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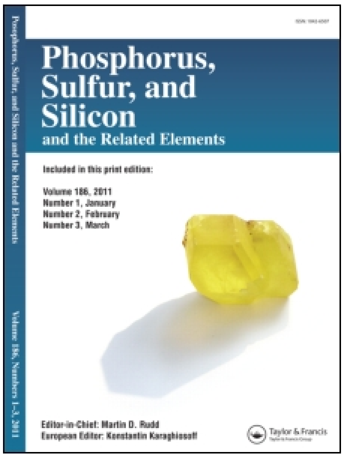

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Stannasiloxanes. Syntheses, Structures, and Surprises

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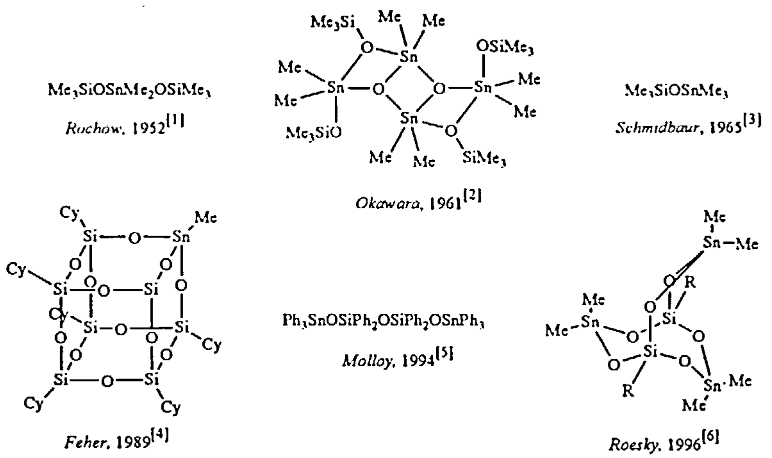
Recent results are reported on the syntheses and structures of novel six-and eight-membered stannasiloxane rings, of stannasiloxane complexes, and of the first well-defined organoelement oxides containing three different metals/metalloids.

Keywords: silicon; tin; intramolecular coordination; polymer

INTRODUCTION

The first stannasiloxane was reported as early as 1952[1] but so far there has been no systematic study on this class of compounds, although a variety of species containing the Si-O-Sn fragment have been synthesized over the years. Randomly selected representative examples are shown below (CHART 1).



$Me_3SiOSnMe_2OSiMe_3$

Rochow, 1952[1]

Okawara, 1961[2]

$Me_3SiOSnMe_3$

Schmidbaur, 1965[3]

Feher, 1989[4]

$Ph_3SnOSiPh_2OSiPh_2OSnPh_3$

Molloy, 1994[5]

Roesky, 1996[6]

CHART 1

The lack of systematic investigations on stannasiloxanes is even more surprising when taking into account that such compounds are thought to be intermediates in the technically important organotin catalyzed polycondensation of silanols[7,8]. Furthermore, cyclic stannasiloxanes might be suitable precursors in thermally or catalytically induced ring-opening polymerizations (ROPs) to give organotin modified polysiloxanes[9,10].

There are several methods for the synthesis of stannasiloxanes involving the reaction of organosilanols with organochlorostannanes in presence of a base[6], the reaction of organosilanols with organotin oxides[5,11], or the lithium halide elimination from organosilanolates and organohalostannanes[12]. The treatment of highly acidic silica surfaces with tetraorganotin compounds or triorganotin hydrides also gives rise to the formation of Si-O-Sn linkages[13].

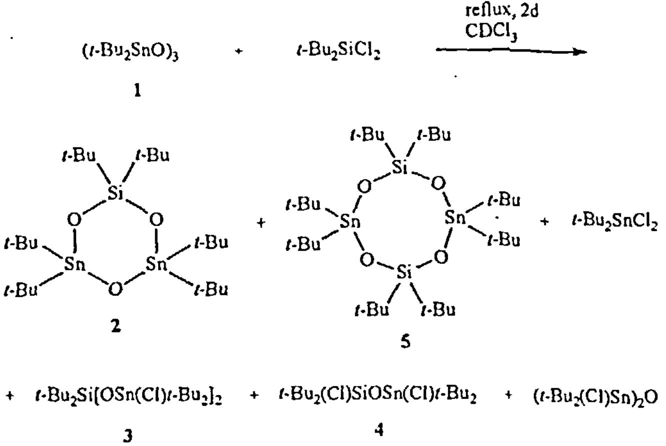
An interesting approach to stannasiloxanes was reported in the late sixties and early seventies by Davies and Harrison who reacted diorganotin oxides with organochlorosilanes. However, the products obtained were characterized only by elemental analyses and infra red spectroscopy[14].

In this communication systematic studies are reported on the reaction of $(t\text{-Bu}_2\text{SnO})_3$ (1) with a variety of organosilanes such as R_2SiX_2 (R = Ph, *t*-Bu; X = Cl, F, OH) and $t\text{-BuSiF}_3$.

All compounds presented here have been characterized by means of NMR spectroscopy and/or X-ray analysis.

RESULTS AND DISCUSSION

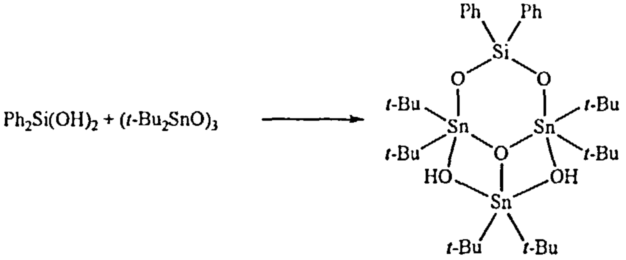
The reaction of di-*tert.*-butyltin oxide $(t\text{-Bu}_2\text{SnO})_3$ (1) and di-*tert.*-butyldichlorosilane $t\text{-Bu}_2\text{SiCl}_2$ gave a clear solution from which the six- and eight-membered stannasiloxane rings 2 and 5 have been isolated and completely characterized (SCHEME 1)[15].



SCHEME 1

In addition, the ^{119}Sn and ^{29}Si NMR spectra showed the presence of the open-chain stannasiloxanes **3** and **4** as well as di-*tert.*-butyltin dichloride and tetra-*tert.*-butyldichlorodistannoxane (SCHEME 1).

The reaction of di-*tert.*-butyltin oxide (**1**) with diphenylsilanediol $Ph_2Si(OH)_2$ provided the unusual stannasiloxane complex **6** (EQUATION 1)[11].

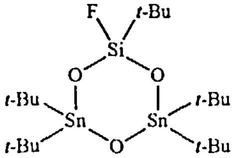


6

(1)

Complex **6** can be regarded as a model compound for organotin oxide grafted on a silica surface. ^{119}Sn NMR studies reveal that in $CDCl_3$ solution it is in equilibrium with the six-membered stannasiloxane ring $Ph_2Si(OSn\textit{t}\text{-}Bu_2)_2O$, $(\textit{t}\text{-}Bu_2SnO)_3$, and water[11].

The reaction of di-*tert.*-butyltinoxide (**1**) with *tert.*-butyltrifluorosilane $\textit{t}\text{-}BuSiF_3$ was also rather complex and NMR studies of the crude reaction mixture provided evidence for the existence of fluoro substituted open-chain and cyclic stannasiloxanes **7** - **10** (CHART 2)[15].



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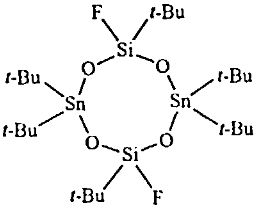

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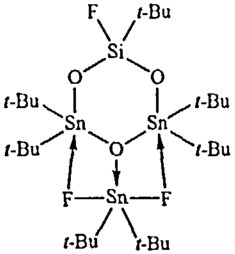


9

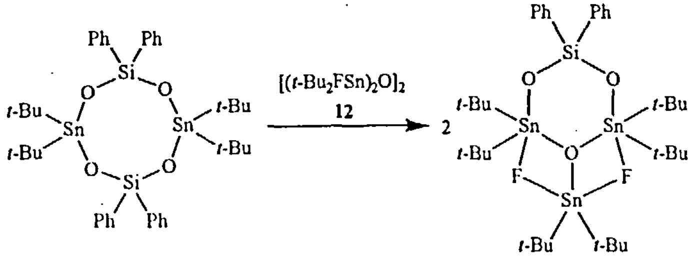
$t\text{-}Bu_2Sn(OSiF_2t\text{-}Bu)_2$

10

CHART 2

The eight-membered stannasiloxane ring **8** was isolated and completely characterized.

The synthesis of the fluoro substituted stannasiloxane complex **13** was achieved by reaction of the eight-membered stannasiloxane ring **11** with the tetra-*tert*.-butyldifluorodistannoxane dimer $[(t\text{-}Bu_2FSn)_2O]_2$ **12** (EQUATION 2).

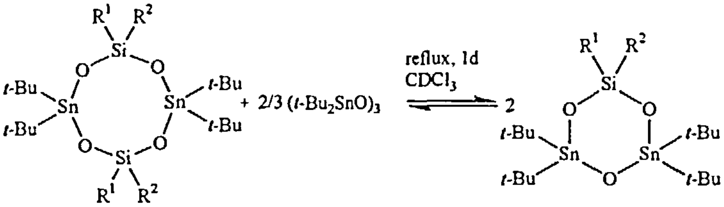


11 **13**

(2)

The latter was synthesized from 1,2-di-*tert.*-butyltetrafluorodisilane ($(t\text{-BuF}_2\text{Si})_2$) and di-*tert.*-butyltin oxide (**1**)[16]. It is the first fluorine containing tetraorganodistannoxane.

The eight-membered stannasiloxane rings **14** - **16** undergo redistribution reactions with di-*tert.*-butyltin oxide **1** to give the six-membered stannasiloxane rings **17-19**, of which only **17** could be isolated (EQUATION 3).



(3)

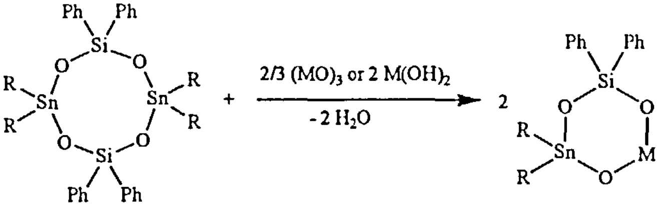
14, $R^1 = R^2 = t$-Bu
15, $R^1 = t$-Bu, $R^2 = F$
16, $R^1 = R^2 = Ph$

17, $R^1 = R^2 = t$-Bu
18, $R^1 = t$-Bu, $R^2 = F$
19, $R^1 = R^2 = Ph$

The reaction according to EQUATION 3 is controlled by the kinetic lability of the Sn-O bonds and entropy gain. The latter favors the six-membered rings **17-19** in solution and compensates their higher ring strain in comparison with the corresponding eight-membered rings **14-16**.

The ring strain in eight-membered stannasiloxane rings is increased by introducing intramolecularly coordinating 3-dimethylaminopropyl groups at tin which changes the coordination geometry at the latter from tetrahedral to octahedral. As result of this ring strain the eight-membered stannasiloxane ring **20** reacts with di-*tert.*-butyltin oxide **1**, di-*tert.*-butylgermanediol $t\text{-Bu}_2\text{Ge(OH)}_2$, and phenylboronic acid PhB(OH)_2

give the corresponding six-membered organoelement oxides **21** - **23** (EQUATION 4)[17]. To the best of our knowledge compounds **22** and **23** are the first such examples containing three different metals/metalloids.



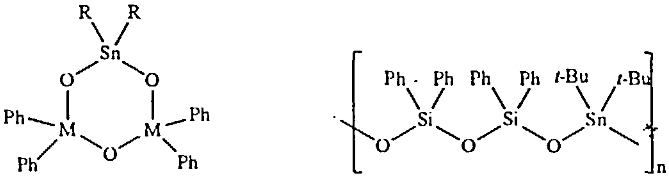
(4)

20, R = $(CH_2)_3NMe_2$

21, M = *t*-Bu_2Sn
22, M = *t*-Bu_2Ge
23, M = PhB

In an attempt to synthesize a six-membered stannasiloxane ring containing one tin and two silicon atoms we reacted di-*tert.*-butyldichlorostannane *t*-Bu_2SnCl_2 with 1,1,3,3-tetraphenyl-1,3-disiloxane-1,3-diol $[Ph_2(OH)Si]_2O$ in the presence of a base[10].

Surprisingly, the compound (**24**) obtained from this reaction is a six-membered ring in solution but forms the first well-defined polystannasiloxane **24a** in the solid state (CHART 3)[10].



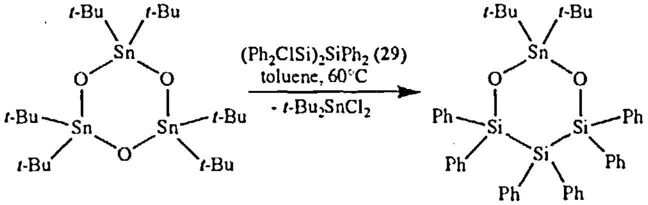
24, M = Si, R = *t*-Bu
25, M = Si, R = $(CH_2)_3NMe_2$
26, M = Ge, R = *t*-Bu
27, M = Si, R = $Cp(CO)_2Fe$
28, M = Si, R = $Cp(CO)_3W$

24a

CHART 3

These results initiated systematic studies on the factors which control the spontaneous polymerization of six-membered stannasiloxane and stannagermoxane rings. So far, we have prepared and characterized the compounds **25** - **28** (CHART 3) in which the R groups at tin are intramolecularly coordinating 3-dimethylaminopropyl groups (**25**) or transition metal fragments (**27**, **28**), or in which the silicon atoms are replaced by germanium (**26**). All of these compounds are six-membered rings in solution and in the solid state.

The same holds for the six-membered stannasiloxane ring **30** which has been obtained by the reaction of di-*tert.*-butyltin oxide **1** with the trisilane **29** (EQUATION 5)[18].



30

(5)

CONCLUSIONS

The chemistry of stannasiloxanes is controlled by the kinetic lability of the Sn-O and the kinetic stability of the Si-O bonds. The reaction of (t-Bu$_2$SnO)$_3$ with organohalo- and organohydroxysilanes is a complementary route for the synthesis of novel stannasiloxanes. [t-Bu$_2$SnOSiPh$_2$OSiPh$_2$O] is the first well-defined polystannasiloxane and a model compound to study ring opening polymerization. The polymerization behavior of six-membered stannasiloxane rings can be tuned by *(i)* electronic effects (introduction of transition metal fragments at tin) or *(ii)* by change of the coordination geometry at tin (intramolecular Sn-N coordination).

The kinetic stabilization of the Sn-O bond by intramolecular Sn-N coordination allows isolation of well-defined mixed organoelement oxides such as $\{[Me_2N(CH_2)_3]_2SnOSiPh_2OMO\}$ (M = *t*-Bu_2Sn, *t*-Bu_2Ge, PhB).

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