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A functional model for lanthanide doped silicate materials: synthesis of an apically substituted samarium silsesquioxane complex

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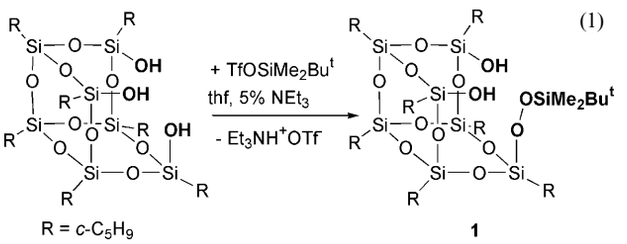
Steric protection of a trisilanol silsesquioxane (also referred to as a silasesquioxane) by one TBDMS group ($SiMe_2Bu^t$) generated a new siloxanolate ligand, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OTBDMS)$ **1**, that allows only restricted access to a co-ordinated metal. Lithiation afforded the stable complex $(c\text{-}C_5H_9)_7Si_7O_9(OLi)_2(OTBDMS)$, which has allowed the generation of a samarium adduct $[Sm(OC_6H_3Bu^t_2\text{-}2,6)\{(c\text{-}C_5H_9)_7Si_7O_9(O)(OLi)(OTBDMS)\}_2]$. A structural study of this samarium adduct revealed two unusual features: an absence of stabilising M–O interactions with the siloxane core, and retention of one apical aryloxide group at the trivalent metal, through which the chemistry of a silica-functionalised Ln^{3+} ion might be modelled. X-Ray crystallography also revealed the dimeric hydrogen bonded structure of the disilanol ligands. The disilanol ligand **1** may also readily be converted into a dithallium salt, providing a potential precursor for further f-element derivatives of this disilanolate moiety.

Introduction

The soluble polyhedral POSS oligomer $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$, formally derived from hydrolytic cleavage of $[(c\text{-}C_5H_9)Si(OH)_3]$ from an Si_8 silsesquioxane cube (see eqn. (1))[1] displays remark-



(1)

ably similar structural and electronic properties to those observed for hydroxylated silica surfaces (POSS = partially oligomerised silsesquioxane). A range of complexes have been synthesized which incorporate a metal at the empty vertex and serve as molecular models for metal-doped silicate surfaces, as well as precursors for metal–silica composites.[2]

Metallosilsesquioxanes mimic their surface-bound counterparts in many ways, with the silsesquioxane framework conferring greater Lewis acidity on the metal in comparison to other silanolate ligand models.[2a] For example, Group 4 and 5 derivatives are highly active catalysts for alkene polymerisation after activation by trialkylaluminium or triarylboron reagents.[3] However, this activation proceeds *via* reactions of the type that would strip a metal from a solid support. A catalyst derived from a lanthanide metal should not be subject to such a problem.

The aim of our study was to generate a functional model for a silica surface bonded f-block ion catalyst by ensuring that the remaining co-ordination site of the Ln^{3+} ion remains accessible. Silicate catalysts doped with f-block ions find use in a number of technologically important organic transformations,[4] whilst examples of lanthanide silsesquioxane derivatives (unlike their d- and p-block counterparts) remain scarce. Also the only lanthanide derivatives structurally characterised to date show strong electrostatic interactions between the metal and Si–O–Si framework oxygen atoms.[5] We have incorporated the particularly bulky TBDMS ($SiMe_2Bu^t$) group to partially block the missing vertex of the silsesquioxane,[6] and to prevent access of the siloxane oxygen atoms to the primary co-ordination sphere of the metal.

Herein we report the synthesis of a new disilanol, and an aryloxide-functionalised samarium derivative which is covalently bound to a bridged pair of silsesquioxanes solely *via* siloxide oxygen atoms.

Results and discussion

Silylation to protect and solubilise the POSS trisilanol

Disilanol **1** may be generated from treatment of $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$ with TBDMS triflate ($CF_3SO_3SiMe_2Bu^t$) in a 5% triethylamine–thf solvent mixture, eqn. (1). The TBDMS group greatly enhances the solubility of **1** in hydrocarbon solvents and forms a thermally stable adduct. Care was taken during the reaction to ensure liberated triflic acid, anticipated to lead to framework cleavage, was immediately precipitated as its ammonium salt.[1c]

Additional resonances observed in the ^{29}Si NMR spectrum were consistent with the lowered pseudo-symmetry of the ligand **1** relative to the parent trisilanol. The molecular structure, determined by single crystal X-ray crystallography (Fig. 1), confirms that functionalisation occurred with retention of configuration and that even the bulky TBDMS group still allows the molecules to form bridged dimers *via* silanol hydrogen bonds. The symmetry of each dimer is close to C_{2v} and the TBDMS groups lie above and below the silanol O_4 plane, the groups bonded to O(200) and O(400) utilising the flexibility of the pivot Si atoms to flex away from the siloxane core without significant distortion of any O–Si–O angle (see Table 1). Intramolecular O···O distances of 2.694(9) and 2.748(9) Å for the silanol groups are similar to the intermolecular distances of 2.639(9) and 2.708(8) Å between opposing O···O pairs. This creates a more symmetrical $[OH]_4$ core than in other monosilylated dimers,[8] which tend to exhibit two

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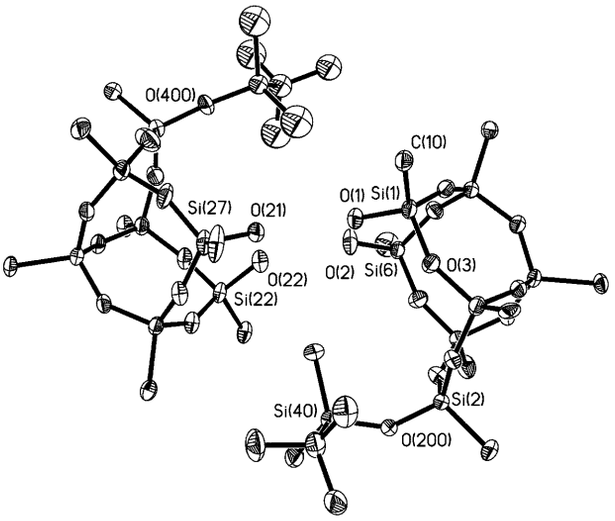


Fig. 1 ORTEP[7] drawing of compound **1**. For clarity, displacement ellipsoids are at 25% probability and CH_2 carbon atoms are omitted.

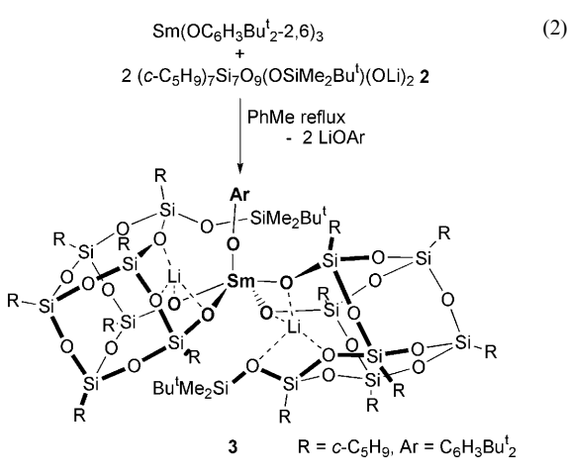
Table 1 Selected distances (Å) and angles (°) for compounds **1** and **3**

1		**3**	
Si(1)–O(1)	1.619(7)	Sm–O(800)	2.183(5)
Si(1)–C(10)	1.833(8)	Sn–O(1)	2.306(7)
Si(2)–O(200)	1.596(6)	Sm–O(2)	2.314(6)
Si(6)–O(2)	1.611(6)	Sm–O(21)	2.304(6)
Si(27)–O(21)	1.640(6)	Sm–O(22)	2.306(7)
Si(22)–O(22)	1.648(7)	O(800)–C(800)	1.268(8)
O(1)···O(21)	2.708(8)	Li(1)–O	1.91(2)–2.32(2)
O(1)···O(22)	3.810(9)	Li(2)–O	1.92(2)–2.37(2)
		Si(2)–O(2)	1.592(6)
O(1)–Si(1)–O(3)	108.2(4)	O(1)–Sm–O(22)	88.8(2)
Si(2)–O(200)–Si(40)	146.6(4)	O(2)–Sm–O(21)	167.0(2)
		Sm–O(2)–Si(2)	141.8(4)
		Si(7)–O(3)–Si(40)	143.0(4)

long and two short O···O distances. This strong, symmetrical hydrogen bonding is retained by **1** in arene solution (as judged by ^{1}H NMR spectroscopy);[6,8] the mutual enhancement of acidity of adjacent hydroxyls for molecular as well as macromolecular silanol functionalities should allow the production of new metal derivatives of **1**.

Functionalised metal derivatives of compound 1

Happily, we were able to lithiate the disilanol to give [(*c*-C_5H_9)$_7$-$Si_7O_9(OLi)_2$(OTBDMS)] **2**, without collapse of the siloxane framework (see below),[5b,9] even using *tert*-butyllithium, eqn. (2).



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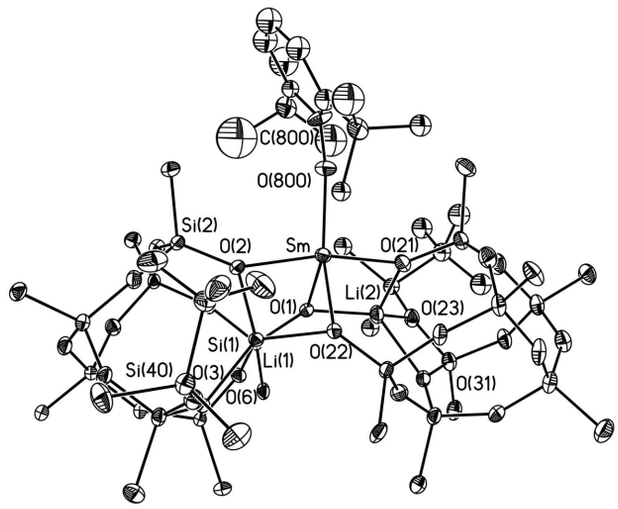


Fig. 2 ORTEP drawing of compound **3**. Details as in Fig. 1.

For us, the lithium salt **2** has provided the simplest route into lanthanide silsesquioxane chemistry.

The reaction of compound **2** with half an equivalent of base-free [Sm(OC$_6$H$_3$Bu$^t_2$-2,6)$_3$] in refluxing toluene for at least 24 h effected the elimination of two equivalents of lithium 2,6-di-*tert*-butylphenolate, leaving one aryloxide ligand untouched, to generate **3**. Extraction with hexanes followed by recrystallisation afforded analytically pure primrose-yellow crystals of **3**·thf in 56% yield. Complex **3** is soluble in aprotic hydrocarbons and thermally stable to 180 °C. ^{1}H NMR spectroscopy of the isolated product showed one molecule of co-ordinated thf which may be eliminated by heating *in vacuo* (160 °C, 10^{-4} mbar) for 4 h, to give the material from which X-ray quality crystals were obtained. The targeting of a samarium derivative of the silsesquioxane ligand was originally chosen since the intermediate size of the trivalent ion makes it a good representative of the lanthanides, whilst the metal is still amenable to study by NMR spectroscopy. This spectroscopy was initially considered to be crucial in characterising any reaction products, since well diffracting crystals of silsesquioxane derivatives are rare. In fact, incorporation of the OTBDMS group into the silanol has allowed us to obtain well diffracting crystals of a surprising number of complexes.

Importantly, the new f-element metallosilsesquioxane **3** (Fig. 2) still has a readily exchangeable co-ordinated aryloxide; the large metal centre is supported by only silanolate oxygen atoms, and displays no interactions with framework oxygen atoms. The approximate C_2 orientation of the two TBDMS groups protects the periphery of the Sm^{3+} ion from further electrostatic interactions with siloxane oxygen atoms and thereby prevents any access of other metal complexes or solvent to the inter- and intra-molecular [Si–O]$_2$ bridges.

The Sm has immediate contacts with only five oxygen atoms, but notably none of these derives from Si–O–Si moieties. The apical Sm–O distance of 2.183(5) Å is barely longer by the 3σ criterion (up to 0.03 Å) than that in homoleptic aryloxides.[10]

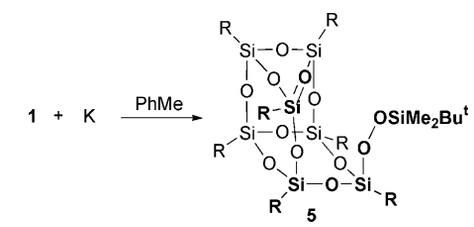
The formation of metal siloxide bonds to independent siloxane cages only marginally reduces the symmetry of the silsesquioxane; the four Sm–OSi distances are remarkably similar in the solid state, ranging from 2.304(6) to 2.314(6) Å (Table 1). These are all attenuated by bonding to the incorporated Li^+ ions, which are diametrically opposed and encapsulated within the silsesquioxane framework. The geometry around both Li(1) and Li(2) is essentially tetrahedral, but with a wide variation in Li–O distances (accounted for by differentiating between siloxane and silanolate oxygen types). For Li(1) distances lie between 1.91(2) and 2.32(2) Å and for Li(2) between 1.92(2) and 2.37(2) Å.

Other derivatives of compound 1

In addition to preparing the dilithium salt of compound **1** quantitatively, the dithallium salt **4** may also be generated from treatment of **1** with two equivalents of thallium ethoxide (eqn. (3)). An yttrium derivative analogous to **3** was also

$$\mathbf{1} + 2\,\mathrm{TlOEt} \xrightarrow{\mathrm{PhMe}} \underset{\mathbf{4}}{(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_2Bu^t)(OTl)_2} + 2\,\mathrm{EtOH} \quad (3)$$

prepared *via* reaction of the tris(aryloxide) with **1**, although due to the similar size of these ions one must be cautious about extrapolating the potential reactivity of **1** or **2** further. We have successfully treated ligand **1** and its salts **2** and **3** with main group metal alkoxides,[11] and anticipate **4** will provide access to further new f-element derivatives. As would be anticipated, the reaction of **1** with an equivalent of high purity potassium metal in hexane or toluene proceeds at room temperature to give a siloxane **5**, arising from formal elimination of H_2O from **1** (eqn. (4)). It may be noted that the same siloxane **5** may also be derived from the reaction of **1** with thallium cyclopentadienide. Very recently, we have reported the structure determination of **5** (see *Acta Crystallogr.*, *Sect. E*, 2001, **57**, o131).



(4)

Conclusion

Incorporation of the TBDMS protecting group into a silsesquioxane generates a soluble disilanol that is readily dilithiated to give a thermally stable salt. A new f-block derivative of this silsesquioxane has been characterised which displays facial co-ordination of the metal centre, as might be observed for a silica-surface bound f-block ion. The TBDMS group prevents metal co-ordination by more than one siloxide group and also prevents framework oxygen atoms from interacting with the large metal centre. The complex also retains one co-ordinated ligand, which may lead to reactivity similar to that of a 'surface-bound' metal ion. The bulky ligand should provide an exciting new class of co-ordinatively accessible silsesquioxane derivatives; a study of the reaction chemistry of compound **3** and catalytic activity of its derivatives is progressing.

Experimental

General procedures

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium, toluene; potassium, THF; NaK, pentane). The compounds $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ and $[Sm(OC_6H_3Bu^t_2\text{-}2,6)_3]$ were prepared by literature methods.[1,12] All other reagents were procured commercially from Aldrich and used without further purification. Elemental analysis data were obtained by Mr Trevor Spencer at the University of Nottingham.

^1H, ^{13}C, ^7Li and ^{29}Si NMR spectra were recorded on a Bruker AMX300 spectrometer, referenced internally to residual solvent proton resonance, and/or externally to aqueous 1 M LiCl or TMS. Benzene-d_6 was refluxed over potassium, and vacuum transferred prior to use. IR spectra were run as Nujol mulls (KBr disc) on a Nicolet Avatar 360 instrument. Melting points were obtained in sealed glass capillaries under dinitrogen and are reported uncorrected. Mass spectra (EI and FAB) were run by Mr Tony Hollingworth on a VG autospec instrument.

Preparations

$(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OTBDMS)$ 1. To a suspension of the cyclopentylsilsesquioxane trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (6.4 g, 7.31 mmol) in thf (20 ml) and triethylamine (1.72 ml, 10.1 mmol) at −30 °C was added a thf solution of $CF_3SO_3SiMe_2Bu^t$ (1.932 g, 7.31 mmol, 10 ml), with stirring over 20 min. The suspension was allowed to warm to room temperature over 48 h, during which time it became transparent. Removal of volatiles under reduced pressure afforded a pale pink solid, which was extracted with pentane and filtered through a bed of Celite. Concentration and cooling of the solution afforded colourless crystalline $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OTBDMS)$ **1** in 54% yield (3.91 g). mp 199–201 °C. NMR (C_6D_6): δ_H (300 MHz) 3.98 (s, 2H, Si–OH), 1.89, 1.70, 1.51 (br m, 56H, CH_2 of $c\text{-}C_5H_9$), 1.12 (m, 7H, CH of $c\text{-}C_5H_9$), 1.05 (s, 9H, Bu^t) and 0.28 (s, 6H, Me_2); δ_C (75.5 MHz) 28.3, 28.1, 28.0, 27.9, 27.85, 27.6, 27.5, 27.4 (CH_2 of $c\text{-}C_5H_9$), 26.0 ($SiCMe_3$), 24.6, 23.6, 23.1, 22.9, 22.8 (CH of $c\text{-}C_5H_9$), 18.45 ($SiCMe_3$) and −2.8 ($SiMe_2$); δ_{Si} (59.62 MHz) −53.2 (s, 1Si), −56.1 (s, 2Si), −62.9 (s, 1Si), −63.7 (s, 1Si), −65.9 (s, 2Si) and −66.8 (s, 1Si). $\tilde{\nu}_{max}$ (Nujol)/cm^{-1} 3286br m, 1113vs, 870w, 837w, 786w, 723w and 500w. *m*/*z* (EI): 975 ($[M - 13]^+$, 4), 931 ($[M - Bu^t]^+$, 4), 913 ($[M - OH_2(Bu^t)]^+$, 100), 901 ($[M - OH_2(C_5H_9)]^+$, 89), 789 ($[M - (OH)(SiBu^t)\text{-}(SiC_5H_9)]^+$, 8) and 67 ($[C_5H_7]^+$, 13%). Calc. for $C_{41}H_{80}O_{12}Si_8$: C, 49.75; H, 8.15. Found: C, 49.82; H, 8.26%.

No substitution was achieved using $SiMe_2Bu^tCl$ with any of NEt_3, pyridine or DABCO.

$(c\text{-}C_5H_9)_7Si_7O_9(OLi)_2(OTBDMS)$ 2. To a thf solution of compound **1** (197.8 mg, 0.2 mmol, 5 ml) was added a pentane solution of $LiBu^t$ (25.6 mg, 0.4 mmol, 10 ml) with stirring, at −80 °C over 2 min. The colourless solution was allowed to warm to 20 °C over 2 h. Removal of volatiles under reduced pressure afforded a colourless solid which was identified as >96% pure $(c\text{-}C_5H_9)_7Si_7O_9(OLi)_2(OTBDMS)$ **2**, by NMR spectroscopy. Extraction with pentane followed by concentration and cooling of the solution afforded colourless crystalline **2** in 89% yield (190 mg). mp 240–243 °C. NMR (C_6D_6): δ_H (300 MHz) 1.97, 1.75, 1.55 (br m, 56H, CH_2 of $c\text{-}C_5H_9$), 1.26–1.10 (m, 7H, CH of $c\text{-}C_5H_9$), 1.10 (s, 9H, Bu^t) and 0.40 (s, 6H, Me_2); δ_C (75.5 MHz) 29.5, 28.6, 28.4, 28.2, 28.1, 28.0, 27.7, 27.5, 27.5, 27.4 (CH_2 of $c\text{-}C_5H_9$), 25.9 ($SiCMe_3$), 25.3, 24.7, 24.2, 23.5, 23.0 (CH of $c\text{-}C_5H_9$), 18.4 ($SiCMe_3$) and −2.6 ($SiMe_2$); δ_{Li} (116.6 MHz) 0.83. $\tilde{\nu}_{max}$ (Nujol)/cm^{-1} 1547w, 1252m, 1084s, 911w, 872w, 836w, 784w, 723m and 506m. *m*/*z* (FAB) 975 ($[M - 25]^+$, 5), 913 ($[M - Li_2OBu^t]^+$, 100) and 901 ($[M - Li_2O(C_5H_9)]^+$, 91%). Calc. for $C_{41}H_{78}Li_2O_{12}Si_8$: C, 49.26; H, 7.66. Found: C, 49.20; H, 7.81%.

$[Sm(OC_6H_3Bu^t_2\text{-}2,6)\{(c\text{-}C_5H_9)_7Si_7O_9(OLi)(O)(OTBDMS)\}_2]$ 3. A high-pressure ampoule was charged with a magnetic stirrer bar, compound **2** (876 mg, 0.816 mmol), $[Sm(OC_6H_3Bu^t_2\text{-}2,6)_3]$ (313 mg, 0.408 mmol) and toluene (50 ml). The yellow solution was stirred for two hours, then heated to reflux for 24 h. Volatiles were removed under reduced pressure, and the pale yellow solid was extracted with hexanes, filtered, concentrated and cooled to yield yellow crystals of **3**·thf in 56% yield (554 mg). Heating *in vacuo* (160 °C, 10^{-4} mbar) for 4 h gave a yellow material which was recrystallised from hexanes to give **3**. mp 224–227 °C. NMR (298 K, C_6D_6): δ_H (300 MHz) 8.69 (d, *J* 8, 2H, OAr), 8.31 (t, *J* 8 Hz, 1H, OAr), 7.05br m, 5.12br s, 3.76br m, 3.4–1.18br m, 1.18–0.82sh m, 0.44 to −0.15br m, −1.23m, −2.56m (124H, $SiOC_5H_9$), 0.78 (s, 18H, $SiMe_2Bu^t$), −0.47 (s, 12H, $SiMe_2Bu^t$), −0.70 (s, 12H, $SiMe_2Bu^t$) and −1.88 (d, 18H, $OC_6H_3Bu^t$); δ_C (75.5 MHz) 140.0, 117.0 (C_{quat} OAr), 128.5, 125.0 (CH of OAr), 36.2 (CH_{quat} of $C_6H_3Bu^t_2$), 30.4 (CH_3 of

$C_6H_3Bu^t_2$), 32.5, 28.4, 26.4, 23.6, 23.2, 22.8, 19.4 (CH of C_5H_9), 32.2, 31.3, 30.8, 30.2, 30.1 (CH_2 of C_5H_9), 29.0–28.8, 28.3–27.1, 26.0–25.4 (19 distinct CH_2 of C_5H_9), 18.6 (C_{quat} of $SiBu^t$), 1.1 (CH_3 of $SiBu^t$), −2.8, −3.1 ($SiMe_2$); δ_{Li} (116.6 MHz) −3.01. $\tilde{\nu}_{max}$ (Nujol)/cm^{-1} 2181w, 1958w, 1582s, 837w, 786w, 723w and 500w. *m*/*z* (EI): 1849 ($[M - (C_5H_9)_4(OAr)(Me)]^+$, 12), 1701 ($[M - (OSiC_5H_9)_3(TBDMS)(Ar) + H]^+$, 84) and 1124 ($[(SiC_5H_9)_7O_{11}(TBDMS)(Sm)]^+$, 100%). Calc. for $C_{100}H_{185}Li_2O_{26}Si_{16}Sm$: C, 49.69; H, 7.71. Found: C, 49.74; H, 7.75%.

Treatment of disilanol **1** with rigorously purified $[Sm(OC_6H_3Bu^t_2\text{-}2,6)_3]$ gave elimination of phenol, and a samarium-containing product with similar NMR spectroscopic characteristics to those of **3**. However, this material remains amorphous even after removal of traces of eliminated phenol and has so far resisted crystallisation or further purification attempts.

(*c*-$C_5H_9)_7Si_7O_9(OTl)_2$(OTBDMS) 4. To a toluene solution of compound **1** (514 mg, 0.52 mmol, 10 ml) was added TlOEt (73.7 μl, 1.04 mmol) with stirring. After further stirring of the colourless solution for 8 h, volatiles were removed under reduced pressure to yield an oily colourless solid. Washing with cold pentane (−78 °C, 4 × 5 ml) afforded (*c*-$C_5H_9)_7Si_7O_9(OTl)_2$(OTBDMS), **4** as a white powder in 58% yield (420 mg). NMR (C_6D_6): δ_H (300 MHz) 2.00, 1.81, 1.57 (br m, 56H, CH_2 of *c*-C_5H_9), 1.18 (m, 7H, CH of *c*-C_5H_9), 1.09 (s, 9H, Bu^t) and 0.30 (s, 6H, Me_2); δ_C 28.8, 28.5, 28.4, 28.3, 28.0, 27.9, 27.8, 27.6, 27.5, 27.4 (CH_2 of *c*-C_5H_9), 26.3 ($SiCMe_3$), 24.2, 23.8, 23.8, 23.2, 23.2 (CH of *c*-C_5H_9), 18.6 ($SiCMe_3$) and 1.36 ($SiMe_2$). $\tilde{\nu}_{max}$ (Nujol)/cm^{-1} 1090s, 1043s, 951m, 874m, 834w, 779w, 499w and 467m. *m*/*z* (FAB) 1331 ($[M - Tl + (C_5H_9)Si_2O]^+$, 4), 1114 ($[M - TlO_3Si]^+$, 4), 1054 ($[M - TlO_4Bu^tMe]^+$, 5), 954 ($[M - Tl_2O_2]^+$, 7), 939 ($[M - Tl_2O_2CH_3]^+$, 2), 906 ($[M - Tl_2O_5]^+$, 100) and 205 ($[TlH]^+$, 100). Calc. for $C_{41}H_{78}O_{12}Si_8Tl_2\cdot 0.5C_7H_8$: C, 37.05; H, 5.72. Found: C, 37.15; H, 5.72%.

(*c*-$C_5H_9)_7Si_7O_9$(O)(OTBDMS) 5. A toluene solution of compound **1** (317 mg, 0.32 mmol, 10 ml) was transferred onto high purity potassium lumps (25.0 mg, 0.64 mmol) and either sonicated or stirred vigorously for 4 h. Removal of volatiles under reduced pressure afforded a colourless solid. Extraction with pentane, followed by concentration and cooling to −30 °C, afforded colourless, highly crystalline **5** in 74% yield (231 mg). NMR (C_6D_6): δ_H (300 MHz) 2.03, 1.74, 1.60 (br m, 56H, CH_2 of *c*-C_5H_9), 1.22 (m, 7H, CH of *c*-C_5H_9), 1.07 (s, 9H, Bu^t) and 0.29 (s, 6H, Me_2); δ_C (75.5 MHz) 28.2, 27.9, 27.8, 27.7, 27.5, 27.4, 27.4, 27.3, 27.2 (CH_2 of *c*-C_5H_9), 26.0 ($SiCMe_3$), 24.3, 23.2, 23.0, 22.9, 22.1 (CH of *c*-C_5H_9), 18.4 ($SiCMe_3$) and −2.9 ($SiMe_2$). $\tilde{\nu}_{max}$ (Nujol)/cm^{-1} 1460s, 1258m, 1107s, 1065s and 638w. *m*/*z* (FAB) 955 ($[M - Me]^+$, 3), 903 ($[M - (C_5H_7)]^+$, 7), 358 ($[(C_5H_9)_2Si_2O_3(OSiMeBu^t)]^+$, 16), 205 ($[Si_3O_4Bu^t]^+$, 50) and 154 ($[(C_5H_9)_2O]^+$, 65%). Calc. for $C_{41}H_{78}O_{11}Si_8$: C, 50.68; H, 8.09. Found: C, 50.61; H, 8.44%.

X-Ray crystallography

Crystal data for complex 1. $C_{41}H_{80}O_{12}Si_8$, $M = 989.77$, monoclinic, space group = *Cc* (no. 9), $a = 22.0658(10)$, $b = 17.1093(8)$, $c = 29.2595(9)$ Å, $\beta = 105.651(2)°$, $U = 10636.8(8)$ Å^3, $T = 150(2)$ K, $Z = 8$, μ(Mo-Kα) = 0.255 mm^{-1}, 15030 unique reflections (R_{int} 0.113) used in all calculations. Final *R*1 [7633, $F > 4\sigma(F)$] = 0.0758 and *wR*(all F^2) 0.215. Positional disorder of some cyclopentyl groups was identified and modelled, and the partial atoms refined as isotropic. Hydroxyl H atoms were not located and H atoms on pivot atoms for disorder components were not placed. Other H atoms were placed geometrically.

Crystal data for complex 3. $C_{96}H_{177}Li_2O_{25}Si_{16}Sm$, $M = 2345.07$, orthorhombic, space group = $Pca2_1$ (no. 29), $a = 17.540(2)$, $b = 31.945(3)$, $c = 21.300(2)$ Å, $U = 11935(2)$ Å^3, $T = 150(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.717 mm^{-1}, 28966 unique reflections (R_{int} 0.113) used in all calculations. Final *R*1 [17406, $F > 4\sigma(F)$] = 0.0766 and *wR*(all F^2) 0.199. Positional disorder in the aryloxide group and some cyclopentyl groups was identified and modelled, with the partial atoms refined as isotropic. Hydrogen atoms on pivot atoms for disorder components were not placed. Other H atoms were placed geometrically.

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See http://www.rsc.org/suppdata/dt/b0/b009123p/ for crystallographic files in .cif format.

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