

# Lanthanide Chalcogenolate Complexes: Synthesis and Crystal Structures of the Isoleptic Series [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>ER] (E = O, S, Se, Te; Tp<sup>Me,Me</sup> = *tris*-3,5-Dimethylpyrazolylborate)

Anna C. Hillier,<sup>†</sup> Sung-Ying Liu,<sup>†</sup> Andrea Sella,<sup>\*,†</sup> and Mark R. J. Elsgood<sup>‡</sup>

Christopher Ingold Laboratories, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., and Department of Chemistry, Bedson Building, University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.

Received December 22, 1999

A series of lanthanide complexes containing a chalcogenolate ligand supported by two Tp<sup>Me,Me</sup> (*tris*-3,5-dimethylpyrazolylborate) groups has been prepared and crystallized and provides direct comparisons of bonding to hard and soft ligands at lanthanide centers. Reaction of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] with NaOR (R = Ph, Ph-Bu<sup>t</sup>) gives [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>OR] (**1a** and **1b**, respectively) in good yields. Reductive cleavage of dichalcogenides by samarium(II) was used to prepare the heavier congeners. Complexes of the type [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>ER] for E = S, R = Ph (**2a**), E = S, R = Ph-4-Me (**2b**), E = S, R = CH<sub>2</sub>Ph (**2c**), E = Se, R = Ph (**3a**), E = Se, R = Ph-4-Bu<sup>t</sup> (**3b**), E = Se, R = CH<sub>2</sub>Ph (**3c**), and E = Te, R = Ph (**4**) have been prepared together with the corresponding complexes with Tp<sup>Me,Me,4-Et</sup> as ancillary. The X-ray crystal structures of **1b**, **2b**, **3a**, **3b**, and **4** have been determined. The crystal of **1b** (C<sub>40</sub>H<sub>57</sub>B<sub>2</sub>N<sub>12</sub>OSm·C<sub>7</sub>H<sub>8</sub>) was monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.6845(6) Å, *b* = 18.5573(11) Å, *c* = 24.4075(14) Å, β = 91.616(2)°, *Z* = 4. The crystal of **2b** (C<sub>37</sub>H<sub>51</sub>B<sub>2</sub>N<sub>12</sub>SSm) was monoclinic, *P*2<sub>1</sub>/*n*, *a* = 15.0154(9) Å, *b* = 13.1853(8) Å, *c* = 21.1254(13) Å, β = 108.628(2)°, *Z* = 4. The crystal of **3a** (C<sub>36</sub>H<sub>49</sub>B<sub>2</sub>N<sub>12</sub>SeSm·C<sub>7</sub>H<sub>8</sub>) was triclinic, *P*1̄, *a* = 10.7819(6) Å, *b* = 19.3011(10) Å, *c* = 23.0235(12) Å, α = 79.443(2)°, β = 77.428(2)°, γ = 89.827(2)°, *Z* = 4. The crystal of **3b** (C<sub>40</sub>H<sub>57</sub>B<sub>2</sub>N<sub>12</sub>SeSm) was triclinic, *P*1̄, *a* = 10.1801(6) Å, *b* = 10.2622(6) Å, *c* = 23.4367(14) Å, α = 88.313(2)°, β = 86.268(2)°, γ = 62.503(2)°, *Z* = 2. The crystal of **4** (C<sub>36</sub>H<sub>49</sub>B<sub>2</sub>N<sub>12</sub>TeSm·C<sub>7</sub>H<sub>8</sub>) was monoclinic, *P*2<sub>1</sub>/*c*, *a* = 18.7440(10) Å, *b* = 10.3892(6) Å, *c* = 23.8351(13) Å, β = 94.854(2)°, *Z* = 4. The compounds form an isoleptic series of seven-coordinate complexes with terminal chalcogenolate ligands. Examination of **1b** and other crystallographically characterized lanthanide alkoxides suggests that there is little correlation between bond angle and bond length. The structures of **3a** and **3b**, however, contain molecules in which one of the pyrazolylborate ligands undergoes a major distortion arising from twisting around a B–N bond so as to give an effectively eight-coordinate complex with π-stacking of the phenyl group with one pyrazolyl ring. These distortions shed light on the fluxionality of these systems.

## Introduction

The lanthanides have long been regarded as good examples of hard metal centers, and their chemistry has been dominated by hard atom donors such as ethers, amines, amides, etc.<sup>1</sup> In recent years, however, there has been considerable interest in the preparation of complexes containing soft donor atoms, in particular those of group 16.<sup>2</sup> This is driven in part because such complexes are thought to be good starting materials for the preparation of binary chalcogenides of the lanthanides, which are of considerable technological interest, but also from a desire to improve the understanding of such hard–soft interactions. Recently a number of reports have appeared which suggest that a simple ionic model for lanthanide chalcogenolate bonding may be simplistic.<sup>3</sup> However, the number of simple complexes between which detailed structural comparisons may be made is rather small.

A number of strategies have been used in the preparation of chalcogenolate complexes. The reaction of lanthanide halides

with the alkali-metal chalcogenolates has been used, but often suffers from problems arising from the incorporation of units of alkali metal or metal halide into the product.<sup>4–8</sup> Protonolysis methods, starting from amides or alkyls, were used in early work and avoid halide contamination,<sup>4,9</sup> although “-ate” complexes have been prepared by protonolysis also.<sup>10,11</sup> An alternative approach involving the direct insertion of chalcogen atoms into lanthanide–carbon bonds requires the presence of ancillary ligands.<sup>12,13</sup> Redox methods offer a convenient route to the preparation of chalcogenolates. The reductive cleavage of diaryl

- (4) Aspinall, H.; Bradley, D.; Hursthouse, M.; Sales, K.; Walker, N. *J. Chem. Soc., Chem. Commun.* **1985**, 1585–1586.
- (5) Gornitzka, H.; Edelmann, F. T.; Jakob, K. *J. Organomet. Chem.* **1992**, *436*, 325–332.
- (6) Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159–3160.
- (7) Tatsumi, K.; Amemiya, T.; Kawaguchi, H.; Tani, K. *J. Chem. Soc., Chem. Commun.* **1993**, 773–774.
- (8) Berardini, M.; Emge, T. J.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537–1538.
- (9) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 932–934.
- (10) Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem., Intl. Ed. Engl.* **1985**, *24*, 985–987.
- (11) Schumann, H.; Albrecht, I.; Gallagher, M.; Hahn, E.; Muchmore, C.; Pickardt, J. *J. Organomet. Chem.* **1988**, *349*, 103–115.
- (12) Beletskaya, I. P.; Voskoboinikov, A. Z.; Shestakova, A. K.; Schumann, H. *J. Organomet. Chem.* **1993**, *463*, C1–C2.

<sup>†</sup> University College London.

<sup>‡</sup> University of Newcastle.

(1) Kaltsoyannis, N.; Scott, P. *The f-Elements*; Oxford University Press: Oxford, 1999.

(2) Nief, F. *Coord. Chem. Rev.* **1998**, *178–80*, 13–81.

(3) Berardini, M.; Lee, J.; Freedman, D.; Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, *36*, 5772–5776.

dichalcogenides either by divalent complexes<sup>14–17</sup> or by the elemental lanthanide itself has proven to be a powerful method for the synthesis of a wide range of compounds. In the case of europium and ytterbium such reactions may be conveniently carried out in liquid ammonia, a solvent in which these metals dissolve.<sup>18,19</sup> The use of lanthanide–mercury amalgams has allowed the synthesis of a wide range of complexes both divalent and trivalent.<sup>19–22</sup> Organometallic complexes have been prepared by carrying out the reaction in the presence of cyclooctatetraene and a catalytic amount of iodine.<sup>23,24</sup>

Few of the reports referred to in the previous section describe terminal chalcogenolates, and systematic comparisons of structurally related complexes from oxygen to tellurium are rare. We and others have recently prepared divalent complexes of the elements europium, samarium, and ytterbium, with two pyrazolylborates as ancillary ligands.<sup>25–27</sup> These complexes react by oxidation with a wide variety of reagents such as azobenzene,<sup>25</sup> dioxygen,<sup>28</sup> and halogens and halocarbons.<sup>29</sup> The considerable steric crowding around the metal results in a variety of unusual monomeric complexes including the first terminal fluoride and hydroxo species.<sup>30,31</sup> In this paper we report on the behavior of an isostructural series of chalcogenolate complexes prepared either by metathesis or by reductive cleavage of the E–E bonds of aryldichalcogenides by the highly reducing Sm(II) center. Some of this work has been communicated previously.<sup>32</sup>

## Experimental Section

All preparations and manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen.<sup>33,34</sup> Oxygen-free nitrogen was purified by passage over columns containing

3 Å molecular sieves and MnO.<sup>35</sup> All solvents were predried over 5 Å molecular sieves or sodium wire and distilled under nitrogen from appropriate drying agents {Na (toluene), K (benzene, tetrahydrofuran), Na/K alloy (petroleum ether, bp 40–60 °C, pentane, diethyl ether)} before use.

[Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] (Tp<sup>Me,Me</sup> = tris-3,5-dimethylpyrazolylborate) was prepared by reaction of samarium diiodide and 2 equiv of sodium hydrotris(3,5-dimethylpyrazolyl)borate.<sup>36</sup> [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>] was prepared analogously using potassium hydrotris(3,5-dimethyl-4-ethylpyrazolyl)borate.<sup>37</sup> [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] was prepared by reaction of SmCl<sub>3</sub> with 2 equiv of KTp<sup>Me,Me</sup> in THF.<sup>38</sup> Disulfides, diselenides, and ditellurides were prepared by standard methods or purchased from Aldrich and used as received.

Infrared spectra were recorded as KBr pellets on a Nicolet 205 FTIR spectrometer. NMR spectra were recorded in solution using Varian XL-200 and VXR-400 spectrometers operating at 200 (<sup>1</sup>H), 400 (<sup>1</sup>H), and 100.6 (<sup>13</sup>C) MHz. Spectra were calibrated using residual proton (<sup>1</sup>H) and solvent resonances (<sup>13</sup>C) and are reported relative to tetramethylsilane. Elemental analyses were determined by Mr. Alan Stones of the University College London Analytical Services.

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>OPh], 1a.** [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] (0.20 g, 0.26 mmol) and sodium phenoxide (0.030 g, 0.26 mmol) were mixed in a Schlenk tube under nitrogen. THF (30 cm<sup>3</sup>) was added and the mixture stirred for 18 h, during which time a fine translucent precipitate appeared. The solvent was removed under reduced pressure and the resultant white residue extracted with toluene (30 cm<sup>3</sup>). The volume of extract was reduced to 10 cm<sup>3</sup> under reduced pressure. Pure material was obtained by leaving this solution in a freezer (–20 °C) overnight. Yield: 0.15 g (69%). Anal. Calcd for C<sub>36</sub>H<sub>49</sub>N<sub>12</sub>B<sub>2</sub>O<sub>2</sub>Sm: C, 51.61; H, 5.89; N, 20.06. Found: C, 51.31; H, 5.87; N, 20.11. IR (KBr): 2566 (BH), cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ –1.87 (s, 18H, 3-Me); 3.32 (s, 18H, 5-Me); 5.44 (s, 6H, 4-CH); 7.71 (t, 1H, *p*-Ph) 8.26 (m, 2H, *m*-Ph); 11.05 (d, 2H, *o*-Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K): δ 9.9 (q, 3 or 5Me); 14.4 (q, 5 or 3Me); 104.5 (d, C–H); 116.0 (d, Ph); 123.1 (s, Ph); 130.4 (d, Ph); 145.1 (s, C(3) or C(5)); 148.2 (s, C(5) or C(3)).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>OPh-4-Bu], 1b.** [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] (0.20 g, 0.26 mmol) and sodium 4-*tert*-butylphenoxide (0.045 g, 0.26 mmol) were mixed in a Schlenk tube under nitrogen. THF (30 cm<sup>3</sup>) was added and the mixture stirred overnight. The solvent was removed from the suspension under reduced pressure, and the resultant white residue was extracted with toluene (30 cm<sup>3</sup>). The volume of extract was reduced to 10 cm<sup>3</sup> under reduced pressure. Colorless crystals of the product were obtained by leaving this solution in a freezer (–20 °C) overnight. Yield: 0.14 g (61%). Anal. Calcd for C<sub>40</sub>H<sub>60</sub>N<sub>12</sub>B<sub>2</sub>O<sub>2</sub>Sm·C<sub>7</sub>H<sub>8</sub>: C, 57.12; H, 6.63; N, 17.02. Found: C, 56.90; H, 6.56; N, 17.21. IR (KBr): 2552 (BH) cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ –1.79 (s, 18H, 3-Me); 1.83 (s, 9H, Bu<sup>t</sup>); 3.29 (s, 18H, 5-Me); 5.41 (s, 6H, 4-CH); 8.18 (d, 2H, *m*-Ph); 10.88 (d, 2H, *o*-Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K): δ (10.2 (q, 3 or 5Me); 14.3 (q, 5 or 3Me); 32.3 (q, Bu<sup>t</sup>); 68.1 (s, C); 104.5 (d, C–H); 118.5 (d, Ph); 126.9 (s, Ph); 128.5 (d, Ph); 145.0 (s, C(3) or C(5)); 148.3 (s, C(5) or C(3)).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SPh], 2a.** [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] (0.20 g, 0.27 mmol) was placed in a Schlenk flask under N<sub>2</sub>. Toluene (20 cm<sup>3</sup>) was added, and the flask was then cooled to –78 °C in a dry ice–acetone slush bath. Diphenyl disulfide (0.031 g, 0.14 mmol) dissolved in toluene (30 cm<sup>3</sup>) was added dropwise and the mixture stirred overnight. The suspension turned from deep purple to a clear pale yellow solution as the mixture warmed. The solution was then concentrated to 15 cm<sup>3</sup> under reduced pressure and cooled to –20 °C, yielding pale yellow microcrystals. Yield: 0.17 g (74%). Anal. Calcd for C<sub>36</sub>H<sub>49</sub>N<sub>12</sub>B<sub>2</sub>SSm: C, 50.51; H, 5.77; N, 19.65. Found: C, 50.31; H, 5.54; N, 19.37. IR (KBr): 2566 (BH), cm<sup>–1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.67 (s, 18H, 3-Me); 2.28 (s, 18H, 5-Me); 5.44 (s, 6H, 4-CH); 7.52 (t, 1H, *p*-Ph); 7.60 (t, 2H, *m*-Ph); 9.50 (d, 2H, *o*-Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 13.3 (q, 3 or 5Me); 13.4 (q, 5 or 3Me); 106.0 (d, C–H); 121.0 (d, Ph);

- (13) Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. *Organometallics* **1993**, *12*, 4723.
- (14) Berg, D. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1858–1863.
- (15) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853.
- (16) Recknagel, A.; Noltemeyer, M.; Stalke, D.; Pieper, U.; Schmidt, H.-G.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *411*, 347–356.
- (17) Edelmann, F. T.; Rieckhoff, M.; Haiduc, I.; Silaghidumitrescu, I. *J. Organomet. Chem.* **1993**, *447*, 203–208.
- (18) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, *33*, 2743–2747.
- (19) Mashima, K.; Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A. *Inorg. Chem.* **1996**, *35*, 93–99.
- (20) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523–2524.
- (21) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 3215–3219.
- (22) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179–6185.
- (23) Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1847–1848.
- (24) Mashima, K.; Nakayama, Y.; Nakamura, A.; Kanehisa, N.; Kai, Y.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 85–91.
- (25) Takats, J.; Zhang, X. W.; Day, V. W.; Eberspacher, T. A. *Organometallics* **1993**, *12*, 4286–4288.
- (26) Maunder, G. H.; Sella, A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1994**, 885–886.
- (27) Santos, I.; Marques, N. *New J. Chem.* **1995**, *19*, 551–571.
- (28) Zhang, X. W.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828–7829.
- (29) Liu, S. Y.; Maunder, G. H.; Day, V. W.; Sella, A.; Takats, J.; Marques, N.; Santos, I. Manuscript in preparation.
- (30) Takats, J. Personal communication.
- (31) Lin, G. Y.; McDonald, R.; Takats, J. Manuscript in preparation.
- (32) Hillier, A. C.; Liu, S. Y.; Sella, A.; Elsegood, M. R. *J. Alloys Compds.* **2000**, *303–304*, 83–93.
- (33) McNally, S.; Cooper, N. J. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; McNally, S., Cooper, N. J., Eds.; American Chemical Society: Washington, DC, 1987; Vol. 357, pp 6–22.
- (34) Errington, R. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie: London, 1997.

- (35) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
- (36) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.
- (37) Maunder, G. H. Ph.D. Thesis, University of London, 1995.
- (38) Liu, S.-Y. Ph.D. Thesis, University of London, 1996.

**Table 1.** Summary of Crystal Data and Structure Determination for Compounds **1b**·C<sub>7</sub>H<sub>8</sub>, **2b**, **3a**·C<sub>7</sub>H<sub>8</sub>, **3b**, and **4**·C<sub>7</sub>H<sub>8</sub>

compd	<b>1b</b> ·C <sub>7</sub> H <sub>8</sub>	<b>2b</b>	<b>3a</b> ·C <sub>7</sub> H <sub>8</sub>	<b>3b</b>	<b>4</b> ·C <sub>7</sub> H <sub>8</sub>
empirical formula	C <sub>40</sub> H <sub>57</sub> B <sub>2</sub> N <sub>12</sub> O <sub>8</sub> Sm·C <sub>7</sub> H <sub>8</sub>	C <sub>37</sub> H <sub>51</sub> B <sub>2</sub> N <sub>12</sub> SSm	C <sub>36</sub> H <sub>49</sub> B <sub>2</sub> N <sub>12</sub> SeSm·C <sub>7</sub> H <sub>8</sub>	C <sub>40</sub> H <sub>57</sub> B <sub>2</sub> N <sub>12</sub> SeSm	C <sub>36</sub> H <sub>49</sub> B <sub>2</sub> N <sub>12</sub> TeSm·C <sub>7</sub> H <sub>8</sub>
fw	986.08	867.93	992.94	956.91	1041.58
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
<i>a</i> , Å	10.6845(6)	15.0154(9)	10.7819(6)	10.1801(6)	18.7440(10)
<i>b</i> , Å	18.5573(11)	13.1853(8)	19.3011(10)	10.2622(6)	10.3892(6)
<i>c</i> , Å	24.4075(14)	21.1254(13)	23.0235(12)	23.4367(14)	23.8351(13)
α, deg			79.443(2)	88.313(2)	
β, deg	91.616(2)	108.628(2)	77.428(2)	86.268(2)	94.854(2)
γ, deg			89.827(2)	62.503(2)	
<i>V</i> , Å <sup>3</sup>	4837.5(5)	3963.4(4)	4593.8(4)	2167.2(2)	4624.9(4)
<i>Z</i>	4	4	4	2	4
ρ <sub>calcd</sub> , g cm <sup>-3</sup>	1.354	1.455	1.421	1.466	1.496
μ, mm <sup>-1</sup>	1.262	1.578	2.09	2.238	1.932
<i>R</i> <sup>a</sup>	0.0323	0.0350	0.0282	0.0305	0.0479
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0703	0.0769	0.0647	0.0675	0.0932
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
<i>T</i> , °C	-113	-113	-113	-113	-113

<sup>a</sup> Conventional  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  for "observed" reflections having  $F_o^2 > 2\sigma(F_o^2)$ . <sup>b</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]$  for all data.

128.7 (s, Ph); 134.1 (d, Ph); 145.4 (s, C(3) or C(5)); 151.3 (s, C(5) or C(3)); 157.9 (d, Ph).

**Preparation of [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>SPh], 2a'.** [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>] (13 mg, 0.014 mmol) and diphenyl sulfide (PhSSPh) (ca. 1 mg, 0.009 mmol) were mixed and 1 cm<sup>3</sup> C<sub>6</sub>D<sub>6</sub> added. The solution immediately became orange, turning yellow within 5 min, and was transferred to an NMR tube which was sealed in vacuo. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.65 (s, 18H, 3-Me), 0.97 (t, 18H, CH<sub>3</sub>), 2.13 (q, 12H, CH<sub>2</sub>), 2.30 (s, 18H, 5-Me), 7.48 (m, 2H, *m*-H), 7.59 (t, 1H, *p*-H), 9.35 (d, 2H, *o*-H).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SPh-4-Me], 2b.** The reaction was carried out analogously to the preparation of **2a**. Yield: 60 mg (52%). Anal. Calcd for C<sub>37</sub>H<sub>51</sub>N<sub>12</sub>B<sub>2</sub>SSm: C, 51.07; H, 5.91; N, 19.33. Found: C, 50.92; H, 5.93; N, 19.04. IR (KBr): 2562 (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.42 (s, 18H, Me); 1.29 (s, 3H, MePh); 1.40 (s, 18H, Me); 5.31 (s, 6H, CH); 7.41 (d, 2H, *J* = 7.9 Hz, *m*-Ph); 9.37 (d, 2H, *J* = 7.9 Hz, *o*-Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K): δ 12.9 (q, 3 or 5Me); 13.5 (q, 5 or 3Me); 21.4 (q, MePh); 105.4 (d, C(4)); 128.6 (d, Ph); 133.2 (d, Ph); 145.0 (s, C(3) or C(5)); 150.4 (s, C(5) or C(3)).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SCH<sub>2</sub>Ph], 2c.** Toluene (20 cm<sup>3</sup>) was added to a mixture of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] (0.30 g, 0.40 mmol) and (SCH<sub>2</sub>-Ph)<sub>2</sub> (0.050 g, 20 mmol) at room temperature. The mixture was stirred and warmed gently, during which time the purple color faded and the solution became yellow. After filtration the solution was concentrated under reduced pressure and cooled overnight to -20 °C to give yellow microcrystals. Yield: 125 mg (34%). IR (KBr): 2540 (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298K): δ 0.44 (s, 18H, 3-Me); 2.33 (s, 18H, 5-Me); 5.74 (s, 6H, 4-CH); 7.07 (s, 2H, CH<sub>2</sub>Ph); 7.50 (t, 1H, *p*-H), 7.79 (t, 2H, *m*-H, *J* = 7.3 Hz); 9.08 (d, 2H, *o*-H, *J* = 7.3 Hz).

**Preparation of [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>SCH<sub>2</sub>Ph], 2c'.** To a purple suspension of [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>] (0.20 g, 0.20 mmol) in toluene (40 cm<sup>3</sup>) cooled to -78 °C was added (SCH<sub>2</sub>Ph)<sub>2</sub> (27 mg, 11 mmol). The mixture was stirred at -78 °C, then allowed to warm to room temperature, and stirred for a further 48 h, during which time it turned yellow. After filtration the solvent was removed under reduced pressure to leave a yellow powder. After the powder was dissolved in pentane (15 cm<sup>3</sup>) and the solution cooled to -30 °C, yellow crystals were obtained. Yield: 69 mg (30%). Anal. Calcd for C<sub>49</sub>H<sub>79</sub>N<sub>12</sub>B<sub>2</sub>SSm: C, 56.79; H, 7.29; N, 16.22. Found: C, 56.21; H, 7.27; N, 15.84. IR (KBr): 2540 (sh) (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.51 (s, 18H, 3-Me); 1.01 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>); 2.18 (q, 12H, CH<sub>2</sub>); 2.31 (s, 18H, 5-Me); 7.09 (s, 2H, CH<sub>2</sub>Ph); 7.50 (t, 1H, *p*-H), 7.77 (t, 2H, *m*-H); 9.04 (d, 2H, *o*-H).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SePh], 3a.** The compound was prepared by analogy with **2a**. Yield: 74 mg (34%). Anal. Calcd for C<sub>36</sub>H<sub>49</sub>N<sub>12</sub>B<sub>2</sub>SeSm·C<sub>7</sub>H<sub>8</sub>: C, 52.01; H, 5.79; N, 16.93. Found: C, 51.67; H, 5.92; N, 16.99. IR (KBr): 2550 (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.74 (s, 18H, Me); 2.18 (s, 18H, Me); 5.45 (s, 6H, CH); 7.30 (m, 3H, Ph); 9.00 (m, 2H, *o*-Ph). <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 183 K): δ -3.10 (br

s, 6H, 3-Me); -1.60 (br s, 6H, 3-Me); 2.25 (br s, 6H, 5-Me); 2.40 (br s, 6H, 5-Me); 3.20 (br s, 6H, 5-Me); 4.60 (s, 6H, 3-Me); 4.85 (s, 2H, 4-CH); 5.45 (s, 2H, 4-CH); 6.10 (s, 2H, 4-CH); 7.75 (br d, 2H, *m*-CH); 9.62 (br d, 2H, *o*-CH).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SePh-4-Bu], 3b.** The compound was prepared by analogy with **2a**. Yield: 83 mg (41%). Anal. Calcd for C<sub>40</sub>H<sub>57</sub>N<sub>12</sub>B<sub>2</sub>SeSm: C, 50.03; H, 5.99; N, 17.52. Found: C, 49.98; H, 5.90; N, 17.35. IR (KBr): 2541, 2462 (sh) (ν<sub>BH</sub>), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.50 (s, 18H, 3-Me); 1.47 (s, 9H, Bu<sup>1</sup>); 2.44 (s, 18H, 5-Me); 5.47 (s, 6H, CH); 7.37 (d, 2H, *m*-Ph); 8.76 (m, 2H, *o*-Ph). <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 208 K): δ -2.51 (s, 6H, 3-Me); -1.34 (s, 6H, 3-Me); 1.70 (s, 9H, Bu<sup>1</sup>); 2.44 (s, 3H, 5-Me); 2.72 (s, 3H, 5-Me); 3.41 (s, 3H, 5-Me); 4.84 (s, 3H, 3-Me); 5.12 (s, 2H, 4-CH); 5.70 (s, 3H, 4-CH); 6.36 (s, 3H, 4-CH); 7.75 (br d, 2H, *m*-Ph); 9.62 (br d, 2H, *o*-Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 13.5 (q, 3 or 5Me); 13.6 (q, 5 or 3Me); 31.6 (q, Bu<sup>1</sup>); 105.6 (d, C-H); 124.6 (d, Ph); 124.8 (d, Ph); 135.8 (s, h); 145.4 (s, C(3) or C(5)); 150.9 (s, C(5) or C(3)).

**Preparation of [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>SeC<sub>6</sub>H<sub>4</sub>-4-Bu], 3b'.** The reaction was carried out by analogy with the preparation of **2a'**. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.68 (s, 3-Me), 0.99 (t, CH<sub>3</sub>), 1.63 (s, Bu<sup>1</sup>), 2.17 (q, CH<sub>2</sub>), 2.29 (d, 5-Me), 7.45 (d, *m*-H), 9.16 (d, *o*-H).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SeCH<sub>2</sub>Ph], 3c.** To a purple suspension of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] (200 mg, 0.27 mmol) in toluene (10 cm<sup>3</sup>) was added (SeCH<sub>2</sub>Ph)<sub>2</sub> (46 mg, 0.14 mmol). The mixture was stirred at room temperature overnight and then warmed gently to 50 °C for 15–20 min, during which time it turned yellow. After filtration the volume of the solution was reduced. Orange yellow microcrystals were obtained on cooling to -20 °C. Yield: 55 mg (22%). IR (KBr): 2540 (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 0.37 (s, 18H, 3-Me); 2.44 (s, 18H, 5-Me); 3.13 (s, 1H, CH<sub>2</sub>Ph); 5.63 (s, 6H, 4-CH); 6.72 (s, 2H, CH<sub>2</sub>Ph); 7.50 (m, 1H, *p*-H), 7.77 (t, 2H, *m*-H); 8.29 (d, 2H, *o*-H). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 183 K): δ -3.68 (br s, 6H, 3-Me); -2.30 (br s, 6H, 3-Me); 1.87 (br s, 6H, 5-Me); 2.42 (br s, 6H, 3-Me); 2.86 (br s, 6H, 3-Me); 5.12 (br s, 2H, 4-CH); 5.33 (br s, 2H, 4-CH); 5.68 (br s, 2H, 4-CH); 6.33 (br s, 6H, 3-Me); 7.43 (m, 1H, *p*-H); 7.80 (m, 2H, *m*-H), 8.82 (d, 2H, *o*-H); 9.03 (br s, 2H, CH<sub>2</sub>Ph).

**Preparation of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>TePh], 4.** The compound was prepared by analogy with **2a**. Anal. Calcd for C<sub>36</sub>H<sub>49</sub>N<sub>12</sub>B<sub>2</sub>TeSm: C, 45.48; H, 5.15; N, 17.68. Found: C, 44.67; H, 5.22; N, 17.04. IR (KBr): 2554 (BH), cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.70 (s, 18H, 3-Me), 2.13 (s, 18H, 5-Me), 5.47 (s, 6H, 4-CH), 7.35 (t, 2H, *J* = 7 Hz, *m*-CH), 7.48 (t, 1H, *J* = 7 Hz, *p*-CH), 9.47 (d, 2H, *J* = 7 Hz, *o*-CH).

**Preparation of [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>TePh], 4'.** The reaction was carried out by analogy with the preparation of **2a'**. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.65 (s, 3-Me), 0.96 (t, CH<sub>3</sub>), 2.15 (q, CH<sub>2</sub>), 2.22 (s, 5-Me), 7.20 (m, *m*-H), 7.31 (t, *p*-H), 9.06 (d, *o*-H).

**Crystallographic Studies.** Crystal data and some refinement details are given in Table 1. Further details of the structure refinements are given in the Supporting Information.

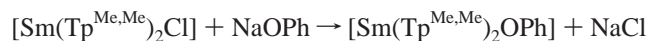


All intensity measurements were made on a Bruker AXS SMART 1K CCD area detector diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data sets were collected at low temperature (160 K). Intensities were integrated from more than a hemisphere of data recorded on narrow frames,  $0.3^\circ$  in  $\omega$ ; cell parameters were refined from the observed setting angles of all strong reflections. Semiempirical absorption corrections were applied on the basis of symmetry-equivalent and repeated data.

The structures were solved by direct methods (Patterson synthesis for **1b**·C<sub>7</sub>H<sub>8</sub>) and refined by full-matrix least squares on  $F^2$  values for all data with anisotropic displacement parameters. H-atoms were included in a riding model with  $U_{\text{iso}}$  set to be 1.2 times that of the carrier atom (1.5 times for methyl H). In **1b**·C<sub>7</sub>H<sub>8</sub> the molecule of toluene was refined, with geometry restraints, as disordered over two sets of interpenetrating positions with an occupancy ratio of 68.4:31.6(8). In **3a**·C<sub>7</sub>H<sub>8</sub> there are two samarium complexes with different conformations and two molecules of toluene in the asymmetric unit. One toluene molecule was ordered and the other refined as disordered over two sets of interpenetrating and partially shared positions with an occupancy ratio of 77.5:22.5(5). For the disordered toluene, restraints were applied to both geometry and displacement parameters and H-atoms were omitted. Programs were standard Bruker AXS control and integration software and members of the SHELX family (Bruker AXS Inc., Madison, WI, and G. M. Sheldrick, University of Göttingen, Germany). Selected bond lengths and angles are listed in the figure captions. Complete results are to be found in the Supporting Information.

## Results

**Synthesis.** When [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] is stirred in THF with 1 equiv of sodium phenoxide, a white precipitate of sodium chloride forms rapidly and a very pale solution results. Removal of solvent followed by extraction into toluene yields [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>OPh], **1a**, which may be crystallized as fine colorless needles by cooling to low temperature.



The complex is soluble in common organic solvents such as dichloromethane, THF, and toluene and has been characterized by elemental analysis and infrared and NMR spectroscopy. An analogous product was obtained using the *para*-substituted alkoxide Na(OPh-4-Bu<sup>t</sup>), which gave the petrol-soluble complex [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>OPh-4-Bu<sup>t</sup>], **1b**. Attempts to prepare analogues of **1a** and **1b** with other alkoxides were unsuccessful. For example, in our hands sodium methoxide, ethoxide, and *tert*-butoxide all failed to give characterizable products. Similarly 2,6-disubstituted phenoxides did not give tractable products, which we presume to be a result of the extreme steric congestion arising from the *ortho* substituents.

Attempts to use the salt metathesis strategy for the preparation of thiolates were not successful as mixtures of products were obtained, presumably as a result of salt incorporation. This parallels the experience of Bianconi, who reported extensive chloride incorporation when preparing divalent ytterbium and samarium tellurolates.<sup>39</sup> For these complexes we therefore resorted to an oxidative strategy, starting from the samarium(II) complex [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>],<sup>25,26</sup> in a manner analogous to that used by Andersen and Edlmann for the preparation of metallocene complexes.<sup>14,16</sup>

Stirring [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] with PhSSPh in a 2:1 mole ratio in THF led to gradual dissolution of the purple starting material, yielding a turbid white solution. Subsequent attempts to obtain a pure product were not successful, although the <sup>1</sup>H NMR

spectra of the crude materials suggested the presence of the desired product. The use of toluene as a solvent and milder conditions, namely, starting the reaction at  $-78^\circ\text{C}$  and warming slowly to room temperature, yielded a clear, pale yellow solution from which [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SPh], **2a**, could be recovered at low temperature as a pale yellow solid.



The reductive cleavage of E–E bonds can be extended to the other members of group 16. Thus, pale yellow [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>-SPh-4-Me], **2b**, bright yellow [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SePh], **3a**, and [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SePh-4-Bu<sup>t</sup>], **3b**, and orange [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>TePh], **4**, could be obtained. They are thermally robust although rather air sensitive. With the exception of **3b**, the infrared spectra of these complexes are very similar, giving a single sharp band around  $2550 \text{ cm}^{-1}$  arising from the expected B–H stretch of a tridentate pyrazolylborate.<sup>40</sup> **3b** on the other hand shows two B–H bands at  $2541$  and  $2463 \text{ cm}^{-1}$ . The latter band is  $80\text{--}90 \text{ cm}^{-1}$  lower than in all other tridentate pyrazolylborate complexes prepared by us previously and suggests a significant difference in the binding mode of the ancillary ligand.

Consistent with an electron-transfer mechanism, the reactions were complete within minutes for the ditelluride, were somewhat slower for the diselenide, and required overnight stirring at room temperature in the case of the disulfides. Analogous compounds [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>SPh], **2a'**, [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>SePh-4-Bu<sup>t</sup>], **3b'**, and [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>TePh], **4'**, were obtained in NMR-scale reactions starting from the toluene-soluble [Sm(Tp<sup>Me,Me,4-Et</sup>)<sub>2</sub>].<sup>37</sup> These reactions proceeded more rapidly than with [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>], and the products were only analyzed by <sup>1</sup>H NMR spectroscopy.

Reaction of [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] with dibenzyl disulfide and diselenide (PhCH<sub>2</sub>EECH<sub>2</sub>Ph, E = S, Se) in toluene was considerably slower and required gentle warming of the solution, but eventually resulted in a color change similar to that of the diaryl disulfides. (This behavior is in contrast to that of the metals themselves, which do not react readily with the dibenzyl compounds.<sup>41</sup>) The toluene-soluble products **2c** (E = S) and **3c** (E = Se) could be isolated in microcrystalline form, but we were unable to obtain reliable elemental analyses as a result of cocrystallization of an unidentified minor product, visible by NMR, but inseparable even after several crystallizations. On the other hand, the Tp<sup>Me,Me,4-Et</sup> analogue, **2c'**, was isolated in analytically pure form and gave a NMR spectrum very similar to that of **2c**.

Attempts were also made to cleave the P–P bond in tetraphenyldiphosphine (Ph<sub>2</sub>PPPPh<sub>2</sub>). No reaction was observed even after prolonged heating, in stark contrast to the behavior observed by Evans and co-workers for decamethylsamarocene and further confirming the diminished reactivity of the Tp<sup>Me,Me</sup> systems relative to the metallocenes.<sup>42</sup>

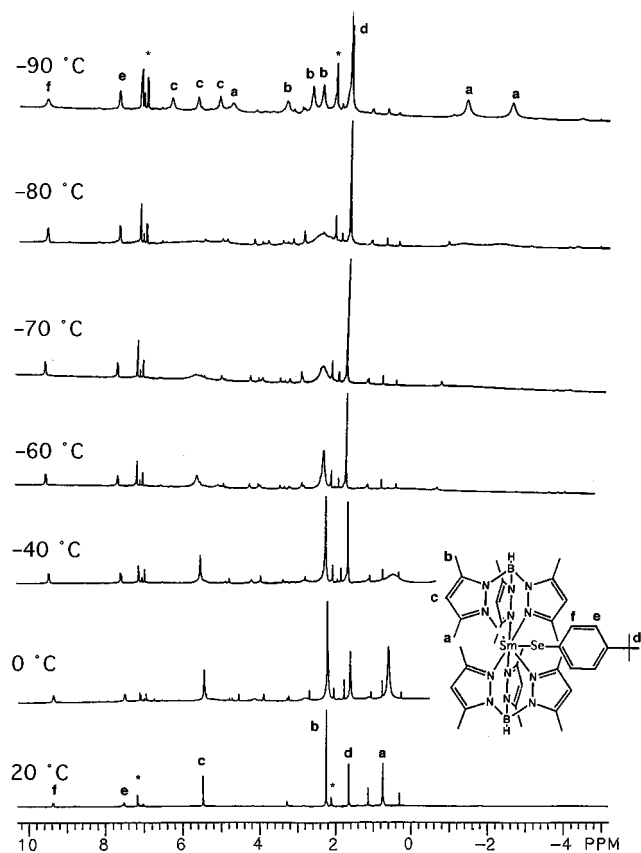
**NMR Spectra.** The room temperature <sup>1</sup>H NMR spectra of the complexes **1a**, **1b**, **2a**, **2b**, **3b**, and **4** are broadly similar, with three peaks in the ratio of 3:3:1 assigned to the trispyrazolylborate ligands, somewhat shifted by the presence of the paramagnetic samarium(III) center, and corresponding peaks for the phenyl groups. The doublet assigned to the *ortho* protons of the phenyl groups showed quite marked shifts downfield,

(40) Apostolidis, C.; Rebizant, J.; Kanellakopoulos, B.; Ammon, R. v.; Dornberger, E.; Müller, J.; Powietzka, B.; Nuber, B. *Polyhedron* **1997**, *16*, 1057–1068.

(41) Brennan, J. G. Personal communication.

(42) Evans, W. J.; Leman, J. T.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1996**, *35*, 4283–4291.

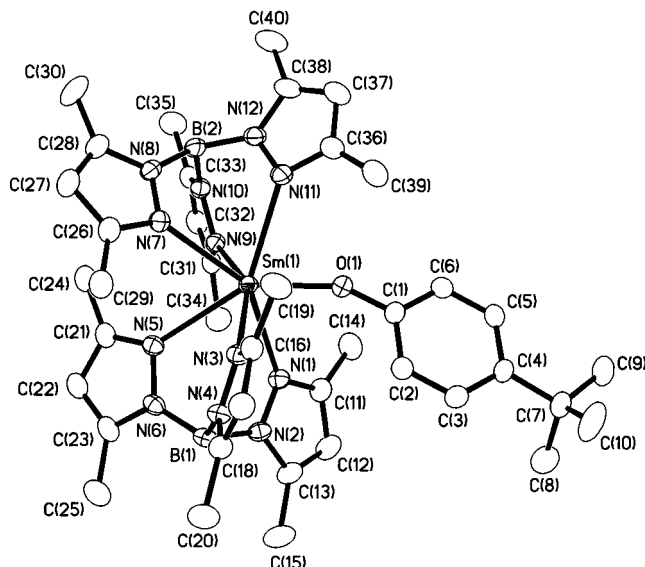
(39) Strzelecki, A. R.; Liker, C. L.; Helsel, B. A.; Utz, T.; Lin, M. C.; Bianconi, P. A. *Inorg. Chem.* **1994**, *33*, 5188–5194.



**Figure 1.**  $^1\text{H}$  NMR (400 MHz) spectra of **3b** recorded in toluene- $d_8$  between room temperature and  $-90\text{ }^\circ\text{C}$ .

particularly for the phenoxides. This is in stark contrast to the aromatic protons of the nonfluxional  $C_2$ -symmetric complex  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2(\text{PhNNPh})]$ , which are shifted by several tens of parts per million to high and low field.<sup>25</sup> The chemical shifts of the  $\text{Tp}^{\text{Me,Me}}$  groups of complexes **1–4** are similar to those of the pyrazolyl groups of  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{X}]$  ( $\text{X} = \text{F}, \text{Cl}, \text{OTf}$ ), which are known to be seven-coordinate both in the solid state and in solution.<sup>43</sup> We note that the chemical shifts of the 3-methyl groups in **1a** and **1b** are significantly upfield of those of the other complexes although the structure of **1b** (vide infra) reveals no particular feature to which the difference could be attributed. Thus, the room temperature NMR spectra of these compounds are rather structurally uninformative and are suggestive of molecular complexes with a fluxional coordination sphere.

Cooling **1a** and **1b** to  $-80\text{ }^\circ\text{C}$  resulted in some broadening and shifting of the  $^1\text{H}$  NMR signals associated with the pyrazolylborate ligands. The changes were considerably more marked for **2a**, **2b**, and **4**, with the peaks assigned to the 3-methyl protons of the pyrazolylborates broadening and disappearing into the baseline. Cooling **3a** and **3b** in toluene led, however, to progressive broadening of the resonances in the  $^1\text{H}$  NMR spectrum (shown in Figure 1) associated with the pyrazolylborates, together with small shifts in the peaks associated with the selenolate group which arise as a result of the Curie dependence of the chemical shift of a paramagnetic molecule. By  $-90\text{ }^\circ\text{C}$  the spectrum had begun to sharpen once more, and six broad resonances assigned to the methyl groups and three owing to the methine protons of the  $\text{Tp}^{\text{Me,Me}}$  ligand had been resolved, consistent with a structure of  $C_2$  symmetry.



**Figure 2.** Molecular structure of **1b** (hydrogen atoms and the toluene molecule of crystallization omitted for clarity).

The slow exchange limit was not reached above the freezing point of the solvent. The spectra are nevertheless similar in appearance to those that have been observed for more crowded eight-coordinate species including  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2(\text{PhNNPh})]^{25}$  and, at low temperature,  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2(\text{S}_2\text{CNR}_2)]^{44}$

The  $^1\text{H}$  NMR spectra of the benzyl complexes **2c** and **3c** were very similar to each other, showing the three peaks expected for a fluxional molecule with equivalent  $\text{Tp}^{\text{Me,Me}}$  ligands. The benzyl group gave three multiplets in the aryl region together with a sharp singlet around  $\delta$  7 integrating for two protons, assigned to the methylene hydrogens of the benzyl fragment, strongly shifted by their proximity to the samarium center. On cooling **2c** and **3c** in toluene- $d_8$ , similar changes were observed. The peaks associated with the pyrazolylborate ligands broadened into the baseline and had resolved into nine broad peaks by  $-90\text{ }^\circ\text{C}$ , although the slow exchange limit could not be reached before the solvent froze. As with **3a** and **3b** the spectrum was consistent with a  $C_2$ -symmetric coordination sphere. The phenyl protons of the chalcogenolate shifted only slightly with temperature. The benzyl methylene protons, on the other hand, shifted dramatically by more than 2 ppm downfield and broadened severely at  $-90\text{ }^\circ\text{C}$ , suggesting perhaps that at this temperature the exchange of the two hydrogen environments might be slowing.

Because complexes **1–4** represent a complete series of isoleptic chalcogenolate complexes of the lanthanides, attempts were made to grow single crystals for X-ray analysis with a view to obtaining better insight into their bonding and the NMR spectra. These efforts were successful for **1b**, **2b**, **3a**, **3b**, and **4**.

**X-ray Crystallography. Complex 1b.** The alkoxide **1b** crystallized from toluene in the space group  $P2_1/c$  with a molecule of toluene included in the lattice. The molecular structure is shown in Figure 2. No unusual intermolecular contacts were noted. The molecule consists of a seven-coordinate molecular complex with two tridentate pyrazolylborates and the phenoxide in the first coordination sphere of the samarium. The average M–N distance, 2.572(5) Å (range 2.473(2)–2.666(2) Å), is similar to those observed in the corresponding seven-

(43) Liu, S.-Y.; Maunder, G. H.; Sella, A.; Stephenson, M.; Tocher, D. A. *Inorg. Chem.* **1996**, *35*, 76–82.

(44) Lopes, I.; Hillier, A. C.; Liu, S. Y.; Domingos, A.; Galvao, A.; Sella, A.; Marques, N. Manuscript in preparation.

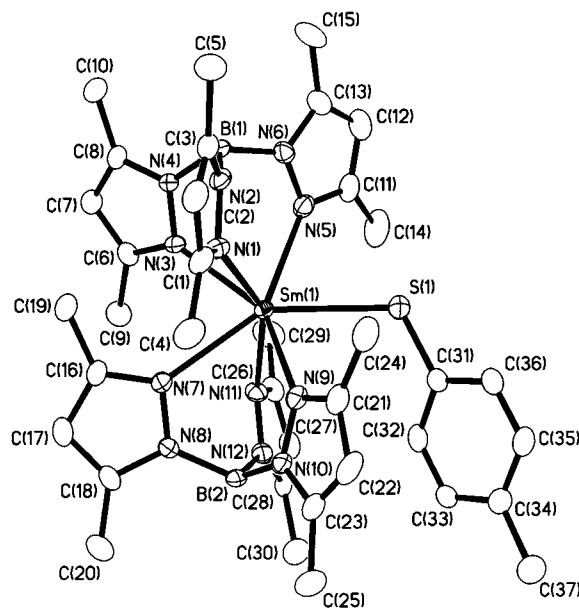
**Table 2.** Selected Bond Distances and Angles for **1b**·C<sub>7</sub>H<sub>8</sub>, **2b**, **3aα**, and **4**·C<sub>7</sub>H<sub>8</sub>.

	<b>1b</b> ·C <sub>7</sub> H <sub>8</sub>	<b>2b</b>	<b>3aα</b>	<b>4</b> ·C <sub>7</sub> H <sub>8</sub>
Sm(1)–E	2.159(2)	2.8620(9)	2.9390(3)	3.1874(4)
Sm(1)–N(1)	2.571(2)	2.492(2)	2.650(2)	2.497(4)
Sm(1)–N(3)	2.473(2)	2.546(2)	2.530(2)	2.633(3)
Sm(1)–N(5)	2.637(2)	2.581(3)	2.513(2)	2.530(3)
Sm(1)–N(7)	2.563(2)	2.634(3)	2.445(2)	2.617(3)
Sm(1)–N(9)	2.524(2)	2.479(3)	2.609(2)	2.455(4)
Sm(1)–N(11)	2.666(2)	2.456(2)	2.510(2)	2.594(2)
Sm(1)–O(1)–C(1)	153.7(2)	114.56(11)	111.18(8)	108.29(9)
max BNNSm torsion	26.8	34.4	16.7	47.7

coordinate [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>Cl] (2.565(3) Å) and [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>F] (2.577 Å).<sup>45</sup> The coordination sphere may be regarded as being distorted pentagonal bipyramidal with N(3) and N(9) occupying the apical sites. The axial sites are bent with a N(3)–Sm–N(9) angle of 153.32(7)°, the distortion arising from the geometrical requirements of the Tp<sup>Me,Me</sup> ligands. As expected for these two least crowded sites, the Sm–N distances (2.473(2) and 2.524(2) vs the average Sm–N<sub>eq</sub> = 2.609(4) Å) (Table 2) are slightly shorter than those in the equatorial girdle.<sup>46</sup> The two Tp<sup>Me,Me</sup> ligands are mutually staggered and bent back from each other at an angle of 143°, as measured by the B–Sm–B angle, a bend angle quite typical of lanthanide bis-Tp<sup>Me,Me</sup> systems.<sup>27</sup>

The boron atoms are both tetrahedral, and the Tp<sup>Me,Me</sup> ligands show the typical twisting of the pyrazolyl rings about the B–N bond, necessary to accommodate the phenoxide group. Thus, the B–N–N–Sm torsion angles for rings N(1)N(2) and N(11)N(12) are 17.1° and 26.8°, respectively. The phenoxide ligand lies in the cleft between pyrazolyls N(1)N(2) and N(3)N(4) and shows a distinct bend at oxygen of 153.7(2)°, presumably resulting from the need to relieve steric crowding with the methyl group (C(39)). There is no evidence for  $\pi$ -interactions between the aromatic group and the pyrazolyls. The Sm–O distance is 2.159(2) Å, similar to those observed in the closely related anthraquinone complex [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>-( $\mu$ -C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>)] (2.138(8) Å)<sup>47</sup> and the metallocenes [Cp\*<sub>2</sub>Sm(O-2,3,5,6-Me<sub>4</sub>C<sub>6</sub>H)<sub>2</sub>] (2.13(1) Å), [Cp\*<sub>2</sub>Sm]<sub>2</sub>(O<sub>2</sub>C<sub>16</sub>H<sub>10</sub>) (2.08(2) Å),<sup>48</sup> and [Cp\*<sub>2</sub>Sm]<sub>2</sub>(O<sub>2</sub>C<sub>16</sub>H<sub>10</sub>) (2.099(9) Å)<sup>49</sup> and to the average terminal aryloxide distance in {Sm( $\mu$ -O- $\eta^6$ -Ar)(OAr)<sub>2</sub>} (Ar = 2,6-Pr<sup>i</sup>C<sub>6</sub>H<sub>3</sub>) (2.101(6) Å).<sup>50</sup>

**Complex 2b.** The thiolate **2b** crystallized from toluene in the space group *P2<sub>1</sub>/n*. The molecular structure is shown in Figure 3. The structure is broadly similar to that reported for **1b**, with a seven-coordinate pentagonal bipyramidal metal center coordinated to two pyrazolylborates in  $\eta^3$  fashion with a terminal thiolate ligand. No unusual intermolecular contacts were noted. Nitrogen atoms N(1) and N(11) adopt pseudoaxial positions with N(11)–Sm(1)–N(1) = 150.1°. The equatorial plane has a mean deviation from planarity of 0.2502 Å. The pyrazolylborate ligands are bent back by 152.8°, as measured by the B(1)–Sm(1)–B(2) angle. The average Sm–N distance is 2.531(6) Å (range 2.456(2)–2.634(3) Å) (Table 2), slightly shorter than in **1b**, presumably owing to the less effective donation to the Lewis

**Figure 3.** Molecular structure of **2b** (hydrogen atoms omitted for clarity).

acidic metal center by the softer thiolate ligand, which results in the ancillary ligands being drawn in to compensate. This is also reflected in the Sm–B distances (3.488 and 3.544 Å). Although the boron atoms are essentially tetrahedral but pyrazolyl rings (N(1)N(2), N(5)N(6), and N(11)N(12)) are twisted about their B–N bonds such that the ring planes are at angles of 28.9°, 31.3°, and 34.4°, respectively, to the Sm–B vectors, significantly greater than in the “parent” complex [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>] (20.8°)<sup>25,26</sup> and in **1b**.

The Sm–S distance in **2a**, 2.8260(9) Å, is similar to those observed in other complexes possessing terminal thiolate ligands, for example, [Sm(SPh)<sub>3</sub>(HMPA)<sub>3</sub>] (2.821(1) Å), [(py)<sub>2</sub>(THF)–Sm(SC<sub>6</sub>H<sub>2</sub>Pr<sup>i</sup><sub>3</sub>)<sub>3</sub>] (2.740(2) Å), and [(THF)<sub>3</sub>Sm( $\mu$ –(SC<sub>6</sub>H<sub>2</sub>–Pr<sup>i</sup><sub>3</sub>)(SC<sub>6</sub>H<sub>2</sub>Pr<sup>i</sup><sub>3</sub>)<sub>3</sub>)] (2.908(6) Å),<sup>20</sup> and slightly longer than that observed in [Sm(SC<sub>6</sub>H<sub>2</sub>–2,4,6–Bu<sup>t</sup><sub>3</sub>)<sub>3</sub>] (av Sm–S = 2.644(5) Å),<sup>9</sup> which relies on Sm–CH<sub>3</sub> interactions to saturate the metal coordination sphere. The only system comparable to that of **2b**, possessing bulky ancillaries together with a single terminal thiolate ligand, is provided by the metallocene [YbCp\*<sub>2</sub>(SPh)(NH<sub>3</sub>)],<sup>51</sup> which has two independent molecules in the asymmetric unit, with Yb–S distances of 2.670(3) and 2.679(3) Å. On changing the metal(III) ion from Sm to Yb, the ionic radius decreases by 0.14 Å<sup>52</sup> or 0.09 Å.<sup>53</sup> Somewhat to our surprise, the average difference in M–S bond length between [Sm(Tp<sup>Me,Me</sup>)<sub>2</sub>SPh-4-Me] and [YbCp\*<sub>2</sub>(SPh)(NH<sub>3</sub>)] is 0.153 Å, suggesting that the steric demand of two Tp<sup>Me,Me</sup> ligands is roughly comparable to that of two Cp\* ligands plus one small donor such as ammonia. The thiolate ligand is significantly bent with a Sm–S–C angle of 114.6(1)°, consistent with there being comparatively little overlap between the lone pairs on the sulfur and the vacant samarium 5d orbitals. The phenyl group, however, shows an apparent  $\pi$ -stacking interaction with one pyrazolyl group, the centroid to centroid distance being 3.444 Å.

**Complex 3a.** The selenolate **3a** crystallized in the space group *P1̄* as large bright yellow blocks. Two independent molecules, **3aα** and **3aβ**, with significantly different conformations, were

(45) Hillier, A. C.; Liu, S. Y.; Maunder, G. H.; McDonald, R.; Sella, A.; Takats, J.; Zhang, X. W. Manuscript in preparation.

(46) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.

(47) Hillier, A. C. Ph.D. Thesis, University of London, 1998.

(48) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191–195.

(49) Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693–1703.

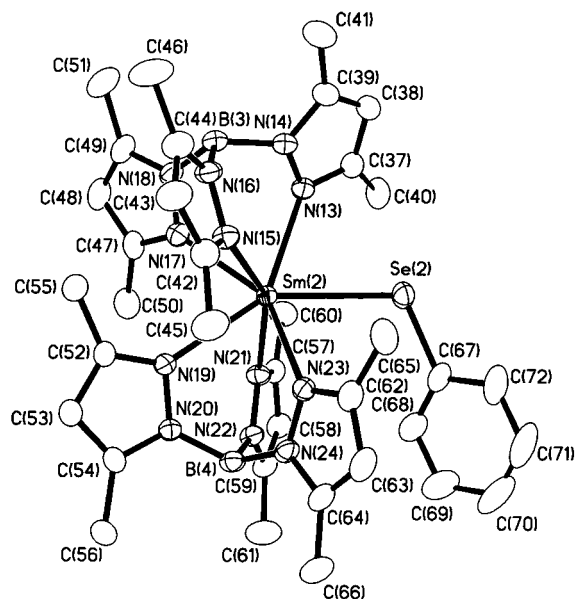
(50) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 3487–3497.

(51) Zalkin, A.; Henly, T. J.; Andersen, R. A. *Acta Crystallogr.* **1987**, *C43*, 233–236.

(52) Emsley, J. *The Elements*; Oxford University Press: Oxford, 1989.

(53) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.





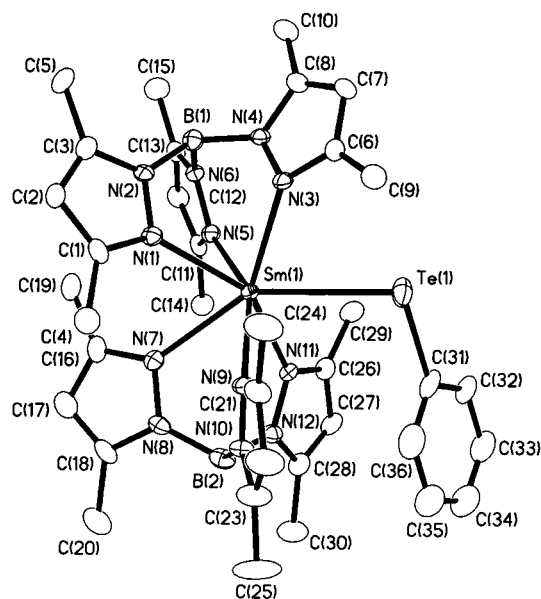
**Figure 4.** Molecular structure of **3aα** (hydrogen atoms and toluene molecules omitted for clarity).

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **3aβ** and **3b**

	<b>3aβ</b>		<b>3b</b>	
Sm(1)–E	2.9621(3)	Sm(1)–E	2.9457(3)	
Sm(1)–N(1)	2.740(2)	Sm(1)–N(1)	2.858(2)	
Sm(1)–N(3)	2.534(2)	Sm(1)–N(3)	2.736(2)	
Sm(1)–N(5)	2.491(2)	Sm(1)–N(5)	2.499(2)	
Sm(1)–N(7)	2.442(7)	Sm(1)–N(7)	2.492(2)	
Sm(1)–N(9)	2.636(2)	Sm(1)–N(9)	2.467(2)	
Sm(1)–N(11)	2.470(2)	Sm(1)–N(11)	2.594(2)	
Sm(1)–Se(1)–C(31)	110.97(8)	Sm(1)–O(1)–C(31)	108.29(9)	
max BNNSm torsion	83.7	max BNNSm torsion	91.3	

found in the asymmetric unit. The structure of **3aα** will be discussed here, while that of **3aβ** will be discussed later. The molecular structure of **3aα** is shown in Figure 4, and selected bond angles and distances are given in Table 2. The molecular structure is broadly similar to those of **1b** and **2b** with isolated  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{SePh}]$  units having a seven-coordinate, distorted pentagonal bipyramidal, metal center. The average Sm–N distance is 2.543(5) Å (range 2.445(2)–2.650(2) Å) similar to that in **2b**. The Sm–Se distance, 2.9390(3) Å, which is slightly longer than those observed by Edlmann and co-workers in the metallocene analogue  $[\text{Cp}^*\text{Sm}(\text{SeC}_6\text{H}_2\text{-2,4,6-(CF}_3)_3)]$  (2.919–(2) Å)<sup>16</sup> and by Brennan in terminal seven-coordinate selenolates for  $[(\text{py})_2\text{Sm}(\text{SePh})(\mu\text{-SePh})_3\text{Na}(\text{py})_2]_2$  (2.908(1) Å)<sup>54</sup> and  $[(\text{py})_3\text{-Sm}(\text{SePh})(\mu\text{-SePh})_2]_2$  (2.9129(14) and 2.8968(11) Å),<sup>55</sup> is consistent with the considerable steric congestion at the samarium center. The Sm–Se–C angle, 110.97(8)°, is slightly more acute than that observed in **2b**, as expected. This is less open than the angle at selenium in  $[\text{Cp}^*\text{Sm}(\text{SeC}_6\text{H}_2\text{-2,4,6-(CF}_3)_3)]$  (126.4(1)°)<sup>16</sup> but compares closely with the corresponding angles in  $[(\text{py})_3\text{Sm}(\mu\text{-SePh})(\text{SePh})_2]_2$  of 109.2(2)° and 114.2(2)° and in  $\text{Yb}(\text{SePh})_2(\text{Py})_4$  of 103.7(2)°.<sup>18</sup> Presumably the bulky  $\text{CF}_3$  *ortho* substituents are responsible for the straightening of the M–Se–C bond in the metallocene complex.

The twisting of the pyrazolyl rings in **3aα** is more pronounced than in the previous cases with maximum twists about the B–N



**Figure 5.** Molecular structure of **4** (hydrogen atoms and the toluene of crystallization omitted for clarity).

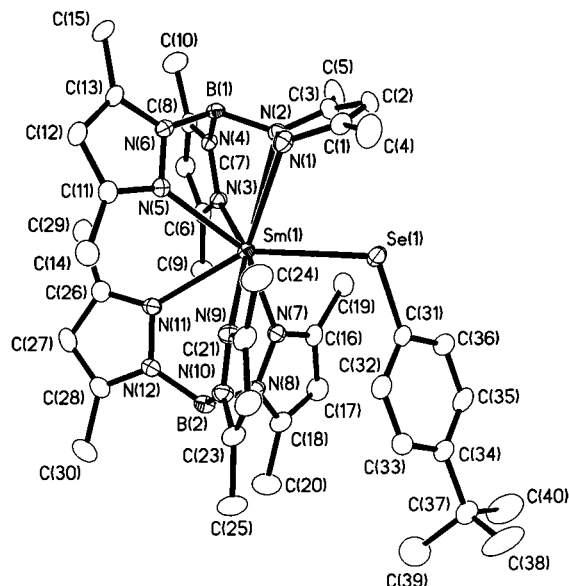
bonds of 51.2° and 16.7°, respectively. The twisting is accompanied by a significant difference in Sm–B distances, 3.486 and 3.589 Å, respectively, although these distances are normal for a seven-coordinate system.

**Complex 4.** The telluroate **4** crystallized as small orange blocks in the space group  $P2_1/c$  as a toluene solvate, and the structure is shown in Figure 5. The molecular structure of the complex is quite similar to those of **1b**, **2b**, and **3aα**, consisting of discrete  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{TePh}]$  units. No unusual intermolecular contacts were noted. The metal center is seven-coordinate with a distorted pentagonal bipyramidal geometry, N(5) and N(9) occupying the pseudoaxial positions. The samarium–tellurium distance, 3.1874(4) Å (Table 2), is slightly longer than that observed by Edlmann in  $[\text{Cp}^*\text{Sm}(\text{TeC}_6\text{H}_2\text{-2,4,6-(CH}_3)_3)]$ , 3.088(2) Å,<sup>16</sup> suggesting much more severe steric congestion than in the corresponding selenium analogues discussed above. On the other hand, the acute Sm–Te–C angle in **4** of 104.83–(13)° does not correlate with the considerably wider angle of 123.5(3)° observed for Edlmann’s metallocene, consistent with the idea that the angle at the chalcogen atom is relatively “soft” and highly dependent upon steric congestion in the second coordination sphere of the metal center. As with **2** and **3aα**, one ring on each ligand twists significantly (19.3° and 47.7°) around the B–N bond. A graphitic-type interaction occurs between the phenyl ring and pyrazolyl ring 6 (N(11)N(12)), with a centroid-to-centroid distance of 3.537 Å. The average Sm–N distance is 2.538 Å (range 2.455(4)–2.633(3) Å), slightly longer than in the thiolate, again presumably due to the larger size of the tellurium atom. The axial nitrogens N(5) and N(9) of the pentagonal bipyramid are bent with a N(5)–Sm(1)–N(9) angle of 151.5°. The equatorial plane has a mean deviation from planarity of 0.2847 Å, larger than that observed for **1b** (0.2239 Å) and comparable to that of the thiolate **2**. The pyrazolylborate ligands are bent back from each other, with a B(1)–Sm–B(2) angle of 148.4°.

**Complexes 3aβ and 3b.** The selenolate **3b** crystallized from toluene as large air-sensitive orange blocks in the space group  $P\bar{1}$  and the structure is extremely similar to that of **3aβ**. The molecular structure of **3b** is shown in Figure 6, and selected interatomic distances and angles for both **3aβ** and **3b** are given in Table 3. No unusual intermolecular contacts were noted in

(54) Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5327–5334.

(55) Lee, J.; Freedman, D.; Melman, J. H.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 2512–2519.



**Figure 6.** Molecular structure of **3b** (hydrogen atoms omitted for clarity).

either structure. The complex consists of two  $\text{Tp}^{\text{Me,Me}}$  ligands and a phenyl selenolate in the metal coordination sphere. However, in contrast to the other complexes in this series, which are rigorously seven-coordinate, one of the Tp ligands in each complex binds normally through three nitrogens (N(7), N(9), N(11)), while the other shows a highly unusual distortion away from the normal  $C_3$  symmetry. Thus, while two of the pyrazolyl groups are aligned approximately parallel to the B–Sm vector, the third is twisted sideways such that both nitrogen atoms interact with the metal. Such distortions have been observed before in the structurally related uranium(III) complex  $[\text{U}(\text{Tp}^{\text{Me,Me}})_2]^{56}$  and very recently in  $[\text{Tp}^{\text{But,Me}}\text{Yb}(\eta\text{-C}_5\text{H}_4\text{-SiMe}_3)]^{57}$ . The torsion angles of  $83.7^\circ$  (**3a $\beta$** ) and  $91.3^\circ$  (**3b**) are similar to those observed in the uranium complex ( $87.4^\circ$ ) and  $75.3(3)^\circ$  in that of ytterbium. Indeed, for **3b**, N(2) is in fact closer to the samarium than N(1) (2.736(2) vs 2.858(2) Å). The sums of the angles around N(2) ( $350^\circ$ , **3a $\beta$** ;  $348^\circ$ , **3b**) suggest the atom to be slightly pyramidal. Further evidence for the interaction can be seen from a comparison of the Sm–B distances (3.314 Å, **3a $\beta$** ; 3.291 Å, **3b**), which are considerably shorter than in other seven-coordinate compounds (av 3.50 Å). Thus, the extreme twisting of the third pyrazolyl group gives rise to deepening of the boat conformation, the Sm–N–N angle decreasing from the normal  $115\text{--}120^\circ$  to about  $113^\circ$ . The difference between the two  $\text{Tp}^{\text{Me,Me}}$  ligands therefore accounts for the markedly different B–H stretching bands in the infrared spectrum noted above. Interestingly Takats and co-workers report the infrared spectrum of  $[\text{U}(\text{Tp}^{\text{Me,Me}})_2]$  as having a single band at  $2482\text{ cm}^{-1}$ , a value intermediate between the two noted for **3b**.<sup>56</sup>

The Sm–Se distances [2.9621(3), **3a $\beta$** ; 2.9457(3), **3b**] are longer than in **3a $\alpha$** , reflecting the increased coordination number for these species. In both structures the  $\text{Tp}^{\text{Me,Me}}$  groups are mutually staggered and the phenyl groups of the selenolate ligands lie in the wedge between two pyrazolyl groups of the undistorted Tp ligand parallel to one of the pyrazolyl rings with centroid-to-centroid distances of 3.631 Å **3a $\beta$** ) and 3.607 Å (**3b**),

once more suggesting a graphitic interaction. A further possible secondary interaction occurs between each selenium atom and a pyrazolyl ring, with short Se–pyrazolyl ring–centroid distances (3.262 Å, **3a $\beta$** ; 3.232 Å, **3b**).

## Discussion

We have previously shown that the structures of the bis- $\text{Tp}^{\text{Me,Me}}$  complexes depend quite critically upon the ionic radius of the metal ion, and on the bonding properties and the steric demand of the potential third ligand. Where the third ligand is a particularly poor donor such as the triflate anion, changing the ionic radius of the metal results in expulsion of the ligand from the coordination sphere.<sup>43</sup> On the other hand, the halide complexes are seven-coordinate when the halide is small and hard, fluoride and chloride, while the iodide adopts a six-coordinate ion-separated structure.<sup>37</sup> In the case of the chalcogenolate complexes, all four adopt molecular structures, suggesting that it is neither the size nor the softness of the iodide which causes its expulsion from the coordination sphere, but rather that an ionic structure maximizes the lattice energy of the overall structure. The salt is presumably less stable for the larger and unsymmetrical phenyltelluroate anion. In the presence of excess  $\text{PhTeTePh}$ , it is possible to crystallize the salt  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2](\text{TePh})_3$ .<sup>58</sup>

The structural differences between this series of complexes show a number of interesting features. First of all, whereas the Sm–E distances for the S, Se, and Te complexes can be predicted quite accurately from the sum of the corresponding single bond covalent radii, the Sm–O distance is significantly shorter than this.<sup>52</sup> Thus, we might expect the Sm–O distance to be on the order of 2.32 Å rather than the 2.159 Å actually found. The behavior seen for this series of complexes therefore parallels that of the zirconium chalcogenolates studied by Parkin, who has argued convincingly that the shortening of the Zr–O bond need not be due to  $\pi$ -donor overlap from the oxygen to the metal.<sup>59</sup> Rather, it may simply be due to the enhanced ionicity of the Zr–O bond arising from the greater electronegativity of oxygen relative to its heavier congeners and its smaller size, both of which lead to more extreme charge polarization. This trend is in line with the classic Shomaker–Stevenson equation, which corrects interatomic bond distances for differences in electronegativity.<sup>60</sup>

As expected, the Sm–E–C angles show a consistent trend toward more acute angles, paralleling that seen for the corresponding hydrides  $\text{H}_2\text{E}$ , [ $\text{H}_2\text{O}$  ( $104.5^\circ$ ),  $\text{H}_2\text{S}$  ( $92.2^\circ$ ),  $\text{H}_2\text{Se}$  ( $91.0^\circ$ ),  $\text{H}_2\text{Te}$  ( $89.5^\circ$ )], where no  $\pi$ -bonding is possible. However, the angles at oxygen in complexes of the type  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{OR}]$ , such as the related semiquinone and alkoxide complexes, vary considerably between  $150^\circ$  and  $170^\circ$ ,<sup>30,61</sup> suggesting this to be quite a soft deformation. Indeed, a plot of Sm–O distance versus Sm–O–C angle for structures of trivalent aryloxides in the Cambridge Structural Database (Figure 7) shows virtually no correlation between these two parameters, the Sm–O–C bond angle varying between  $150^\circ$  and  $179^\circ$ . Both Parkin<sup>59</sup> and Rothwell<sup>64</sup> have made similar observations for group 4 and group 5 complexes, indicating that the bond angle is a poor predictor of bond order. This view is

(58) Hillier, A. C.; Liu, S. Y.; Sella, A.; Elsegood, M. R. *J. Angew. Chem., Intl. Ed. Engl.* **1999**, *38*, 2745–2747.

(59) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900–5909.

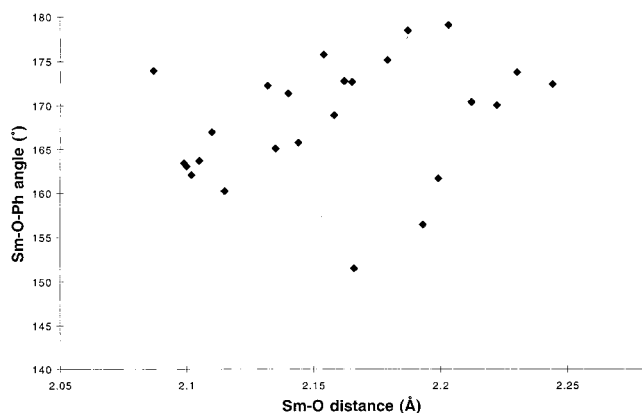
(60) Shomaker, V.; Stephenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37–40.

(61) Marques, N. Personal communication.

(56) Sun, Y. M.; McDonald, R.; Takats, J.; Day, V. W.; Eberspacher, T. A. *Inorg. Chem.* **1994**, *33*, 4433–4434.

(57) Ferrence, G. M.; McDonald, R.; Morissette, M.; Takats, J. *J. Organomet. Chem.*, submitted for publication.





**Figure 7.** Sm–O–C angle (deg) versus Sm–O bond length for terminal unconstrained trivalent samarium alkoxides in the Cambridge Structural Database.

supported by the computational studies of Cundari.<sup>65</sup> Analogous computational studies for the lanthanides are currently in progress.<sup>62</sup>

All of the complexes crystallized as part of this study show marked distortions of the pyrazolylborate ligands away from  $C_3$  symmetry as a result of twisting of individual pyrazolylborate ligands around the B–N bond, and such distortions have been observed in other systems.<sup>63</sup> The fact that this twisting appears to be far more marked for the lanthanide complexes than for transition-metal and main group elements suggests that it arises in part from the mismatch between the bite angle of these ligands and the large size of the ion itself. This mismatch is further corroborated by the rapid transfer of the  $Tp^{R,R}$  ligand from the lanthanide to smaller ions such as magnesium.<sup>37</sup> In addition the pyrazolyl groups closest to the chalcogenolate ligand are invariably the most distorted, suggesting that accommodation of the third ligand is also important. However, the large range of twist angles, and the isolation of a “normal” seven-coordinate molecule, **3a $\alpha$** , and the highly distorted **3a $\beta$**  in the same crystal, suggests that the twisting of the rings has a very soft potential. Hence, crystal packing forces, including intramolecular  $\pi$ – $\pi$  interactions, play a considerable role in determining the precise extent of twisting.

The extreme distortions of the pyrazolylborate seen for **3a $\beta$**  and **3b** (as well as  $[U(Tp^{Me,Me})_2I]^{56}$  and  $[Yb(Tp^{But,Me})(C_5H_4SiMe_3)]^{57}$ ) are also interesting in view of the many examples of pyrazolylborate fragmentation that have been reported anecdotally. Thus, twisting of the B–N bond may activate the bond toward nucleophilic attack by adventitious water, for example, and may therefore be regarded as forming a part of the trajectory leading ultimately to B–N bond cleavage. We note that the selenolate appears to be somewhat more moisture sensitive than either of the other members of the series. Indeed, several fragmented products have been isolated from attempts to crystallize the complex.<sup>38</sup> Similarly,  $Sm(Tp^{Me,Me})_2Br$  is significantly more difficult to isolate in pure form than the other halides, suggesting that similar distortions may occur for that complex also.<sup>45</sup>

Until this study the NMR spectra of other seven-coordinate  $[Sm(Tp^{Me,Me})_2X]$  systems have been consistently uninformative with regard to the coordination sphere and have failed to give any hints of the underlying structural equilibria.<sup>43</sup> Although the slow exchange limit is almost reached for **2c**, **3a**, **3b**, and **3c**, it is clear that the thiolates **2a** and **2b** and telluroate **4** behave analogously even if the fluxionality cannot be frozen out. In each case a  $C_2$  structure is observed rather than the  $C_1$  structure observed in the solid state. The  $C_2$  symmetry is nevertheless consistent with the distorted pentagonal bipyramidal coordination spheres around the metal centers, and it implies that the phenyl groups of the chalcogenolate ligand remain highly mobile in solution. The fluxionality presumably involves concerted rotations of the two pyrazolylborate ligands around their respective B–Sm axes. Qualitatively at least, the barriers to the fluxionality appear to correlate with the extent of the distortion of pyrazolylborate groups. Since it is only in the structures of the heavier chalcogenolates that we observe  $\pi$ -stacking of the rings, we presume that these interactions contribute to making the coordination sphere less mobile than in their lighter analogues. The tighter angle around the chalcogen atom also makes this more likely for the heavier elements than for oxygen, presumably also increasing the steric demand of the ligand. Neither the sterics nor the stacking interactions are however sufficient to hinder the motion of the phenyl group significantly. The greater length and flexibility of the benzyl group may make such stacking easier and could therefore account for the reduced fluxionality for **2c** and **3c**. The sudden broadening of the methylene group observed at  $-90$  °C may be an indication of progressive slowing of the motion of the benzyl group, but our failure to reach the slow exchange limit precluded the possibility of observing NOE effects between the methylene and the pyrazolyl protons. It also precludes quantitative experiments because of the difficulty of separating Curie effects on the chemical shifts from those of the dynamics.

## Conclusions

We have isolated a series of complexes which are essentially isostructural, with similar coordination geometries around the metal center. The Sm–O bond appears unusually short, and although this may be attributed to  $\pi$ -donation from the oxygen to the samarium, the variability in the angle at oxygen suggests that its deformation is quite facile. Hence, the shortness in the bond length may well be attributed to a large ionic contribution to the bonding. The considerable steric congestion in these systems is reflected in our observation that the fluxionality of the coordination sphere can be observed on lowering the temperature. There is some evidence that  $\pi$ – $\pi$  interactions between the ligands may contribute to the rigidity of the system. Finally, we have observed further examples of extreme deformation of the pyrazolylborate ligand, which suggest that it may be more flexible than believed hitherto.

**Acknowledgment.** We are grateful to the Royal Society and the University of London Central Research Fund for support, to the EPSRC for a studentship to A.C.H. (Grant GR/K11338) and for provision of the X-ray diffractometer, and to the Formosa Chemical Co. for study leave to S.Y.L. We thank Prof. W. Clegg for use of the X-ray diffractometer and associated computer programs and facilities in Newcastle. We are grateful to Dr. Abil Aliev for assistance with recording the NMR spectra, to Profs. J. Takats, N. Marques, and J. G. Brennan for helpful discussions, to Drs. D. A. Tocher and S. McWhinnie for gifts of disulfides and diselenides, and to Prof. R. J. H. Clark for his

(62) Kaltsoyannis, N.; Russo, M. R.; Sella, A. Unpublished results.

(63) Clark, R. J. H.; Liu, S. Y.; Maunder, G. H.; Sella, A.; Elsegood, M. R. *J. Chem. Soc., Dalton Trans.* **1997**, 2241–2247.

(64) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963–968.

(65) (a) Benson, M. T.; Cundari, T. R.; Lim, S. J.; Nguyen, H. D.; Pierce-Beaver, K. *J. Am. Chem. Soc.* **1994**, *116*, 3955–3966. (b) Benson, M. T.; Bryan, J. C.; Burrell, A. K.; Cundari, T. R. *Inorg. Chem.* **1995**, *116*, 2348–2355.

interest and support. We acknowledge the Cambridge Crystallographic Data Centre for the data in Figure 7.

**Supporting Information Available:** Listing of references for crystal structures used in generating Figure 7 and X-ray crystallographic files in CIF format for the crystal structures of  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{OPh-4-}$

$\text{Bu}^i]\cdot\text{C}_7\text{H}_8$ ,  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{SPH-4-Me}]$ ,  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{SePh}]\cdot\text{C}_7\text{H}_8$ ,  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{SePh-4-Bu}^i]$ , and  $[\text{Sm}(\text{Tp}^{\text{Me,Me}})_2\text{TePh}]\cdot\text{C}_7\text{H}_8$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC9914793