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Inorganica Chimica Acta 359 (2006) 4769-4773

www.elsevier.com/locate/ica

Neutral and cationic rare-earth metal alkyl complexes that contain bis(2-methoxyethyl)(trimethylsilyl)amine, a neutral [ONO]-type ligand

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Received 13 March 2006; accepted 10 April 2006 Available online 22 April 2006

Dedicated to Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann.

Abstract

Neutral tris(trimethylsilylmethyl) complexes $[Ln(CH_2SiMe_3)_3(L)](Ln = Sc (1), Lu (2))$ and cationic bis(trimethylsilylmethyl) complexes $[Ln(CH_2SiMe_3)_2(L)(THF)]^+[BPh_4]^-$, (Ln = Sc (3), Lu (4)) that contain bis(2-methoxyethyl)(trimethylsilyl)amine $(L = Me_3SiN(CH_2-CH_2OMe)_2)$ as a neutral, tridentate ligand were synthesized and characterized by NMR spectroscopy. X-ray structural analysis was performed for the scandium complex 1 and exhibited a distorted octahedral coordination geometry with a facially arranged ligand at the neutral scandium center. NMR spectroscopy corroborated the coordination of the tertiary amine function of the ligand to the metal. Complexes 3 and 4 expand the still limited range of cationic rare-earth metal alkyl complexes with known neutral, multidentate ligands. © 2006 Elsevier B.V. All rights reserved.

Keywords: Scandium; Lutetium; Rare-earth metals; Cations; Coordination chemistry

1. Introduction

In contrast to the numerous neutral and anionic complexes, only recently have cationic rare-earth organometallic complexes been described [1]. The increased attention to these cationic complexes is caused by the growing interest in the development of more active catalysts for olefin polymerization [2]. In particular, a number of post-metallocene alkyl complexes of the rare-earth metals have been described [3]. The majority of these complexes incorporate mono- and dianionic ligands. Examples of neutral, multidentate ligands for the coordination of cationic rare-earth metal alkyl complexes include 1,4,7-trimethyl-1,4,7-triazacyclononane [4], tris(3,5-dimethylpyrazolyl)methane [4b], $1,1,1-\text{tri}\{2-[(S)-4-\text{isopropyl}]\circ xazolyl\}$ ethane [5] and 1,4, 7-trithiacyclononane [6]. We have recently succeeded in utilizing crown ethers to isolate and structurally fully characterize an extensive series of rare earth metal alkyl cations [7]. Here we report the use of bis(2-methoxyethyl)(trimethylsilyl)amine ($L = Me_3SiN(CH_2CH_2OMe)_2$) as a neutral, chelating ligand to coordinate neutral and cationic scandium and lutetium alkyl complexes and their characterization by NMR spectroscopy and X-ray crystallography.

2. Experimental

2.1. General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Anhydrous lanthanoid trichlorides (Aldrich or Strem) were used as received. $[Ln(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ complexes [7c] and bis(2-methoxyethyl)(trimethylsilyl)-amine [8] were synthesized according to the literature procedures. Solvents and all other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Varian Unity 500 spectrometer (¹H, 499.6 MHz; ¹³C, 125.6 MHz; ¹¹B, 160.3 MHz) at 25 °C. Chemical shifts for ¹H and ¹³C NMR spectra were

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referenced internally using the residual solvent resonances and reported relative to tetramethylsilane, ¹¹B NMR spectra were referenced externally to a 1 M solution of NaBH₄ in D₂O. Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg-Universität Mainz, Germany. In many cases the results were not satisfactory and the best values from repeated runs were given. Moreover the results were inconsistent from run to run and therefore not reproducible. We ascribe this difficulty observed also by other workers to the extreme sensitivity of the material [9]. Metal analysis was performed by complexometric titration using xylenol orange as indicator [10].

2.2. Syntheses

2.2.1. Synthesis of $[Sc(CH_2SiMe_3)_3\{(MeOCH_2CH_2)_2N-SiMe_3\}]$ (1)

Anhydrous scandium trichloride (454 mg, 3.00 mmol) was stirred in THF (3 mL) at ambient temperature overnight. After addition of pentane (23 mL) and diethyl ether (23 mL), the suspension was treated dropwise at ambient temperature with a solution of LiCH₂SiMe₃ (806 mg, 8.56 mmol) in pentane (9 mL). The resulting colorless suspension was stirred at this temperature for 2 h. After filtration, the solvent was removed from the clear colorless filtrate at 0 °C in vacuo. The resulting oily yellow residue was extracted with pentane $(2 \times 40 \text{ mL})$ at 0 °C and the extracts treated with a solution of bis(2-methoxyethyl)(trimethylsilyl)amine (585 mg, 2.85 mmol) in pentane (5 mL) at 0 °C. After stirring for 2 h at this temperature and filtering, the solvent was evaporated in vacuo. Washing the oily residue with hexamethyldisiloxane (5 mL) and drying in vacuo afforded a colourless powder of 1 (597 mg, 36%). Single crystals suitable for X-ray analysis were obtained from a saturated toluene solution at -30 °C. ¹H NMR (C₆D₅CD₃): $\delta = -0.04$ (6H, s, ScCH₂SiCH₃), 0.08 (9H, s, NSiCH₃), 0.35 (27H, s, ScCH₂SiCH₃), 2.42 (4H, t, ${}^{3}J_{HH} = 5.8 \text{ Hz}, \text{ NC}H_{2}\text{C}H_{2}\text{O}), 3.08 (4\text{H}, \text{t}, {}^{3}J_{HH} = 5.8 \text{ Hz}, \text{ NC}H_{2}\text{C}H_{2}\text{O}), 3.22 (6\text{H}, \text{s}, \text{OC}H_{3}).$ $(C_6D_5CD_3)$: $\delta = -0.7$ (NSiCH₃), 4.5 (ScCH₂SiCH₃), 42.4 (br, ScCH₂SiCH₃), 46.5 (NCH₂CH₂O), 60.6 (OCH₃), 72.6 (NCH₂CH₂O). Anal. Calc. for C₂₁H₅₆NO₂ScSi₄: C, 49.27; H, 11.02; N, 2.74; Sc, 8.78. Found: C, 45.68; H, 12.47; N, 3.86; Sc. 8.78%.

2.2.2. Synthesis of $[Lu(CH_2SiMe_3)_3\{(MeOCH_2CH_2)_2N-SiMe_3\}]$ (2)

Anhydrous lutetium trichloride (840 mg, 3.00 mmol) was stirred in THF (10 mL) at 40 °C overnight. After evaporation of the solvent, the residue was suspended in pentane (20 mL) and treated with a solution of LiCH₂SiMe₃ (856 mg, 9.09 mmol) in pentane (20 mL) at -78 °C. The resulting colorless suspension was allowed to warm to 0 °C and stirred at this temperature for 1 h and for an additional 2 h at room temperature. After filtration at 0 °C, the clear colorless filtrate was treated with a solution of bis(2-

methoxyethyl)(trimethylsilyl)amine (616 mg, 3.00 mmol) in pentane (5 mL) at 0 °C. After stirring for 2 h at this temperature and filtering, the solvent was evaporated in vacuo. Washing the oily residue with hexamethyldisiloxane (5 mL) and drying in vacuo afforded a colorless powder of **2** (971 mg, 50%). ¹H NMR (C₆D₅CD₃): $\delta = -0.79$ (6H, s, LuCH₂SiCH₃), 0.08 (9H, s, NSiCH₃), 0.36 (27H, s, LuCH₂-SiCH₃), 2.18 (4H, br, NCH₂CH₂O), 3.00 (4H, t, ³J_{HH} = 5.5 Hz, NCH₂CH₂O), 3.25 (6H, s, OCH₃). ¹³C{¹H} NMR (C₆D₅CD₃): $\delta = -1.2$ (NSiCH₃), 5.1 (LuCH₂SiCH₃), 42.2 (LuCH₂SiCH₃), 46.0 (NCH₂CH₂O), 61.4 (OCH₃), 72.1 (NCH₂CH₂O). *Anal.* Calc. for C₂₁H₅₆LuNO₂Si₄: C, 39.29; H, 8.79; N, 2.18; Lu, 27.25. Found: C, 35.27; H, 8.68; N, 2.63; Lu, 27.19%.

2.2.3. Synthesis of $[Sc(CH_2SiMe_3)_2\{(MeOCH_2CH_2)_2N-SiMe_3\}$ (THF) $]^+[BPh_4]^-(3)$

A solution of bis(2-methoxyethyl)(trimethylsilyl)amine (103 mg, 0.500 mmol) in THF (5 mL) was added dropwise to a solution of $[Sc(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (377 mg, 0.500 mmol) in THF (15 mL) at 0 °C. After stirring at this temperature for 30 min, all volatiles were evaporated. Washing with pentane (10 mL) and drying in vacuo at 0 °C afforded a colorless powder of 3 (331 mg, 81%). ¹H NMR (THF- d_8): $\delta = -0.22$ (4H, s, ScC H_2 SiCH₃), -0.05 (18H, s, ScCH₂SiCH₃), 0.03 (9H, s, NSiCH₃), 2.90 (4H, t, ${}^{3}J_{\text{HH}} = 6.1 \text{ Hz}, \text{ NC}H_2\text{C}H_2\text{O}), 3.24 (6H, s, \text{OC}H_3), 3.26$ (4H, t, ${}^{3}J_{HH} = 6.1 \text{ Hz}$, NCH_2CH_2O), 6.73 (4H, t, ${}^{3}J_{\rm HH} = 7.2$ Hz, Ph-4), 6.87 (8H, t, ${}^{3}J_{\rm HH} = 7.2$ Hz, Ph-3), 7.27 (8H, br, Ph-2). ¹³C{¹H} NMR (THF- d_8): $\delta = 0.3$ (ScCH₂SiCH₃), 3.5 (NSiCH₃), 45.0 (br, ScCH₂SiCH₃), 47.9 (NCH₂CH₂O), 58.5 (OCH₃), 73.6 (NCH₂CH₂O), 121.6 (Ph-4), 125.5 (Ph-3), 136.8 (Ph-2), 164.8 (q, ${}^{11}B{}^{1}H{}$ ${}^{1}J_{\rm BC} = 49.4$ Hz, Ph-1). NMR (THF- d_8): $\delta = -6.6$. Anal. Calc. for C₄₅H₇₃BNO₃ScSi₃: C, 66.23; H, 9.02; N, 1.72; Sc, 5.51. Found: C, 66.37; H, 9.22; N, 1.69; Sc, 5.56%.

2.2.4. Synthesis of $[Lu(CH_2SiMe_3)_2\{(MeOCH_2CH_2)_2N-SiMe_3\}$ $(THF)]^+[BPh_4]^-$ (4)

A solution of bis(2-methoxyethyl)(trimethylsilyl)amine (103 mg, 0.500 mmol) in THF (5 mL) was added dropwise to a solution of $[Lu(CH_2SiMe_3)_2(THF)_3]^+[BPh_4]^-$ (443 mg, 0.500 mmol) in THF (15 mL) at 0 °C. After stirring at this temperature for 30 min all, volatiles were evaporated. Washing with pentane (10 mL) and drying in vacuo at 0 °C afforded a colorless powder of 4 (354 mg, 75%). ¹H NMR (THF- d_8): $\delta = -1.01$ (4H, s, LuC H_2 SiC H_3), -0.05(18H, s, LuCH₂SiCH₃), 0.03 (9H, s, NSiCH₃), 2.91 (4H, t, ${}^{3}J_{HH} = 6.1$ Hz, NCH₂CH₂O), 3.24 (6H, s, OCH₃), 3.28 $(4H, t, {}^{3}J_{HH} = 6.1 \text{ Hz}, \text{ NCH}_2\text{C}H_2\text{O}), 6.73 (4H, t,$ ${}^{3}J_{\rm HH} = 7.2$ Hz, Ph-4), 6.87 (8H, t, ${}^{3}J_{\rm HH} = 7.2$ Hz, Ph-3), 7.28 (8H, br, Ph-2). ¹³C{¹H} NMR (THF- d_8): $\delta = -0.1$ (LuCH₂SiCH₃), 4.1 (NSiCH₃), 39.8 (LuCH₂SiCH₃), 47.9 (NCH₂CH₂O), 58.5 (OCH₃), 73.7 (NCH₂CH₂O), 121.7 (Ph-4), 125.5 (Ph-3), 136.8 (Ph-2), 164.8 (q, ${}^{1}J_{BC} = 49.4$ Hz, Ph-1). ¹¹B{¹H} NMR (THF- d_8): $\delta = -6.6$. Anal. Calc. for



Scheme 1. Synthesis of the neutral and cationic complexes.

C₄₅H₇₃BLuNO₃Si₃: C, 57.13; H, 7.78; Lu, 18.49; N, 1.48. Found: C, 55.80; H, 7.68; Lu, 18.38; N, 1.49%.

2.3. X-ray investigation

2.3.1. Crystal data for 1

 $C_{21}H_{56}NO_2ScSi_4$, M = 511.99, crystal dimensions $0.73 \times 0.36 \times 0.12$ mm, space group $P2_1/n$, a = 9.7075(9) Å, b = 15.661(2) Å, c = 21.467(2) Å, $\beta = 102.991(4)^{\circ}$, $U = 3180.1(6) \text{ Å}^3$, Z = 4, $D_c = 1.069 \text{ g/cm}^3$, μ (Mo K α) = 0.398 mm^{-1} , T = 120(2) K, θ range $1.62-26.09^{\circ}$, number of reflections 29134, number of unique reflections 6276, number of parameters 276, $R_1 = 0.0529$, $wR_2 = 0.1310$ $(I \ge 2\sigma(I)), R_1 = 0.0845, wR_2 = 0.1498$ (all data). Experimental data were collected on a Bruker AXS diffractometer with graphite monochromated Mo K α radiation using ϕ and ω scans. The data collection as well as the data reduction and correction for absorption were carried out using the program system SMART [11]. The structure was solved by direct methods using SHELXS-86 [12] and refined with anisotropic displacement parameters for all non-hydrogen atoms by full-matrix least-squares based on F^2 using SHELXL-97 [13]. Hydrogen atoms were included into calculated positions with isotropic displacement parameters and were allowed to ride on the carbon atoms. For the graphical representation, ORTEP-III for Windows was used as implemented in the program system WINGX [14].

3. Results and discussion

The reaction of the neutral, in situ generated tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ [15] with bis(2-meth-oxyethyl)(trimethylsilyl)amine L (L = Me_3SiN(CH_2CH_2O-Me)_2) in toluene afforded the neutral complexes [Ln-(CH_2SiMe_3)_3(L)] (Ln = Sc (1), Lu (2)) in moderate yield.

The cationic complexes $[Ln(CH_2SiMe_3)_2(L)(THF)]^+[BPh_4]^-$ (Ln = Sc (3), Lu (4)) were obtained in good yield starting from the cationic bis(alkyl) complexes $[Ln(CH_2SiMe_3)_2-(THF)_3]^+[BPh_4]^-$ [7c] via exchange of THF by bis(2-methoxyethyl)(trimethylsilyl)amine (Scheme 1). Although the THF ligands in the cationic complexes are deemed to be less labile than in the neutral complexes [7], exchange of THF against L is smooth owing to the chelate effect.

Single crystals of 1 suitable for crystallography were obtained from a saturated toluene solution at -30 °C. Fig. 1 depicts the ORTEP diagram of the molecular structure of 1 in the solid state. The structure shows a distorted octahedral coordination geometry around the metal center with the ligand L coordinating to the scandium center in a facial manner. The Sc-O bond distances of 2.308(2) and 2.341(2) A correspond to values found in other organometallic scandium complexes with ether ligands,¹ whereas the Sc-N bond length of 2.584(2) Å is slightly longer than those in other organometallic scandium complexes with a tertiary amine ligand.² This may be due to the reduced basicity of the silvlamine donor. In the only other crystallographically characterized scandium complex with a silvlamine donor $([Sc{N(SiMe_3)(CH_2CH_2NSiMe_3)_2}Cl(THF)])$, the donor group is incorporated in a dianionic ligand, thus leading to a shorter Sc-N bond distance of 2.456(2) Å for the silylamine [16i]. The Sc-C bond lengths between 2.237(3) and 2.270(3) Å are in the range of those reported for other scandium complexes with a trimethylsilylmethyl ligand.³

¹ Sc–O(ether) separations between 2.098(15) and 2.423(3) Å have been reported, see Ref. [7c,16a–16o]. ² Sc–N(tertiony, aming) =

 $^{^{2}}$ Sc–N(tertiary amine) separations between 2.223(3) and 2.564(4) Å have been reported, see Ref. [16i,17a–17f].

³ Sc-C(CH₂SiMe₃) separations between 2.166(2) and 2.295(3) Å have been reported, see Ref. [5,7c,16c,16g,16i–16o,17d,17e,18].



Fig. 1. Molecular Structure of compound 1 with the atomic numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (°): Sc-C1 2.237(3), Sc-C5 2.270(3), Sc-C9 2.250(3), Sc-O1 2.308(2), Sc-O2 2.341(2), Sc-N 2.584(2); and C1–Sc–N 158.53(10), C5–Sc–O1 161.49(9), C9–Sc–O2 164.28(10), C1–Sc–C5 98.72(11), C1–Sc–O1 92.96(9), O1–Sc-O2 79.83(8).

Notably the Sc–C1 bond *trans* to the amine donor shows the shortest distance.

The NMR spectra of the toluene-soluble neutral complexes **1** and **2** revealed signals for the trimethylsilylmethyl groups comparable to other related complexes. For the coordinated ligand L, an upfield shift of all resonances compared to the free ligand in the same solvent could be detected. The ¹H NMR spectrum of the free ligand (toluene- d_8) showed two doublets with a coupling constant of $J_{\rm HH} = 6.0$ Hz at 2.94 ppm (NCH₂CH₂O) and 3.20 ppm (NCH₂CH₂O) for the ethylene link and two singlets for the methyl groups at 0.12 ppm (SiCH₃) and 3.12 ppm (OCH₃). For complexes **1** and **2**, resonances of the corresponding groups could be detected at 2.42 and 2.18 ppm (NCH₂CH₂O), 3.08 and 3.00 ppm (NCH₂CH₂O) 0.08 and 0.08 ppm (SiCH₃) and 3.22 and 3.25 ppm (OCH₃), respectively.

NMR spectroscopic studies for the toluene insoluble cationic complexes 3 and 4 were carried out in THF- d_8 . Again, all the expected signals could be observed as well-separated resonances. The cation-independent resonance at $\delta = -6.6$ ppm in the ¹¹B{¹H} NMR spectrum for both complexes 3 and 4 might be attributed to the separated ions in solution on the NMR time scale.

Attempts at generating the dications $[Ln(CH_2SiMe_3)L-(THF)_x]^{2+}$ have failed, as we failed to observe any significant ethylene polymerization activity for both neutral and cationic complexes under standard conditions (activation by $[PhNMe_2H][B(C_6F_5)_4]$ under 1 bar ethylene in toluene).

4. Conclusions

We have shown that bis(2-methoxyethyl)(trimethylsilyl)amine can be used as a neutral, tridentate [ONO]-type ligand suitable for the coordination of neutral tris(trimethylsilylmethyl) and cationic bis(trimethylsilylmethyl) complexes of the smallest rare earth metals, scandium and lutetium.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. Dr. U. Englert for recording the crystallographic data.

Appendix A. Supplementary material

CCDC-601302 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.04.018.

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