



# Double InMe<sub>2</sub> insertion into a 12-membered Si<sub>4</sub>O<sub>6</sub>Li<sub>2</sub> inorganic ring system coordinated to praseodymium

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## ARTICLE INFO

### Article history:

Received 5 October 2009

Received in revised form 13 November 2009

Accepted 15 November 2009

Available online 16 December 2009

Dedicated to Prof. C.N.R. Rao on the occasion of his 75th birthday.

### Keywords:

Praseodymium

Disiloxanediolates

Indium

Inorganic ring systems

X-ray structure

## ABSTRACT

A novel transformation of a lanthanide(III) disiloxanediolate complex with trimethylindium is reported. Treatment of the praseodymium “inorganic metallocene” complex  $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{DME})\}_2]\text{PrCl}(\text{DME})$  (**5**) with  $\text{InMe}_3$  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  $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O})_2\}]$  (**6**). The novel ionic product **6** was structurally authenticated by single-crystal X-ray diffraction.

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## 1. Introduction

The chemistry of metallasiloxanes derived from silanediols, disiloxanediols and related Si–OH species continues to be an area of vigorous research activities [1–7] because such compounds are valuable precursors for metal oxides and silicates [2,3] as well as models for silica-supported heterogeneous catalysts [1,4], or are catalytically active themselves [5]. A particularly useful ligand in this field is the tetraphenyldisiloxanediolate dianion,  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ , which gives rise to a variety of unusual and unexpected structures especially when combined with alkali metals [6] and early transition metals [2b,6,7]. The starting material tetraphenyldisiloxanediol,  $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$ , is readily accessible from cheap precursors [8]. Soluble alumosiloxanes have become increasingly important in recent years [9], and some exciting chemistry has been developed by Veith and co-workers around the polycyclic aluminum tetraphenyldisiloxanediolate derivative  $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_4$  [10]. A rare example of an indium disiloxanediolate,  $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\text{InMe}[\mu\text{-Li}(\text{THF})_2]_2]$  was prepared from  $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$  and  $\text{Li}[\text{InMe}_4]$  [11].

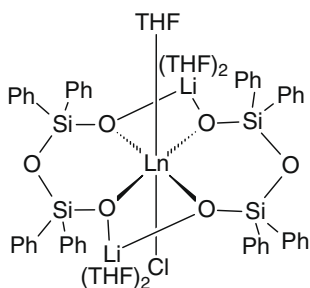
Group 3 metal (Sc, Y) and lanthanide complexes containing the  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$  ligand have been investigated in our laboratory [12]. It was discovered that the small  $\text{Sc}^{3+}$  and  $\text{Y}^{3+}$  ions form heterobimetallic complexes in which the Group 3 metal is located in

the center of a 12-membered  $\text{Si}_4\text{O}_6\text{Li}_2$  inorganic ring system formed by two lithium disiloxanediolate units. Additional chloro functions and solvent molecules are arranged in the *trans*-positions. Thus these complexes can be regarded as “metallacrown” derivatives of scandium and yttrium (Scheme 1).

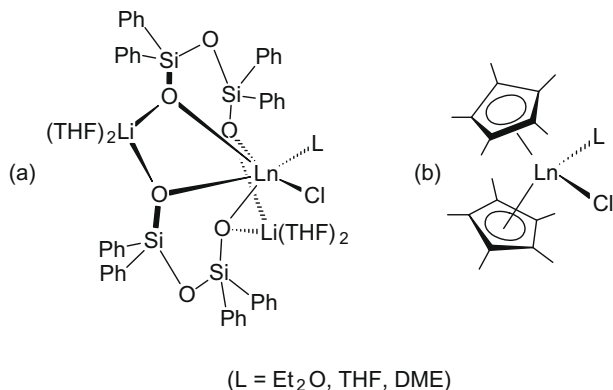
In contrast, large  $\text{Ln}^{3+}$  ions such as  $\text{Pr}^{3+}$  or  $\text{Sm}^{3+}$  do not fit into the center of the 12-membered  $\text{Si}_4\text{O}_6\text{Li}_2$  inorganic ring system but are significantly displaced, leading to a series of bis(disiloxanediolate) complexes which have been termed “inorganic lanthanide metallocenes” [12]. It was shown that this new class of heterobimetallic lanthanide disiloxanediolates (Scheme 2a) shares structural similarities with the well-known bent metallocenes containing pentamethylcyclopentadienyl ( $=\text{C}_5\text{Me}_5$ ) ligands (Scheme 2b). The latter form a large and well-investigated class of organolanthanides with many of them displaying high catalytic activities in various olefin transformations [13]. In both cases two bulky ligands are coordinated to the central lanthanide ion in a bent geometry, leaving room for functional groups X (X = Cl, N(SiMe<sub>3</sub>)<sub>2</sub>, alkyl, H, etc.) as well as additional solvent molecules S (S = Et<sub>2</sub>O, THF, etc.).

Recently, novel transformations of lanthanide(III) disiloxanediolates with Group 13 metal trialkyls were reported. Treatment of the scandium metallacrown complex  $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{DME})\}_2]\text{ScCl}(\text{THF})$  (**1**) with  $\text{AlMe}_3$  according to Scheme 3 resulted in an Li–Al exchange reaction and formation of the heterotrimetallic inorganic ring system  $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}\text{AlMe}_2]\text{ScCl}(\text{THF})$  (**2**) [14].

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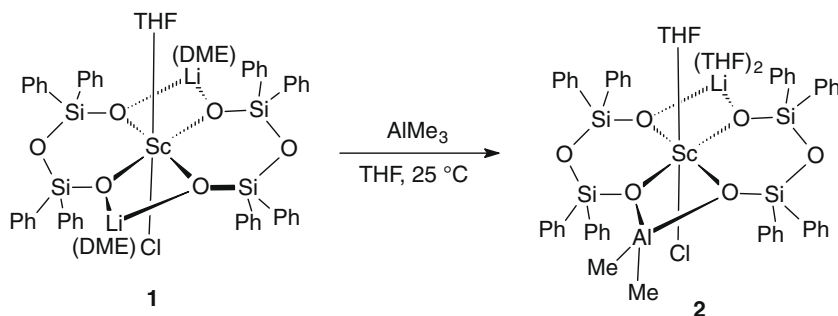


**Scheme 1.** The “metallacrown form” of lanthanide-bis(disiloxanediolates) [12].

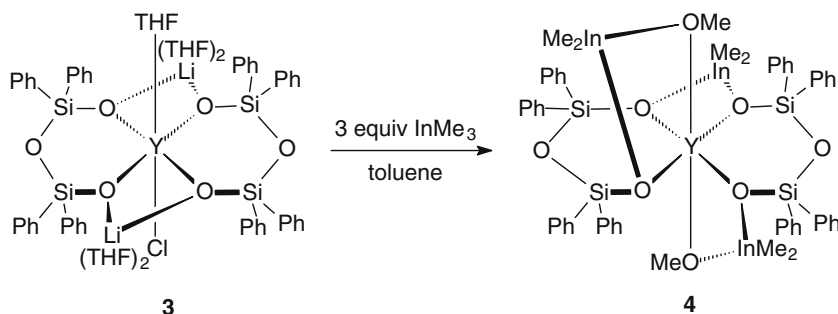


**Scheme 2.** The “inorganic metallocene form” of lanthanide-bis(disiloxanediolates) [12].

The related yttrium metallacrown  $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]YCl(THF)$  (**3**) was found to react with  $InMe_3$  under formation of the heterobimetallic Y/In disiloxanediolate complex  $[\{(Ph_2SiO)_2O\}_2\{InMe_2(OMe)\}_2InMe_2]Y$  (**4**, Scheme 4). In the latter, two monomeric



**Scheme 3.** Formation of  $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}AlMe_2]ScCl(THF)$  (**2**) [14].



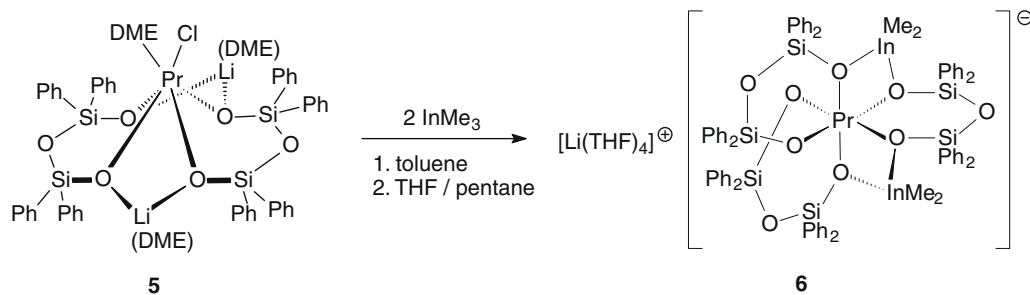
**Scheme 4.** Formation of  $[\{(Ph_2SiO)_2O\}_2\{InMe_2(OMe)\}_2InMe_2]Y$  (**4**) [14].

$Me_2InOMe$  ligands are stabilized through coordination to yttrium [14].

Surprisingly, although closely related, these two reactions took an entirely different course. Similar transformations of the “inorganic metallocene”-type lanthanide-bis(disiloxanediolates) in the presence of Group 13 metal trialkyls have thus far not been studied. We report here the reaction of the praseodymium “inorganic metallocene” complex  $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]PrCl(DME)$  (**5**) with trimethylindium which resulted in formation of the novel ionic complex  $[Li(THF)_4][Pr\{O(SiPh_2O)InMe_2OSiPh_2OSiPh_2O\}_2]$  (**6**).

## 2. Results and discussion

For a first study of a reaction between an “inorganic metallocene”-type lanthanide bis(disiloxanediolate) and a Group 13 metal trialkyl we chose the praseodymium complex  $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]PrCl(DME)$  (**5**) [12c] as a typical representative of this series. Treatment of this starting material with trimethylindium in a THF/toluene solvent mixture resulted in a colorless reaction mixture from which colorless crystals could be isolated. Spectroscopic data (IR, MS and NMR) provided only negligible information on the nature of the reaction product. Due to the paramagnetic nature of  $Pr^{3+}$  the NMR spectra of the product were not fully interpretable (<sup>1</sup>H) or could not be measured at all (<sup>13</sup>C, <sup>29</sup>Si). The observation of ten broad signals assigned to the phenyl protons in the <sup>1</sup>H NMR spectrum indicated a low symmetry in the product, while multiplets at  $\delta$  3.54 and 1.70 ppm clearly showed the presence of coordinated THF, presumably coordinated to Li as in **5** and not to the central Pr atom. With a range of  $\delta$  12.58–5.92 ppm the C<sub>6</sub>H<sub>5</sub> signals experience a stronger paramagnetic shift than those in the starting material **5** ( $\delta$  7.07–5.42 ppm) [12]. The compound is virtually insoluble in hydrocarbon solvents and diethyl ether, but well-formed single-crystals suitable for X-ray diffraction could be grown from a concentrated solution in THF. The crystal structure determination revealed the formation of an unexpected anionic complex as illustrated in Scheme 5.



Scheme 5. Synthesis of  $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O})_2\}]$  (**6**).

Table 1

Crystal data and structure refinement for  $\text{C}_{92}\text{H}_{104}\text{In}_2\text{LiO}_{13}\text{PrSi}_6 \cdot 2\text{THF}$  (**2**).

Identification code	ip28a
Empirical formula	$\text{C}_{100}\text{H}_{120}\text{In}_2\text{LiO}_{15}\text{PrSi}_6$
Formula weight	2107.99
<i>T</i> (K)	133(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	19.6351(2)
<i>b</i> (Å)	23.1638(2)
<i>c</i> (Å)	44.2559(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	20128.6(3)
<i>Z</i>	8
Density (calculated) (Mg/m <sup>3</sup> )	1.296
Absorption coefficient (mm <sup>-1</sup> )	1.056
<i>F</i> (0 0 0)	8032
Crystal size (mm <sup>3</sup> )	0.50 × 0.30 × 0.05
$\theta$ Range for data collection (°)	1.94–28.28
Index ranges	–25 ≤ <i>h</i> ≤ 25, –30 ≤ <i>k</i> ≤ 27, –57 ≤ <i>l</i> ≤ 58
Reflections collected	170 259
Independent reflections	24 844 [ <i>R</i> <sub>int</sub> = 0.0771]
Completeness to $\theta = 28.00^\circ$	99.5%
Absorption correction	Numerical
Maximum and minimum transmission	0.9957 and 0.9774
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	24 844/0/1032
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.030
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0509, <i>wR</i> <sub>2</sub> = 0.1208
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0672, <i>wR</i> <sub>2</sub> = 0.1291
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.186 and –1.415

According to the X-ray diffraction study, the product obtained from treatment of **5** with 2 equivalents of  $\text{InMe}_3$  is the ionic complex  $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O})_2\}]$  (**6**). Crystal data and structure refinement details are listed in Table 1, and selected bond lengths and angles for **6** are summarized in Table 2. Fig. 1 depicts the overall molecular structure of **6**, while the core structure of **6** is shown in Fig. 2.

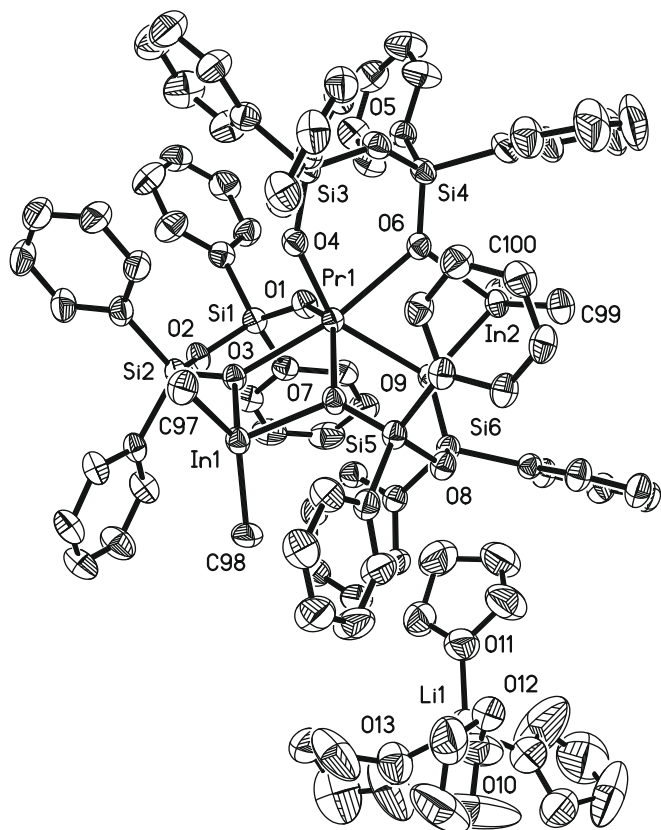
In the course of the reaction, not only two  $\text{Li}(\text{DME})$  units were replaced by  $\text{InMe}_2$  moieties, but an extensive ligand rearrangement is encountered as well. While in the starting material **5**, two lithium disiloxanediolate ligands are coordinated to the central praseodymium, the anion in **6** formally comprises three disiloxanediolate dianions. The coordination number in compound **5** is 7 with the central praseodymium being coordinated to the tetradentate  $\text{Si}_4\text{O}_6\text{Li}_2$  inorganic ring, a chelating DME ligand and a chlorine. The replacement of  $\text{Li}(\text{DME})$  fragments by  $\text{InMe}_2$  units leads to complete disruption of the metallacrown ring and formation of a

Table 2

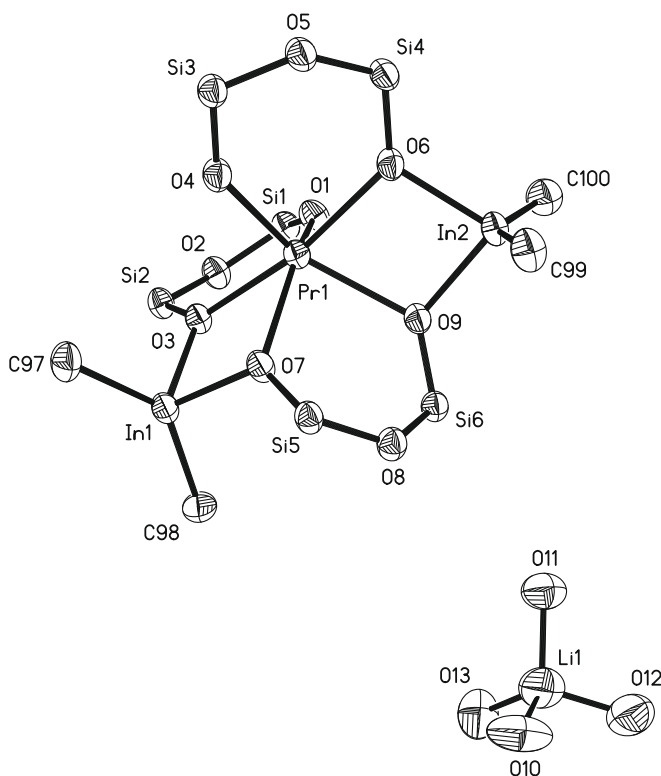
Selected bond lengths (Å) and angles (°) for  $\text{C}_{92}\text{H}_{104}\text{In}_2\text{LiO}_{13}\text{PrSi}_6 \cdot 2\text{THF}$  (**2**).

$\text{In}(1)–\text{Pr}(1)$	3.6559(3)	$\text{Pr}(1)–\text{O}(4)$	2.249(2)
$\text{In}(1)–\text{O}(3)$	2.168(2)	$\text{Pr}(1)–\text{O}(1)$	2.252(3)
$\text{In}(1)–\text{O}(7)$	2.185(2)	$\text{Pr}(1)–\text{O}(3)$	2.450(2)
$\text{In}(1)–\text{C}(98)$	2.141(4)	$\text{Pr}(1)–\text{O}(6)$	2.454(2)
$\text{In}(1)–\text{C}(97)$	2.141(4)	$\text{Pr}(1)–\text{O}(7)$	2.459(2)
$\text{In}(2)–\text{Pr}(1)$	3.6588(3)	$\text{Pr}(1)–\text{O}(9)$	2.479(2)
$\text{In}(2)–\text{O}(6)$	2.173(2)	$\text{Li}(1)–\text{O}(10)$	1.864(13)
$\text{In}(2)–\text{O}(9)$	2.184(2)	$\text{Li}(1)–\text{O}(11)$	1.910(11)
$\text{In}(2)–\text{C}(99)$	2.139(4)	$\text{Li}(1)–\text{O}(13)$	1.922(11)
$\text{In}(2)–\text{C}(100)$	2.144(5)	$\text{Li}(1)–\text{O}(12)$	1.951(14)
$\text{C}(98)–\text{In}(1)–\text{C}(97)$	139.16(17)	$\text{O}(1)–\text{Pr}(1)–\text{O}(6)$	91.57(9)
$\text{C}(98)–\text{In}(1)–\text{O}(3)$	108.64(15)	$\text{O}(3)–\text{Pr}(1)–\text{O}(6)$	168.54(8)
$\text{C}(97)–\text{In}(1)–\text{O}(3)$	101.56(14)	$\text{O}(4)–\text{Pr}(1)–\text{O}(7)$	93.93(9)
$\text{C}(98)–\text{In}(1)–\text{O}(7)$	107.29(14)	$\text{O}(1)–\text{Pr}(1)–\text{O}(7)$	143.52(9)
$\text{C}(97)–\text{In}(1)–\text{O}(7)$	103.99(14)	$\text{O}(3)–\text{Pr}(1)–\text{O}(7)$	70.32(8)
$\text{O}(3)–\text{In}(1)–\text{O}(7)$	81.00(9)	$\text{O}(6)–\text{Pr}(1)–\text{O}(7)$	119.74(8)
$\text{C}(98)–\text{In}(1)–\text{Pr}(1)$	117.44(12)	$\text{O}(4)–\text{Pr}(1)–\text{O}(9)$	140.34(9)
$\text{C}(97)–\text{In}(1)–\text{Pr}(1)$	103.39(12)	$\text{O}(1)–\text{Pr}(1)–\text{O}(9)$	98.08(9)
$\text{O}(3)–\text{In}(1)–\text{Pr}(1)$	40.44(6)	$\text{O}(3)–\text{Pr}(1)–\text{O}(9)$	119.00(8)
$\text{O}(7)–\text{In}(1)–\text{Pr}(1)$	40.81(6)	$\text{O}(6)–\text{Pr}(1)–\text{O}(9)$	70.54(8)
$\text{C}(99)–\text{In}(2)–\text{C}(100)$	138.93(17)	$\text{O}(7)–\text{Pr}(1)–\text{O}(9)$	77.62(8)
$\text{C}(99)–\text{In}(2)–\text{O}(6)$	106.46(14)	$\text{O}(4)–\text{Pr}(1)–\text{In}(1)$	91.43(6)
$\text{C}(100)–\text{In}(2)–\text{O}(6)$	104.19(14)	$\text{O}(1)–\text{Pr}(1)–\text{In}(1)$	114.35(7)
$\text{C}(99)–\text{In}(2)–\text{O}(9)$	105.34(14)	$\text{O}(3)–\text{Pr}(1)–\text{In}(1)$	35.03(6)
$\text{C}(100)–\text{In}(2)–\text{O}(9)$	105.58(14)	$\text{O}(6)–\text{Pr}(1)–\text{In}(1)$	153.99(6)
$\text{O}(6)–\text{In}(2)–\text{O}(9)$	81.65(9)	$\text{O}(7)–\text{Pr}(1)–\text{In}(1)$	35.50(6)
$\text{C}(99)–\text{In}(2)–\text{Pr}(1)$	113.87(11)	$\text{O}(9)–\text{Pr}(1)–\text{In}(1)$	101.94(5)
$\text{C}(100)–\text{In}(2)–\text{Pr}(1)$	107.20(13)	$\text{O}(4)–\text{Pr}(1)–\text{In}(2)$	113.05(6)
$\text{O}(6)–\text{In}(2)–\text{Pr}(1)$	40.53(6)	$\text{O}(1)–\text{Pr}(1)–\text{In}(2)$	93.73(7)
$\text{O}(9)–\text{In}(2)–\text{Pr}(1)$	41.26(6)	$\text{O}(3)–\text{Pr}(1)–\text{In}(2)$	153.37(6)
$\text{O}(4)–\text{Pr}(1)–\text{O}(1)$	110.14(10)	$\text{O}(6)–\text{Pr}(1)–\text{In}(2)$	35.13(6)
$\text{O}(4)–\text{Pr}(1)–\text{O}(3)$	93.13(8)	$\text{O}(7)–\text{Pr}(1)–\text{In}(2)$	101.74(6)
$\text{O}(1)–\text{Pr}(1)–\text{O}(3)$	81.06(8)	$\text{O}(9)–\text{Pr}(1)–\text{In}(2)$	35.52(6)
$\text{O}(4)–\text{Pr}(1)–\text{O}(6)$	81.12(8)	$\text{In}(1)–\text{Pr}(1)–\text{In}(2)$	134.006(8)
$\text{O}(10)–\text{Li}(1)–\text{O}(11)$	114.4(6)	$\text{O}(10)–\text{Li}(1)–\text{O}(12)$	110.9(6)
$\text{O}(10)–\text{Li}(1)–\text{O}(13)$	107.2(6)	$\text{O}(11)–\text{Li}(1)–\text{O}(12)$	105.6(6)
$\text{O}(11)–\text{Li}(1)–\text{O}(13)$	110.1(5)	$\text{O}(13)–\text{Li}(1)–\text{O}(12)$	108.4(6)

formally tetraanionic  $[\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O})_2]^{4-}$  17-membered inorganic chain ligand wrapped around the central praseodymium as a hexadentate ligand. The negative charge of the resulting anion is compensated by a  $[\text{Li}(\text{THF})_4]^+$  cation. Bond lengths and angles around the central praseodymium in **6** are unexceptional with  $\text{Pr}–\text{O}$  distances ranging from 2.249(2) to 2.479(2) Å. These values are in good agreement with other structurally characterized lanthanide disiloxanediolate complexes [12,14]. For example, in the closely related praseodymium bis(disiloxanediolate) derivative  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}\}\text{Pr}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  [12] the  $\text{Pr}–\text{O}$  distances to the disiloxanediolate ligands range from 2.301(2) to 2.346(2) Å, while the average  $\text{Pr}–\text{O}$  distance in  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Li}(\text{DME})\}_2\}\text{PrCl}(\text{DME})$  (**5**) is 2.370(2) Å [12]. Further comparison with literature values is difficult as apparently no other praseodymium siloxides have been structurally characterized in the past. The compound  $\text{Pr}(\text{O}–$



**Fig. 1.** ORTEP view of the molecular structure of  $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{O}-\text{SiPh}_2\text{OSiPh}_2\text{O}_2)\}_2]$  (**6**) with thermal ellipsoids at the 50% probability level (H atoms are not shown for clarity).



**Fig. 2.** ORTEP view of the core structure of  $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{O}-\text{SiPh}_2\text{OSiPh}_2\text{O}_2)\}_2]$  (**6**) with thermal ellipsoids at the 50% probability level.

$\text{SiPh}_3)_3(\text{THF})_3\cdot\text{THF}$  [15] has been reported, but its structure has not been determined by X-ray methods. The O–Pr–O angles in **6** indicate a highly distorted octahedral coordination environment (cf. Table 2). The average In–O distance in **6** is 2.178(2) Å. The value compares favorably with those reported for  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{InMe}_2(\text{OMe})\}_2\text{InMe}_2\text{Y}\}$  (**4**) where the In–O distances range from 2.161(3) to 2.211(3) Å [14].

In summarizing the results reported here, all reactions between lanthanide-bis(disiloxanediolates) with Group 13 metal trialkyls took a very different course. The first reaction of this type using the Pr “inorganic metallocene” derivative **5** and trimethylindium produced an unusual anionic 6-coordinated reaction product **6** containing a formally tetraanionic  $[\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O}_2)]^{4-}$  17-membered inorganic chain ligand. Further investigations in this field will certainly reveal an even greater diversity of this reaction system.

### 3. Experimental

#### 3.1. General procedures

The reaction was conducted in flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. All solvents were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under vacuum prior to use. The starting materials  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Li}(\text{DME})\}_2\}\text{PrCl}(\text{DME})$  (**1**) [12c] and  $\text{InMe}_3$  [16] were prepared according to the literature procedures. NMR spectra were recorded in  $\text{THF}-d_8$  solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Microanalysis of **6** was performed using a Leco CHNS 923 apparatus. The intensity data of **6** were collected on a Stoe IPDS 2T diffractometer with  $\text{Mo K}\alpha$  radiation. The data were collected with the Stoe XAREA [17] program using  $\omega$ -scans. Numeric absorption correction was applied for compound **6** using XRED32 [17]. The space group was determined with XRED32 [17] program. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on  $F^2$  using SHELXL-97 [18]. Data collection parameters are given in Table 1.

#### 3.2. Synthesis of $[\text{Li}(\text{THF})_4][\text{Pr}\{\text{O}(\text{SiPh}_2\text{OInMe}_2\text{OSiPh}_2\text{OSiPh}_2\text{O}_2)\}_2]$ (**6**)

0.33 g (2.1 mmol) of  $\text{InMe}_3$ , dissolved in 30 ml of toluene, were added to a solution of 1.0 g (0.7 mmol) of  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]_2\{\text{Li}(\text{DME})\}_2\}\text{PrCl}(\text{DME})$  (**5**) in THF (50 ml) and the reaction mixture was stirred for 1 h at room temperature. A small amount of white precipitate was removed by filtration and the clear, colorless filtrate was evaporated to dryness. Recrystallization of the white residue from 10 ml of THF at –20 °C afforded **6** as colorless crystals in 58% yield (0.86 g). M.p. 185–187 °C (dec.). Analysis ( $\text{C}_{100}\text{H}_{120}\text{In}_2\text{LiO}_{15}\text{Pr}_6$ ,  $M_w = 2107.99$  g/mol): C, 57.44 (calcd. 56.98), H, 5.50 (5.74)%. IR (KBr): 3075mw, 3051mw, 2999m ( $\nu_{\text{CH}}$  phenyl), 2918m, 2803m ( $\nu_{\text{CH}_2}$ ,  $\nu_{\text{CH}_3}$ ), 1566m, 1470m, 1448s, 1373m, 1301m, 1243m, 1188m ( $\nu$  ring phenyl, CH rocking,), 1126vs ( $\nu_{\text{as}}$  Si–O–Si), 1065s, 1035s ( $\nu_{\text{as}}$  C–O–C), 1009vs, 997s (Si–O–Si), 923m, 740m (CH wagging), 695s ( $\delta$  ring–Si); 528s, 498m, 469m ( $\delta$  ring)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 400.1 MHz):  $\delta = 12.58, 11.46, 11.15, 9.43, 8.33, 8.02, 7.37, 6.59, 6.29, 5.92$  (s br,  $\text{C}_6\text{H}_5$ ); 3.95, 3.00, 2.22 (s br, rel. int. 2:1:2,  $\text{InMe}_2$ ); 3.54, 1.70 (m, THF) ppm.

### 4. Supplementary material

CCDC 749435 contains the supplementary crystallographic data for (**6**). These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgements

This work was generously supported by the Deutsche Forschungsgemeinschaft (SPP 1166 “Lanthanoid-spezifische Funktionalitäten in Molekül und Material”). Financial support by the Otto-von-Guericke-Universität Magdeburg is also gratefully acknowledged.

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