

## The First Neutral, Mononuclear 4f Metal Thiolates and New Methods for Corresponding Aryl Oxides and Bis(trimethylsilyl)amidest

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The first neutral, mononuclear 4f metal thiolates, [Sm(SAr)<sub>3</sub>] **1** and [Yb(SAr)<sub>2</sub>(dme)<sub>2</sub>] **2**, have been prepared and X-ray characterised [ $\langle\text{Sm-S}\rangle$  2.645(9) Å,  $\langle\text{Yb-S}\rangle$  2.756(8) Å], **1** from [Sm(CHR'<sub>2</sub>)<sub>3</sub>] + 3ArSH and **2** from [Yb(NR'<sub>2</sub>)<sub>2</sub>(dme)<sub>2</sub>] [obtained from Yb + Sn(NR'<sub>2</sub>)<sub>2</sub>]; **1** was not readily accessible from ArSH and Yb in liquid NH<sub>3</sub>, although replacing ArSH by Ar'OH yielded [Yb(OAr')<sub>2</sub>(thf)<sub>3</sub>] [Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,4,6; Ar' = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4; R' = SiMe<sub>3</sub>, dme = (MeOCH<sub>2</sub>)<sub>2</sub>, thf = OC<sub>4</sub>H<sub>8</sub>].

We report the synthesis of the first mononuclear 4f metal thiolates [Sm(SAr)<sub>3</sub>] **1** [eqn. (1)] and [Yb(SAr)<sub>2</sub>(dme)<sub>2</sub>] **2** (Scheme 1) (Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,4,6; dme = MeOCH<sub>2</sub>-CH<sub>2</sub>OMe). Compound **2** is also the first 4f metal(II)-sulfur complex.

The choice of a metal alkyl as precursor, eqn. (1), is likely to have widespread application. It has the convenience that the alkane by-product is unreactive and readily removed; its use appears previously to have been restricted to lithium thiolates, as for LiSAr(OEt<sub>2</sub>).<sup>1</sup> Selection of a metal bis(trimethylsilyl)-amide (*e.g.* **3** in Scheme 1) as precursor is more general, as for

M(SAr)<sub>2</sub> (M = Ge, Sn or Pb)<sup>1</sup> or [{Cd(μ-SAr)(SAr)}<sub>2</sub>].<sup>2</sup> Whereas [SmR<sub>3</sub>] is known,<sup>3</sup> a lanthanide(II) alkyl has not yet appeared in the literature; YbR<sub>2</sub>(thf)<sub>*n*</sub> can be prepared but is not readily accessible [R = CH(SiMe<sub>3</sub>)<sub>2</sub>, thf = OC<sub>4</sub>H<sub>8</sub>].<sup>4</sup> The compound [Yb(NR'<sub>2</sub>)<sub>2</sub>(dme)<sub>2</sub>]<sup>5a</sup> **3** with 2ArSH yielded **2** (reaction iii in Scheme 1). Both [Yb(NR'<sub>2</sub>)<sub>2</sub>(dme)]<sup>5</sup> [from Yb + Hg(NR'<sub>2</sub>)<sub>2</sub>]<sup>5b</sup> and [Eu(NR'<sub>2</sub>)<sub>2</sub>(dme)<sub>2</sub>]<sup>6</sup> have been described (R' = SiMe<sub>3</sub>). The synthesis of **3**, from Yb + Sn(NR'<sub>2</sub>)<sub>2</sub> (reaction ii in Scheme 1), is novel, although a similar procedure has been used to convert Ca into [Ca(NR'<sub>2</sub>)<sub>2</sub>(dme)<sub>2</sub>].<sup>7</sup> The -SAr ligand was introduced into coordination chemistry in 1983.<sup>1</sup>

Attempts to make an ytterbium(II) thiolate from Yb in liquid ammonia and ArSH in thf did not yield a characterised product, but the corresponding reaction using Ar'OH (reaction i in Scheme 1) to yield the known<sup>8</sup> ytterbium aryl

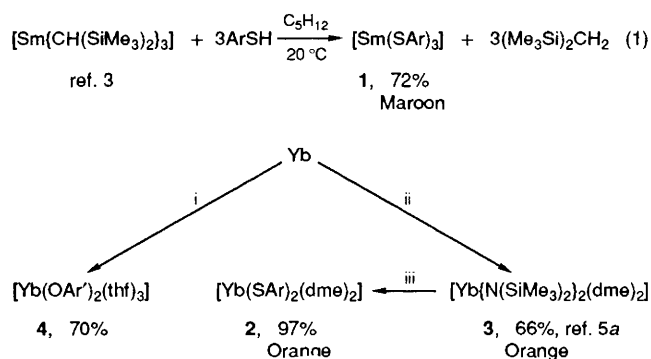
<sup>†</sup> No reprints available.

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**Table 1** Comparative selected structural data for some crystalline lanthanide metal thiolates

Compound	$d(\text{Ln-S})/\text{\AA}$	$\angle(\text{SLnS}')/^\circ$	CN of Ln	Ref.
[Sm(SAr) <sub>3</sub> ] <b>1</b>	2.645(9) av.	119.4(2) av.	3	This work
[Yb(SAr) <sub>2</sub> (dme) <sub>2</sub> ] <b>2</b>	2.756(8)	124.4(2)	6	This work
[{Ce( $\eta$ -C <sub>5</sub> H <sub>4</sub> Bu <sup>t</sup> ) <sub>2</sub> ( $\mu$ -SPri)} <sub>2</sub> ]	2.882(2) av.	78.9(1)	4	10
[{Gd[N(SiMe <sub>3</sub> ) <sub>2</sub> ( $\mu$ -SBu <sup>t</sup> ) <sub>2</sub> ]} <sub>2</sub> ]	2.791(5) av.	70.9(2)	4	11
[La( $\eta$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ( $\mu$ -SBu <sup>t</sup> ) <sub>2</sub> Li(thf) <sub>2</sub> ]	2.715(4) av.	73.6(1)	4(+4) <sup>a</sup>	12

<sup>a</sup> An  $\eta$ -cyclopentadienyl may be taken as occupying one (or three) coordination sites around the metal; CN = coordination number.



**Scheme 1** New routes to some ytterbium(II) complexes. Abbreviations: Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,4,6; Ar' = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4; thf = OC<sub>4</sub>H<sub>8</sub>; dme = (MeOCH<sub>2</sub>)<sub>2</sub>. Reaction conditions: i, Ar'OH in thf added to Yb in NH<sub>3</sub> (l) at -78 °C, then at 20 °C; ii, Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, thf, reflux, 8 h, and subsequent recrystallisation (C<sub>6</sub>H<sub>14</sub>-dme); iii, 2ArSH, C<sub>6</sub>H<sub>14</sub>, 20 °C. Characterisation: NMR spectroscopy,  $\ddagger$  X-ray data (for **2**, Fig. 2), and comparison with literature data for **4**.<sup>8</sup>

oxide [Yb(OAr')<sub>2</sub>(thf)<sub>3</sub>] **4** was effective (Ar' = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4). Similar use of liquid ammonia for reactions of lanthanide metals has yielded [Yb( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(NH<sub>3</sub>)(thf)]<sup>9a</sup> [Eu( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(thf)] and [Yb( $\eta$ -C<sub>8</sub>H<sub>8</sub>)(NC<sub>5</sub>H<sub>5</sub>)<sub>3</sub>] $\frac{1}{2}$ NC<sub>5</sub>H<sub>5</sub>.<sup>9b</sup>

The crystalline compounds **1–3** gave satisfactory analytical and NMR $\ddagger$  data, and single crystal X-ray diffraction studies $\S$

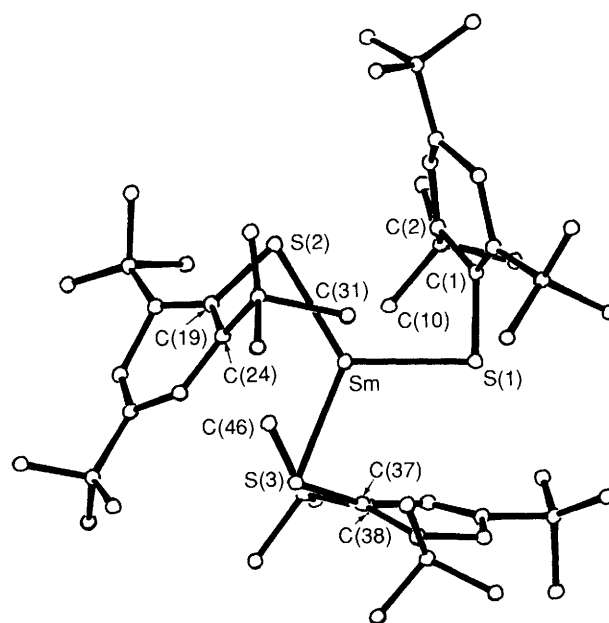
$\ddagger$  NMR spectroscopic data: **1**: <sup>1</sup>H NMR (80 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 298 K):  $\delta$  -2.27 (*o*-Bu<sup>t</sup>), 2.09 (*p*-Bu<sup>t</sup>), 8.21 (*m*-H); <sup>13</sup>C (90 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 298 K):  $\delta$  28.18 [*o*-C(CH<sub>3</sub>)<sub>3</sub>], 37.32 [*o*-C(CH<sub>3</sub>)<sub>3</sub>], 31.50 [*p*-C(CH<sub>3</sub>)<sub>3</sub>], 39.82 [*p*-C(CH<sub>3</sub>)<sub>3</sub>], 145.6 (*o*-C), 130.8 (*m*-C), 150.2 (*p*-C) (*ipso*-C not observed). **2**: <sup>1</sup>H NMR (360 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.45 (*p*-Bu<sup>t</sup>), 1.59 (Me of dme), 1.99 (*o*-Bu<sup>t</sup>), 3.09 (CH<sub>2</sub> of dme), 7.54 (*m*-H); <sup>191</sup>Yb NMR (63.02 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  485 [rel. to [Yb( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(thf)]<sub>2</sub>].

$\S$  Crystal data [*T* 295 K, Enraf-Nonius CAD-4 diffractometer, Mo-K $\alpha$  radiation ( $\lambda$  = 0.71069 Å)], no crystal decay, full-matrix least-squares refinement with Sm, Yb and S atoms anisotropic, H atoms fixed,  $w = 1/\sigma^2(F)$ .

**1**, C<sub>54</sub>H<sub>87</sub>S<sub>3</sub>Sm, *M* = 982.8, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 10.181(9), *b* = 37.510(15), *c* = 14.389(6) Å,  $\beta$  = 99.76(5)°, *U* = 5415.4 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.21 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 12.3 cm<sup>-1</sup>, specimen 0.5 × 0.5 × 0.5 mm, 7182 unique reflections for 2 <  $\theta$  < 22°, 3508 with  $|F^2| > \sigma(F^2)$  used in the refinement where  $\sigma(F^2) = \{\sigma(I) + (0.04I)^2\}^{1/2}/Lp$ . An absorption correction (max. 1.64 and min. 0.64) was applied after isotropic refinement (anisotropically refining C atoms produced several negative thermal parameters); *R* = 0.12 and *R*<sub>w</sub> = 0.14. A final difference map had peaks up to 1.4 e Å<sup>-3</sup> near the Sm atom.

**2**, C<sub>44</sub>H<sub>78</sub>O<sub>4</sub>S<sub>2</sub>Yb, *M* = 908.3, tetragonal, space group *I*4<sub>2</sub>d (No. 122), *a* = *b* = 21.850(3), *c* = 22.937(3) Å, *U* = 10950.4 Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.10 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 18.1 cm<sup>-1</sup>, specimen 0.3 × 0.3 × 0.1 mm, 1474 unique reflections for 0 <  $\theta$  < 22°, 1166 with  $|F^2| > 2\sigma(F^2)$  used in the refinement where  $\sigma(F^2) = \{\sigma^2(I) + (0.00I)^2\}^{1/2}/Lp$ , absorption correction (max. 1.34 and min. 0.73); *R* = 0.067, *R*<sub>w</sub> = 0.093. The molecule lies on a crystallographic two-fold rotation axis. No difference in *R* or *R*<sub>w</sub> for opposite absolute structure.

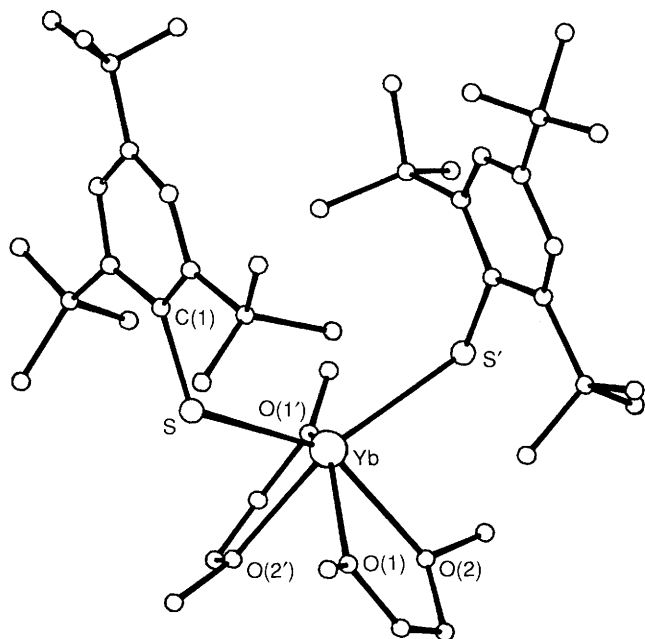
Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** The molecular structure of [Sm(SC<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,4,6)<sub>3</sub>] **1** and atom numbering scheme. Selected bond distances and angles: Sm-S(1) 2.646(7), Sm-S(2) 2.652(9), Sm-S(3) 2.634(9), Sm...C(1) 3.13(2) Å, Sm...C(19) 2.97(2), Sm...C(37) 2.88(3), Sm...C(2) 3.31(2) Å, Sm...C(24) 3.11(2), Sm...C(38) 3.29(3), Sm...C(10) 2.98(2) Å, Sm...C(31) 2.85(3), Sm...C(46) 3.23(4) Å; S(1)-Sm-S(2) 122.4(2)°, S(1)-Sm-S(3) 112.2(2)°, S(2)-Sm-S(3) 123.7(3)°, Sm-S(1)-C(1) 87.9(7)°, Sm-S(2)-C(19) 82.4(9)°, Sm-S(3)-C(37) 78.5(9)°.

on compounds **1** (Fig. 1) and **2** (Fig. 2) established the molecular structures. The only previously X-ray-characterised lanthanide metal thiolates were [Ce( $\eta$ -C<sub>5</sub>H<sub>4</sub>Bu<sup>t</sup>)<sub>2</sub>(SPri)]<sub>2</sub>,<sup>10</sup> [Gd(NR'<sub>2</sub>)<sub>2</sub>( $\mu$ -SBu<sup>t</sup>)<sub>2</sub>],<sup>11</sup> and [Lu( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(SBu<sup>t</sup>)<sub>2</sub>Li(thf)<sub>2</sub>];<sup>12</sup> comparative Ln-S and S-Ln-S bond lengths and angles for these and complexes **1** and **2** are shown in Table 1. Complexes **1** and **2** are the first lanthanide metal (Ln) complexes to have terminally bound thiolato ligands; not surprisingly, therefore, they have short Ln-S bond lengths. X-Ray data are also available for two complexes isolectic with **1**, [M(SAr)<sub>3</sub>] (M = Al or Ga);<sup>13</sup> these have an almost planar MS<sub>3</sub> core with <Al-S> 2.185(8) Å and <Ga-S> 2.205(8) Å. Bivalent M(SAr)<sub>2</sub> complexes to have been similarly characterised are Sn(SAr)<sub>2</sub>,<sup>14</sup> [M(SAr)( $\mu$ -SAr)]<sub>2</sub> (M = Mn,<sup>14</sup> Fe, Co,<sup>14</sup> or Cd<sup>2</sup>), and [Zn(SAr)<sub>2</sub>(OEt<sub>2</sub>)].<sup>15</sup> Crystallographic data on Ln-S complexes are now available for the five thiolates (Table 1) and for [Yb( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>( $\eta^2$ -S<sub>2</sub>CNMe<sub>2</sub>)] [*<*Yb-S 2.70(1) Å],<sup>16</sup> [Yb{(NR')<sub>2</sub>SPh}( $\eta^2$ -S<sub>2</sub>CNMe<sub>2</sub>)] [*<*Yb-S 2.716(3) Å],<sup>17</sup> and [Sm( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>( $\eta^2$ -S<sub>2</sub>CNMe<sub>2</sub>)] [Sm-S 2.808(2) Å].<sup>18</sup>

The SmS<sub>3</sub> skeleton in complex **1** approximates to having *D* symmetry, although the S-Sm-S angles deviate from the trigonal by up to 7.8°. The Sm atom is 0.149(2) Å from the S-Sm-S plane. The Sm-S-C angles are acute, 78.5(9) to 87.9(7)°. Or *tert*-butyl group on each -SAr ligand has short Sm...C(M



**Fig. 2** The molecular structure of  $[\text{Yb}(\text{SC}_6\text{H}_2\text{Bu}'_3\text{-}2,4,6)_2(\text{dme})_2]$  **2** and atom numbering scheme. Selected bond lengths and angles: Yb–S 2.756(8), Yb–O(1) 2.41(2), Yb–O(2) 2.66(2) Å; S–Yb–S' 124.4(2), S–Yb–O(1) 89.6(5), S–Yb–O(1') 112.3(5), S–Yb–O(2) 149.7(6), S–Yb–O(2') 83.0(6), O(1)–Yb–O(2) 65.8(8), O(1)–Yb–O(1') 133.0(7), O(1)–Yb–O(2') 77.1(8), Yb–S–C(1) 125.0(8)°.

contacts, av. 3.02(3) Å, and the *ipso*- and *ortho*-carbons are close to the metal, av. 3.12(2) Å.  $\gamma$ -Agostic interactions were previously observed in the parent alkyl  $[\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ ,  $\text{Sm}\cdots\text{C}(\text{Me})$  2.85(3) Å,<sup>3</sup> and, as for **1**, are attributable to the coordinative unsaturation of a formally three-coordinate lanthanide metal complex; they were also found in  $[\text{M}(\text{SAr})_3]$  (M = Al or Ga).<sup>13</sup>

In **2** the Yb atom, which lies on a crystallographic two-fold rotation axis, has distorted octahedral coordination with a large angle of 124.4(2)° between the *cis*-SAr groups, and a small bite angle of 65.8(8)° for the dme ligand. The Yb–S bond length is 2.756(8) Å, whilst the Yb–O bonds are 2.66(2) Å *trans* to S and 2.41(2) Å *trans* to O.

We thank SERC and Leverhulme Trust for support, SERC and ICI plc Chemicals and Polymers Group (and Dr P. J. V. Jones) for a CASE award to R. G. S., and the Turkish Academy (TUBITAK) and the Royal Society for a grant for B. C.

Received, 2nd April 1992; Com. 2/01744J

## References

- 1 P. B. Hitchcock, M. F. Lappert, B. J. Samways and E. L. Weinberg, *J. Chem. Soc., Chem. Commun.*, 1983, 1492.
- 2 M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 638.
- 3 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 1007.
- 4 S. A. Holmes and M. F. Lappert, unpublished work.
- 5 (a) T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271; (b) Yu. F. Rad'kov, E. A. Fedorova, S. Ya. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *Zh. Obshch. Khim.*, 1985, **55**, 2153.
- 6 T. D. Tilley, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1982, **21**, 2644.
- 7 H. Westerhausen, *Inorg. Chem.*, 1991, **30**, 90.
- 8 G. B. Deacon, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, P. MacKinnon and R. H. Newnham, *J. Chem. Soc., Chem. Commun.*, 1989, 935.
- 9 (a) A. L. Wayda, I. Mukerji, J. L. Dye and R. D. Rogers, *Organometallics*, 1987, **6**, 1328; (b) A. L. Wayda, J. L. Dye and R. D. Rogers, *Organometallics*, 1984, **3**, 1605.
- 10 S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 1623.
- 11 H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585.
- 12 H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Munchmore and J. Pickardt, *J. Organomet. Chem.*, 1988, **349**, 103.
- 13 K. Ruhlant-Senge and P. P. Power, *Inorg. Chem.*, 1991, **30**, 2633.
- 14 P. P. Power and S. C. Shoner, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 330.
- 15 P. P. Power and S. C. Shoner, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1403.
- 16 T. D. Tilley, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1982, **21**, 2644.
- 17 M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke and F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 894.
- 18 A. Recknagel, M. Noltemeyer, D. Stalke, U. Pieper, H.-G. Schmidt and F. T. Edelmann, *J. Organomet. Chem.*, 1991, **411**, 347.