



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 682 (2003) 263–266

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

Synthesis and structural characterization of unusual amido samarium(III) complexes

Blanca Martín-Vaca^a, Anca Dumitrescu^a, Heinz Gornitzka^a, Didier Bourissou^{a,*},
Guy Bertrand^{a,b}

^a Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex 04, France

^b Department of Chemistry, UCR-CNRS Joint Research Chemistry Laboratory (UMR 2282), University of California, Riverside, CA 92521-0403, USA

Received 20 June 2003; received in revised form 1 August 2003; accepted 1 August 2003

Abstract

Reaction of SmCl_3 with two and three equivalents of lithium hexamethyldisilylamide affords the amido samarium complexes **1** and **2** in 62 and 58% yield, respectively. Single crystal X-ray diffraction studies reveal the covalent dimeric structure of **1** and ion-pair monomeric structure of **2**. The factors that control the coordination number and aggregation state of these complexes are discussed.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Samarium; N ligands; X-ray diffraction; Zwitterions; Ion pairs

1. Introduction

Lanthanide(III) complexes are powerful catalysts for various organic transformations. Organolanthanides and especially metallocene derivatives have proven to be highly efficient for olefin transformations [1], while lanthanide alkoxides, triflates and halides were used in Lewis acid catalyzed organic transformations [2]. Homoleptic lanthanide(III) amides, initially prepared by Bradley et al. [3], are used as main-element constituents in metal–organic chemical vapor deposition (MOCVD) of superconducting metal oxides as well as volatile dopant sources in MOCVD processes with applications in the opto- and micro-electronic industry [4]. They are also promising homogeneous catalysts, as suggested by their activity for the Tishchenko reaction [5] and the ring-opening polymerisation of lactones [6].

Due to the large effective ionic radii of rare-earth elements, lanthanide derivatives usually adopt coordination numbers (CN) up to 9 or even 12 [7]. Among the ways to induce lower CN (from 3 to 6) and monomeric

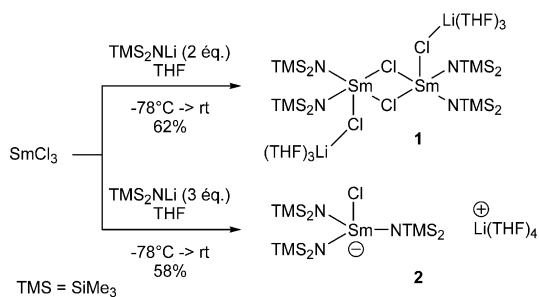
or at least well-defined structures, the use of sterically demanding amido ligands has attracted considerable attention over the last 10 years. Accordingly, various samarium(III) amides have been reported and structural determinations have revealed a broad range of coordination modes. Here we report the synthesis of the bis- and tris-amido samarium(III) complexes $\{(\mu\text{-Cl})\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-Cl})\text{Li}(\text{THF})_3\}_2$ (**1**) and $\{\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3(\text{Cl})\}[\text{Li}(\text{THF})_4]$ (**2**), respectively. Single crystal X-ray diffraction studies reveal the covalent dimeric structure of **1** and ion-pair monomeric structure of **2**. The factors that control the coordination number and aggregation state in these unusual complexes are discussed.

2. Results and discussion

Compounds **1** and **2** are prepared by reaction of anhydrous SmCl_3 with two and three equivalents of lithium hexamethyldisilylamide in tetrahydrofuran (Scheme 1). Evaporation of the solvent, extraction with pentane and crystallisation at -20°C afford white single crystals in good yields (**1**: 62%, **2**: 58%). The solid

* Corresponding author. Fax: +33-5-61-55-8204.

E-mail address: dbouriss@chimie.ups-tlse.fr (D. Bourissou).

Scheme 1. Synthesis of compounds **1** and **2**.

structure of both compounds have been determined by X-ray analysis.

Compound **1** adopts a dimeric structure (Fig. 1) consisting of two Sm[N(SiMe₃)₂]₂(μ-Cl)Li(THF)₃ units bridged by two chlorine atoms. As observed in [Sm(NR₂)₂(μ-Cl)(THF)₂] (R = *c*-Hex or TMS) (**A**) [8a,b] and {[TMSNCH₂CH₂)₂NMe]Sm(μ-Cl)(THF)}₂ (**B**) [8c], the (SmCl)₂ core is perfectly planar and centered on the crystallographical inversion center of the molecule. The coordination sphere of the samarium is not completed by a THF molecule, as observed in complexes **A** [9] and **B**, but by an additional chlorine atom. This exocyclic chlorine atom bridges the samarium center with a Li(THF)₃ unit, which ensures the overall electroneutrality of the molecule. So far, a similar situation has only been observed in the tris-amido complex {Sm(NR₂)₃(μ-Cl)[Li(THF)₃]}₂ (R₂ = -SiMe₂CH₂CH₂SiMe₂-) (**C**) [10]. The samarium adopts in **1** a distorted trigonal bipyramide geometry (CN of 5). The pseudo-equatorial plane is defined by the two

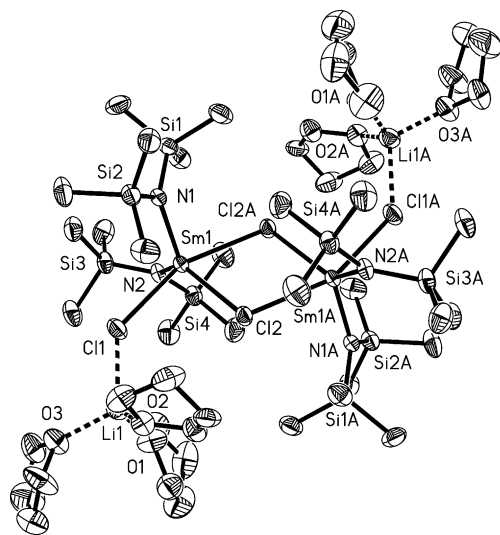


Fig. 1. Molecular structure of **1** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond length (Å) and bond angles (°): Sm1–N1 2.275(4), Sm1–N2 2.296(4), Sm1–Cl1 2.7436(13), Sm1–Cl2 2.8127(12), Li1–Cl1 2.353(10); Sm1–Cl(2)–Sm1A 106.40(4), Cl2–Sm1–Cl2A 73.60(4), Cl1–Sm1–Cl2A 156.75(4), N1–Sm1–N2 116.07(16), N1–Sm1–Cl2 112.05(11), N2–Sm1–Cl2 131.46(12).

nitrogen centers and one of the chlorine of the (SmCl)₂ core, while the two remaining chlorine atoms occupy pseudo-axial positions [Cl1–Sm1–Cl2A 156.75(4)°]. Noteworthy, the Sm–Cl exocyclic bond distance is slightly shorter than the endocyclic one [Sm1–Cl1: 2.7436(13) Å, Sm1–Cl2: 2.8127(12) Å].

Not surprisingly, the introduction of a third bulky amido ligand around the samarium center results in a monomeric complex, as revealed by the solid-state structure of **2** (Fig. 2). Interestingly, the compound adopts an unusual ion-pair structure featuring a tetracoordinate *ate* complex and the Li(THF)₄⁺ unit [11]. The samarium adopts a distorted tetrahedral geometry (sum of the N–Sm–N bond angles 349.9°), and as expected, the Sm–Cl bond distance [2.631(2) Å] is significantly shorter than those observed in Sm–Cl–M bridges. Compared to that observed in **1**, the Sm–Cl–Li bridge is probably precluded in **2** due to steric reasons.

The coordination sphere of monomeric tris-amido samarium complexes is usually completed with solvent molecules (as observed in [Sm(Nc-Hex)₃(THF)] (**D**) [8a], {Sm[N(SiHMe₂)₂]₃(THF)₂} (**E**) [12] or [Sm(NHC₆F₅)(THF)₃] **F** [13]). Tetracoordinate *ate* complexes of tris-amido samarium(III) derivatives have also been structurally characterized, but only with an additional nitrogen- or oxygen-based anionic ligand [14]. Although coordination of an additional chlorine atom has been observed in complex **C**, it resulted in a zwitter-ion rather than ion-pair structure. The difference observed between **2** and **C** most probably results from the higher steric hindrance of the acyclic compared to the cyclic disilylamido ligand. Complexes **1** and **2** are promising candidates for ring-opening poly-

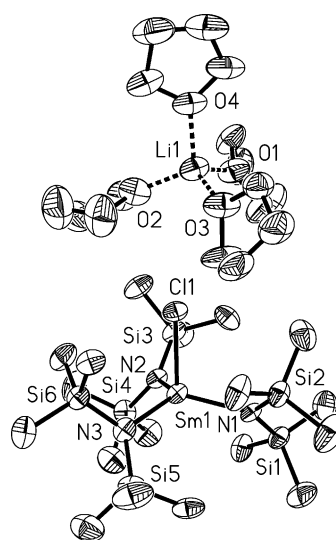


Fig. 2. Molecular structure of **2** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond length (Å) and bond angles (°): Sm1–Cl1 2.631(2), Sm1–N1 2.311(7), Sm1–N2 2.328(7), Sm1–N3 2.324(7); N1–Sm1–N2 114.9(3), N1–Sm1–N3 117.3(3), N2–Sm1–N3 117.7(3).

merization of lactones, and the influence of the precise structure of these amido samarium complexes on their catalytic properties certainly deserves to be studied.

3. Experimental

All reactions were performed under argon atmosphere using standard Schlenk tube techniques. Solvents were dried by standard procedures and distilled prior to use.

3.1. General procedure for the preparation of $\{(\mu\text{-Cl})\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-Cl})\text{Li}(\text{THF})_3\}_2$ (**1**) and $\{\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3(\text{Cl})\}[\text{Li}(\text{THF})_4]$ (**2**)

One equivalent of *n*-butyllithium (20 ml, 31.06 mmol, 1.6 M in hexane) was added to a solution of hexamethyldisilazane (5 g, 31.06 mmol) in THF (20 ml) at -78°C . The solution was stirred at room temperature (r.t) for 2 h, cooled again at -78°C and added dropwise to a suspension of anhydrous SmCl_3 (3.98 g, 15.53 mmol for **1** and 2.65 g, 10.35 mmol for **2**) in 20 ml of THF. After stirring for 4 h at r.t., removal of the solvent under vacuum (0.1 mmHg) and extraction with pentane, colourless crystals were obtained at -20°C (**1**: 7.37 g, 62% yield and **2**: 6.23 g, 58% yield).

3.2. Crystal data

Data for both structures were collected at low-temperature using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with graphite-monochromate Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97 [15] and refined with all data on F^2 using SHELXL-97 [16]. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined using a riding model.

3.2.1. $\{(\mu\text{-Cl})\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-Cl})\text{Li}(\text{THF})_3\}_2$ (**1**)

$\text{C}_{24}\text{H}_{60}\text{Cl}_2\text{LiN}_2\text{O}_3\text{Si}_4\text{Sm}$, $M = 765.29$; triclinic, space group $P\bar{1}$; $T = 193 \text{ K}$; $a = 12.1900(11)$, $b = 13.1323(12)$, $c = 15.0591(14) \text{ \AA}$; $\alpha = 101.279(2)$, $\beta = 106.926(2)$, $\gamma = 114.555(2)^\circ$; $V = 1954.0(3) \text{ \AA}^3$; $Z = 2$; $D_{\text{calc}} = 1.301 \text{ g cm}^{-3}$; $R [I > 2\sigma(I)] = 0.0531$, wR_2 (all data) = 0.1510 for 7735 independent reflections, 365 parameters, GOF = 1.068.

3.2.2. $\{\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3(\text{Cl})\}[\text{Li}(\text{THF})_4]$ (**2**)

$\text{C}_{39}\text{H}_{93}\text{ClLiN}_3\text{O}_{4.5}\text{Si}_6\text{Sm}$, $M = 1037.44$; monoclinic, space group $P2_1/n$; $T = 193 \text{ K}$; $a = 16.844(3)$, $b = 16.086(2)$, $c = 25.056(4) \text{ \AA}$; $\beta = 109.493(3)^\circ$; $V = 6400.2(17) \text{ \AA}^3$; $Z = 4$; $D_{\text{calc}} = 1.077 \text{ g cm}^{-3}$; $R [I > 2\sigma(I)] = 0.0645$, wR_2 (all data) = 0.1691 for 6549 independent reflections, 698 parameters, GOF = 1.199.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 216286 and 216287 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support of this work by the Centre National de la Recherche Scientifique, the University Paul Sabatier (France) is gratefully acknowledged.

References

- [1] F.T. Edelman, Top. Curr. Chem. 179 (1996) 247.
- [2] T. Imamoto, Lanthanides in Organic Synthesis, Academic Press, London, 1994.
- [3] (a) D.C. Bradley, J.S. Ghotra, F.A. Hart, J. Chem. Soc. Chem. Commun. (1972) 349.; (b) D.C. Bradley, J.S. Ghotra, F.A. Hart, J. Chem. Soc. Dalton (1973) 1021.
- [4] (a) W.S. Rees, Jr, O. Just, D.S. Van Derver, J. Mater. Chem. 9 (1999) 249; (b) W.S. Rees, Jr, O. Just, H. Schumman, R. Weimann, Angew. Chem. Int. Ed. Engl. 35 (1996) 419.
- [5] (a) H. Berberich, P.W. Roesky, Angew. Chem. Int. Ed. Engl. 37 (1998) 1569; (b) M.R. Bürgstein, H. Berberich, P.W. Roesky, Chem. Eur. J. 7 (2001) 3078.
- [6] (a) S. Agarwal, M. Karl, K. Dehnicke, G. Seybert, W. Massa, A. Greiner, J. Appl. Polym. Sci. 73 (1999) 1669; (b) E. Martin, P. Dubois, R. Jérôme, Macromolecules 33 (2000) 1530.
- [7] K. Dehnicke, A. Greiner, Angew. Chem. Int. Ed. Engl. 42 (2003) 1340.
- [8] (a) R.K. Minhas, Y. Ma, J.I. Song, S. Gambarotta, Inorg. Chem. 35 (1996) 1866; (b) M. Karl, G. Seybert, W. Massa, S. Agarwal, A. Grenier, K. Dehnicke, Z. Anorg. Allg. Chem. 625 (1999) 1405; (c) A. Dumitrescu, B. Martín-Vaca, H. Gornitzka, J.-B. Cazaux, D. Bourissou, G. Bertrand, Eur. J. Inorg. Chem. (2002) 1948.
- [9] The related complex **A** ($R = \text{TMS}$) has been prepared by the redistribution route from SmCl_3 and $[\text{Sm}(\text{NTMS}_2)_3]$, which clearly explains the structural differences observed with **1**.
- [10] O. Just, W.S. Rees, Jr, Inorg. Chem. 40 (2001) 1751.
- [11] The synthesis of $[\text{Sm}(\text{NTMS}_2)_3]$ was first reported in 1972 by Bradley et al., but no x-ray analysis has been performed so far. Its monomeric solvent-free structure was supported by molecular weight determination. The formation of complex **2** probably results from a somewhat different work-up. The solvent was not removed under high vacuum for **2**, which might explain the presence of residual THF and thus the observed ion-pair structure.

- [12] G.W. Rabe, G.P.A. Yap, *Z. Kristallogr. New Cryst. Struct.* 215 (2000) 457.
- [13] D.R. Click, B.L. Scott, J.G. Watkin, *Chem. Commun.* (1999) 633.
- [14] (a) W.J. Evans, M.A. Ansari, J.W. Ziller, *Inorg. Chem.* 35 (1996) 5435;
(b) M. Karl, A. Dashti-Mommertz, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* 624 (1998) 355;
(c) M. Karl, G. Seybert, W. Massa, K. Harms, S. Aggarwal, R. Maleika, W. Stelter, W. Heitz, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* 625 (1999) 1301.
- [15] G.M. Sheldrick, *Acta Crystallogr. Sect A* 46 (1990) 467.
- [16] G.M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.