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Organometallic Compounds of the Lanthanides. 141.[1] Synthesis, Molecular Structure, and Solution Behavior of Some Lanthanum(III) and Ytterbium(II) Complexes Containing New Tridentate 1,2- and 1,3-Bis(2-(dimethylamino)ethyl)cyclopentadienyl Ligands[†]

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$K[C_5H_4(CH_2CH_2NMe_2)]$ reacts with 2-(dimethylamino)ethyl chloride in THF, forming an inseparable 1.5:1 mixture of isomeric 1,2- and 1,3-disubstituted bis((dimethylamino)ethyl)-cyclopentadiene, which on deprotonation with KH gives a mixture of the corresponding potassium salts $K[1,2\text{-}C_5H_3(CH_2CH_2NMe_2)_2]$ ($K[1,2\text{-}Do_2C_5H_3]$; **1**) and $K[1,3\text{-}C_5H_3(CH_2CH_2NMe_2)_2]$ ($K[1,3\text{-}Do_2C_5H_3]$; **2**). Addition of $LaI_3(THF)_3$ to the mixture of **1** and **2** suspended in THF causes the formation of the half-sandwich complexes $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2)LaI_2(THF)$ (**3**) and $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,3)LaI_2(THF)$ (**4**), which can successfully be separated because of their different crystal shapes. The analogous reaction with $YbI_2(THF)_2$ causes the precipitation of crystalline $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2)YbI(THF)_2$ (**5**). The noncrystallizing 1,3-isomer left in solution reacts with $(C_5Me_5)Na$, forming the polymeric mixed-metallocene *ate* complex $\{Na[\mu_2\text{-}(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,3)(\eta^5\text{-}C_5Me_5)Yb(\mu_2\text{-}I)Yb[\mu_2\text{-}(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,3)(\eta^5\text{-}C_5Me_5)\}_n$ (**6**). The reaction of **5** with $(C_5Me_5)K$ or $(C_5H_4{}^tBu)Na$ results in the formation of the sandwich complexes $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2)Yb(\eta^5\text{-}C_5H_4{}^tBu)$ (**7**) and $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2)Yb(\eta^5\text{-}C_5Me_5)$ (**8**), respectively. The novel compounds have been characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. Additionally, X-ray structural analyses of **3**−**8** were performed.

Introduction

Metal complexes with donor-functionalized cyclopentadienyl ligands have been studied intensively during the past decade because of their potential application as catalysts in polymerization processes.[2] Recently we reported on the synthesis and characterization of a number of complexes of trivalent and divalent lanthanides with mono-N- and mono-O-functionalized cyclopentadienyl ligands.[2p,t,u] The additional intramolecular coordination of the Lewis base function of the cyclopentadienyl substituent to the metal center reduces or even prevents the coordination of solvent molecules. In general, such intramolecularly stabilized cyclopentadienyl complexes are less sensitive to hydrolysis and oxidation in air compared to their nonfunctionalized analogues. The synthesis of the first bis-functionalized cyclopentadienyl ligand, $1,3\text{-}C_5H_3(SiMe_2CH_2P^iPr_2)_2$, and of its zirconium complexes has been reported by Fryzuk et al.[3] Rhodium complexes containing both 1,2- and 1,3-bis(phosphinopropyl)cyclopentadienyl ligands were reported by Nelson et al.,[4] and the rhodium complex $[\{1,3\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\}RhCl]BF_4$ was described by Saunders et al.[5] The only example of a complex with a bis-oxygen-functionalized cyclopentadienyl ligand is the zirconium complex $[1,2\text{-}C_5H_3(CH_2CH_2OMe)_2]ZrCl_3$.[6] Scandium complexes with cyclopentadienyl ligands incorporating both an amido and an amine function have been synthesized by Piers et al.[7]

Since so far no bis-amino-functionalized cyclopentadienyls have been used in complexation reactions and lanthanide complexes of cyclopentadienyl systems containing two donor-functionalized side chains are not known at all, we started to prepare such a ligand system in order to study its coordination behavior toward lanthanum(III) and ytterbium(II) iodide, expecting in-

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[†] Dedicated to Professor Max Schmidt on the occasion of his 75th birthday.

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Table 1. ^{1}H and ^{13}C{^{1}H} NMR Data for 1−4

		^{1}H NMR			^{13}C{^{1}H} NMR	
	solvent	δ (ppm)	assignt	*J* (Hz)	δ (ppm)	assignt
1	THF-d_8	5.14 (d, 2H), 5.08 (t, 1H)	1,2-Do$_2$Cp*H*	^{3}*J*(H,H) 2.2	118.2	Cp*C*CH$_2$
		2.49−2.44 (m, 4H)	N*CH$_2$*CH$_2$		103.7	Cp*C*H
		2.33−2.27 (m, 4H)	NCH$_2$*CH$_2$*		102.2	Cp(*C*H)$_2$
		2.08 (s, 12H)	(*CH$_3$*)$_2$N		64.1	N*C*H$_2$
					45.6	(*C*H$_3$)$_2$NCH$_2$
					29.5	NCH$_2$*C*H$_2$
2	THF-d_8	5.27 (t, 1H), 5.19 (d, 2H)	1,3-Do$_2$Cp*H*	^{4}*J*(H,H) 3.0	115.4	Cp*C*CH$_2$
		2.49−2.44 (m, 4H)	N*CH$_2$*CH$_2$		104.0	Cp(*C*H)$_2$
		2.33−2.27 (m, 4H)	NCH$_2$*CH$_2$*		102.8	Cp*C*H
		2.09 (s, 12H)	(*CH$_3$*)$_2$N		63.5	N*C*H$_2$
					45.8	(*C*H$_3$)$_2$NCH$_2$
					27.3	NCH$_2$*C*H$_2$
3	pyridine-d_5	6.59 (d, 2H), 6.43(t, 1H)	1,2-Do$_2$Cp*H*	^{3}*J*(H,H) 3.0	128.9	Cp*C*CH$_2$
		3.64 (m, 4H)	O*CH$_2$*CH$_2$		116.0	Cp(*C*H)$_2$
		3.27−2.93 (m, 2H)	NCH*H*CH$_2$		114.3	Cp*C*H
		2.99−2.85 (m, 2H)	NCH*H*CH$_2$		67.5, 25.5	THF
		2.81−2.61 (m, 4H)	NCH$_2$*CH$_2$*		63.5	N*C*H$_2$
		2.44 (s, 12H)	(*CH$_3$*)$_2$N		45.8	(*C*H$_3$)$_2$NCH$_2$
		1.59 (m, 4H)	OCH$_2$*CH$_2$*		26.1	NCH$_2$*C*H$_2$
4	pyridine-d_5	6.95 (t, 1H), 6.53 (d, 2H)	1,3-Do$_2$Cp*H*	^{4}*J*(H,H) 2.6	129.9	Cp*C*CH$_2$
		3.64 (m, 4H)	O*CH$_2$*CH$_2$		116.7	Cp*C*H
		3.39−3.15 (m, 2H)	NCH*H*CH$_2$		115.4	Cp(*C*H)$_2$
		2.95−2.70 (m, 2H)	NCH*H*CH$_2$		67.5, 25.5	THF
		2.62−2.45 (m, 4H)	NCH$_2$*CH$_2$*		63.0	N*C*H$_2$
		2.36 (s, 12H)	(*CH$_3$*)$_2$N		45.6	(*C*H$_3$)$_2$NCH$_2$
		1.59 (m, 4H)	OCH$_2$*CH$_2$*		26.6	NCH$_2$*C*H$_2$

teresting results concerning the mutual ring positions of the two side chains and the fluxional behavior of the complexes in solution.

Experimental Section

All operations involving organometallic compounds were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques in dry, oxygen-free solvents. Melting points and decomposition temperatures were measured on a hot-stage microscope in vacuum-sealed (0.01 mbar) capillaries and are uncorrected. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz, ^{13}C, 50.32 MHz) spectrometer at room temperature. The NMR spectroscopic data are cited in Tables 1 and 2. All chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residues of the deuterated solvents. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311A instrument. Only characteristic fragments and 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. Reasonably satisfactory analyses could be obtained by using a special Schlenk tube and small aluminum cans for weighing these extremely sensitive compounds, but not in all cases, because of their especially high sensitivity toward traces of moisture and air of some compounds. 2-(Dimethylamino)ethyl chloride hydrochloride was used as purchased from Aldrich. Free 2-(dimethylamino)ethyl chloride was obtained by treatment of the hydrochloride with sodium hydroxide prior to use. K[$C_5H_4(CH_2CH_2NMe_2)$] was prepared according to published procedures.[8] Recrystallization from THF resulted in the crystalline adduct [K(THF)]-[{$C_5H_4(CH_2CH_2NMe_2)$}], which was characterized by X-ray diffraction. Its molecular structure will be published elsewhere.

[1,2-Bis(2-(dimethylamino)ethyl)cyclopentadienyl]-potassium (1) and [1,3-Bis(2-(dimethylamino)ethyl)cyclopentadienyl]potassium (2). To a suspension of [K(THF)]-[{$C_5H_4(CH_2CH_2NMe_2)$}] (9.3 g, 37.6 mmol) in THF (140 mL) was added dropwise 2-(dimethylamino)ethyl chloride (4.2 g, 39.0 mmol). The mixture was stirred for 0.5 h at room temperature and then for 12 h at reflux temperature. Then, water (250 mL) was added, the organic layer separated, dried over Na_2SO_4, and concentrated at reduced pressure, and the residual oil distilled under a vacuum (69−79 °C, 10^{-2} Torr), yielding 6.73 g (86%) of a mixture of 1,2- and 1,3-bis(2-(dimethylamino)ethyl)cyclopentadiene as a light-yellow transparent liquid. A solution of this liquid (6.35 g, 30.4 mmol) in

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Table 2. ^{1}H and ^{13}C{^{1}H} NMR Data for 5−8

		^{1}H NMR			^{13}C{^{1}H} NMR		
	solvent	δ (ppm)	assign	J (Hz)	δ (ppm)	assign	$^1J(^{171}$Yb,^{13}C) (Hz)
5	THF-d_8	5.67 (s, 1H), 5.54 (s, 2H)	1,2-Do$_2$CpH		119.3	CpCCH$_2$	
		3.59 (m, 8H)	OCH_2CH$_2$		107.5	CpCH	
		2.54 (s, 8H)	NCH_2CH_2		105.2	Cp(CH)$_2$	
		2.33 (s, 12H)	(CH_3)$_2$N		68.2	THF	
		1.71 (m, 8H)	OCH$_2$CH_2		64.8	NCH$_2$	
					47.3	(CH$_3$)$_2$NCH$_2$	
					26.3	NCH$_2$$CH_2$	
					27.2	THF	
6	THF-d_8	5.52 (t, 1H), 5.45 (d, 2H)	1,3-Do$_2$CpH	^4J(H,H) 2.1	120.0	CpCCH$_2$	
		2.59 (m, 2H)	NCHHCH$_2$		111.2	CpCCH$_3$	
		2.49 (m, 2H)	NCHHCH$_2$		107.1	CpCH	
		2.29 (m, 4H)	NCH$_2$CH_2		105.8	Cp(CH)$_2$	
		2.23 (s, 12H)	(CH_3)$_2$N		64.7	NCH$_2$	
		1.93 (s, 15H)	CpCH_3		45.8	(CH$_3$)$_2$NCH$_2$	
					28.4	NCH$_2$$CH_2$	
					12.2	CpCCH$_3$	
7	C$_6$D$_6$	6.31 (t, 1H), 5.71 (d, 2H)	1,2-Do$_2$CpH	^3J(H,H) 3.2, ^2J(Yb,H) 12.9, 7.7,	136.2	CpCC(CH$_3$)$_3$	5.4
		5.99 (t, 2H), 5.61 (t, 2H)	^{t}Bu-CpH	^3J(H,H) 2.6, ^2J(Yb,H) 10.3	117.5	CpCCH$_2$	5.4
		2.5−2.0 (m, 8H)	NCH_2CH_2		107.7	Cp(CH)$_2$	6.5
		1.88 (s, 12H)	(CH_3)$_2$N		106.6	^{t}Bu-CpC	7.5
		1.61 (s, 9H)	(CH_3)$_3$C		105.3	CpCH	6.5
					104.2	^{t}Bu-CpC	5.2
					64.4	NCH$_2$	
					48.1	(CH$_3$)$_2$NCH$_2$	
					44.2	(CH$_3$)$_2$NCH$_2$	
					33.4	C(CH$_3$)$_3$	
					32.2	C(CH$_3$)$_3$	
					25.2	NCH$_2$$CH_2$	
8	C$_6$D$_6$	6.25 (t, 1H), 5.38 (d, 2H)	1,2-Do$_2$CpH	^3J(H,H) 3.4, ^2J(Yb,H) 13.3, 8.2	116.7	CpCCH$_2$	5.4
		2.5−1.7 (m, 8H)	NCH_2CH_2		111.8	CpCCH$_3$	6.4
		2.15 (s, 15H)	(CH_3)Cp		108.2	Cp(CH)$_2$	6.4
		1.89 (s, 12H)	(CH_3)$_2$N		107.5	CpCH	7.5
					64.7	NCH$_2$	
					47.1	(CH$_3$)$_2$NCH$_2$	
					43.0	(CH$_3$)$_2$NCH$_2$	
					26.3	NCH$_2$$CH_2$	
					12.0	CpCH$_3$	
8	THF-d_8	5.64 (t, 1H), 5.68 (d, 2H)	1,2-Do$_2$CpH	^3J(H,H) 3.4, ^2J(Yb,H) 12.9, 8.2	117.5	CpCCH$_2$	4.9
		2.9−2.4 (m, 8H)	NCH_2CH_2		111.8	CpCCH$_3$	7.1
		2.33 (s, 12H)	(CH_3)Cp		107.9	Cp(CH)$_2$	6.5
		1.92 (s, 15H)	(CH_3)$_2$N		107.1	CpCH	7.6
					65.4	NCH$_2$	
					45.9	(CH$_3$)$_2$NCH$_2$	
					25.9	NCH$_2$$CH_2$	
					11.9	CpCH$_3$	

THF (50 mL) was added within 2 h with stirring to a suspension of KH (1.1 g, 27.4 mmol) in THF (70 mL). The pale yellow precipitate formed was filtered off and dried under a vacuum, yielding 6.45 g (95%) of a mixture of **1** and **2** (1.5:1 ratio, demonstrated by ^{1}H NMR spectroscopy). Anal. Calcd for $C_{13}H_{23}N_2K$ (mol wt 246.44): C, 63.36; H, 9.41; N, 11.37. Found: C, 63.83; H, 8.79; N, 10.25.

Diiodo[1,2-bis(2-(dimethylamino)ethyl)cyclopentadienyl](tetrahydrofuran)lanthanum(III) (3) and Diiodo[1,3-bis(2-(dimethylamino)ethyl)cyclopentadienyl](tetrahydrofuran)lanthanum(III) (4). To a stirred suspension of a mixture of **1** and **2** (1.72 g, 6.97 mmol) in THF (40 mL) was added $LaI_3(THF)_3$ (5.05 g, 6.86 mmol). The mixture was stirred for 30 min at room temperature. Then the solution was separated from precipitated KI by filtration. After the clear solution was concentrated under a vacuum to a volume of 15 mL, 3.16 g (68.5%) of colorless crystals of **3** (elongated blocks) and **4** (large cubic crystals) were isolated. Manual separation of the crystals gave 1.34 g (29%) of **3** and 1.80 g (39%) of **4**; both **3** and **4** decomposed at ∼180 °C. **3**: MS (195 °C, ^{139}La; *m/z* (%)) 208.1 (0.7) $[C_5H_3(CH_2CH_2NMe_2)_2]^+$, 58.1 (100) $[Me_2NCH_2]^+$. Anal. Calcd for $C_{17}H_{31}I_2N_2OLa\cdot{}^1/_2C_4H_8O$ (mol wt 708.2): C, 32.22; H, 4.98; N, 3.96. Found: C, 31.38; H, 5.39; N, 2.25. **4**: MS (251 °C, ^{139}La; *m/z* (%)) 599.8 (2) $[M - THF]^+$, 473.1 (100) $[M - THF - I]^+$, 414.9 (5) $[M - THF - I - CH_2NMe_2]^+$, 58.1 (96) $[Me_2NCH_2]^+$. Anal. Calcd for $C_{17}H_{31}I_2N_2OLa$ (mol wt 672.15): C, 30.38; H, 4.65; N, 4.17. Found: C, 29.92; H, 5.02; N, 4.13.

Iodo[1,2-bis(2-(dimethylamino)ethyl)cyclopentadienyl]bis(tetrahydrofuran)ytterbium(II) (5). A mixture of **1** and **2** (1.55 g, 6.29 mmol) was added to a solution of $YbI_2(THF)_2$ (3.45 g, 6.03 mmol) in THF (50 mL). The mixture was stirred for 3 h at room temperature; the red-orange solution that formed was filtered off and reduced to a volume of 15 mL by evaporation of the solvent under a vacuum at 50 °C. Cooling to −28 °C caused precipitation of 1.49 g (38%) of **5** as orange crystals, mp 212 °C dec. MS (271 °C, ^{174}Yb; *m/z* (%)): 588.3 (4) $[M - C_5H_3]^+$, 508.0 (10) $[M - 2THF]^+$, 380.9 (4) $[M - 2THF - I]^+$, 300.8 (2) $[YbI]^+$, 207.2 (7) $[C_5H_3(CH_2CH_2NMe_2)]^+$, 58.1 (100) $[Me_2NCH_2]^+$. Anal. Calcd for $C_{21}H_{39}N_2O_2IYb$ (mol wt): C, 38.72; H, 6.03; N, 4.30; Yb, 26.56. Found: C, 37.14; H, 5.88; N, 4.92; Yb, 26.34.

Sodium Iodobis{[1,3-bis(2-(dimethylamino)ethyl)cyclopentadienyl](pentamethylcyclopentadienyl)}diytterbium(II) (6). The residual THF solution which is left after isolation of **5** was added to a suspension of Cp*Na (0.59

Table 3. Crystal Data and Structure Refinement for 3−5

	3	4	5
empirical formula	$C_{17}H_{31}I_2LaN_2O\cdot{}^1/_2C_4H_8O$	$C_{17}H_{31}I_2LaN_2O$	$C_{21}H_{39}N_2O_2IYb$
fw	708.20	672.15	651.48
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
a (Å), α (deg)	17.5679(3), 90	8.5876(1), 90	9.4725(1), 90
b (Å), β (deg)	9.5385(1), 109.139(1)	15.2281(2), 90	8.4049(2), 98.831(1)
c (Å), γ (°)	15.4491(1), 90	17.1304(2), 90	15.1456(4), 90
V (Å^3)	2445.73(5)	2240.19(5)	1191.53(4)
Z	4	4	2
D(calcd) (g/cm^3)	1.923	1.993	1.816
μ(Mo Kα) (mm^{-1})	4.283	4.669	5.237
F(000)	1352	1272	636
cryst size (mm^3)	0.54 × 0.12 × 0.16	0.48 × 0.26 × 0.40	0.32 × 0.32 × 0.48
θ_{min}, θ_{max} (deg)	1.13, 27.50	1.79, 27.50	1.36, 27.50
index ranges	$-22 \le h \le 18, -12 \le k \le 8, -19 \le l \le 20$	$-11 \le h \le 9, -17 \le k \le 19, -22 \le l \le 19$	$-5 \le h \le 12, -9 \le k \le 10, -19 \le l \le 17$
no. of rflns collected	18 239	17 486	5927
no. of indep rflns	5576 (R(int) = 0.0577)	5141 (R(int) = 0.0372)	4635 (R(int) = 0.0355)
max, min transmissn	0.6883, 0.3644	0.4291, 0.2271	0.3215, 0.2313
no. of data, restraints, params	5576, 0, 257	5141, 0, 212	4635, 1, 249
GOF on F^2	1.004	1.059	1.007
R indices ($I > 2\sigma(I)$)	$R = 0.0330$, $R_w = 0.0610$	$R = 0.0249$, $R_w = 0.0496$	$R = 0.0468$, $R_w = 0.0982$
R indices (all data)	$R = 0.0555$, $R_w = 0.0679$	$R = 0.0285$, $R_w = 0.0509$	$R = 0.0591$, $R_w = 0.1040$
abs structure param		0.01(2)	0.278(17)
max, min resid electron density (e/Å^3)	1.051, −1.282	1.013, −0.645	2.181, −1.618

g, 3.74 mmol) in THF (20 mL). The mixture turned dark purple immediately. The solvent was removed under a vacuum, and the residue was washed twice with toluene (15 mL) and was then extracted with THF (30 mL). Again this THF extract was treated with toluene (20 mL), resulting in the formation of 1.26 g (53%) of deep red crystals of **6**, mp 240 °C dec. MS (242 °C, ^{174}Yb; m/z (%)): 588.2 (4) [1,3-$Do_2C_5H_3YbI$]$^+$, 516.1 (22) [1,3-$Do_2C_5H_3YbCp^*$]$^+$, 381.0 (100) [1,3-$Do_2C_5H_3Yb$]$^+$, 308.0 (4) [Cp*Yb]$^+$, 58.1 (95) [Me_2NCH_2]$^+$. Anal. Calcd for $C_{46}H_{76}IN_4NaYb_2\cdot C_7H_8$ (mol wt 1273.21): C, 50.00; H, 6.65; N, 4.40; Yb, 27.18. Found: C, 51.12; H, 5.93; N, 4.19; Yb, 27.11.

(1,2-Bis(2-(dimethylamino)ethyl)cyclopentadienyl)(*tert*-butylcyclopentadienyl)ytterbium(II) (7). A mixture of **5** (0.9 g, 1.38 mmol) and $^tBuC_5H_4Na$ (0.2 g, 1.38 mmol) turned immediately purple when 25 mL of THF was added. The mixture was stirred for a few minutes, and the solvent was removed under a vacuum. The residue was extracted with diethyl ether (2 × 20 mL). Concentration of the clear solution to 15 mL caused crystallization of 0.54 g (78%) of dark red **7**, mp 219 °C dec. MS (136 °C, ^{174}Yb; m/z (%)): 502.1 (100) [M]$^+$, 379.0 (59) [M − ^{t}BuCp]$^+$, 321.0 (8) [M − ^{t}BuCp − CH_2NMe_2]$^+$, 295.0 (14) [(^{t}BuCp)Yb]$^+$, 279.0 (16) [M − ^{t}BuCp − CH_2NMe_2 − CH_2CH_2]$^+$, 58.1 (78) [Me_2NCH_2]$^+$. Anal. Calcd for $C_{22}H_{36}N_2Yb$ (mol wt 501.57): C, 52.68; H, 7.23; N, 5.59; Yb, 34.50. Found: C, 51.30; H, 6.17; N, 6.10; Yb, 34.57.

(1,2-Bis(2-(dimethylamino)ethyl)cyclopentadienyl)(pentamethylcyclopentadienyl)ytterbium(II) (8). In analogy to the synthesis of **7**, complex **5** (1.1 g, 1.68 mmol) was treated with Cp*K (0.28 g, 1.61 mmol) in 25 mL of THF. Recrystallization from diethyl ether afforded 0.68 g (82%) of deep purple crystals of **8**: mp 195 °C dec. MS (193 °C, ^{174}Yb; m/z (%)): 516.1 (18) [M]$^+$, 380.9 (68) [M − Cp*]$^+$, 321.9 (8) [M − Cp* − CH_2NMe_2]$^+$, 306.8 (11) [Cp*Yb]$^+$, 279.0 (3) [M − ^{t}BuCp − CH_2NMe_2 − CH_2CH_2]$^+$, 58.1 (100) [Me_2NCH_2]$^+$. Anal. Calcd for $C_{23}H_{38}N_2Yb$ (mol wt 515.59): C, 53.58; H, 7.43; N, 5.43; Yb, 33.56. Found: C, 52.95; H, 7.19; N, 5.98; Yb, 33.40.

X-ray Structure Determination. The crystal data and details of data collection are given in Tables 3 and 4. The data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) with an area detector by use of ω scans at 173 K. The structures were solved by direct methods using SHELXS-97[9] and were refined on F^2 using all reflections with SHELXL-97.[10] All non-hydrogen atoms in **3**−**5**, **7**, and **8** were refined anisotropically. The carbon atoms of the disordered toluene solvent molecules in **6** were refined isotropically; all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The idealized methyl groups were allowed to rotate around their X−C bond. Absolute structure parameters were determined using the Flack parameters[11] with SHELXL-97. SADABS[12] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors are summarized in Tables 3 and 4. The geometrical aspects of the structures were analyzed by using the PLATON program.[13]

Results and Discussion

Ligand Synthesis. In analogy to the synthetic approach to mono-N-donor-functionalized cyclopentadienyl derivatives,[2,14] the treatment of ((2-(dimethylamino)ethyl)cyclopentadienyl)potassium with 2-(dimethylamino)ethyl chloride in THF results in the formation of an isomeric mixture of 1,2- and 1,3-bis(2-(dimethylamino)ethyl)cyclopentadiene (1,2-$Do_2C_5H_4$ and 1,3-$Do_2C_5H_4$) along with additional isomers arising from prototropic shifts. The introduction of the second N-functionalized substituent to the cyclopentadienyl ring requires prolonged heating of the reaction mixture under reflux conditions. Workup of the reaction mixture affords a light yellow oil which distills continuously in a temperature range of 69−79 °C/10^{-2} Torr, thus not allowing a separation of the isomers (the temperatures necessary to distill the product at pressures of 0.1−1 Torr cause extensive decomposition). However, the ratio of the

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(10) Sheldrick, G. M. SHELXL-97 Program for the Refinement of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1997.

(11) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

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(13) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

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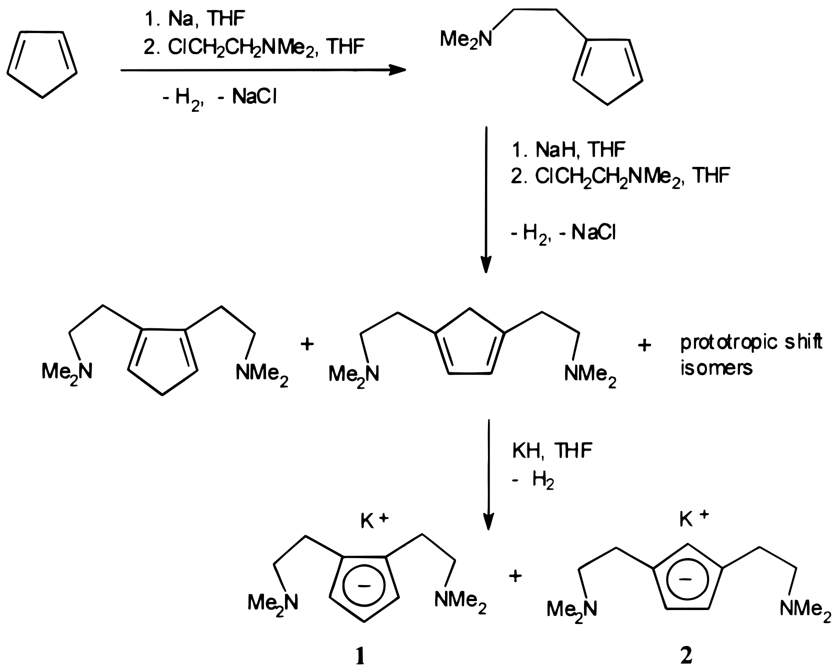
Table 4. Crystal Data and Structure Refinement for 6−8

	6	**7**	**8**
empirical formula	$C_{46}H_{76}IN_4NaYb_2 \cdot C_7H_8$	$C_{22}H_{36}N_2Yb$	$C_{23}H_{38}N_2Yb$
fw	1273.21	501.57	515.59
cryst syst	orthorhombic	orthorhombic	triclinic
space group	*Pbcn* (No. 60)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a (Å), α (deg)	13.6957(1), 90	8.5441(2), 90	10.4367(1), 103.334(1)
b (Å), β (deg)	19.1068(1), 90	15.7446(3), 90	14.9603(2), 105.658(1)
c (Å), γ (°)	21.2924(1), 90	16.1012(3), 90	15.3926(1), 93.699(1)
V (Å^3)	5571.82(6)	2165.99(8)	2231.06(4)
Z	4	4	4
D(calcd) (g/cm^3)	1.518	1.538	1.535
μ(Mo Kα) (mm^{-1})	3.933	4.324	4.200
F(000)	2536	1008	1040
cryst size (mm^3)	0.44 × 0.18 × 0.08	0.36 × 0.10 × 0.08	0.26 × 0.14 × 0.04
θ_{min}, θ_{max} (deg)	1.91, 25.50	1.81, 27.50	1.41, 27.50
index ranges	$-16 \le h \le 16, -23 \le k \le 23, -25 \le l \le 16$	$-11 \le h \le 9, -20 \le k \le 17, -20 \le l \le 20$	$-13 \le h \le 13, -15 \le k \le 19, -19 \le l \le 14$
no. of rflns collected	34 172	16 830	17 149
no. of indep rflns	5176 (R(int) = 0.0960)	4967 (R(int) = 0.0735)	10 100 (R(int) = 0.0471)
max, min transmissn	0.7934, 0.5760	0.7758, 0.5560	0.5494, 0.4078
no. of data, restraints, params	5176, 35, 283	4967, 0, 233	10 100, 0, 487
GOF on F^2	1.053	1.092	0.979
R indices ($I > 2\sigma(I)$)	$R = 0.0421$, $R_w = 0.0678$	$R = 0.0454$, $R_w = 0.0738$	$R = 0.0419$, $R_w = 0.0687$
R indices (all data)	$R = 0.0771$, $R_w = 0.0772$	$R = 0.0635$, $R_w = 0.0788$	$R = 0.0832$, $R_w = 0.0798$
abs structure param		−0.020(19)	
max, min resid electron density (e/Å^3)	0.721, −0.665	2.167, −1.270	2.098, −0.888

Scheme 1



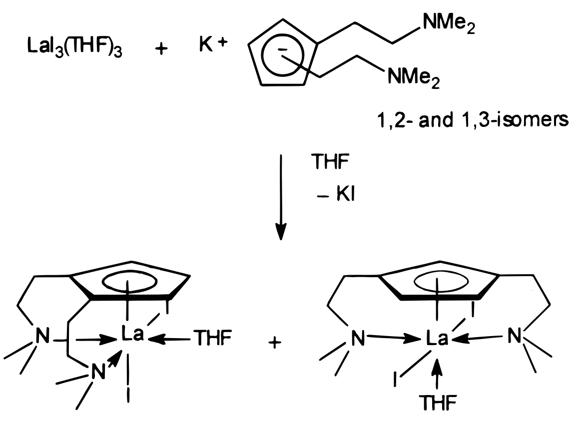
integral intensities of the resonances appearing in the ^1H NMR spectrum of the distillate showing six distinct *N*-methyl singlets and overlapping multiplets in the "aromatic" region indicates that the product consists of a 1.5:1 mixture of 1,2- and 1,3-$Do_2C_5H_4$.

Deprotonation of the mixture of the isomeric cyclopentadienes with KH in THF gives the potassium salts K[1,2-$C_5H_3(CH_2CH_2NMe_2)_2$] (**1**) and K[1,3-$C_5H_3(CH_2CH_2NMe_2)_2$] (**2**), which precipitate from the THF solution (Scheme 1). Both compounds are also only slightly soluble in pyridine and insoluble in alkanes and aromatic hydrocarbons. **1** and **2** cannot be separated by fractional extraction with THF but can be characterized by NMR spectroscopic measurements.

The ^1H NMR spectrum of THF-d_8 solutions of the mixture containing **1** and **2** shows four well-resolved resonances in the Cp region, two somewhat poorly resolved signals for the CH_2-CH_2 bridges, and two sharp NCH_3 signals. $^1H-^1H$ and $^1H-^{13}C$ NMR COSY measurements allow their unambiguous assignment. On the basis of the fact that the molar amounts of **1** and **2** in the mixture are not equal (ca. 1.5:1), all ^{13}C NMR frequencies can be clearly assigned (Table 1).

Lanthanum(III) Complexes. The metathetical reaction of the mixture of **1** and **2** with the lanthanum(III) iodide $LaI_3(THF)_3$ in THF at room temperature produces the two lanthanum(III) half-sandwich complexes (1,2-$Do_2C_5H_3$)LaI_2(THF) (**3**) and (1,3-$Do_2C_5H_3$)-

Scheme 2



3 **4**

$LaI_2(THF)$ (**4**) (Scheme 2). After separation of the immediately formed potassium iodide and concentration of the filtrate, the compounds **3** and **4** crystallize simultaneously from the solution as colorless, well-shaped crystals. Once being formed as crystals, the complexes **3** and **4** lose their solubility. Fortunately, the crystals of **3** and **4** are of different shape, thus allowing a manual separation. Complex **3** crystallizes as elongated blocks, whereas complex **4** forms cubic crystals. Both compounds decompose without melting at temperatures of about 180 °C.

The ^1H NMR spectrum of pure **3** in pyridine shows the expected two signals for the protons of the C_5H_3 fragment (δ 6.59 (d, 2H) and 6.43 (t, 1H)), only one singlet signal for the NCH_3 protons (δ 2.44, 12H), and three sets of overlapping multiplets centered at δ 3.12 (2H), 2.92 (2H), and 2.71 (4H) for the methylene protons of the side chains. A quite similar ^1H NMR spectrum is observed for pure **4** with two signals for the C_5H_3 protons (δ 6.95 (t, 1H) and 6.53 (d, 2H)), a singlet for the NCH_3 protons (δ 2.36 (12H)), and three multiplets centered at δ 3.27 (2H), 2.78 (2H), and 2.54 (4H) for the methylene protons. From the multiplet structure of the CH_2 resonances, which indicates the nonequivalence of the methylene protons, it can be inferred that the N atoms of both donor side arms coordinate the lanthanum ion even in such a basic solvent such as pyridine. The $^{13}C\{^1H\}$ NMR spectra of **3** and **4** show six singlets, one for the *N*-methyl groups, two for the methylene groups of the side chains, and three for the ring carbon atoms (Table 1).

It is noteworthy that the mass spectra of **3** and **4** recorded under EI conditions differ substantially. Whereas for **3** no molecular fragments were detected in the temperature range 20–260 °C, the mass spectrum of **4** shows the unsolvated molecular fragments $[(1,3\text{-}Do_2C_5H_3)LaI_2]^+$ and $[(1,3\text{-}Do_2C_5H_3)LaI]^+$ with intensities of 2 or 100%, respectively.

Molecular Structures of the Lanthanum Complexes 3 and 4. The crystals of **3** and **4** separating directly from the reaction solution can be used for single-crystal X-ray diffraction analyses without further purification by recrystallization. Details of the crystal data collections and the structure refinements are listed in Table 3, the ORTEP drawings[15] of the molecular structures of **3** and **4** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are presented in Table 5. Complex **3**, containing the 1,2-substituted cyclopentadienyl ligand, crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit is

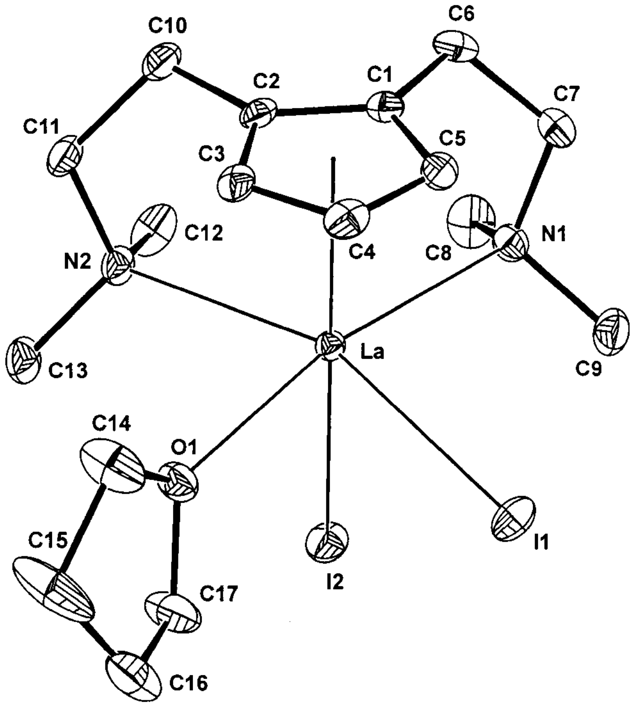


Figure 1. ORTEP plot[15] of the molecular structure and numbering scheme of **3**, with 30% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

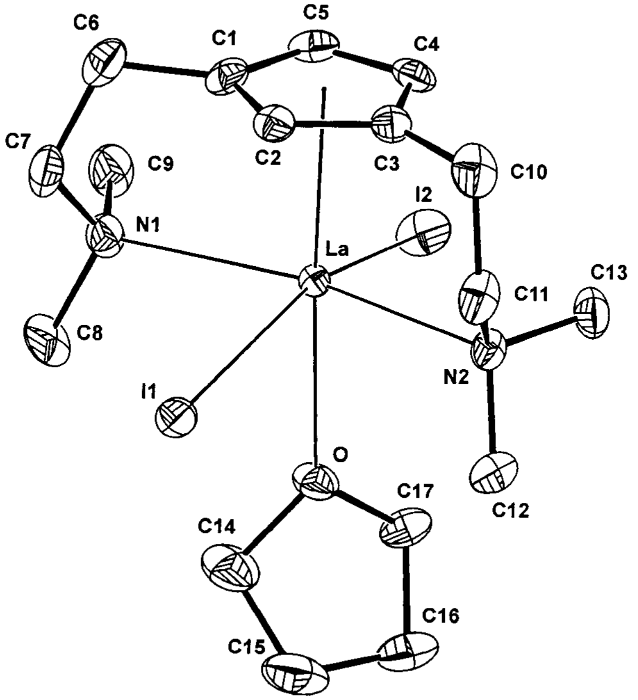


Figure 2. ORTEP plot[15] of the molecular structure and numbering scheme of **4**, with 40% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

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[15] Zsolnai, L.; Pritzkow, H. ZORTEP, ORTEP Program for PC; Universität Heidelberg, Heidelberg, Germany, 1994.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 3−5 with Estimated Standard Deviations

	3	4	5
	Bond Distances and Angles		
Ln−Cp[a,b]	2.511(2)	2.519(2)	2.466(5)
Ln−I(1)	3.1974(4)	3.2681(4)	3.2529(8)
Ln−I(2)	3.2287(4)	3.1696(4)	
Ln−N(1)	2.820(4)	2.728(4)	2.753(9)
Ln−N(2)	2.772(3)	2.712(4)	2.762(9)
Ln−O(1)	2.558(3)	2.593(3)	2.500(8)
Ln−O(2)			2.522(8)
I(1)−Ln−Cp	101.55(4)	100.66(4)	170.54(13)
I(2)−Ln−Cp	167.05(5)	100.73(4)	
O(1)−Ln−Cp	102.65(9)	176.62(8)	103.8(2)
O(2)−Ln−Cp			101.3(2)
N(1)−Ln−Cp	89.97(9)	89.69(11)	91.4(2)
N(2)−Ln−Cp	89.64(9)	90.68(8)	90.5(2)
O(1)−Ln−N(1)	167.10(11)	93.65(12)	163.5(3)
O(1)−Ln−N(2)	79.96(11)	85.98(11)	87.4(3)
I(1)−Ln−I(2)	88.346(10)	157.990(13)	
N(2)−Ln−N(1)	103.11(11)	162.94(12)	98.9(3)
	Ring Slippage		
Ln−Cp	0.074	0.043	0.086

[a] Ln = La for **3** and **4** and Yb for **5**. [b] Cp defines the centroid of the ring atoms C1−C5.

represented by one molecule of the complex and half of a disordered THF molecule located on a center of inversion. In contrast, complex **4**, bearing the 1,3-substituted cyclopentadienyl ligand, crystallizes in the orthorhombic space group $P2_12_12_1$. Both complexes **3** and **4** show similar molecular geometries. Two nitrogen atoms, two iodine atoms, the oxygen atom of the coordinated THF molecule, and the centroid position of the Cp ring form a slightly distorded pseudo octahedron around the lanthanum. However, the different coordination requirements of the cyclopentadienyl ligands lead to different positions of the iodine atoms and of the THF molecule relative to the metal center.

In complex **3**, the equatorial plane is occupied by two *cis*-arranged nitrogen atoms, the THF oxygen, and one iodine atom, while the second iodine atom and the Cp ring occupy the apical positions. The La−I bonds are almost of equal length (3.1974 and 3.2287 Å). To the best of our knowledge, this is the first example of a complex of the type $CpLnX_2(L)_3$ in which the LnX_2 fragment exhibits such a geometry.

In complex **4**, the equatorial plane is occupied by the two *trans*-positioned nitrogen atoms of the cyclopentadienyl side arms and the two iodine atoms. The ring centroid and the THF oxygen occupy the apical positions of the distorted octahedron. The coordination environment of the metal in **4** corresponds to that in monocyclopentadienyl complexes of the type $CpLnX_2(THF)_3$ (Ln = lanthanide, X = Cl, Br, I)[16] and is similar to that in the naphthalene lanthanum complex $[\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8][LaI_2(THF)_3]_2$,[17] in which the halogen atoms are also *trans*-positioned in the equatorial plane. Unexpectedly, and in contrast to **3**, the La−I bond lengths (3.1696 and 3.2681 Å) differ significantly, with the last value being the longest Ln−I distance ever estimated in lanthanoid iodine complexes. This fact agrees well with the kind of fragmentation of **4** observed in the mass spectrum under EI conditions.

The La−N bonds in **3** (2.772 and 2.820 Å) are longer than those in **4** (2.712 and 2.728 Å), probably caused by steric strains between the *cis*-coordinated Me_2N groups in **3**, and are comparable to those in $Cp_2La[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (2.788 and 2.755 Å).[18] The La−N bonds of both **3** and **4** are considerably shorter than those in $(Me_2NCH_2CH_2C_5H_4)_3La$ (2.898 Å).[19] The La−$Cp_{centroid}$ distances are almost the same in both **3** and **4** (2.511 and 2.519 Å, respectively) and fairly close to those in other monocyclopentadienyl lanthanum derivatives.[20]

Ytterbium(II) Complexes. The treatment of mixtures of **1** and **2** with equimolar amounts of YbI_2 in THF affords only the 1,2-isomeric half-sandwich ytterbium(II) complex $(1,2\text{-}Do_2Cp)YbI(THF)_2$ (**5**) in ca. 40% yield (Scheme 3). Compound **5** crystallizes from the filtered and concentrated solution as large orange blocks. All attempts to isolate the analogous complex containing the $1,3\text{-}Do_2Cp$ ligand did not succeed. However, addition of $(C_5Me_5)Na$ (Cp*Na) to the THF solution remaining after the separation of **5**, followed by treatment with toluene, yields dark red crystals of a mixed ytterbium complex containing both the $1,3\text{-}Do_2Cp$ ligand and the Cp* ligand, $\{Na[(1,3\text{-}Do_2Cp)(Cp^*)Yb]_2(I)(C_7H_8)]_n$ (**6**). Also, compound **5** reacts with the cyclopentadienides $(^tBuC_5H_4)Na$ and Cp*K in THF to give the mixed complexes $(1,2\text{-}Do_2Cp)Yb(^tBuC_5H_4)$ (**7**) and $(1,2\text{-}Do_2Cp)Yb(Cp^*)$ (**8**), respectively (Scheme 3). **5** and **6** are soluble in THF but insoluble in diethyl ether, toluene, and hexane. Addition of **5** to pyridine (py) causes decomposition into $YbI_2(py)_4$ and unidentified products. **7** and **8** are readily soluble in THF, diethyl ether, and benzene. **5**−**8** melt with decomposition in the temperature range 195−240 °C, with the highest value observed for polymeric **6**.

In the ^1H NMR spectrum of the diamagnetic **5**, recorded in THF-d_8 at 200−293 K, all signals are significantly broadened, showing no spin−spin coupling structure. The resonances of the ring protons show chemical shifts of δ 5.67 (1H) and 5.54 (2H). The protons of the methylene or the NCH_3 groups give rise to broad singlets at δ 2.54 (8H) or 2.33 (12H), respectively. The appearance of the $^{13}C\{^1H\}$ NMR spectrum is rather similar, with the exception that the resonances of the methylene groups can be distinguished. These data confirm two points: (i) both donor functions of the cyclopentadienyl ligand are coordinated to the metal even in THF solution; (ii) a mirror inversion of two crown-type cycles $Cp{-}CH_2{-}CH_2\text{-}(Me_2)N{-}Yb$ forced by limited rotation of the Cp ring around the $Cp_{centroid}{-}Yb$ axis takes place in solution. This is consistent with published data[21] and the data we obtained by structural analysis. In the ^1H NMR spectrum of **6**, recorded in THF-d_8, the signals of the ring protons (t, δ 5.52, 1H; d, δ 5.45, 2H) and of the methylene protons (m, δ 2.59,

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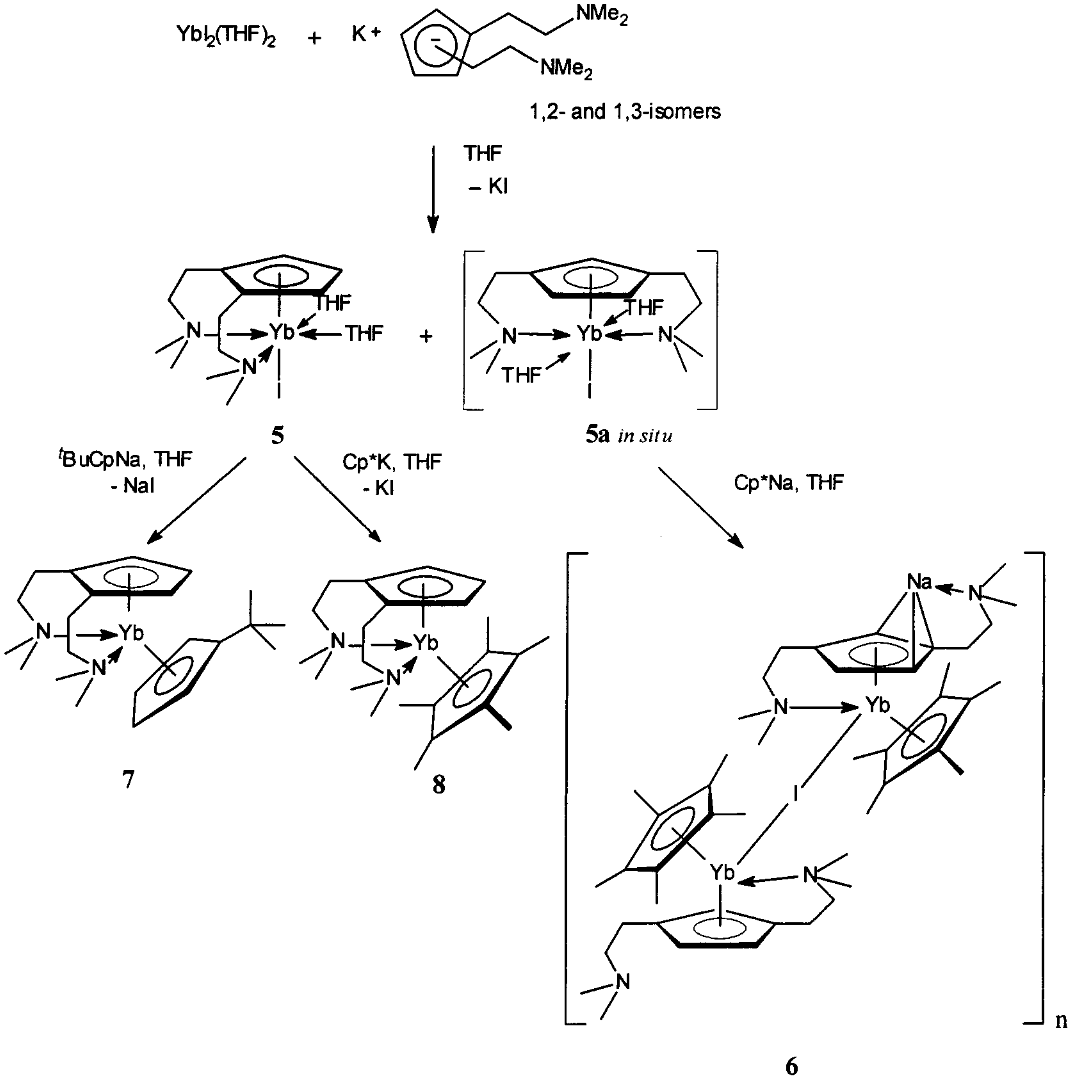
Scheme 3



2H; m, δ 2.49, 2H; m, δ 2.29, 4H) are at least poorly resolved, suggesting that in solution either both nitrogen atoms of the 1,3-Do$_2$Cp ligand coordinate the Yb^{2+} ion or both are turned away from the metal center. Taking into account that considerable steric problems will arise if, along with the Cp* ligand and the Cp ring of the 1,3-Do$_2$Cp ligand, also the two side chains are coordinated to the metal, the last case would be the most probable one. The existence of a mono-N-coordinated species in solution can be excluded, since in this case three ring ^{1}H signals of equal intensity should appear in the spectrum. Since the low-temperature NMR spectra of **6** do not differ significantly from its ambient-temperature spectra, dynamic processes can also be excluded.

The ^{1}H NMR spectrum of **7** in benzene-d_6 shows two well-resolved signals for the disubstituted as well as for the monosubstituted cyclopentadienyl ligand (Table 2), a complex signal structure for the side chains of the 1,2-Do$_2$Cp ligand ranging from δ 2.5 to 2.0, a sharp signal for the *tert*-butyl protons, and an extremely broad signal for the NCH$_3$ protons. The ^{13}C NMR spectrum of **7** consists of 12 resonances, with the two CH$_3$N signals being also extremely broadened. ^{1}H−^{1}H, ^{1}H−^{13}C NMR COSY, and ^{13}C DEPT spectroscopic measurements allow an unambiguous assignment of the signals. The nonequivalence of the NCH$_3$ groups in solution can be explained by a rigid coordination of the side chains to the ytterbium ion, causing different positions of the methyl groups relative to the metal. A careful inspection of the ^{1}H and ^{13}C NMR spectra of **7** reveals small additional couplings only for the Cp ring resonances, thus excluding side rotation bands. It is possible to suggest that ^{1}H−^{171}Yb and ^{13}C−^{171}Yb couplings cause those additional spin−spin spectra, since the relative intensities of the peaks observed are consistent with the natural abundance of this ytterbium isotope (^{171}Yb: spin $^1/_2$, natural abundance 14.27%).[22] Similar $J(^{13}\text{C}-^{171}\text{Yb})$ couplings can be observed in the spectra of (C$_5$Me$_5$)$_2$Yb(THF)$_2$ in THF-d_8, Cp*Yb[Si(SiMe$_3$)$_3$](THF)$_2$ (10 Hz),[23] and of dialkylytterbium compounds (158−265 Hz).[24]

The ^{1}H and ^{13}C NMR spectra of **8** in benzene-d_6 are very similar to those of **7**, including the ^{1}H−^{171}Yb and ^{13}C−^{171}Yb couplings of the resonances arising from the Cp ring atoms, and show only the differences connected

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Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for 6−8 with Estimated Standard Deviations

	6	7	8
Bond Distances and Angles			
Yb−Cp(1)[a]	2.440(3)	2.394(4)	2.417(3)/2.415(3)
Yb−Cp(2)[a]	2.431(3)	2.451(5)	2.452(3)/2.456(3)
Na−Cp(1)	2.545(3)		
Yb−N(1)[b]	2.606(5)	2.585(7)	2.635(5)/2.627(5)
Yb−I	3.1001(2)		
Na−N(2)	2.495(5)		
Yb−N(2)[c]		2.623(5)	2.640(5)/2.636(6)
Na−C(1)	2.930(6)		
Na−C(2)	2.776(6)		
Na−C(3)	2.675(6)		
Na−C(4)	2.757(6)		
Na−C(5)	2.923(6)		
Cp(1)−Yb−Cp(2)	132.34(8)	141.44(12)	133.10(12)/133.11(12)
I−Yb−Cp(1)	106.06(6)		
I−Yb−Cp(2)	107.71(6)		
N(1)−Yb−Cp(1)	93.31(15)	93.90(19)	93.36(14)/92.93(14)
N(2)−Yb−Cp(1)		94.15(17)	92.40(14)/92.85(14)
N(1)−Yb−Cp(2)	118.40(14)	109.09(18)	116.13(15)/117.22(14)
N(2)−Yb−Cp(2)		111.62(19)	117.24(13)/116.57(15)
N(1)−Yb−N(2)		98.8(2)	96.79(15)/96.03(17)
N(1)−Yb−I	91.11(13)		
Yb−I−Yb′	180		
Cp(1)−Na−Cp(1)″	127.16(13)		
N(2)−Na−N(2)″	102.4(3)		
Yb−Cp(1)−Na	172.56(12)		
Yb−Cp(1)*−Na[a]	157.53		
Ring Slippage			
Cp(1)−(Yb)	0.082	0.079	0.046/0.063
Cp(2)−(Yb)	0.064	0.104	0.070/0.088
Cp(1)−(Na)	0.319		

[a] Cp defines the centroid of the ring atoms Cp(1) (C(1)−C(5) for **6** and **7** and C(101)−C(105)/C(201)−C(205) for **8**), Cp(2) (C(14)−C(18)), and Cp(1)* (C(2),C(3),C(4)). [b] N(11)/N(21) for **8**. [c] N(12)/N(22) for **8**. Symmetry transformations used to generate equivalent atoms: (′) $-x + 1, -y + 1, -z + 1$; (″) $-x + 1, y, -z + {}^{3}/_{2}$.

with the exchange of ^{t}BuCp for Cp* as the second ligand of the Yb^{2+} ion. As for **7**, ${}^{1}H-{}^{1}H$ and ${}^{1}H-{}^{13}C$ NMR COSY as well as ${}^{13}C$ DEPT measurements were applied to ensure the assignment of the signals of **8**. If **8** is dissolved in THF-d_8, the signal associated with the protons of the $(CH_3)_2N$ groups becomes sharp and the two very broad signals associated with the carbon atoms of the $(CH_3)_2N$ groups change into one broad signal, thus indicating that in nonpolar solvents such as benzene both donating side chains of the 1,2-Do_2Cp ligand will be fixed to the metal, whereas in polar solvents such as THF the side chains compete with the solvent with respect to their coordination to the metal.

The EI mass spectra of the complexes **5** and **6** show no molecular ion peaks. The most intense metal-containing fragments are $[(1,2\text{-}Do_2Cp)YbI]^+$ (10%) for **5** and $[(1,3\text{-}Do_2Cp)Yb]^+$ (100%) for **6**. In the mass spectra of **7** and **8** the molecular ion peaks appear at 136 or 193 °C with 100 or 18% intensity, respectively. The most intense metal-containing fragment in the spectrum of **8**, $[1,3\text{-}Do_2CpYb]^+$ (68%), corresponds to that in **6**.

Molecular Structures of the Ytterbium Complexes 5−8. The crystal data collection and structure refinement data for **5** are given in Table 3 and those for **6**−**8** in Table 4. Selected bond distances and angles for **5** are given in Table 5 and those for **6**−**8** in Table 6.

The large well-shaped elongated blocks of **5** suitable for single-crystal X-ray diffraction analysis were obtained by crystallization from THF. The half-sandwich ytterbium(II) complex **5** crystallizes in the monoclinic space group $P2_1$ with two molecules in the unit cell. The calculation of the absolute structure parameter x indicated a racemic twinning for the selected crystal. The value of x was refined to 0.278(17); therefore, the ratio of the two enantiomorphs is approximately 72:28. The discrete molecules show a distorted-octahedral structure (Figure 3) similar to that of the lanthanum(III) complex **3**, except that the equatorial iodine in **3** is replaced by a second THF. The *cis*-arranged Me_2N donor units and the THF molecules form the equatorial plane, while the ring part of the 1,2-Do_2Cp ligand and the iodine atom occupy the axial positions ($Cp_{centroid}-Yb-I = 170.54°$). The monomeric structure of **5** is unique, because all other ytterbium complexes of analogous empirical composition form halogen-bridged dimers $[RYbX(L)_n]_2$ (R = alkyl,[24] cyclopentadienyl;[25] X = halogen; L = coordinating solvent such as THF or Et_2O). In contrast to **3**, there is no mirror plane in **5** incorporating $Cp_{centroid}-Yb-I$, since the α-carbon atoms of the cyclopentadienyl side arms are turned clockwise around the $Cp_{centroid}-Yb$ axis. With regard to the difference in ionic radii of La(III) and Yb(II), the Yb−I bond length in **5** (3.2529 Å) is somewhat longer than the La−I distances in **3** (3.1974 and 3.2287 Å), while the distance $Cp_{centroid}-Yb$ (2.466 Å) in **5** is somewhat shorter than the corresponding value in **3** (2.511 Å). The smaller angle N−Yb−N (98.9°) in **5** compared to that in **3** (N−La−N, 103.1°) is probably the result of less repulsion of the two Me_2N groups caused by the clockwise turning of the α-carbon atoms of the side chains. The distances Yb−N (2.753 and 2.762 Å) fall into the range found for the La−N distances in **3** (2.772 and 2.820 Å).

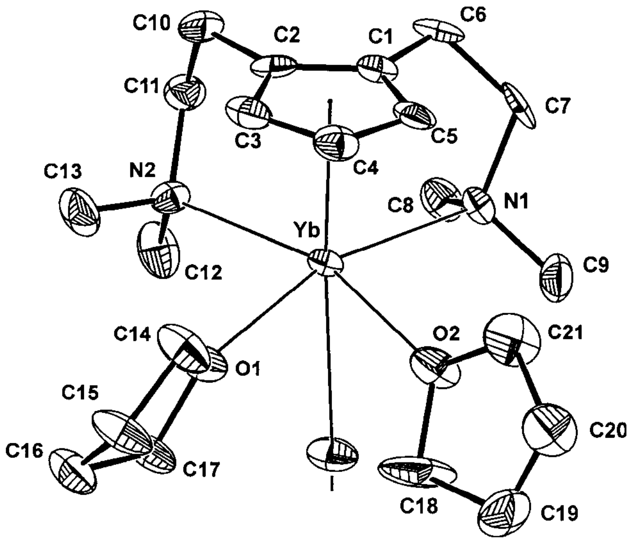

Figure 3. ORTEP plot[15] of the molecular structure and numbering scheme of **5**, with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

X-ray-quality crystals of **6** were obtained from a THF/toluene mixture. Complex **6** crystallizes in the orthorhombic space group *Pbcn*. **6** is a polymer consisting of infinite chains formed by $[Na\{\mu_2\text{-}1,3\text{-}Do_2Cp\}Yb(\mu_2\text{-}I)Yb\text{-}\{\mu_2\text{-}1,3\text{-}Do_2Cp\}]$ units (Figure 4). Each ytterbium atom is further η^5-coordinated by a C_5Me_5 ligand. The iodine atom is located on a center of inversion with equal distances to the ytterbium atoms of the linear

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(25) Constantine, S. P.; De Lima, G. M.; Hitchcock, P. B.; Keates, J. M.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2421.

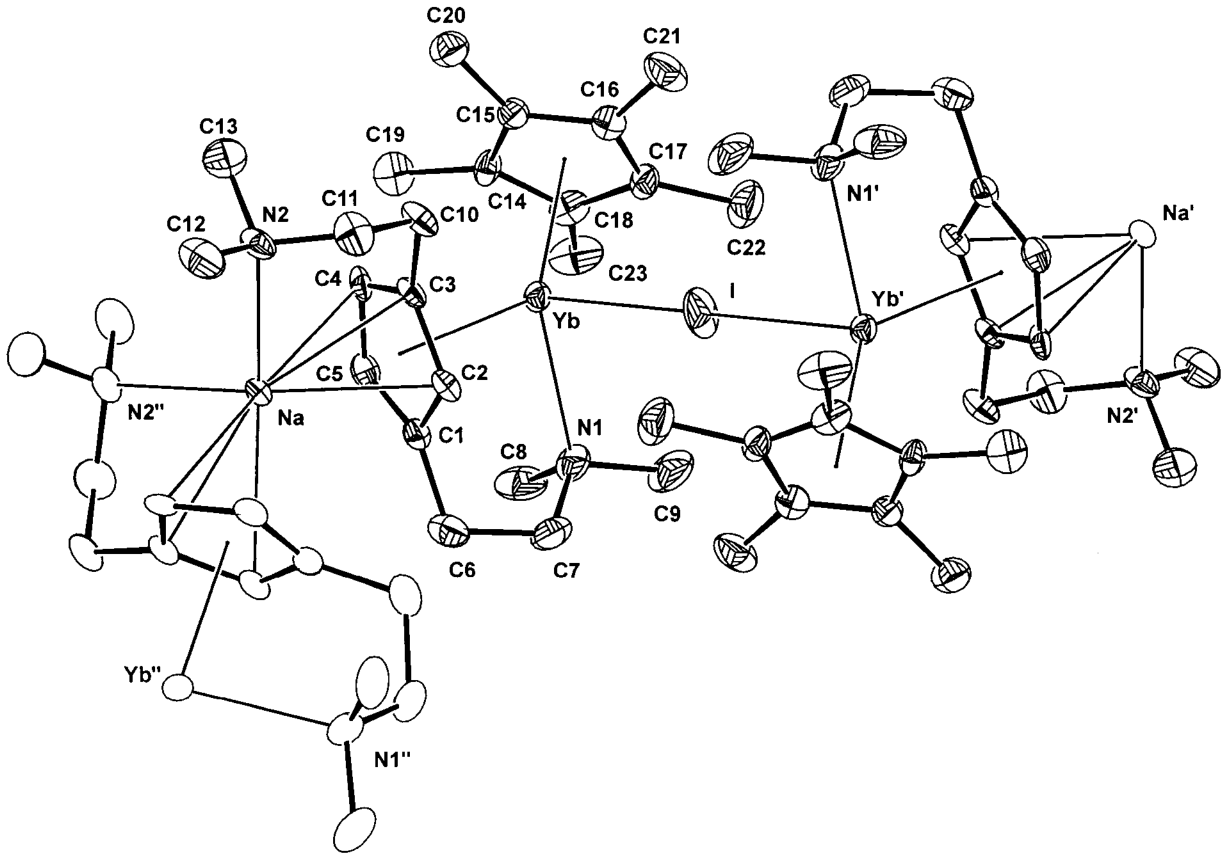

Figure 4. ORTEP plot[15] of the molecular structure and numbering scheme of **6**, with 30% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (′) $-x + 1$, $-y + 1$, $-z + 1$; (″) $-x + 1$, y, $-z + {}^{3}/_{2}$.

Yb−I−Yb unit (180°). However, the unexpectedly large thermal ellipsoid of the iodine atom suggests that in different molecular units of the polymer the Yb−I−Yb angle slightly deviates from 180°. Nevertheless, the geometry of this fragment is rather rare in organolanthanide chemistry. The linear arrangement Yb−F−Yb, but with different Yb−F distances (2.317 and 2.084 Å), was established only for the mixed-valence ytterbium complex $Cp^*_2Yb^{II}(\mu\text{-}F)Yb^{III}Cp^*_2$.[26] The Yb−I distances in **6** (3.1001 Å each) are somewhat shorter than in the complex $[Cp^*(THF)_2Yb(\mu\text{-}I)_2YbCp^*(THF)_2]$ (3.134 and 3.175 Å)[25] and remarkably shorter than in **5** (3.2529 Å). The angle 1,3-Do_2Cp−Yb−Cp* (132.34°) and the distances of the ytterbium atom to the ring centers (1,3-Do_2Cp−Yb, 2.440 Å; Cp*−Yb, 2.431 Å) fall into the range found for $\{C_5H_4(CH_2CH_2NMe_2)\}_2Yb$[27] and Cp^*_2-$Yb(py)_2$.[28] Only one of the two N atoms of each 1,3-Do_2-Cp ligand is bonded to ytterbium, whereas the second N atom coordinates a sodium atom. The bond length Yb−N (2.606 Å) in **6** is much shorter than that in the half-sandwich complex **5** (2.753 and 2.762 Å) but similar to that in the ytterbium(II) complex $\{C_5H_4(CH_2CH_2$-$NMe_2)\}_2Yb$ (2.58 Å) containing mono-Me_2N-functionalized Cp ligands.[27] The Na−N bond length is 2.495 Å. The distances of the sodium atom to the carbon atom of the ring part of the 1,3-Do_2Cp ligand range from 2.675 to 2.930 Å with the shortest contact to the carbon atom bearing the side arm involved into the Na−N coordination. The angle $Cp_{centroid}$−Na−$Cp_{centroid}$ is 127.16°. The asymmetric unit of **6** contains a toluene molecule which is disordered about a 2-fold rotation axis. All C−C distances of the phenyl ring and all C−C−C angles belonging to the phenyl and methyl groups were restrained to be equal. Furthermore, the carbon atoms of the solvent molecule were restrained to lie on a common plane.

Crystals of **7** and **8** suitable for single-crystal X-ray analysis were grown from diethyl ether. **7** crystallizes in the orthorhombic space group $P2_12_12_1$ and **8** in the triclinic space group $P\bar{1}$. The X-ray analysis of two different crystals of **7** revealed two mirror isomers which differ in the position of the *tert*-butyl substituent. The asymmetric unit of **8** contains two crystallographically independent molecules. In the monomeric and solvent-free molecules of **7** (Figure 5) and **8** (Figure 6) the ytterbium atoms are coordinated by both donor atoms of the 1,2-Do_2Cp ligand. The structures of **7** and **8** resemble the distorted-tetrahedral geometry of other $Cp_2Yb(L)_2$ complexes with the formal coordination number 8.[16] In comparison to complex **5**, possessing the same coordination number, the distances of the ytterbium atoms to the ring center of the 1,2-Do_2Cp ligand are remarkably shorter (2.466 Å (**5**), 2.394 Å (**7**), 2.417/2.415 Å (**8**)). The distances $^{t}BuCp_{centroid}$−Yb (2.451 Å) and $Cp^*_{centroid}$−Yb (2.452/2.456 Å) in **7** or **8** are similar to

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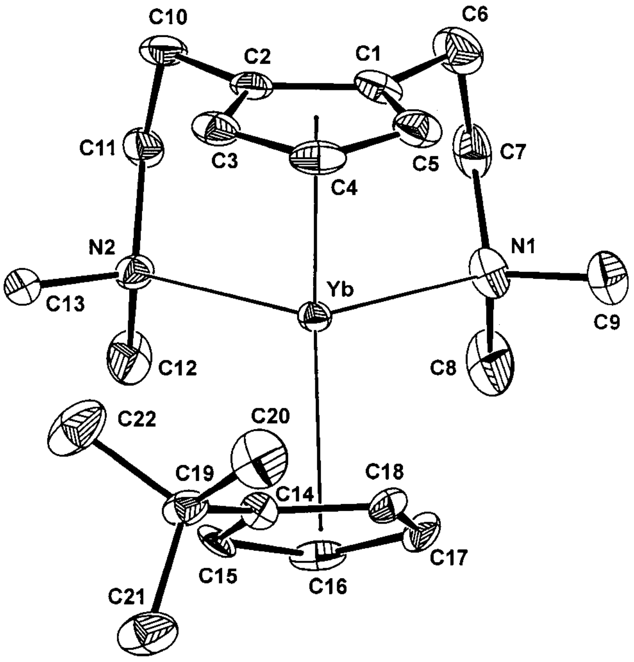

Figure 5. ORTEP plot[15] of the molecular structure and numbering scheme of **7**, with 30% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

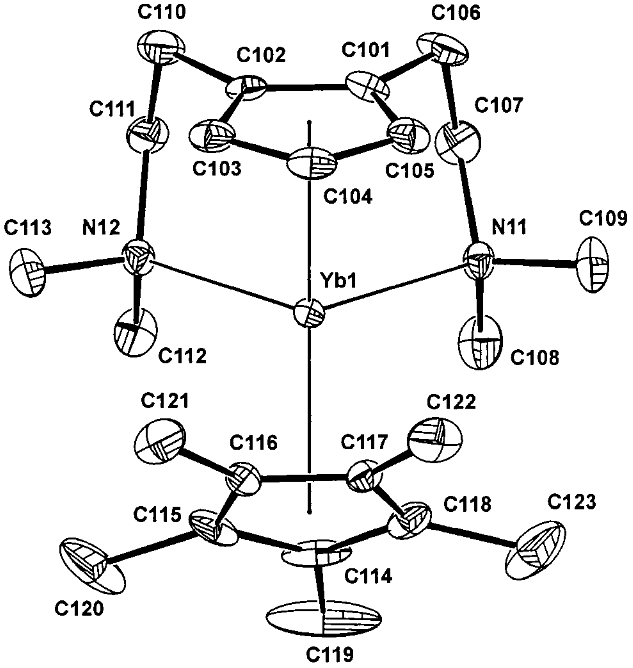

Figure 6. ORTEP plot[15] of the molecular structure and numbering scheme of **8**, with 30% probability thermal ellipsoids. Only one of the two crystallographically independent molecules is shown. All hydrogen atoms are omitted for clarity

those in $(^t\mathrm{BuC_5H_4})_2\mathrm{Yb(THF)_2}$[29] or $\mathrm{Cp^*{}_2Yb(py)_2}$,[28] respectively. While the 1,2-Do$_2$Cp−Yb−Cp* angle in **8** (133.1°) is typical for bent divalent lanthanidocenes, the 1,2-Do$_2$Cp−Yb−^{t}BuCp angle of 141.44° in **7** shows a certain tendency toward coplanarity, which is realized in $(\mathrm{C_5}(^i\mathrm{Pr})_5)_2\mathrm{Eu}$ (Cp−Eu−Cp = 153.8°).[30] The methyl groups of the Cp* ring in **8** and the quaternary carbon atom of the ^{t}Bu group in **7** are bent out of the ring plane away from the ytterbium atoms by up to 0.25(1) and 0.22(2) Å, respectively. The α-carbon atoms of the side arms of the 1,2-Do$_2$Cp ligands deviate from the ring plane toward the ytterbium atoms by up to 0.04(1) and 0.05(1) Å, respectively. In contrast to the ytterbium complex **5**, the geometry of the side chains in **7** and **8** is symmetric relative to the plane containing the metal atom and the centroids of the ligands. The N−Yb−N angles in **7** (98.8°) and **8** (96.79/96.03°) are similar to that in **5** (98.9°) but differ from that in $\{\mathrm{C_5H_4(CH_2CH_2NMe_2)}\}_2\mathrm{Yb}$ (104.0°).[28] However, the distances Yb−N in **7** (2.585, 2.623 Å) and **8** (2.635, 2.640/2.627, 2.636 Å) are significantly shorter than in **5** (2.753, 2.762 Å) but are somewhat longer than in $\{\mathrm{C_5H_4(CH_2CH_2NMe_2)}\}_2\mathrm{Yb}$ (2.57, 2.58 Å).[28]

Conclusion

We prepared half-sandwich and bent mixed-sandwich complexes of lanthanum(III) and ytterbium(II) with the novel 1,2- and 1,3-bis(2-(dimethylamino)ethyl)cyclopentadienyl ligands by metathetic reactions of La(III) and Yb(II) iodides with the potassium salts of the ligands. The intramolecular coordination of the donor atoms of the side chains was confirmed by X-ray structure determination for all complexes **3**−**8**. The different coordination requirements of the 1,2- and the 1,3-donor-functionalized ligands cause a specific coordination geometry around the metal centers in the isomeric half-sandwich lanthanum complexes **3** and **4**. Using the stabilizing influence of the 1,2-donor-functionalized ligand, we were able to isolate the first monomeric monocyclopentadienyl ytterbium(II) complex. The nonequivalence of the ^{13}C NMR signals of the *N*-methyl groups in **7** and **8** in benzene solution confirms strong $\mathrm{Me_2N{\rightarrow}Yb}$ coordination. In contrast, the appearance of a broadened singlet signal for these groups in THF solution indicates that the N-donor atoms compete with the coordinating solvent molecules. Investigations concerning the catalytic activity of the complexes for the block polymerization of styrene are in progress.

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Supporting Information Available: Full details of the X-ray structures of complexes **3**−**8**, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropical thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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