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A Functionalized Cyclooctatetraene as Ligand in Organolanthanide Chemistry

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o-(Chlorodimethylsilyl)-*N*,*N*-dimethylaniline was prepared and characterized by NMR and X-ray crystallography. Reaction of this reagent with $K_2C_8H_8$ gives selectively 1,4-bis[(*o*-dimethylsilyl)-*N*,*N*-dimethylaniline]cycloocta-2,5,7-triene. Further reaction with 2 equiv *n*-BuLi affords a new functionalized cyclooctatetraenide, Li_2-1,4-$R_2C_8H_6$ (R = *o*-(dimethylsilyl)-*N*,*N*-dimethylaniline). The new ligand is a useful starting material for the preparation of organolanthanide sandwich complexes, $[Li(diglyme)_2]^+[Ln(1,4\text{-}R_2C_8H_6)_2]^-$ (Ln = Nd, Sm). These metal complexes were characterized by NMR and X-ray crystallography. They are the first examples of structurally characterized cyclooctatetraene complexes with a donor functionality attached to the eight-membered ring.

Introduction

The work of Bercaw and Shapiro in which one ring of an *ansa* metallocene was replaced by a *tert*-butyl amido group has produced an enormous amount of interest in functionalized cyclopentadienyl ligands containing an additional coordination site.[1] Today, group 4 metal complexes containing an amido cyclopentadienyl ligand have gained considerable importance as homogeneous polymerization catalysts in the presence of methyl alumoxane.[2] In addition to the complexes used for catalytic applications a huge number of main group and transition metal complexes containing the cyclopentadienyl ligand (or its derivatives) in which at least one additional coordination site is tethered via a bridge to the five-membered ring such as BR_2,[3] $-CH{=}CH_2$,[4] NR,[1,2,5] NR_2,[6] PR_2,[7] O,[8] OR,[9] and SR[10] are also known.[11]

In contrast to the large number of bi- and multifunctionalized cyclopentadienyl complexes, almost no comparable cyclooctatetraene (COT) compound is known. Only two functionalized di-η^8-cyclooctatetraene uranium complexes (uranocenes), $U(C_8H_7R)_2$ (R = CH_2NMe_2, $(CH_2)_3NMe_2$), which could not be characterized by single-crystal X-ray studies have been reported.[12] Since we are interested in the development of alternatives to cyclopentadienyl-based ligands for organolanthanide chemistry, we have begun to study the properties of functionalized cyclooctatetraene complexes. In this contribution, we report the design, synthesis, and implementation of the new ligand 1,4-bis[(*o*-dimethylsilyl)-*N*,*N*-dimethylaniline]cyclooctatetraenide dianion

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together with its application as a ligand in organolanthanide chemistry.

Experimental Section

General Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware either on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled Braun Atmospheres glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na wire. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable flasks. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were performed on a Bruker IFS 28; mass spectra were recorded at 70 eV on a Varian MAT 711. Elemental analyses were performed in the microanalytical laboratory of the author's institute (S. Ariman). Dipotassium cyclooctatetraenide[13] and *o*-lithium *N*,*N*-dimethylaniline[14] were prepared by literature procedures.

***o*-(Chlorodimethylsilyl)-*N*,*N*-dimethylaniline (1).** To a solution of 142 mL of dimethyldichlorosilane in 100 mL of pentane was added a solution of 30.1 g (0.24 mol) of *o*-lithium *N*,*N*-dimethylaniline in 50 mL of pentane. A white precipitate was immediately formed. The mixture was then stirred for 3 h at room temperature and filtered, and the residue washed with pentane (2 × 25 mL). The extracts were combined and the solvent was removed in a vacuum. The remaining yellow liquid was purified by vacuum distillation (bp 60 °C/10^{-2} mm). White crystals of the product formed slowly at room temperature: yield, 13.7 g (27%); mp, 30 °C. ^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.63 (s, 6H, CH_3Si), 2.22 (s, 6H, CH_3N), 6.96 (d, 1H, Ph, J(H,H) = 8.2 Hz), 7.08 (t, 1H, Ph, J(H,H) = 7.3 Hz), 7.19 (t, 1H, Ph, J(H,H) = 7.6 Hz), 8.03 (d, 1H, Ph, J(H,H) = 7.0 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): δ 4.8 (CH_3-Si), 47.4 (CH_3N), 122.5 (Ph), 127.3 (Ph), 130.1 (Ph), 132.8 (Ph), 137.1 (Ph), 161.4 (Ph). ^{29}Si NMR (C_6D_6, 49.7 MHz, 25 °C): δ 15.5. EI/MS (70 eV) m/z: 213 ($[M]^+$, rel int 61.55), 198 ($[M - CH_3]^+$, 25.89), 183 ($[M - C_2H_6]^+$, 20.14), 178 ($[M - Cl]^+$ 26.29), 120 ($[C_8H_{10}N]^+$, 100). Anal. Calcd for $C_{10}H_{16}ClNSi$: C, 56.18; H, 7.54; N, 6.55; Found: C, 56.68; H, 7.90; N, 6.52.

1,4-Bis[(*o*-dimethylsilyl)-*N*,*N*-dimethylaniline]cycloocta-2,5,7-triene (2). To a stirred solution of 5.65 g (31 mmol) of dipotassium cyclooctatetraenide in 25 mL of THF at 0 °C was added slowly a solution of 13.4 g (63 mmol) of **1** in 25 mL of THF. The mixture was allowed to warm to room temperature and stirred for a further 3 h. The solvent was removed in a vacuum, and the residue was extracted with pentane (3 × 15 mL). The extracts were combined, and the solvent was removed in a vacuum. A brown oil remained, which was used without further purification as starting material for the synthesis of **3**. Yield: 11.7 g (82%). ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): δ 0.41 (d, 12H, CH_3Si), 2.65 (s, 12H, CH_3N), 3.39−3.45 (m, 2H, COT), 5.48−5.62 (m, 4H, COT), 5.85−5.92 (m, 2H, COT), 7.19−7.55 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz, 25 °C): δ −2.7 (CH_3Si), −2.6 (CH_3Si), 30.7 (COT), 47.3 (CH_3N), 122.0 (Ph), 125.3 (Ph), 127.7 (COT), 128.8 (COT), 129.3 (Ph), 130.2 (COT), 130.7 (Ph), 136.3 (Ph), 161.6 (Ph). ^{29}Si NMR ($CDCl_3$, 49.7 MHz, 25 °C): δ −3.1.

Dilithium 1,4-Bis[(*o*-dimethylsilyl)-*N*,*N*-dimethylaniline]cyclooctatetraenide (THF-adduct) (3). To a stirred solution of 10.6 g (23 mmol) of **2** in 40 mL of THF at −78 °C slowly was added 35.9 mL (58 mmol) of a 1.6 M solution of *n*-BuLi in hexane. The solution was allowed to warm to room temperature with stirring for another 12 h; during this time the color of the solution changed from yellow to red-brown. The solvent was removed in a vacuum, and the residue was dissolved in 40 mL of pentane. A brown precipitate was formed on cooling to −78 °C and was collected by filtration and dried in a vacuum. Yield, 7.5 g (53%). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 0.60 (s, 12H, CH_3Si), 1.72−1.79 (m, 8H, THF), 2.63 (s, 12H, CH_3N), 3.57−3.63 (m, 8H, THF), 5.88−5.93 (m, 2H, COT), 6.20−6.24 (m, 2H, COT), 6.32 (s, 2H, COT), 6.83−6.89 (m, 4H, Ph), 7.11−7.14 (m, 4H, Ph). ^{7}Li NMR (THF-d_8, 116.6 MHz, 25 °C): δ −6.9. $^{13}C\{^1H\}$ NMR (THF-d_8, 62.9 MHz, 25 °C): δ 2.4 (CH_3Si), 47.0 (CH_3N), 85.7 (COT), 89.7 (COT), 95.5 (COT), 95.9 (COT), 120.2 (Ph), 123.5 (Ph), 129.0 (Ph), 138.1 (Ph), 141.5 (Ph), 161.1 (Ph). ^{29}Si NMR (THF-d_8, 49.7 MHz, 25 °C): δ −5.1.

$[Li(diglyme)_2]^+[Nd(1,4\text{-}R_2C_8H_6)_2]^-$ (4a). A 15 mL sample of THF was condensed at −196 °C onto a mixture of 115 mg (0.46 mmol) of $NdCl_3$ and 510 mg (0.83 mmol) of **3**. Then the mixture was stirred for 12 h at room temperature. The solvent was evaporated in a vacuum, 15 mL of diethyl ether was condensed onto the mixture, and the dark green solution was filtered. A 2 mL portion of the solution was taken off and diluted with another 4 mL of diethyl ether. Finally, a mixture of 8 mL of pentane and 0.1 mL of diglyme was layered on top. After 2−6 weeks green crystals were obtained. Yield: 90 mg (62%). IR (KBr [cm^{-1}]): 2955 (m), 1458 (s), 1260 (s), 1029 (s), 808 (vs), 749 (m). Anal. Calcd for $C_{68}H_{104}LiN_4NdO_6Si_4$: C, 61.08; H, 7.84; N, 4.19. Found: C, 60.57; H, 7.99; N, 3.89.

$[Li(diglyme)_2]^+[Sm(1,4\text{-}R_2C_8H_6)_2]^-$ (4b). A 15 mL sample of THF was condensed at −196 °C onto a mixture of 229 mg (0.89 mmol) of $SmCl_3$ and 1.0 g (1.62 mmol) of **3**, and the mixture was stirred for 12 h at room temperature. The solvent was evaporated in a vacuum, and 15 mL of diethyl ether was condensed onto the residue. The brown solution was filtered, and 4 mL of the filtrate was taken off and diluted by another 4 mL of diethyl ether. Finally, a mixture of 10 mL of pentane and 0.1 mL of diglyme was layered on top. After 2−6 weeks brown crystals were obtained. Yield: 215 mg (74%). IR (KBr [cm^{-1}]): 2931 (m), 1474 (m), 1111 (m), 1083 (m), 1049 (m), 932 (m), 827 (m), 809 (s) 725 (m). ^{1}H NMR (THF-d_8, 250 MHz, 25 °C): δ 0.11 (s, 24H, CH_3Si), 3.26 (s, 12H, CH_3O), 3.41−3.51 (m, 16H, CH_2O), 4.54 (s, 12H, CH_3N), 5.27 (s, 12H, CH_3N), 5.34 (d, 4H, Ph, J(H,H) = 6.4 Hz), 5.96 (d, 4H, Ph, J(H,H) = 6.4 Hz), 6.49 (d, 4H, Ph, J(H,H) = 7.5 Hz), 6.60 (t, 4H, Ph, J(H,H) = 7.6 Hz), 11.73 (br, 4H, COT), 13.49 (br, 4H, COT), 14.00 (br, 4H, COT). Anal. Calcd for $C_{68}H_{104}LiN_4O_6Si_4Sm$: C, 60.80; H, 7.80; N, 4.17. Found: C, 60.12; H, 8.03; N, 3.85.

X-ray Crystallographic Studies of 1. Crystals of $C_{10}H_{16}ClNSi$ (**1**) were grown from a benzene solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −70 °C cold stream of a STOE STADI IV diffractometer. Subsequent computations were carried out on a SGI Power Challenge.

Lattice parameters were determined for 30 angle reflections set in the range $15.0° < 2\theta < 24.0°$. Systematic absences and successful refinement of the proposed structure showed **1** to crystallize in the space group *Pbca* (No. 61). Intensities of two standard reflections were measured every 2 h of X-ray exposure and showed no significant variations. The structure was solved by direct methods (SHELXS-86[15]) and refined by full-matrix least-squares methods using the program SHELXL-93.[16] All non-hydrogen atoms were refined anisotropically. The

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hydrogen atom positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 1925 observed reflections ($I > 2.0\sigma(I)$) and 122 variable parameters and converged with R1 = 0.0451, wR2 = 0.1368. The maximum and minimum peaks on the final difference Fourier map were 0.421 and −0.317 e$^-$/Å^3, respectively. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-408822, the name of the author, and the journal citation.

X-ray Crystallographic Studies of 4a. Crystals of $C_{68}H_{104}LiN_4NdO_6Si_4$ (**4a**) were grown from a pentane/diethyl ether/diglyme solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C cold stream of a STOE IPDS diffractometer. Subsequent computations were carried out on a SGI Power Challenge.

Systematic absences and successful refinement of the proposed structure showed **4a** to crystallize in the space group $P2_1/n$ (No. 14). The structure was solved by the Patterson method (SHELXS-86[15]) and refined by full-matrix least-squares methods using the program SHELXL-93.[16] All non-hydrogen atoms were refined anisotropically except C(56)−C(68) and O. The hydrogen atom positions were calculated in ideal geometry and were not refined. The final cycle of full-matrix least-squares refinement was based on 9966 observed reflections ($I > 2.0\sigma(I)$) and 655 variable parameters and converged with R1 = 0.0587, wR2 = 0.1683. The maximum and minimum peaks on the final difference Fourier map were 1.824 and −0.738 e$^-$/Å^3, respectively. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-408823, the name of the author, and the journal citation.

Results and Discussion

The synthesis of a new functionalized cyclooctatetraene, 1,4-$R_2C_8H_6$ (R = *o*-(dimethylsilyl)-*N*,*N*-dimethylaniline), will be discussed, followed by the synthesis and structural characterization of biscyclooctatetraene lanthanide complexes $[Li(diglyme)_2]^+[Ln(1,4\text{-}R_2C_8H_6)_2]^-$ (Ln = Nd, Sm).

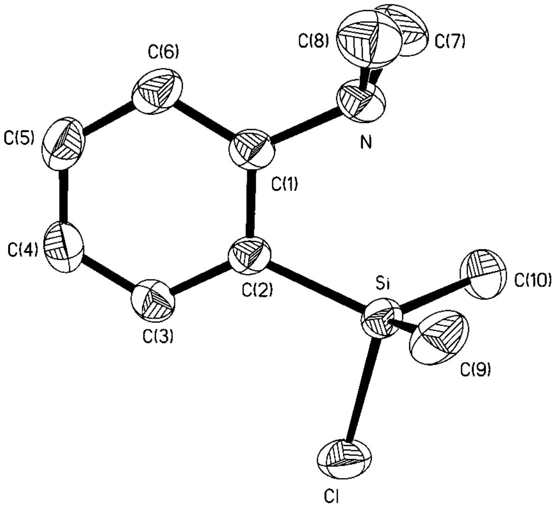
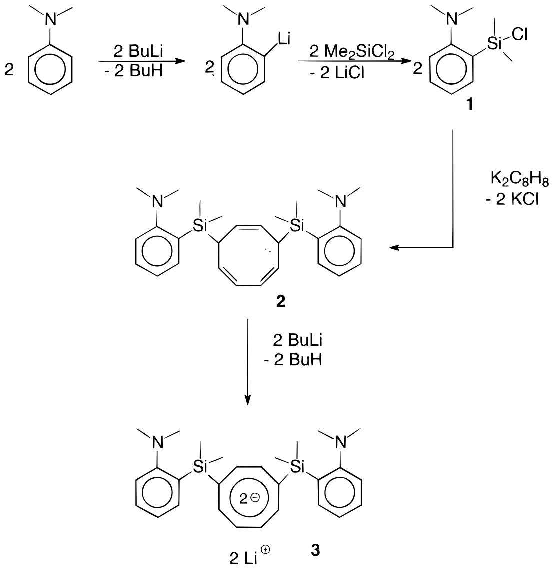


Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass 50% probability.

Scheme 1



Ligand Design and Synthesis. In contrast to bifunctionalized cyclopentadienes, which can be simply prepared by reacting cyclopentadienyl with some haloalkanes, bi- and multifunctional COTs cannot be obtained in the same way by using K_2COT. In reactions with haloalkanes the higher base strength of the COT dianion causes the formation of elimination instead of addition products. To avoid elimination reactions, the key step of the ligand synthesis is the incorporation of a silicon atom into the side chain in the α-position to the eight-membered ring. The synthesis of the ligand system as the dilithio salt is shown in Scheme 1. This is achieved by the synthesis of *o*-(chlorodimethylsilyl)-*N*,*N*-dimethylaniline (**1**), which was prepared by reaction of dichlorodimethylsilane with *o*-lithium *N*,*N*-dimethylaniline.[14] **1** is an extremely moisture sensitive colorless solid with a very low melting point. It is one of the rare structurally characterized examples of an aminochlorosilane in which the amino function is not directly attached to the silicon atom.[17,18] **1** was characterized by MS, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and elemental analysis. The ^{29}Si NMR resonance (δ 15.5) is shifted to higher field compared to $RMeSiCl_2$ (R = diphenylpyridylmethyl) (δ −20.7).[18] The molecular structure of **1** was probed further by single-crystal X-ray diffraction (Figure 1). Data collection and selected bond lengths and angles are given in Tables 1 and 2, respectively. In contrast to the bis(trimethylsilyl)pyridylmethyl ligand, where an interaction between the nitrogen atom and the silicon atom is observed,[18] no significant interaction of these two groups is seen in **1** (Si−N 2.842(3) Å). On the other hand, there is a distorted tetrahedral coordination sphere around the silicon atom having bond angles of C(2)−Si−C(9) 110.68(10)°, C(2)−Si−Cl 99.51(7)°, and C(2)−Si−C(10) 122.30(11)°. This is also indicated by the significantly different bond length of 0.12 Å for the methyl groups attached to the silicon atom (Si−C(10) 1.780(2) Å and

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Table 1. Crystallographic Details for *o*-(Chlorodimethylsilyl)-*N*,*N*-dimethylaniline (1)

formula	$C_{10}H_{16}ClNSi$
formula wt	213.78
space group	*Pbca* (No. 61)
a, Å	10.6407(8)
b, Å	11.8656(6)
c, Å	18.6455(15)
V, Å^3	2354.1(3)
Z	8
T, °C	−70(2)
radiation	Mo Kα (λ =0.71069 Å)
ρ(calc), g/cm^3	1.206
abs corr	ψ-scans
data collected, deg	$4.3° < 2\theta < 57.0°$
reflections collected	2298
independent reflections	2298
observed reflections	1925 [$I > 2\sigma(I)$]
μ, mm^{-1}	0.385
R1^a	0.0451
wR2^b	0.1368

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of *o*-(Chlorodimethylsilyl)-*N*,*N*-dimethylaniline (1)

Si−C(2)	1.843(2)	Si−Cl	2.222(1)
Si−C(9)	1.908(3)	Si−N	2.842(3)
Si−C(10)	1.780(2)		
C(2)−Si−C(10)	122.30(11)	C(2)−Si−Cl	99.51(7)
C(9)−Si−C(10)	108.86(13)	C(9)−Si−Cl	116.76(9)
C(2)−Si−C(9)	110.68(10)	C(10)−Si−Cl	98.31(9)

Scheme 2

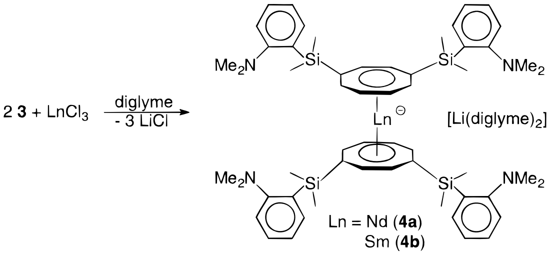

Table 3. Crystallographic Details for 4a and 4b

	4a	**4b**
formula	$C_{68}H_{104}LiN_4NdO_6Si_4$	$C_{68}H_{104}LiN_4O_6Si_4Sm$
formula wt	1337.09	1343.21
space group	$P2_1/c$ (No. 14)	*Pccn* (No. 56)
a, Å	16.708(3)	16.010(3)
b, Å	26.589(5)	19.282(4)
c, Å	17.855(4)	23.175(4)
β, deg	112.76(3)	
V, Å^3	7314(3)	7154(2)
Z	4	4
T, °C	−73(2)	−73(2)
diffractometer	STOE IPDS	STOE IPDS
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
ρ(calc), g/cm^3	1.214	
data collected, deg	$4.04° < 2\theta < 50.0°$	$3.15° < 2\theta < 42.0°$
abs corr	none	none
reflections collected	52 582	7868
independent reflections	12807 [R(int) = 0.0551]	4112 [R(int) = 0.0753]
observed reflections	9966 [$I > 2\sigma(I)$]	2409
μ, mm^{-1}	0.824	
R1^a	0.0587	
wR2^b	0.1683	

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of 4a

Nd−C(1)	2.714(5)	Si(1)−C(1)	1.875(5)
Nd−C(2)	2.696(5)	Si(1)−C(11)	1.906(5)
Nd−C(29)	2.735(5)	Si(3)−C(29)	1.867(5)
Nd−C(30)	2.694(5)	Si(3)−C(39)	1.907(6)
C(1)−Nd−C(2)	30.3(2)	C(29)−Nd−C(30)	30.5(2)
C(1)−Nd−C(29)	143.0(2)	Si(1)−C(1)−Nd	130.4(2)
C(1)−Nd−C(30)	173.3(2)	Si(3)−C(29)−Nd	130.6(3)
C(2)−Nd−C(29)	173.0(2)	C(1)−Si(1)−C(11)	106.5(2)
C(2)−Nd−C(30)	156.3(2)	C(29)−Si(3)−C(39)	106.3(2)

Si−C(9) 1.908(3) Å, respectively). Even though no intramolecular influence of the Me_2N group is observed, there is a strong intermolecular influence in solution, which is shown by a much higher moisture sensitivity of **1** compared to other R_3SiCl compounds. An intermolecular coordination of the nitrogen atom onto the silicon center might weaken the Si−Cl and therefore promote a decomposition reaction.

Reaction of 2 equiv of **1** with K_2COT affords selectively 1,4-bis[(*o*-dimethylsilyl)-*N*,*N*-dimethylaniline]-cycloocta-2,5,7-triene (**2**) (Scheme 1). The substitution pattern of **2** is easily identified by ^1H NMR spectroscopy. It was shown by Cloke et al. that 1,4-bis(trimethylsilyl)-cycloocta-2,5,7-triene shows a characteristic AXY pattern for the allyl protons as well as a symmetric multiplet for the olefin protons.[19] Reaction of **2** with 2 equiv of *n*-BuLi affords the dilithium salt **3** as a brown crystalline solid after recrystallization from pentane. **3** crystallizes with approximately 2 equiv of THF. The ^{29}Si NMR resonance of **3** (δ −5.1) is shifted only slightly upfield compared to **2** (δ −3.1). The strong high-field shift of the resonance in the ^7Li NMR spectrum (δ −6.9) of **3** indicates a symmetric localization of the lithium atom above and below the aromatic eight-membered ring.[20]

Metal Complexes. The synthesis of the organolanthanide sandwich complex $[Li(diglyme)_2]^+[Ln(1,4\text{-}R_2C_8H_6)_2]^-$ (R = *o*-(dimethylsilyl)-*N*,*N*-dimethylaniline; Ln = Nd (**4a**), Sm (**4b**)) (Scheme 2) was performed by transmetalation of **3** with anhydrous neodymium or samarium trichloride. After extraction with diethyl ether and crystallization from diethyl ether/pentane compound **4** crystallizes in the presence of diglyme. First, **4** separates out as an oil. The oil usually crystallizes after two to six weeks at room temperature. The molecular structure of **4** consists of an ion pair composed of a $[Li(diglyme)_2]^+$ cation and an $[Ln(1,4\text{-}R_2C_8H_6)_2]^-$ anion. Both complexes **4a** and **4b** have been characterized by standard analytical and spectroscopic techniques. Single crystals were obtained for both compounds, but a full refinement of the single-crystal X-ray structure was possible only for **4a**. Data collection and selected bond lengths and angles are given in Tables 3 and 4, respectively. The anion of **4a** (Figure 2) is a typical example of a COT sandwich complex with two planar aromatic eight-membered rings. Anions of comparable unsubstituted COT complexes of the type $[Ln(COT)_2]^-$ have been described for various lanthanide elements including scandium and yttrium.[21] The Nd−C

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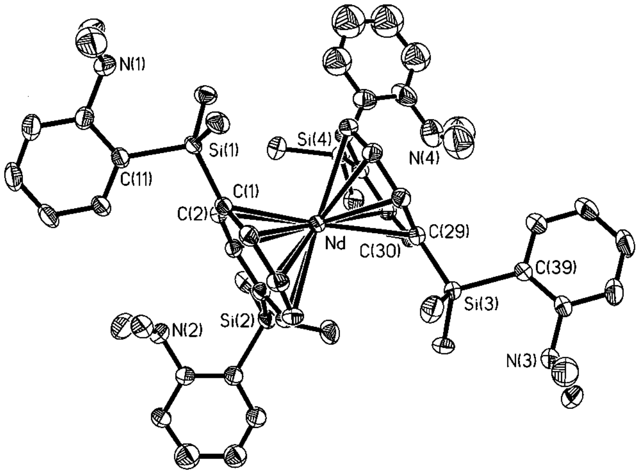

Figure 2. Perspective ORTEP view of the molecular structure of the anion of **4a**. Thermal ellipsoids are drawn to encompass 30% probability.

bond distances in **4a** range from 2.696(5) to 2.787(5) Å (av 2.739(5) Å) and are in the range expected from other [Nd(COT)$_2$] compounds.[22] There is a tetrahedral coordination sphere around the silicon atoms having C−Si−C bond angles in the range 105.3(3)−114.2(3)°. The carbon atoms in the sandwich unit are in a nearly eclipsed conformation, whereas the substituents are staggered. The dimethylamino group of the aniline ring is turned away from the neodymium center. Thus, neither intra- or intermolecular coordination is observed in the solid state. There is an octahedral arrangement of the two diglyme molecules around the lithium cation.

As a result of the paramagnetism of the samarium(III) atom, the ^{1}H NMR signals of **4b** are distributed over a wide range (+14.0 to 0.1 ppm), allowing a clear determination of the resonances. The signal due to the protons of the eight-membered ring in **4b** shows broad resonances which have a marked downfield shift (δ 14.00, 13.49, and 11.73) compared to K[Sm(COT)$_2$] (δ −11.4).[22b] Surprisingly, the signal due to the Me$_2$N group is split into two singlets. Spin−lattice relaxation (T_1) measurements were performed for the protons of complex **4b** in order to probe the proximity of the dimethylamino group to the paramagnetic Sm(III) center.[23] Static or transitory Sm−N interactions should result in efficient electron−nuclear dipolar relaxation ($\sim 1/r^6$)[24] of the Me$_2$N spin system. The T_1 values increase along the pendent chains as the Me$_2$N group is approached. This suggests that coordination of the Me$_2$N group to the samarium atom is negligible in solution. Coordination of the Me$_2$N group to the lithium cation in solution may therefore be the reason for the splitting of the ^{1}H NMR signals of this group.

Summary

In summary, a new type of multifunctional cyclooctatetraene with two aniline groups attached via a silicon bridge to the eight-membered ring has been introduced into organolanthanide chemistry, and the anionic sandwich complexes [Ln(1,4-R$_2$C$_8$H$_6$)$_2$]$^-$ were obtained. These are the first examples of structurally characterized cyclooctatetraene complexes with a donor functionality attached to the eight-membered ring. Further reactions at these functional groups are currently under investigation.

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Supporting Information Available: X-ray experimental details, including tables of positional and anisotropic displacement parameters and bond lengths and angles (21 pages). Ordering information is given on any current masthead page.

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