

A Novel Binuclear Samarium(II) Complex Bearing Mixed Cyclopentadienide/Siloxide Ligands: [(C₅Me₅)Sm{μ-OSi(O^tBu)₃}₃Sm]. Synthesis, Structure, Electron-Transfer, and Unusual Metal-Coordination Reactions

Masayoshi Nishiura, Zhaomin Hou,* and Yasuo Wakatsuki

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan, and PRESTO, Japan Science and Technology Agency (JST)

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The reaction of (C₅Me₅)₂Sm(thf)₂ with 1.5 equiv of (tBuO)₃SiOH in toluene gave the unsymmetrical binuclear Sm(II) complex [(C₅Me₅)Sm{μ-OSi(O^tBu)₃}₃Sm] (**1**) in 93% isolated yield. The use of 1 equiv of (tBuO)₃SiOH in this reaction also afforded **1** albeit in low yield. Addition of 4 equiv of hexamethylphosphoric triamide (hmpa) to a toluene solution of **1** gave (C₅Me₅)Sm{OSi(O^tBu)₃}₂(hmpa)₂ (**2**) as the only isolable product. The reaction of **1** with 1 equiv of azobenzene in toluene gave the corresponding binuclear Sm(III) azobenzene-dianion complex [(C₅Me₅)Sm{μ-OSi(O^tBu)₃}₂(μ,η¹:η²-N₂Ph₂)SmOSi(O^tBu)₃] (**3**) in 64% isolated yield. When **1** was treated with ArOH (Ar = C₆H₂(Bu-2,6-Me-4) or phenylacetylene in toluene, a novel trinuclear Sm(II)/Sm(III) mixed valence “inverse sandwich” complex, [(tBuO)₃SiO]₃Sm^{III}-(μ,η⁵:η⁵-C₅Me₅)Sm^{II}{μ-OSi(O^tBu)₃}₃Sm^{II}] (**4**), was isolated (ca. 20%). Complex **4** could alternatively be obtained in high yields (80–85%) by reaction of **1** with 1 equiv of the Sm(III) tris(siloxide) complex Sm{OSi(O^tBu)₃}₃(thf)₂ (**5**) or [Sm{μ-OSi(O^tBu)₃}₂{OSi(O^tBu)₃}₂]₂ (**8**), through coordination of the C₅Me₅ unit to the Sm(III) center. Similarly, the reactions of **1** with Gd{OSi(O^tBu)₃}₃(thf)₂ (**6**) and Sm(OSiPh₃)₃(thf)₃·(thf) (**7**) yielded the corresponding Sm(II)/Gd(III) heterometallic complex [(tBuO)₃SiO]₃Gd^{III}(μ,η⁵:η⁵-C₅Me₅)Sm^{II}{μ-OSi(O^tBu)₃}₃Sm^{II}] (**9**) (88%) and the Sm(II)/Sm(III) mixed valence complex [{Ph₃SiO]₃Sm^{III}(μ,η⁵:η⁵-C₅Me₅)Sm^{II}{μ-OSi(O^tBu)₃}₃Sm^{II}] (**10**) (78%), respectively. The reaction of **1** with the Sm(II) silylamido complex Sm{N(SiMe₃)₂}₂(thf)₂ in toluene yielded a linear pentanuclear Sm(II) ion-pair complex, [Sm^{II}{μ-OSi(O^tBu)₃}₃Sm^{II}(μ,η⁵:η⁵-C₅Me₅)Sm^{II}{μ-OSi(O^tBu)₃}₃Sm^{II}]-[Sm^{II}{N(SiMe₃)₂}₃] (**11**). Complexes **1**, **3**, **4**, and **8–11** have all been structurally characterized by X-ray crystallographic studies.

Introduction

The organometallic chemistry of Sm(II) has witnessed rapid progress in the last two decades.¹ In this development, the samarocene(II) complexes such as (C₅Me₅)₂-Sm(thf)_n (n = 0–2)² have occupied an especially important place. The high reactivity of the metallocene complexes is attributed mostly to their good solubility and the strong reducing power of Sm(II). In principle, heteroleptic Sm(II) complexes bearing one C₅Me₅ and one monodentate anionic ancillary ligand should offer a sterically and electronically unique environment for the Sm(II) center.^{1f} However, this type of complex has

received less attention because of difficulty in isolation. By use of appropriate ligand combinations, we recently isolated and structurally characterized a series of the mixed-ligand-supported Sm(II) complexes, such as [(C₅-Me₅)Sm(μ-OAr)]₂ (Ar = C₆H₂(Bu-2,4,6)),³ [(C₅Me₅)Sm(ER)-(C₅Me₅)K(thf)₂]_n (ER = C₆H₂(Bu-2,6-Me-4), SC₆H₂(Pr-2,4,6), N(SiMe₃)₂, PH(C₆H₂(Bu-2,4,6)), SiH₃, CH(SiMe₃)₂),⁴ Me₂Si(C₅Me₄)(NPh)Sm(thf)_x,⁵ and Me₂Si(C₅Me₄)(PC₆H₂(Bu-2,4,6))Sm(thf)₃,⁶ and found that such heteroleptic Sm(II) complexes could show unique reactivity that differs from those of the homoleptic analogues.^{1f,4–6} The importance of the steric and electronic factors of the monodentate anionic ligands in determining the struc-

* Corresponding author. E-mail: houzh@riken.jp.

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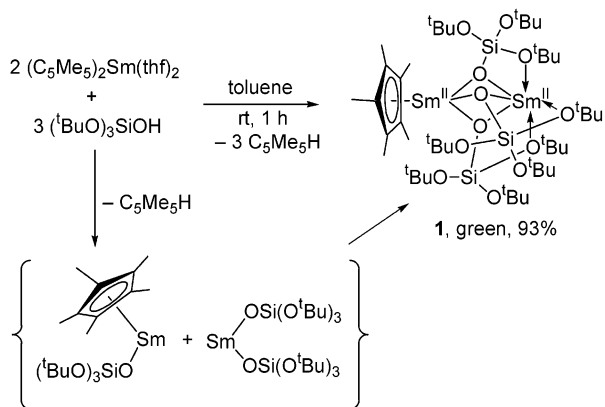
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Scheme 1



ture and reactivity of these complexes was well recognized. Preparation of related heteroleptic Sm(II) complexes bearing different ligating moieties is, therefore, of obvious interest.⁷

In this paper, we wish to report a novel binuclear Sm(II) complex that bears mixed pentamethylcyclopentadienide/siloxide ligands, [(C₅Me₅)Sm{μ-OSi(O^tBu)₃}₃-Sm]. This complex exhibits unprecedented features both in structure and in reactivity. In addition to the “normal” reducing chemistry of Sm(II), it shows unusual coordination ability to a Lewis acidic metal center such as Sm(II), Sm(III), or Gd(III) via the C₅Me₅ part to yield a new class of polynuclear Sm(II) or mixed valence Sm(II)/Ln(III) complexes that possess novel “inverse sandwich” structures.

Results and Discussion

Synthesis and Structure of Sm(II) Complexes Bearing Mixed Cyclopentadienide/Siloxide Ligands. To prepare a Sm(II) complex bearing mixed cyclopentadienide/siloxide ligands, partial protonation of (C₅Me₅)₂Sm(thf)₂ with a silanol was employed, analogously to our previous preparation of the Sm(II) mixed cyclopentadienide/aryloxide complexes such as [(C₅Me₅)Sm(μ-OAr)]₂ (Ar = C₆H₂/Bu₃-2,4,6).³ Unexpectedly to us, however, the reaction of (C₅Me₅)₂Sm(thf)₂ with 1 equiv of (tBuO)₃SiOH in toluene yielded the unsymmetrical binuclear complex [(C₅Me₅)Sm{μ-OSi(O^tBu)₃}₃-Sm] (**1**), together with the unreacted (C₅Me₅)₂Sm(thf)₂. Complex **1** could be viewed formally as a combination of the expected partial protonation product [(C₅Me₅)Sm{OSi(O^tBu)₃}] and the full protonation product Sm{OSi(O^tBu)₃}₂ (Scheme 1). The use of 1.5 equiv of (tBuO)₃SiOH, therefore, afforded **1** in 93% isolated yield (Scheme 1).

An X-ray analysis established that the two Sm(II) atoms in **1** are bridged by three OSi(O^tBu)₃ ligands, in which one Sm end (Sm1) is capped by a C₅Me₅ ligand, while the other Sm end (Sm2) is wrapped by three O^tBu groups of the siloxide ligands via the neutral oxygen atoms (O4, O5, and O6) (Figure 1 and Table 1). The siloxide bridges are asymmetric. The bond distances of the Sm1–O(siloxide) bonds (av 2.440(3) Å) are signifi-

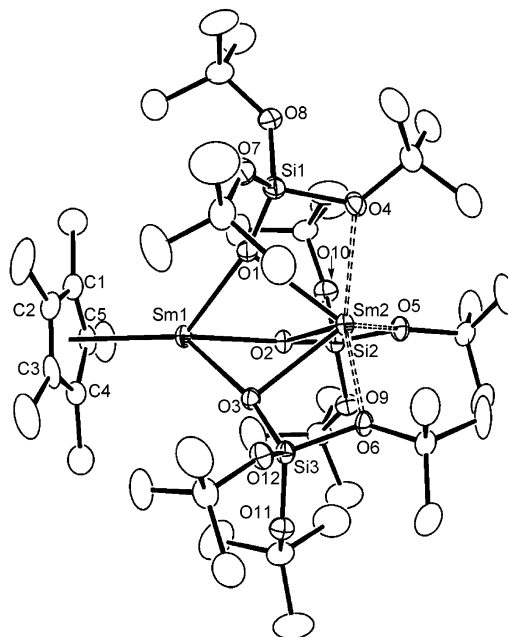


Figure 1. ORTEP drawing of **1**. The lattice solvent is omitted for clarity.

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

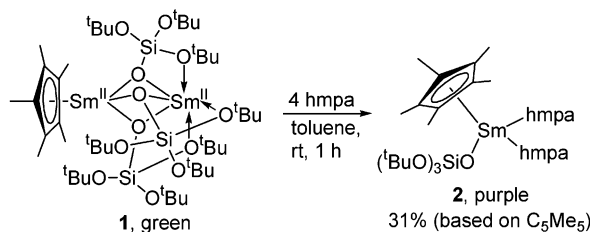
Sm1–C1	2.867(5)	Sm1–C2	2.863(6)
Sm1–C3	2.830(6)	Sm1–C4	2.834(5)
Sm1–C5	2.846(5)		
Sm1–O1	2.432(3)	Sm1–O2	2.438(3)
Sm1–O3	2.450(3)	Sm2–O1	2.494(3)
Sm2–O2	2.523(3)	Sm2–O3	2.503(3)
Sm2–O4	2.649(3)	Sm2–O5	2.597(3)
Sm2–O6	2.643(3)	Si1–O1	1.586(3)
Sm1...Sm2	3.4485(5)		
O1–Sm1–O2	78.7(1)	Sm1–O1–Sm2	88.84(9)
Sm1–O2–Sm2	88.06(9)	Sm1–O3–Sm2	88.3(1)
O1–Sm2–O2	76.3(1)	O1–Sm2–O4	58.22(9)

cantly shorter than those of the Sm2–O(siloxide) bonds (av 2.507(3) Å), both of which can, however, be compared with those of the Sm–O bonds in [(C₅Me₅)Sm(μ-OAr)]₂ (Ar = C₆H₂/Bu₃-2,4,6) (av 2.469(6) Å).³ The distance between the two Sm atoms in **1** (3.4485(5) Å) is much shorter than that found in [(C₅Me₅)Sm(μ-OAr)]₂ (3.8418(5) Å).³ The ∠Sm1–O–Sm2 bond angles in **1** (av 88.41(8)°) are therefore much smaller than those in [(C₅Me₅)Sm(μ-OAr)]₂ (102.2(2)°).³ As expected, the bond distances of the Sm2–O(^tBu) coordination bonds (av 2.630(3) Å) are much longer than those of the Sm–O(siloxide) bonds, but comparable with those between Sm(II) and a neutral oxygen donor ligand found in other Sm(II) complexes such as (C₅Me₅)₂Sm(thf)₂ (2.63(1) Å)² and [(C₅Me₅)Sm(μ-I)(thf)₂]₂ (2.64(1) Å).² The average bond distance of the Sm–C(C₅Me₅) bonds in **1** (2.848(6) Å) can be compared with those in (C₅Me₅)₂-Sm(thf)₂ (2.86(2) Å)² and (C₅Me₅)Sm(ER)(hmpa)₂ (ER = OC₆H₂/Bu₂-2,6-Me-4 (2.860(6) Å),^{7c} N(SiMe₃)₂ (2.86(2) Å);^{4b} hmpa = hexamethylphosphoric triamide) but longer than those in [(C₅Me₅)Sm(μ-OAr)]₂ (Ar = C₆H₂/Bu₃-2,4,6) (2.78(1) Å)³ and [(C₅Me₅)Sm(μ-I)(thf)₂]₂ (2.81(2) Å).²

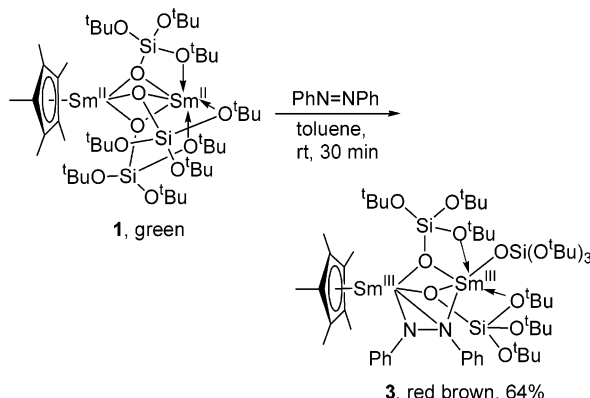
The ¹H NMR spectrum of **1** in C₆D₆ showed a sharp singlet for C₅Me₅ at δ 9.37 and a broad peak for the ^tBu groups at δ 3.10. No other signals were observed. This suggests that the binuclear structure of **1** was

(7) For examples of Cp-free, mixed-ligand-supported Sm(II) complexes, see: (a) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575. (b) Hasinoff, L.; Takats, J.; Zhang, X. W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833. (c) Hou, Z.; Fujita, A.; Yoshimura, T.; Jesorka, A.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Inorg. Chem.* **1996**, *35*, 7190.

Scheme 2

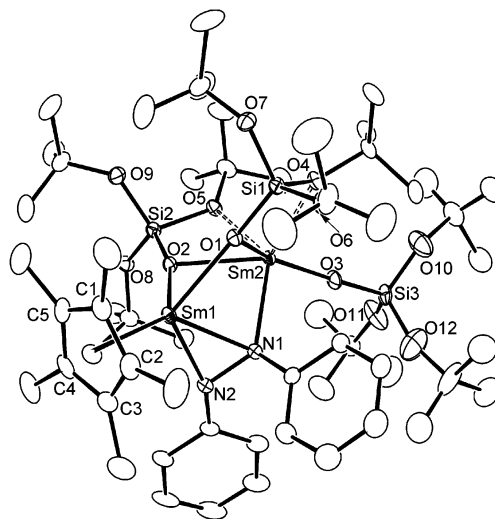


Scheme 3



retained in C_6D_6 . In $THF-d_8$, however, more signals (δ 2.08 (s, 18 H, tBu), 1.50 (s, 36 H, tBu)) were observed in addition to those at δ 9.00 (s, 15 H, C_5Me_5) and 3.20 (br s, 27 H, tBu), suggesting that dissociation of **1** into $(C_5Me_5)Sm\{OSi(O^tBu)_3\}(thf)_x$ and $Sm\{OSi(O^tBu)_3\}_2(thf)_x$ might occur in THF.⁸ Addition of 4 equiv of hmpa (hexamethylphosphoric triamide) to a toluene solution of **1** afforded $(C_5Me_5)Sm(OSi(O^tBu)_3)(hmpa)_2$ (**2**) as the only isolable product (Scheme 2).⁸

Reduction of Azobenzene by $[(C_5Me_5)Sm\{\mu-O Si(O^tBu)_3\}_2Sm]$ (1**).** The reaction of **1** with 1 equiv of azobenzene in toluene at room temperature afforded the corresponding Sm(III) binuclear complex $[(C_5Me_5)Sm\{\mu-O Si(O^tBu)_3\}_2(\mu, \eta^1: \eta^2-N_2Ph_2)SmOSi(O^tBu)_3]$ (**3**) in 64% isolated yield (Scheme 3). The two Sm(III) centers in **3** are bridged by two siloxide ligands and one azobenzene dianion unit (Figure 2 and Table 2). The third siloxide ligand is bonded to one Sm atom (Sm2) in a terminal fashion, to which two neutral O^tBu groups of the bridging siloxide ligands are also bonded by the oxygen atoms (O4 and O5). As in **1**, the other Sm end (Sm1) is capped by a "terminal" C_5Me_5 ligand. The azobenzene unit in **3** is oriented in a *cis*-fashion, which is similar to that in $[Me_2Si(C_5Me_4)(NPh)Yb(thf)(\mu, \eta^2: \eta^3-N_2Ph_2)Yb(NPh)(C_5Me_4)SiMe_2]$ ⁵ but in contrast with the *trans* orientation in $\{(C_5Me_5)_2Sm\}_2(\mu, \eta^1: \eta^1-N_2Ph_2)$.⁹ One (N1) of the two N atoms of the azobenzene unit in **3** bridges two Sm atoms, while the other N atom (N2) is bonded terminally to only one Sm atom (Sm1). The bond distance of the terminal Sm1–N2 bond (2.228(3) Å) is significantly shorter than those of the bridging Sm–N

Figure 2. ORTEP drawing of **3**.Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Sm1–C1	2.751(4)	Sm1–C2	2.745(5)
Sm1–C3	2.705(4)	Sm1–C4	2.723(4)
Sm1–C5	2.735(4)		
Sm1–O1	2.338(3)	Sm1–O2	2.342(2)
Sm1–N1	2.451(3)	Sm1–N2	2.228(3)
Sm2–O1	2.489(2)	Sm2–O2	2.436(2)
Sm2–O3	2.131(3)	Sm2–O4	2.520(3)
Sm2–O5	2.522(3)	Sm2–N1	2.392(3)
N1–N2	1.449(4)	Sm1...Sm2	3.4044(3)
O1–Sm1–O2	75.05(9)	N1–Sm1–N2	35.7(1)
Sm1–O1–Sm2	89.63(8)	Sm1–O2–Sm2	90.87(8)
Sm1–N1–Sm2	89.3(1)	O1–Sm2–O4	58.92(8)
Sm2–O3–Si3	173.1(2)		

bonds (Sm1–N1 = 2.451(3) Å and Sm2–N1 = 2.392(3) Å), but comparable with those of the terminal Sm–N bonds found in $Sm(\eta^2-Ph_2CNPh)(OC_6H_2^tBu_2-2,6-Me-4)(thf)_3$ (2.255(6) Å)¹⁰ and $Sm(\eta^2-C_{12}H_8CNPh)(OC_6H_2^tBu_2-2,6-Me-4)(thf)_3$ (2.270(4) Å).¹⁰ Similarly, the bond distance of the terminal Sm2–O3 siloxide bond in **3** (2.131(3) Å) is much shorter than those of the bridging Sm–O bonds (av 2.463(2) Å), but comparable with those of the terminal Sm–O siloxide bonds reported for $Sm(OSiPh_3)_3(thf)_3$ (av 2.170(2) Å).¹¹ The average bond distance of the Sm–C(C_5Me_5) bonds in **3** (2.732(7) Å) is typical for Sm(III)–C(C_5Me_5) bonds and shorter than that in the Sm(II) complex **1** (2.848(6) Å). The bond distance of the N1–N2 bond in **3** (1.449(4) Å) is typical for a N–N single bond.^{5,9}

The straightforward formation of **3** in the present reaction demonstrates that the binuclear Sm(II) complex **1** could act as a two-electron reducing agent, each Sm(II) center donating one electron to a substrate.

Reactions of $[(C_5Me_5)Sm\{\mu-O Si(O^tBu)_3\}_2Sm]$ (1**) with Phenylacetylene and an Aryl Alcohol.** In an attempt to prepare a mixed alkoxide/siloxide Sm(II) complex by alcoholysis (protonation) of the C_5Me_5 ligand in **1**, the reaction of **1** with 1 equiv of $ArOH$ ($Ar = C_6H_2^tBu_2-2,6-Me-4$) was carried out in toluene (Scheme 4). However, this reaction yielded a novel trinuclear Sm(II)/Sm(III) mixed valence complex $[(^tBuO)_3SiO)_3Sm^{III}$.

(8) The analogous aryloxide and silylamido complexes, such as $(C_5Me_5)Sm(OAr)(hmpa)_2$ ($Ar = OC_6H_2^tBu_2-2,6-Me-4$)^{7c} and $(C_5Me_5)Sm(N(SiMe_3)_2)(hmpa)_2$ ^{4b} have been reported previously. An attempt to prepare "Sm $\{OSi(O^tBu)_3\}_2$ " by the reaction of $Sm\{N(SiMe_3)_2\}_2(thf)_2$ with 2 equiv of $HOSi(O^tBu)_3$ in toluene yielded an unidentified oily product.

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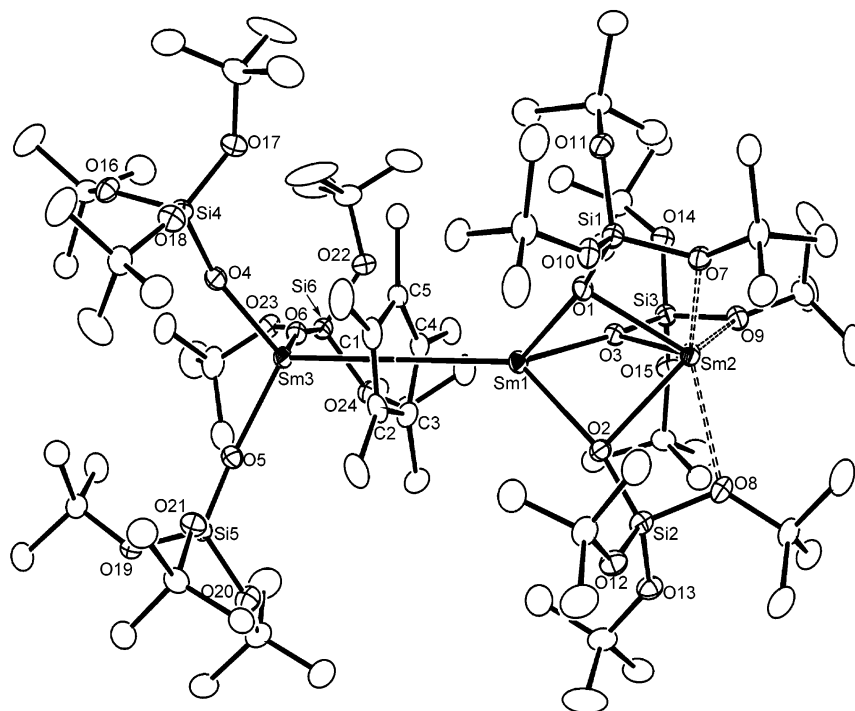
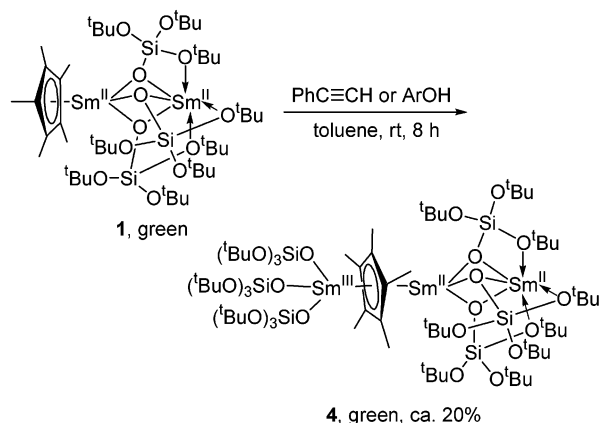


Figure 3. ORTEP drawing of **4**. Only one of the two independent molecules is shown.

Scheme 4



$(\mu, \eta^5: \eta^5\text{-C}_5\text{Me}_5)\text{Sm}^{\text{II}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}\}$ (**4**) as the only isolable product. The reaction of **1** with phenylacetylene also afforded **4** similarly. Complex **4** could be viewed formally as a combination of the binuclear Sm(II) complex **1** and a mononuclear Sm(III) tris(siloxide) complex $\text{Sm}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3$ through coordination of the C_5Me_5 ligand of **1** to the Sm(III) center (Figure 3 and Table 3). The bond distances of the Sm(II)–O siloxide bonds in **4** (av Sm1–O = 2.409(7) Å, Sm2–O = 2.522(7) Å) are comparable with those in **1** (2.440(3) and 2.507(3) Å). The bond distances of the Sm1–C(C_5Me_5) in **4** (av 2.91(1) Å) are, however, significantly longer than those in **1** (av 2.848(6) Å), because of the coordination of the C_5Me_5 ligand to a Sm(III) center (Sm3). The bond distances of the Sm3–C(C_5Me_5) bonds in **4** (av 2.82(1) Å) are comparable with those of the Sm(III)–C(C_5H_5) bonds found in the Sm(II)/Sm(III) mixed valence complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu, \eta^2: \eta^5\text{-C}_5\text{H}_5)\text{Sm}(\text{C}_5\text{Me}_5)_2$ (2.800(4) Å).¹² The Sm3–O bond distances in **4** (av 2.179(7) Å) can be compared with those of the Sm–

Table 3. Summary of Selected Bond Lengths (Å) and Angles (deg) for $(\text{R}_3\text{SiO})_3\text{Ln}(\mu\text{-Cp}^*)\text{Sm}^{\text{I}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}$

R: Ln:	4 (two molecules)		9	10
	O ^t Bu Sm	O ^t Bu Sm	O ^t Bu Gd	Ph Sm
Sm ¹ –C(Cp [*])(av)	2.91(1)	2.91(1)	2.899(9)	2.930(7)
Sm ¹ –O1	2.400(7)	2.435(6)	2.385(5)	2.391(5)
Sm ¹ –O2	2.415(6)	2.391(7)	2.395(5)	2.370(5)
Sm ¹ –O3	2.420(6)	2.391(6)	2.410(6)	2.384(5)
Sm ² –O1	2.559(6)	2.529(7)	2.495(5)	2.537(5)
Sm ² –O2	2.479(7)	2.533(6)	2.498(6)	2.502(5)
Sm ² –O3	2.538(7)	2.493(7)	2.526(5)	2.525(4)
Sm ² –O7	2.615(7)	2.613(6)	2.628(6)	2.588(5)
Sm ² –O8	2.618(7)	2.651(7)	2.579(6)	2.611(5)
Sm ² –O9	2.602(7)	2.628(7)	2.605(6)	2.578(5)
Ln–C(Cp [*])(av)	2.81(1)	2.82(1)	2.76(1)	2.776(8)
Ln–O4	2.186(7)	2.188(6)	2.151(6)	2.162(5)
Ln–O5	2.176(7)	2.179(6)	2.132(6)	2.160(5)
Ln–O6	2.173(7)	2.170(6)	2.134(6)	2.162(4)
Sm ¹ ...Sm ²	3.4491(9)	3.4438(9)	3.4293(7)	3.4357(6)
Sm ¹ –O1–Sm ²	88.1(2)	87.8(2)	89.3(2)	88.4(2)
Sm ¹ –O2–Sm ²	89.6(2)	88.7(2)	89.0(2)	89.7(2)
Sm ¹ –O3–Sm ²	88.1(2)	89.7(2)	88.0(2)	88.8(1)
Ln–O–Si(av)	164.1(5)	163.7(5)	164.5(4)	160.3(3)
Sm ¹ –Cp [*] (centroid)–Ln	177.7	174.3	175.3	176.4

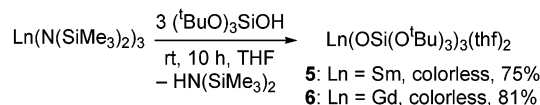
OSiPh_3 bonds in the Sm(III) siloxide complex $\text{Sm}(\text{OSiPh}_3)_3(\text{thf})_3$ (2.170(2) Å).¹¹

The trinuclear Sm(II)/Sm(III) complex **4** was stable in C_6D_6 , as shown by the ^1H NMR spectrum. The $\text{C}_5\text{-Me}_5$ group showed a singlet at δ 15.72 (in contrast with δ 9.37 in **1**), and the siloxide ligands gave two singlets at δ 3.10 (for the Sm(II) part) and δ 1.21 (for the Sm(III) part), respectively. In THF, dissociation of **4** into **1** and $\text{Sm}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3(\text{thf})_2$ seemed to occur.

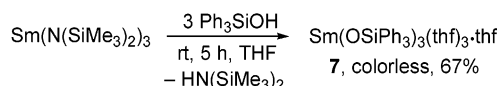
Apparently, the formation of **4** in the present reactions requires oxidation of **1** to generate a Sm(III) tris(siloxide) complex such as $\text{Sm}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3$. The coordination of another molecule of **1** to the Sm(III) center of the in-situ-generated $\text{Sm}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3$ via the C_5Me_5 ligand would afford **4** straightforwardly, although iden-

(12) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.

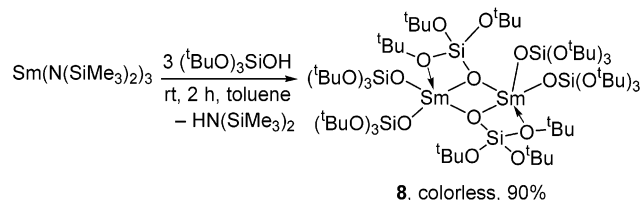
Scheme 5



Scheme 6

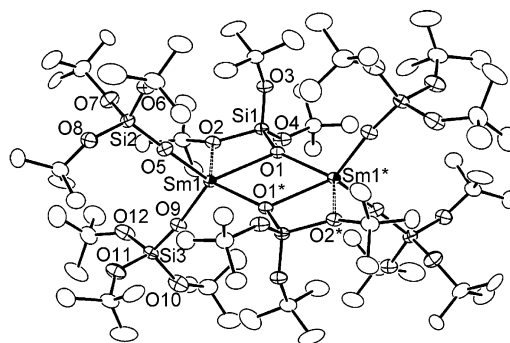


Scheme 7



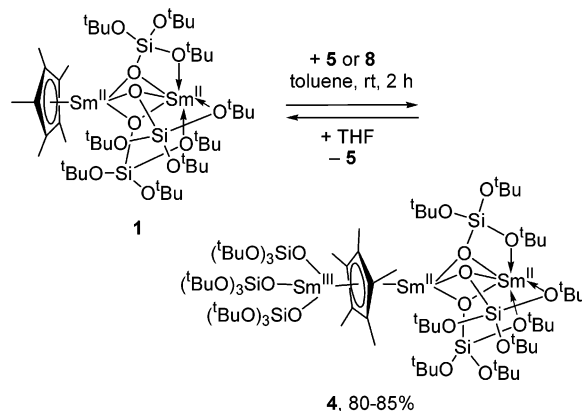
tification of other coproducts in these reactions was difficult.^{13,14} To further confirm the coordination ability of the binuclear Sm(II) complex **1** to a Ln(III) center, the reaction of **1** with well-defined lanthanide(III) siloxide complexes was then carried out.

Synthesis of Lanthanide(III) Siloxide Complexes. To probe the coordination ability of **1** to a Ln(III) center, we needed to prepare appropriate lanthanide(III) siloxide complexes first. The acid–base reactions between $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$ and 3 equiv of $(\text{tBuO})_3\text{SiOH}$ in THF gave straightforwardly the corresponding Ln(III) siloxide complexes $\text{Ln}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3(\text{thf})_2$ (Ln = Sm (**5**), Gd (**6**)) (Scheme 5). Similarly, the reaction of $\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_3$ with 3 equiv of Ph_3SiOH afforded $\text{Sm}(\text{OSiPh}_3)_3(\text{thf})_3 \cdot (\text{thf})$ (**7**) (Scheme 6).¹⁵ When the reaction of $\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_3$ with $(\text{tBuO})_3\text{SiOH}$ was carried out in toluene, the THF-free, dimeric Sm(III) complex $[\text{Sm}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_2]_2$ (**8**) was obtained (Scheme 7). Complex **8** possesses a crystallographic inversion center at the center of the molecule, in which the two Sm atoms are bridged by two siloxide ligands and each Sm is also bonded to two terminal siloxide ligands (Figure 4 and Table 4). Moreover, each of the two Sm centers is coordinated by a O^tBu group of the bridging siloxide ligands, while no interaction between the O^tBu groups of the terminal siloxide ligands and the Sm atoms is observed. It is noteworthy that the bond distance of the neutral $\text{Sm}\text{--}\text{O}^t\text{Bu}$ coordination bond ($\text{Sm1}\text{--}\text{O}(2) = 2.180(5) \text{ \AA}$) is unusually short, and is even shorter than those of the terminal $\text{Sm}\text{--}\text{O}$ siloxide covalent bonds (cf. $\text{Sm1}\text{--}\text{O5} = 2.216(6) \text{ \AA}$, $\text{Sm1}\text{--}\text{O9} = 2.257(6) \text{ \AA}$). Meanwhile, the $\text{Si1}\text{--}\text{O2}$ (Sm-coordinated O^tBu) bond distance ($1.906(7) \text{ \AA}$) is much longer

Figure 4. ORTEP drawing of **8**.Table 4. Selected Bond Lengths (Å) and Angles (deg) for **8**

Sm1–O1	2.701(6)	Sm1–O1*	2.503(6)
Sm1–O2	2.180(5)	Sm1–O5	2.216(6)
Sm1–O9	2.257(6)	Si1–O1	1.499(5)
Si1–O2	1.906(7)	Si1–O3	1.597(7)
Si1–O4	1.493(7)	Si2–O5	1.710(7)
Si2–O6	1.684(8)	Si2–O7	1.525(8)
Si2–O8	1.610(8)	Si3–O9	1.698(7)
Si3–O10	1.67(1)	Si3–O11	1.57(1)
Si3–O12	1.601(9)		
O1–Sm1–O1*	58.1(2)	Sm1–O5–Si2	168.7(4)
O1–Si1–O2	107.5(3)		

Scheme 8



than those of other $\text{Si}\text{--}\text{O}^t\text{Bu}$ bonds (Table 4), and the bond distances of the bridging $\text{Sm}\text{--}\text{siloxide}$ bonds in **8** ($\text{Sm1}\text{--}\text{O1} = 2.701 \text{ \AA}$, $\text{Sm1}\text{--}\text{O1}^* = 2.503 \text{ \AA}$, Table 4) are significantly longer than those found in the Sm(III) siloxide complex **3** ($2.338(3)\text{--}2.489(2) \text{ \AA}$). These data suggest that the negative charge of the bridging siloxide ligands in **8** might be delocalized, to some extent, to the Sm-coordinated O^tBu oxygen atoms (O2 and O2^*). An analogous interaction between the metal center and the ipso carbon of one of the phenyl rings in the bridging triphenylsiloxide ligand in $[\text{Ce}\{\mu\text{-OSiPh}_3\}\{\text{OSiPh}_3\}_2]_2$ was also observed previously.^{15b}

Coordination of $[(\text{C}_5\text{Me}_5)\text{Sm}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}]$ (1**) to a Ln(III) Center.** The reaction of either the bis-(thf)-coordinated Sm(III) complex **5** or the dimeric complex **8** with **1** in toluene easily yielded the adduct **4** in high yield (Scheme 8). Similarly, the reaction of **6** or **7** with **1** afforded straightforwardly the corresponding Sm(II)/Gd(III) heterometallic complex $[(\text{tBuO})_3\text{SiO}]_3\text{Gd}^{\text{III}}(\mu, \eta^5\text{-C}_5\text{Me}_5)\text{Sm}^{\text{II}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}$ (**9**) (Scheme 9) or the Sm(II)/Sm(III) complex $[(\text{Ph}_3\text{SiO})_3\text{Sm}^{\text{III}}(\mu, \eta^5\text{-C}_5\text{Me}_5)\text{Sm}^{\text{II}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}]$ (**10**)

(13) For examples of oxidation of Sm(II) species by aryl alcohols, see: (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. (c) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191.

(14) Oxidation of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{thf})_2$ by phenylacetylene to give the Sm(III) complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}\equiv\text{CPh})(\text{thf})$ was reported. See: Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124.

(15) $\text{Sm}(\text{OSiPh}_3)_3(\text{thf})_3$ (**7**) is a known compound, which was previously obtained by reaction of $\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}_2\text{SmF}$ with Ph_3SiOH .¹¹ The Y^{15a} , La^{15a} , and Ce^{15b} analogues have also been reported previously. See: (a) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1723. (b) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963.

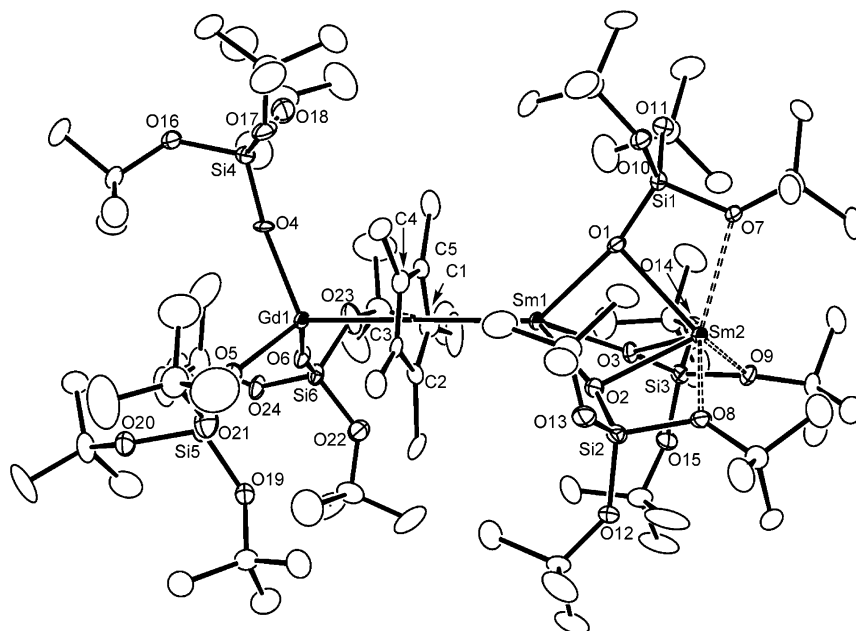
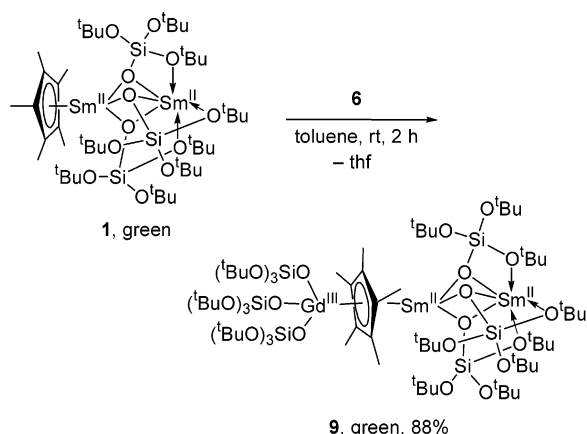
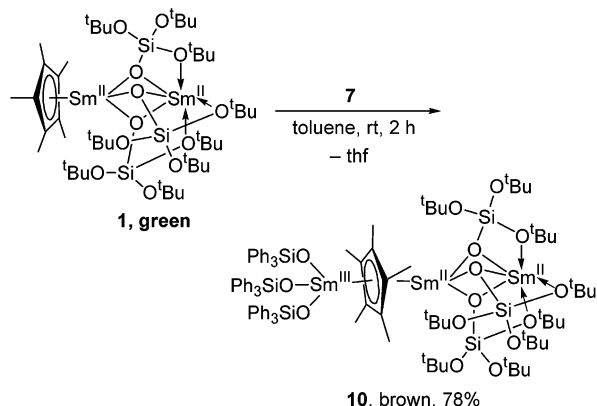


Figure 5. ORTEP drawing of **9**. The lattice solvent is omitted for clarity.

Scheme 9



Scheme 10



(Scheme 10), respectively. The ORTEP drawings of **9** and **10** are shown in Figures 5 and 6, respectively. The selected bond lengths and angles are summarized in Table 3. Their structural data are comparable with each other and also with those of **4**, and therefore are not further discussed here.

The easy formation of **4**, **9**, and **10** from the reactions of **1** with **5–8** demonstrates that the coordination ability

of the C_5Me_5 unit in **1** is strong enough to replace a thf ligand and to break a $\text{Sm(III)}-\text{O}$ siloxide bridging bond. These results suggest that the reactions of **1** with appropriate Ln(III) complexes could offer a general route to the corresponding Sm(II)/Ln(III) homo- or heterometallic mixed valence lanthanide complexes. Mixed valence lanthanide complexes, in particular those of heterometallic complexes, remained rare.^{16,17}

Coordination of $[(\text{C}_5\text{Me}_5)\text{Sm}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}]$ (1**) to a Sm(II) Center.** To see if **1** can coordinate to a Sm(II) center, the reaction of $\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2$ with **1** was carried out in toluene. From this reaction, an unexpected pentanuclear Sm(II) ion-pair complex, $[\text{Sm}^{\text{II}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}(\mu, \eta^5\text{-C}_5\text{Me}_5)\text{Sm}^{\text{II}}\{\mu\text{-OSi}(\text{O}^t\text{Bu})_3\}_3\text{Sm}^{\text{II}}][\text{Sm}^{\text{II}}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (**11**), was isolated (Scheme 11). The cation part in **11** contains four Sm(II) atoms, each two of which are bridged by three siloxide ligands, similarly to that in **1** (Figure 7 and Table 5). One Sm end of each binuclear Sm(II) unit is bonded to an identical C_5Me_5 ligand on the opposite side to form a novel “ $\text{Sm(II)}_2\text{-C}_5\text{Me}_5\text{-Sm(II)}_2$ ” inverse sandwich structure, while the other Sm end is wrapped by three O^tBu groups of the siloxide ligands via the oxygen atoms. In the anion part of **11**, a Sm(II) ion is surrounded by three $[\text{N}(\text{SiMe}_3)_2]^-$ ligands. The whole molecule of **11** is of very high symmetry. A crystallographic 3-fold axis passes through all of the five Sm(II) atoms and the center of the C_5Me_5 ring, and therefore, the C_5Me_5 unit in **11** is disordered into a “ C_6 -

(16) For previous examples of mixed valence homo-lanthanide complexes, see: (a) Bocella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710. (b) Burns, C. J.; Berg, D. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 272. (c) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 136. (d) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y. F.; Zakharov, L. N. *J. Organomet. Chem.* **1992**, 429, 27. (e) Deacon, G. B.; Forsyth, C. M.; Junk, P. J.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **1999**, 5, 1452. (f) Deacon, G. B.; Gitlits, A.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1999**, 1213. (g) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, 19, 817. See also ref 12.

(17) The only previously reported heterobimetallic organolanthanide complex was an “ate” complex, $[\text{Yb}(\text{thf})_6][\text{Ce}(\text{cot}''')]$ ($\text{cot}''' = \eta^8\text{-1,3,6-(Me}_3\text{Si)}_3\text{C}_8\text{H}_5$). See: Reissmann, U.; Lameyer, L.; Stalke, D.; Poremba, P.; Edelmann, F. T. *Chem. Commun.* **1999**, 1865.

[illegible]

The formation of **11** could be explained by the reaction path shown in Scheme 11. The coordination of the C₅-Me₅ unit of **1** to the Sm(II) center of Sm{N(SiMe₃)₂}₂-(thf)₂ should give **A** straightforwardly. A similar reaction was confirmed in the case of Ln(III) complexes such as **4**, **9**, and **10** as described above. Replacement of the “[Cp₂(SiMe₃)₂N]₂Sm(C₅Me₅)” part of **A** by another molecule of **1** via the C₅Me₅ coordination would give the ion-pair complex **B**. Ligand exchange reaction between the anion part of **B** and Sm{N(SiMe₃)₂}₂(thf)₂ could afford **11**, with release of the possible coproduct [(C₅Me₅)SmN(SiMe₃)₂].¹⁹

In contrast with the previously reported reaction between $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{thf})_2$ and an aryl alcohol ArOH ($\text{Ar} = \text{OC}_6\text{H}_2\text{Bu}-2,6\text{-Me}-4$), which yielded quantitatively the symmetrical dimeric $\text{Sm}(\text{II})$ complex $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-OAr})_2]$ that bears two bridging aryloxy ligands and

(18) Brady, E. D.; Clark, D. L.; Gordon, J. C.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Walkin, J. G. *Inorg. Chem.* **2003**, *42*, 6682.

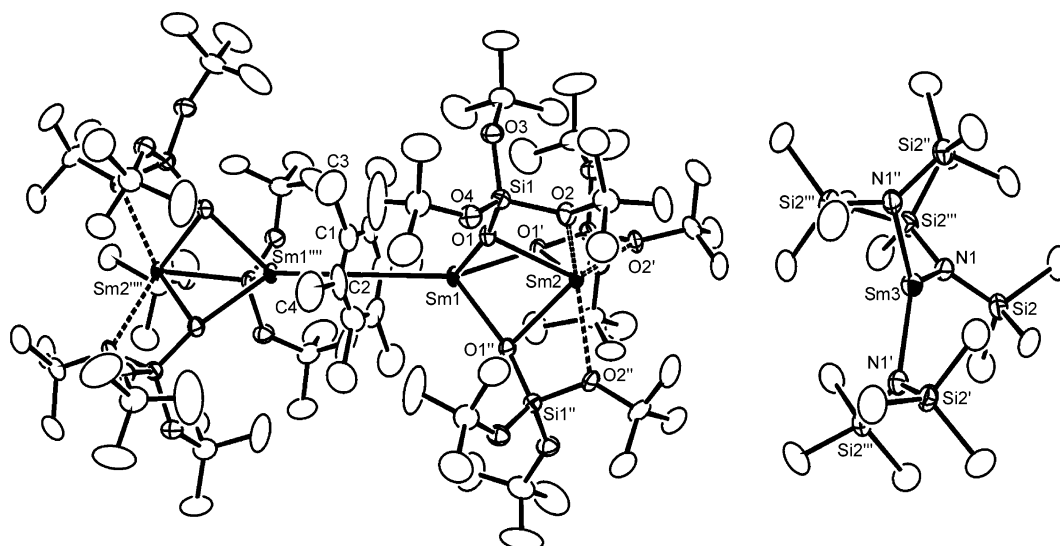


Figure 7. ORTEP drawing of **11**. The C_5Me_5 ligand is disordered. Symmetry transformations are used to generate equivalent atoms: ' = $-x+y, -x+1, z$, '' = $-y+1, x-y+1, z$, ''' = $x, x-y+1, -z+3/2$, '''' = $-y+1, -x+1, -z+1/2$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **11**

Sm1–C1	2.915(5)	Sm1–C2	2.935(5)
Sm1–C(Cp*)(av.)	2.925(5)	Sm1–O1	2.392(3)
Sm2–O1	2.518(3)	Sm2–O2	2.594(4)
Sm3–N1	2.463(7)	Sm1...Sm2	3.4258(6)
Sm1–O1–Sm2	88.5(1)	Sm1–Cp*(centroid)–Sm1*	180
N1–Sm3–N1*	120		

two terminal C_5Me_5 ligands,³ the reaction of $(C_5Me_5)_2Sm(thf)_2$ with $(tBuO)_3SiOH$ led to the preferred formation of the unsymmetrical dimeric complex $[(C_5Me_5)_2Sm\{\mu-O\text{Si}(O^tBu)_3\}_3Sm]$ (**1**), in which the two Sm(II) centers are bridged by three siloxide ligands and only one of the two Sm(II) atoms is bonded to a C_5Me_5 ligand. The binuclear Sm(II) complex **1** could act as a two-electron-transfer agent (one from each Sm(II) center) for the reduction of azobenzene to yield the corresponding Sm(III) azobenzene-dianion complex **3**. More remarkably, complex **1** could act as a neutral coordination ligand for Lewis acidic lanthanide metal centers via the C_5Me_5 part. Thus, the reaction of **1** with $Sm\{N(SiMe_3)_2\}_2(thf)_2$ yielded the novel polynuclear Sm(II) complex **11**, and the reactions with Ln(III) siloxide complexes such as **5–8** afforded the corresponding polynuclear Sm(II)/Ln(III) mixed valence homo- and heterometallic organolanthanide complexes (e.g., **4**, **9**, and **10**), which possess novel “inverse sandwich” structures.

Experimental Section

General Methods. All reactions 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 being passed 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 ensure both were always below 1 ppm. Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. 1H and ^{13}C NMR spectra were recorded on a JNM-EX 270 (FT, 270 MHz) spectrometer. Elemental analyses were performed by the Chemical Analysis Team, Advanced Development and Supporting Center of RIKEN. There seemed a trend that the observed value for carbon was lower than that expected for this series of siloxide complexes, in particular, the larger polynuclear complexes **4** and **9–11**. This is probably due to possible formation of incombustible carbide species.²⁰ Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump–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). $LnCl_3$ were purchased from STREM. $(tBuO)_3SiOH$ was obtained from AZmax Co. Ltd. $(C_5Me_5)_2Sm(thf)_2$,² $Sm\{N(SiMe_3)_2\}_2(thf)_2$,^{7a} and $Ln\{N(SiMe_3)_2\}_3$ ($Ln = Sm, Gd$)²¹ were prepared according to literature methods.

$[(C_5Me_5)_2Sm\{\mu-O\text{Si}(O^tBu)_3\}_3Sm]$ (1**).** A toluene solution (20 mL) of $(tBuO)_3SiOH$ (5.95 g, 22.5 mmol) was added to a toluene solution (50 mL) of $(C_5Me_5)_2Sm(thf)_2$ (8.46 g, 15 mmol) at room temperature under magnetic stirring. The solution color changed immediately from purple to green. After the mixture was stirred for 2 h, the solvent was removed under reduced pressure. The residue was washed with hexane and dried to give **1** as a green powder (8.55 g, 93% yield). Single crystals of **1** could be grown from a concentrated hot toluene solution. 1H NMR (C_6D_6 , 22 °C): δ 9.37 (s, 15 H, C_5Me_5), 3.1 (br s, 81 H, tBu). 1H NMR ($THF-d_6$, 22 °C): δ 9.00 (s, 15 H, C_5Me_5), 3.20 (br s, 27 H, tBu), 2.08 (s, 18 H, tBu), 1.50 (s, 36 H, tBu). An informative ^{13}C NMR spectrum was not obtained, because of the influence of the paramagnetic Sm(II) ion. Anal. Calcd for $C_{46}H_{96}O_{12}Si_3Sm_2$: C, 45.06; H, 7.89. Found: C, 44.82; H, 7.89.

$(C_5Me_5)_2Sm\{OSi(O^tBu)_3\}_2(hmpa)_2$ (2**).** A toluene solution (2 mL) of hexamethylphosphoric triamide (hmpa) (717 mg, 4 mmol) was added to a toluene solution (10 mL) of **1** (1.23 g, 1 mmol) at room temperature. The solution color changed from green to purple-brown immediately. After the mixture was stirred for 1 h, the solvent was removed under reduced

(19) Identification of the possible coproduct $[(C_5Me_5)_2Sm\{N(SiMe_3)_2\}]$ was difficult in the present case because of difficulty in separation. Its hmpa adduct, $[(C_5Me_5)_2Sm\{N(SiMe_3)_2\}(hmpa)_2]$, was reported previously,^{4b} which could be easily derived from the reaction of $(C_5Me_5)_2Sm(thf)_2$ with 1 equiv of $Sm\{N(SiMe_3)_2\}_2(thf)_2$ in toluene. Its ArO analogue, $[(C_5Me_5)_2Sm(OAr)]_2$, was also known.³

(20) A similar phenomenon was also observed previously. For examples, see ref 6 and references therein.

(21) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

pressure. The residue was dissolved in hexane to give a purple-brown solution, and the volume of the solution was reduced under vacuum to precipitate purple powder. The precipitate was collected by decanting the solution and was recrystallized from a hot hexane solution to afford **2** as dark purple needle crystals (283 mg, 0.31 mmol, 31% yield based on C_5Me_5). ^1H NMR (C_6D_6 , 22 °C): δ 7.99 (s, 15 H, C_5Me_5), 4.80 (br s, 36 H, Me), 3.20 (br s, 27 H, 'Bu). The connection of the molecule was determined by an X-ray analysis, but further refinement was not allowed because of poor quality of the crystal. Anal. Calcd for $\text{C}_{34}\text{H}_{78}\text{O}_6\text{N}_6\text{SiP}_2\text{Sm}$: C, 45.00; H, 8.66; N, 9.26. Found: C, 44.33; H, 8.73; N, 8.98. The lower value found for carbon might be due to possible formation of incombustible carbide species.²⁰

[(C₅Me₅)Sm{ μ -OSi(O'Bu)₃}₂(μ , η^1 : η^2 -N₂Ph₂)SmOSi(O'Bu)₃]} (3). Azobenzene (364 mg, 2 mmol) in toluene (2 mL) was added to a green solution of **1** (2.452 g, 2 mmol) in toluene (30 mL). The solution color changed from green to red brown immediately. After the solution was stirred at room temperature for 30 min, the solvent was concentrated and was then left to stand at room temperature for 2 weeks to afford **3** as red-brown needle crystals (1.80 g, 64%). ^1H NMR (C_6D_6 , 22 °C): δ 4.53 (br s, 10 H, Ph), 2.92 (br s, 15 H, C_5Me_5), 2.63 (s, 27 H, 'Bu), -1.55 (br s, 54 H, 'Bu). Anal. Calcd for $\text{C}_{58}\text{H}_{106}\text{N}_2\text{O}_{12}\text{Si}_3\text{Sm}_2$: C, 49.46; H, 7.59; N, 1.99. Found: C, 48.93; H, 7.63; N, 1.79.

[(('BuO)₃SiO)₃Sm^{III}(μ , η^5 : η^5 -C₅Me₅)Sm^{II}{ μ -OSi(O'Bu)₃}₃Sm^{II}]} (4). Method A: To a toluene solution (5 mL) of **1** (245 mg, 0.2 mmol) was added ArOH (Ar = C₆H₂/Bu₂-2,6-Me-4) (44 mg, 0.2 mmol) in 5 mL of toluene. The mixture was stirred at room temperature for 8 h. Reduction of the solution volume under reduced pressure gave green precipitates, which were collected and recrystallized from a hot toluene solution to give **4** as green blocks (65 mg, 23% yield based on Sm). The reaction of **1** with phenylacetylene also gave **4** similarly. Method B: A toluene solution (5 mL) of **1** (245 mg, 0.2 mmol) was added to a toluene solution (5 mL) of **5** (217 mg, 0.2 mmol) at room temperature. After the mixture was stirred for 2 h, the solvent was removed under reduced pressure. The residue was washed with hexane and dried to give **4** (370 mg, 85% yield). The reaction of **1** (245 mg, 0.2 mmol) with **8** (188 mg, 0.1 mmol) also gave **4** (355 mg, 82%). Dark green blocks of **4** suitable for X-ray analysis were obtained by recrystallization from a concentrated hot toluene solution. ^1H NMR (C_6D_6 , 22 °C): δ 15.72 (s, 15 H, $\text{C}_5\text{Me}_5), 3.1 (br s, 81 H, 'Bu), 1.21 (s, 81 H, 'Bu). Anal. Calcd for $\text{C}_{82}\text{H}_{177}\text{O}_{24}\text{Si}_6\text{Sm}_3$: C, 45.45; H, 8.23. Found: C, 44.68; H, 8.25. The lower value found for carbon might be due to possible formation of incombustible carbide species.²⁰$

Sm{OSi(O'Bu)₃}₃(thf)₂ (5). A mixture of Sm{N(SiMe₃)₂}₃ (1.26 g, 2 mmol) and ('BuO)₃SiOH (1.59 g, 6 mmol) in 20 mL of THF was stirred at room temperature for 10 h. The volatiles were removed under reduced pressure to give a white powder, which was recrystallized from hot hexane to give **5** as colorless blocks (1.63 g, 75%). Complex **5** could also be obtained in quantitative yield by dissolving **8** in THF and drying under reduced pressure. ^1H NMR (C_6D_6 , 22 °C): δ 1.87 (br s, 81 H, 'Bu), 0.94 (br s, 8 H, THF), 0.04 (br s, 8 H, THF). The ^1H NMR spectrum seemed to be concentration dependent. Anal. Calcd for $\text{C}_{44}\text{H}_{97}\text{O}_{14}\text{Si}_3\text{Sm}$: C, 48.71; H, 9.01. Found: C, 48.66; H, 8.91.

Gd{OSi(O'Bu)₃}₃(thf)₂ (6). Starting from Gd{N(SiMe₃)₂}₃ (638 mg, 1 mmol), complex **6** was obtained as a white powder (884 mg, 81%) in a manner analogous to that described for the synthesis of **5**. An informative ^1H NMR spectrum was not obtained for **6**, because of the influence of the paramagnetic Gd(III) ion. Anal. Calcd for $\text{C}_{44}\text{H}_{97}\text{O}_{14}\text{Si}_3\text{Gd}$: C, 48.41; H, 8.96. Found: C, 48.44; H, 8.96.

Sm(OSiPh₃)₃(thf)₃ (7). A mixture of Sm{N(SiMe₃)₂}₃ (1.26 g, 2 mmol) and Ph₃SiOH (1.66 g, 6 mmol) in 20 mL of THF was stirred at room temperature for 5 h. The solvent and hexamethyldisilazane were removed under reduced pressure

to give a white powder, which was then dissolved in THF. After reduction of solution volume under reduced pressure, ether was slowly added to precipitate **7** as colorless blocks (1.70 g, 67%). The crystals were dried for 8 h under reduced pressure, but the lattice solvent of THF could not be removed.¹⁵ ^1H NMR (C_6D_6 , 22 °C): δ 8.33 (br s, 18 H, *o*-Ph), 7.23 (br s, 27 H, *m,p*-Ph), 2.27 (br s, 16 H, THF), 0.58 (br s, 16 H, THF). Anal. Calcd for $\text{C}_{70}\text{H}_{77}\text{O}_7\text{Si}_3\text{Sm}$: C, 66.46; H, 6.14. Found: C, 65.93; H, 6.18.

[Sm{OSi(O'Bu)₃}₂{ μ -OSi(O'Bu)₃}₂] (8). Addition of a toluene solution (5 mL) of ('BuO)₃SiOH (793 mg, 3 mmol) to a pale yellow toluene solution (10 mL) of Sm(N(SiMe₃)₂)₃ (632 mg, 1 mmol) gave a colorless reaction mixture immediately, which was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was washed with hexane and dried to give **8** as a white powder (847 mg, 90%). Single crystals of **8** for X-ray structural analysis were obtained by slow evaporation of a toluene solution in the glovebox for 2 weeks. ^1H NMR (C_6D_6 , 22 °C): δ 2.24, 1.45, 1.30 (the integrations were dependent on concentration). Anal. Calcd for $\text{C}_{36}\text{H}_{81}\text{O}_{12}\text{Si}_3\text{Sm}$: C, 45.97; H, 8.68. Found: C, 46.07; H, 8.88.

[{('BuO)₃SiO}₃Gd^{III}(μ , η^5 : η^5 -C₅Me₅)Sm^{II}{ μ -OSi(O'Bu)₃}₃Sm^{II}]} (9). Starting from **6** (328 mg, 0.3 mmol), complex **9** was obtained as a green powder (574 mg, 88%) in a manner analogous to that described for the synthesis of **4** (method B). Dark green crystals of **9** were obtained from a hot benzene solution. An informative ^1H NMR spectrum was not obtained for **9**, because of the influence of the paramagnetic Gd(III) ion. Anal. Calcd for $\text{C}_{82}\text{H}_{177}\text{O}_{24}\text{Si}_6\text{Sm}_2\text{Gd}$: C, 45.31; H, 8.21. Found: C, 44.41; H, 7.96. The lower value found for carbon might be due to possible formation of incombustible carbide species.²⁰

[(Ph₃SiO)₃Sm^{III}(μ , η^5 : η^5 -C₅Me₅)Sm^{II}{ μ -OSi(O'Bu)₃}₃-Sm^{II}]} (10). A toluene solution (5 mL) of **1** (245 mg, 0.2 mmol) was added to a toluene solution (5 mL) of **7** (253 mg, 0.2 mmol) at room temperature. The solution color changed from green to brown immediately. After the mixture was stirred for 2 h, the solvent was removed under reduced pressure. The residue was washed with hexane and dried to give **10** (344 mg, 78% yield). Dark brown blocks of **10** suitable for X-ray analysis were obtained by recrystallization from a concentrated hot toluene solution. ^1H NMR (C_6D_6 , 22 °C): δ 14.2 (s, 15 H, C_5Me_5), 6.65–7.35 (m, 45 H, Ph), 2.1 (br s, 81 H, 'Bu). Anal. Calcd for $\text{C}_{100}\text{H}_{141}\text{O}_{15}\text{Si}_6\text{Sm}_3$: C, 54.53; H, 6.45. Found: C, 52.10; H, 6.35. The lower value found for carbon might be due to possible formation of incombustible carbide species.²⁰

[Sm^{II}{ μ -OSi(O'Bu)₃}₃Sm^{II}(μ , η^5 : η^5 -C₅Me₅)Sm^{II}{ μ -OSi(O'Bu)₃}₃Sm^{II}][Sm^{II}{N(SiMe₃)₂}₃] (11). To a toluene solution (5 mL) of Sm{N(SiMe₃)₂}₂(thf)₂ (123 mg, 0.2 mmol) was added a toluene solution (5 mL) of **1** (245 mg, 0.2 mmol). The brown mixture was stirred at room temperature for 24 h and filtered through a frit. The solvent was removed under reduced pressure to give brown powders, which after recrystallization from toluene yielded **11** (ca. 48 mg, 16%) as brown crystals together with some green powders (possibly [(C₅Me₅)Sm{N(SiMe₃)₂}]). A complete separation of **11** and the green powders was difficult, but single crystals of **11** suitable for X-ray analysis could be selected. ^1H NMR (C_6D_6 , 22 °C): δ 9.8 (br s, 15 H, C_5Me_5), 3.0 (s, 36 H, SiMe₃), 0.3 (s, 18 H, SiMe₃), 1.5 (br 162 H, 'Bu). Anal. Calcd for $\text{C}_{100}\text{H}_{231}\text{N}_3\text{O}_{24}\text{Si}_{12}\text{Sm}_5$: C, 40.73; H, 7.90; N, 1.43. Found: C, 39.10; H, 7.64; N, 1.31. The lower value found for carbon might be due to possible formation of incombustible carbide species.²⁰

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 sealed in thin-walled glass capillaries. Data collections of **4** and **8** were performed on a Rigaku R-AXISII diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71070 Å), and the structures were solved by using the tXsan software package. Data

Table 6. Summary of Crystallographic Data of 1, 3 and 4

	1·0.5 C ₆ H ₆	3	[4] ₂
formula	C ₄₉ H ₉₉ O ₁₂ Si ₃ Sm ₂	C ₅₈ H ₁₀₆ N ₂ O ₁₂ Si ₃ Sm ₂	C ₁₆₄ H ₃₅₄ O ₄₈ Si ₁₂ Sm ₆
fw	1265.25	1408.42	2167.00
cryst syst	triclinic	monoclinic	triclinic
space group	<i>P</i> 1 (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 1 (No. 2)
<i>a</i> (Å)	12.734(1)	12.1289(6)	26.528(3)
<i>b</i> (Å)	13.242(1)	21.118(1)	27.179(6)
<i>c</i> (Å)	22.661(2)	28.325(1)	19.299(4)
α (deg)	105.899(2)	90	108.12(2)
β (deg)	91.251(2)	94.302(1)	100.72(1)
γ (deg)	117.569(2)	90	62.218(9)
<i>V</i> (Å ³)	3207.8(6)	7234.6(6)	11686(4)
<i>Z</i>	2	4	2
<i>D</i> _{calcd} (g cm ^{−3})	1.310	1.293	1.232
μ (mm ^{−1})	1.917	1.708	1.605
<i>T</i> (°C)	−100	20	−100
no. of reflns collected	17 824	54 606	29 778
no. of reflns with <i>I</i> > 2σ(<i>I</i>)	12 971	19 297	28 709
no. of variables	627	726	2190
GOF	0.888	1.000	1.607
<i>R</i>	0.0417	0.0495	0.0685
<i>R</i> _w	0.0523	0.1046	0.1520

Table 7. Summary of Crystallographic Data of 8–11

	8	9·2.5C ₆ H ₆	10·3toluene	11
formula	C ₇₂ H ₁₆₂ O ₂₄ Si ₆ Sm ₂	C ₉₇ H ₁₉₂ O ₂₄ GdSi ₆ Sm ₂	C ₁₂₁ H ₁₆₅ O ₁₅ Si ₆ Sm ₃	C ₁₀₀ H ₂₃₁ N ₃ O ₂₄ Si ₁₂ Sm ₅
fw	1881.26	2369.00	2479.12	2948.71
cryst syst	monoclinic	triclinic	triclinic	trigonal
space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 3 ₁ <i>c</i> (No. 163)
<i>a</i> (Å)	26.042(5)	13.922(2)	15.733(1)	19.0414(8)
<i>b</i> (Å)	14.383(3)	18.802(2)	18.049(2)	19.0414(8)
<i>c</i> (Å)	27.99(3)	26.762(3)	25.542(2)	29.821(2)
α (deg)	90	106.655(2)	96.315(2)	90
β (deg)	98.60(5)	96.617(2)	103.866(2)	90
γ (deg)	90	109.171(2)	112.789(2)	120
<i>V</i> (Å ³)	10366(11)	6167(1)	6323(1)	9363.8(8)
<i>Z</i>	4	2	2	2
<i>D</i> _{calcd} (g cm ^{−3})	1.205	1.276	1.302	1.046
μ (mm ^{−1})	1.249	1.588	1.488	1.663
<i>T</i> (°C)	20	−100	−100	−100
no. of reflns collected	10 152	38 927	41 955	71 373
no. of reflns with <i>I</i> > 2σ(<i>I</i>)	7262	26 499	27 893	9007
no. of variables	497	1155	1241	238
GOF	1.353	0.944	0.953	1.011
<i>R</i>	0.0454	0.0704	0.0606	0.0503
<i>R</i> _w	0.1136	0.0954	0.1113	0.1924

collections of **1**, **3**, **9**, **10**, and **11** were performed on a Bruker CCD APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. Molecular structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and not refined. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Tables 5 and 6.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1**, **3**, **4**, and **8–11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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