Synthesis and structure of a heterotrimetallic (Li/Er/In), heptacyclic metallasiloxane cage compound

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The unusual heterotrimetallic (Li/Er/In), heptacyclic metallasiloxane cage compound \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\{\text{InMe}_4\}\text{Er} (2)\] has been prepared in 98% yield by reaction of the erbium bis(disiloxanediolate) derivative \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{Cl} (1)\] with trimethylindium, InMe_3. The product was structurally characterized by single-crystal X-ray diffraction.

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Well-defined molecular metal siloxides (= metallasiloxanes) comprising M–O–Si functionalities attract significant interest due to their diverse potential applications [1]. Not only are metal siloxides excellent molecular models for silica-supported heterogeneous metal catalysts [2], but they can also serve as precursors for new materials [3], nanoparticles [4], well-defined surface species [5], and homogeneous catalysts [6]. A particularly useful and versatile precursor for a large variety of metal siloxides is the simple and readily accessible 1,1,3,3-tetrahydroxy-trisiloxane-1,3-diol, \((\text{HO})\text{SiPh}_2\text{OSiPh}_2\text{O} (\text{OH})\), which forms stable complexes with virtually all metallic elements across the Periodic Table ranging from lithium to uranium [1,7]. Among these, lanthanide disiloxanediolates form a well-investigated class of compounds [1]. Most prominent are heterometallic lanthanide bis(disiloxanediolates) of the type \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{S})_n\}_2\text{LnCl} (\text{S} = \text{Ln} = \text{rare-earth metal; } S = \text{Er}_2\text{O}, \text{THF, DME; } n = 1, 2)\]. In these complexes, two formally monoanionic \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{S})_n\}\] forms a twelve-membered \(\text{Si}_4\text{O}_6\text{Li}_2\) inorganic ring system. While the smaller ions like \(\text{Sc}^3+,\text{Y}^3+\), or \(\text{Lu}^3+\) fit into the center of the \(\text{Si}_4\text{O}_6\text{Li}_2\) ring (Scheme 1, A), the larger ions such as \(\text{Er}^{3+},\text{Ho}^{3+}\) (B), \(\text{Pr}^{3+}\) or \(\text{Nd}^{3+}\) (C) are more or less displaced from the center of the twelve-membered rings [1,7a].

Initial reactivity studies revealed that unusual heterometallic products could be isolated from reactions of these lanthanide bis(disiloxanediolates) with Group 13 metal trialkyls. Scheme 2 illustrates the outcome of reactions of type A complexes \((\text{Ln} = \text{Sc, Y})\) with \(\text{AlMe}_3\) and \(\text{InMe}_3\), resp. Treatment of the Sc complex with \(\text{AlMe}_3\) resulted in a Li–Al exchange reaction and formation of the heterometallic (Li/Sc/Al) inorganic ring system \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{AlMe}_3\{\text{ScCl}\cdot\text{THF}\}\]. The related yttrium complex reacted with \(\text{InMe}_3\) under formation of a heterobimetallic (Y/In) disiloxanediolate complex in which two monomeric \(\text{Me}_3\text{InMeO}\) ligands are stabilized through coordination to yttrium [7b].

Yet another, completely different product was obtained when a praseodymium complex of type C was treated with trimethylindium (Scheme 3). This reaction resulted in double insertion of \(\text{InMe}_2\) units into the 12-membered \(\text{Si}_4\text{O}_6\text{Li}_2\) inorganic ring system attached to praseodymium and formation of the novel ionic product \[\text{[Li}(\text{THF})_4]_2\{\text{Pr}[\text{O} \text{SiPh}_2\text{O}\text{Me}_3\text{SiPh}_2\text{O}\text{SiPh}_2\text{O} \text{SiPh}_2\text{O}]_2\}\] [7c].

Thus far, all reactions of \(\text{Ln}-\text{bis(disiloxanediolates)}\) with Group 13 metal trialkyls had resulted in entirely different reaction products (Schemes 2 and 3). Complexes of the structural type B (Scheme 1) are formed with intermediate-sized \(\text{Ln}^{3+}\) ions such as \(\text{Er}^{3+}\) and \(\text{Ho}^{3+}\). In the present study, we found that a reaction of the type B erbium bis(disiloxanediolate) complex \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{ErCl} (1)\] with trimethylindium yet again took an entirely different course (Scheme 4).

The reaction of \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{ErCl} (1)\] with trimethylindium was carried out in toluene solution using a molar ratio of 1:3 [8]. The reaction mixture was first stirred at r.t. and then refluxed for 1 h. After removal of a small amount of insoluble material (presumably \(\text{Li}[\text{InMe}_4]\)) by filtration, the product 2 crystallized directly from the concentrated filtrate in the form of colorless prisms. Meaningful NMR spectra of 2 could not be obtained due to the strongly paramagnetic nature of the \(\text{Er}^{3+}\) ion. After all, as is characteristic for the chemistry of metal disiloxanediolates, the usual combination of spectroscopic

Dedicated to Professor Michael Veith on the occasion of his 70th birthday.

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methods and elemental analyses largely failed to provide sufficiently detailed information about the structure of the product. Fortunately, well-formed colorless single-crystals suitable for X-ray diffraction were obtained after several unsuccessful attempts when a saturated solution in a 1:1 mixture of THF and C6H6 was left to stand at r.t. for a few days [9].

The crystal structure determination revealed the unexpected formation of the unusual heterotrimetallic (Li/Er/In), heptacyclic metallasiloxane cage compound \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_3\{(\text{Li}(\text{THF})_2)_2\}\text{InMe}\]Er (2). Fig. 1 shows the molecular structure (a), the heptacyclic core (b), as well as selected bond lengths and angles. The compound crystallizes in the triclinic space group P-1 with one equivalent of THF and C6H6 in the unit cell. Certainly the most surprising result of the reaction shown in Scheme 4 is the complete rearrangement of the bis(disiloxanediolate) starting material \[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{(\text{Li}(\text{THF})_2)_2\}\text{ErCl}\] (1) under formation of an erbium tris(disiloxanediolate) complex. As is shown in Fig. 1a, the central erbium atom is coordinated in a severely distorted octahedral fashion by six disiloxanediolate oxygen atoms. O–Er–O angles to the oxygens in trans-positions of the coordination octahedron are O3–Er–O4 154.47(10)°, O6–Er–O7 151.41(10)°, and O1–Er–O9 160.18(10)°, while those between oxygens in cis-positions are in the fairly wide range of O1–Er–O4 71.04(9)° (O1–Er–O4) to 108.48(10)° (O3–Er–O7). Two disiloxanediolate oxygens are bridged in the usual manner (cf. Scheme 1) by a Li(THF)_2^+ unit. The tetrahedral coordination geometry around lithium is also severely distorted. Here, the O–Li–O angles are in the wide range between 90.8(3)° (O6–Li–O9) and 125.4(10)° (O6–Li–O10). In contrast to all previously found examples [7], indium is incorporated in the product in the form of a formally dicaticonic monomethylindium unit, InMe^2+. Together with the Li(THF)_2^+ moiety and the Er^3+ ion, this compensates the six negative charges of the three disiloxanediolate dianions. The monomethylindium unit bridges three disiloxanediolate oxygens to give a tricyclic Er(μ-O)_3In cage resembling [1,1,1]-tricyclooctane. The resulting overall heterotrimetallic structure comprises a heptacyclic core consisting of three six-membered ErO₃Si₂ chelate rings, three four-membered ErO₂In rings and one four-membered ErO₂Li ring (Fig. 1b). With 2.110(3) Å (Er–O3) the shortest Er–O bond is formed with a disiloxanediolate oxygen bonded only to erbium. Slightly longer are the Er–O bonds within the ErO₂Li ring (Er–O6 2.168(3) Å, Er–O9 2.176(3) Å), while the longest Er–O bonds are formed with the oxygens bridging erbium and indium (Er–O1 2.390(3) Å, Er–O4 2.392(2) Å, and Er–O7 2.359(3) Å). In the recently reported erbium disiloxanediolate cluster (C₆H₅)₂Si₂O₃(μ-InMe₂)Er₂(THF)₂LiCl₂ the Er–O bonds were found to be in the range of 2.183(3)–2.235(3) Å [10]. Another rare example of a structurally verified complex comprising Er–O–Si bonds is the carborane species \[\{(\text{Na}_2(\text{THF})_{11})\{(\eta^5:σ\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10}))\{(μ^-\eta^5:σ\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6))\text{Er}\}}\] with 2.051(2) Å the Er–O(Si) distance in this compound is comparably short, indicating the presence of metal dπ–oxygen pπ interactions.

At this stage it is certainly premature to speculate about the reason for the different reaction modes of lanthanide bis(disiloxanediolates) with Group 13 metal trialkyls. As has been pointed out earlier [7], the lanthanide bis(disiloxanediolates) can be viewed as lanthanide complexes of metalla-crown ethers. It seems reasonable to assume that
the degree of displacement of the central lanthanide ion from the Si₄O₆Li₂ ring accounts for the observed difference modes of reactivity. Further studies in that direction are clearly warranted.

In summarizing the results reported here, we succeeded in the preparation and structural characterization of a novel trimetallic (Li/Er/In), heptacyclic metallasiloxane cage compound, [(Ph₂SiO)₂O₃{Li(THF)₂}InMe]Er (2). The formation of this unusual product underlines the diversity of reactions between lanthanide bis(disiloxanediolates) and Group 13 metal trimethyl compounds.

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Appendix A. Supplementary material

Crystallographic data for the crystal structure reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition code CCDC 972154 (2). Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2014.09.013.

References

(b) L.G. Hubert-Pfalzgraf, N. Touati, S.V. Pasko, J. Vaissermann, A. Abrutis, Polyhedron 24 (2005) 3066–3073;
(c) A. Abrutis, L.G. Hubert-Pfalzgraf, S. Pasko, N. Touati, V. Kazlauskiene, Vacuum 81 (2013) 13–17;
The reaction mixture was stirred overnight, refluxed for 1 h and filtered through a P4 glass-frit to separate a white precipitate from the clear, almost colorless solution. After reducing the volume of the solution in vacuum to 15 ml the product crystallized in form of colorless prisms. These crystals were suitable of X-ray analysis. For analysis, the compound was thoroughly dried in vacuum at 50–70 °C for 4 h to remove residual solvents. Yield: 1.10 g (98%). Mp: 135–140 °C (dec). Anal. calcld for C81H79LiErInO11Si6 (Mr = 1686.04): C 57.70%; H 4.72%. Found: C 57.35%; H 4.46%.

Mass spectrum (EI): m/z 792 (2%) [(Ph2SiO)4], 715 (10%) [(Ph2SiO)2OLiErInCH3], 637 (18%) [(Ph2SiO)2OLiErInCH3–Ph], 594 (100%) [(Ph2SiO)2OLiErInCH3–Ph], 438 (45%) [(Ph2SiO)2OLiErInCH3–2Ph]. IR (KBr): 3134w, 3068m, 3047m, 3000m, 2955m, 2932m, 2830w, 1960w, 1894w, 1826w, 1774w, 1635w, 1591m, 1485m, 1428s, 1306w, 1305w, 1240w, 1186w, 1121vs, 1036s, 1020s, 1009s, 953s, 899s, 742s, 710vs, 700vs, 683m, 668w, 521s, 497s, and 411w cm⁻¹. NMR resonances could not be assigned due to strong broadening and shifting of the signals as an effect of the paramagnetic Er³⁺ ion.

The intensity data of 2 were registered on an Oxford Diffraction Nova A diffractometer using mirror-focussed CuKα radiation. Absorption corrections were applied using the multi-scan method. The structure was solved by direct methods (SHELXL-97) and refined by full matrix least-squares methods on F² using SHELXL-97 [12]. Full crystal data and structure refinement parameters are summarized in Table S1, while bond lengths and angles are listed in Table S2 in the Supplementary information.

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