0}$ were treated with 0.41 g (1.8 mmol) of **23** in 50 mL of THF. A 0.31 g (33%) amount of brown crystals of **2b** was obtained from 15 mL of THF/ether (1:1) at −78 °C. Mp: 131 °C dec.

MS (^{152}Sm, 180 °C; *m*/*z* (relative intensity, %)): 550 (4) [M]$^+$, 351 (2) [Sm($C_5H_4CH_2CH$(Ph)OMe)]$^+$, 318 (1) [Sm($C_5H_4CH_2CH$-(Ph)OMe) − CH_4O]$^+$, 121 (100) [C_8H_9O]$^+$. Anal. Calcd for $C_{28}H_{30}O_2Sm$ (M_r = 548.91): C, 61.27; H, 5.51. Found: C, 60.94; H, 5.32.

Bis(η^5:η^1-(*S*)-[2-methoxy-2-phenylethyl]cyclopentadienyl)ytterbium(II) (3c). Analogously to **1a** 0.79 g (1.4 mmol) of $YbI_2(THF)_{2.3}$ was treated with 0.67 g (2.8 mmol) of **23** in 50 mL of THF. A 0.57 g (71%) amount of dark brown crystals of **2c** was obtained from 10 mL of THF/ether (2:1) at −78 °C. Mp: 111 °C dec.

^{1}H NMR (THF-d_8, 400 MHz): δ 7.33−7.20 (m, 10H, C_6H_5), 5.70 (m, 4H, C_5H_4), 5.66 (m, 4H, C_5H_4), 4.64 (m, 2H, C*H*), 3.10 (s, 6H, CH_3), 2.87−2.84 (m, 4H, CH_2 and C*H*). ^{13}C{^{1}H} NMR (THF-d_8, 100.64 MHz): δ 143.31 (C_6−C), 129.30, 128.45, 127.89 (C_6H_5), 118.16 (C_5−C), 106.19 (m, C_5H_4), 88.29 (C*H*), 57.32 (CH_3), 40.76 (CH_2). MS (^{174}Yb, 200 °C; *m*/*z* (relative intensity, %)): 571 (1) [M]$^+$, 373 (1) [Yb($C_5H_4CH_2CH$(Ph)-OMe)]$^+$, 341 (1) [Yb($C_5H_4CH_2CH$(Ph)OMe) − CH_4O]$^+$, 121 (100) [C_8H_9O]$^+$. Anal. Calcd for $C_{28}H_{30}O_2Yb$ (M_r = 571.59): C, 58.84; H, 5.29. Found: C, 58.97; H, 5.53.

Bis(η^5:η^1-(*S*)-[2-(dimethylamino)propyl]cyclopentadienyl)calcium (2a). Analogously to **1a** 0.75 g (2.6 mmol) of CaI_2 was treated with 1.00 g (5.2 mmol) of **24** in 120 mL of THF. A 0.78 g (88%) amount of colorless crystals of **3a** was obtained from 30 mL of toluene at −78 °C. Mp: 221 °C dec. $[\alpha]^{25}_D$ = +16.2° (c = 2.35, THF).

^{1}H NMR (toluene-d_8, 200 MHz): δ 6.29 (m, 2H, C_5H_4), 6.02 (m, 2H, C_5H_4), 5.77 (m, 2H, C_5H_4), 5.49 (m, 2H, C_5H_4), 2.61−2.24 (m, 6H, C*H* and CH_2), 1.83 (s, 12H, N−CH_3), 0.59 (d, J = 6.3 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, 100.64 MHz): δ 121.52 (C_5−C), 108.89, 107.38, 104.85 (C_5H_4), 64.95 (*C*H), 40.59, 40.49 (N−CH_3), 35.76 (CH_2), 10.18 (C−CH_3). MS (180 °C; *m*/*z* (relative intensity, %)): 340 (57) [M]$^+$, 190 (85) [Ca($C_5H_4CH_2CH$(Me)NMe_2)]$^+$, 72 (100) [$C_4H_{10}N$]$^+$. Anal. Calcd for $C_{20}H_{32}CaN_2$ (M_r = 340.57): C, 70.53; H, 9.47; N, 8.23. Found: C, 70.22; H, 9.73; N, 8.55.

Bis(η^5:η^1-(*S*)-[2-(dimethylamino)propyl]cyclopentadienyl)samarium(II) (2b). Analogously to **1a** 0.66 g (1.2 mmol) of $SmI_2(THF)_{2.0}$ was treated with 0.46 g (2.4 mmol) of **24** in 60 mL of THF. A 0.36 g (65%) amount of dark brown crystals of **3b** was obtained from 10 mL of toluene at −28 °C. Mp: 213 °C dec.

MS (240 °C; *m*/*z* (relative intensity, %)): 456 (2) [M]$^+$, 304 (5) [Sm($C_5H_4CH_2CH$(Me)NMe_2)]$^+$, 72 (100) [$C_4H_{10}N$]$^+$. Anal. Calcd for $C_{20}H_{32}N_2Sm$ (M_r = 450.85): C, 53.28; H, 7.15; N, 6.21. Found: C, 52.72; H, 6.98; N, 6.19.

Bis(η^5:η^1-(*S*)-[2-(dimethylamino)propyl]cyclopentadienyl)ytterbium(II) (2c). Analgously to **1a** 0.68 g (1.2 mmol) of $YbI_2(THF)_{2.3}$ was treated with 0.46 g (2.4 mmol) of **24** in 60 mL of THF. A 0.38 g (67%) amount of dark red crystals of **3c** was obtained from 20 mL of toluene at −28 °C. Mp: 194 °C dec.

^{1}H NMR (toluene-d_8, 200 MHz): δ 6.30 (m, 2H, C_5H_4), 5.87−5.78 (m, 4H, C_5H_4), 5.31 (m, 2H, C_5H_4), 2.61−2.52 (m, 4H,

Table 1. Crystal Data and Structure Refinement for 2c, 3a, and 4a

	2c	3a	4a
empirical formula	$C_{20}H_{32}N_2Yb$	$C_{28}H_{30}CaO_2$	$C_{30}H_{36}CaN_2$
fw	473.52	438.60	464.69
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group (No.)	$P2_12_12_1$ (18)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)
a, b, c (Å)	8.009(3), 8.176(3), 14.939(2)	12.202(5), 13.105(4), 15.109(2)	12.882(3), 8.1490(14), 25.138(5)
α, β, γ (deg)	90.0, 90.0, 90.0	90.0, 90.0, 90.0	90.0, 90.0, 90.0
V (Å^3)	978.2(5)	2415.9(12)	2638.8(10)
Z	2	4	4
D_{calcd} (g cm^{-3})	1.608	1.206	1.170
$F(000)$	472	936	1000
μ(Mo Kα) (cm^{-1})	0.4782	0.281	0.257
abs structure param	0.03(2)	0.08(7)	−0.03(8)
cryst size (mm)	0.16 × 0.12 × 0.10	0.39 × 0.30 × 0.30	0.48 × 0.27 × 0.09
temp (K)	162(3)	162(3)	193(2)
radiation (Å)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
$\theta^{min}, \theta^{max}$ (deg)	2.8, 52.00	4.12, 47.86	3.24, 45.88
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan (deg)	0.81 + 0.35 tan θ	0.72 + 0.35 tan θ	0.92 + 0.35 tan θ
horiz and vert aperture (mm)	2.5, 2.5	2.2, 2.2	2.6, 2.6
ref rflns	3	3	3
data set			
h^{min}, h^{max}	0, 9	0, 13	0, 14
k^{min}, k^{max}	0, 10	0, 14	0, 8
l^{min}, l^{max}	−18, +18	−17, +17	−27, +27
total unique no. of rflns	2118/1819	2467/2177	3546/3142
no. of obsd data ($I > 2\sigma(I)$)	1808	2168	3137
intensity, variation	none	DIFABS: min 0967, max 1.353, av 1.062	DIFABS: min 0.780, max 1.540, av 1.153
N_{ref}, N_{par}	1808, 108	2168, 282	3137, 298
R, R_w ($I > 2\sigma(I)$), S	0.0248, 0.0592, 1.092	0.0442, 0.1317, 1.113	0.0562, 0.1277, 0.982
weighting scheme	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
max and av shift/error	<0.001	<0.001	<0.001
min and max residual density (e Å^{-3})	max 1.717, min −1.852	max 0.185, min −0.299	max 0.244, min −0.207

CH_2), 2.26−2.05 (m, 2H, CH), 1.91 (s, 12H, N−CH_3), 0.61 (d, J = 6.3 Hz, 6H, C−CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, 50.32 MHz): δ 121.04 (C_5−C), 107.96, 106.47, 105.84, 104.66 (C_5H_4), 66.03 (CH), 44.11 (N−CH_3), 35.45 (CH_2), 34.94 (N−CH_3), 10.49 (C−CH_3). MS (180 °C; m/z (relative intensity, %)): 477 (1) [M]$^+$, 326 (2) [Yb($C_5H_4CH_2CH$(Me)NMe_2)]$^+$, 72 (100) [$C_4H_{10}N$]$^+$. Anal. Calcd for $C_{20}H_{32}N_2Yb$ (M_r = 473.53): C, 50.73; H, 6.81; N, 5.92. Found: C, 50.69; H, 7.02; N, 6.14.

Bis(η^5:η^1-(*S*)-[2-(dimethylamino)-1-phenylethyl]cyclopentadienyl)calcium (4a). Analogously to **1a** 0.38 g (1.3 mmol) of CaI_2 was treated with 0.56 g (2.6 mmol) of **25** in 50 mL of THF. A 0.29 g (48%) amount of colorless crystals of **4a** was obtained from 10 mL of toluene at −28 °C. Mp: 154 °C dec. [α]$^{25}_D$ −24.4° (c = 0.06, THF).

^{1}H NMR (THF-d_8, 400 MHz): δ 7.33 (d, J = 7.6 Hz, 4H, C_6H_5), 7.17 (dd, J = 7.6, 7.4 Hz, 4H, C_6H_5), 7.07 (t, J = 7.4 Hz, 2H, C_6H_5), 5.88 (m, 4H, C_5H_4), 5.79 (m, 2H, C_5H_4), 5.63 (m, 2H, C_5H_4), 4.03 (dd, J = 12.3, 3.7 Hz, 2H, CH_2), 3.16 (dd, J = 12.3, 12.0 Hz, 2H, CH), 2.46 (dd, J = 12.0, 3.7 Hz, 2H, CH_2), 2.41 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 100.64 MHz): δ 145.43 (C_6−C), 128.77, 128.74 (C_6H_5), 126.89 (C_5−C), 126.51 (C_6H_5), 110.09, 108.47, 106.23, 103.23 (C_5H_4), 72.24 (CH_2), 47.11 (CH_3), 44.58 (CH). MS (180 °C; m/z (relative intensity, %)): 464 (3) [M]$^+$, 252 (24) [Ca(C_5H_4CH(Ph)CH_2-NMe_2)]$^+$, 58 (100) [C_3H_8N]$^+$. Anal. Calcd for $C_{30}H_{36}CaN_2$ (M_r = 464.71): C, 77.54; H, 7.81; N, 6.03. Found: C, 77.33; H, 7.60; N, 5.93.

Bis(η^5:η^1-(*S*)-[2-(dimethylamino)-1-phenylethyl]cyclopentadienyl)samarium(II) (4b). Analogously to **1a** 0.72 g (1.3 mmol) of $SmI_2(THF)_{2.0}$ was treated with 0.56 g (2.6 mmol) of **25** in 50 mL of THF. A 0.30 g (40%) amount of dark green crystals of **4b** was obtained from 10 mL of toluene at −28 °C. Mp: 117 °C dec.

MS (^{152}Sm, 240 °C; m/z (relative intensity, %)): 576 (26) [M]$^+$, 364 (8) [Sm(C_5H_4CH(Ph)CH_2NMe_2)]$^+$, 58 (100) [C_3H_8N]$^+$. Anal. Calcd for $C_{30}H_{36}N_2Sm$ (M_r = 574.99): C, 62.67; H, 6.31; N 4.87. Found: C, 62.40; H, 6.36; N, 4.70.

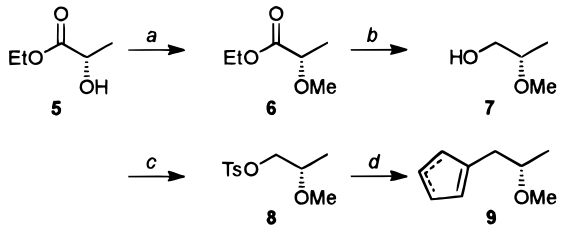
Bis(η^5:η^1-(*S*)-[2-(dimethylamino)-1-phenylethyl]cyclopentadienyl)ytterbium(II) (4c). Analgously to **1a** 0.86 g (1.5 mmol) of $YbI_2(THF)_{2.3}$ was treated with 0.78 g (3.0 mmol) of **25** in 60 mL of THF. A 0.38 g (44%) amount of dark red crystals of **4c** was obtained from 20 mL of toluene at −28 °C. Mp: 108 °C dec.

^{1}H NMR (THF-d_8, 400 MHz): δ 7.30 (d, J = 7.2 Hz, 4H, C_6H_5), 7.13 (dd, J = 7.2, 6.9 Hz, 4H, C_6H_5), 7.03 (t, J = 6.9 Hz, 2H, C_6H_5), 5.75 (m, 4H, C_5H_4), 5.69 (m, 2H, C_5H_4), 5.47 (m, 2H, C_5H_4), 3.97 (m, 2H, CH_2), 3.19 (dd, J = 12.0, 11.9 Hz, 2H, CH), 2.57 (m, 2H, CH_2), 2.42 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 50.32 MHz): δ 145.00 (C_6−C), 128.75, 126.61 (C_6H_5), 126.44 (C_5−C), 126.34 (C_6H_5), 109.04, 107.44, 104.40, 102.57 (C_5H_4), 72.97 (CH_2), 47.03 (CH_3), 44.21 (CH). MS (^{174}Yb, 180 °C; m/z (relative intensity, %)): 598 (2) [M]$^+$, 386 (4) [Yb(C_5H_4-CH(Ph)CH_2NMe_2)]$^+$, 58 (100) [C_3H_8N]$^+$. Anal. Calcd for $C_{30}H_{36}N_2Yb$ (M_r = 597.67): C, 60.29; H, 6.07; N, 4.69. Found: C, 60.18; H, 5.92; N, 4.33.

X-ray Structure Determination of 2c. Suitable crystals were obtained from toluene. A dark red, block-shaped crystal was selected by using a device similar to that reported by Veith and Bärnighausen,[9] 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 controlled by a Compaq Deskpro 386s. The cell parameters were obtained from the angles of 25 reflections in the range of 5.02° < θ < 10.16°. 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 intensities of three check reflections monitored after 2 h showed only statistical fluctuations during the course of the data collection. The crystal orientation was checked every 200 intensity measurements by scanning 3 reflections. A new orientation matrix was automatically

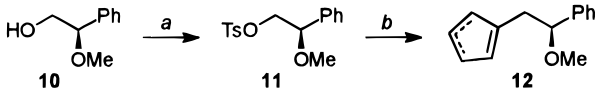
(9) Veith, M.; Bärninghausen, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 1806.

Scheme 1



[a] Ag_2O, MeI, CH_3CN, reflux, 12 h, 73 %. [b] LAH, ether, 0 °C, 2 h, 71 %. [c] TsCl, py, 0 °C → rt, 12 h, 80 %. [d] NaCp, THF, 0 °C, 4 h, 61 %.

Scheme 2



[a] TsCl, py, 0 °C → rt, 12 h, 83 %. [b] NaCp, THF, 0 °C → rt, 60 %.

calculated from a list of 25 recentered reflections in case the angular change was greater than 0.1°. The raw data were corrected for Lorentz, polarization, and absorption effects.[10] Refinements in space group $P22_12_1$ were successful. The position of the Yb atom was determined from a three-dimensional Patterson synthesis (SHELXS86).[11] The calculated difference Fourier map (SHELXL93)[12] 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.[13] The final residual of least squares is R = 2.48%. Data reduction was performed using a IBM RISC System/6000,340.[14] All other calculations were undertaken with SHELXL93.[12] The geometrical aspects of the structure were analyzed by using the PLUTON program.[15]

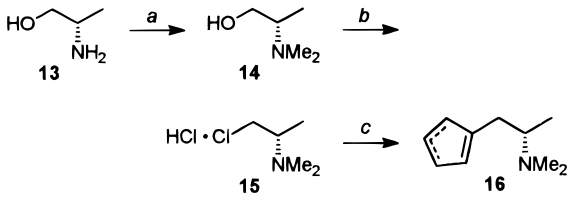
X-ray Structure Determination for 3a and 4a. Suitable colorless, block-shaped crystals were obtained from toluene. The general procedure for solving the structure is outlined above. The cell parameters were obtained from the angles of 25 reflections in the range of 12.66° < θ < 22.94° (**3a**) and 13.28° < θ < 20.26° (**4a**), respectively. Refinements in space group $P2_12_12_1$ were successful. The structures were solved with direct methods (SHELXS86).[11] After all atoms were added to the model of the structure, an empirical absorption correction was applied (DIFABS;[10] minimum absorption correction, maximum absorption correction, average). Final residuals of least squares are R = 4.42% (**3a**) and R = 5.62% (**4a**). 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 numbers CSD-404769 (**2c**), CSD-404891 (**3a**), and CSD-404768 (**4a**), the authors, and the full citation of the journal.

Results and Discussion

Ligand Synthesis. (*S*)-(2-Methoxypropyl)cyclopentadiene was synthesized analogously to literature procedures[4] by starting from ethyl (*S*)-(−)-lactate (**5**; $[\alpha]^{14}_D$ = −10° (neat)), as shown in Scheme 1. Methylation of **5** yielded the corresponding methyl ester (13%) as a byproduct of the ethyl ester **6**. Lithium aluminum hydride reduction of the esters led to alcohol **7**. Treatment of **7** with *p*-toluenesulfonyl chloride gave the desired **8** in high yields. In the same way the tosylate **11** is obtained from (*R*)-(−)-2-methoxy-2-phenylethanol (**10**; $[\alpha]^{20}_D$ = −133° (*c* = 1, acetone)) (Scheme 2). Reaction of **8** and **11** with cyclopentadienylsodium provided the chiral, nonracemic cyclopentadienes as a 1:1 mixture of two pairs of isomers **9** and **12**.[4] The overall yields for the syntheses of (*S*)-(2-methoxypropyl)-cyclopentadiene and (*S*)-(2-methoxy-2-phenylethyl)-cyclopentadiene are 25% and 50%, respectively. No evidence of racemization at the stereocenter was detected, and therefore, the products are considered to have the same optical purity as the starting material.

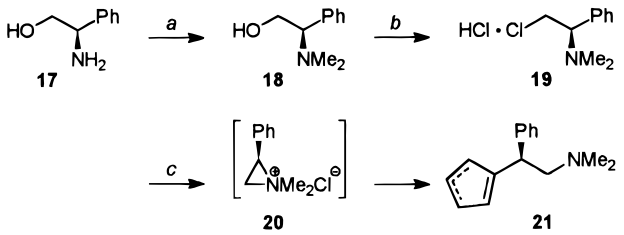
In the case of the N-substituted ligand systems (*S*)-[2-(dimethylamino)propyl]cyclopentadienyl and (*S*)-[2-

Scheme 3



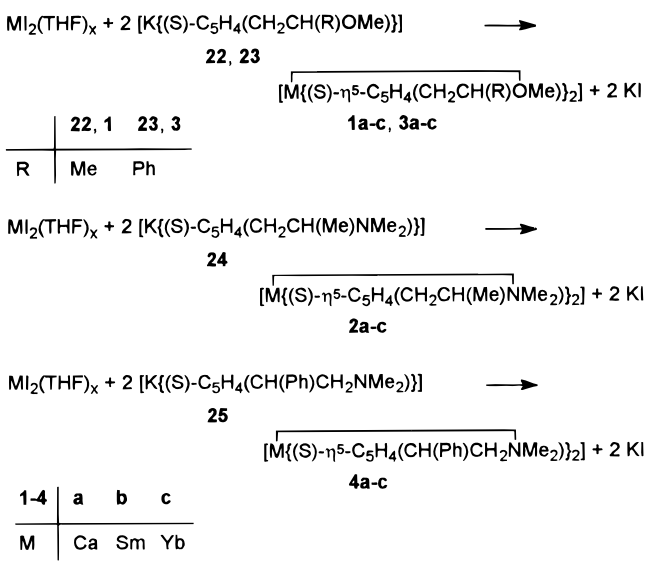
[a] 2 equiv HCO_2H, 2 equiv HCHO, 80 °C, 24 h, 73 %. [b] $SOCl_2$, 0 °C → rt, 1 h, 44 %. [c] 2.5 equiv NaCp, THF/HMPA, 0 °C → reflux, 4 h, 58 %.

Scheme 4



[a] 2 equiv HCO_2H, 2 equiv HCHO, 80 °C, 24 h, 88 %. [b] $SOCl_2$, 0 °C → rt, 1 h, 39 %. [c] 2.5 equiv NaCp, THF/HMPA, 0 °C → reflux, 4 h, 88 %.

Scheme 5



	22, 1	**23, 3**
R	Me	Ph

1-4	**a**	**b**	**c**
M	Ca	Sm	Yb

(10) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158.
(11) Sheldrick, G. M. SHELXS 86 Program for Crystal Structure Determination; Universität Göttingen, Göttingen, Germany, 1986.
(12) Sheldrick, G. M. SHELXL 93 Program for Crystal Structure Determination; Universität Göttingen, Göttingen, Germany, 1993.
(13) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321. (b) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891. (c) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(14) Kretschmar, M. CAD4/PC-Version; Universität Tübingen, Tübingen, Germany, 1994.
(15) Spek, A. L. PLUTON, University of Ütrecht, Ütrecht, The Netherlands, 1992.

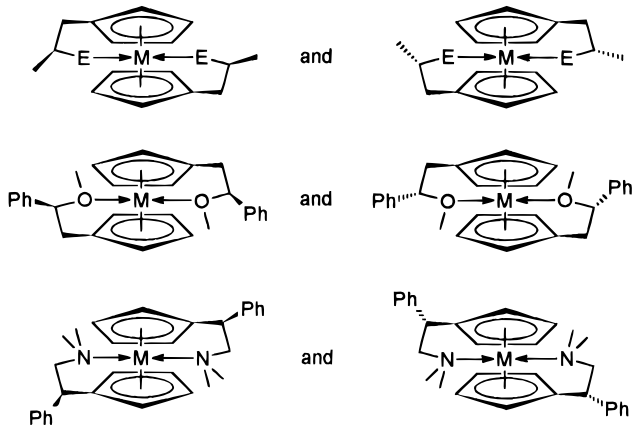


Figure 1. Possible diastereomeric forms of the complexes **1**−**4** (M = Ca, Sm, Yb; E = OMe, NMe_2).

(dimethylamino)-1-phenylethyl]cyclopentadienyl, the hydrochlorides **15** and **19** have been prepared, by a method similar to that described in the literature[7] (Schemes 3 and 4). The readily available amino alcohols **13** and **17** were N-methylated with formaldehyde and formic acid and afterwards converted to the hydrochlorides **15** and **19** by treatment with thionyl chloride. The (*S*)-[2-(dimethylamino)propyl]cyclopentadiene could easily be prepared as a 1:1 mixture of isomers (**16**) with an overall yield of 19%, when **15** was treated with 2.5 equiv of cyclopentadienylsodium in THF/HMPA.[16] Again no reaction takes place at the stereocenter, and therefore enantiomeric purity can be assumed to be retained from the starting material. Application of the same reaction conditions to **19** gave (*S*)-[2-(dimethylamino)-1-phenylethyl]cyclopentadiene as a 1:1 mixture of the isomers **21** instead of (*S*)-[2-(dimethylamino)-2-phenylethyl]-cyclopentadiene, caused by reaction via the intermediate aziridinium ion **20**.[17] Because of the complete inversion at the stereogenic center, the absolute configuration of the product is *S*.

Complexes. The isomeric mixtures of the chiral, nonracemic functionalized cyclopentadienes were deprotonated with potassium hydride to the corresponding cyclopentadienyl anions. Reaction of the potassium salts **22**−**25** with Ca, Sm, and Yb diiodide cleanly gave the metallocenes **1**−**4** (Scheme 5). Crystallization from THF/hexanes, THF/ether, ether/hexanes, or toluene afforded the complexes in 33−88% isolated yields. The intensely colored Sm and Yb compounds as well as the colorless Ca derivatives are air- and moisture-sensitive and soluble in polar solvents like THF. Additionally, **1c**, **2a**−**c**, **3a**, and **4a**−**c** are also soluble in aromatic solvents such as toluene. Melting points for the metallocenes range from 111 to 221 °C, decreasing from Ca to Sm to Yb for each ligand. The complexes were characterized by elemental analyses, NMR spectroscopy, and mass spectrometry.

In all cases the NMR spectra at room temperature show signals for the protons and carbons with the expected chemical shifts, proton intensity, and coupling pattern. In the ^{1}H NMR spectra up to four signals appear for the protons of the cyclopentadienyl rings at low field. All spectra show one signal for the single proton of the stereocenter, two for the two diastereotopic protons of the methylene group, and one for the methoxy and dimethylamino group, respectively. Additionally, a doublet is observed at high field for the methyl group adjacent to the stereocenter in **1a,c** and **2a,c**, whereas the phenyl-containing compounds **3a,c** and **4a,c** show the corresponding signals at low field. In all compounds investigated the two cyclopentadienyl ligands are magnetically equivalent. The fact that no signals attributable to coordinated THF were observed, the low coordination number for only two cyclopentadienyl rings, and the electronic situation at the Lewis acidic metal center all suggest that the oxygen and nitrogen donor atoms are coordinated to the metal. This permits the existence of two diastereomeric forms, as shown in Figure 1. However, only one set of signals is observed

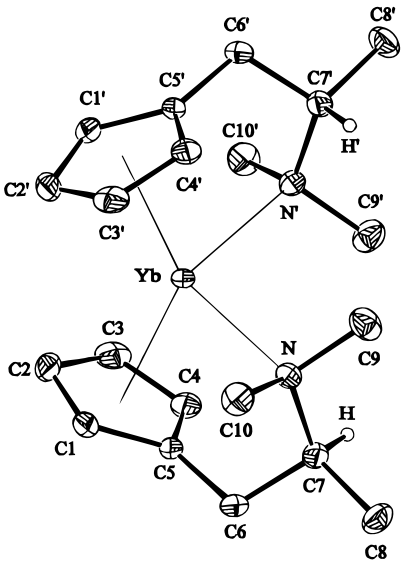


Figure 2. ORTEP plot[19] of the molecular structure and numbering scheme of **2c**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except those on the chiral center are omitted.

Table 2. Selected Bond Lengths (Å) for 2c with Estimated Standard Deviations

Yb−Cp[a]/Cp′[a]	2.400(5)	Yb−C(2)	2.696(5)
Yb−N′[b]	2.603(4)	N−C(9)	1.461(6)
Yb−N	2.603(4)	N−C(10)	1.471(6)
Yb−C(5)	2.665(5)	N−C(7)	1.495(7)
Yb−C(5′)[b]	2.665(5)	C(5)−C(4)	1.400(7)
Yb−C(4)	2.678(5)	C(5)−C(1)	1.413(6)
Yb−C(4′)[b]	2.678(5)	C(5)−C(6)	1.506(7)
Yb−C(1)	2.677(5)	C(1)−C(2)	1.402(8)
Yb−C(1′)[b]	2.677(5)	C(2)−C(3)	1.440(9)
Yb−C(3)	2.698(5)	C(4)−C(3)	1.386(8)
Yb−C(3′)[b]	2.698(5)	C(6)−C(7)	1.525(7)
Yb−C(2′)[b]	2.696(5)	C(7)−C(8)	1.530(7)

[a] Cp defines the centroid of the ring atoms Cp (C(1)−C(5)) and Cp′ (C(1′)−C(5′)). [b] Symmetry transformation used to generate equivalent atoms: *x*, −*y*, −*z*.

Table 3. Selected Bond Angles (deg) for 2c with Estimated Standard Deviations

Cp[a]−Yb−Cp′[a]	134.03(16)	C(9)−N−C(10)	108.7(4)
Cp[a]−Yb−N′	114.30(15)	C(9)−N−C(7)	111.0(4)
N−Yb−Cp[a]	94.25(15)	C(10)−N−C(7)	111.8(4)
N′−Yb−Cp′[a]	94.25(15)	C(5)−C(6)−C(7)	113.5(4)
N−Yb−Cp′[a]	114.30(15)	N−C(7)−C(6)	110.9(4)
N′−Yb−N	103.1(2)	N−C(7)−C(8)	114.9(4)
		C(6)−C(7)−C(8)	110.5(4)

[a] Cp defines the centroid of the ring atoms Cp (C(1)−C(5)) and Cp′ (C(1′)−C(5′)).

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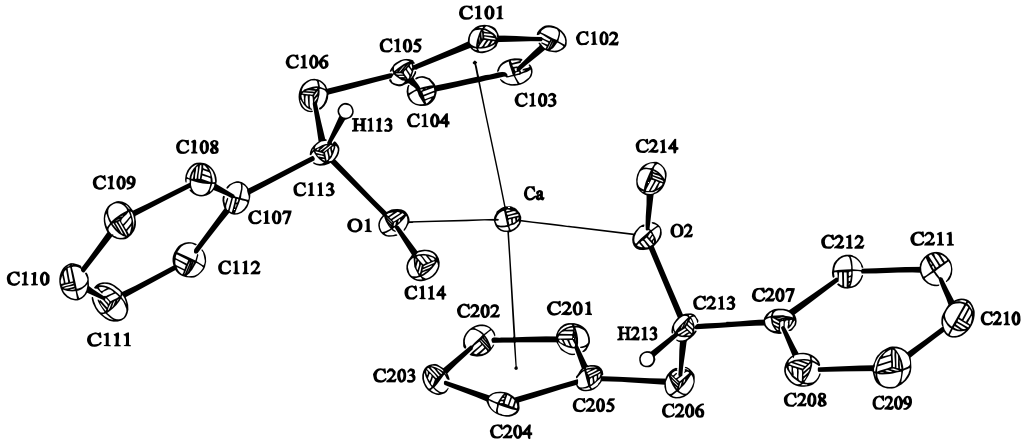

Figure 3. ORTEP plot[19] of the molecular structure and numbering scheme of **3a**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except those on the chiral center are omitted.

for the cyclopentadienyl ring and the donor-substituted chain in the ^{1}H and ^{13}C NMR spectra at room temperature, and no resolution of these signals is observed even at −78 °C. This could be because the minor isomer is in too small an amount, only the most highly crystalline diastereomer has been isolated, or a rapid exchange between the two forms occurs.

All mass spectra recorded between 60 and 240 °C show the molecular ion as the peak with the highest mass and a fragment formed by loss of one cyclopentadienyl ligand with the expected isotopic pattern for the elements.

Values for the optical rotations of the complexes could only be obtained for the colorless Ca compounds, because the high extinction coefficient of the intensely colored solutions of the Sm and Yb compounds does not permit exact measurements.

Molecular Structure of [Yb{(*S*)-η^5:η^1-$C_5H_4(CH_2$-CH(Me)NMe_2)}$_2$] (2c). A crystal suitable for X-ray diffraction analysis was obtained by recrystallization from toluene. The structure of one of the two identical well-separated molecules in the unit cell of **2c** is shown in Figure 2, the crystallographic data are compiled in Table 1, and selected structural data are given in Tables 2 and 3. Both dimethylamino groups are intramolecularly coordinated to the Yb atom, and only one possible diastereomeric conformation (Figure 1) is present. Overall, the structure of **2c** closely resembles the distorted-tetrahedral geometry of [Yb{η^5:η^1-$C_5H_4(CMe_2CH_2C_5H_4N$-2)}$_2$][20] with N−Yb−N′ = 103.10° and Cp−Yb−Cp′ = 134.04° (Cp defines the centroid of the ring atoms C(1)−C(5), the atoms marked with primes are constructed through rotation by the 2-fold axis); the latter is the angle with the largest deviation from the ideal tetrahedral geometry. The Yb−N distance is, at 2.603(4) Å, only slightly longer than those reported for [$(C_5Me_5)_2$-Yb(C_5H_5N)$_2$][18] (2.586(7) and 2.544(6) Å, respectively) and [Yb{η^5:η^1-$C_5H_4(CMe_2CH_2C_5H_4N$-2)}$_2$][20] (2.494(7) and 2.469(7) Å, respectively). In the near-planar cyclopentadienyl ligands the C−C bond distances range from 1.39 to 1.44 Å, and each of the aromatic carbons is almost evenly bonded to the Yb center (2.67−2.70 Å). The structure shows that the side chain is coordinated to the Yb atom in a zigzag fashion with an *S* configuration at the stereocenter (C(7)).

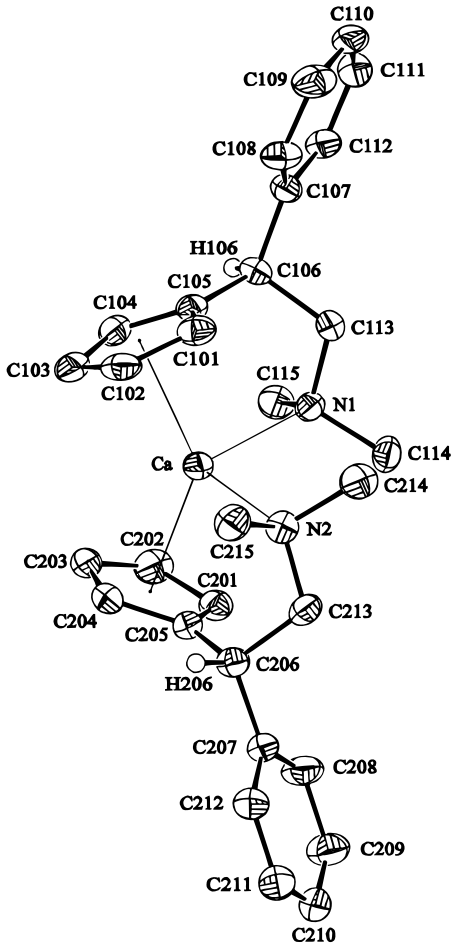

Figure 4. ORTEP plot[19] of the molecular structure and numbering scheme of **4a**, with 30% probability thermal ellipsoids. For clarity, all hydrogens except those on the chiral center are omitted.

Molecular Structure of [Ca{(*S*)-η^5:η^1-$C_5H_4(CH_2$-CH(Me)OMe)}$_2$] (3a) and [Ca{(*S*)-η^5:η^1-$C_5H_4(CH_2$-(Ph)CH_2NMe_2)}$_2$] (4a). Suitable crystals for X-ray crystallography were also obtained from toluene. Figures 3 (**3a**) and 4 (**4a**) show the structure of one of the four identical molecules found in the unit cell for each complex. The experimental data and the selected bond parameters are included in Tables 1 and 4−7. The

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Table 4. Selected Bond Lengths (Å) for 3a with Estimated Standard Deviations

Ca−O(1)	2.400(4)	Ca−O(2)	2.417(5)
Ca−C(101)	2.686(5)	Ca−C(201)	2.653(7)
Ca−C(102)	2.703(5)	Ca−C(202)	2.686(6)
Ca−C(103)	2.671(6)	Ca−C(203)	2.681(5)
Ca−C(104)	2.634(7)	Ca−C(204)	2.656(6)
Ca−C(105)	2.632(6)	Ca−C(205)	2.640(6)
Ca−Cp(1)[a]	2.382	Ca−Cp(2)[a]	2.379
O(1)−C(113)	1.456(6)	O(2)−C(213)	1.455(7)
O(1)−C(114)	1.443(9)	O(2)−C(214)	1.439(7)
C(101)−C(105)	1.399(8)	C((201)−C(205)	1.404(10)
C(105)−C(106)	1.504(8)	C(205)−C(206)	1.500(9)
C(106)−C(113)	1.540(10)	C(206)−C(213)	1.552(9)
C(107)−C(113)	1.506(8)	C(207)−C(213)	1.497(8)

[a] Cp defines the centroid of the ring atoms Cp(1) (C(101)−C(105)) and Cp(2) (C(201)−C(205)).

Table 5. Selected Bond Angles (deg) for 3a with Estimated Standard Deviations

O(1)−Ca−O(2)	102.54(16)	Cp[a](1)−Ca−Cp[a](2)	139.7
O(1)−Ca−Cp[a](1)	92.55(13)	O(2)−Ca−Cp[a](2)	94.76
O(1)−Ca−Cp[a](2)	109.42(14)	O(2)−Ca−Cp[a](1)	113.43
C(114)−O(1)−C(113)	111.8(4)	C(214)−O(2)−C(213)	111.3(5)
O(1)−C(113)−C(106)	108.4(5)	O(2)−C(213)−C(206)	106.8(5)
O(1)−C(113)−C(107)	109.8(4)	O(2)−C(213)−C(207)	112.0(5)
C(107)−C(113)−C(106)	112.6(5)	C(207)−C(213)−C(206)	111.9(4)
C(105)−C(106)−C(113)	113.4(5)	C(205)−C(206)−C(213)	114.4(5)

[a] Cp defines the centroid of the ring atoms Cp(1)(C(101)−C(105)) and Cp(2)(C(201)−C(205)).

geometry around the Ca center in **4a** is, with Cp(1)−Ca−Cp(2) = 137.33° and N(1)−Ca−N(2) = 101.31°, very similar to that around the Yb center of **2c**. The same is true for the Ca complex **3a**, with Cp(1)−Ca−Cp(2) = 139.70° and O(1)−Ca−O(2) = 102.54°. The Cp(1)−Ca−Cp(2) angles may be compared to those found in [Ca{η^5-$C_5H_4(CMe_3)$}$_2$(THF)$_2$][20] (133.3°) and [Ca{η^5-C_5H_4Me}$_2$(DME)][21] (134.8°). The Ca−O bond lengths of 2.400(4) and 2.417(5) Å, respectively, are also in good agreement with [Ca{η^5-$C_5H_4(CMe_3)$}$_2$(THF)$_2$][20] (2.405(4) and 2.398(4) Å, respectively) and [Ca{η^5-C_5H_4Me}$_2$(DME)][21] (2.404(1) Å). The Ca−N distances are 2.558(5) and 2.601(5) Å, respectively. The mean Ca−C bond length of 2.68 Å for **4a** is the same as in [Ca{η^5-C_5H_4Me}$_2$(DME)];[21] that for **3a** is, at 2.66 Å, in the same range. Both solid-state structures show the chelating arm coordinated in zigzag fashion, where *S* is the absolute configuration at the stereocenter (C(113)/C(213) for **3a**; C(106)/C(206) for **4a**).

Conclusion. We have prepared novel chiral metallocenes of the divalent lanthanides samarium(II) and ytterbium(II) and the alkaline-earth metal calcium involving new chiral, nonracemic donor-functionalized cyclopentadienyl ligands. The enantiomeric purity of the stereogenic centers in the ligands as well as the intramolecular coordination of the donor arm has been confirmed by X-ray structural analyses carried out for the three complexes **2c**, **3a**, and **4a**. We will continue to examine these systems with respect to their potential use in catalytic reactions.

Table 6. Selected Bond Lengths (Å) for 4a with Estimated Standard Deviations

Ca−N(1)	2.558(5)	Ca−N(2)	2.601(5)
Ca−C(101)	2.643(6)	Ca−C(201)	2.649(6)
Ca−C(102)	2.672(6)	Ca−C(202)	2.663(6)
Ca−C(103)	2.716(6)	Ca−C(203)	2.684(7)
Ca−C(104)	2.705(6)	Ca−C(204)	2.701(6)
Ca−C(105)	2.663(6)	Ca−C(205)	2.693(6)
Ca−Cp[a](1)	2.400(30)	Ca−Cp[a](2)	2.397(30)
N(1)−C(113)	1.485(7)	N(2)−C(213)	1.476(7)
N(1)−C(114)	1.496(7)	N(2)−C(214)	1.498(8)
N(2)−C(215)	1.474(7)	N(1)−C(115)	1.476(7)
C(101)−C(105)	1.412(8)	C(201)−C(205)	1.383(8)
C(105)−C(106)	1.514(8)	C(205)−C(206)	1.502(8)
C(106)−C(113)	1.533(8)	C(206)−C(207)	1.532(7)
C(106)−C(107)	1.533(8)	C(206)−C(213)	1.533(9)

[a] Cp defines the centroid of the ring atoms Cp(1)(C(101)−C(105)) and Cp(2)(C(201)−C(205)).

Table 7. Selected Bond Angles (deg) for 4a with Estimated Standard Deviations

N(1)−Ca−N(2)	101.31(16)	Cp[a](1)−Ca−Cp[a](2)	137.33(13)
N(1)−Ca−Cp[a](2)	113.38(13)	N(2)−Ca−Cp[a](1)	112.16(16)
N(1)−Ca−Cp[a](1)	95.53(13)	N(2)−Ca−Cp[a](2)	93.64(13)
C(113)−N(1)−C(114)	108.4(5)	C(213)−N(2)−C(214)	107.7(5)
C(115)−N(1)−C(113)	109.5(4)	C(213)−N(2)−C(215)	111.5(4)
C(115)−N(1)−C(114)	107.8(5)	C(215)−N(2)−C(214)	107.6(5)
N(1)−C(113)−C(106)	112.9(4)	N(2)−C(213)−C(206)	113.0(5)
C(105)−C(106)−C(113)	110.4(5)	C(205)−C(206)−C(213)	110.6(5)
C(113)−C(106)−C(107)	107.4(5)	C(207)−C(206)−C(213)	108.4(5)
C(105)−C(106)−C(107)	117.2(5)	C(205)−C(206)−C(207)	116.3(5)

[a] Cp defines the centroid of the ring atoms Cp(1) (C(101)−C(105)) and Cp(2) (C(201)−C(205)).

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Supporting Information Available: Full details of the X-ray structures of complexes **2c**, **3a**, and **4a**, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters (18 pages). Ordering information is given on any current masthead page.

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