

# Synthesis of Arenethiolate Complexes of Divalent and Trivalent Lanthanides from Metallic Lanthanides and Diaryl Disulfides: Crystal Structures of $\{[Yb(hmpa)_3]_2(\mu\text{-SPh})_3\}[\text{SPh}]$ and $\text{Ln}(\text{SPh})_3(\text{hmpa})_3$ (Ln = Sm, Yb; hmpa = Hexamethylphosphoric Triamide)

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Received January 18, 1995<sup>©</sup>

A convenient and one-pot synthetic method of lanthanide thiolate compounds was developed. An excess of metallic samarium, europium, and ytterbium directly reacted with diaryl disulfides in THF to give selectively Ln(II) thiolate complexes,  $[\text{Ln}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3]_2$  (**1**, Ln = Sm; **2**, Ln = Eu; Ar = 2,4,6-triisopropylphenyl),  $\text{Yb}(\text{SAr})_2(\text{py})_4$  (**3**, py = pyridine), and  $[\{\text{Ln}(\text{hmpa})_3\}_2(\mu\text{-SPh})_3][\text{SPh}]$  (**6**, Ln = Sm; **7**, Ln = Eu; **8**, Ln = Yb; hmpa = hexamethylphosphoric triamide). Reaction of metallic lanthanides with 3 equiv of disulfides afforded Ln(III) thiolate complexes,  $\text{Ln}(\text{SAr})_3(\text{py})_n(\text{thf})_{3-n}$  (**9a**, Ln = Sm,  $n = 3$ ; **9b**, Ln = Sm,  $n = 2$ ; **10**, Ln = Yb,  $n = 3$ ) and  $\text{Ln}(\text{SPh})_3(\text{hmpa})_3$  (**11**, Ln = Sm; **12**, Ln = Eu; **13**, Ln = Yb). Thus, Ln(II) and Ln(III) thiolate complexes were prepared from the same source by controlling the stoichiometry of the reactants. X-ray analysis of **8** revealed that **8** has the first ionic structure composed of triply bridged dinuclear cation and benzenethiolate anion [**8**, orthorhombic, space group  $P2_12_12_1$  with  $a = 21.057(9)$ ,  $b = 25.963(7)$ ,  $c = 16.442(8)$  Å,  $V = 8988(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.040$ ,  $R_w = 0.039$  for 5848 reflections with  $I > 3\sigma(I)$  and 865 parameters]. The monomeric structures of **11** and **13** were revealed by X-ray crystallographic studies [**11**, triclinic, space group  $P\bar{1}$  with  $a = 14.719(3)$ ,  $b = 17.989(2)$ ,  $c = 11.344(2)$  Å,  $\alpha = 97.91(1)$ ,  $\beta = 110.30(2)$ ,  $\gamma = 78.40(1)^\circ$ ,  $V = 2751.9(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.045$ ,  $R_w = 0.041$  for 7111 reflections with  $I > 3\sigma(I)$  and 536 parameters; **13**, triclinic, space group  $P\bar{1}$  with  $a = 14.565(2)$ ,  $b = 17.961(2)$ ,  $c = 11.302(1)$  Å,  $\alpha = 97.72(1)$ ,  $\beta = 110.49(1)$ ,  $\gamma = 78.37(1)^\circ$ ,  $V = 2706.0(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.031$ ,  $R_w = 0.035$  for 9837 reflections with  $I > 3\sigma(I)$  and 536 parameters]. A comparison with the reported mononuclear and dinuclear lanthanide thiolate complexes has been made to indicate that the Ln–S bonds weakened by the coordination of HMPA to lanthanide metals have ionic character.

## Introduction

Lanthanide metals are highly electropositive elements and have rather high reactivities in general. We are concerned with the synthesis of lanthanide thiolate compounds from metallic lanthanides since these compounds have attracted current interest in the field of organic synthesis<sup>1</sup> and as rational molecular precursors to materials.<sup>2</sup> These compounds have been synthesized by the reaction of lanthanide halides with alkali salts of thiolates.<sup>3–5</sup> In these preparations, the rather strong interaction of lanthanide cations with the alkali-metal halides sometimes renders the isolation and purification of the products difficult. To avoid this difficulty, the reaction of alkyl or amido lanthanide complexes with thiols<sup>6–8</sup> and the oxidative reaction of low-

valent organosamarium or ytterbium complexes with organic disulfides<sup>9–11</sup> have been applied. Lanthanide compounds such as halide,<sup>12–15</sup> alkoxide,<sup>16–18</sup> amide,<sup>19</sup> and organolanthanide compounds<sup>20–27</sup> have been directly prepared from metallic lanthanides and this is the most effective synthetic strategy. Here we describe the details of the selective formation of divalent

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<sup>©</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1995.

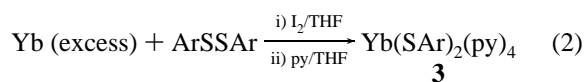
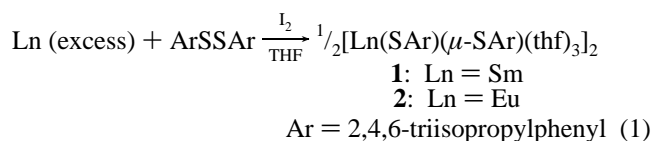
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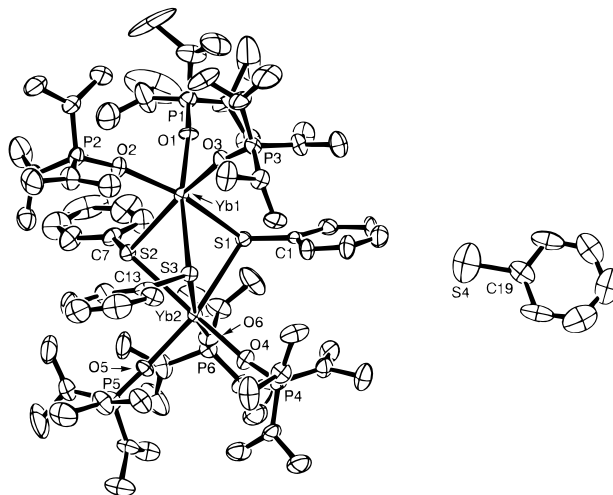
and trivalent samarium, europium, and ytterbium arenethiolate complexes by the direct reaction of lanthanide metals with diaryl disulfides, some details of which have been communicated.<sup>28</sup>

## Results and Discussion

**Synthesis of Bis(thiolato)lanthanide(II).** The binuclear bis-(2,4,6-triisopropylbenzenethiolate) complexes of samarium(II) and europium(II), [Ln(SAr)( $\mu$ -SAr)(thf)<sub>3</sub>]<sub>2</sub> (**1**, Ln = Sm; **2**, Ln = Eu; SAr = 2,4,6-triisopropylbenzenethiolate), were prepared by a direct reaction between a 2-fold excess of metallic lanthanide and bis(2,4,6-triisopropylphenyl) disulfide in THF in the presence of a catalytic amount (ca. 3 mol %) of iodine (eq 1). This reaction did not proceed at all without iodine. The lanthanide metal was quantitatively consumed within 24 h at 50 °C. Dimeric structures bearing bridging thiolate and terminal thiolate ligands for **1** and **2** have been revealed by the crystallographic study.<sup>28</sup> In the case of dialkyl disulfide such as di(*tert*-butyl) disulfide or dimethyl disulfide, no reaction was observed under the same conditions. Once isolated as crystals, complexes **1** and **2** gradually became opaque due to the loss of THF ligands, resulting in the formation of [Ln(SAr)<sub>2</sub>(thf)<sub>n</sub>]<sub>2</sub> (Ln = Sm, *n* = 1; Ln = Eu, *n* = 2), based on elemental analyses. The similar reaction of metallic Yb with bis(2,4,6-triisopropylphenyl) disulfide in THF gave an orange oily product, from which black crystals of Yb(SAr)<sub>2</sub>(py)<sub>4</sub> (**3**) were obtained on the addition of an excess of pyridine to the solution (eq 2). Recently, Brennan *et al.* reported the preparation of Yb(SPh)<sub>2</sub>(py)<sub>4</sub> (**4**) by the reaction of diphenyl disulfide with the solvated Yb metal ion in liquid ammonia or Yb/Hg amalgam in THF,<sup>2</sup> and Nief *et al.* reported the preparation of [Yb( $\mu$ -SPh)( $\eta^5$ -C<sub>4</sub>-Me<sub>4</sub>P)(thf)<sub>2</sub>]<sub>2</sub> (**5**) from metallic Yb and C<sub>4</sub>Me<sub>4</sub>PSPH in THF.<sup>29</sup>



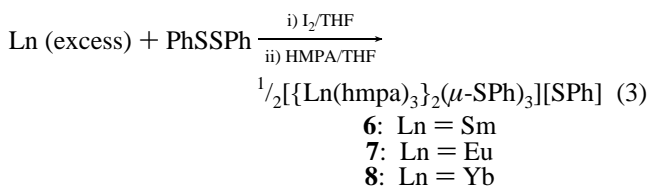
When diphenyl disulfide was used instead of the bulky substituted diaryl disulfide, the isolation of the product from the unreacted metal was hampered by the low solubility. This was solved by the use of HMPA as a ligand. This point has been noted in the case where uranium thiolates were dissolved by using HMPA.<sup>30,31</sup> The reaction of excess ytterbium metal with diphenyl disulfide under the same condition as eq 1 afforded a suspension of a sparingly soluble red powder, which dissolved upon successive addition of 4 equiv of HMPA to the suspension to give a dark red solution. Removal of the unreacted metal followed by concentration and cooling of the



**Figure 1.** ORTEP drawing of cationic and anionic parts of **8** with a numbering scheme; 20% probability ellipsoids.

supernatant solution gave the HMPA adduct of ytterbium(II) complex, [Yb(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>[SPh] (**8**), as dark red crystals (eq 3). Samarium (**6**) and europium (**7**) derivatives were also prepared similarly. The structure of **6–8** was assumed to be the cationic dimer structure, which was based on the X-ray analysis of **8** (*vide infra*).

In the case of the preparation of **6**, the reaction of excess samarium metal and diphenyl disulfide was carried out in the presence of HMPA to afford the product together with a contamination of the tris(benzenethiolate) complex Sm(SPh)<sub>3</sub>(hmpa)<sub>3</sub>. Thus, the yield of the Sm(II) thiolate complex is lowered by the coordination of HMPA on samarium, forming a mononuclear Sm(III) complex. This is consistent with the fact that the addition of HMPA to the solution of LnI<sub>2</sub> (Ln = Sm and Yb) in THF greatly accelerates the electron transfer reactions.<sup>32</sup> All of these complexes are highly sensitive to air and moisture. Especially, it was difficult to purify **6** and **7**, resulting in poor elemental analysis data.



### Molecular Structures of [Yb(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>[SPh] (**8**).

The molecular structure of **8** is shown in Figure 1, and the selected bond distances and angles are listed in Table 1. A single-crystal X-ray analysis of **8** revealed that complex **8** has the ionic structure composed of triply bridged dinuclear cation and benzenethiolate anion, *i.e.*, [Yb(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>[SPh], in sharp contrast to the neutral dimer structure found for **1** and **2**.<sup>28</sup> There is no significant contact between cationic and anionic molecules. To our knowledge, this is the first example of the cationic thiolate complex of lanthanide element together with thiolate as a counteranion.

In the cationic part of complex **8**, each ytterbium metal has distorted octahedral geometry coordinated by three HMPA ligands and three bridging benzenethiolate ligands in facial fashion. Such triply bridged structures are common for thiolate complexes of transition metals.<sup>33,34</sup> Each phenyl plane is nearly

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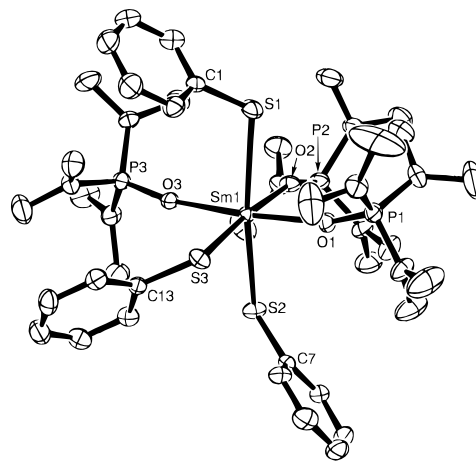
**Table 1.** Selected Bond Distances (Å) and Angles (deg) of **8**

Bond Distances			
Yb(1)–S(1)	2.902(4)	Yb(2)–S(1)	2.897(4)
Yb(1)–S(2)	2.916(4)	Yb(2)–S(2)	2.930(4)
Yb(1)–S(3)	2.936(3)	Yb(2)–S(3)	2.922(4)
Yb(1)–O(1)	2.351(8)	Yb(2)–O(4)	2.319(10)
Yb(1)–O(2)	2.344(9)	Yb(2)–O(5)	2.320(8)
Yb(1)–O(3)	2.343(10)	Yb(2)–O(6)	2.319(9)
S(1)–C(1)	1.74(2)	S(2)–C(7)	1.75(1)
S(3)–C(13)	1.78(2)	S(4)–C(19)	1.75(2)
Bond Angles			
S(1)–Yb(1)–S(2)	78.3(1)	S(1)–Yb(2)–S(2)	78.1(1)
S(1)–Yb(1)–S(3)	78.8(1)	S(1)–Yb(2)–S(3)	79.1(1)
S(2)–Yb(1)–S(3)	77.5(1)	S(2)–Yb(2)–S(3)	77.52(10)
S(1)–Yb(1)–O(2)	165.8(3)	S(1)–Yb(2)–O(5)	168.2(2)
S(2)–Yb(1)–O(3)	166.6(2)	S(2)–Yb(2)–O(4)	165.8(3)
S(3)–Yb(1)–O(1)	168.3(2)	S(3)–Yb(2)–O(6)	168.8(3)
Yb(1)–S(1)–C(1)	117.9(5)	Yb(2)–S(1)–C(1)	117.9(5)
Yb(1)–S(2)–C(7)	117.7(7)	Yb(2)–S(2)–C(7)	122.2(6)
Yb(1)–S(3)–C(13)	116.4(5)	Yb(2)–S(3)–C(13)	115.6(5)
Yb(1)–O(1)–P(1)	171.3(6)	Yb(2)–O(4)–P(4)	169.6(7)
Yb(1)–O(2)–P(2)	170.2(7)	Yb(2)–O(5)–P(5)	172.7(6)
Yb(1)–O(3)–P(3)	167.5(7)	Yb(2)–O(6)–P(6)	167.9(7)
Yb(1)–S(1)–Yb(2)	87.13(10)	Yb(1)–S(2)–Yb(2)	86.25(9)
Yb(1)–S(3)–Yb(2)	86.02(8)		

perpendicular to the Yb1–Yb2 vector. The bridging Yb–S distances (av 2.917(4) Å) are 0.1 Å longer than those of [Yb( $\mu$ -SPh)( $\eta^5$ -C<sub>4</sub>Me<sub>4</sub>P)(thf)<sub>2</sub>]<sub>2</sub> (**5**) (av 2.817(3) Å).<sup>29</sup> On the other hand, Yb–O(hmpa) distances (av 2.334(9) Å) of **8** are in the range of those previously reported for other divalent ytterbium complexes, e.g., [Yb( $\mu$ -OCPh<sub>2</sub>)(hmpa)<sub>2</sub>]<sub>2</sub> [2.28(3) Å],<sup>35</sup> Yb(OC<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>2</sub>-2,6-Me-4)<sub>2</sub>(hmpa)<sub>2</sub> [2.298(7) Å],<sup>35</sup> Yb[ $\mu$ -OC{Mo(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(hmpa)<sub>4</sub> [2.33(1) Å],<sup>36</sup> and [Yb(hmpa)<sub>4</sub>(thf)<sub>2</sub>]<sub>2</sub> [2.357(6) Å].<sup>37</sup> The strong coordination of polar HMPA ligands to the ytterbium metal elongates the Yb–S bonds and this effect might result in the heterolysis of one Yb–S bond to make the complex ionic.

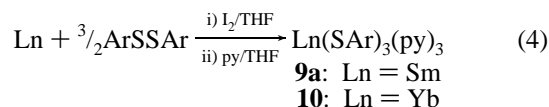
The Yb–S–C angles of **8** [115.6(5)–122.2(6)°, av 118.0(6)°] are in the range of those reported for other 6-coordinated ytterbium(II) thiolates.<sup>2,6</sup> The sums of angles around S(1) [322.9°], S(2) [326.6°], and S(3) [318.0°] are smaller than 360°, indicating that the sulfur atoms in **8** are not planar. The Yb–O–P angles of **8** [167.5(7)–172.7(6)°, av 169.9(7)°] are slightly larger than those of 6-coordinated ytterbium(III) thiolate (**13**, *vide infra*).

**Synthesis of Tris(thiolato)lanthanide(III).** The reaction of a lanthanide metal powder with 3 equiv of bis(2,4,6-triisopropylphenyl) disulfide in THF in the presence of a catalytic amount of iodine gave oily compounds, whose formula can be speculated from the final product as Ln(SAr)<sub>3</sub>(thf)<sub>n</sub>. Addition of pyridine to the reaction mixture resulted in the formation of Ln(SAr)<sub>3</sub>(py)<sub>3</sub> (**9a**, Ln = Sm; **10**, Ln = Yb) as orange and red crystals in 39% and 30% yields, respectively (eq 4). When the crude crystals of **9a** were recrystallized from THF, one of the pyridine ligands on **9a** was replaced by a THF ligand to afford Sm(SAr)<sub>3</sub>(py)<sub>2</sub>(thf) (**9b**), whose formula was revealed by X-ray crystallography.<sup>28</sup> The reaction of the isolated Sm(II) complex **1** with bis(2,4,6-triisopropylphenyl) disulfide in THF also resulted in the formation of Sm(III) complex **9a** after the

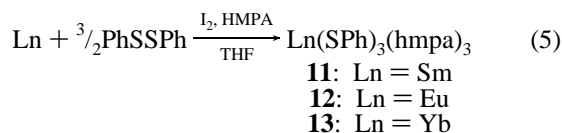


**Figure 2.** ORTEP drawing of **11** with a numbering scheme; 20% probability ellipsoids. The solvated THF molecule and all hydrogen atoms are omitted for clarity.

treatment with pyridine. Although this reaction must also occur at the initial stage of the reaction for the preparation of **1** in eq 1, **1** could be isolated in good yield. This suggests that the samarium(III) thiolates might be reduced to samarium(II) by metallic samarium in the condition without HMPA. These tris(triisopropylbenzenethiolate) complexes **9a**, **9b**, and **10** are air- and moisture-sensitive and easily lose thf and pyridine ligands, resulting in the poor elemental analysis. The reaction of metallic europium did not give tris(thiolate) complexes but afforded complex **2**. The smaller negative value of the oxidation potential of Eu than Sm and Yb is consistent with the above finding.



The direct reaction of metallic samarium and diphenyl disulfide in THF gave an insoluble yellow powder. When the reaction was carried out in the presence of 3 equiv of HMPA, Sm(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (**11**) was obtained as THF-soluble colorless crystals in 77% yield. Similarly, the europium (**12**) and ytterbium (**13**) derivatives were prepared in moderate yields (eq 5). This is in sharp contrast to the fact that the reaction of metallic europium with more than 3 equiv of bis(2,4,6-triisopropylphenyl) disulfide in THF, without HMPA, did not give europium(III) tris(thiolate). However, this is consistent with the fact that the addition of HMPA to the solution of LnI<sub>2</sub> (Ln = Sm and Yb) in THF greatly accelerates the electron-transfer reactions.<sup>32</sup> These lanthanide(III) benzenethiolates bearing HMPA ligands are relatively stable in air compared to the other lanthanide thiolates reported in this paper, but they are deliquescent. Elemental analysis of these complexes indicated that they have one THF as a solvent molecule, which was further confirmed by crystallographic studies of **11** and **13** (*vide infra*). In the case of other lanthanide metals such as lanthanum, praseodymium, dysprosium, and neodymium, the rate of the reaction was much slower than that of Sm, Eu, and Yb.



**Molecular Structures of Sm(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (**11**) and Yb(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (**13**).** The molecular structure of compound **11** is shown in Figure 2 and the selected bond distances and angles

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**Table 2.** Selected Bond Distances (Å) and Angles (deg) in **11** and **13**

	<b>11</b>	<b>13</b>
Bond Distances		
Ln-S(1)	2.815(2)	2.740(1)
Ln-S(2)	2.837(2)	2.727(1)
Ln-S(3)	2.811(2)	2.718(1)
Ln-O(1)	2.307(4)	2.181(3)
Ln-O(2)	2.318(4)	2.232(2)
Ln-O(3)	2.271(4)	2.212(3)
S(1)-C(1)	1.756(8)	1.752(4)
S(2)-C(7)	1.734(7)	1.756(4)
S(3)-C(13)	1.770(7)	1.768(4)
O(1)-P(1)	1.495(4)	1.492(3)
O(2)-P(2)	1.501(4)	1.495(2)
O(3)-P(3)	1.498(4)	1.494(3)
Bond Angles		
S(1)-Ln-S(2)	162.87(7)	164.33(4)
S(1)-Ln-S(3)	99.87(7)	97.42(3)
S(1)-Ln-O(1)	85.2(1)	86.98(7)
S(1)-Ln-O(2)	83.0(1)	80.93(7)
S(1)-Ln-O(3)	91.2(1)	95.41(7)
S(2)-Ln-S(3)	97.25(6)	98.25(4)
S(2)-Ln-O(1)	95.8(1)	91.99(7)
S(2)-Ln-O(2)	80.0(1)	83.42(7)
S(2)-Ln-O(3)	87.0(1)	85.30(7)
S(3)-Ln-O(1)	88.6(1)	93.14(7)
S(3)-Ln-O(2)	175.8(1)	176.85(7)
S(3)-Ln-O(3)	94.2(1)	88.04(7)
O(1)-Ln-O(2)	88.6(2)	89.46(10)
O(1)-Ln-O(3)	175.8(2)	177.18(9)
O(2)-Ln-O(3)	88.8(2)	89.44(10)
Ln-S(1)-C(1)	115.6(3)	117.7(1)
Ln-S(2)-C(7)	116.8(2)	117.2(1)
Ln-S(3)-C(13)	111.5(2)	113.2(1)
Ln-O(1)-P(1)	161.8(3)	169.1(2)
Ln-O(2)-P(2)	162.8(3)	162.3(2)
Ln-O(3)-P(3)	169.2(3)	161.7(2)

found in **11** are summarized in Table 2. Compound **13** has essentially the same structure as **11**, and only the selected bond distances and angles are given in Table 2. Comparative Ln-S bond distances and Ln-S-C bond angles for these complexes and the known samarium and ytterbium thiolates are shown in Table 3.

Both complexes **11** and **13** have essentially the same mononuclear pseudooctahedral geometry with three benzene thiolato ligands and three HMPA ligands in meridional fashion as observed previously for complexes **9b** and **10**.<sup>28</sup> The Ln-S distances [2.811(2)–2.837(2) Å, av 2.821(2) Å] of **11** are significantly longer than those found for the other two known samarium(III) complexes bearing terminal thiolato ligands, *e.g.*, Sm(SC<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3</sub>-2,4,6)<sub>3</sub> (**14**) [2.634(9)–2.652(9) Å, av 2.645(9) Å]<sup>6</sup> and **9b** [2.720(3)–2.751(3) Å, av 2.740(3) Å].<sup>28</sup> Complex **13** [2.718(1)–2.740(1) Å, av 2.728(3) Å] has the longest Yb-S bonds among the reported ytterbium(III) complexes bearing terminal thiolate ligand, *e.g.*, Yb(SPh)(NH<sub>3</sub>)(η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (**15**) [2.670(3) and 2.679(3) Å, av 2.675(3) Å]<sup>41</sup> and **10** [2.622(7)–2.665(6) Å; av 2.648(6) Å].<sup>28</sup> Thus the coordination of HMPA to the lanthanide metals elongates the Ln-S bonds and presumably weakens them, as described for complex **8**.

The Sm-O(hmpa) distances of **11** are slightly, but significantly, shorter than those reported in the 5-coordinated samarium(III) complex, Sm{OC(Ph)=CCH=CHCH<sub>2</sub>CH=CH}<sub>2</sub>(OC<sub>6</sub>H<sub>2</sub>-

Bu<sup>t</sup><sub>2</sub>-2,6-Me-4)(hmpa)<sub>2</sub> [av 2.333(10) Å],<sup>26</sup> and the Yb-O(hmpa) distances of **13** are comparable to those reported in YbCl<sub>3</sub>(hmpa)<sub>3</sub> [av 2.224(9) Å]<sup>44</sup> and [Yb(H<sub>2</sub>O)<sub>5</sub>(hmpa)<sub>2</sub>]Cl<sub>3</sub> [av 2.178(7) Å].<sup>44</sup> These Ln-O(hmpa) distances of **11** and **13** are also comparable to those found in divalent lanthanide complexes such as SmI<sub>2</sub>(hmpa)<sub>4</sub> [av 2.500(6) Å], [Yb(hmpa)<sub>4</sub>(thf)<sub>2</sub>]I<sub>2</sub> [av 2.357(6) Å],<sup>37</sup> and **8** [av 2.334(9) Å] on taking into account the difference of ionic radii of Ln<sup>2+</sup> and Ln<sup>3+</sup> [0.19–0.20 Å for Sm(II/III) and 0.15–0.16 Å for Yb(II/III)].<sup>45</sup>

Among the three Yb-S bonds in the complex **13**, the bond distance of Yb-S3 trans to O2 is shorter than those of the other Yb-S bond cis to O2. Such a tendency has been seen in the Yb-Cl bonds in the 6-coordinated ytterbium(III) complex YbCl<sub>3</sub>(hmpa)<sub>3</sub>.<sup>44</sup> The rather large angles of Ln-O-P (ca. 161–169°) as well as the observed bond distances of **11** and **13** indicate that the donation of an oxygen atom of HMPA to lanthanide metal elongates the Ln-S bond cis to HMPA.

For the 6-coordinated trivalent complexes bearing a terminal thiolate ligand, the Ln-S distances of **9b** (2.740(3) Å), **11** (2.821(2) Å), **10** (2.648(6) Å) and **13** (2.728(3) Å) are apparently shorter than those of divalent complexes such as **1**, **2**, **4**, and **18**, indicating that the Ln-S distance is a simple summation of ionic radii of Ln<sup>2+</sup> or Ln<sup>3+</sup> with that of S<sup>2-</sup>.<sup>45</sup> As a result, complexes **11** and **13** are best described by using an ionic bond model.

## Conclusion

The synthesis of divalent and trivalent lanthanide arenethiolate complexes has been achieved by the direct reaction of some metallic lanthanides with diaryl disulfides. The oxidation states of the lanthanides in the product can be controlled by the stoichiometry of the reactants. The X-ray analysis of the divalent ytterbium thiolate [{Yb(hmpa)<sub>3</sub>]<sub>2</sub>(μ-SPh)<sub>3</sub>][SPh] (**8**) has revealed that **8** has ionic structure composed of a triply bridged dinuclear cation and a benzenethiolate anion. The X-ray crystallographic studies of tris(benzenethiolate) complexes of trivalent lanthanides Sm(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (**11**) and Yb(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (**13**) have revealed their monomeric pseudooctahedral structure. The elongated Ln-S bond lengths in these complexes indicate that the coordination of HMPA somewhat weakens the Ln-S bonds and the ionic nature of these Ln-S bonds are clearly confirmed.

## Experimental Section

**General.** All manipulations involving air- and moisture-sensitive lanthanide compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. THF and hexane were dried over sodium benzophenone ketyl and then distilled before use.

<sup>1</sup>H NMR (270 MHz) spectra were measured on a JEOL GSX-270 spectrometer. Elemental analyses were performed at the Elemental Analysis Center of Faculty of Science, Osaka University. All melting points were measured in sealed tubes and were not corrected.

**Synthesis of [Sm(SAr)(μ-SAr)(thf)<sub>3</sub>]<sub>2</sub> (**1**).** To samarium metal powder (453 mg, 3.01 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (712 mg, 1.51 mmol) in THF (40 mL) was added a catalytic amount of iodine (12 mg, 0.05 mmol). The reaction mixture was stirred at 50 °C for 24 h. A dark green solution was separated from the unreacted metal. Concentration of the solution, addition of hexane, and cooling to -20 °C afforded dark green prisms of **1** (351 mg, 28% yield). Further concentration and cooling the mother liquor gave second, third, and fourth crops of crystals. The total yield was 74%. Mp 160–178 °C (dec). Anal. Calcd for C<sub>34</sub>H<sub>54</sub>OS<sub>2</sub>Sm: C, 58.90; H, 7.85. Found: C, 58.94; H, 8.25.

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**Table 3.** Comparative Structural Data of Lanthanide Thiolate Complexes

complexes <sup>a</sup>	$d(\text{Ln}-\text{S})/\text{\AA}^b$	$\angle(\text{LnSC})/\text{deg}^b$	mode <sup>c</sup>	CN <sup>d</sup>	ref
[Sm(SAr)( $\mu$ -SAr)(thf) <sub>3</sub> ] <sub>2</sub> ( <b>1</b> )	2.908(6) 3.017(6)	124.0(8) 123.7(7)	terminal bridging	6	28
Sm(SAr) <sub>3</sub> (py) <sub>2</sub> (thf) ( <b>9b</b> )	2.740(3)	121.8(3)	terminal	6	28
Sm(SPh) <sub>3</sub> (hmpa) <sub>3</sub> ( <b>11</b> )	2.821(2)	114.6(2)	terminal	6	this work
Sm(SC <sub>6</sub> H <sub>2</sub> Bu <sup>t</sup> <sub>3</sub> -2,4,6) <sub>3</sub> ( <b>14</b> )	2.645(9)	82.9(8)	terminal	3	6
[Sm( $\mu$ -SPh)( $\eta$ -C <sub>8</sub> H <sub>8</sub> )(thf) <sub>2</sub> ] <sub>2</sub> ( <b>16</b> )	2.924(8)	121.4(7)	bridging	8	42
[Sm( $\mu$ -SAr)( $\eta$ -C <sub>8</sub> H <sub>8</sub> )(thf) <sub>2</sub> ] <sub>2</sub> ( <b>17</b> )	2.883(6)	127.0(8)	bridging	7	42
Yb(SAr) <sub>3</sub> (py) <sub>3</sub> ( <b>10</b> )	2.648(6)	116.8(8)	terminal	6	28
Yb(SPh) <sub>3</sub> (hmpa) <sub>3</sub> ( <b>13</b> )	2.728(3)	116.0(1)	terminal	6	this work
( $\eta$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Yb(SPh)(NH <sub>3</sub> ) ( <b>15</b> )	2.675(3)	118.5(3)	terminal	8	41
[{Yb(hmpa) <sub>3</sub> ] <sub>2</sub> ( $\mu$ -SPh) <sub>3</sub> ][SPh] ( <b>8</b> )	2.917(4)	118.0(6)	bridging	6	this work
Yb(SC <sub>6</sub> H <sub>2</sub> Bu <sup>t</sup> <sub>3</sub> -2,4,6) <sub>2</sub> (dme) <sub>2</sub> ( <b>18</b> )	2.756(8)	125.0(8)	terminal	6	6
[Yb( $\mu$ -SPh)( $\eta$ <sup>5</sup> -C <sub>4</sub> Me <sub>4</sub> P)(thf) <sub>2</sub> ] <sub>2</sub> ( <b>5</b> )	2.817(3)		bridging	7	29
Yb(SPh) <sub>2</sub> (py) <sub>4</sub> ( <b>4</b> )	2.827(3)	101.6(3)	terminal	6	2

<sup>a</sup> Ar = 2,4,6-triisopropylphenyl. <sup>b</sup> Averaged value in the complex. <sup>c</sup> Bonding mode of the thioleto ligand. <sup>d</sup> CN = coordination number.  $\eta$ -Cyclopentadienyl and  $\eta$ -cyclooctatetraenyl may be taken as occupying three and four coordination sites around the metal, respectively.

**Table 4.** Crystal Data and Data Collection Parameters

complex	<b>8</b>	<b>11</b>	<b>13</b>
formula	C <sub>60</sub> H <sub>128</sub> O <sub>6</sub> N <sub>18</sub> P <sub>6</sub> S <sub>4</sub> Yb <sub>2</sub>	C <sub>40</sub> H <sub>77</sub> O <sub>4</sub> N <sub>9</sub> P <sub>3</sub> S <sub>3</sub> Sm	C <sub>40</sub> H <sub>77</sub> O <sub>4</sub> N <sub>9</sub> P <sub>3</sub> S <sub>3</sub> Yb
crystal system	orthorhombic	triclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , $\text{\AA}$	21.057(9)	14.719(3)	14.565(2)
<i>b</i> , $\text{\AA}$	25.963(7)	17.989(2)	17.961(2)
<i>c</i> , $\text{\AA}$	16.442(8)	11.344(2)	11.302(1)
$\alpha$ , deg		97.91(1)	97.72(1)
$\beta$ , deg		110.30(2)	110.49(1)
$\gamma$ , deg		78.40(1)	78.37(1)
<i>V</i> , $\text{\AA}^3$	8988(5)	2751.9(9)	2706.0(7)
<i>Z</i>	4	2	2
<i>D</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.373	1.312	1.363
abs coeff, cm <sup>-1</sup>	23.19	13.14	19.76
unique data [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	5848	7111	9837
no. of variables	865	536	536
<i>R</i> <sup>a</sup>	0.040	0.045	0.031
<i>R</i> <sub>w</sub> <sup>b</sup>	0.039	0.041	0.035

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

**Synthesis of [Eu(SAr)( $\mu$ -SAr)(thf)<sub>3</sub>]<sub>2</sub> (**2**).** This complex was prepared and isolated in a manner similar to that of **1**. The total yield was 56%. Mp >300 °C (dec). Anal. Calcd for C<sub>38</sub>H<sub>62</sub>O<sub>2</sub>S<sub>2</sub>Eu: C, 59.51; H, 8.15. Found: C, 59.10; H, 8.51.

**Synthesis of Yb(SAr)<sub>2</sub>(py)<sub>4</sub> (**3**).** To a suspension of ytterbium metal (172 mg, 0.99 mmol) with a solution of bis(2,4,6-triisopropylphenyl) disulfide (435 mg, 0.92 mmol) in THF (40 mL) was added a catalytic amount of iodine (5 mg, 0.02 mmol). The reaction mixture was stirred at 50 °C for 24 h. After removal of an excess of ytterbium metal, the addition of pyridine (1 mL) to the solution caused an immediate change of the color from orange yellow to black. Recrystallization afforded black microcrystals of **3** (407 mg, 46% yield), mp 170–215 °C (dec). Anal. Calcd for C<sub>30</sub>H<sub>66</sub>N<sub>4</sub>S<sub>2</sub>Yb: C, 62.54; H, 6.93; N, 5.83. Found: C, 61.85; H, 6.85; N, 6.25. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C)  $\delta$  8.56 (s, 8 H, py), 7.67 (t, 4 H, py), 7.26 (m, 8 H, py), 6.73 (s, 4 H, *m*-H), 4.23 (brs, 4 H, *o*-CHMe<sub>2</sub>), 2.75 (brs, 2 H, *p*-CHMe<sub>2</sub>), 1.18 (m, 36 H, *o*- and *p*-CHMe<sub>2</sub>).

**Synthesis of [{Sm(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>][SPh] (**6**).** To samarium metal (912 mg, 6.07 mmol) and diphenyl disulfide (684 mg, 3.13 mmol) in THF (30 mL) was added a catalytic amount of iodine (20 mg, 0.08 mmol). The reaction mixture was stirred at 50 °C for 24 h to give a mixture of a black powder and unreacted metal. When the HMPA (2.20 mL, 12.6 mmol) was added to the reaction mixture, the black powder gradually dissolved within 1 h. Removal of the metal followed by recrystallization gave black prisms of **6** (241 mg, 8% yield). Further concentration and cooling the mother liquor gave a second crop. The total yield was 29%. Mp 87–93 °C (dec). Anal. Calcd for C<sub>30</sub>H<sub>64</sub>N<sub>9</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>Sm: C, 39.76; H, 7.12; N, 13.91. Found: C, 37.65; H, 7.20; N, 13.45.

**Synthesis of [{Eu(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>][SPh] (**7**).** This complex was prepared and isolated in a manner similar to that of **6**, as yellow crystals

(13% yield), mp 162–164 °C (dec). Anal. Calcd for C<sub>30</sub>H<sub>64</sub>-EuN<sub>9</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>: C, 39.69; H, 7.11; N, 13.88. Found: C, 37.16; H, 7.07; N, 13.38.

**Synthesis of [{Yb(hmpa)<sub>3</sub>]<sub>2</sub>( $\mu$ -SPh)<sub>3</sub>][SPh] (**8**).** This complex was prepared and isolated in a manner similar to that of **6**, as dark red crystals (46% yield), mp 135–137 °C (dec). Anal. Calcd for C<sub>30</sub>H<sub>64</sub>N<sub>9</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>Yb: C, 38.79; H, 6.94; N, 13.57. Found: C, 38.65; H, 7.01; N, 13.33. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C)  $\delta$  7.48 (d, 4 H, *o*-H), 6.74 (m, 4 H, *m*-H), 6.55 (t, 2 H, *p*-H), 2.95 (d, 54 H, Me-(hmpa)).

**Synthesis of Sm(SAr)<sub>3</sub>(py)<sub>3</sub> (**9a**).** From Sm Metal. To samarium metal powder (151 mg, 1.00 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (727 mg, 1.54 mmol) in THF (40 mL) was added a catalytic amount of iodine (6 mg, 0.02 mmol). Stirring the mixture at 50 °C for 24 h afforded a red-orange solution. After removal of a small amount of insoluble impurities, pyridine (1 mL) was added. Concentration, addition of hexane, and cooling to –20 °C afforded orange microcrystals of **9a** (305 mg, 28% yield). Further concentration and cooling the mother liquor gave a second crop. The total yield was 39%. Mp 160–164 °C. Anal. Calcd for C<sub>60</sub>H<sub>84</sub>N<sub>3</sub>S<sub>3</sub>Sm: C, 65.88; H, 7.74; N, 3.84. Found: C, 65.12; H, 7.62; N, 3.76. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C)  $\delta$  8.45 (d, 6 H, py), 7.64 (t, 3 H, py), 7.22 (m, 6 H, py), 6.70 (s, 6 H, *m*-H), 4.76 (m, 6 H, *o*-CHMe<sub>2</sub>), 2.67 (m, 3 H, *p*-CHMe<sub>2</sub>), 1.28 (d, 36 H, *o*-CHMe<sub>2</sub>), 1.15 (d, 18 H, *p*-CHMe<sub>2</sub>).

**From complex 1.** To a dark green solution of **1** (258 mg, 0.15 mmol) in THF (3 mL) was added a solution of bis(2,4,6-triisopropylphenyl) disulfide (75 mg, 0.16 mmol) in THF (1 mL). Stirring the mixture at room temperature for 12 h afforded an orange solution. Addition of pyridine (0.1 mL) followed by concentration, addition of hexane, and cooling to –20 °C afforded orange crystals of **9a** (114 mg, 34% yield).

**Table 5.** Atomic Coordinates of Complex **8**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Yb(1)	0.01299(2)	0.17582(2)	0.85014(3)	3.94(1)	C(13)	-0.0423(9)	0.0514(5)	0.7190(8)	5.4(4)
Yb(2)	0.03126(2)	0.17608(2)	0.60822(3)	3.94(1)	C(14)	-0.1022(10)	0.0675(7)	0.703(1)	7.6(6)
S(1)	0.1056(2)	0.2198(1)	0.7394(2)	4.77(9)	C(15)	-0.1538(9)	0.0335(10)	0.697(2)	10.9(8)
S(2)	-0.0679(2)	0.2131(1)	0.7188(2)	4.77(9)	C(16)	-0.142(1)	-0.018(1)	0.707(2)	11.0(9)
S(3)	0.0241(2)	0.0935(1)	0.7286(2)	4.70(8)	C(17)	-0.084(1)	-0.0356(8)	0.723(2)	11.2(8)
S(4)	0.4429(4)	0.0487(3)	0.7616(7)	18.4(4)	C(18)	-0.0315(9)	-0.0021(6)	0.727(1)	7.4(5)
P(1)	0.0253(2)	0.2942(2)	0.9857(3)	5.4(1)	C(19)	0.524(1)	0.0421(6)	0.744(2)	8.9(7)
P(2)	-0.1419(2)	0.1348(2)	0.9481(3)	5.7(1)	C(20)	0.546(2)	0.022(1)	0.671(2)	11.7(10)
P(3)	0.1225(2)	0.0954(2)	0.9813(3)	5.1(1)	C(21)	0.609(3)	0.013(2)	0.662(3)	16(1)
P(4)	0.1569(2)	0.0928(2)	0.5086(3)	5.2(1)	C(22)	0.651(2)	0.029(1)	0.719(3)	15(1)
P(5)	-0.0937(2)	0.1294(2)	0.4604(3)	6.0(1)	C(23)	0.626(2)	0.050(1)	0.786(2)	13(1)
P(6)	0.0499(2)	0.2980(2)	0.4846(3)	5.2(1)	C(24)	0.563(2)	0.0564(8)	0.800(1)	11.3(8)
O(1)	0.0250(5)	0.2464(3)	0.9383(5)	5.3(2)	C(25)	0.1144(9)	0.3290(8)	0.887(1)	9.5(6)
O(2)	-0.0796(4)	0.1512(4)	0.9190(6)	5.9(3)	C(26)	0.117(1)	0.357(2)	1.038(3)	38(2)
O(3)	0.0749(4)	0.1273(4)	0.9404(6)	5.9(3)	C(27)	0.068(1)	0.248(1)	1.116(1)	14(1)
O(4)	0.1065(5)	0.1280(4)	0.5386(6)	5.9(3)	C(28)	-0.026(2)	0.313(1)	1.133(2)	26(1)
O(5)	-0.0449(4)	0.1512(3)	0.5141(5)	5.5(3)	C(29)	-0.094(1)	0.310(1)	0.948(2)	12.2(9)
O(6)	0.0512(5)	0.2487(4)	0.5301(5)	6.2(3)	C(30)	-0.027(2)	0.388(1)	0.970(2)	34(2)
N(1)	0.0839(9)	0.3295(7)	0.962(1)	11.8(6)	C(31)	-0.200(1)	0.133(1)	1.091(1)	14.0(9)
N(2)	0.031(1)	0.2846(6)	1.0809(10)	10.8(6)	C(32)	-0.1032(9)	0.1817(10)	1.087(1)	11.1(7)
N(3)	-0.0387(8)	0.3258(9)	0.977(1)	14.4(8)	C(33)	-0.2242(10)	0.2102(9)	0.925(2)	13.8(9)
N(4)	-0.1475(7)	0.1514(7)	1.0439(9)	8.5(5)	C(34)	-0.2169(8)	0.1454(8)	0.820(1)	8.9(6)
N(5)	-0.2050(6)	0.1585(5)	0.9026(10)	6.6(4)	C(35)	-0.2070(10)	0.0447(9)	0.941(1)	11.5(8)
N(6)	-0.1508(7)	0.0724(5)	0.9334(10)	7.8(4)	C(36)	-0.0931(10)	0.0403(7)	0.932(1)	8.6(6)
N(7)	0.1326(6)	0.0363(5)	0.9418(10)	6.4(4)	C(37)	0.1548(9)	0.0294(6)	0.862(1)	7.5(5)
N(8)	0.1928(6)	0.1205(5)	0.9710(8)	6.4(4)	C(38)	0.0827(10)	-0.0017(8)	0.967(2)	10.7(7)
N(9)	0.1046(8)	0.0874(7)	1.0752(9)	8.9(5)	C(39)	0.2523(8)	0.0939(8)	0.982(1)	9.2(6)
N(10)	0.1448(7)	0.0800(6)	0.4136(9)	7.7(4)	C(40)	0.1998(8)	0.1764(8)	0.966(1)	8.8(6)
N(11)	0.2254(6)	0.1167(6)	0.5252(9)	6.9(4)	C(41)	0.146(1)	0.061(1)	1.134(1)	16(1)
N(12)	0.1607(7)	0.0349(5)	0.5534(9)	6.9(4)	C(42)	0.050(1)	0.1043(9)	1.112(1)	12.9(9)
N(13)	-0.1595(7)	0.1603(7)	0.469(1)	8.5(5)	C(43)	0.094(1)	0.0981(8)	0.369(1)	9.5(7)
N(14)	-0.0713(7)	0.1338(5)	0.3660(7)	6.8(4)	C(44)	0.186(1)	0.0486(10)	0.365(1)	11.9(8)
N(15)	-0.1069(8)	0.0689(6)	0.483(1)	8.5(5)	C(45)	0.2340(7)	0.1714(8)	0.533(1)	8.0(5)
N(16)	-0.0188(7)	0.3087(5)	0.4462(9)	8.3(5)	C(46)	0.2853(8)	0.0903(8)	0.517(1)	10.2(7)
N(17)	0.1016(7)	0.2966(5)	0.4136(9)	7.8(4)	C(47)	0.1123(10)	-0.0025(8)	0.530(2)	12.1(8)
N(18)	0.0663(8)	0.3467(5)	0.5437(10)	8.6(5)	C(48)	0.182(1)	0.0304(8)	0.634(1)	10.2(7)
C(1)	0.1842(7)	0.2003(6)	0.7491(8)	4.9(4)	C(49)	-0.2017(9)	0.173(1)	0.401(2)	17(1)
C(2)	0.2340(8)	0.2352(6)	0.7535(9)	6.7(5)	C(50)	-0.1861(8)	0.173(1)	0.545(1)	12.0(8)
C(3)	0.2987(8)	0.2179(9)	0.759(1)	8.4(6)	C(51)	-0.0442(9)	0.1814(7)	0.3347(10)	9.0(6)
C(4)	0.3118(9)	0.1667(10)	0.764(1)	9.1(7)	C(52)	-0.084(1)	0.0949(8)	0.304(1)	11.2(7)
C(5)	0.2632(8)	0.1332(8)	0.759(1)	8.2(6)	C(53)	-0.051(1)	0.0368(8)	0.500(1)	9.2(7)
C(6)	0.2021(7)	0.1482(6)	0.749(1)	6.0(5)	C(54)	-0.165(1)	0.0429(9)	0.473(1)	12.7(9)
C(7)	-0.0914(9)	0.2779(6)	0.722(1)	6.1(5)	C(55)	-0.0767(8)	0.298(1)	0.494(1)	12.9(10)
C(8)	-0.0463(9)	0.3182(7)	0.733(1)	9.3(6)	C(56)	-0.031(1)	0.331(1)	0.370(2)	16(1)
C(9)	-0.070(2)	0.3676(8)	0.736(2)	13(1)	C(57)	0.120(1)	0.2506(9)	0.373(1)	11.3(8)
C(10)	-0.130(2)	0.3819(9)	0.734(2)	18(1)	C(58)	0.127(1)	0.342(1)	0.373(1)	13.6(9)
C(11)	-0.174(1)	0.343(1)	0.715(2)	14(1)	C(59)	0.118(1)	0.3450(8)	0.598(2)	13.2(9)
C(12)	-0.152(1)	0.2917(7)	0.713(1)	8.9(6)	C(60)	0.033(2)	0.3951(9)	0.537(2)	19(1)

**Synthesis of Sm(SAR)<sub>3</sub>(py)<sub>2</sub>(thf) (9b).** Complex **9a** (348 mg) was redissolved in THF followed by addition of hexane, concentration, and cooling the mixture to -20 °C to give orange crystals (5 mg) of **9b**. Further concentration and cooling of the mother liquor to -20 °C to give a second crop (83 mg). The total yield was 24%. Mp 163–167 °C. Anal. Calcd for C<sub>59</sub>H<sub>87</sub>N<sub>2</sub>O<sub>5</sub>Sm: C, 65.20; H, 8.07; N, 2.58. Found: C, 63.86; H, 8.09; N, 2.54. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C) δ 8.45 (d, 4 H, py), 7.64 (t, 2 H, py), 7.21 (m, 4 H, py), 6.71 (s, 6 H, *m*-H), 4.77 (m, 6 H, *o*-CHMe<sub>2</sub>), 2.68 (m, 3 H, *p*-CHMe<sub>2</sub>), 1.29 (d, 36 H, *o*-CHMe<sub>2</sub>), 1.15 (d, 18 H, *p*-CHMe<sub>2</sub>).

**Synthesis of Yb(SAR)<sub>3</sub>(py)<sub>3</sub> (10).** This complex was prepared and isolated in a manner similar to that of **9a**, as red crystals. The total yield was 30%. Mp 198–201 °C. Anal. Calcd for C<sub>60</sub>H<sub>84</sub>N<sub>3</sub>S<sub>3</sub>Yb: C, 64.54; H, 7.58; N, 3.76. Found: C, 63.70; H, 7.77; N, 3.34.

**Synthesis of Sm(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (11).** To samarium metal (402 mg, 2.67 mmol), diphenyl disulfide (883 mg, 4.05 mmol), and HMPA (1.40 mL, 8.05 mmol) in THF (30 mL) was added a catalytic amount of iodine (21 mg, 0.08 mmol). The reaction mixture was stirred at 50 °C for 24 h to give a brown solution. Removal of a small amount of insoluble impurities followed by cooling to -20 °C afforded colorless crystals of **11** (2.10 g, 77% yield), mp 142–146 °C. Anal. Calcd for C<sub>40</sub>H<sub>77</sub>N<sub>9</sub>O<sub>4</sub>P<sub>3</sub>S<sub>3</sub>Sm: C, 44.17; H, 7.14; N, 11.59. Found: C, 43.96;

H, 7.28; N, 11.69. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C) δ 7.01 (m, 3 H, *p*-H), 6.76 (d, 6 H, *o*-H), 6.35 (brs, 6 H, *m*-H), 2.58 (d, 54 H, Me(hmpa)).

**Synthesis of Eu(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (12).** This complex was prepared and isolated in a manner similar to that of **11**, as dark red crystals (70% yield), mp 128–131 °C. Anal. Calcd for C<sub>40</sub>H<sub>77</sub>EuN<sub>9</sub>O<sub>4</sub>P<sub>3</sub>S<sub>3</sub>: C, 44.11; H, 7.13; Eu, 13.95; N, 11.57. Found: C, 43.96; H, 7.14; N, 11.81. <sup>1</sup>H NMR (270 MHz, THF-*d*<sub>8</sub>, 30 °C) δ 11.63 (brs, 6 H, *m*- or *o*-H), 8.81 (brs, 3 H, *p*-H), 6.66 (brs, 6 H, *m*- or *o*-H), 1.90 (d, 54 H, Me(hmpa)).

**Synthesis of Yb(SPh)<sub>3</sub>(hmpa)<sub>3</sub> (13).** This complex was prepared and isolated in a manner similar to that of **11**, as yellow crystals (79% yield), mp 187–190 °C. Anal. Calcd for C<sub>40</sub>H<sub>77</sub>N<sub>9</sub>O<sub>4</sub>P<sub>3</sub>S<sub>3</sub>Yb: C, 43.27; H, 6.99; N, 11.35. Found: C, 43.27; H, 7.11; N, 11.39.

**Crystallographic Data Collections and Structure Determination of 8, 11, and 13.** The crystals of **8**, **11**, and **13** suitable for X-ray diffraction sealed in glass capillaries under argon atmosphere were mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo Kα radiation. Three standard reflections were chosen and monitored every 150 reflections. Measured nonequivalent reflections with *I* > 3.0σ(*I*) were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan.

**Table 6.** Atomic Coordinates of Complex **11**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Sm(1)	0.25566(3)	0.23309(2)	0.03776(4)	3.251(8)	C(10)	0.1066(7)	-0.0406(6)	-0.3644(9)	7.0(3)
S(1)	0.2191(2)	0.3835(1)	0.1393(3)	6.95(7)	C(11)	0.1252(6)	-0.0684(5)	-0.2524(10)	6.2(3)
S(2)	0.2848(2)	0.0720(1)	0.0019(2)	4.89(5)	C(12)	0.1773(6)	-0.0333(4)	-0.1420(8)	4.9(2)
S(3)	0.2886(2)	0.2611(1)	-0.1806(2)	4.94(5)	C(13)	0.4102(5)	0.2232(4)	-0.1766(6)	4.1(2)
P(1)	-0.0136(1)	0.2883(1)	-0.1361(2)	4.83(5)	C(14)	0.4562(6)	0.1506(4)	-0.1369(7)	5.0(2)
P(2)	0.1996(2)	0.1620(1)	0.2991(2)	4.37(5)	C(15)	0.4621(6)	0.2632(4)	-0.2197(7)	5.4(2)
P(3)	0.5170(1)	0.2272(1)	0.2501(2)	4.25(5)	C(16)	0.5553(7)	0.2329(6)	-0.2221(9)	6.8(3)
O(1)	0.0894(3)	0.2510(2)	-0.0724(4)	4.4(1)	C(17)	0.5495(7)	0.1218(5)	-0.1396(8)	6.2(3)
O(2)	0.2209(3)	0.2040(2)	0.2088(4)	4.3(1)	C(18)	0.5992(6)	0.1618(6)	-0.1821(9)	7.1(3)
O(3)	0.4167(3)	0.2214(2)	0.1578(4)	4.2(1)	C(19)	0.0451(8)	0.3735(7)	-0.258(1)	13.7(5)
N(1)	-0.0194(5)	0.3670(4)	-0.1932(7)	6.7(2)	C(20)	-0.072(1)	0.4372(6)	-0.170(2)	22.3(8)
N(2)	-0.0749(5)	0.3035(4)	-0.0374(8)	7.2(2)	C(21)	-0.0333(7)	0.3330(6)	0.089(1)	9.1(4)
N(3)	-0.0684(5)	0.2328(4)	-0.2573(7)	6.7(2)	C(22)	-0.1786(8)	0.3012(9)	-0.076(1)	16.7(6)
N(4)	0.1315(5)	0.0979(3)	0.2246(6)	4.8(2)	C(23)	-0.1387(9)	0.2583(7)	-0.376(1)	14.3(5)
N(5)	0.2986(5)	0.1189(4)	0.3994(6)	5.3(2)	C(24)	-0.0568(8)	0.1536(5)	-0.2437(10)	10.0(3)
N(6)	0.1376(5)	0.2226(3)	0.3756(6)	5.2(2)	C(25)	0.1624(7)	0.2984(5)	0.4175(9)	7.8(3)
N(7)	0.5090(5)	0.2850(4)	0.3713(6)	5.1(2)	C(26)	0.0739(7)	0.2016(5)	0.4340(9)	7.6(3)
N(8)	0.5701(4)	0.1429(3)	0.2988(6)	5.1(2)	C(27)	0.3264(7)	0.1270(5)	0.5350(8)	7.4(3)
N(9)	0.5855(4)	0.2590(4)	0.1904(6)	5.0(2)	C(28)	0.3709(7)	0.0695(5)	0.3514(8)	7.9(3)
C(1)	0.2990(6)	0.4433(4)	0.1367(8)	4.7(2)	C(29)	0.1506(7)	0.0202(5)	0.2564(9)	7.9(3)
C(2)	0.3130(6)	0.4557(5)	0.0272(9)	6.1(3)	C(30)	0.0582(6)	0.1118(5)	0.1034(8)	6.7(3)
C(3)	0.3740(8)	0.5039(6)	0.026(1)	8.3(4)	C(31)	0.6805(7)	0.2237(5)	0.187(1)	9.8(4)
C(4)	0.4225(8)	0.5411(6)	0.135(1)	8.9(4)	C(32)	0.4321(7)	0.2858(5)	0.4231(8)	7.3(3)
C(5)	0.4122(9)	0.5299(6)	0.246(1)	9.2(4)	C(33)	0.5777(7)	0.3352(5)	0.4379(8)	8.2(3)
C(6)	0.3499(8)	0.4801(5)	0.2476(10)	7.4(3)	C(34)	0.6430(7)	0.1307(5)	0.4222(9)	8.7(3)
C(7)	0.2136(5)	0.0325(4)	-0.1401(7)	3.9(2)	C(35)	0.5631(6)	0.0755(5)	0.2104(9)	7.1(3)
C(8)	0.1951(6)	0.0616(4)	-0.2548(8)	5.4(2)	C(36)	0.5467(6)	0.3274(5)	0.1218(9)	7.3(3)
C(9)	0.1416(7)	0.0247(6)	-0.3665(8)	7.0(3)					

**Table 7.** Atomic Coordinates of Complex **13**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Yb(1)	0.25488(1)	0.232904(9)	0.04246(2)	2.718(3)	C(10)	0.1093(4)	-0.0369(3)	-0.3656(5)	6.1(1)
S(1)	0.2182(1)	0.37976(6)	0.1359(1)	5.69(3)	C(11)	0.1266(4)	-0.0666(3)	-0.2539(6)	5.6(1)
S(2)	0.28294(8)	0.07713(6)	0.00651(9)	3.96(2)	C(12)	0.1781(3)	-0.0302(2)	-0.1414(4)	4.4(1)
S(3)	0.28911(8)	0.26152(6)	-0.1673(1)	4.16(2)	C(13)	0.4100(3)	0.2214(2)	-0.1688(3)	3.54(9)
P(1)	-0.00970(8)	0.28745(6)	-0.1335(1)	4.09(2)	C(14)	0.4605(4)	0.2625(3)	-0.2157(4)	4.6(1)
P(2)	0.19817(9)	0.16421(6)	0.29791(10)	3.63(2)	C(15)	0.5530(4)	0.2320(3)	-0.2235(5)	6.0(1)
P(3)	0.51323(8)	0.22664(6)	0.24896(10)	3.56(2)	C(16)	0.5977(4)	0.1606(4)	-0.1851(5)	6.1(1)
O(1)	0.0943(2)	0.2500(1)	-0.0682(2)	3.67(6)	C(17)	0.5493(4)	0.1187(3)	-0.1390(5)	5.7(1)
O(2)	0.2200(2)	0.2061(1)	0.2077(2)	3.75(6)	C(18)	0.4565(3)	0.1492(2)	-0.1304(4)	4.2(1)
O(3)	0.4118(2)	0.2210(1)	0.1575(2)	3.72(6)	C(19)	0.0491(5)	0.3734(4)	-0.2553(9)	11.9(3)
N(1)	-0.0158(3)	0.3670(2)	-0.1899(4)	5.8(1)	C(20)	-0.0668(9)	0.4380(4)	-0.1595(9)	17.0(4)
N(2)	-0.0731(3)	0.3019(3)	-0.0370(4)	6.2(1)	C(21)	-0.0320(5)	0.3314(4)	0.0919(6)	7.7(2)
N(3)	-0.0634(3)	0.2320(2)	-0.2558(4)	5.53(10)	C(22)	-0.1802(5)	0.2999(6)	-0.0790(9)	14.6(3)
N(4)	0.1307(3)	0.0991(2)	0.2253(3)	4.24(9)	C(23)	-0.1341(6)	0.2585(4)	-0.3740(7)	10.8(2)
N(5)	0.2984(3)	0.1226(2)	0.4006(3)	4.61(9)	C(24)	-0.0527(5)	0.1518(3)	-0.2433(6)	7.9(2)
N(6)	0.1346(3)	0.2257(2)	0.3729(3)	4.62(9)	C(25)	0.1592(4)	0.3012(3)	0.4148(5)	6.6(2)
N(7)	0.5066(3)	0.2851(2)	0.3700(3)	4.57(9)	C(26)	0.0694(4)	0.2035(3)	0.4307(5)	6.6(2)
N(8)	0.5682(3)	0.1426(2)	0.2997(3)	4.46(8)	C(27)	0.3238(4)	0.1299(3)	0.5367(4)	6.6(2)
N(9)	0.5812(2)	0.2588(2)	0.1874(3)	4.41(9)	C(28)	0.3740(4)	0.0720(3)	0.3569(5)	6.7(2)
C(1)	0.2980(3)	0.4410(2)	0.1353(4)	4.2(1)	C(29)	0.1505(4)	0.0217(3)	0.2594(5)	6.7(2)
C(2)	0.3118(4)	0.4543(3)	0.0263(5)	5.3(1)	C(30)	0.0550(4)	0.1120(3)	0.1016(5)	5.5(1)
C(3)	0.3726(5)	0.5053(3)	0.0277(6)	7.0(2)	C(31)	0.6768(4)	0.2220(3)	0.1823(7)	8.1(2)
C(4)	0.4212(5)	0.5430(3)	0.1372(8)	7.9(2)	C(32)	0.4294(4)	0.2862(3)	0.4241(4)	6.0(1)
C(5)	0.4102(5)	0.5307(4)	0.2452(7)	7.8(2)	C(33)	0.5783(4)	0.3346(3)	0.4374(5)	6.8(2)
C(6)	0.3490(4)	0.4794(3)	0.2461(5)	6.2(1)	C(34)	0.6427(4)	0.1317(3)	0.4248(5)	7.4(2)
C(7)	0.2133(3)	0.0367(2)	-0.1390(4)	3.25(8)	C(35)	0.5617(4)	0.0754(3)	0.2113(5)	5.8(1)
C(8)	0.1944(3)	0.0660(3)	-0.2538(4)	4.6(1)	C(36)	0.5408(4)	0.3282(3)	0.1202(5)	6.0(1)
C(9)	0.1433(4)	0.0290(3)	-0.3654(5)	6.2(1)					

The structure of **8** was solved by direct methods<sup>46</sup> and those of **11** and **13** were solved by the heavy-atom Patterson methods.<sup>46,47</sup> In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed by using the TEXSAN crystallographic software package. The THF molecule in **11** and **13** showed disordered form, and the occupancy of the disordered atoms

was fixed at 0.5. All other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were not refined.

The pertinent details of data collection and the final cell dimensions for **8**, **11**, and **13** are given in Table 4. Atomic coordinates of **8**, **11**, and **13** are listed in Tables 5, 6 and 7, respectively.

**Acknowledgment.** A.N. thanks to the Ministry of Education, Science and Culture, Japan, for support of this research (Specially Promoted Research No. 06101004).

**Supporting Information Available:** Tables of complete crystal data, hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles and ORTEP drawings for **8**, **11**, and **13** (37 pages). Ordering information is given on any current masthead page.

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