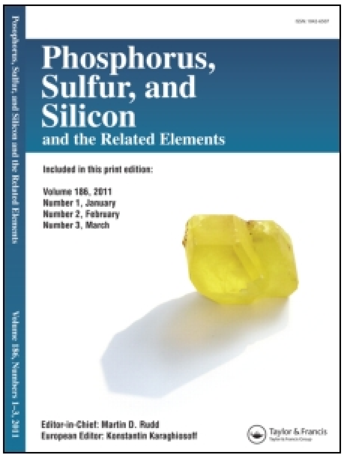

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Oxygen Transfer Reactions between Tris(Di-*t*-Butyltinoxide), $[(t\text{-Bu})_2SnO]_3$, and Ph_2GeCl_2, Et_2GeCl_2 and $PhBCl_2$

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The reactions between tris-(di-*t*-butyltinoxide), (**1**, $\{t\text{-Bu}_2SnO\}_3$), and R_2GeCl_2 in methylene chloride results in the quantitative transformation to $(R_2GeO)_3$ and $t\text{-Bu}_2SnCl_2$, R = Ph (**2**) and Et (**3**). A similar reaction between **1** and $PhBCl_2$ led to the quantitative formation of $(PhBO)_3$ (**4**). In the latter case intermediates were observed by following the reaction via ^{119}Sn NMR. If the tin oxide reagent was replaced by a sila-distanna analog, $[Ph_2SiO(t\text{-Bu}_2SnO)_2]$ (**5**) the corresponding sila-digerma complex was produced, $[Ph_2SiO(Ph_2GeO)_2]$ (**6**) along with some **2**. A crystal structural analysis of **6** is presented.

Keywords: tinoxide; oxygen transfer; germanium dichloride; boron dichloride

INTRODUCTION

In 1954 Anderson reported a series of reactions between hexaethyltin oxide and halo-silanes, -germanes and -boranes which effectively transferred oxygen from the tin oxide to the other element [1]. Some typical examples are described in equation 1.

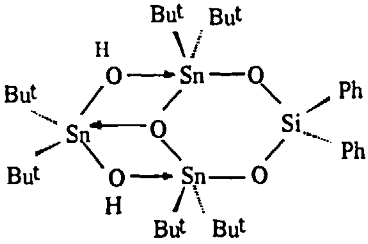
$3\ Ph_2SiF_2 + 3\ Et_3Sn\text{-}O\text{-}SnEt_3 \rightarrow (Ph_2SiO)_3 + 6\ Et_3SnF$ (1)

$2\ (i\text{-}Pr)_3GeCl + Et_3Sn\text{-}O\text{-}SnEt_3 \rightarrow (i\text{-}Pr)_3GeOGe(i\text{-}Pr)_3 + 2\ Et_3SnCl$ (2)

$3\ EtOBCl_2 + 3\ Et_3Sn\text{-}O\text{-}SnEt_3 \rightarrow (EtOBO)_3 + 6\ Et_3SnCl$ (3)

There has been some recent interest in the similar reactivity of cyclic tin oxides with silyl chlorides and hydroxides involving oxygen transfer reactions, including the isolation and characterization of unusual self-assembled intermediates [2,3]. For example, we serendipitously observed that a reaction mixture containing di-t-butyltin dichloride and silicon grease resulted in a unique self-assembled planar 8 membered ring illustrated in Figure 1 [2].

Figure 1



Such compounds were later reported by the Jurkschat group, using a more conventional and rationale syntheses [3]. These authors further noted that such compounds transform into, *inter alia*, mixed sila-distanna oxide cycles, Figure 2.

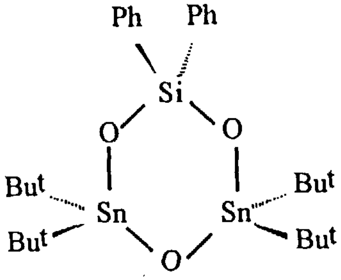


Figure 2

During our studies in the general area of group 14 chemistry we have investigated some aspects of the generality of the oxygen transfer reaction from the trimeric tin oxide system, $(t\text{-}Bu_2SnO)_3$, **1**, since, based upon the seminal work of Anderson [1], it would be surprising if this were limited to silicon. We now report the reactions between **1** and R_2GeCl_2, R = Ph, Et, and a boron analog, $PhBCl_2$, that lead to $(R_2GeO)_3$, **2** (R = Ph), **3** (R = Et), and $(PhBO)_3$, **4**, respectively. The reaction between $[Ph_2SiO(t\text{-}Bu_2SnO)_2]$, **5**, and Ph_2GeCl_2 is also reported together with the single crystal structure of the product from this reaction, i.e. $[Ph_2SiO(Ph_2GeO)_2]$, **6**.

EXPERIMENTAL

Synthesis of 1,1,3,3,5,5-hexaphenyl-2,4,6-trioxa-1,3,5-trigermane cyclohexane (2)

A mixture of $(t\text{-}Bu_2SnO)_3$ (0.89 g, 1.18 mmol) and Ph_2GeCl_2 (1.0 g; 3.3 mmol) was heated at reflux in CH_2Cl_2 (30 mL) for 7h under an inert atmosphere (N_2). The solution was cooled and the solvent was removed under reduced pressure to give the mixture of $t\text{-}Bu_2SnCl_2$ and $(Ph_2GeO)_3$. The $t\text{-}Bu_2SnCl_2$ was removed from the mixture by washing with hexane leaving a white residue (0.9 g). The white residue was recrystallized from hexane to yield **1** as a white crystalline material (0.6 g, 31%); m. pt. 149-150 °C (lit. 149 °C) [7].

NMR: ^1H ($CDCl_3$, ppm): 7.3-7.6 ppm (Ph)

^{13}C ($CDCl_3$, ppm): 136.7;134.0;130.7;128.6.

Synthesis of 1,1,3,3,5,5-hexaethyl-2,4,6-trioxa-1,3,5-trigermane cyclohexane (3)

In an analogous manner to that described above, starting with a mixture of $(t\text{-}Bu_2SnO)_3$ (1.01 g, 1.34 mmol) and Et_2GeCl_2 (1.0 g, 4.05 mmol), we obtained the title material in 67% yield. Separation of **3** from $t\text{-}Bu_2SnCl_2$ was performed by recrystallization of the latter material. The germoxane **3** was confirmed by spectral data and mass spectrometric analysis.

NMR: ^{1}H ($CDCl_3$, ppm): 0.36, 0.06

^{13}C ($CDCl_3$, ppm): 11.8, 6.6

MS (m/e, %): 411(35), 383(11), 355(9).

Synthesis of 1,3,5-triphenyl-2,4,6-trioxa-1,3,5-triboroncyclo hexane (4)

To a solution of (t-$Bu_2SnO)_3$ (0.85 g; 1.13 mmol) in 10 mL of toluene, was added $PhBCl_2$ (0.5 g, 3.4 mmol). The solution was stirred at room temperature for 19 h during which the mixture transformed from a cloudy incompletely dissolved mixture to a clear transparent solution. The solution was heated at reflux for 3 h, cooled, and the solvent was removed under reduced pressure to give the mixture of t-Bu_2SnCl_2 and $(PhBO)_3$. The t-Bu_2SnCl_2 was removed from the mixture by washing with hexane leaving a white residue (250 mg). The residue was recrystallized from hexane to yield **4** as a white crystalline material, (200 mg, 17.5%), m. pt. = 215-217 °C; mixed m. pt. with an authentic sample 216 °C, (lit. 214-216 °C) [8]

NMR: ^{1}H ($CDCl_3$, ppm): 7.5-8.2.

^{13}C ($CDCl_3$, ppm): 136.1; 133.8 (ipso); 133.1; 128.4

In a separate experiment we followed the above reaction using ^{119}Sn NMR by titrating the tin oxide (70 mg; 0.093 mmol) with $PhBCl_2$ (15 mg; 0.094 mmol). Subsequent to addition of 30% equivalent needed for complete transformation, all the starting material had been consumed and a single ^{119}Sn resonance appeared at −101.6 ppm with another at −168.8 ppm. Further addition, 40%, 60%, and 80% equivalent of $PhBCl_2$ led to the disappearance of these resonances and the transient appearance of peaks at −106.7 and −128.2 ppm, together with that representing $(t\text{-}Bu)_2SnCl_2$ at 57.8 ppm. Subsequent to complete addition (100%) only the latter resonance remained.

Synthesis of 1,1,3,3,5,5-hexaphenyl-2,4,6-trioxa-5-sila-1,3-digermane cyclohexane (6)

A mixture of $[Ph_2SiO((t\text{-}Bu_2)_2SnO)_2]$ (5) [3] (0.5 g, 0.72 mmol) and Ph_2GeCl_2 (0.40 g, 1.4 mmol) was heated at reflux in CH_2Cl_2 (25 mL) for 12 h under an inert atmosphere (N_2). The solution was cooled and the solvent was removed under reduced pressure to give a mixture of $t\text{-}Bu_2SnCl_2$, $[Ph_2SiO(Ph_2GeO)_2]$ and $(Ph_2GeO)_3$. The $t\text{-}Bu_2SnCl_2$ was removed from the mixture by washing with hexane leaving a white residue (0.41g). The white residue was recrystallized from hexane and it gave **6** and **2** as white crystals (0.325g; 36.0% yield), m. pt. 156 °C. We were unable to completely purify **6** and remove all traces of **2**.

NMR: ^{1}H ($CDCl_3$, ppm): 7.2-7.6 ppm (Ph)

^{13}C ($CDCl_3$, ppm): 135.2; 134.1; 131.1; 128.8 (C of PhGe)

137.2; 134.9; 130.1; 128.0 (C of PhSi)

HRMS: Average molecular mass = 683.899. maximum peak mass = 684.04. The experimental and theoretical mass spectral isotope distribution for the parent ion of **6** are equivalent.

Reaction between $(Ph_2GeO)_3$ and $Ph_2Si(OH)_2$

A mixture of $(Ph_2GeO)_3$ (0.63 g, 0.87 mmol) and $Ph_2Si(OH)_2$ (0.18 g, 0.82 mmol) was heated at reflux in toluene (30 mL) for 2 days. The solution was cooled, and the solvent was removed under reduced pressure to give a white residue. The white residue was recrystallized from hexane and it gave **2** as white crystals (0.350 g; 43 % yield), m. pt. 150 ^{0}C (lit 149° C)[7].

NMR : ^1H ($CDCl_3$, ppm): 7.3-7.6 (Ph)

^{13}C ($CDCl_3$, ppm):136.7; 134.0; 130.7; 128.6

Xray Data Collection on 6

A white fragment of **6**, approximate dimensions 0.38 x 0.45 x 0.30 mm., was mounted in a random orientation at the tip of glass fiber for X-ray examination and data collection. All data were collected at room temperature on a Siemens R3m/v single-crystal diffractometer with graphite-monochromated Mo Kα radiation; λ(MoKα) = 0.71073. Unit cell parameters and standard deviations were obtained by least-squares fit of 49 randomly selected reflections in the 2θ range of 15-30°. They indicated monoclinic symmetry, which was confirmed by oscillation photographs around each crystallographic axis. Intensity data were collected in the ω-scan mode with a scan range of 1.2° in ω and a variable speed of 4-20 deg./min. Background counts were taken with stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored every 197 reflections and showed no intensity decay. The collection was conducted over the reciprocal space region with $0 \leq h \leq 10$, $0 \leq k \leq 20$ and $-19 \leq l \leq 19$. A total of 4630 reflections were collected producing, after merging symmetry equivalents, a set of 4189 unique reflections with an reliability parameter $R_{int.}$= 2.6%. The data were corrected for Lorentz polarization and extinction effects but no absorption correction was applied.

Structure Refinement

Analysis of the data set based on cell parameters, systematically absent reflections and counting statistics lead to selection of space group $P2_{1/n}$ (No. 14). The structure was solved by direct methods and refined by full-matrix least-squares, based on F, in a Micro Vax II computer using the VMS version of the SHELEXTL-PLUS software package by Siemens. Ge and Si at the statistically occupied sites were refined isotropically. The quantity minimized was $\Sigma w(Fo\text{-}Fc)^2$. All non-hydrogen atoms were placed at calculated positions with C-H bond distances of 0.96Å and average isotropic thermal parameters of 0.08.

The weighting scheme has the form $w^{-1}=\sigma^2(F)+gF^2$ with g=0.0004 .The extinction correction has the form $F^* = F[\ 1 + 0.002\chi F^2 / \sin(2\theta)\ ]^{1/4}$ with $\chi = 0.0063$. The final R factors have the form $R=\Sigma|Fo-Fc|/\Sigma Fo$ and $Rw=[w|Fo-Fc|^2/\Sigma Fo^2]^{1/2}$. Reflections with intensities giving F values smaller than three times their standard deviation from their mean value were treated as unobserved. For the last cycle of refinement of 365 parameters and 3306 reflections, the maximum and mean Δ/σ were 7.428 and 0.562, the maximum and minimum residual electron densities were 3.62 and -1.36 electrons per Å^3 and the final R-values, as defined above, were R=0.1079 and R*w*=0.1328. No efforts were made to improve the R*w* values by changing the weighting scheme. Selected crystallographic parameters and bond angles and lengths for **6** compared to those of **2** and **7** (hexaphenyl-trigermoxane-, **2**, and -trisiloxane, **7** respectively) are provided in Table 1. A complete set of atomic coordinates, data for the collection and refinement and full bond lengths and angles are available from the authors upon request.

TABLE 1. Cell parameters, average bond lengths, and ring conformation*

	a	b	c	α	β	γ	V
2	10.038	18.614	17.727	90.00	90.43	90.00	3312
6	10.004	18.551	17.692	90.00	90.58	90.00	3283
7	10.123	15.802	20.245	90.00	90.00	90.00	3238

	Ge/Si-O	Ge/Si-C	E-O-E	Ring conformation
2	1.769	1.928	128.6	Boat
6	1.746	1.894	130.2	Twisted
7	1.639	1.853	132.1	Planar

- a, b, c, bond lengths in Å; α, β, δ in degrees, V in $Å^3$.

DISCUSSION

The reactions between **1** and both R_2GeCl_2, R = Ph, Et, and $PhBCl_2$ in methylene chloride at room temperature led to rapid oxygen transfer reactions outlined in equations 4 and 5.

$$(t\text{-}Bu_2SnO)_3 + 3\ R_2GeCl_2 \rightarrow (R_2GeO)_3 + 3\ t\text{-}Bu_2SnCl_2 \qquad (4)$$

$$(t\text{-}Bu_2SnO)_3 + 3\ PhBCl_2 \rightarrow (PhBO)_3 + 3\ t\text{-}Bu_2SnCl_2 \qquad (5)$$

Both reactions are very fast and essentially quantitative as monitored by NMR spectroscopy. In the case of the reaction described in equation 5 with $PhBCl_2$, we performed a titration by progressive addition of $PhBCl_2$ to the tin oxide solution, following the progress of the reaction by ^{119}Sn NMR. Upon addition of one equivalent a precipitate formed which could be dissolved by either warming, or further addition of $PhBCl_2$. At this stage NMR analysis showed little if any t-Bu_2SnCl_2, but complete removal of **1**. A major new ^{119}Sn resonance appeared at −101.6 ppm, followed upon further addition of $PhBCl_2$, by transient resonances at −106.7 and −128.2 ppm. Complete addition of $PhBCl_2$ resulted in observation of t-$BuSnCl_2$ (57.8 ppm). These results suggest the possible intermediacy of [t-$(Bu_2SnO)_2PhBO$] analogous to that formed with silicon (^{119}Sn = −107 ppm) [3], and [t-$(Bu_2SnO)(PhBO)_2$]. We have not pursued this chemistry.

In a second type of reaction we found that the two tin atoms in [$Ph_2SiO(t$-$Bu_2SnO)_2$] (**5**) are also reactive in this type of chemistry. Thus, the reaction of **5** with Ph_2GeCl_2 led to the formation of the digerma analog, **6**, in which both the t-Bu_2Sn groups had been replaced by Ph_2Ge groups, equation 6.

$$\mathbf{5} + Ph_2GeCl_2 \rightarrow [Ph_2SiO(Ph_2GeO)_2] + t\text{-}Bu_2SnCl_2 \qquad (6)$$

In the reaction product, small amounts of $(Ph_2GeO)_3$ (**2**) were observed. The source of this by-product is not known. In a separate experiment we reacted **6** with an excess of Ph_2GeCl_2 under the same reaction conditions; however, we were unable to observe any significant transformation of **6** to **2**.

We obtained crystals of the new digermasiloxane **6**, and the structure is presented in Figure 3; selected bond angles and lengths are presented in Table 1. The unit cell parameters and cell volume of **6** are similar but smaller than those reported for 2,2,4,4,6,6-hexaphenyl-1,3,5-trioxa-2,4,6-trigermanecyclohexane (**2**) [9], but larger than the trisiloxane analog (7) [10]. The site occupancy for all three metalloid sites was allowed to refine and produced an average value of 0.80 (Ge), close to a 2/3-1/3 Ge-Si theoretical site occupancy. The statistically distributed Ge and Si had to be refined isotropically but nonetheless, the refinement improved significantly, from R = 0.145 for a trigermoxane to R = 0.108 for the digermasiloxane.

The cell parameters, average bond lengths and heterocycle conformation for $C_{36}H_{30}O_3SiGe_2$ are intermediate between $C_{36}H_{30}O_3Ge_3$, 2, and $C_{36}H_{30}O_3Si_3$, 7 [9,10], as shown in Table 2, and Figure 3. Thus despite the high R value, we think that along with the structure refinement the data provides strong evidence of isomorphous substitution among Ge and Si in the heterocyclic ring.

The driving force for these reactions seems to be the relative bond energies of the E-O and E-Cl bond. For silicon, germanium and boron these favour the E-O bond, the transformations E-Cl → E-O being approximately 80 kJ/mole **exo**thermic [4,5,6]. On the other hand for tin the corresponding transformation is **endo**thermic by about the same amount. The extent to which the reactions can result in only partial substitution remains to be determined by more experimental data and theoretical considerations. As noted in the experimental section no reaction occurred between $(Ph_2GeO)_3$ and $Ph_2Si(OH)_2$.

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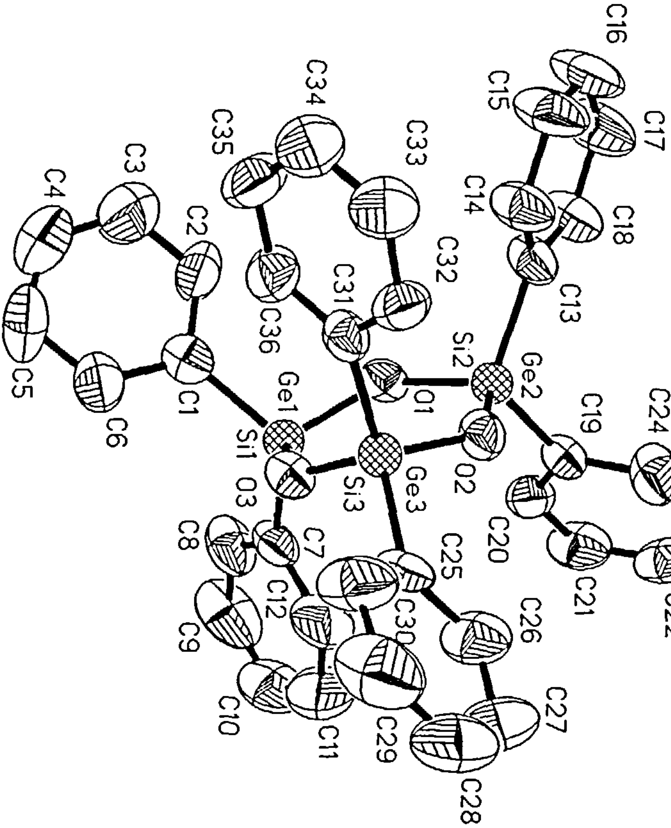

Figure 3. Structure of $Ph_6SiGe_2O_3$.

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