least-squares techniques. After anisotropic refinement of the Fe-, C-, and O-atom positions ($R = 0.066$, $R_w = 0.090$), it was possible to find all hydrogen atom positions from a difference Fourier calculation. These were included isotropically in the final refinement cycles. Table IX shows the final atomic coordinates; Tables I, II, and III contain selected bond distances, angles, and planes, respectively.

For **5a** the positions of all atoms except hydrogen were found in a Fourier analysis. The positions of hydrogen atoms at C8 and C16 were calculated [d(C–H) = 1.0 Å, $U = 0.05$], but the other hydrogen atom positions could be taken from a difference Fourier analysis. After an empirical correction for absorption the refinement was carried out by full-matrix least-squares techniques. All non-hydrogen atoms were included anisotropically in the final refinement cycles. Table X shows the final atomic coordinates; Tables VI and VII contain selected bond distances and angles.

Acknowledgment. We are indebted to Mr. K. Schneider and Mrs. R. Schrader for experimental assistance. We thank Dr. W. E. Klotzbücher and Dr. K. Seevogel for IR and ORD/CD measurements, respectively, and Prof. J. Takats for helpful discussions.

Registry No. 2, 88657-71-0; **3a**, 115224-73-2; [(–)-**3a**], 115224-75-4; **3b**, 115224-76-5; 4, 65582-71-0; **5a**, 115160-53-7; **5b**, 115224-74-3; **6**, 115160-52-6; (η^2-diethyl formarate)FeCO$_4$, 53150-33-7; (η^2-methyl acrylate)$_2$Fe(CO)$_3$, 56323-91-2.

Supplementary Material Available: Tables of crystal data and details of data collection, atomic fractional coordinates, atomic thermal parameters, and bond distances and angles for **3a** and **5a** (12 pages); listings of structure factors for **3a** and **5a** (31 pages). Ordering information is given on any current masthead page.

Organometallic Compounds of the Lanthanides. 42.[1] Bis(dimethoxyethane)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)lanthanide Complexes

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The trichlorides of Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu react with NaC_5H_5 in tetrahydrofuran in the presence of dimethoxyethane (dme) with formation of bis(cyclopentadienyl)lanthanide chloride complexes of the types $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(dme)$. The reactions of these organolanthanide halide complexes with (trimethylsilyl)lithium in dme yield compounds of the type $[Li(dme)_2][(C_5H_5)_2Ln(SiMe_3)_2]$ (Ln = Sm, Dy, Ho, Er, Tm, Lu). $(C_5H_5)_2Sm(\mu\text{-}Cl)_2Na(dme)$ reacts with (trimethylgermyl)lithium in dme/pentane with formation of $[Li(dme)_3][(C_5H_5)_3SmClSm(C_5H_5)_3]$ (**7a**). The new compounds have been characterized by elemental analyses and IR and NMR spectra. The structure of $[Li(dme)_3][(C_5H_5)_3SmClSm(C_5H_5)_3]$ (**7a**) has been elucidated through complete X-ray analysis. The crystals are monoclinic with $a = 14.00$ (1) Å, $b = 13.38$ (2) Å, $c = 23.49$ (3) Å, $\beta = 93.37$ (9)°, space group $P2_1/n$, $Z = 4$, and $R = 0.0411$ for 4671 reflections. The $[Cp_3SmClSmCp_3]^-$ anion consists of two Cp_3Sm units bridged by a chlorine atom with Sm–Cl distances of 2.827 (2) and 2.798 (2) Å.

Introduction

Organolanthanides are generally known as hard Lewis acids.[2] Thus the most thermodynamically stable compounds are formed between the lanthanide acceptors and carbon, halogen, or oxygen donors.[3] Only a few examples of organometallic compounds of the lanthanides with bonds to soft donors such as S,[4,5] Se,[6,7] P,[8–13] or As[14] are known. We reported the synthesis of the first bis(cyclopentadienyl)lanthanide triphenylgermyl and triphenylstannyl complexes,[15] and recently we have been successful in synthesizing $[Li(dme)_3][(C_5H_5)_2Sm(SiMe_3)_2]$, the first organometallic compound with a lanthanide to silicon bond.[16] The lanthanide–silicon bond might possess a high degree of "covalency" because of the good donor properties of the trimethylsilyl ligand, although the bonding in organoactinides and organolanthanides is considered to be ionic.[17]

We have investigated the synthesis of the whole series of bis(cyclopentadienyl)bis(trimethylsilyl)lanthanide de-

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rivatives and have succeeded in isolating and characterizing a number of sodium chloride adducts of bis(cyclopentadienyl)lanthanide chlorides as well as of bis(dimethoxyethane)lithium bis(cyclopentadienyl)bis(trimethylsilyl)lanthanide complexes. The synthesis and characterization by single-crystal X-ray structural analysis of tris(dimethoxyethane)lithium bis[tris(cyclopentadienyl)samarium] chloride are also described.

Experimental Section

Due to the air and moisture sensitivity of these compounds, all syntheses were carried out with the rigorous exclusion of oxygen and water by using Schlenk tubes in an atmosphere of dried, oxygen-free argon, which was purified by passage through a copper catalyst (BASF) to remove oxygen and P_4O_{10} supported on alumina (Merck) to remove water. The solvents used were dried and freed of oxygen by refluxing and keeping over potassium and distilling under argon prior to use. Anhydrous rare-earth chlorides were prepared from the pure oxides (Auer-Remy, West Germany) by reaction with NH_4Cl.[18] NaC_5H_5 was prepared in THF from freshly distilled C_5H_6 and cleaned sodium. The THF was pumped off and the dry THF-free NaC_5H_5 washed with dme and stored under argon. $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ were prepared by reaction of Me_3SiCl or Me_3GeCl with activated Li in ether following the procedures of Rösch et al.[19]

^1H and ^{13}C NMR spectra were obtained in sealed 5- or 10-mm tubes on a Bruker WP 80 or WH 270 MHz spectrometer. Elemental analyses were performed by a Perkin-Elmer CHN-Analyzer 240 (C, H, N) or by a Perkin-Elmer 2380 atomic absorption spectrometer (Ge). Satisfactory analyses could be obtained by using a special Schlenk tube, and small aluminum cans for weighing these extremely sensitive compounds. Metal analyses were carried out by complexometric titration against dithizone.[20] Melting points were determined in capillaries sealed under vacuum.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichlorosamarate(III) (3a). Dry THF-free NaC_5H_5 3.43 g (38.9 mmol) was added at room temperature to a slurry of 5.0 g (19.5 mmol) of $SmCl_3$ in 100 mL of dme. The mixture was stirred for 2 h, subsequently allowed to stand overnight, and decanted from insoluble residues. After concentration of the clear solution to about 40 mL and cooling to −30 °C, yellow needles of **3a** crystallize in 70% yield (6.33 g). Anal. Calcd for $C_{14}H_{20}Cl_2NaO_2Sm$: C, 36.18; H, 4.34; Cl, 15.26; Sm, 32.38. Found: C, 35.97; H, 4.65; Cl, 15.10; Sm, 32.15.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichlorogadolinate(III) (3b). This compound was prepared from 2.39 g (9.07 mmol) of $GdCl_3$ and 1.59 g (18.1 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 1.25 g (30%) of yellowish **3b**. Anal. Calcd for $C_{14}H_{20}Cl_2GdNaO_2$: C, 35.66; H, 4.28; Cl, 15.04; Gd, 33.35. Found: C, 36.91; H, 4.87; Cl, 15.00; Gd, 32.98.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichloroterbate(III) (3c). This compound was prepared from 2.5 g (9.42 mmol) of $TbCl_3$ and 1.66 g (18.8 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 3.2 g (72%) of brownish **3c**. Anal. Calcd for $C_{14}H_{20}Cl_2NaO_2Tb$: C, 35.54; H, 4.27. Found: C, 35.49; H, 4.95.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichlorodysprosate(III) (3d). This compound was prepared from 5 g (18.6 mmol) of $DyCl_3$ and 3.72 g (37.2 mmol) of NaC_5H_5 in 100 mL of dme by using the method described for **3a**: yield 5.76 g (65%) of yellowish **3d**. Anal. Calcd for $C_{14}H_{20}Cl_2DyNaO_2$: C, 35.28; H, 4.23. Found: C, 33.51; H, 5.60.

Bis(dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichloroholmiate(III) (3e). This compound was prepared from 2.5 g (9.21 mmol) of $HoCl_3$ and 1.62 g (18.4 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 1.8 g (35%) of yellow **3e**. Anal. Calcd for $C_{18}H_{30}Cl_2HoNaO_4$: C, 37.98; H, 5.31; Ho, 28.97. Found: C, 37.70; H, 4.92; Ho, 29.00.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichloroerbate(III) (3f). This compound was prepared from 2.6 g (9.5 mmol) of $ErCl_3$ and 1.67 g (19 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 1.83 g (40%) of pink **3f**. Anal. Calcd for $C_{14}H_{20}Cl_2ErNaO_2$: C, 34.93; H, 4.19; Er, 34.73. Found: C, 36.86; H, 4.22; Er, 35.09.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichlorothulate(III) (3g). This compound was prepared from 2.5 g (9.08 mmol) of $TmCl_3$ and 1.6 g (18 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 3.25 g (74%) of yellow needles of **3g**. Anal. Calcd for $C_{14}H_{20}Cl_2NaO_2Tm$: C, 34.80; H, 4.17. Found: C, 34.63; H, 4.50.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichloroytterbate(III) (3h). This compound was prepared from 3.50 g (12.4 mmol) of $YbCl_3$ and 2.20 g (25 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 4.71 g (78%) of yellow crystals of **3h**. Anal. Calcd for $C_{14}H_{20}Cl_2NaO_2Yb$: C, 34.51; H, 4.14; Cl, 14.55; Yb, 35.51. Found: C, 34.63; H, 4.58; Cl, 14.90; Yb, 35.00.

(Dimethoxyethane-*O*,*O*′)sodium Bis(cyclopentadienyl)dichlorolutetate(III) (3i). This compound was prepared from 3.6 g (12.8 mmol) of $LuCl_3$ and 2.25 g (25.6 mmol) of NaC_5H_5 in 70 mL of dme by using the method described for **3a**: yield 4.9 g (78%) of colorless **3i**. Anal. Calcd for $C_{14}H_{20}Cl_2LuNaO_2$: C, 34.37; H, 4.12; Lu, 35.77. Found: C, 34.01; H, 4.20; Lu, 35.31.

(Trimethylsilyl)lithium (4). A 250-mL Schlenk-flask, furnished with a pressure-equalized dropping funnel, was charged with 2 g (300 mmol) of activated lithium and 80 g of NaCl suspended in 150 mL of absolute pentane. $Hg(SiMe_3)_2$ (10 g, 28.8 mmol in 50 mL of pentane) was added dropwise over a period of 2 h. An intensive red color was observed after some minutes, which turned to light yellow after 32 h at room temperature. The resulting solution was decanted from the Hg precipitate and concentrated. A pyrophoric white powder precipitated, which was solvent-free stable only for a few hours, but for several days, if kept in pentane solution at −30 °C.

Tris(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)samarate(III) (5a). NaC_5H_5 (0.84 g, 9.4 mmol) was added to a suspension of $SmCl_3$ in 70 mL of dme. After 3 h of stirring, the reaction mixture was cooled to −78 °C and 18.8 mL of a 0.2 M solution of $LiSiMe_3$ in pentane added slowly. Then the mixture was warmed to room temperature, stirred for additional 14 h, decanted from the LiCl formed, and concentrated to 20 mL, and 20 mL of pentane was added. After the mixture was cooled to −23 °C for 1 week, yellow crystals of $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$ were collected in 20% yield, based on $SmCl_3$. The crystals lose one dme ligand while drying them in vacuo, yielding a yellow powder of **5a**; decomp pt, 86 °C. Anal. Calcd for $C_{28}H_{58}LiO_6Si_2Sm$: C, 47.75; H, 8.31; Sm, 21.35. Found: C, 46.55; H, 7.25; Sm, 22.12. Calcd for $C_{24}H_{48}LiO_4Si_2Sm$: C, 46.93; H, 7.89; Sm, 24.48. Found: C, 46.55; H, 7.25; Sm, 23.23.

Bis(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)dysprosiate(III) (5d). This compound was prepared from 7.8 g (16 mmol) of $(C_5H_5)_2Dy(\mu\text{-}Cl)_2Na(dme)$ and 81 mL of a 0.2 M solution of $LiSiMe_3$ in pentane in 100 mL of dme by using the method described for **5a** but starting with **3d**: yield 3.2 g (35%) of brownish **5d**; decomp pt, 92 °C. Anal. Calcd for $C_{24}H_{48}DyLiO_4Si_2$: C, 46.03; H, 7.72; Dy, 25.95. Found: C, 45.21; H, 6.94; Dy, 26.00.

Bis(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)holmiate(III) (5e). This compound was prepared from 3.6 g (6.3 mmol) of $(C_5H_5)_2Ho(\mu\text{-}Cl)_2Na(dme)$ and 31 mL of a 0.2 M solution of $LiSiMe_3$ in pentane in 70 mL of dme by using the method described for **5a**: yield 1.7 g (44%) of yellow crystals of **5e**; decomp pt, 82–86 °C. Anal. Calcd for $C_{24}H_{48}HoLiO_4Si_2$: C, 45.85; H, 7.69; Ho, 25.23. Found: C, 45.26; H, 7.20; Ho, 26.80.

Bis(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)erbate(III) (5f). This compound was prepared from 2.04 g (3.23 mmol) of $(C_5H_5)_2Er(\mu\text{-}Cl)_2Na(dme)$ and 46.5 mL of a 0.2 M solution of $LiSiMe_3$ in

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pentane in 70 mL of dme by using the method described for **5d**: yield 2.1 g (35%) of yellow **5f**; decomp pt, 73–76 °C. Anal. Calcd for $C_{24}H_{48}ErLiO_4Si_2$: C, 45.69; H, 7.66; Er, 26.51. Found: C, 46.17; H, 7.10; Er, 26.20.

Bis(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)thulate(III) (5g). This compound was prepared from 5.1 g (11 mmol) of $(C_5H_5)_2Tm(\mu\text{-}Cl)_2Na(dme)$ and 55.5 mL of a 0.2 M solution of $LiSiMe_3$ in pentane in 100 mL of dme by using the method described for **5d**: yield 1.1 g (15%) of green crystals of **5g**; decomp pt, 78–82 °C. Anal. Calcd for $C_{24}H_{48}LiO_4Si_2Tm$: C, 45.56; H, 7.64; Tm, 26.70. Found: C, 45.70; H, 7.24; Tm, 26.90.

Tris(dimethoxyethane-*O*,*O*′)lithium Bis(cyclopentadienyl)bis(trimethylsilyl)lutetate(III) (5i). This compound was prepared from 4.79 g (10.3 mmol) of $(C_5H_5)_2Lu(\mu\text{-}Cl)_2Na(dme)$ and 51 mL of a 0.2 M solution of $LiSiMe_3$ in pentane in 70 mL of dme by using the method described for **5d**: yield 3.2 g (42%) of yellowish crystals of $[Li(dme)_3][(C_5H_5)_2Lu(Si(CH_3)_3)_2]$; decomp pt, 87 °C yielding yellowish **5i**, decomp pt, 127 °C. Anal. Calcd for $C_{28}H_{58}LiLuO_6Si_2$: C, 46.14; H, 8.03; Lu, 24.00. Found: C, 46.15; H, 7.96; Lu, 24.04. Calcd for $C_{24}H_{48}LiLuO_4Si_2$: C, 45.13; H, 7.57; Lu, 27.39. Found: C, 45.51; H, 7.73; Lu, 27.96.

(Trimethylgermyl)lithium (6). A 0.2 M solution of **6** in pentane was prepared from 35 g (80 mmol) of $Hg(GeMe_3)_2$, 1.13 g (160 mmol) of lithium, and 40 g of NaCl in 100 mL of absolute pentane by using the method described for **4**: yield 100 mL of a 0.2 M solution which has to be kept in the dark at −30 °C.

Reaction of 3a with $LiGeMe_3$. Isolation of 7a. $LiGeMe_3$ (70 mL of a 0.12 M solution, 8.4 mmol) in pentane was dropped slowly to a solution of 5.8 g (12.5 mmol) of **3a** in 70 mL of dme. After 4 h at room temperature, the clear solution was decanted from undissolved material, concentrated until the beginning of a precipitation of fine crystals, and cooled to −78 °C. Yellow needles of **7a** precipitated the next day: yield 2.25 g (18%); decomp pt, 192 °C. Anal. Calcd for $C_{42}H_{60}ClLiO_6Sm_2$: C, 50.25; H, 6.01; Cl, 3.53; Sm, 29.95. Found: C, 53.36; H, 6.34; Cl, 3.50; Sm, 30.05. From the decanted solution crystallize yellow needles of $[(C_5H_5)_2SmCl]_2$. Anal. Calcd for $C_{10}H_{10}ClSm$: C, 38.01; H, 3.18; Cl, 11.22; Sm, 47.58. Found: C, 37.30; H, 3.28; Cl, 10.58; Sm, 48.10.

Tris(dimethoxyethane)lithium Bis(tricyclopentadienylsamarium)trimethylgermane (8a). **3a** (5.7 g, 12 mmol) in 70 mL of dme reacts with 68 mL of a 0.18 M solution of $LiGeMe_3$ (12.3 mmol) in pentane following the procedure described above to give yellow crystals of **8a**, yield 2.9 g (22%). Anal. Calcd for $C_{45}H_{69}GeLiO_6Sm_2$: C, 49.76; H, 6.39; Li, 0.64; Ge, 6.68; Sm, 27.69. Found: C, 46.91; H, 7.62; Li, 0.64; Ge, 6.58; Sm, 28.06.

X-ray Data Collection, Structure Determination, and Refinement for 7a. Suitable crystals of **7a** were obtained through recrystallization from a dme solution. The crystals were stored under dme. A small amount of this suspension was transferred into a device similar to that reported by Veith and Bärnighhausen.[21] An irregular shaped crystal with an approximate diameter of 0.3 mm was selected, glued with grease on top of a glass fiber, and placed in the nitrogen beam of the diffractometer. Initial investigations revealed the crystal system to be monoclinic. Final lattice parameters were determined from a least-squares refinement of the angular settings of 15 strong, accurately centered reflections. All intensities $-h \rightarrow h, -k \rightarrow k, 0 \rightarrow l$ in the 2θ range $5° \leqslant 2\theta \leqslant 45°$ were measured at 173 (5) K, applying ω–2θ scans and Mo K_α radiation (λ = 0.71069 Å). Three intensity check reflections were measured every 50 reflections.

The raw data were corrected for fluctuation of check reflections and Lorentz and polarization effects and converted into structure factors. No absorption correction was made (μ = 25.99 cm^{-1}). From the systematic absent reflections ($0k0$, k odd; $h0l$, $h + l$ odd) the space group was determined to be $P2_1/n$ (alternate setting of $P2_1/c$, No. 14).

The positional parameters for the two samarium atoms were calculated from the Patterson map. A difference Fourier map based on the metal atom phases revealed the positions of all other non-hydrogen atoms in the asymmetric unit. The positional parameters of these atoms were refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen positions were calculated but not refined and added to the structure model with a constant isotropic temperature factor ($U_{iso,H}$ = 0.06 Å^2).[22] A difference Fourier map based on the final

Table I. Crystal and Data Collection Parameters for $[Li(dme)_3][((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]$ (7a)[a]

formula	$C_{42}H_{60}O_6ClLiSm_2$
fw	1004.05
space group	$P2_1/n$
a, Å	14.00 (1)
b, Å	13.38 (2)
c, Å	23.49 (3)
β, deg	93.37 (9)
V, Å^3	4394
Z	4 (ion pairs)
ρ_{calcd}, g/cm^3	1.52
μ, cm^{-1}	25.99
$F(000)$	2016
diffractometer	Syntex $P2_1$
radiatn, λ, Å	Mo $K\alpha$, 0.71069
temp, K	173 (5)
scan technique	ω–2θ
data collected	$\bar{h}\rightarrow h$, $\bar{k}\rightarrow k$, $0\rightarrow l$
2θ limits	$1° \leq 2\theta \leq 45°$
no. of unique data	5743
no. of obsd data, $I \geq 3\sigma(I)$	4355
R $(= \sum[\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert]/\sum\lvert F_o\rvert)$	0.034
R_w $(= [\sum w\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/\sum w\lvert F_o\rvert^2]^{1/2})$	0.046
no. of parameters	507
corrections	anomalous dispersion, Lorentz, polarization

[a] Estimated standard deviations of the last significant digit are given in parentheses.

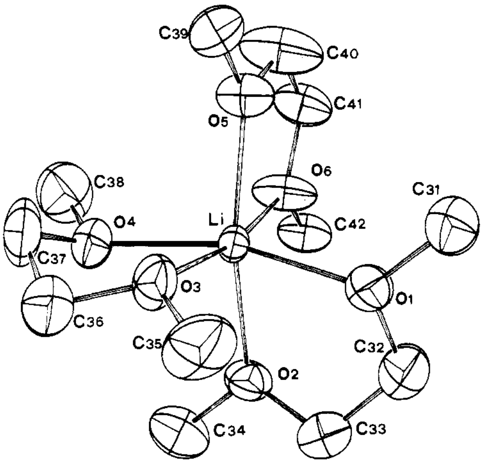

Figure 1. ORTEP drawing of the cation $[Li(dme)_3]^+$ of **7a** showing the atom numbering.

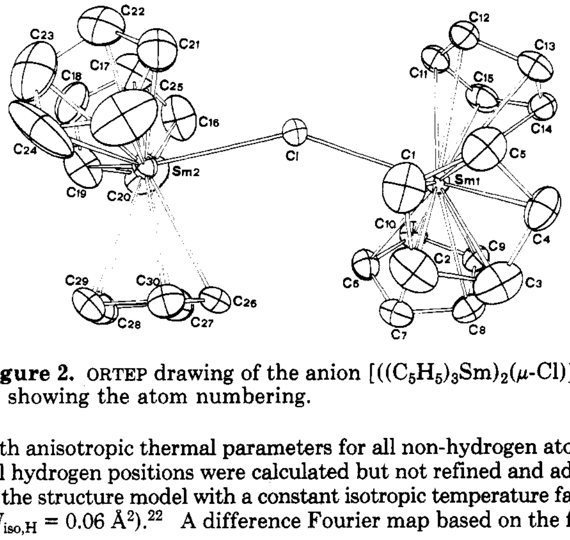

Figure 2. ORTEP drawing of the anion $[((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]^-$ of **7a** showing the atom numbering.

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Table II. Final Positional Parameters of $[Li(dme)_3][((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]$ (7a) with Standard Deviations of the Last Significant Digit in Parentheses

atom	x/a	y/b	z/c
Sm1	0.74783 (2)	0.39340 (3)	0.47453 (1)
Sm2	0.75209 (2)	0.21811 (3)	0.16093 (1)
Cl	0.75098 (13)	0.09059 (12)	0.06496 (7)
C1	0.9322 (5)	−0.0791 (7)	0.0814 (4)
C2	0.8886 (6)	−0.1486 (8)	0.1145 (4)
C3	0.8782 (5)	−0.2371 (7)	0.0835 (4)
C4	0.9147 (5)	−0.2220 (6)	0.0300 (4)
C5	0.9492 (5)	−0.1238 (6)	0.0294 (4)
C6	0.5932 (5)	−0.1006 (6)	0.0906 (3)
C7	0.6504 (5)	−0.1779 (6)	0.1142 (3)
C8	0.6483 (5)	−0.2549 (6)	0.0733 (3)
C9	0.5902 (5)	−0.2255 (5)	0.0250 (3)
C10	0.5555 (5)	−0.1303 (6)	0.0369 (3)
C11	0.7016 (5)	0.0073 (6)	−0.0701 (3)
C12	0.8004 (5)	−0.0110 (6)	−0.0728 (3)
C13	0.8111 (6)	−0.1131 (6)	−0.0843 (3)
C14	0.7204 (7)	−0.1583 (6)	−0.0883 (3)
C15	0.6534 (6)	−0.0821 (6)	−0.0810 (3)
C16	0.5925 (7)	0.2705 (9)	0.0918 (5)
C17	0.6484 (6)	0.3559 (8)	0.0942 (4)
C18	0.6489 (6)	0.3937 (7)	0.1481 (5)
C19	0.5943 (7)	0.3313 (9)	0.1796 (4)
C20	0.5593 (6)	0.2561 (8)	0.1460 (6)
C21	0.9211 (6)	0.2584 (7)	0.1108 (4)
C22	0.8809 (5)	0.3479 (8)	0.1161 (4)
C23	0.8794 (7)	0.3720 (9)	0.1718 (6)
C24	0.9231 (8)	0.2974 (14)	0.2033 (4)
C25	0.9493 (6)	0.2236 (8)	0.1647 (6)
C26	0.7346 (8)	0.0273 (6)	0.2048 (3)
C27	0.6569 (7)	0.0789 (8)	0.2233 (4)
C28	0.6924 (9)	0.1494 (8)	0.2644 (4)
C29	0.7922 (9)	0.1411 (7)	0.2685 (4)
C30	0.8168 (6)	0.0644 (6)	0.2327 (4)
Li	0.7419 (8)	0.4143 (9)	0.8515 (5)
O1	0.6461 (4)	0.2957 (4)	0.8418 (3)
O2	0.6299 (4)	0.4620 (4)	0.8986 (3)
C31	0.6550 (7)	0.2062 (7)	0.8094 (4)
C32	0.5670 (8)	0.3049 (9)	0.8696 (6)
C33	0.5557 (6)	0.3946 (7)	0.9025 (5)
C34	0.6172 (6)	0.5497 (7)	0.9311 (5)
O3	0.8267 (4)	0.3518 (4)	0.9193 (3)
O4	0.8273 (4)	0.5397 (4)	0.8796 (2)
C35	0.8078 (8)	0.2669 (8)	0.9513 (5)
C36	0.8733 (8)	0.4263 (9)	0.9550 (4)
C37	0.9027 (7)	0.5123 (8)	0.9203 (5)
C38	0.8487 (8)	0.6223 (7)	0.8465 (5)
O5	0.8394 (4)	0.3508 (5)	0.7930 (2)
O6	0.7003 (4)	0.4914 (5)	0.7734 (2)
C39	0.9298 (7)	0.3104 (9)	0.8095 (5)
C40	0.8401 (7)	0.4008 (9)	0.7404 (4)
C41	0.7358 (9)	0.4332 (9)	0.7264 (4)
C42	0.6101 (8)	0.5247 (10)	0.7581 (6)

Table III. Selected Bond Distances (Å) for $[Li(dme)_3][((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]$ (7a) with Estimated Standard Deviations of the Last Significant Digit in Parentheses[a]

Bond Distances			
Anion			
Sm1–Cl	2.798 (2)	Sm2–Cl	2.827 (2)
Sm1–Cp1	2.514 (8)	Sm2–Cp4	2.500 (10)
Sm1–Cp2	2.499 (7)	Sm2–Cp5	2.492 (10)
Sm1–Cp3	2.501 (7)	Sm2–Cp6	2.501 (9)
Cation			
Li–O1	2.083 (13)	Li–O2	2.074 (12)
Li–O3	2.103 (12)	Li–O4	2.142 (13)
Li–O5	2.167 (12)	Li–O6	2.155 (12)

[a] Cp denotes the centroid of the cyclopentadienyl ring.

Table IV. Selected Bond Angles (deg) for $[Li(dme)_3][((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]$ (7a) with Estimated Standard Deviations of the Last Significant Digit in Parentheses[a]

Bond Angles			
Anion			
Cp1–Sm1–Cp2	117.1 (3)	Cp4–Sm2–Cp5	116.3 (4)
Cp1–Sm1–Cp3	117.3 (3)	Cp4–Sm2–Cp6	118.5 (3)
Cp2–Sm1–Cp3	116.3 (2)	Cp5–Sm2–Cp6	117.0 (4)
Cp1–Sm1–Cl	99.8 (2)	Cp4–Sm2–Cl	98.6 (2)
Cp2–Sm1–Cl	101.9 (2)	Cp5–Sm2–Cl	99.9 (3)
Cp3–Sm1–Cl	98.4 (2)	Cp6–Sm2–Cl	100.3 (2)
Sm1–Cl–Sm2	146.52 (6)		
Cation			
O1–Li–O2	77.9 (4)	O1–Li–O3	96.4 (5)
O1–Li–O4	167.3 (6)	O1–Li–O5	93.3 (5)
O1–Li–O6	97.5 (5)	O2–Li–O3	97.4 (5)
O2–Li–O4	91.1 (5)	O2–Li–O5	169.8 (6)
O2–Li–O6	97.6 (5)	O3–Li–O4	78.4 (4)
O3–Li–O5	88.6 (5)	O3–Li–O6	161.4 (6)
O4–Li–O5	98.2 (5)	O4–Li–O6	90.3 (5)
O5–Li–O6	78.3 (4)		

[a] Cp denotes the centroid of the cyclopentadienyl rings.

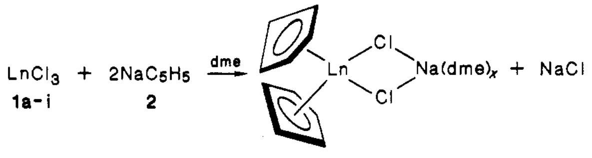
structure model showed no strong peaks (maximum 0.97 e/Å^3, minimum −0.87 e/Å^3).

Additional data pertinent to the crystal structure determination are summarized in Table I; final atomic positional parameters are listed in Table II. The atomic numbering scheme followed in these listings is identified in Figures 1 and 2. Selected interatomic distances and angles are listed in Tables III and IV.

All calculations were performed with the use of the program SHELX.[23] Atomic scattering factors for Sm and Li were taken from the tabulations of Cromer and Manri[24] and anomalous dispersion terms from Cromer and Liberman.[25]

Results and Discussion

Synthesis of Bis(cyclopentadienyl)lanthanide Chloride Complexes. Lanthanide trichlorides $LnCl_3$ (**1**) react with powdered, solvent-free cyclopentadienylsodium (**2**) in the molar ratio 1:2 in dimethoxyethane (dme) at room temperature to give $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(C_4H_{10}O_2)$.



3a-i

Ln = Sm, Gd, Tb, Dy, Er, Tm, Yb, Lu; $x = 1$
Ln = Ho; $x = 2$

The sodium chloride complexes can be isolated with one (**3a–d**, **3f–i**) dimethoxyethane as the stabilizing base for sodium. Only in the case of the holmium complex **3e**, two dme ligands could be found. The crystalline compounds are stable at room temperature, when isolated from the dme solution. They lose dme slowly at 20 °C (0.001 mbar), yielding dinuclear complexes $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Ln(C_5H_5)_2$,[26-28] which are also formed during decomposition of **3a–i** between 60 and 90 °C. They can be sublimed between 160 and 180 °C (0.001 mbar). **3e** does not decompose in the 60–80 °C range. It sublimes at 178 °C (0.001 mbar) with evolution of dme. A holmium complex with only one dme ligand could not be detected.

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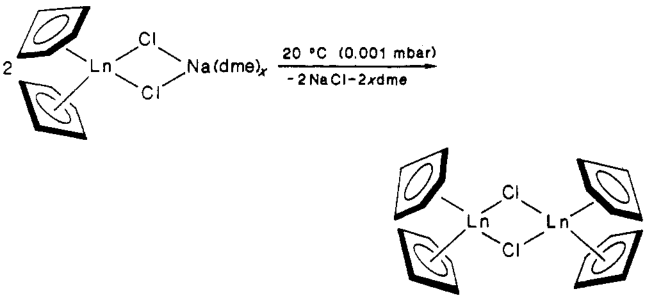
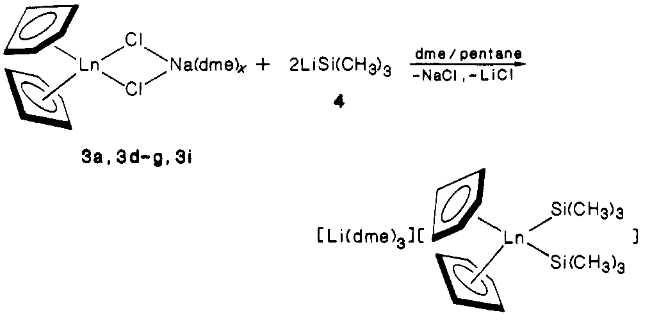


Ln = Sm, Gd, Tb, Dy, Er, Tm, Yb, Lu; x = 1
Ln = Ho; x = 2

Synthesis of Bis(cyclopentadienyl)bis(trimethylsilyl)lanthanide Complexes. Reaction of $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(dme)_x$ (Ln = Sm, Dy, Ho, Er, Tm, Lu) with an equimolar amount of $LiSi(CH_3)_3$, prepared from $Hg(Si(CH_3)_3)_2$ and activated lithium in a slurry of sodium chloride in pentane, does not yield the expected complexes $(C_5H_5)_2LnSi(CH_3)_3$, but instead the cation–anion pairs $[Li(dme)_3][(C_5H_5)_2Ln(Si(CH_3)_3)_2]$. The same compounds are formed in higher yields using a molar ratio of $(C_5H_5)_2Ln(\mu\text{-}Cl)_2Na(dme)_x$:$LiSi(CH_3)_3$ = 1:2.

$$Hg(Si(CH_3)_3)_2 + 2Li \xrightarrow{NaCl/pentane} 2LiSi(CH_3)_3 + Hg$$



4

3a, 3d–g, 3i

5a, 5d–g, 5i

Ln = Sm, Dy, Ho, Er, Tm, Lu

The yellow (**5a,e**), brownish (**5d**), pink (**5f**), green (**5g**), and colorless (**5i**) complexes are extremely sensitive toward moisture and air. They decompose slowly at room temperature, even when kept in an argon atmosphere. The lithium cation is stabilized by three dme ligands, when precipitated from the solvent below 0 °C. Such cation–anion pairs having a hexacoordinated lithium cation could be isolated and analyzed in the case of the lutetium complex **5i** and characterized by an X-ray structural analysis for the samarium derivative **5a**. For the complexes containing dysprosium (**5d**), holmium (**5e**), erbium (**5f**), and thulium (**5g**), elemental analyses showed only tetracoordinated lithium cations $[Li(dme)_2]^+$. All six complexes investigated decompose upon heating above 75 °C. **5d**, **5f**, and **5g** loose the coordinated dme completely at 92°, 73–76°, or 78–82 °C, respectively. **5a** and **5i** loose dme first at 94° or 87 °C, respectively, yielding yellow powders, secondly at 136° or 127 °C, respectively, and in a third step at 178 and 204 °C, respectively, yielding black decomposition products.

Hydrolysis of $[Li(dme)_2][(C_5H_5)_2Ln(SiMe_3)_2]$ yields trimethylsilane which was identified by its absorption in the IR spectrum[29] at 2123 cm^{-1}.

Reaction of $(C_5H_5)_2Sm(\mu\text{-}Cl)_2Na(dme)$ with $LiGe(CH_3)_3$. Bis(cyclopentadienyl)samarium chloride reacts with lithium trimethylgermane (**6**), prepared from $Hg(Ge(CH_3)_3)_2$ and activated lithium in pentane in the presence of NaCl, in a different way compared to lithium trimethylsilane. The reaction of **3a** with $LiGe(CH_3)_3$ in the molar ratio 1:1 in pentane at room temperature yielded a small amount of a yellow powder, which was soluble in dme. After this solution was cooled to −78 °C, yellow needles precipitated, which could be identified to be a complex formed from tris(cyclopentadienyl)samarium and lithium chloride. Hexamethyldigermane could be detected as another product formed.

$$2\underset{\mathbf{3a}}{(C_5H_5)_2Sm(\mu\text{-}Cl)_2Na(dme)} + \underset{\mathbf{6}}{LiGe(CH_3)_3} \xrightarrow{dme} \underset{\mathbf{7a}}{[Li(dme)_3][(C_5H_5)_3Sm\text{-}Cl\text{-}Sm(C_5H_5)_3]} + (CH_3)_3GeGe(CH_3)_3$$

This reaction could not be understood completely until now. We could isolate the same complex **7a** along with other not identified products, from the reaction of $(C_2H_5)_3SiH$ with $(C_5H_5)_2Sm(\mu\text{-}CH_3)_2Li(tmed)$, which was contaminated with **3a**. An X-ray structural analysis gave exactly the same result: a cation–anion pair with the cation formed of a lithium, coordinated in this case by two tmed ligands.[30] In both reactions, redistribution occurs, resulting in the formation of $Sm(C_5H_5)_3$ which forms a very stable anionic dinuclear complex with a chlorine atom bridging two samariums. Another example of this type of redistribution reactions forming anion-bridged dinuclear tris(cyclopentadienyl)lanthanide complexes is the reaction of $(C_5H_5)_2LuCl(THF)$ with NaH in THF, which resulted in the formation of $[Na(THF)_6][(C_5H_5)_3Lu\text{-}H\text{-}Lu(C_5H_5)_3]$ and $LuCl_3$.[31] Recently, we could show that tris(cyclopentadienyl)samarium reacts with lithium azide, LiN_3, giving another example of those complexes: $[Li(dme)_3][(C_5H_5)_3Sm\text{-}NNN\text{-}Sm(C_5H_5)_3]$.[32]

Excess of $LiGe(CH_3)_3$ results in the formation of another dinuclear tris(cyclopentadienyl)samarium complex, now bridged by a trimethylgermyl unit, which could be characterized by elemental analyses:

$$(C_5H_5)_2Sm(\mu\text{-}Cl)_2Na(dme) + 4LiGe(CH_3)_3 \xrightarrow{dme/pentane} \underset{\mathbf{8a}}{[Li(dme)_3][((C_5H_5)_3Sm)_2Ge(CH_3)_3]}$$

The extremely air-sensitive compound **8a** is hydrolyzed with formation of C_5H_6 and $(CH_3)_3GeH$ besides LiOH and samarium hydroxide.

NMR Spectroscopy. The ^1H NMR data of the diamagnetic lutetium complexes **3i** and **5i** as well as some data of the paramagnetic complexes **3a–g**, **5a–g**, **7a**, and **8a** are given in Table V. The diamagnetic derivatives show the expected ^1H signals in THF-d_8 for the cyclopentadienyl groups, the trimethylsilyl group, and the dme ligands.

The spectra of the paramagnetic compounds show broadened signals with half widths up to 8100 Hz for **3b**.

Molecular Structure of $[Li(dme)_3][(Cp_3Sm)_2Cl]$ (7a). The compound exists as a discrete cation–anion pair. The anion $[((C_5H_5)_3Sm)_2(\mu\text{-}Cl)]^-$ shown in Figure 2 consists of two $(C_5H_5)_3Sm$ units bridged by a chlorine atom. The decacoordinated samarium atoms lie in the center of two trigonal pyramids with the centroids of the cyclopentadienyl rings forming the bases and the chlorine atom as the mutual apex. The cyclopentadienyl rings are bonded in η^5 fashion with Sm–C bond lengths ranging from 2.726 (11) to 2.806 (8) Å (mean, 2.766 Å). This value agrees well with the mean Sm–C distances in $(C_5H_5)_3Sm(C_5H_5N)$[33]

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Table V. ^{1}H NMR Spectral Data for Bis(cyclopentadienyl)lanthanide Complexes 3a–i, Bis(cyclopentadienyl)bis(trimethylsilyl)lanthanide Complexes 5a–i, and Compounds 7a and 8a in THF-d_8 at 30 °C[a]

compd	$\delta(C_5H_5)$	$\delta[(CH_3)_3Si]$	δ(dme)	
$Cp_2Sm(\mu\text{-}Cl)_2Na(dme)$ (**3a**)[b]	12.74		−1.07	−1.39
$Cp_2Gd(\mu\text{-}Cl)_2Na(dme)$ (**3b**)	4.3		3.3	
$Cp_2Tb(\mu\text{-}Cl)_2Na(dme)$ (**3c**)	157		−0.8	−1.5
$Cp_2Dy(\mu\text{-}Cl)_2Na(dme)$ (**3d**)	43.1		3.2	
$Cp_2Ho(\mu\text{-}Cl)_2Na(dme)_2$ (**3e**)	178		1.3	
$Cp_2Er(\mu\text{-}Cl)_2Na(dme)$ (**3f**)	−13.6		−0.22	−1.54
$Cp_2Tm(\mu\text{-}Cl)_2Na(dme)$ (**3g**)	−85			
$Cp_2Lu(\mu\text{-}Cl)_2Na(dme)$ (**3i**)[b]	6.34		3.14	2.90
$[Li(dme)_3][Cp_2Sm(SiMe_3)_2]$ (**5a**)	11.52	0.108	3.45	3.26
5a[b]	12.09	0.18	3.26	3.15
$[Li(dme)_2][Cp_2Dy(SiMe_3)_2]$ (**5d**)	5.88	−0.005	3.45	3.28
$[Li(dme)_2][Cp_2Ho(SiMe_3)_2]$ (**5e**)	164.2	−78.80	5.56	
$[Li(dme)_2][Cp_2Er(SiMe_3)_2]$ (**5f**)	−68.27	48.35	3.60	
$[Li(dme)_2][Cp_2Tm(SiMe_3)_2]$ (**5g**)	−56.7	3		
$[Li(dme)_3][Cp_2Lu(SiMe_3)_2]$ (**5i**)	5.94	0.10	3.43	3.27
5i[b]	6.13	0.515	3.15	3.07
$[Li(dme)_3][(Cp_3Sm)_2Cl]$ (**7a**)	11.09		3.42	3.26
$[Li(dme)_3][(Cp_3Sm)_2GeMe_3]$ (**8a**)	10.23	0.158[c]	3.43	3.27

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$. [b] In C_6D_6 [c] $\delta[(CH_3)_3Ge]$.

(2.753 (5), 2.779 (5), 2.766 (5) Å), $[(CH_3C_5H_4)_2SmCC\text{-}t\text{-}C_4H_9]_2$[11] (2.72 (4), 2.71 (4) Å), and $(C_9H_7)_3Sm$[34] (2.75 Å), but it is not in agreement with the Sm–C distances found in **5a** (average 2.61 Å).[35] The Sm–Cl distances are 2.827 (2) and 2.798 (2) Å, which is quiet long but compares well with the Sm–Cl distances in two (pentamethylcyclopentadienyl)samarium complexes containing Sm–Cl–Sm bridges, 2.849 (7)–2.892 (7) Å in $[(C_5Me_5)_2SmCl]_3$ and 2.76 (1)–2.89 (1) Å in $(C_5Me_5)_{10}Sm_5Cl_5$(tetraglyme),[36] and with the Nd–Cl distance in $[Na(THF)_6][((C_9H_7)_3Nd)_2(\mu\text{-}Cl)]$[37] (2.82 Å). The cyclopentadienyl(centroid)–Sm–cyclopentadienyl(centroid) angles average 117° with a range of ±1.4°. In previously reported f-element compounds with a trigonal-pyramidal arrangement the corresponding angles are 117.4 ± 0.8° in $(CH_3C_5H_4)_3Nd$,[38] 117 ± 1.3° in $(C_5H_5)_3U(C_6H_5)$,[39] and 118.9° in $(C_5H_5)_3Pr\cdot CNC_6H_{11}$.[40] The Sm–Cl–Sm angle (146.52 (6)°) is smaller then the Sm–Cl–Sm angles in $[(C_5Me_5)_2SmCl]_3$ (154.0 (3) and 158.2 (3)°) and in $(C_5Me_5)_{10}Sm_5Cl_5$(tetraglyme) (164.8 (4) and 165.1 (4)°)[36] and the Y–Cl–Y angle in $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$[41] (162.8 (2)°). In the neodymium complex $[Na(THF)_6][((C_9H_7)_3Nd)_2(\mu\text{-}Cl)]$[37] the chlorine atom lies on a center of symmetry; therefore the chlorine bridge is linear in contrast to that of **7a**. The bonding parameters associated with the $[Li(dme)_3]^+$ cations of **7a** are normal.

Acknowledgment. We thank the Fonds der Chemischen Industrie for generous support of this work, which was also supported by the Deutsche Forschungsgemeinschaft and by special grants of the TU Berlin within the exchange program TU Berlin/University of Oklahoma.

Registry No. **3a**, 115339-67-8; **3b**, 115339-69-0; **3c**, 115339-71-4; **3d**, 115339-73-6; **3e**, 115339-75-8; **3f**, 115339-77-0; **3g**, 115339-79-2; **3h**, 115339-81-6; **3i**, 115339-83-8; **4**, 18000-27-6; **5a**, 95156-25-5; **5d**, 115339-85-0; **5e**, 115339-87-2; **5f**, 115339-89-4; **5g**, 115339-91-8; **5i**, 115339-92-9; **6**, 18489-76-4; **7a**, 115339-94-1; **8a**, 115339-96-3; $Hg(GeMe_3)_2$, 13915-91-8.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, and selected least-squares planes for **7a** (8 pages); a listing of observed and calculated structure factors for **7a** (26 pages). Ordering information is given on any current masthead page.

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