

# Synthesis, Reactivity, and Stability of Di- and Trivalent Samarium Amides

Ravinder K. Minhas, Yinlin Ma, Jae-Inh Song, and Sandro Gambarotta\*

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Received September 27, 1995<sup>⊗</sup>

SmCl<sub>3</sub>(THF)<sub>3</sub> (THF = tetrahydrofuran) reacts with anionic dialkylamides R<sub>2</sub>N<sup>−</sup> [R = Cy (cyclohexyl), i-Pr (isopropyl), Ph (phenyl)] to give different products, depending on the nature of the R substituents. Reaction with Cy<sub>2</sub>NLi in a 1:2 molar ratio formed [(Cy<sub>2</sub>N)<sub>2</sub>Sm(μ-Cl)(THF)]<sub>2</sub> (**1**) in 80% yield, whereas reaction with (i-Pr)<sub>2</sub>NLi under similar conditions gave [(i-Pr<sub>2</sub>N)<sub>2</sub>SmCl<sub>3</sub>(Li(TMEDA))<sub>2</sub>] (**2**). Partial loss of THF from complex **1** reorganized the molecule into the tetranuclear (Cy<sub>2</sub>N)<sub>6</sub>Sm<sub>4</sub>Cl<sub>6</sub>(THF)<sub>2</sub> (**3**). Attempts to reduce complex **1** with a number of reagents gave [(Cy<sub>2</sub>N)<sub>3</sub>SmTHF]·toluene (**5**), while [(Cy<sub>2</sub>N)<sub>4</sub>SmLi(THF)] (**4**) was isolated upon alkylation reactions carried out with either NpLi or NfLi [Np = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>; Nf = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>Ph]. Direct synthesis of Sm(II) amides from SmI<sub>2</sub>(THF)<sub>2</sub> starting material was successful only in the case of diphenylamide anion (Ph<sub>2</sub>N<sup>−</sup>). Depending on the stoichiometry, -ate (Ph<sub>2</sub>N)<sub>4</sub>Sm[Na(TMEDA)]<sub>2</sub> (**6**) or neutral [(Ph<sub>2</sub>N)<sub>2</sub>Sm(THF)<sub>4</sub>]·THF (**7**) was obtained. The crystal structures of **1–7** were demonstrated by X-ray diffraction analysis. Crystal data are as follows. **1**: C<sub>56</sub>H<sub>105</sub>N<sub>4</sub>O<sub>2</sub>Sm<sub>2</sub>Cl<sub>2</sub>, triclinic, *P* $\bar{1}$ , *a* = 14.344(1) Å, *b* = 23.897(2) Å, *c* = 10.2031(9) Å,  $\alpha$  = 88.479(9)°,  $\beta$  = 121.83(1)°,  $\gamma$  = 93.73(1)°, *Z* = 2. **2**: C<sub>24</sub>H<sub>60</sub>N<sub>6</sub>SmCl<sub>3</sub>Li<sub>2</sub> triclinic, *P* $\bar{1}$ , *a* = 11.552(1) Å, *b* = 15.483(1) Å, *c* = 11.330(1) Å,  $\alpha$  = 101.69(1)°,  $\beta$  = 106.13(1)°,  $\gamma$  = 88.89(2)°. **3**: C<sub>80</sub>H<sub>148</sub>N<sub>6</sub>Cl<sub>6</sub>O<sub>2</sub>Sm<sub>4</sub>, triclinic, *P* $\bar{1}$ , *a* = 16.508(1) Å, *b* = 16.7795(9) Å, *c* = 16.4030(8) Å,  $\alpha$  = 89.794(1)°,  $\beta$  = 88.688(2)°,  $\gamma$  = 79.531(1)°, *Z* = 2. **4**: C<sub>56</sub>H<sub>106</sub>N<sub>4</sub>O<sub>2</sub>LiSm, orthorhombic, *Pna*2<sub>1</sub>, *a* = 16.6145(9) Å, *b* = 17.5858(9) Å, *c* = 19.7754(9) Å, *V* = 5778.0(9) Å<sup>3</sup>, *Z* = 4. **5**: C<sub>47</sub>H<sub>82</sub>N<sub>3</sub>O<sub>2</sub>Sm, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.250(2) Å, *b* = 23.305(2) Å, *c* = 19.088(1) Å,  $\beta$  = 100.90(1)°, *Z* = 4. **6**: C<sub>60</sub>H<sub>72</sub>N<sub>8</sub>SmNa<sub>2</sub>, tetragonal, *I*4<sub>1</sub>/*acd*, *a* = 18.0004(9) Å, *c* = 34.106(1) Å, *Z* = 8. **7**: C<sub>44</sub>H<sub>60</sub>N<sub>2</sub>O<sub>5</sub>Sm, monoclinic, *C*2, *a* = 19.066(1) Å, *b* = 11.932(1) Å, *c* = 9.200(1) Å,  $\beta$  = 93.89(1)°, *Z* = 2.

## Introduction

In the past few years, lanthanide chemistry has been one of the most rapidly developing areas of organometallic chemistry.<sup>1</sup> A significantly low radial extension and ionic character is a distinctive characteristic of these elements, which implies that the chemical behavior is mainly determined by electrostatic and steric factors rather than by the interactions between the metal and ligand orbitals. In other words, the choice of the ligand donor atom and the tuning of its steric bulk are central to the stabilization of these complexes and to the prevention of unwanted features such as decomposition, disproportionation, and ligand scrambling.

Among the lanthanides that exist in the +2 oxidation state (Eu<sup>+2</sup>, Yb<sup>+2</sup>, Sm<sup>+2</sup>), samarium is the most reactive due to its high reduction potential (−1.55 V),<sup>2</sup> and consequently its complexes are the most difficult to stabilize. Cyclopentadienyl anions<sup>3</sup> and the cyclooctatetraenyl dianion<sup>4</sup> are two classes of ligands which have been successfully used for the stabilization of Sm(II) species. In particular, (C<sub>5</sub>Me<sub>5</sub>)<sup>−</sup> has allowed the isolation of some of the most highly reactive organolanthanide derivatives,<sup>5</sup> providing new classes of complexes,<sup>6</sup> unusual structural types,<sup>7</sup> and spectacular reactivity patterns.<sup>8</sup> More

recently, the sterically demanding tris(pyrazolyl)borate, which similar to Cp\* is a 6e<sup>−</sup> donor and has similar steric requirements, has also proved to be able to stabilize the Sm(II)<sup>9</sup> metal center.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, February 15, 1996.

- (1) (a) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299, and references cited therein. (b) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283, and references cited therein. (c) Marks, T. J.; Ernst, R. D. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982. (d) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131.
- (2) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.
- (3) Watt, G. W.; Gillow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 775.
- (4) Wayda, A. L.; Cheng, S.; Mukeiji, I. *J. Organomet. Chem.* **1987**, *330*, C17.

- (5) (a) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.
- (6) (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401. (b) Evans, W. J.; Engerer, S. C.; Neville, A. C. *J. Am. Chem. Soc.* **1978**, *100*, 331. (c) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007. (d) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. In *Fundamentals of Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3. (e) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Organometallics* **1995**, *14*, 3.
- (7) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270. (c) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285. (d) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389. (e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877. (f) Evans, W. J.; Keyer, R. K.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837. (g) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928. (h) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1989**, *111*, 3329.
- (8) (a) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. *Organometallics* **1993**, *12*, 4664. (b) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671. (c) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292. (d) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (e) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (f) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (g) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. G.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (h) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440. (i) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.
- (9) (a) Takats, J.; Zhang, X. W.; Day, V. W.; Eberspacher, T. A. *Organometallics* **1993**, *12*, 4286. (b) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828.

Apart from these ligands, only less than a handful of compounds, containing divalent samarium, have been reported with oxygen,<sup>10</sup> nitrogen,<sup>11</sup> and phosphorus<sup>12</sup> donor based ligands.

Recently, we have reported that a tetraanionic porphyrinogen ligand promoted the formation of either an unusual Sm dinitrogen complex<sup>13</sup> or a divalent bis-samarium species,<sup>14</sup> depending on the reaction conditions. These findings suggested to us that N-donor based ligands might be suitable for the stabilization of the Sm(II) metal center and may well provide promising reactivity patterns. With this respect, anionic dialkylamides are one of the most versatile families of ligands.<sup>15</sup> A feature that makes these ligands especially attractive is their basicity, which is important for both the stabilization of a wide range of oxidation states and for promoting di- and polynuclear aggregation, through bridging interactions of the nitrogen donor atom. Another attractive characteristic of these ligands is a virtually unlimited possibility of adjusting the steric hindrance by selecting the appropriate organic moieties bound to nitrogen. Given this scenario, it is at least surprising that the chemistry of samarium(II) amides is limited to a few reports.<sup>11</sup>

These observations prompted us to start a project on the synthesis, characterization, and reactivity of samarium(II) amides. Since some difficulties were anticipated for the employment of  $\text{SmI}_2(\text{THF})_2$  as a starting material, we have also preliminarily explored the preparation of sterically encumbered samarium(III) amide complexes, which might be further reduced toward divalent species.

Herein we describe our findings.

## Experimental Part

All operations were performed under an inert atmosphere of a nitrogen filled drybox or by use of standard Schlenk-type glassware in combination with a nitrogen-vacuum line.  $\text{SmCl}_3(\text{THF})_3$ <sup>16</sup> and  $\text{SmI}_2(\text{THF})_2$ <sup>17</sup> were prepared according to the literature procedures.  $\text{Cy}_2\text{NH}$ ,  $i\text{-Pr}_2\text{NH}$ , and TMEDA (Aldrich) were distilled prior to use over Na and K metals. The corresponding lithium salts ( $\text{R}_2\text{NLi}$ ) were prepared by treating the hexane solutions of the amines with stoichiometric amounts of  $n\text{-BuLi}$ .  $\text{NpLi}$  and  $\text{NfLi}$  [ $\text{Np} = \text{CH}_2\text{C}(\text{CH}_3)_3$ ;  $\text{Nf} = \text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$ ] were obtained by refluxing the solutions of the

corresponding chlorides with finely dispersed metallic lithium under Ar atmosphere. The NaH and KH suspensions in mineral oil (Aldrich) were washed with hexane, dried, and stored under nitrogen in sealed ampules.  $\text{NaBH}_4$ ,  $\text{TMSN}_3$ , and  $\text{NaHBEt}_3$  were used as received (Aldrich).  $\text{C}_6\text{D}_6$  was dried over Na/K alloy, vacuum transferred into an ampule, and stored under nitrogen. Na/Hg and Li naphthalenide were prepared according standard procedures. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were prepared inside the drybox, and the measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods,<sup>18</sup> and corrections for underlying diamagnetism were applied to the data.<sup>19</sup> Elemental analyses were carried out by using a Perkin-Elmer Series II CHN/O 2400 analyzer.

**[( $\text{Cy}_2\text{N}$ )<sub>2</sub>Sm( $\mu\text{-Cl}$ )(THF)]<sub>2</sub> (1).** The addition of  $\text{Cy}_2\text{NLi}$  (15.7 g, 83.8 mmol) at room temperature to a stirred solution of  $\text{SmCl}_3(\text{THF})_3$  (19.8 g, 41.8 mmol) in THF (150 mL) turned the color of the solution orange. The stirring was continued for an additional 3 h followed by removal of the solvent in vacuo. The residual crystalline solid was redissolved in toluene (150 mL), and LiCl was filtered out. Orange crystals of **1** (20.8 g, 33 mmol, 81%) separated upon allowing the filtrate to stand overnight at  $-30^\circ\text{C}$ . Anal. Calcd (Found) for  $\text{C}_{56}\text{H}_{104}\text{N}_4\text{O}_2\text{Sm}_2\text{Cl}_2$ : C, 54.37 (53.99); H, 8.47 (8.19); N, 4.53 (4.44). IR (KBr, Nujol mull,  $\text{cm}^{-1}$ ): 2661 (m), 1454 (sh), 1376 (s), 1249 (m), 1157 (w), 1145 (sh), 1120 (sh), 1025 (s, br), 983 (m), 944 (sh), 919 (w), 877 (m, br), 842 (m), 798 (m), 777 (m), 725 (m), 665 (sh), 651 (sh), 597 (m), 572 (m), 493 (m).  $\mu_{\text{eff}} = 2.30\mu_{\text{B}}$ .

**[( $i\text{-Pr}_2\text{N}$ )<sub>2</sub>SmCl<sub>3</sub>(LiTMEDA)]<sub>2</sub> (2).** The addition of TMEDA (4.5 mL, 29.8 mmol) to a solution of  $\text{SmCl}_3(\text{THF})_3$  (7.0 g, 14.8 mmol) in THF (60 mL), followed by the addition of lithium diisopropylamide (3.2 g, 29.8 mmol), quickly turned the color of the solution orange. The stirring was continued for about 3 h. The solvent was evaporated in vacuo, and the residual oil was redissolved in toluene (80 mL). After removal of LiCl by filtration and standing at  $-30^\circ\text{C}$  for 2 days, the resulting solution yielded orange crystals of **2** (3.3 g, 4.7 mmol, 32%). Anal. Calcd (Found) for  $\text{C}_{24}\text{H}_{60}\text{N}_6\text{SmCl}_3\text{Li}_2$ : C, 40.98 (40.77); H, 8.60 (8.48); N, 11.95 (12.05). IR (KBr, Nujol mull,  $\text{cm}^{-1}$ ): 1461 (sh), 1405 (w), 1376 (m, br), 1351 (m), 1290 (m), 1251 (w), 1180 (sh), 1130 (w), 1114 (w), 1101 (m), 1062 (m), 1035 (m), 1016 (m), 948 (m), 917 (sh), 842 (w), 792 (sh), 769 (w), 723 (w), 586 (w), 518 (w), 482 (m).  $\mu_{\text{eff}} = 1.58\mu_{\text{B}}$ .

**( $\text{Cy}_2\text{N}$ )<sub>6</sub>Sm<sub>4</sub>Cl<sub>6</sub>(THF)<sub>2</sub> (3).** A suspension of [( $\text{Cy}_2\text{N}$ )<sub>2</sub>Sm( $\mu\text{-Cl}$ )(THF)]<sub>2</sub> (2.1 g, 1.7 mmol) in toluene (40 mL) was warmed and stirred at  $60^\circ\text{C}$  for about 24 h. The resultant clear orange solution was evaporated to dryness in vacuo and the residual solid redissolved in hexane. Dark red crystals of **3** (0.8 g, 0.39 mmol, 47%) separated upon standing overnight at room temperature. Anal. Calcd (Found) for  $\text{C}_{80}\text{H}_{148}\text{N}_6\text{Cl}_6\text{O}_2\text{Sm}_4$ : C, 47.10 (46.88); H, 7.31 (7.19); N, 4.12 (4.33). IR (KBr, Nujol mull,  $\text{cm}^{-1}$ ): 1455 (sh, br), 1376 (m), 1342 (w), 1247 (m), 1157 (w), 1141 (m), 1118 (sh, br), 1081 (w), 1033 (m, br), 981 (m), 943 (sh), 889 (sh), 840 (m), 798 (m), 775 (m), 723 (w), 655 (sh), 615 (w), 572 (m), 495 (sh), 440 (m), 420 (m).  $\mu_{\text{eff}} = 4.25\mu_{\text{B}}$ .

**[( $\text{Cy}_2\text{N}$ )<sub>4</sub>SmLi(THF)]·THF (4). Method A.** A stirred orange suspension of **1** (5.5 g, 4.4 mmol) in diethyl ether (140 mL) was treated with  $\text{NpLi}$  (0.7 g, 8.9 mmol) at room temperature. The reaction was very slow, and the stirring was continued for about 20 h. The solvent was evaporated to dryness in vacuo, and the residual solid was redissolved in hexane (30 mL). Filtration of LiCl followed by cooling of the clear orange solution at  $-30^\circ\text{C}$  yielded yellow crystals of **4** (1.3 g, 1.36 mmol, 17%) over a period of 1 week. Anal. Calcd (Found)

- (10) (a) Sen, A.; Chebolu, V.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1821. (b) Evans, W. J.; Anwender, R.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5. (c) Berardini, M.; Enige, T. J.; Breuman, J. C. *Inorg. Chem.* **1995**, *34*, 5327. (d) White, J. P., III; Deng, H.; Boyd, E. P.; Gallucci, J.; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 1685. (11) (a) Chebolu, V.; Whittle, R. R.; Sen, A. *Inorg. Chem.* **1985**, *24*, 3082. (b) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575. (c) Evans, W. J.; Rabe, G. W.; Ziller, J. W. *Inorg. Chem.* **1994**, *33*, 3072. (d) Evans, W. J.; Rabe, G. W.; Ziller, J. W. *Organometallics* **1994**, *13*, 1641. (12) (a) Nief, F.; Ricard, L. J. *Organomet. Chem.* **1994**, *464*, 149. (b) Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 4521. (13) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477. (14) Song, J.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2141. (15) (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. *Metal and Metalloid Amides*; Ellis Woodrow: Chichester, England, 1980; and references cited therein. (b) Beydoun, N.; Duchateau, R.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1992**, 244. (c) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986. (d) Gambarotta, S.; Edema, J. J. H.; Minhas, R. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1503. (e) Berno, P.; Hao, S.; Minhas, R. K.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417. (f) Song, J. I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927. (g) Bardley, D. C.; Cooperwhaite, R. G. *Inorg. Synth.* **1978**, *18*, 112. (h) Alyea, E. C.; Bradley, D. C.; Copperwhaite, R. G.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1973**, 185. (i) Alyea, E. C.; Bradley, D. C.; Copperwhaite, R. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1580. (j) Berno, P.; Minhas, R. K.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052. (16) (a) Anhydrous  $\text{SmCl}_3$  was prepared following a standard procedure: Freeman, J. H.; Smith, M. L. *J. Inorg. Nucl. Chem.* **1958**, *7*, 224. (b) It was transformed in the corresponding tetrahydrofuranate: Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

- (17) (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (b) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941. (c) Evans, W. J.; Gummerscheimer, T. S.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 8999. (d) Okaue, Y.; Isobe, T. *Inorg. Chim. Acta* **1988**, *144*, 143. (18) Mabbs, M. B.; Machin, D. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973. (19) Foesse, G.; Gorter, C. J.; Smit, L. J. *Constantes Selectionnees, Diamagnetisme, Paramagnetisme Relaxation Paramagnetique*; Masson: Paris, 1957.

for  $C_{56}H_{104}N_4O_2LiSm$ : C, 65.76 (64.99); H, 10.25 (10.34); N, 5.48 (5.12). IR (KBr, Nujol mull,  $cm^{-1}$ ): 1452 (sh), 1376 (sh), 1340 (m), 1261 (w), 1197 (w), 1176 (m), 1130 (m), 1103 (m), 1087 (w), 1047 (sh), 983 (w), 960 (w), 944 (sh), 917 (w), 887 (sh), 842 (m), 796 (m), 723 (w), 655 (m), 626 (m), 613 (sh), 568 (w), 495 (m), 470 (m).  $\mu_{eff} = 2.07\mu_B$ .

**Method B.** A stirred orange suspension of **1** (4.9 g, 4.0 mmol) in diethyl ether (140 mL) was treated with  $NfLi$  (1.21 g, 8.5 mmol) at room temperature, and the stirring was continued for about 24 h. The solvent was evaporated to dryness in vacuo, and the residual solid was redissolved in hexane (30 mL). The resulting solution was filtered to remove  $LiCl$  and allowed to stand at  $-30^\circ C$  over a period of 1 week, upon which yellow crystals of **4** (1.1 g, 1.15 mmol, 28%) separated.

**[Sm(Cy<sub>2</sub>N)<sub>3</sub>(THF)]·toluene (5).** **Method A.** The addition of  $Cy_2NLi$  (1.3 g, 7.1 mmol) to the stirred solution of  $SmCl_3(THF)_3$  (1.2 g, 2.5 mmol) in THF (30 mL) at room temperature turned the color instantaneously pale yellow. The solvent was evaporated in vacuo, and the residual crystalline solid was redissolved in toluene (30 mL). After filtration of  $LiCl$ , the clear solution was allowed to stand at  $-30^\circ C$  for 2 days, upon which pale yellow single crystals of **5** (0.9 g, 1.18 mmol, 72%) separated.

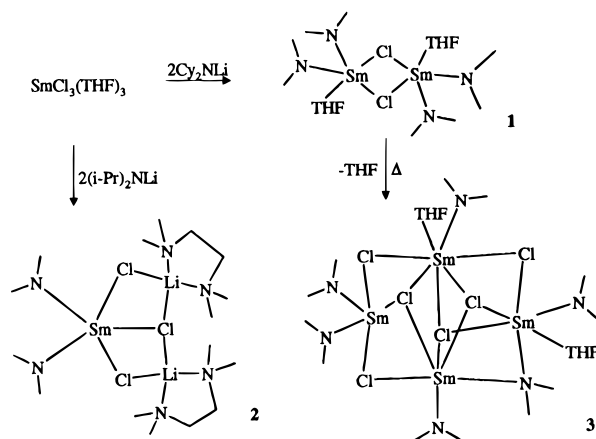
**Method B.** A stirred solution of **1** (1.3 g, 1.0 mmol) in THF (40 mL) was treated with lithium naphthalenide (3.3 mmol) prepared under Ar in THF, at  $-78^\circ C$ . The reaction was instantaneous, and the color of the solution became burgundy red. During the warming to room temperature, the color turned orange-brown. The solvent was evaporated in vacuo and the residual oil redissolved in toluene (20 mL). A small amount of black solid was removed by filtration, and the resultant clear solution was allowed to stand for 7 days at  $-30^\circ C$ , upon which yellow crystals of **5** (0.3 g, 0.4 mmol, 20%) separated. Anal. Calcd (Found) for  $C_{47}H_{82}N_3OSm$ : C, 65.98 (65.33); H, 9.66 (9.61); N, 4.91 (4.78). IR (KBr, Nujol mull,  $cm^{-1}$ ): 2661 (m), 1450 (br, s), 1376 (m), 1340 (w), 1240 (m), 1195 (w), 1174 (w), 1143 (sh), 1118 (sh), 1085 (m), 1064 (m), 1030 (br, s), 983 (m), 960 (w), 944 (sh), 920 (m), 887 (m), 867 (m), 840 (m), 796 (m), 775 (m), 727 (sh), 694 (m), 655 (sh), 646 (w), 620 (sh), 573 (sh), 489 (sh), 465 (m), 440 (m).  $\mu_{eff} = 1.60\mu_B$ .

**(Ph<sub>2</sub>N)<sub>4</sub>Sm[Na(TMEDA)]<sub>2</sub> (6).** A clear solution of  $Ph_2NH$  (4.1 g, 24.0 mmol) in THF (70 mL) was stirred with  $NaH$  (1.2 g, 50.0 mmol) and refluxed for 6 h. After removal of excess  $NaH$  by filtration, the addition of  $SmI_2(TMEDA)_2^{20}$  (3.85 g, 6.0 mmol) turned the color dark brown. The reaction mixture was stirred for 24 h, and dark green crystals of **6** (3.8 g, 3.4 mmol, 57%) were obtained from the resulting dark brown solution, upon standing for 2 days at  $-30^\circ C$ . Anal. Calcd (Found) for  $C_{60}H_{72}N_8SmNa_2$ : C, 65.42 (65.27); H, 6.59 (6.39); N, 10.17 (10.34). IR (KBr, Nujol mull,  $cm^{-1}$ ): 1577 (sh), 1560 (s), 1460 (sh, br), 1376 (m), 1330 (s), 1305 (sh), 1199 (s), 1170 (m), 1076 (s), 1037 (s), 1020 (s), 987 (m), 948 (s), 883 (s), 864 (w), 827 (w), 804 (m), 788 (w), 750 (sh), 694 (sh), 516 (sh), 495 (m).  $\mu_{eff} = 3.61\mu_B$ .

**[(Ph<sub>2</sub>N)<sub>2</sub>Sm(THF)<sub>4</sub>]·THF (7).** A solution of  $Ph_2NH$  (1.8 g, 10.7 mmol) in THF (50 mL) was stirred and refluxed with  $KH$  (0.7 g, 17.5 mmol) for 1 h and then filtered. A solution of  $SmI_2(THF)_2$  (2.9 g, 5.3 mmol) in THF (50 mL) was added at room temperature under  $N_2$ . The reaction mixture was stirred for 24 h, and the color turned very dark grey. The resulting solution was concentrated and allowed to stand for 2 days at  $-30^\circ C$ , upon which dark blue crystals of **7** separated (3.4 g, 3.9 mmol, 75%). Anal. Calcd (Found) for  $C_{44}H_{60}N_2O_5Sm$ : C, 62.37 (61.82); H, 7.14 (6.81); N, 3.31 (3.54). IR (KBr, Nujol mull,  $cm^{-1}$ ): 1581 (sh), 1462 (s, br), 1378 (sh), 1288 (m), 1261 (m), 1171 (s), 1075 (m), 1025 (m), 874 (w), 800 (m), 749 (sh), 694 (sh).  $\mu_{eff} = 3.80\mu_B$ .

**(Ph<sub>2</sub>N)<sub>4</sub>SmNa(TMEDA) (8).** The addition of trimethylsilyl azide (0.2 mL) to a stirred solution of **6** (1.14 g, 1.0 mmol) in THF (50 mL) immediately changed the color to orange. After removal of the solvent by evaporation in vacuo, the oily residue was dissolved in toluene (20 mL). The resulting solution was filtered and layered with hexane (20 mL), yielding orange single crystals of **8** (0.5 g, 0.5 mmol, 52%). Anal. Calcd (found) for  $C_{54}H_{56}N_6SmNa$ : C, 67.39 (67.23); H, 5.87 (5.80); N, 8.73 (9.06). IR (KBr, Nujol mull,  $cm^{-1}$ ): 1581 (sh), 1567 (sh), 1470 (sh, br), 1376 (m), 1330 (w), 1305 (br), 1286 (br), 1193 (m),

## Scheme 1



1174 (m), 1080 (s), 1025 (s), 991 (m), 910 (s), 888 (br, w), 817 (m, br), 748 (sh), 694 (sh), 649 (w), 520 (sh), 497 (sh).  $\mu_{eff} = 1.65\mu_B$ .

**X-ray Crystallography.** Data were collected at temperature in the range of  $-140$  to  $-157^\circ C$  using the  $\omega - 2\theta$  scan technique to a maximum  $2\theta$  value of  $50.0^\circ$  for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were averaged. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects and for absorption (DIFABS). The structures were solved by direct as well as Fourier methods. The non-hydrogen atoms positions were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps but not refined. Two carbon atoms of the cyclohexyl rings of complexes **1** and one methyl group of the TMEDA molecule of complex **2** showed rather large thermal parameters which resolved in the formation of rather elongated thermal ellipsoids. This behavior, which is not surprising for crystal structures of molecules containing cyclohexyl rings, is possibly indicative of some disorder. However, any attempt to model the disorder by splitting the occupancy over two or more positions failed. Nevertheless, it was possible to successfully refine anisotropically their positions while improving the final agreement factors. In the case of complexes **3–5** full anisotropic refinement for all of the non-hydrogen atoms was not possible due to the tendency of some carbon atoms to give negative thermal parameters. These particular atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with  $[I > 2.5\sigma(I)]$ . Neutral atomic scattering factors were taken from Cromer and Waber.<sup>21</sup> Anomalous dispersion effects were included in  $F_{calc}$ . All calculations were performed using the TEXSAN package on a Digital VAX station. Details on crystal data and structure solution are given in Table 1. Selected bond distances and bond angles are given in Table 2. Listing of atomic coordinates and thermal parameters are given as Supplementary Information.

## Results and Discussion

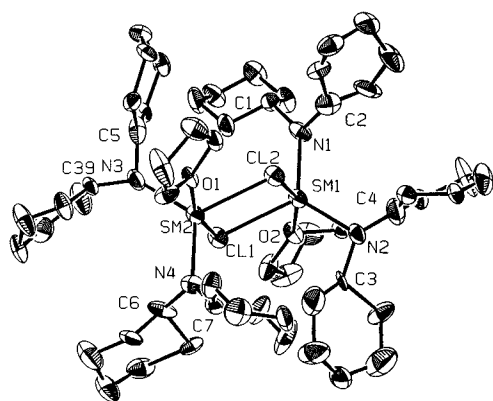
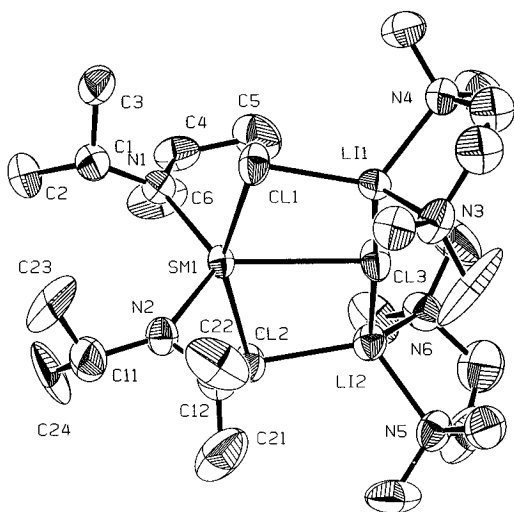
The reaction at room temperature of  $SmCl_3(THF)_3$  with 2 equiv of  $Cy_2NLi$  formed an orange-yellow, air-sensitive solution from which orange crystals of dimeric  $[(Cy_2N)_2Sm(\mu-Cl)(THF)]_2$  (**1**, Scheme 1) were isolated in good yield upon crystallization from toluene. While the formulation was inferred from combustion analysis data, the magnetic moment ( $\mu_{eff} = 2.30\mu_B$  per dimeric unit) was significantly higher than expected for the  $f^5$  electronic configuration of a  $Sm(III)$  metal center. The structure of **1** was elucidated by X-ray crystal structure. Complex **1** is dimeric with two  $(Cy_2N)_2Sm(THF)$  units bridged by two chlorine atoms (Figure 1). Each Sm has a distorted trigonal bipyramidal geometry. The equatorial plane is bound

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

**Table 1.** Crystal Data and Structure Analysis Results

	1	2	3	4	5	6	7
formula	C <sub>56</sub> H <sub>104</sub> O <sub>2</sub> N <sub>4</sub> Sm <sub>2</sub> Cl <sub>2</sub>	C <sub>24</sub> H <sub>60</sub> N <sub>6</sub> Li <sub>2</sub> SmCl <sub>3</sub>	C <sub>80</sub> H <sub>148</sub> N <sub>6</sub> O <sub>2</sub> Cl <sub>6</sub> Sm <sub>4</sub>	C <sub>56</sub> H <sub>106</sub> O <sub>2</sub> N <sub>4</sub> SmLi	C <sub>47</sub> H <sub>82</sub> N <sub>3</sub> SmO	C <sub>60</sub> H <sub>72</sub> N <sub>8</sub> SmNa <sub>2</sub>	C <sub>44</sub> H <sub>60</sub> O <sub>5</sub> N <sub>2</sub> Sm
fw	1238.18	703.42	2040.41	1024.82	855.58	1101.66	847.37
cryst syst	triclinic	triclinic	triclinic	orthorhombic	monoclinic	tetragonal	monoclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>I</i> 4 <sub>1</sub> / <i>acd</i>	<i>C</i> 2
<i>a</i> (Å)	14.344(1)	11.552(1)	16.508(1)	16.6145(9)	10.250(2)	18.0004(9)	19.006(1)
<i>b</i> (Å)	23.897(1)	15.483(1)	16.7795(9)	17.5858(9)	23.305(2)		11.932(1)
<i>c</i> (Å)	10.2031(9)	11.330(1)	16.4030(8)	19.7754(9)	19.088(1)	34.106(1)	9.200(1)
$\alpha$	88.479(9)	101.69(1)	89.794(1)				
$\beta$ (deg)	121.83(1)	106.13(1)	88.688(2)		100.90(1)		93.89(1)
$\gamma$ (deg)	93.73(1)	88.89(2)	79.531(1)				
<i>V</i> (Å <sup>3</sup> )	2965(1)	1904.8(6)	4466.8(7)	5778.0(9)	4477(2)	11051(1)	2088.1(6)
<i>Z</i>	2	2	2	4	4	8	2
radiation	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
(Mo K $\alpha$ Å)							
<i>T</i> (°C)	-156	-145	-140	-157	-153	-143	-147
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.387	1.226	1.517	1.178	1.269	1.324	1.348
$\mu$ <sub>calcd</sub> (cm <sup>-1</sup> )	20.99	17.78	28.26	10.57	13.50	11.24	14.53
<i>R</i> , <i>R</i> <sub>w</sub> , GoF. <sup>a</sup>	0.031, 0.042	0.035, 0.047	0.062, 0.078	0.069, 0.083	0.071, 0.091	0.028, 0.037	0.021, 0.027

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

**Figure 1.** ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.**Figure 2.** ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.

by two nitrogen atoms of two amides and one bridging chlorine atom [ $\text{Cl1-Sm1-Cl2} = 78.9(1)^\circ$ ,  $\text{Cl1-Sm1-O2} = 80.9(2)^\circ$ ,  $\text{Cl1-Sm1-N1} = 115.8(3)^\circ$ ,  $\text{Cl1-Sm1-N2} = 124.4(4)^\circ$ ,  $\text{Cl2-Sm1-O2} = 159.8(2)^\circ$ ,  $\text{Cl2-Sm1-N1} = 100.6(4)^\circ$ ,  $\text{N1-Sm1-N2} = 119.1(5)^\circ$ ], while the oxygen atom of one THF molecule and the second bridging chlorine are placed on the axis. The geometry around the N atoms of the amides [ $\text{Sm1-N1} = 2.19(1) \text{ \AA}$ ,  $\text{Sm1-N2} = 2.23(1) \text{ \AA}$ ] is almost trigonal planar [ $\text{Sm1-N1-C1} = 136.5(9)^\circ$ ,  $\text{Sm1-N1-C2} = 107.4(9)^\circ$ ,  $\text{C1-N1-C2} = 112(1)^\circ$ ]. The  $\text{Sm}_2\text{Cl}_2$  core is perfectly planar [torsion angle

$\text{Cl1-Sm1-Cl2-Sm2} = 0.0(1)^\circ$ ] with slightly different Sm-Cl and Sm-N bond distances [ $\text{Sm1-Cl1} = 2.782(4) \text{ \AA}$ ,  $\text{Sm1-Cl2} = 2.819(5) \text{ \AA}$ ,  $\text{Sm2-Cl1} = 2.819(5) \text{ \AA}$ ,  $\text{Sm2-Cl2} = 2.782(4) \text{ \AA}$ ].

Reaction of  $\text{SmCl}_3(\text{THF})_3$  with diisopropylamide lithium, which may be considered comparable to the cyclohexyl substituents in terms of steric hindrance, showed a remarkably different behavior. When the reaction was carried out under comparable reaction conditions, intractable materials were obtained. However, a new crystalline complex **2** was isolated when the reaction was carried out in the presence of TMEDA (Scheme 1). The formula, indicated by combustion analysis and X-ray fluorescence data, suggested a monomeric structure for the complex. The molecular structure of **2** was elucidated by single crystal X-ray diffraction analysis confirming the complex to be monomeric with a Sm atom placed in the center of a distorted trigonal bipyramid bound by two N atoms of two amide groups and three chloride atoms [ $\text{Cl1-Sm1-Cl2} = 155.69(5)^\circ$ ,  $\text{Cl3-Sm1-N1} = 119.9(1)^\circ$ ,  $\text{Cl3-Sm1-N2} = 121.7(1)^\circ$ ,  $\text{N1-Sm1-N2} = 118.3(2)^\circ$ ] (Figure 2). Two N atoms from two amides [ $\text{Sm1-N1} = 2.218(5) \text{ \AA}$ ,  $\text{Sm1-N2} = 2.202(5) \text{ \AA}$ ] and one chlorine [ $\text{Sm1-Cl3} = 2.888(2) \text{ \AA}$ ] define the equatorial plane, while the other two chlorine atoms are placed on the axial positions, forming somewhat shorter Sm-Cl distances [ $\text{Sm1-Cl1} = 2.764(2) \text{ \AA}$ ,  $\text{Sm1-Cl2} = 2.754(2) \text{ \AA}$ ]. The three chlorine atoms also bridge two Li(TMEDA) units, forming a narrow Cl-Sm-Cl angle [ $\text{Cl1-Sm1-Cl3} = 78.08(5)^\circ$ ]. The equatorial chlorine atom bridges the two lithium cations, forming an almost linear Li-Cl-Li array [ $\text{Li1-Cl3-Li2} = 175.5(4)^\circ$ ]. Each Li atom bears a molecule of TMEDA, which completes the pentacoordination of the alkali metal cation.<sup>22</sup> The geometry around the N atoms of the amides significantly deviates from the trigonal planar configuration [ $\text{Sm1-N1-C1} = 112.1(4)^\circ$ ,  $\text{Sm1-N1-C4} = 130.6(4)^\circ$ ,  $\text{C1-N1-C4} = 116.9(5)^\circ$ ] expected from the  $\text{sp}^2$  hybridization of the amide nitrogen atom.

Both complexes **1** and **2** showed thermal instability in the solution of nonpolar solvents, where a slow decomposition occurred. Conversely, the two complexes are indefinitely stable at room temperature in the solid state. As expected, the reaction

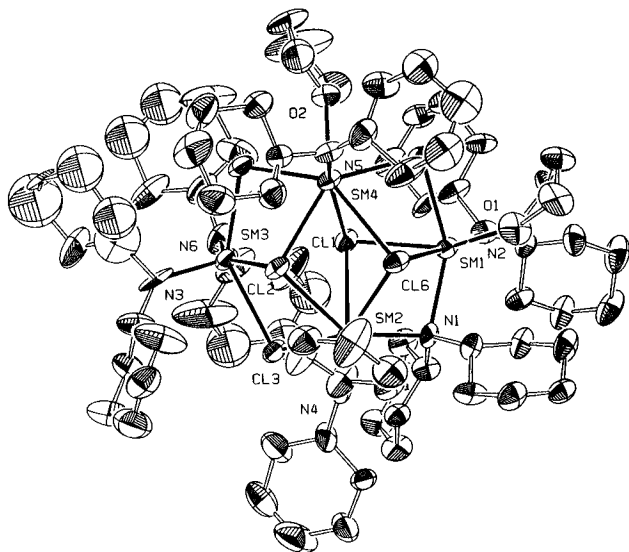
(22) See for example: (a) Brownstein, S. K.; Plouffe, P. Y.; Bensimon, C.; Tse, J. *Inorg. Chem.* **1994**, *33*, 354. (b) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1. (c) Dietrich, H.; Mahdi, W.; Knorr, R. *J. Am. Chem. Soc.* **1986**, *108*, 2462. (d) Olsher, U.; Izatt, R. D.; Bradshaw, J. S.; Dalley, N. K. *Chem. Rev.* **1991**, *91*, 137. (e) Hao, S.; Song, J. I.; Berno, P.; Gambarotta, S. *Organometallics* **1994**, *13*, 1326.

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

Distances						
1	2	3	4	5	6	7
Sm1–Cl1 2.782(4)	Sm1–Cl1 2.764(2)	Sm1–Cl1 2.852(5)	Sm1–N1 2.36(2)	Sm1–N1 2.26(1)	Sm1–N1 2.574(3)	Sm1–N1 2.550(4)
Sm1–Cl2 2.819(5)	Sm1–Cl2 2.754(2)	Sm1–Cl5 2.839(5)	Sm1–N2 2.29(2)	Sm1–N2 2.28(1)	N1–Na1 2.482(3)	Sm1–O1 2.608(3)
Sm2–Cl1 2.819(5)	Sm1–Cl3 2.888(2)	Sm1–Cl6 3.017(5)	Sm1–N3 2.38(2)	Sm1–N3 2.28(1)	Na1–N2 2.411(3)	Sm1–O2 2.631(3)
Sm2–Cl2 2.782(4)	Sm1–N1 2.218(5)	Sm1–N1 2.43(1)	Sm1–N4 2.33(2)	Sm1–O1 2.51(1)		
Sm1–O2 2.573(8)	Sm1–N2 2.202(5)	Sm1–N2 2.20(2)	N1–Li1 2.07(4)			
Sm2–O1 2.368(9)	Cl1–Li1 2.29(1)	Sm2–Cl1 3.092(5)	N3–Li1 2.12(4)			
Sm1–N1 2.19(1)	Cl2–Li2 2.28(1)	Sm2–Cl2 2.873(5)	O1–Li1 1.85(4)			
Sm1–N2 2.23(1)	Cl3–Li1 2.33(1)	Sm2–Cl3 2.709(5)				
Sm2–N3 2.21(1)	Cl3–Li2 2.34(1)	Sm2–Cl6 2.754(5)				
Sm2–N4 2.22(1)		Sm2–N1 2.56(1)				
		Sm2–N1 2.56(1)				
		Sm2–N4 2.11(2)				
		Sm3–Cl2 2.977(5)				
		Sm3–N3 2.13(2)				
		Sm3–N6 2.22(6)				
		Sm4–Cl2 2.850(5)				
		Sm4–Cl6 2.998(5)				

Angles						
1	2	3	4	5	6	7
Cl2–Sm1–N1 100.6(4)	Cl1–Sm1–N1 97.0(1)	Cl1–Sm1–Cl6 71.9(1)	N1–Sm1–N2 126.6(2)	N1–Sm1–N2 108.4(5)	N1–Sm1–N1a 86.9(1)	N1–Sm1–N1a 121.7(2)
Cl2–Sm1–Cl1 78.9(1)	Cl1–Sm1–N2 95.7(1)	Cl1–Sm1–Cl5 76.1(1)	N1–Sm1–N1b 99.7(1)	N1–Sm1–O1 128.0(4)	Sm1–N1–Na1 91.08(9)	N1–Sm1–O1 80.4(1)
Sm1–Cl1–Sm2 101.1(1)	Cl1–Sm1–Cl2 155.69(5)	Cl1–Sm1–N1 82.5(3)	N1–Sm1–N3 87.4(6)	N1–Sm1–N3 109.1(5)	N2–Na1–N2a 78.0(2)	N1–Sm1–O2 126.5(1)
Cl1–Sm1–O2 80.9(2)	Cl1–Sm1–Cl3 78.08(5)	Cl1–Sm1–N2 107.9(4)	N1–Sm1–N1c 152.4(1)	N2–Sm1–O1 93.8(4)	N2–Na1–N1 122.2(1)	O1–Sm1–O2 73.1(1)
Cl1–Sm1–N2 124.4(4)	Cl2–Sm1–Cl3 77.74(4)	N1–Sm1–N2 109.2(5)	N1–Sm1–N4 107.5(7)	N2–Sm1–N3 123.3(5)		O1–Sm1–O1a 145.6(2)
Cl1–Sm1–N1 115.8(3)	Cl2–Sm1–N1 97.1(1)	N1–Sm1–Cl5 143.2(4)	N2–Sm1–N3 105.6(5)	O1–Sm1–N3 95.1(4)		O2–Sm1–O2a 74.7(2)
Cl2–Sm1–O2 159.8(2)	Cl2–Sm1–N2 94.9(1)	N1–Sm1–Cl1 82.5(3)	N2–Sm1–N4 106.4(6)	Sm1–O1–Cl1 131(1)		C6–N1–Cl1 120.8(4)
Cl2–Sm1–N1 100.6(4)	Cl3–Sm1–N1 119.9(1)	N1–Sm1–Cl6 75.0(4)	N3–Sm1–N4 124.4(6)	C5–N1–C28 114(1)		Sm1–N1–C6 104.8(3)
Cl2–Sm1–N2 98.5(5)	Cl3–Sm1–N2 121.7(1)	N1–Sm2–Cl6 77.9(3)	O1–Li1–N1 130(2)	Sm1–N1–C28 120(1)		Sm1–N1–C11 132.8(3)
Cl1–Sm2–Cl2 78.9(1)	N1–Sm1–N2 118.3(2)	N1–Sm2–Cl1 75.8(3)	O1–Li1–N3 127(2)	Sm1–N1–C5 127(1)		
Cl1–Sm2–N3 97.9(1)	Li1–Cl3–Li2 175.5(4)	N1–Sm2–Cl3 112.4(3)	N1–Li1–N3 103(2)	Sm1–N2–Cl11 134(1)		
Cl1–Sm2–N4 98.2(4)	Cl1–Li1–Cl3 100.8(4)	Cl6–Sm2–Cl2 73.2(6)		Sm1–N2–C17 109(1)		
Cl1–Sm2–O1 162.6(2)	Cl1–Li1–N3 120.7(5)	N3–Sm3–N6 109.7(7)		Sm1–N3–C27 129(1)		
Cl2–Sm2–O1 85.6(1)	Cl1–Li1–N4 118.4(5)			Sm1–N3–C33 118(1)		
Cl2–Sm2–N3 124.4(4)	Cl3–Li1–N3 114.1(5)					
Cl2–Sm2–N4 116.6(3)	Cl3–Li1–N4 115.2(5)					
O1–Sm2–N3 84.4(5)	N3–Li1–N4 88.6(4)					
O1–Sm2–N4 95.7(5)	Cl2–Li2–Cl3 100.3(4)					
N3–Sm2–N4 118.7(5)	Cl2–Li2–N5 116.6(5)					
	Cl1–N1–C4 116.9(5)					

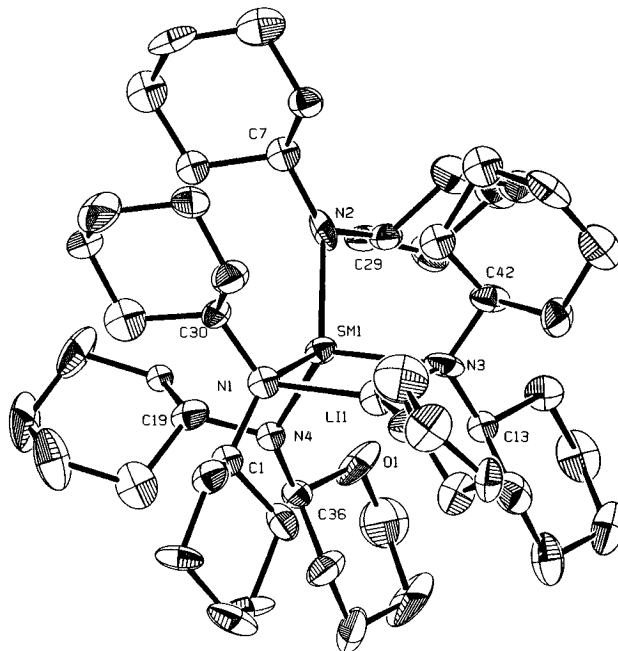


**Figure 3.** ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level.

was greatly accelerated by heating at 60 °C. Unfortunately in the case of **2**, the product of the thermolysis could not be isolated due to its very high solubility. However, in the case of complex **1**, dark-red crystals of  $(\text{Cy}_2\text{N})_6\text{Sm}_4\text{Cl}_6(\text{THF})_2$  (**3**) were isolated in good yield from a red-orange solution (Scheme 1). The combustion analysis and X-ray fluorescence data were consistent with a formulation which indicated partial loss of coordinated THF, thus indicating a probable higher level of nuclearity. The structure was elucidated by an X-ray single crystal structure determination. Complex **3** possesses a tetranuclear core (Figure 3) with four Sm atoms being part of the eight membered ring formed with three bridging chlorides [Sm1–Cl5 = 2.839(5) Å, Sm4–Cl4 = 2.782(5) Å, Sm4–Cl5 = 2.814(6) Å, Sm3–Cl3 = 2.836(5) Å, Sm2–Cl3 = 2.709(5) Å] and one amide [Sm1–N1 = 2.43(1) Å, Sm2–N1 = 2.56(1) Å]. The eight membered ring surrounds three  $\mu^3$ -chlorines, which define a plane perpendicular to that of the  $\text{Sm}_4\text{Cl}_3\text{N}$  ring and bridge the four nonequivalent Sm atoms [Sm1–Cl1 = 2.852(5) Å, Sm2–Cl1 = 3.092(5) Å, Sm4–Cl1 = 3.015(5) Å]. The first Sm atom is six-coordinated, the distorted octahedral geometry being defined by one  $\mu^2$ -bridging amide, three bridging chlorides [Sm1–Cl1 = 2.852(5) Å, Sm1–Cl5 = 2.839(5) Å, Sm1–Cl6 = 3.017(5) Å], one terminal amide [Sm1–N2 = 2.20(2) Å], and a molecule of THF [Sm1–O1 = 2.46(1) Å]. The second Sm atom is also six-coordinated with four bridging chlorides, one bridging amide [Sm2–N1 = 2.56(1) Å], and one terminal amide [Sm2–N4 = 2.11(2) Å]. The third Sm is five-coordinated with three bridging chlorides and two terminal amides [Sm3–N3 = 2.13(2) Å, Sm3–N6 = 2.22(2) Å], while the fourth metal atom is seven-coordinated and is bound to five bridging chlorides, one terminal amide, and a molecule of THF.

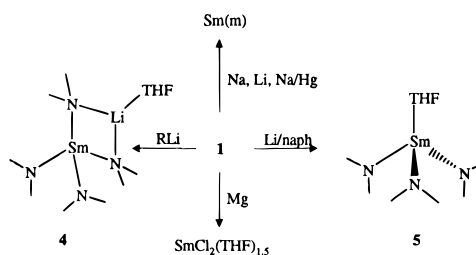
Attempts to replace the bridging chlorides in complex **1** with either  $\text{NpLi}$  or  $\text{NfLi}$  [ $\text{Np} = \text{CH}_2\text{C}(\text{CH}_3)_3$ ;  $\text{Nf} = \text{CH}_2\text{C}(\text{CH}_3)_2\text{-Ph}$ ] did not afford the corresponding alkyl derivative but rather yielded the same product [ $(\text{Cy}_2\text{N})_4\text{SmLi}(\text{THF})$ ·THF (**4**) (Scheme 2). The formulation<sup>23</sup> was indicated by combustion analysis and X-ray fluorescence data which showed the absence of chlorine. The light color of the product suggested that the samarium atom was probably in the trivalent oxidation state.

(23) Other lanthanide complexes with a similar formulation have been reported in the literature: (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 735. (b) Aspinall, H. C.; Moore, S. R.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1993**, 993. (c) Aspinall, H. C.; Tillotson, M. R. *Polyhedron* **1994**, *13*, 3229.



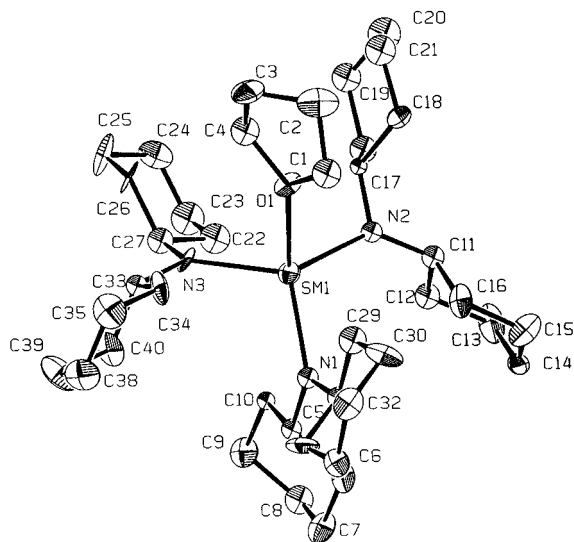
**Figure 4.** ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

## Scheme 2



These observations indicated that a ligand scrambling occurred at the time of the chlorine removal during the alkylation reaction. Accordingly, the yield of complex **4**, although significant, was always rather poor. The crystal structure of **4** revealed the molecule to be mononuclear, consisting of a distorted tetrahedral Sm atom surrounded by four  $\text{Cy}_2\text{N}$  groups [N1–Sm1–N2 = 126.6(6)°, N1–Sm1–N3 = 87.4(6)°, N1–Sm1–N4 = 107.5(7)°, N2–Sm1–N3 = 105.6(5)°]. Two of the four amides bridge a lithium cation, forming an almost planar  $\text{SmN}_2\text{Li}$  core [torsion angle N1–Sm1–N3–Li1 = 3°]. The geometry around the terminal amide nitrogen atoms is trigonal planar with rather distorted angles [Sm1–N2–C7 = 142(1)°, Sm1–N2–C24 = 103(1)°, C7–N2–C24 = 115(2)°], whereas the other two bridging amides possess a distorted tetrahedral geometry [Sm1–N1–C1 = 125(1)°, Sm1–N1–C30 = 103(1)°, Sm1–N1–Li1 = 86(1)°, C1–N1–C30 = 116(2)°, C1–N1–Li1 = 102(2)°]. The Sm–N bond distances with the bridging tetrahedral nitrogen atoms are only slightly longer [Sm1–N1 = 2.36(2) Å, Sm1–N3 = 2.38(2) Å] than those formed by the terminal trigonal planar nitrogen atoms [Sm1–N2 = 2.29(2) Å, Sm1–N4 = 2.33(2) Å]. The trigonal coordination geometry of the Li cation is completed by one molecule of THF forming an almost perfectly linear Sm–Li–O vector [Sm1–Li1–O1 = 179(2)°].<sup>27</sup>

Attempts to reduce the Sm(III) dimer (**1**) using a variety of reducing agents (Na, Li, Na/Hg,  $\text{NaHBEt}_3$ ) invariably led to either metallic Sm or some intractable materials (Scheme 2). Interestingly enough, the reduction of **1** with Mg powder gave a high yield of a deep-green, very air-sensitive solid whose combustion analysis and X-ray fluorescence data were consistent with the formulation  $\text{SmCl}_2(\text{THF})_2$ . Conversely, reduction with



**Figure 5.** ORTEP plot of **5**. Thermal ellipsoids are drawn at the 50% probability level.

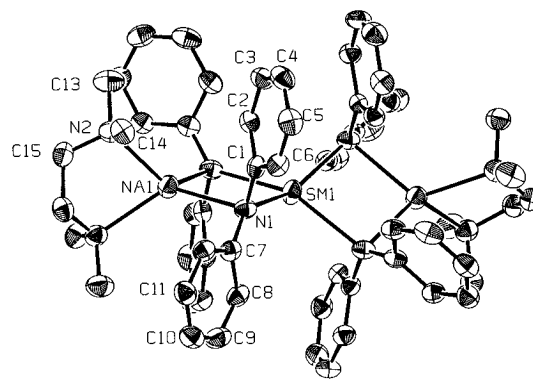
lithium/naphthalide gave metallic Sm and yellow crystals of  $[\text{Sm}(\text{Cy}_2\text{N})_3(\text{THF})]\cdot\text{toluene}$  (**5**), probably as a result of the formation of an unstable  $\text{Sm}(\text{Cy}_2\text{N})_2$  species followed by disproportionation into Sm(III) and  $\text{Sm}^0$ . Complex **5** was more conveniently prepared by reaction of  $\text{SmCl}_3(\text{THF})_3$  with 3 equiv of  $\text{Cy}_2\text{NLi}$ . Attempts to remove THF from the coordination sphere of the samarium atom and to prepare a solvent-free  $\text{Sm}(\text{Cy}_2\text{N})_3$  species by the azeotropic removal of THF in toluene were unsuccessful, as only a highly soluble intractable oil was obtained. Complex **5** is monomeric with Sm having a distorted tetrahedral geometry defined by the three nitrogen atoms of the three  $\text{Cy}_2\text{N}$  groups and one oxygen atom from a THF molecule [ $\text{O1-Sm1-N1} = 128.0(4)^\circ$ ,  $\text{O1-Sm1-N2} = 93.8(4)^\circ$ ,  $\text{O1-Sm1-N3} = 95.1(4)^\circ$ ,  $\text{N1-Sm1-N2} = 108.4(5)^\circ$ ,  $\text{N2-Sm1-N3} = 123.3(5)^\circ$ ,  $\text{N1-Sm1-N3} = 109.1(5)^\circ$ ] (Figure 5). In spite of the fact that the large steric bulk of the amides tends to reduce the N-Sm-O angles, the O1-Sm-N1 angle is the largest about the samarium atom. This can probably be ascribed to the fact that the THF molecule is oriented in the direction of one of the cyclohexyl rings on N1, thus being probably responsible for the anomalously large angle with respect to the other O-Sm-N angles of the other amides. The Sm-N bond distances are comparable to those of the other complexes reported above [ $\text{Sm1-N1} = 2.26(1) \text{ \AA}$ ,  $\text{Sm1-N2} = 2.28(1) \text{ \AA}$ ,  $\text{Sm1-N3} = 2.28(1) \text{ \AA}$ ].

The failure to prepare samarium(II) amides via reduction of Sm(III) precursors possibly indicates that these species may possess an intrinsic instability toward disproportionation. This is further emphasized by the fact that the utilization of  $\text{SmI}_2(\text{TMEDA})_2$ <sup>20</sup> as starting material yielded, upon reaction with 2 equiv of  $\text{R}_2\text{NLi}$ , unidentified complexes, but whose light-yellow color strongly indicated the presence of the metal in the +3 oxidation state. Similar to the case of the Zr(III) halides,<sup>24</sup> the instability of these particular samarium(II) amides might be ascribed to their ability to form dinuclear structures which readily disproportionate to metallic Sm and anionic Sm(III) species. Another possibility is that metallacyclic structures, similar to those observed in the case of vanadium<sup>25</sup> and niobium<sup>26</sup> amide derivatives, would be formed via C-H  $\sigma$ -bond metathesis.

(24) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; Spek, L. A. *Organometallics* **1989**, *8*, 2948.

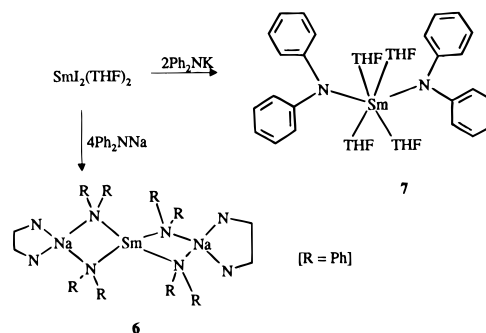
(25) Berno, P.; Minhas, R.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.

(26) Berno, P.; Gambarotta, S. *Organometallics*, in press.



**Figure 6.** ORTEP plot of **6**. Thermal ellipsoids are drawn at the 50% probability level.

### Scheme 3

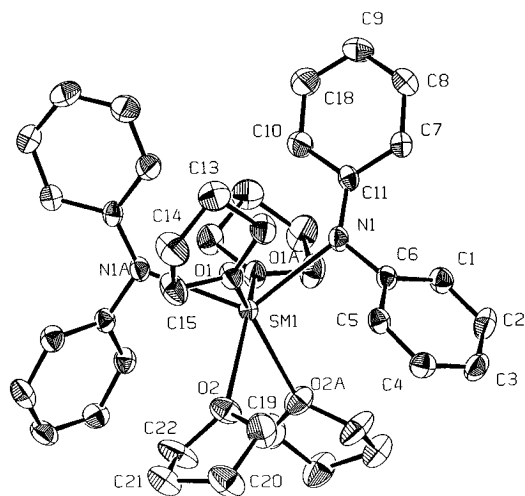


In order to probe this second possibility, the reaction of  $\text{SmI}_2(\text{TMEDA})_2$  with  $\text{R}_2\text{NNa}$  having no  $\alpha$ -H (e.g.,  $\text{Ph}_2\text{NNa}$ ) was examined. The reaction using a 1:4 stoichiometry of reagents yielded a four-coordinate metallate samarium(II) amide  $(\text{Ph}_2\text{N})_4\text{SmNa}_2(\text{TMEDA})_2$  (**6**) (Scheme 3). This complex showed the characteristic resonances of the aromatic group in the IR spectrum. Combustion analysis data were consistent with the proposed formulation. The high magnetic moment of **6** ( $\mu_{\text{eff}} = 3.61\mu_{\text{B}}$ ) falls in the expected range observed for other Sm(II) derivatives.<sup>28</sup>

The structure of complex **6** consists of a discrete mononuclear species with the Sm atom lying in the center of a symmetrically distorted tetrahedron [ $\text{N1-Sm1-N1c} = 152.4(1)^\circ$ ] defined by the N atoms of four amides groups [ $\text{N1-Sm1-N1a} = 86.9(1)^\circ$ ,  $\text{N1-Sm1-N1b} = 99.7(1)^\circ$ ] (Figure 6). Each pair of amides bridges the Sm to one peripheral sodium atom [ $\text{Na1-N1} = 2.482(3) \text{ \AA}$ ], pointing the aromatic rings above and below the  $\text{SmN}_2\text{Na}$  plane [torsion angle  $\text{Sm1-N1-Na1-N1a} = 0.0(1)^\circ$ ]. The geometry around N atoms of the amides is therefore distorted tetrahedral [ $\text{Sm1-N1-C1} = 99.6(2)^\circ$ ,  $\text{Sm1-N1-C7} = 134.6(2)^\circ$ ,  $\text{Na1-N1-C1} = 102.1(2)^\circ$ ,  $\text{Na1-N1-C7} = 99.4(2)^\circ$ ,  $\text{C1-N1-C7} = 120.6(3)^\circ$ ]. All the amides are equidistant from Sm forming Sm-N bond distances [ $\text{Sm1-N1} = 2.574(3) \text{ \AA}$ ] which are slightly lengthened with respect to the other Sm(III) amide complexes reported in this work, probably as a result of the difference in ionic radius. One molecule of TMEDA completes the tetrahedral coordination sphere of each Na cation [ $\text{Na1-N2} = 2.411(3) \text{ \AA}$ ,  $\text{N1-Na1-N1a} = 91.0(1)^\circ$ ,  $\text{N1-Na1-N2} = 123.9(1)^\circ$ ].

(27) See for example: (a) Fraenkel, G.; Winchester, W. R.; Williard, P. G. *Organometallics* **1989**, *8*, 2308. (b) Evans, W. J.; Drummond, D. K.; Hanusa, T. P. *J. Organomet. Chem.* **1989**, *376*, 311. (c) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1446. (d) Karsch, H. H.; Zellner, K.; Gamper, S.; Muller, G. *J. Organomet. Chem.* **1991**, *414*, C39. (e) Karsch, H. H.; Richter, R.; Paul, M.; Riede, J. *J. Organomet. Chem.* **1994**, *474*, C1.

(28) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299.



**Figure 7.** ORTEP plot of **7**. Thermal ellipsoids are drawn at the 50% probability level.

The stability of complex **6** may be ascribed not only to the absence of  $\alpha$ -H but also to the steric protection provided to the divalent metal center by the four bulky amide groups, which prevents polynuclear aggregation and subsequent disproportionation. This idea is further supported by the fact that the samarium atom possesses a rather unusual tetrahedral coordination geometry. In order to test this second possibility, the synthesis of a neutral and less encumbered Sm(II) compound was attempted. The reaction of  $\text{SmI}_2(\text{THF})_2$  with  $\text{Ph}_2\text{NK}$  in a 1:2 ratio at room temperature and in THF gave a high yield of analytically pure  $[(\text{Ph}_2\text{N})_2\text{Sm}(\text{THF})_4] \cdot \text{THF}$  (**7**). The formulation was indicated by combustion analysis, while the absence of iodine was clearly shown by X-ray fluorescence. The magnetic moment calculated on the basis of the proposed formulation ( $\mu_{\text{eff}} = 3.80\mu_{\text{B}}$ ) was also as expected for the  $f^6$  electronic configuration of a Sm(II) metal center. The formulation was confirmed by an X-ray crystal structure.

The coordination geometry of the samarium atom in complex **7** (Figure 7) is defined by two nitrogen atoms of the amide groups and the oxygen atoms of four THF molecules [ $\text{O1}-\text{Sm1}-\text{O1a} = 145.6(2)^\circ$ ,  $\text{O1}-\text{Sm1}-\text{O2} = 73.1(1)^\circ$ ,  $\text{O1}-\text{Sm1}-\text{O2a} = 139.6(1)^\circ$ ,  $\text{O1}-\text{Sm1}-\text{N1} = 80.4(1)^\circ$ ] and may be considered as trigonal prismatic. A similar geometry was previously found in the structure of  $(\text{CBZ})_2\text{Sm}(\text{THF})_4$ .<sup>11e</sup> The Sm-N [ $\text{Sm1}-\text{N1} = 2.550(4) \text{ \AA}$ ] and Sm-O distances [ranging from 2.608 to 2.631  $\text{ \AA}$ ] are rather normal and compare well with those of the other complexes reported in this work. The nitrogen atoms of two amides have a slightly distorted trigonal

planar geometry [ $\text{Sm1}-\text{N1}-\text{C6} = 104.8(3)^\circ$ ,  $\text{Sm1}-\text{N1}-\text{C11} = 132.8(3)^\circ$ ,  $\text{C1}-\text{N1}-\text{C11} = 120.8(4)^\circ$ ].

The deviation of complex **7** from the regular octahedral geometry is rather bizarre and might be caused by the steric repulsion between the two amides which are roughly *cis* positioned. However, this behavior cannot be easily interpreted on the exclusive basis of steric considerations since a simple *trans* arrangement, with the two amides aligned and four equatorial THF, should in principle release the steric compression in the molecule and afford a regular octahedral structure. Similar to the case of samarocene,<sup>5</sup> the possibility that the distortion might be caused by electronic rather than steric factors cannot be conclusively excluded at this stage.

Both complexes **6** and **7** are stable in both solid state and solution, showing no tendency to dimerize or disproportionate. In addition to the absence of  $\alpha$ -H and to the moderate steric hindrance, a third possible cause for the stability of these two Sm(II) complexes might be that the corresponding Sm(III) species  $(\text{Ph}_2\text{N})_3\text{Sm}(\text{THF})$  or  $(\text{Ph}_2\text{N})_4\text{SmNa}$ , formed as a result of the disproportionation reaction, may be unstable. To test this latest possibility, we have attempted the preparation of Sm(III) diphenylamide complexes. While the direct reaction of  $\text{SmCl}_3(\text{THF})_3$  with 3 or 4 equiv of  $\text{Ph}_2\text{NNa}$  failed, the Sm(III) anionic metallate  $(\text{Ph}_2\text{N})_4\text{SmNa}(\text{TMEDA})$  (**8**) was obtained via reaction of the Sm(II) derivative **6** with  $\text{Me}_3\text{SiN}_3$  through a rather complicated reaction, which obviously required decomposition of the azide and possible elimination of  $\text{NaN}_3$ . The reaction afforded an orange colored solution which yielded orange crystals of thermally stable **8**. The complex was characterized on the basis of microanalytical and IR data.

This result indicates that the stability of complexes **6** and **7** cannot be ascribed to the lack of stability of the disproportionation products, and, therefore, the absence of  $\alpha$ -H in the amide ligand is more likely to be responsible for the stabilization of the divalent oxidation state of samarium. However, it is also possible that electronic factors are of importance in determining the stability of these species.

**Acknowledgment.** This work was supported by the National Science and Engineering Council of Canada (NSERC) through a strategic and operating grant.

**Supporting Information Available:** Tables listing atomic coordinates, anisotropic thermal parameters, bond distances and angles, and torsion angles for all of the complexes and figures showing the ORTEP diagrams of complexes **1** and **4** (122 pages). Ordering information is given on any current masthead page.

IC951253+