Novel Heteroleptic Samarium(II) Complexes Bearing both Aryloxide and Pentamethylcyclopentadienide Ligands

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Reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of ArOH (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^tBu) or $Sm(OAr)_2(THF)_3$ in toluene gave almost quantitatively the corresponding heteroleptic unsolvated dimeric Sm(II) complexes $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H (**1a**), Me (**1b**), ^tBu (**1c**)). These heteroleptic complexes are stable in toluene solution and did not undergo ligand redistribution. Addition of 4 equiv of hexamethylphosphoric triamide (HMPA) to a THF solution of **1a**−**c** afforded the corresponding HMPA-coordinated monomeric complexes $(C_5Me_5)Sm(OAr)(HMPA)_2$ (**2a**−**c**) in 90−94% isolated yields. Air-oxidation of **1c** yielded an orange-red Sm(III) complex, $(C_5Me_5)_2Sm(OAr)$ (**3**, Ar = $C_6H_2{}^tBu_3$-2,4,6), in which an agostic interaction between the central Sm(III) ion and an *ortho*-^tBu methyl group was observed. Reaction of **1a**−**c** with 2 equiv of C_5Me_5K in THF yielded the polymeric Sm(II) complexes $[(\mu,\eta^5\text{-}C_5Me_5)Sm(OAr)(\mu,\eta^5\text{-}C_5Me_5)K(THF)_2]_\infty$ (**4a**−**c**), in which the "$(C_5Me_5)K(THF)_2$" unit acted as a neutral coordination ligand. Metathesis reaction of $(ArO)_2Sm(THF)_3$ with C_5Me_5K or $(C_5Me_5)_2Sm(THF)_2$ with ArOK also gave **4a**−**c** in excellent yields. In the solid state, the ArO ligand of **4b** (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) was severely bent toward the central Sm atom (∠Sm−O−Ar 126.7(5)°) and an agostic interaction between the Sm atom and an *ortho*-^tBu methyl group of the ArO ligand was observed. Reaction of **4a**−**c** with 2 equiv of HMPA in THF yielded **2a**−**c** in 90−95% isolated yields.

Introduction

The bis(pentamethylcyclopentadienyl) ligand set $(C_5Me_5)_2$ as a stabilizing and solubilizing moiety has played a particularly important role in the development of the organometallic chemistry of Sm(II).[1] Recent efforts to search for alternative ancillary ligands for this highly reactive species have led to the synthesis and structural characterization of several new Sm(II) complexes, including the bis(silylamide) $Sm(N(SiMe_3)_2)_2(THF)_2$,[2] bis(pyrazolylborate) $Sm(HB(3,5\text{-}Me_2Pz))_2$ (Pz = pyrazolyl),[3] and bis(aryloxide) $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4),[4] and some of them have shown very interesting reactivities.[3b,4b,5] On the other hand, most of the samarium(II) complexes reported so far in the literature contained one or more strongly coordinated etheral solvent ligands. Although unsolvated Sm(II) complexes are known to show much higher reactivities,[1,6] the synthesis of such complexes has been very difficult, since the central Sm(II) ion is extremely susceptible to an attack of etheral solvents.[6a,7]

During our recent studies on lanthanide(II) bis(aryloxide) complexes,[4a,b,5,8] we became interested in heteroleptic samarium(II) complexes which bear both aryloxide (ArO) and C_5Me_5 ligands, since such mixed-ligand systems would probably provide a sterically and electronically new environment which could not be achieved in the case of the homoleptic complexes. To our knowledge, divalent lanthanide complexes which have both ArO and C_5Me_5 ligands are extremely rare.[4a] In this paper, we report the synthesis, structural characterization, and some of the reactivities of a new series of solvated and unsolvated heteroleptic samarium(II) aryloxide/pentamethylcyclopentadienide com-

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(7) To the best of our knowledge, only three homoleptic unsolvated samarium(II) complexes, $(C_5Me_5)_2Sm$,[6a] $Sm(HB(3\text{-}^tBu\text{-}5\text{-}MePz))_2$ (Pz = pyrazolyl),[3a] and $Sm(HB(3,5\text{-}Me_2Pz))_2$,[3c] were reported. In the case of the extremely reactive $(C_5Me_5)_2Sm$, even THF vapor in the glovebox atmosphere could attack the central Sm(II) to give the solvated complexes $(C_5Me_5)_2Sm(THF)_n$ (n = 1, 2).[6a]

(8) (a) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1992**, 722. (b) Hou, Z.; Wakatsuki, Y. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 906.

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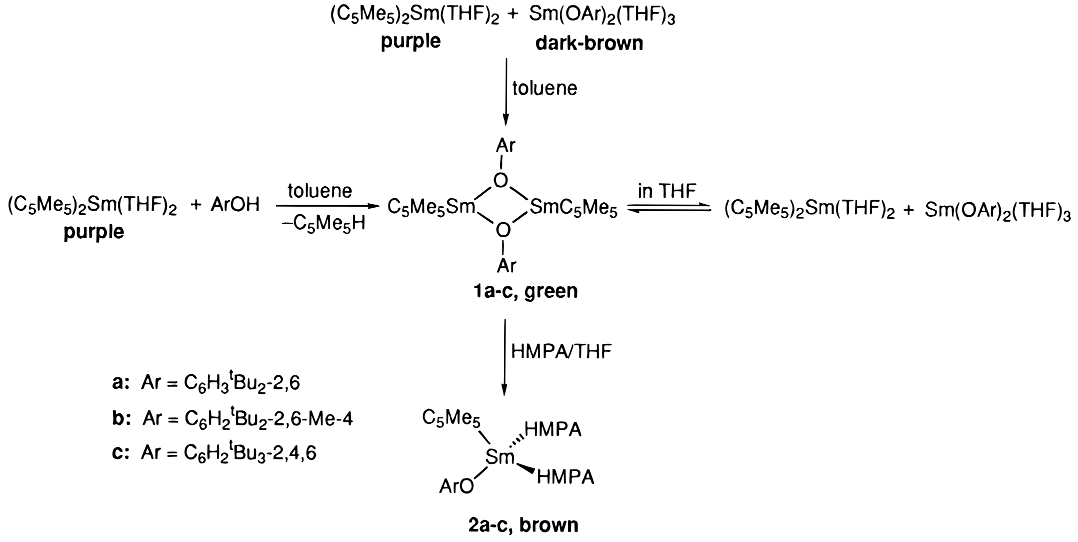
Scheme 1



plexes, some of which have shown unprecedented structural features and reactivities.

Results and Discussion

Unsolvated Heteroleptic Samarium(II) Aryloxide/Pentamethylcyclopentadienide Complexes. One of our initial approaches to heteroleptic samarium(II) aryloxide/pentamethylcyclopentadienide complexes was partial alcoholysis of the bis(pentamethylcyclopentadienyl)samarium(II) complex $(C_5Me_5)_2Sm(THF)_2$[9] by aryl alcohols. 2,6-Di-*tert*-butylphenols (ArOH, Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^{t}Bu) were chosen as a starting material for the aryloxide part, since such phenoxy groups (ArO) have shown a good stabilizing ability for samarium ions.[4,8b,10]

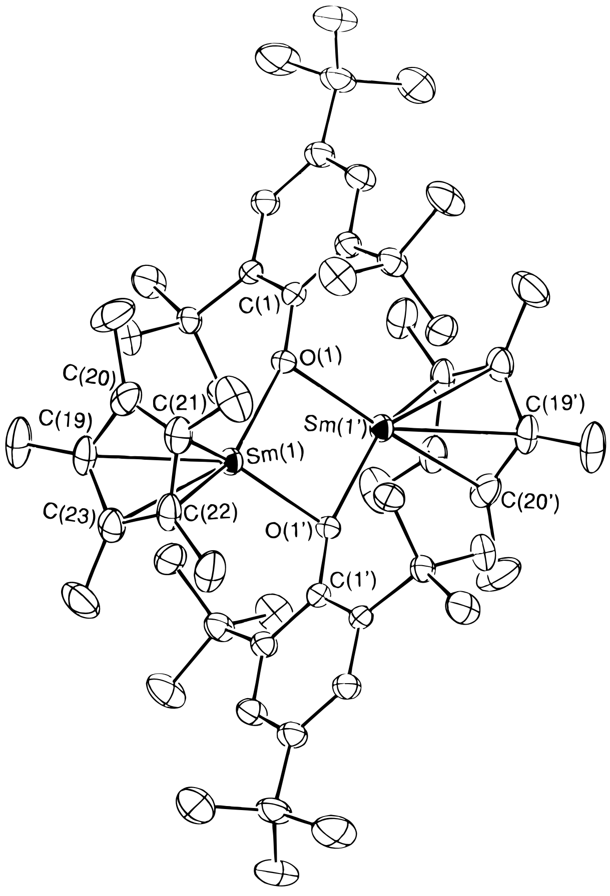


Figure 1. ORTEP drawing of **1c**.

Addition of 1 equiv of $HOC_6H_3{}^tBu_2$-2,6 to a purple toluene solution of $(C_5Me_5)_2Sm(THF)_2$ gradually yielded a green mixture, from which a green crystalline product **1a** was isolated almost quantitatively (Scheme 1). The similar reactions of $(C_5Me_5)_2Sm(THF)_2$ with $HOC_6H_2{}^tBu_2$-2,6-Me-4 and $HOC_6H_2{}^tBu_3$-2,4,6 afforded **1b** and **1c**, respectively. Reaction of 1 equiv of $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^{t}Bu) with $(C_5Me_5)_2Sm(THF)_2$ in toluene also gave **1a**−**c** in almost quantitative yields (Scheme 1). Elemental analyses suggested the formulation of these complexes as "$(C_5Me_5)Sm(OAr)$" (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H (**1a**), Me (**1b**), ^{t}Bu (**1c**)). In the case of **1c**, single crystals suitable for diffraction studies were successfully obtained by slow diffusion of a toluene solution of ArOH (Ar = $C_6H_2{}^tBu_3$-2,4,6) into a toluene solution of $(C_5Me_5)_2Sm(THF)_2$. An X-ray analysis has revealed that **1c** is an unsolvated dimeric samarium(II) complex which bears mixed ArO and C_5Me_5 ligands (Figure 1 and Table 1). The two Sm atoms are bridged by two OAr ligands. A crystallographic inversion center exists at the center of the molecule, and therefore, the $Sm(\mu\text{-}O)_2Sm$ unit is exactly planar. The C(1) and C(1′) atoms are also placed in this plane within 0.05 Å. Both the Cp* (Cp* = C_5Me_5) planes and the phenyl planes of the ArO ligands are almost perpendicular to the $Sm(\mu\text{-}O)_2Sm$ plane, forming dihedral angles of 86° and 92°, respectively. The μ-OAr bridges are unsymmetric. The bond distance of the Sm(1)−O(1) bond (2.425(5) Å) is significantly shorter than that of the Sm(1)−O(1′) bond (2.512(6) Å). These bridging Sm−OAr bonds are longer than those found in the polymeric samarium(II) aryloxide $[KSm(\mu\text{-}OAr)_3(THF)]_\infty$ (2.319(9)−2.362(6) Å) (Ar = $C_6H_2Bu^t_2$-2,6-Me-4)[4c] and as expected, longer than the terminal Sm(II)−OAr bonds found in $Sm(OAr)_2(THF)_3$ (2.29(1)−2.35(1) Å),[4a,d] $(C_5Me_5)Sm(OAr)(HMPA)_2$ (2.345(4) Å),[4a] and $[Sm(OAr)(\mu\text{-}I)(THF)_3]_2$ (2.300(10) Å).[4a] Also reflecting

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[9] Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter; W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

[10] (a) Hou, Z.; Yoshimura, T.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11169. (b) Yoshimura, T.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5382.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1c

Sm(1)···Sm(1′)	3.8418(5)	Sm(1)−O(1)	2.425(5)
Sm(1)−O(1′)	2.512(6)	Sm(1)−C(19)	2.794(9)
Sm(1)−C(20)	2.768(10)	Sm(1)−C(21)	2.756(8)
Sm(1)−C(22)	2.776(10)	Sm(1)−C(23)	2.799(10)
O(1)−C(1)	1.355(8)		
O(1)−Sm(1)−O(1′)	77.8(2)	O(1)−Sm(1)−Cp*(centroid)	133.1(3)
O(1′)−Sm(1)−Cp*(centroid)	148.9(3)	Sm(1)−O(1)−Sm(1′)	102.2(2)
Sm(1)−O(1)−C(1)	160.0(5)	Sm(1′)−O(1)−C(1)	97.8(5)

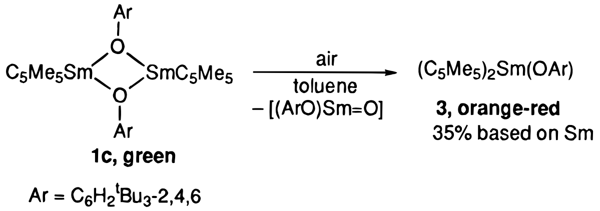
the unsymmetrical bridging feature in **1c**, the angle of Sm(1)−O(1)−C(1) (160.0(5)°) is much larger than that of Sm(1′)−O(1)−C(1) (97.8(5)°) while the former is only slightly smaller than those of Sm−O−Ar (164−179°) found for the terminal ArO ligands in $(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4),[4a] $Sm(OAr)_2(THF)_3$,[4a,d] and $[Sm(OAr)(\mu\text{-}I)(THF)_3]_2$.[4a] The bond distances of the Sm−Cp* bonds in **1c** (average 2.78(1) Å) are almost the same as those found in the unsolvated homoleptic samarium(II) complex $(C_5Me_5)_2Sm$ (average 2.79(1) Å)[6a] but shorter than those in $(C_5Me_5)_2Sm(THF)_2$ (average 2.86 (2) Å)[9] and $(C_5Me_5)Sm(OAr)(HMPA)_2$ (2.860(6) Å).[4a]

Complexes **1a**−**c** are slightly soluble in toluene in the order of **1c** > **1b** > **1a** to give a green solution. Their ^{1}H NMR spectra in C_6D_6 are relatively well-resolved and comparable with each other. The *ortho*-^{t}Bu groups of the ArO ligands appeared as singlets at unusually low fields (δ 33.69 (**1a**), 34.30 (**1b**), 34.40 (**1c**)), while the C_5Me_5 ligands showed singlets at very high fields (δ −5.31 (**1a**), −5.13 (**1b**), −5.10 (**1a**)). Signals for the aromatic protons appeared at δ −0.01 (br s, para) and −0.17 (br s, meta) for **1a**, δ −0.70 (s) for **1b**, and δ −0.27 (s) for **1c**. No signal for the known $(C_5Me_5)_2Sm$[6a] was observed in any of these cases, suggesting that compounds **1a**−**c** in benzene are quite stable and do not undergo ligand redistribution to the homoleptic complexes $(C_5Me_5)_2Sm$ and $(ArO)_2Sm$.

Complexes **1a**−**c** represent the first examples of unsolvated heteroleptic samarium(II) complexes,[7] as well as rare examples of the bulky 2,6-di-*tert*-butylphenoxide-bridged complexes.[4c,11] The isolation of **1a**−**c** in an unsolvated dimeric form rather than a solvated monomeric one suggests that the heteroleptic $(C_5Me_5)Sm(OAr)$ prefers the intermolecular Sm···OAr interaction to the coordination of THF in toluene solution. This is in sharp contrast to the homoleptic "$(ArO)_2Sm$" (Ar = $C_6H_2Bu^t_2$-2,6-Me-4), which was always isolated in the solvated monomeric form, $(ArO)_2Sm(THF)_3$.[4] The unsolvated homoleptic $(C_5Me_5)_2Sm$ was obtained by vacuum sublimation of its THF solvate, $(C_5Me_5)_2Sm(THF)_2$, at high temperature and had to be handled in a THF-free glovebox due to its susceptibility to the attack of THF.[6a,7] For the isolation of **1a**−**c**, such complete exclusion of THF from the reaction system was not required.

The behavior of **1a**−**c** in THF was different from that in toluene. Dissolving **1a**−**c** into THF gave a brown solution, which upon concentration under reduced pressure precipitated $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^{t}Bu). The ^{1}H NMR spectrum of **1b** in THF-d_8 showed complex signals which included those for the known complexes $(C_5Me_5)_2Sm(THF)_2$[9] and $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4).[4c] These results suggest that the heteroleptic complexes **1a**−**c** in THF probably existed in an equilibrium with their homoleptic analogs. Nevertheless, addition of 4 equiv of HMPA to a THF solution of **1a**−**c** afforded the corresponding monomeric HMPA-coordinated heteroleptic complexes $(C_5Me_5)Sm(OAr)(HMPA)_2$ (**2a**−**c**) in 90−94% isolated yields (Scheme 1). Complexes **2a**−**c** all gave well-resolved ^{1}H NMR signals in C_6D_6 without ligand redistribution being observed (see Experimental Section). The synthesis of **2b** by an alternative method and its structural characterization have been recently carried out in our laboratories.[4a]

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with a less bulky aryl alcohol, HOC_6HMe_4-2,3,5,6, has been previously reported to give an orange-yellow samarium(III) complex $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$.[12] In our reactions, the formation of this type of complex was not observed under the inert conditions. However, when a green toluene solution of **1c** was exposed to a trace amount of air, the trivalent samarium complex $(C_5Me_5)_2Sm(OAr)$ (**3**, Ar = $C_6H_2{}^tBu_3$-2,4,6) was obtained as orange-red crystals in 35% yield (based on Sm) (eq 1). Although **3** is an $OC_6H_2{}^tBu_3$-2,4,6 analog of $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$,[12] it has several noteworthy structural features which are brought about by the larger bulkiness of the aryloxide ligand (Figure 2 and Table 2).



(1)

The whole molecule of **3** possesses a mirror symmetry. The Sm(1), O(1), C(1)−C(7), C(9)−C(11), C(13), and C(15) atoms are all placed in this mirror plane, and therefore, the two C_5Me_5 ligands are entirely eclipsed (Figure 2). Within the mirror plane, an agostic interaction between Sm(1) and an *ortho*-^{t}Bu methyl (C(9)) group of the ArO ligand is observed. The Sm(1)···C(9) distance (3.055(7) Å) is comparable with the η^6-arene-Sm bond distances observed in the samarium(III) aryloxide complex $Sm_2(OC_6H_3{}^iPr_2\text{-}2,6)_6$ (2.824(7)-3.160(8) Å).[13,14] The methyl carbon atom C(9) is only 3.584(8) Å away from the methyl carbon atoms C(22) and C(22′)

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[11] As far as we are aware, only the following four 2,6-di-*tert*-butyl-4-methylphenoxide ArO-bridged complexes were previously reported: $[KSm(\mu\text{-}OAr)_3(THF)]_\infty$,[4c] $[(ArO)Yb(\mu\text{-}OAr)]_2$,[11a] $[((Me_3Si)_2N)Yb(\mu\text{-}OAr)]_2$,[11a] and $[Li(\mu\text{-}OAr)(OEt_2)]_2$.[11b] (a) van den Hende, J. R.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1435. (b) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102,* 2086.

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[13] Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33,* 3487.

[14] For a recent review on lanthanide complexes having metal−arene interactions, see: Deacon, G. B.; Shen, Q. *J. Organomet. Chem.* **1996**, *511,* 1.

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

Sm(1)−O(1)	2.144(5)	Sm(1)−C(16)	2.816(6)
Sm(1)−C(17)	2.783(5)	Sm(1)−C(18)	2.742(4)
Sm(1)−C(19)	2.721(6)	Sm(1)−C(20)	2.778(6)
O(1)−C(1)	1.323(8)	Sm(1)···C(9)	3.0555(7)
C(9)···C(22)	3.583(8)	C(14)···C(24)	3.484(10)
C(25)···C(25′)	3.399(10)		
Cp*(centroid)−Sm(1)−Cp*(centroid)	134.6(3)	Sm(1)−O(1)−C(1)	165.8(5)
O(1)−Sm(1)−Cp*(centroid)	112.5(3)	Sm(1)−C(9)−C(7)	128.8(6)
O(1)−Sm(1)−C(9)	61.3(2)		

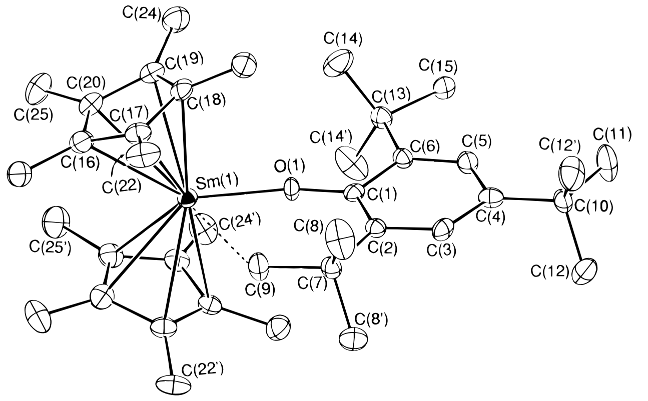

Figure 2. ORTEP drawing of **3**.

in the C_5Me_5 ligands. The methyl carbon atoms C(14) and C(14′) of another *ortho*-^{t}Bu group are as close as 3.484(10) Å to the C_5Me_5 methyl carbon atoms C(24) and C(24′), respectively. The distance between the methyl carbon atoms C(25) and C(25′) of the C_5Me_5 ligands is as short as 3.399(10) Å. These distances are much shorter than the sum of the van der Waals radius of a methyl group (2.0 Å),[15] and considerable van der Waals repulsion between these methyl groups must be present.[12,15] Apparently, due to these steric repulsions, the bond distances of the Sm−Cp* bonds in **3** (average 2.768(6) Å) are much longer than those in $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6) (average 2.68(1) Å),[12] and the Cp*(centroid)−Sm−Cp*(centroid) angle (134.6(3)°) is smaller than that in $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6) (139.1°).[12]

The bond distance of the Sm−OAr bond in **3** (2.144(5) Å) is comparable with that in $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6) (2.13(1) Å)[12] and those in other samarium(III) aryloxide complexes such as (4-Me-2,6-^{t}Bu$_2C_6H_2O)_2SmI(THF)_2$ (2.153(7) Å),[4a] [(4-Me-2,6-^{t}Bu$_2C_6H_2O)_2Sm(\mu$-Cl)(THF)]$_2$ (2.110(7) and 2.135(6) Å),[4a] and $Sm_2(OC_6H_3{}^iPr_2$-2,6)$_6$ (average 2.101(6) Å for terminal).[13] The Sm−O−Ar angle in **3** (165.8(5)°) is smaller than that found in $(C_5Me_5)_2Sm(OC_6HMe_4$-2,3,5,6) (172(1)°)[12] and is among the smallest ones observed so far in samarium(III) aryloxides (163−179°).[4a,b,10,13]

The ^{1}H NMR spectrum of **3** in C_6D_6 was well-resolved. The C_5Me_5 groups appeared at δ 0.77 as a singlet. The aromatic protons of the ArO group gave a singlet at δ 8.32, while the *para*-^{t}Bu group showed a singlet at δ 2.18. The *ortho*-^{t}Bu groups of the ArO ligand appeared as a singlet at very high field (δ −4.51), probably due to the shielding of the Cp* ring current.

Heteroleptic Samarium(II) Aryloxide/Pentamethylcyclopentadienide Complexes with the "(C_5Me_5)K" Ligand. Parallel to the alcoholysis approach described above, the synthesis of heteroleptic samarium(II) aryloxide/pentamethylcyclopentadienide complexes was also attempted by a metathesis reaction of the samarium(II) bis(aryloxide) $Sm(OAr)_2(THF)_3$ with C_5M_5K. Reaction of $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_3{}^tBu_2$-2,6) with 1 equiv of C_5Me_5K in THF afforded a green crystalline product **4a** in about 40% yield (Scheme 2). The use of 2 equiv of C_5Me_5K in this reaction increased the yield of **4a** to 71%. Single crystals suitable for diffraction studies were obtained by recrystallization of **4a** from THF/toluene. It has been revealed that **4a** is a heteroleptic samarium(II) aryloxide/pentamethylcyclopentadienide complex coordinated by a neutral "(μ,η^5-C_5Me_5)K(THF)$_2$" ligand (Figure 3 and Table 3). The intermolecular K···C_5Me_5 interactions constitute a polymeric structure in which each C_5Me_5 is bonded in a μ,η^5-fashion to a Sm atom on one side and to a K atom on the other side. There is a mirror symmetry in this molecule. The mirror plane, which is oriented along the polymer chain, contains Sm(1), K(1), O(1), C(1), C(4), C(11), C(14), C(17), and C(20) and bisects the C(9)−C(9′) and C(15)−C(15′) bonds. The μ-C_5Me_5 bridges are almost symmetric. The lengths of the Sm−Cp*$_{C(9)-C(9')}$ bonds (average 2.86(2) Å) are almost the same as those of the Sm−Cp*$_{C(15)-C(15')}$ bonds (average 2.87(2) Å), both of which are comparable with those reported for $(C_5Me_5)_2Sm(THF)_2$ (average 2.86 (2) Å)[9] and $(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4, 2.860(6) Å)[4a] but longer than those in **1c** (2.78(1) Å) and $(C_5Me_5)_2Sm$ (average 2.79(1) Å).[6a] Similarly, the lengths of the K−Cp*$_{C(15)-C(15')}$ bonds (average 3.15(3) Å) are almost the same as those of the K−Cp*$_{C(9'')-C(9'')}$ bonds (average 3.13(3) Å). These K−Cp* bond distances (average 3.14(3) Å) are slightly longer than those in $[(C_5Me_5)K(py)_2]_\infty$ (py = pyridine) (average 3.030(2) Å),[16] $[(C_5H_4(SiMe_3))K]_\infty$ (average 3.03(1) Å),[17] and $(C_5(CH_2C_6H_5)_5))K(THF)_3$ (average 3.035(5) Å).[18] The distance of the Sm−OAr bond (2.29(2) Å) in **4a** is comparable with those found in other samarium(II) aryloxides, such as $Sm(OAr)_2(THF)_3$ (2.29(1)−2.35(1) Å) (Ar = $C_6H_2Bu^t{}_2$-2,6-Me-4),[4a,d] $(C_5Me_5)Sm(OAr)(HMPA)_2$ (2.345(4) Å),[4a] $[Sm(OAr)(\mu\text{-I})(THF)_3]_2$ (2.300(10) Å),[4a] and $[KSm(\mu\text{-OAr})_3(THF)]_\infty$ (2.319(9)−2.362(6) Å).[4c]

Complex **4a** could be viewed as a $(C_5Me_5)K$ adduct of the monomeric form of **1a**. In fact, reaction of **1a** with 2 equiv of C_5Me_5K in THF gave **4a** in 85% isolated yield (Scheme 2). The similar reactions of **1b,c** with C_5Me_5K afforded **4b,c**. Complexes **4a**−**c** could also be obtained in 80−85% yields by reaction of $(C_5Me_5)_2Sm(THF)_2$ with ArOK in THF (Scheme 2).

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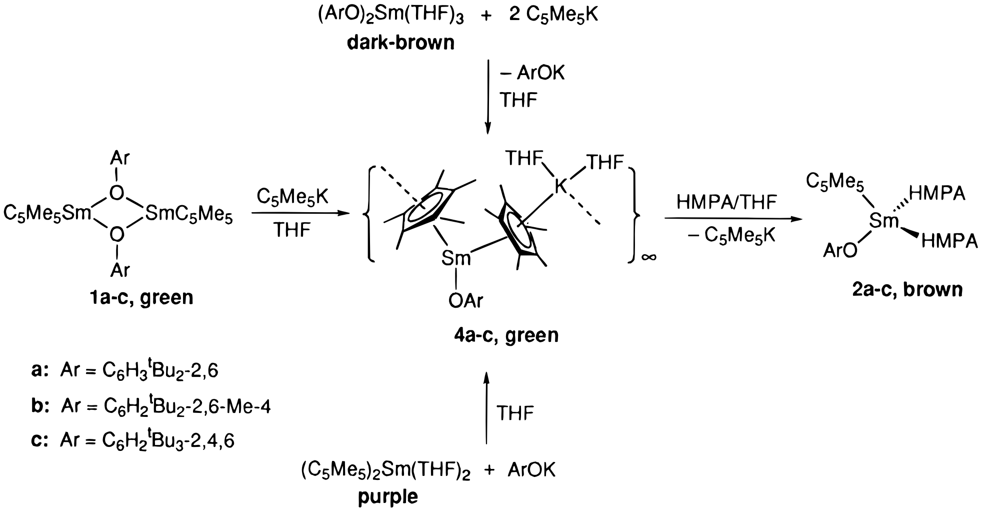
Scheme 2



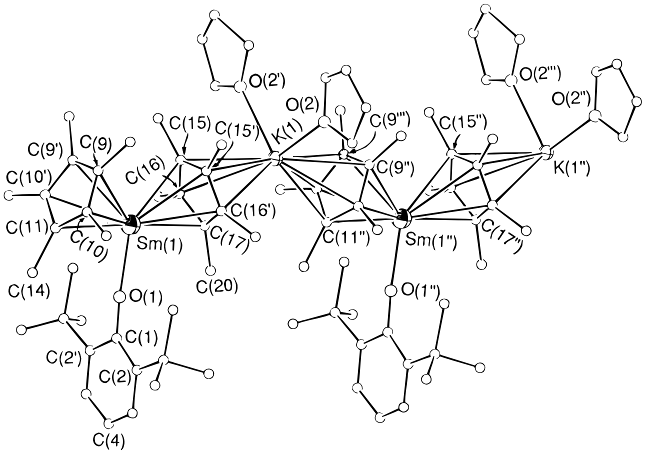


Figure 3. Extended structure of **4a**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4a

Sm(1)−O(1)	2.29 (2)	Sm(1)−C(9)	2.87(3)
Sm(1)−C(10)	2.87(2)	Sm(1)−C(11)	2.84(2)
Sm(1)−C(15)	2.88(2)	Sm(1)−C(16)	2.87(2)
Sm(1)−C(17)	2.86(3)	K(1)−O(2)	2.79(2)
K(1)−C(15)	3.157(15)	K(1)−C(16)	3.142(19)
K(1)−C(17)	3.13(3)	K(1)−C(9″)	3.19(2)
K(1)−C(10″)	3.10(3)	K(1)−C(11″)	3.11(3)
O(1)−C(1)	1.32(3)		

Sm(1)−O(1)−C(1)	175(1)
O(2)−K(1)−O(2′)	103.7(6)
O(1)−Sm(1)-Cp*$_{C(9)-C(9')}$(centroid)	113.2(7)
O(1)−Sm(1)−Cp*$_{C(15)-C(15')}$(centroid)	112.3(7)
Cp*$_{C(9)-C(9')}$(centroid)−Sm(1)−Cp*$_{C(15)-C(15')}$(centroid)	134.5(8)
Cp*$_{C(9'')-C(9''')}$(centroid)−K(1)−Cp*$_{C(15)-C(15')}$(centroid)	142.2(7)

Complex **4b** possesses a polymeric structure similar to that of **4a**, however, the orientation of the ArO group in **4b** is rather different from that in **4a**. As shown in Figure 4 and Table 4, the ArO group in **4b** (Ar = C_6H_2-Bu^t_2-2,6-Me-4) is severely bent toward the central Sm metal, which thus results in an agostic interaction between Sm and a ^{t}Bu methyl (C(10)) group. The Sm−O−Ar angle in **4b** is as small as 126.7(5)°, which is in sharp contrast to that (175(1)°) in **4a**. The Sm(1)···C(10) distance in **4b** is 3.176(8) Å, which is shorter than the shortest intermolecular Sm···C distance (3.22(1) Å) found in $(C_5Me_5)_2$Sm, in which an intermolecular metal···methyl interaction was thought to be present.[6a] The interaction between Sm(1) and C(10) in **4b** is probably stronger than that between Sm(1) and C(9) observed in **3** (Sm(1)···C(9), 3.055(7) Å), since Sm(II) is ca. 0.19 Å larger than Sm(III) when both have the same coordination number.[19] The hydrogen atoms on the C(10) carbon in **4b** could be successfully located by the difference Fourier syntheses. The Sm(1)···H(10A) and Sm(1)···H(10C) distances are 2.81(7) and 2.76(8) Å, respectively, which are virtually shorter than the shortest Yb···H distances (2.85(6) and 2.76(8) Å) observed in

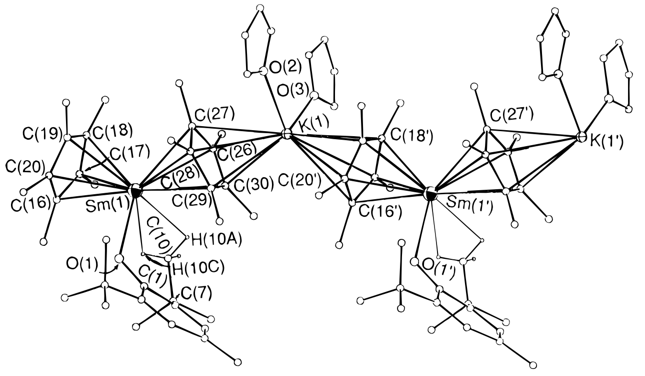


Figure 4. Extended structure of **4b**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4b

Sm(1)−O(1)	2.330(6)	Sm(1)−C(16)	2.897(7)
Sm(1)−C(17)	2.889(7	Sm(1)−C(18)	2.889(8)
Sm(1)−C(19)	2.844(8)	Sm(1)−C(20)	2.859(7)
Sm(1)−C(26)	2.911(7)	Sm(1)−C(27)	2.893(7)
Sm(1)−C(28)	2.877(7)	Sm(1)−C(29)	2.920(6)
Sm(1)−C(30)	2.953(7)	Sm(1)···C(10)	3.176(8)
Sm(1)···H(10A)	2.81(7)	Sm(1)···H(10C)	2.76(7)
K(1)−O(2)	2.888(8)	K(1)−O(3)	2.787(9)
K(1)−C(16)	3.220(8)	K(1)−C(17)	3.214(8)
K(1)−C(18)	3.154(8)	K(1)−C(19)	3.087(8)
K(1)−C(20)	3.110(8)	K(1)−C(26)	3.159(7)
K(1)−C(27)	3.270(7)	K(1)−C(28)	3.214(7)
K(1)−C(29)	3.063(7)	K(1)−C(30)	3.006(7)
O(1)−C(1)	1.317(10)		

O(1)−Sm(1)−Cp*$_{C(16-20)}$(centroid)	101.9(3)
O(1)−Sm(1)−Cp*$_{C(26-30)}$(centroid)	120.4(2)
Cp*$C_{(16-20)}$(centroid)−Sm(1)−Cp*$_{C(26-30)}$(centroid)	137.6(3)
Cp*$_{C(16'-20')}$(centroid)−K(1)−Cp*$_{C(26-30)}$(centroid)	140.2(3)
O(2)−K(1)−O(3)	106.9(3)
Sm(1)−O(1)−C(1)	126.7(5)
Sm(1)−C(10)−C(7)	117.9(5)

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[19] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

$Yb(N(SiMe_3)_2)_2(Me_2PCH_2CH_2PMe_2)$,[20] when the difference in size between Sm(II) and Yb(II) is considered.[21] These data implied that a stronger metal···H interaction was probably present in **4b**, as compared to that in $Yb(N(SiMe_3)_2)_2(Me_2PCH_2CH_2PMe_2)$.[20]

The distances of the Sm-Cp* bonds in **4b** (Sm−$Cp^*_{C(16)-C(20)}$ average 2.876(8), Sm−$Cp^*_{C(26)-C(30)}$ average 2.911(7) Å) are comparable with those in **4a**, and so are the K−Cp* bonds (K−$Cp^*_{C(26)-C(30)}$ average 3.142(7), K−$Cp^*_{C(16')-C(20')}$ average 3.157(8) Å) and the Sm−OAr bond (2.330 Å).

The structural difference between **4a** and **4b** probably resulted from the difference in the steric repulsion of adjacent polymer chains. The presence of a Me group in the para position of the phenyl ring in **4b** would result in a stronger steric repulsion with the adjacent chains and, thus, force the ArO group to bend toward the central metal. The intramolecular metal···methyl interactions probably compensate to some extent the resulting strain. An examination of the packing diagrams of **4a,b** by computer graphics supported this steric consideration.

Complexes **4a**−**c** were almost insoluble in benzene but soluble in THF to give a dark-green solution. Due to their poor solubility in benzene, attempts to measure their ^1H NMR spectra in C_6D_6 were not successful (only the solvent signal was observed). The ^1H NMR spectra of **4a**−**c** in THF-d_8 seemed to be concentration dependent. In dilute THF-d_8 solutions, the ^1H NMR spectra of **4a**−**c** were very similar to those of a mixture of $(C_5Me_5)_2Sm(THF)_2$[9] and KOAr. The C_5Me_5 groups appeared as a singlet at δ 1.59−1.61, which was assignable to those of $(C_5Me_5)_2Sm(THF)_2$,[9] while the signals for the ArO groups showed little influence of the paramagnetic Sm(II) species (see Experimental Section) and could be assigned to KOAr. In concentrated THF-d_8 solutions, the ^1H NMR spectra of **4a**−**c** were very complex and unassignable; two broad signals at δ 15−16 and 6−7 were also observed. These results suggested that **4a**−**c** in THF might exist in an equilibrium with $(C_5Me_5)_2Sm(THF)_2$ and KOAr. In concentrated THF solutions, this equilibrium probably shifted toward **4a**−**c**. In fact, complexes **4a**−**c**, rather than $(C_5Me_5)_2Sm(THF)_2$ and KOAr, were quantitatively obtained when their THF solutions were concentrated.

The coordination of $(C_5Me_5)K(THF)_2$ rather than THF to the Sm(II) ions in **4a**−**c** was surprising to us, since complexes **4a**−**c** were isolated from THF and the Sm(II) ion has been known to be very fond of the coordination of THF.[4,6a,7,9] Moreover, although the (μ,η^5-Cp*)K-type of bridging was previously observed in the polymeric potassium complexes $[(C_5Me_5)K(pyridine)_2]_\infty$[16] and $[(C_5H_4(SiMe_3))K]_\infty$,[17] coordination of a (μ,η^5-Cp*)K unit to a transition metal is, to the best of our knowledge, unprecedented.[22]

The easy formation of **4a**−**c** in the present reactions suggested that the coordinatively unsaturated Sm(II) center in $(C_5Me_5)Sm(OAr)$ preferred the coordination of $(C_5Me_5)K$ to that of THF. Reaction of **4a**−**c** with a more strongly coordinative ligand like HMPA, however, easily substituted the $(C_5Me_5)K$ ligand and gave the HMPA-coordinated monomeric heteroleptic complexes $(C_5Me_5)Sm(OAr)(HMPA)_2$ (**2a**−**c**) in 90−95% isolated yields (Scheme 2).

The observation of metal···methyl interactions in **4b** and the easy formation of **2a**−**c** from **1a**−**c** or **4a**−**c** suggested that the unsolvated Sm(II) centers in **1a**−**c** and **4a**−**c** should be capable of accepting approaches of other appropriate substrates. Further studies on the reactivity of these new complexes are under progress.

Experimental Section

General Methods. All manipulations were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by passing through a Dryclean column (4 Å 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 (4 Å) 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 2 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 during all of the measurements. ^1H 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. Hexamethylphosphoric triamide (HMPA) was distilled from Na under reduced pressure, degassed by the freeze−thaw method (three times), and dried over molecular sieves (4 Å). Deuterated solvents (C_6D_6, THF-d_8) were commercial grade, and degassed by the freeze−thaw method (three times) and dried over fresh Na chips in the glovebox. Samarium metal (40 mesh) was obtained from Rare Metallic Co. and Aldrich. $(C_5Me_5)_2Sm(THF)_2$,[9] C_5Me_5K,[23] and $Sm(OAr)_2(THF)_3$[4a] (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^{t}Bu; only physical data are recorded below) were prepared according to literature procedures. ArOK was synthesized by reaction of ArOH (Ar = $C_6H_2{}^tBu_2$-2,6-R-4, R = H, Me, ^{t}Bu) with K in THF.

$Sm(OC_6H_3{}^tBu_2\text{-}2,6)_2(THF)_3$. ^1H NMR (C_6D_6, 22 °C), δ 11.01 (br s, 12 H, THF), 5.69 (br s, 12 H, THF), 2.50 to −1.50 (br s, 42 H, ArO). ^1H NMR (THF-d_8, 22 °C): δ 0.39 (t, J = 7.5 Hz, 2 H, C_6H_3), −0.37 (s, 36 H, ^{t}Bu), −0.97 (d, J = 7.5 Hz, 4 H, C_6H_3). Crystal data: $C_{40}H_{66}O_5Sm$, M_w = 777.37, orthorhombic, space group $P2_1ab$, a = 19.117(8) Å, b = 21.810(9) Å, c = 10.036(4) Å, U = 4184(3) Å^3, Z = 4, D_c = 1.23 g cm^{-3}. Anal. Calcd for $C_{40}H_{66}O_5Sm$: C, 61.80; H, 8.56. Found: C, 61.58; H, 8.64. Mp: 170−172 °C.

$Sm(OC_6H_2{}^tBu_3\text{-}2,4,6)_2(THF)_3$. ^1H NMR (C_6D_6, 22 °C): δ 9.25 (br s, 12 H, THF), 4.43 (br s, 12 H, THF), 0.18 (s, 36 H, ^{t}Bu), −0.43 (s, 4 H, C_6H_2), −1.71 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{48}H_{82}O_5Sm$: C, 64.81; H, 9.29. Found: C, 65.20; H, 9.33. Mp: 160−162 °C.

$[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_3{}^tBu_2$-2,6) (1a). To a purple toluene solution (5 mL) of $(C_5Me_5)_2Sm(THF)_2$ (1.13 g, 2 mmol) was added ArOH (0.41 g, 2 mmol) in toluene (5 mL).

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(21) Sm(II) is ca. 0.14 Å smaller than Yb(II) when both have the same coordination number.[19]

(22) The presence of K···Cp···Nd interactions in a "ate" complex, $\{K[(C_5H_5)_2Nd(OC_6H_3Me_2\text{-}2,6)_2]\}_\infty$, was recently observed see: Evans, W. J.; Ansari, M. A.; Khan, S. I. *Organometallics* **1995**, *14*, 558.

(23) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

Table 5. Summary of Crystallographic Data

	1c	**3**	**4a**	**4b**
formula	$C_{56}H_{88}O_2Sm_2$	$C_{38}H_{59}OSm$	$C_{42}H_{67}O_3KSm$	$C_{43}H_{69}O_3KSm$
fw	1094.12	682.29	809.50	823.53
cryst syst	trigonal	orthorhombic	monoclinic	triclinic
space group	$R\bar{3}$ (No. 148)	$Pnm2_1$ (No. 31)	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)
a (Å)	32.435(3)	12.256(7)	13.810(2)	13.002(3)
b (Å)	32.435(3)	13.498(7)	17.174(2)	17.202(4)
c (Å)	13.193(2)	10.541(6)	10.338(3)	10.373(6)
α (deg)				91.40(3)
β (deg)			100.80(2)	103.97(3)
γ (deg)				100.38(2)
V (Å^3)	12 019(3)	1744(2)	2408.5(9)	2209(1)
Z	9	2	2	2
D_{calcd} (g cm^{-3})	1.36	1.30	1.12	1.24
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
data collcd	$\pm h, +k, +l$	$+h, +k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$
scan speed (deg/min)	6	6	6	6
2θ range (deg)	3−55	3−50	3−55	3−55
μ (cm^{-1})	44.399	36.795	13.372	14.591
no. of reflns collcd	6771	1860	5046	11038
no. of unique reflns	4419	1687	4579	10152
no. of reflns with ($I_o > 3\sigma(I_o)$)	3627	1604	2086	6090
no. of variables	271	201	226	550
R_{int}	0.03		0.05	0.03
R (%)	3.92	3.51	7.77	4.51
R_w (%)	5.10	4.54	8.68	5.12

The resulting green mixture was stirred at room temperature for 3 h. Evaporation of the solvent gave a green crystalline product, which after washing with toluene afforded analytically pure **1a** (1.88 g, 1.92 mmol, 96% yield). $(C_5Me_5)_2Sm(THF)_2$ and 1 equiv of $(ArO)_2Sm(THF)_3$ were mixed in toluene and also gave **1a** in 97% isolated yield. ^{1}H NMR (C_6D_6, 22 °C): δ 33.69 (s, 36 H, ^{t}Bu), −0.01 (br s, 2 H, *para*-C_6H_3), −0.17 (br s, 4 H, *meta*-C_6H_3), −5.31 (s, 30 H, C_5Me_5). Anal. Calcd for $C_{48}H_{72}O_2Sm_2$: C, 58.72; H, 7.39. Found: C, 58.40; H, 7.32. Mp: 262.5−263.0 °C.

[$(C_5Me_5)Sm(\mu$-OAr)]$_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) (1b). Complex **1b** was synthesized similar to **1a** in 95% yield. ^{1}H NMR (C_6D_6, 22 °C): δ 34.30 (s, 36 H, ^{t}Bu), −0.70 (s, 4 H, C_6H_2), −4.28 (s, 6 H, Me), −5.13 (s, 30 H, C_5Me_5). Anal. Calcd for $C_{50}H_{76}O_2Sm_2$: C, 59.46; H, 7.59. Found: C, 59.88; H, 7.63. Mp: 281−282 °C.

[$(C_5Me_5)Sm(\mu$-OAr)]$_2$ (Ar = $C_6H_2{}^tBu_3$-2,4,6) (1c). Complex **1c** was synthesized similar to **1a** in 96% yield. Slow diffusion of a toluene solution of ArOH into a toluene solution of $(C_5Me_5)_2Sm(THF)_2$ in a U-tube afforded dark-green blocks of **1c**, which were suitable for X-ray analysis. ^{1}H NMR (C_6D_6, 22 °C): δ 34.40 (s, 36 H, *ortho*-^{t}Bu), −0.27 (s, 4 H, C_6H_2), −3.88 (s, 18 H, *para*-^{t}Bu), −5.10 (s, 30 H, C_5Me_5). Anal. Calcd for $C_{56}H_{88}O_2Sm_2$: C, 61.48; H, 8.11. Found: C, 61.33; H, 8.20. Mp: 272.0−272.5 °C.

$(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_3{}^tBu_2$-2,6) (2a). Addition of HMPA (70 μl, 0.4 mmol) to **1a** (98 mg, 0.1 mmol) in THF (5 mL) gave a dark brown solution, which was stirred at room temperature for 1 h. After reduction of the solution volume under reduced pressure, ether was layered to precipitate **2a** as brown blocks (160 mg, 0.188 mmol, 94% yield). For the synthesis of **2a**, isolation of **1a** was not necessary. Addition of 2 equiv of HMPA to a reaction mixture of $(C_5Me_5)_2Sm(THF)_2$ and ArOH in toluene afforded **2a** similarly. ^{1}H NMR (C_6D_6, 22 °C): δ 5.12 (s, 15 H, C_5Me_5), 4.15 (br s, 36 H, NMe), 3.07 (t, J = 7.7 Hz, 1 H, *para*-C_6H_3), 2.81 (s, 18 H, ^{t}Bu), 2.51 (d, J = 7.7 Hz, 2 H, *meta*-C_6H_3). Anal. Calcd for $C_{36}H_{72}N_6O_3P_2Sm$: C, 50.91; H, 8.54; N, 9.89. Found: C, 50.80; H, 8.41; N, 10.01. Mp: 260−262 °C.

$(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) (2b). Complex **2b** was obtained similar to **2a**, by reaction of **1b** with 4 equiv of HMPA in 92% yield. Addition of 2 equiv of HMPA to a reaction mixture of $(C_5Me_5)_2Sm(THF)_2$ and ArOH in toluene also afforded **2b** similarly. Its ^{1}H NMR spectrum and cell parameters were identical to those obtained previously.[4a] ^{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).

$(C_5Me_5)Sm(OAr)(HMPA)_2$ (Ar = $C_6H_2{}^tBu_3$-2,4,6) (2c). Complex **2c** was obtained similar to **2a**, by reaction of **1c** with 4 equiv of HMPA in 90% yield. Addition of 2 equiv of HMPA to a reaction mixture of $(C_5Me_5)_2Sm(THF)_2$ and ArOH in toluene also afforded **2c** similarly. ^{1}H NMR (C_6D_6, 22 °C): δ 5.24 (s, 15 H, C_5Me_5), 4.29 (br s, 36 H, NMe), 2.73 (s, 18 H, *ortho*-^{t}Bu), 2.38 (s, 2 H, C_6H_2), −0.44 (s, 9 H, *para*-^{t}Bu). Anal. Calcd for $C_{40}H_{80}N_6O_3P_2Sm$: C, 53.06; H, 8.91; N, 9.28. Found: C, 53.36; H, 8.84; N, 9.31. Mp: 225−227 °C.

$(C_5Me_5)_2Sm(OAr)$ (Ar = $C_6H_2{}^tBu_3$-2,4,6) (3). A green toluene solution of **1c** (55 mg, 0.05 mmol) in a Schlenk flask was exposed to the air for a few seconds. The color of the solution changed gradually to yellow. Evaporation of the solvent gave a yellow solid, which was redissolved into toluene and filtered. Concentration of the filtrate and addition of hexane afforded **3** as orange-red crystals (24 mg, 0.35 mmol, 35% yield based on Sm). ^{1}H NMR (C_6D_6, 22 °C): δ 8.32 (s, 2 H, C_6H_2), 2.18 (s, 9 H, *para*-^{t}Bu), 0.77 (s, 30 H, C_5Me_5), −4.51 (s, 18 H, *ortho*-^{t}Bu). Anal. Calcd for $C_{38}H_{59}OSm$: C, 66.90; H, 8.72. Found: C, 70.01; H, 8.62. Mp: 182−184 °C.

[$(\mu,\eta^5$-$C_5Me_5)Sm(OAr)(\mu,\eta^5$-$C_5Me_5)K(THF)_2]_\infty$ (Ar = $C_6H_3{}^tBu_2$-2,6) (4a). Method A: addition of a brown THF solution (10 mL) of $(ArO)_2Sm(THF)_3$ (777 mg, 1 mmol) to a THF suspension (2 mL) of C_5Me_5K (348 mg, 2 mmol) gave a green mixture immediately, which was stirred at room temperature for 18 h to yield a dark-green solution. The solution was filtered through a frit and concentrated under reduced pressure. Green blocks of **4a** were precipitated overnight, together with fine colorless powders of KOAr. The KOAr was removed by washing with toluene. A second crop of **4a** could be obtained by similar treatment of the mother liquor. Total yield of **4a**: 575 mg, 0.71 mmol, 71% yield. Using one equiv of C_5Me_5K in this reaction also afforded **2a**, but in a lower yield. Method B: addition of a brown THF solution (10 mL) of **1a** (982 mg, 1 mmol) to a THF suspension (2 mL) of C_5Me_5K (348 mg, 2 mmol) gave a green mixture immediately, which was stirred at room temperature for 5 h to yield a dark-green solution. The solution was filtered through a frit and concentrated under reduced pressure. Addition of toluene precipitated **4a** as green blocks (1376 mg, 1.70 mmol, 85% yield). Method C: addition of a THF solution (5 mL) of ArOK (244 mg, 1 mmol) to a purple THF solution (5 mL) of $(C_5Me_5)_2Sm(THF)_2$ (565 mg, 1 mmol) gave a green solution gradually, which was stirred at room temperature for 5 h. After concentration and addition of toluene, green blocks of **4a** (672 mg, 0.83 mmol, 83% yield) were obtained. ^{1}H NMR (concentration dependent) (THF-d_8, dilute, 22 °C): δ 6.67 (d, 2 H, J = 7.3 Hz, *meta*-C_6H_3), 5.67 (t, 1 H, J = 7.3 Hz, *para*-C_6H_3), 1.59 (s, 30 H, C_5Me_5), 1.34 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{42}H_{67}O_3KSm$: C, 62.32; H, 8.34. Found: C, 62.39; H, 8.41. Mp: 263−264 °C.

[(μ,η^5-C_5Me_5)Sm(OAr)(μ,η^5-C_5Me_5)K(THF)$_2$]$_\infty$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) (4b). Complex **4b** was synthesized similar to **4a**. Method A: 54% yield. Method B: 82% yield. Method C: 85% yields. ^{1}H NMR (concentration dependent) (THF-d_8, dilute, 22 °C): δ 6.49 (s, 2 H, C_6H_2), 2.00 (s, 3 H, Me), 1.59 (s, 30 H, C_5Me_5), 1.32 (s, 18 H, ^{t}Bu). Anal. Calcd for $C_{43}H_{69}O_3KSm$: C, 62.72; H, 8.45. Found: C, 63.09; H, 8.27. Mp: 178−180 °C (decomposed to red solid, which remained up to 300 °C).

[(μ,η^5-C_5Me_5)Sm(OAr)(μ,η^5-C_5Me_5)K(THF)$_2$]$_\infty$ (Ar = $C_6H_2{}^tBu_3$-2,4,6) (4c). Complex **4c** was synthesized similar to **4a**. Method B: 80% yield. Method C: 82% yield. ^{1}H NMR (concentration dependent) (THF-d_8, dilute, 22 °C): δ 6.76 (s, 2 H, C_6H_2), 1.61 (s, 30 H, C_5Me_5), 1.34 (s, 18 H, *ortho*-^{t}Bu), 1.16 (s, 9 H, *para*-^{t}Bu). Anal. Calcd for $C_{46}H_{75}O_3KSm$: C, 63.83; H, 8.73. Found: C, 63.69; H, 8.67. Mp: 273−274 °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 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, λ = 0.710 73 Å, graphite monochromator, ω−2θ scan or ω-scan (for **1c**)). Lattice constants and orientation matrices were obtained by least-squares refinement of 22 reflections with 30° ≤ 2θ ≤ 35°. Three reflections were monitored periodically as a check for crystal decomposition or movement, and no significant 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 5. Structures were solved by direct methods using SIR92 in the CRYSTAN-GM software package. 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 $\sum(|F_o| - |F_c|)^2$. Neutral atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[24] The residual electron densities were of no chemical significance. Crystal data, data collection, and processing parameters are given in Table 5.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1c**, **3**, and **4a,b** (22 pages). Ordering information is given on any current masthead page.

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(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.