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Articles

Heteroleptic Lanthanide Complexes with Aryloxide Ligands. Synthesis and Structural Characterization of Divalent and Trivalent Samarium Aryloxide/Halide and Aryloxide/Cyclopentadienide Complexes

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Synthesis of a new class of heteroleptic samarium aryloxide complexes has been achieved by the use of homoleptic samarium(II) bis(aryloxide) $Sm(OAr)_2(THF)_3$ (**1**, Ar = $C_6H_2Bu^t_2$-2,6-Me-4) as a starting material, which is easily obtained by reaction of $Sm(N(SiMe_3)_2)_2(THF)_2$ with 2 equiv of ArOH in THF. **1** reacts with 1 equiv of SmI_2 in THF to give Sm(II) mixed aryloxide/iodide $[(ArO)Sm(\mu\text{-}I)(THF)_3]_2$ (**2**), which adopts a dimeric structure *via* very weak Sm···I (3.534(2) Å) interactions. Reaction of **2** with C_5Me_5K in THF/HMPA affords the corresponding Sm(II) aryloxide/cyclopentadienide $(C_5Me_5)Sm(OAr)(HMPA)_2$ (**3**). Oxidation of **1** with 0.5 equiv of I_2 in THF gives monomeric samarium(III) aryloxide/iodide $(ArO)_2SmI(THF)_2$ (**4**), while the similar reaction of **1** with $ClCH_2CH_2Cl$ or ^tBuCl in THF affords dimeric samarium(III) aryloxide/chloride $[(ArO)_2Sm(\mu\text{-}Cl)(THF)]_2$ (**5**). Crystal data for **1**: monoclinic, space group $P2_1$, $a = 9.903(3)$ Å, $b = 16.718(5)$ Å, $c = 13.267(2)$ Å, $\beta = 95.17(2)°$, $V = 2187(2)$ Å^3, $Z = 2$, $D_c = 1.223$ g cm^{-3}, $R = 0.0634$. Crystal data for **2**·2THF: monoclinic, space group $P2_1/a$, $a = 18.330(6)$ Å, $b = 14.320(4)$ Å, $c = 13.949(3)$ Å, $\beta = 103.16(2)°$, $V = 3563(2)$ Å^3, $Z = 2$, $D_c = 1.46$ g cm^{-3}, $R = 0.0606$. Crystal data for **3**: triclinic, space group $P\bar{1}$, $a = 10.528(1)$ Å, $b = 12.335(2)$ Å, $c = 19.260(2)$ Å, $\alpha = 101.33(1)°$, $\beta = 95.230(9)°$, $\gamma = 108.54(1)°$, $V = 2293.1(5)$ Å^3, $Z = 2$, $D_c = 1.25$ g cm^{-3}, $R = 0.0358$. Crystal data for **4**: monoclinic, space group $C2/c$, $a = 17.191(7)$ Å, $b = 10.737(6)$ Å, $c = 21.773(7)$ Å, $\beta = 98.80(3)°$, $V = 3971(3)$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $R = 0.0467$. Crystal data for **5**: monoclinic, space group $P2_1/n$, $a = 13.750(3)$ Å, $b = 17.231(3)$ Å, $c = 14.973(6)$ Å, $\beta = 95.81(2)°$, $V = 3529(2)$ Å^3, $Z = 2$, $D_c = 1.31$ g cm^{-3}, $R = 0.0557$.

Introduction

The use of the bis(cyclopentadienyl) ligand sets ($(C_5R_5)_2$, R = H, Me) as stabilizing and solubilizing moieties has been a crucial factor in the development of organolanthanide chemistry.[1] Recently, there has been new impetus toward the search for alternative ligands in an attempt to extend lanthanide chemistry beyond the traditional realm of metallocene complexes.[2] Among possible alternatives, alkoxides (aryloxides) are attractive ligands for the lanthanides since they will have strong metal−ligand bonds and can be sterically fine tuned *via* the selection of a variety of easily available alcohol precursors including bidentate and optically active ones. In comparison with the useful $(C_5R_5)_2LnX$ (X = halide) type complexes,[3] heteroleptic lanthanide alkoxide/halide complexes of type of $(RO)_2LnX$ or (RO)LnX are of particular interest. However, such type of lanthanide complexes has remained very rare,[4,5] probably due to the possible equilibrium between the homoleptic and heteroleptic complexes, which favors the former. In our recent studies on lanthanide aryloxides, we found that 2,6-di-*tert*-butyl-4-methylphenoxide (ArO) served as a good stabilizing ligand for some reactive organic samarium species such as ketyls,[6] pinacolates,[6] and enolates.[7] Further efforts to develop new

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lanthanide systems based on this aryloxide ligand have now led to the isolation of heteroleptic samarium(II) and samarium(III) aryloxide/halide complexes, $[(ArO)Sm(\mu\text{-}I)(THF)_3]_2$ (**2**), $(ArO)_2SmI(THF)_2$ (**4**), and $[(ArO)_2Sm(\mu\text{-}Cl)(THF)]_2$ (**5**). We report herein the synthesis and structural characterization of these new complexes. Formation of samarium(II) aryloxide/cyclopentadienide $(C_5Me_5)Sm(OAr)(HMPA)_2$ (**3**) from **2** is also described.

Experimental Section

General Methods. All manipulations were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under nitrogen atmosphere in an Mbraun glovebox. The argon was purified by passing through a DRYCLEAN column (4A molecular sieves, Nikka Seiko Co.) and a GASCLEAN GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O COMBI-ANALYZER (Mbraun) to assure both were always below 1 ppm. Samples for NMR spectroscopic measurements were prepared in the glovebox. J. Young valve NMR tubes (Wilmad 528-JY) were used to maintain the inert atmosphere all of the time during the measurements. ^{1}H NMR spectra were recorded on a JNM-GSX 500 (FT, 500 MHz) or a JNM-EX 270 (FT, 270 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane. Elemental analyses were performed by the chemical analysis laboratory of The Institute of Physical and Chemical Research (RIKEN). Melting points were measured in sealed N_2-filled capillaries by using a Yanaco micro melting point apparatus. Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone ketyl, degassed by the freeze−thaw method (three times) and dried over fresh Na chips in the glovebox. Hexamethylphosphoramide (HMPA) was distilled from Na under reduced pressure, degassed by the freeze−thaw method (three times) and dried over molecular sieves (4A). Deuterated solvents were commercial grade and were degassed by the freeze−thaw method (three times) and dried over fresh Na chips (C_6D_6, THF-d_8) or 4A molecular sieves (CD_2Cl_2) in the glovebox. Lanthanide metals (40 mesh) were obtained from Rare Metallic Co. and Aldrich. $Sm(N(SiMe_3)_2)_2(THF)_2$,[8] SmI_2,[9] and C_5Me_5K[10] were prepared according to literature.

$Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) (1). To a purple brown THF (50 mL) solution of $Sm(N(SiMe_3)_2)_2(THF)_2$ (4.44 g, 7.21 mmol) was added ArOH (3.18 g, 14.42 mmol) in THF (20 mL). The resulting brown solution was stirred at room temperature for 2 h and was evaporated under vacuum. The residue was washed with hexane and recrystallized from THF/toluene to give **1** as dark brown crystals (4.81 g, 5.97 mmol, 83% yield). A second crop from the mother liquor yielded 0.70 g of **1** (12% yield). ^{1}H NMR (C_6D_6, 22 °C) δ 9.15 (br s, 12 H, THF), 4.20 (br s, 12 H, THF), −0.10 (br s, 36 H, ^{t}Bu), −0.95 (br s, 4 H, C_6H_2), −1.90 (br s, 6 H, Me). Anal. Calcd for $C_{42}H_{70}O_5Sm$: C, 62.67; H, 8.76. Found: C, 62.30; H, 8.81. Mp: 151−153 °C.

$[(ArO)Sm(\mu\text{-}I)(THF)_3]_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) (2). Addition of a dark brown solution of **1** (0.81 g, 1 mmol) in 5 mL of THF to a blue 0.1 M THF solution of SmI_2 (10 mL, 1 mmol) gave immediately a black brown solution. The mixture was stirred at room temperature for 4 h and was filtered. Condensation of the filtrate under reduced pressure precipitated **2** as black crystals (1.04 g after being vacuum-dried; 91% yield for **2** − 4THF). Crystals for X-ray analysis were obtained by slow evaporation of a THF solution in the glovebox. Four of the six THF ligands in **2** were lost under vacuum as suggested by elemental analyses, which were carried out by using samples from different batches. Anal. Calcd for $C_{38}H_{62}O_4I_2Sm_2$ (**2** − 4THF): C, 40.12; H, 5.49. Found: C, 39.50 (40.15); H, 5.79 (5.94). In THF-d_8, an equilibrium between **2** and its homoleptic analogs **1** and SmI_2 was observed. Shift of the equilibrium toward **2** by addition of SmI_2 was also observed by ^{1}H NMR spectroscopy. ^{1}H NMR (**2** − 4THF, in THF-d_8, 22 °C): δ −0.14 (s, 4 H, C_6H_2 for **2**), −0.50 (s, 36 H, ^{t}Bu for **1**), −1.06 (s, 4 H, C_6H_2 for **1**), −1.18 (s, 6 H, Me for **2**), −1.78 (s, 6 H, Me for **1**), −2.80 (s, 36 H, ^{t}Bu for **2**). In C_6D_6, a satisfactory integral was not obtained because the signal for the OAr group was too broad: δ 4.40 (br s, THF), 1.53 (br s, THF), −3.5∼0.5 (very broad, OAr). Mp: 139−141 °C.

$(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) (3). To a THF (5 mL) suspension of C_5Me_5K (0.18 g, 1 mmol) was added a THF solution (10 mL) of $[(ArO)Sm(\mu\text{-}I)(THF)]_2$ (**2** − 4THF) (0.57 g, 0.5 mmol). The dark brown mixture was stirred at room temperature overnight and filtered through a frit. Evaporation of the solvent yielded a dark brown solid, which was insoluble in toluene but became green when rinsed with toluene. Addition of THF gave a dark brown solution, into which HMPA (0.35 mL, 2 mmol) was syringed. After reduction of the solution volume under reduced pressure, ether was layered to precipitate **3** as brown blocks (0.56 g, 0.65 mmol, 65% yield). This reaction could also be done in one pot to obtain **3**. ^{1}H NMR (C_6D_6, 22 °C): δ 5.26 (s, 15 H, C_5Me_5), 4.20 (br s, 36 H, NMe), 2.76 (s, 18 H, ^{t}Bu), 2.24 (s, 2 H, C_6H_2), 0.42 (s, 3 H, Me). Anal. Calcd for $C_{37}H_{74}N_6O_3P_2Sm$: C, 51.47; H, 8.64; N, 9.73. Found: C, 51.10; H, 8.73. N, 9.91. Mp: 258−260 °C.

$(ArO)_2SmI(THF)_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) (4). To a dark brown THF solution (20 mL) of **1** (0.70 g, 0.87 mmol) was added a 0.05 M THF solution of iodine (8.8 mL, 0.44 mmol). The resulting orange solution was stirred at room temperature for 30 min and was vacuum-pumped. The residue was dissolved in warm ether, and the solution volume was reduced under reduced pressure. After a few days, orange blocks of **4** (0.58 g, 78% yield) were precipitated. A second crop from the mother liquor gave 0.08 g of **4** (0.09 mmol, 11% yield). ^{1}H NMR (C_6D_6, 22 °C): δ 8.11 (s, 4 H, C_6H_2), 3.49 (br s, 8H, THF), 2.75 (s, 6 H, Me), 1.20 (s, 36 H, ^{t}Bu), 0.77 (br s, 8 H, THF). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.85 (s, 4 H, C_6H_2), 3.73 (br s, 8H, THF), 2.68 (s, 6 H, Me), 1.64 (br s, 8 H, THF), 1.09 (s, 36 H, ^{t}Bu). ^{13}C NMR (CD_2Cl_2, 22 °C): δ 164.8, 139.1, 128.2, 125.8, 67.2, 36.8, 32.4, 24.9, 22.3. Anal. Calcd for $C_{38}H_{62}O_4ISm$: C, 53.06; H, 7.26. Found: C, 52.90; H, 7.23. Mp: 108−110 °C (decomposed to white powder which remained up to 300 °C).

$[(ArO)_2Sm(\mu\text{-}Cl)(THF)]_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) (5). To a THF solution (30 mL) of **1** (1.05 g, 1.3 mmol) was added $ClCH_2CH_2Cl$ (51 μL, 0.65 mmol) in THF (2 mL). The mixture was stirred at room temperature overnight. During this time the color changed gradually from dark brown to light yellow. Reduction of the solution volume and addition of ether yielded **5** as light yellow crystals (0.68 g, 0.49 mmol, 75%). The similar reaction of **1** with ^{t}BuCl also gave **5** in 70% yield. ^{1}H NMR (C_6D_6, 22 °C): δ 8.08 (s, 8 H, C_6H_2), 2.74 (br s, 20 H, THF, Me), 1.20 (br s, 80 H, THF, ^{t}Bu). ^{1}H NMR (CD_2Cl_2, 22 °C): d 7.78 (s, 8 H, C_6H_2), 2.99 (br s, 8 H, THF), 2.63 (s, 12 H, Me), 1.29 (br s, 8 H, THF), 0.78 (s, 72 H, ^{t}Bu). ^{13}C NMR (CD_2Cl_2, 22 °C): δ 165.9, 138.8, 127.9, 125.6, 69.7, 36.6, 32.1, 24.7, 22.2. Anal. Calcd for $C_{68}H_{108}O_6Cl_2Sm_2$: C, 58.62; H, 7.81. Found: C, 58.65; H, 8.19. Mp: 140−142 °C (decomposed to black powder which remained up to 300 °C).

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope (Wild M3Z, Leica) which was mounted on the glovebox window, and were sealed in thin-walled glass capillaries. Data collections were performed at 20 °C on a Mac Science MXC3K diffractometer (Mo Kα radiation, $\lambda = 0.710\,69$ Å, graphite monochromator, $\omega - 2\theta$ scan) for **2**, **3**, and **4**, and an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator, ω-scan) for **1** and **5**. Lattice constants and orientation matrices were obtained by least-squares refinement of 25 reflections with $30° \leq 2\theta \leq 35°$. Three reflections were monitored periodically as a check for crystal decomposition or movement, and no signifi-

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Table 1. Summary of Crystallographic Data

	1	**2**·2THF	**3**	**4**	**5**
formula	$C_{42}H_{70}O_5Sm$	$C_{62}H_{110}O_{10}I_2Sm_2$	$C_{37}H_{74}N_6O_3P_2Sm$	$C_{38}H_{62}O_4ISm$	$C_{68}H_{108}O_6Cl_2Sm_2$
fw	805.42	1570.17	863.39	860.22	1393.32
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	9.903(3)	18.330(6)	10.528(1)	17.191(7)	13.750(3)
b (Å)	16.718(5)	14.320(4)	12.335(2)	10.737(6)	17.231(3)
c (Å)	13.267(2)	13.949(3)	19.260(2)	21.773(7)	14.973(6)
α (deg)			101.33(1)		
β (deg)	95.17(2)	103.16(2)	95.230(9)	98.80(3)	95.81(2)
γ (deg)			108.54(1)		
V (Å^3)	2187(2)	3563(2)	2293.1(5)	3971(3)	3529(2)
Z	2	2	2	4	2
D_{calcd} (g cm^{-3})	1.22	1.46	1.25	1.44	1.31
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
T (°C)	20	20	20	20	20
μ (cm^{-1})	13.819	25.330	13.886	22.810	17.730
R (%)^a	6.34	6.06	3.58	4.67	5.57
R_w (%)^b	7.38	6.69	4.02	5.30	6.52

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

cant decay was observed. All data were corrected for X-ray absorption effects. The observed systematic absences were consistent with the space groups given in Table 1. Complexes **2**, **3**, and **4** were solved by direct methods using SIR92 in the CRYSTAN-GM software package, and **1** and **5** were solved by the UNICS-III program.[11] Hydrogen atoms were either located from the difference Fourier maps, or placed at calculated positions. Refinements were performed anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms by the block-diagonal least-squares method. The function minimized in the least-squares refinements was $\Sigma(|F_o| - |F_c|)^2$. Neutral atomic scattering factors were taken from the ref 12. The residual electron densities were of no chemical significance. Crystal data, data collection, and processing parameters are given in Table 1.

Results and Discussion

Samarium(II) Bis(aryloxide) Complex $\mathbf{Sm(OAr)_2(THF)_3}$ (1). Reaction of $Sm(N(SiMe_3)_2)_2(THF)_2$[8] with 2 equiv of ArOH (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4) in THF gave the homoleptic samarium(II) bis(aryloxide) **1** as dark brown crystals in 95% yield (eq 1).[6a] Similar synthesis of **1** in hexane solvent was

$$\mathrm{Sm(N(SiMe_3)_2)_2(THF)_2} + 2\mathrm{ArOH} \xrightarrow[-\mathrm{HN(SiMe_3)_2}]{\mathrm{THF}} \underset{\mathbf{1}}{\mathrm{Sm(OAr)_2(THF)_3}} \quad (1)$$

recently reported independently by Evans and co-workers.[2e] Reduction of "$(ArO)_2SmCl$" with sodium was also reported to afford **1** by Shen and co-workers, though information on the starting material and the product yield was not given.[13] It is interesting to note that complex **1** could be crystallized in three forms depending on recrystallization conditions. Dark brown crystals of **1** without any lattice solvent were obtained from THF/toluene co-solvent,[6a] while lattice solvent-containing crystals of **1**·THF[13,14] and **1**·C_7H_8[2e] were precipitated from pure THF and toluene, respectively. Crystals of **1**[6a] and **1**·THF[13] were found to be suitable for X-ray analysis, while serious decomposition of **1**·C_7H_8 was observed during data collection.[2e]

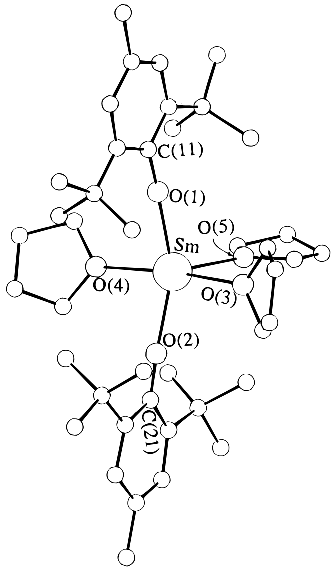

Figure 1. X-ray structure of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Sm−O(1)	2.331(11)	Sm−O(2)	2.347(13)
Sm−O(3)	2.601(14)	Sm−O(4)	2.640(14)
Sm−O(5)	2.568(15)	O(1)−C(11)	1.29(2)
O(2)−C(21)	1.38(2)		
O(1)−Sm−O(2)	151.1(4)	O(1)−Sm−(3)	87.5(4)
O(1)−Sm−O(4)	86.7(4)	O(1)−Sm−O(5)	110.2(5)
O(2)−Sm−O(3)	95.8(4)	O(2)−Sm−O(4)	87.8(4)
O(2)−Sm−O(5)	98.6(4)	O(3)−Sm−O(4)	173.4(4)
O(3)−Sm−O(5)	81.1(5)	O(4)−Sm−O(5)	103.9(5)
Sm−O(1)−C(11)	174(1)	Sm−O(2)−C(21)	167(1)

The structure of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. Similar to the structure in **1**·THF,[13,15] **1** possesses a distorted trigonal bipyramid structure, in which two THF ligands (O(3) and (O(4)) are placed at the apical, and the ArO groups (O(1) and O(2)) together with one THF ligand (O(5)) are laid at the equatorial positions (∠O(3)−Sm−O(4) = 173.4(4)°; ∠O(1)−Sm−O(2) = 151.1(4)°) (Figure 1 and Table 2).[15] This is in contrast to the square pyramidal ytterbium(II) aryloxide $Yb(OAr)_2(THF)_3$ (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4).[16] The Sm−OAr bond lengths in **1** (2.331(11) and 2.347(13) Å) are comparable with those reported for another samarium(II) aryloxide complex, which has a

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[13] Qi, G.-Z.; Shen, Q.; Lin, Y.-H. *Acta Crystallogr., Sect. C* **1994**, *50*, 1456.

[14] Although **1**·THF was previously reported to be crystallized from THF/toluene,[13] we obtained crystals of **1** from THF/toluene, and **1**·THF from pure THF.

[15] The structure of **1** was inappropriately described previously as the ArO ligands occupying the apical positions and the three THF ligands taking the equatorial positions. See ref 13.

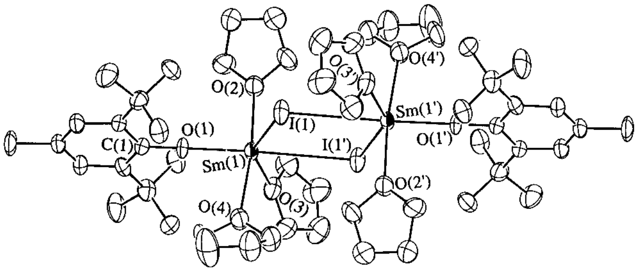

Figure 2. X-ray structure of **2**.

Scheme 1

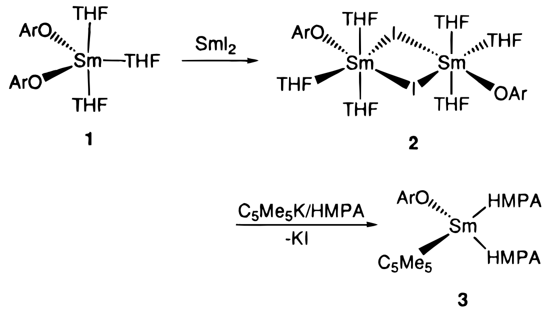

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **2**

Sm(1)−I(1)	3.308(2)	Sm(1)−I(1′)	3.534(2)
Sm(1)−O(1)	2.300(10)	Sm(1)−O(2)	2.570(11)
Sm(1)−O(3)	2.589(13)	Sm(1)−O(4)	2.570(12)
O(1)−C(1)	1.356(17)		
I(1)−Sm(1)−I(1′)	74.2(1)	I(1)−Sm(1)−O(1)	112.2(3)
I(1)−Sm(1)−O(2)	97.3(3)	I(1)−Sm(1)−O(3)	146.3(3)
I(1)−Sm(1)−O(4)	90.6(4)	I(1′)−Sm(1)−O(1)	173.5(3)
I(1′)−Sm(1)−O(2)	92.0(3)	I(1′)−Sm(1)−O(3)	72.2(3)
I(1′)−Sm(1)−O(4)	94.4(3)	O(1)−Sm(1)−O(2)	86.5(4)
O(1)−Sm(1)−O(3)	101.4(4)	O(1)−Sm(1)−O(4)	86.4(4)
O(2)−Sm(1)−O(3)	86.8(4)	O(2)−Sm(1)−O(4)	170.9(4)
O(3)−Sm(1)−O(4)	89.0(5)	Sm(1)−I(1)−Sm(1′)	105.8(1)
Sm(1)−O(1)−C(1)	178.5(10)		

polymeric structure and contains a KOAr unit, [KSm(μ-OC$_6$H$_2$-Bu$^t_2$-2,6-Me-4)$_3$(THF)]$_\infty$ (2.319(9)−2.362(6) Å).[2e]

Samarium(II) Aryloxide/Iodide [(ArO)Sm(μ-I)(THF)$_3$]$_2$ (2). Reaction of **1** with 1 equiv of SmI$_2$ in THF gave the heteroleptic samarium(II) aryloxide/iodide **2** as dark brown crystals in 91% isolated yield (Scheme 1). An X-ray analysis reveals that **2** possesses a dimeric structure in which a crystallographic inversion center exists at the center of the molecule, and each Sm atom is six-coordinated in a distorted octahedral form. (Figure 2 and Table 3). The Sm(μ-I)$_2$Sm unit is exactly planar as required by the crystallographic symmetry. The oxygen atoms of the ArO (O(1) and O(1′)) and two THF (O(3) and O(3′)) ligands are also in this plane (d = 0.03−0.13 Å). The overall structure of **2** can be viewed as replacement of one of the two ArO groups in **1** by an I, followed by dimerization *via* the intermolecular Sm···I interactions, which thus compensate the steric unsaturation caused by this replacement around the Sm atom. The μ-I bridges in **2** are highly unsymmetric. The bond distances of the two short Sm−I bonds (Sm(1)−I(1) = Sm(1′)−I(1′) = 3.308(2) Å) are in the 3.231(1)−3.390(2) Å range of terminal Sm−I bond lengths reported for samarium(II) diiodide complexes such as SmI$_2$(DME)(THF)$_3$,[17] SmI$_2$(O(CH$_2$CH$_2$OMe)$_2$)$_2$[18] and SmI$_2$(HMPA)$_4$,[19] while the two long Sm−I bonds (Sm(1)−I(1′) = Sm(1′)−I(1) = 3.534(2) Å) are longer than those reported for other μ-I bridging Sm(II) complexes, *e.g.*, [Sm(μ-I)$_2$(NCCMe$_3$)$_2$]$_\infty$ (3.260(1) and 3.225(1) Å),[20] [(C$_5$Me$_5$)Sm(μ-I)(THF)$_2$]$_2$ (3.356(2) and 3.459(2) Å),[21] [((Me$_3$Si)$_2$N)Sm(μ-I)(DME)(THF)]$_2$ (3.3414(9) and 3.3553(9) Å).[8] As far as we are aware, these two bonds (Sm(1)−I(1′) = Sm(1′)−(1)) represent the longest Sm−I bonds reported so far in the literature, indicating that the interactions between the two Sm(II) units in **2** are very weak. The Sm−OAr bond distances in **2** (2.300(10) Å) are comparable with those in **1**.

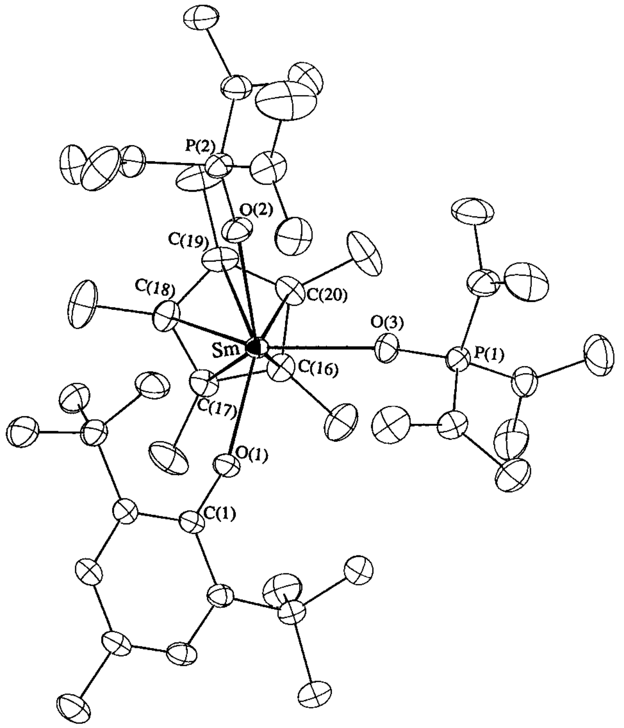

Figure 3. X-ray structure of **3**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **3**

Sm(1)−O(1)	2.345(4)	Sm(1)−O(2)	2.497(5)
Sm(1)−O(3)	2.443(5)	Sm(1)−C(16)	2.827(6)
Sm(1)−C(17)	2.876(7)	Sm(1)−C(18)	2.906(7)
Sm(1)−C(19)	2.868(6)	Sm(1)−C(20)	2.822(6)
P(1)−O(3)	1.481(5)	P(2)−O(2)	1.479(5)
O(1)−C(1)	1.321(7)		
O(1)−Sm(1)−Cp(centroid)	116.1(2)	O(1)−Sm(1)−O(2)	123.3(2)
O(2)−Sm(1)−Cp(centroid)	108.8(2)	O(1)−Sm(1)−O(3)	96.3(2)
O(3)−Sm(1)−Cp(centroid)	114.8(2)	O(2)−Sm(1)−O(3)	89.2(2)
Sm(1)−O(1)−C(1)	163.6(4)	Sm(1)−O(2)−P(2)	173.2(3)
Sm(1)−O(3)−P(1)	165.7(3)		

Samarium(II) Aryloxide/Cyclopentadienide (C$_5$Me$_5$)Sm(OAr)(HMPA)$_2$ (3). In the presence of 2 equiv of HMPA, reaction of **2** with 2 equiv of C$_5$Me$_5$K in THF yielded (C$_5$Me$_5$)Sm(OAr)(HMPA)$_2$ (**3**) as dark brown crystals. An X-ray analysis reveals that the central Sm(II) ion is bonded to one C$_5$Me$_5$, one ArO, and two HMPA ligands in a distorted tetrahedral form (Figure 3 and Table 4). The angle of the ∠O(Ar)−Sm−C$_5$Me$_5$ ring centroid (116°) is smaller than that of the ∠C$_5$Me$_5$ ring centroid−Sm−C$_5$Me$_5$ ring centroid (137°) in

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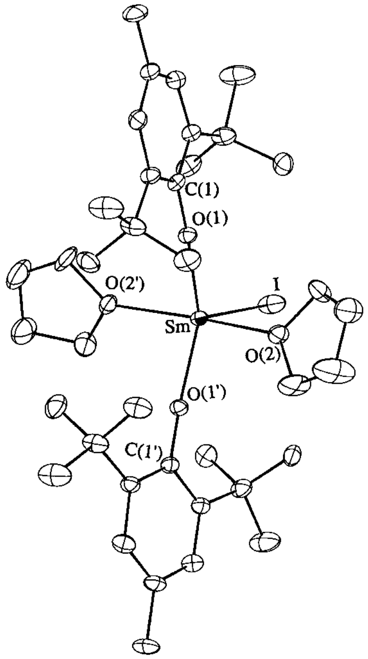


Figure 4. X-ray structure of **4**.

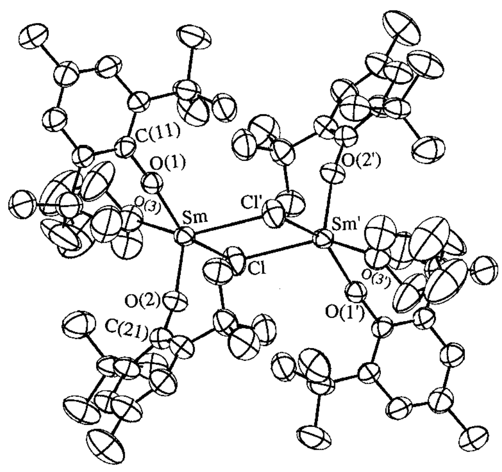
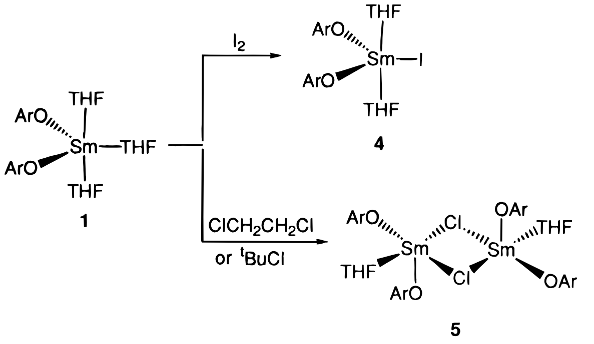


Figure 5. X-ray structure of **5**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of **4**

Sm(1)−I(1)	3.024(2)	Sm(1)−O(1)	2.153(7)
Sm(1)−O(2)	2.424(7)	O(1)−C(1)	1.373(12)
I(1)−Sm(1)−O(1)	107.6(2)	I(1)−Sm(1)−O(2)	95.9(3)
O(1)−Sm(1)−O(1′)	144.7(3)	O(1)−Sm(1)−O(2)	89.2(3)
O(1)−Sm(1)−O(2′)	87.2(3)	O(1′)−Sm(1)−O(2)	87.2(3)
O(1′)−Sm(1)−O(2′)	89.2(3)	O(2)−Sm(1)−O(2′)	168.1(3)
Sm(1)−O(1)−C(1)	175.8(6)		

Scheme 2



$(C_5Me_5)_2Sm(THF)_2$,[21] but slightly larger than that of ∠O(Ar)−Yb−O(Ar) (110°) in $Yb(OAr)_2(HMPA)_2$ (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4).[22] The angle of the ∠O(HMPA)−Sm−O(HMPA) (89°) in **3** is between that in $Yb(OAr)_2(HMPA)_2$ (97°),[22] and that of ∠O(THF)−Sm−O(THF) (83°) in $(C_5Me_5)_2Sm(THF)_2$.[21] The Sm−OAr bond in **3** (2.345(4) Å) is comparable with those in **1** (average 2.339(12) Å) and **2** (2.300(10) Å), and the Sm-Cp bonds (average 2.860(6) Å) are almost the same as those in $(C_5Me_5)_2Sm(THF)_2$ (average 2.86(2) Å).[21]

The ^1H NMR spectrum of **3** in C_6D_6 was consistent with its solid structure. The C_5Me_5 showed a singlet at δ 5.26, and the ArO gave three singlets at δ 5.26 (^tBu), 2.24 (C_6H_2), and 0.42 (Me). HMPA appeared as a broad singlet at δ 4.20.

Complex **3** represents the first example of a lanthanide(II) mixed aryloxide/cyclopentadienide complex. Its formation from **2** demonstrated that heteroleptic lanthanide aryloxide/halide complexes could be used as precursors for the synthesis of new aryloxide-based lanthanide derivatives.

Samarium(III) Aryloxide/Iodide $(ArO)_2SmI(THF)_2$ (4). Oxidation of **1** with 0.5 equiv of I_2 in THF produced the corresponding samarium(III) aryloxide/iodide **4** as orange crystals (Scheme 2). An X-ray analysis shows that **4** has a monomeric structure, in which the central Sm(III) ion is five-coordinated by one I, two ArO, and two THF ligands in a distorted trigonal bipyramid form (Figure 4, Table 5). There is a 2-fold axis which passes through both the Sm and I atoms. Similar to what was observed in **1**, the THF ligands occupy the apical positions, while the more bulky ArO groups together with the I atom are placed at the equatorial vertices. The overall structure of **4** can formally be viewed as substitution of the equatorial THF in **1** with an I atom. Reflecting the feature of a trivalent samarium species,[23] however, the Sm−OAr bonds (2.153(7) Å) in **4** are ca. 0.19 Å shorter than those in **1**, but are in the 2.101(6)−2.243(5) Å range of Sm−OAr bond lengths in samarium(III) aryloxide complexes such as $Sm_2(OC_6H_3Me_2\text{-}2,6)_6$,[24] $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$,[25] and $Sm(OAr)_2$-(fluorenoxy)$(HMPA)_2$ (Ar = $C_6H_3Bu^t{}_2$-2,6).[7b] Similarly, the Sm−I bond (3.024(2) Å) in **4** is shorter than those in **2**, but comparable with that reported for $(C_5Me_5)_2SmI(THF)$ (3.048(2) Å).[26] Complex **4** is the first example of monomeric lanthanide aryloxide/halide complex; three dimeric lanthanide alkoxide/halide complexes, $[(^tBu_3CO)_2Nd(\mu\text{-}Cl)(THF)]_2$,[4] $[YbI_2(\mu\text{-}OMe)(DME)]_2$,[5] and $[YbI(\mu\text{-}OCPh_3)(DME)]_2$,[5] were recently reported.

The ^1H NMR spectrum of **4** in C_6D_6 or CD_2Cl_2 could be easily assigned. In C_6D_6 signals for the ArO groups appeared at δ 8.11 (s, C_6H_2), 2.75 (s, Me), and 1.20 (s, ^tBu), and the THF ligands gave two broad singlets at δ 3.49 and 0.77, respectively.

Samarium(III) Aryloxide/Chloride $[(ArO)_2Sm(\mu\text{-}Cl)(THF)]_2$ (5). Reaction of **1** with $ClCH_2CH_2Cl$ or ^tBuCl in THF afforded the samarium(III) aryloxide/chloride **5** as light yellow crystals in 70∼75% yields (Scheme 2). In contrast to the monomeric iodide **4**, the chloride **5** possesses a dimeric structure, in which a crystallographic inversion center is present at the

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Table 6. Selected Bond Lengths (Å) and Angles (deg) of **5**

Sm−Cl	2.742(3)	Sm−Cl′	2.804(3)
Sm−O(1)	2.135(6)	Sm−O(2)	2.110(7)
Sm−O(3)	2.469(8)	O(1)−C(11)	1.354(11)
O(2)−C(21)	1.350(12)		
Cl−Sm−Cl′	74.50(8)	Cl−Sm−O(1)	98.5(2)
Cl−Sm−O(2)	105.1(2)	Cl−Sm−O(3)	135.4(2)
O(1)−Sm−O(2)	113.2(3)	O(1)−Sm−O(3)	86.3(3)
O(1)−Sm−Cl′	147.3(2)	O(2)−Sm−O(3)	113.6(3)
O(2)−Sm−Cl′	99.4(2)	O(3)−Sm−Cl′	78.0(2)
Sm−Cl−Sm′	105.50(9)	Sm−O(1)−C(11)	165.1(6)
Sm−O(2)−C(21)	167.0(6)		

center of the molecule (Figure 5, Table 6). Each Sm atom in **5** is surrounded by one THF, two Cl, and two ArO ligands in a distorted square-pyramid form. The basal plane is defined by one aryloxide oxygen (O(1)), one THF oxygen (O(3)), and two chlorines (Cl and Cl′). The Sm atom is 0.77 Å above the basal plane. The Sm−OAr bonds (average 2.122(7) Å) in **5** are comparable with those in **4** (2.153(7) Å). The Sm−Cl bond distances (2.742((3) and 2.804(3) Å) are in the 2.60(1)−2.892(7) Å range of the Sm(III)−Cl bond lengths found in $(C_5Me_5)_2SmCl(THF)$,[26] $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$,[27] and $(C_5Me_5)_{10}Sm_5Cl_5(Me(OCH_2CH_2)_4OMe)$.[27]

In the case of the $(C_5Me_5)_2$-coordinated complexes, $(C_5Me_5)_2SmX(THF)$ (X = Cl, I),[26] both iodide and chloride adopted a similar monomeric structure with one THF in the coordination sphere. In contrast, the bis(aryloxide)/chloride **5** adopts a dimeric structure *via* Sm···Cl interactions, while the bis(aryloxide)/iodide **4** has two THF ligands bound to the central Sm atom, though possessing a monomeric form. These structural differences probably resulted from the difference in steric bulkiness and electron-donating ability between the ArO and C_5Me_5 groups.

The ^{1}H NMR spectrum of **5** was to some extent solvent dependent. Signals for the THF ligands and the Me and ^{t}Bu groups of the ArO units were not well separated in C_6D_6, but an easily assignable spectrum was obtained in CD_2Cl_2. The ArO units showed three singlets at δ 7.78 (C_6H_2), 2.63 (Me), and 0.78 (^{t}Bu), while the THF groups gave broad singlets at δ 2.99 and 1.29.

Conclusion

By the use of the easily available homoleptic samarium(II) bis(aryloxide) **1** as a starting material, we have synthesized a new class of aryloxide-based heteroleptic Sm(II) and Sm(III) complexes. The aryloxide/halide complexes **2, 4** and **5** can be viewed as the ArO analogs of the useful "$(Cp')_nLnX$" ($n = 1$, 2; Cp′ = substituted cyclopentadienyls) type complexes. Moreover, the samarium(II) aryloxide/iodide **2**, and aryloxide/cyclopentadienide **3** are of interest as one-electron reductants, in comparison with the useful and well-known homoleptic SmI_2,[9,28] $(C_5Me_5)_2Sm(THF)_2$,[1d] and $(ArO)_2Sm(THF)_3$.[6]

Acknowledgment. This work was partly supported by a grant-in-aid from the Ministry of Education, Science and Culture of Japan.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, bond distances and angles, and detailed crystallographic data for **1**−**5** (23 pages). Ordering information is given on any current masthead page.

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