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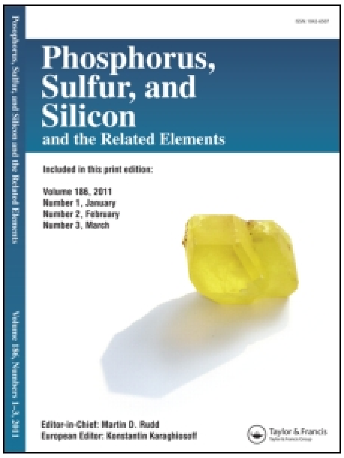

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Intramolecular Mobility in Novel Stannasiloxane Complexes

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The synthesis and dynamic behaviour in solution of the stannasiloxane complexes $[Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O\cdot\textit{t}\text{-}Bu_2SnX_2]$ (**2**, x = OH; **6**, x = F) and $\{[R_2(Me_3SiO)Sn]_2O\}_2$ (**7**, R = Me; **8**, R = Et) are reported.

Keywords: silicon; tin; stannasiloxanes; distannoxanes

INTRODUCTION

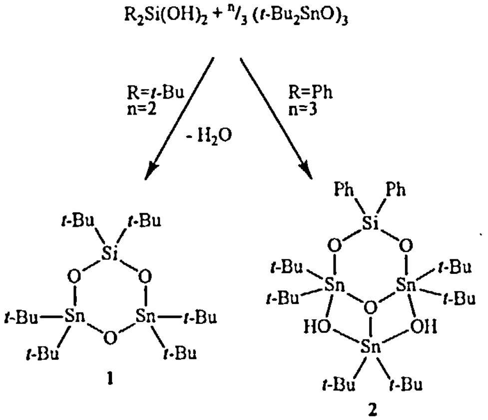
In recent years we have been interested in the chemistry of stannasiloxanes[1]. Metallasiloxanes in general play an important role as soluble molecular model compounds for understanding the surface chemistry of organometal fragments grafted on silica[2]. Organotins bonded to silica show promise in enhancing the activity of some transition metal catalysts[3]. Aside from their application as homogeneous surface mimics metallasiloxanes might also serve as precursors for modified silica materials that can be used as alternatives to those obtained using the common sol-gel approach[4].

Cyclic metallasiloxanes hold potential as precursors for linear polymers with tailor-made compositions and physical properties[5]. Recently, we reported the first well-defined polystannasiloxane $[t\text{-Bu}_2\text{Sn}(\text{Ph}_2\text{SiO})_2\text{O}]_n$. It is accessible via ring opening polymerisation (ROP) from its corresponding monomer[1a]. The industrial polycondensation of organosilanols is efficiently catalysed by small amounts of organotin-oxo compounds and it is very likely that stannasiloxanes are also involved in this process[6].

Here our attention is focused on stannasiloxanes in which tin has higher coordination numbers than four.

RESULTS AND DISCUSSION

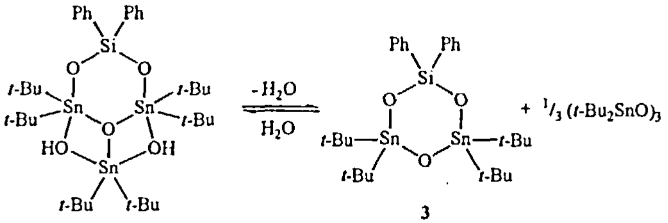
Depending on the identity of the organic group R the reaction of diorganosilanediols $R_2Si(OH)_2$ (R=*t*-Bu, Ph) with hexa-*tert.*-butyltristannoxane $(t\text{-Bu}_2\text{SnO})_3$ gives either the six-membered stannasiloxane ring $(t\text{-Bu}_2\text{Si}(\text{OSn}t\text{-Bu}_2)_2\text{O})$ (**1**) or the stannasiloxane complex $(\text{Ph}_2\text{Si}(\text{OSn}t\text{-Bu}_2)_2\text{O}\cdot t\text{-Bu}_2\text{Sn}(\text{OH})_2)$ (**2**) (SCHEME 1)[1b].



SCHEME 1

Formally, **2** consists of the six-membered ring **3** and t-$Bu_2Sn(OH)_2$ coordinated to it. The $Sn_3O(OH)_2$ structural motif is almost planar and closely related to the more common ladder type $Sn_4O_2X_4$ structural motif of tetraorganodistannoxanes $[R_2XSnOSnXR_2]_2$ (X=F, Cl, Br, I, OH, OOCR)[1c, 7].

In chloroform complex **2** exhibits a unique equilibrium involving the stannasiloxane ring **3**, (t-$Bu_2SnO)_3$ and water (EQUATION 1). This equilibrium is strongly temperature dependent with **2** dominating at lower and **3** dominating at higher temperatures.



2

3

(1)

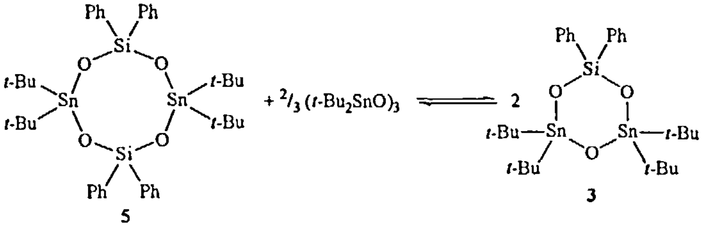
In this equilibrium $t\text{-Bu}_2\text{Sn(OH)}_2$ is assumed to be the initial dissociation product which then immediately self condensates to give $(t\text{-Bu}_2\text{SnO})_3$ and water.

This assumption is supported by the fact that $t\text{-Bu}_2\text{Sn(OH)}_2$ (4) which was prepared by mild hydrolysis of $t\text{-Bu}_2\text{Sn(OMe)}_2$ (EQUATION 2) is itself labile towards self-condensation in both solution and solid state[1b]

$$t\text{-Bu}_2\text{Sn(OMe)}_2 \xrightarrow[-2\,\text{MeOH}]{2\,\text{H}_2\text{O}} \underset{\mathbf{4}}{t\text{-Bu}_2\text{Sn(OH)}_2} \qquad (2)$$

According to ^{119}Sn MAS NMR spectroscopy[1b], the organotin dihydroxide 4 is most likely a dimer with a similar structure to those reported for $(t\text{-Bu}_2\text{Sn(OH)X})_2$ (X=F, Cl, Br[8a], O(S)P(OEt)_2[8b]).

Quantitative *in situ* synthesis of the six-membered stannasiloxane **3** was also achieved by reaction of (*t*-Bu$_2$SnO)$_3$ with the eight-membered stannasiloxane ring [Ph$_2$Si(OSn*t*-Bu$_2$)O]$_2$ **5** (EQUATION 3)[1b].

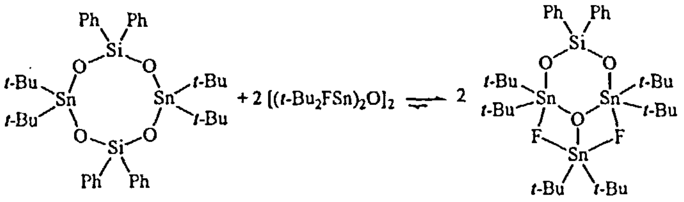


(3)

However, compound **3** could not be isolated. Upon evaporation of a CDCl$_3$ solution containing only **3** the reverse reaction takes place and only the eight-membered stannasiloxane ring **5** and (*t*-Bu$_2$SnO)$_3$ were obtained[1d]. The reverse reaction is most likely driven by release of ring strain in **3**. In solution this ring strain might be compensated by the entropic favor of a greater number of species.

The reaction of *t*-BuSi(OH)$_3$ with (*t*-Bu$_2$SnO)$_3$ provides (*t*-Bu(OH)Si(OSn*t*-Bu$_2$)$_2$O·*t*-Bu$_2$Sn(OH)$_2$), an analogue of **2**[9].

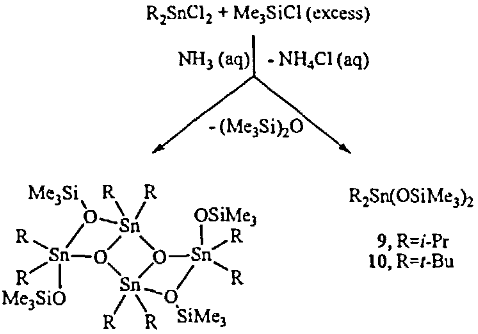
The fluorine-bridged stannasiloxane complex **6** was synthesised by a redistribution reaction of the eight-membered cyclostannasiloxane **5** with tetra-*tert*.-butyldifluorodistannoxane [*t*-Bu$_2$FSnOSnF*t*-Bu$_2$]$_2$[1c] (EQUATION 4).



5 6 (4)

In solution, the stannasiloxane complex **6** shows no tendency to dissociate into *t*-Bu$_2$SnF$_2$ and Ph$_2$Si(OSn*t*-Bu$_2$)$_2$O. However, it is in equilibrium with its starting compounds (EQUATION 4). Unlike the hydroxy-substituted complex **2**, the fluorine-substituted complex **6** is highly sensitive towards moisture and reacts with water to give the eight-membered stannasiloxane ring **5** and *t*-Bu$_2$Sn(OH)F.

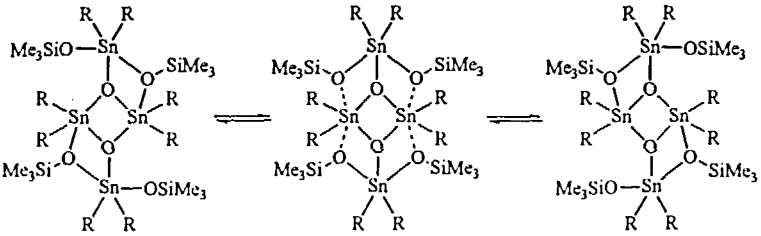
Depending on the identity of the organic group R the cohydrolysis of diorganodichlorostannanes R$_2$SnCl$_2$ (R=Me, Et, *i*-Pr, *t*-Bu) and excess trimethylchlorosilane Me$_3$SiCl in aqueous ammonia affords either the stannasiloxane ladders **7** (R=Me) and **8** (R=Et), or the stannasiloxanes R$_2$Sn(OSiMe$_3$)$_2$ **9** (R=*i*-Pr) and **10** (*t*-Bu) (SCHEME 2). Compounds **7** and **8** were previously synthesized by *Okawara* et al[10], but were not completely characterized.



7, R=Me
8, R=Et

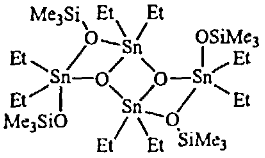
SCHEME 2

For compounds 7 and 8 there is evidence that a wagging process of the bridging and non-bridging $OSiMe_3$ groups occurs in solution at room temperature (SCHEME 3). This phenomenon has previously been reported for other tetraorganodistannoxanes $[R_2XSnOSnXR_2]_2$ with ladder type structures[1c,11].



SCHEME 3

In toluene solution at 90 °C compound 8 is in equilibrium with its monomer 8a , as was evidenced by ^{119}Sn NMR spectroscopy (EQUATION 5).



8

$\rightleftharpoons$ 2 $[Et_2(OSiMe_3)Sn]_2O$ (5)

8a

ACKNOWLEDGEMENTS

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