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Notes

Synthesis and Characterization of Hexakis(trimethylsilyl)digermane and -distannane

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Tris(trimethylsilyl)silyl derivatives of Ge(IV),[1] Sn(II),[2a] Sn(IV),[2b] and Pb(IV)[3] exhibit novel structural behavior owing to the crowding caused by the bulky groups. Our attempt to prepare Pb(II) derivatives[4] led instead to the reaction in eq 1, which

$$\mathrm{PbCl_2 + 2(THF)_3Li[Si(SiMe_3)_3]} \xrightarrow[\mathrm{Et_2O}]{-78\text{ to }+25\ ^\circ\mathrm{C}} \mathrm{[(Me_3Si)_3Si]_2 + Pb + 2LiCl} \quad (1)$$

provided a convenient synthesis of hexakis(trimethylsilyl)disilane in quantitative yield. The structure of the disilane was found to be disordered owing to the presence of solvent in the lattice; nevertheless, bond distances and angles were consistent with the presence of appreciable steric strain in the molecule. Subsequent reports on $(Me_3Si)_3Si–Si(SiMe_3)_3$[5] based on improved structure determinations have dealt further with the steric interactions across the central Si–Si link in that molecule and in other molecules containing $Si(SiMe_3)_3$ substituents. Bock, Meuret, and Ruppert proposed using the X–Y–Y–X dihedral angles in $X_3Y–YX_3$ (X = $SiMe_3$) molecules as a criterion of overcrowding.[5b] A study of ionization energies from photoelectron spectra revealed that $Si(SiR_3)$ groups are markedly electron releasing.[5b] This interest in $(Me_3Si)_3E–E(SiMe_3)_3$ (E = group 14 element) species, coupled with a desire to determine whether the method in eq 1 can be extended, has led us to investigate its use for preparing digermane and new distannane derivatives.

Experimental Section

Materials and Procedures. $GeCl_4$ and $SnCl_4$ were from Strem and Aldrich, respectively, $PbCl_2$ was from Lancaster Synthesis, and tris(trimethylsilyl)methane was from Aldrich. The lithium germyl, $(THF)_{2.5}LiGe(SiMe_3)_3$, was prepared according to the published procedure,[6] with the minor modification of using halide-free methyllithium. Experimental details have been described elsewhere.[3]

Reaction of $PbCl_2$ and $LiC(SiMe_3)_3$. An ether solution (100 mL) of $LiC(SiMe_3)_3$ (17.2 mmol) (prepared in situ from 4.00 g, 17.2 mmol, of $HC(SiMe_3)_3$ and 15 mL of 1.56 M LiMe in THF[7]) was added dropwise to a cold (–78 °C) suspension of $PbCl_2$ (2400 mg, 8.6 mmol) in ether (50 mL). After 45 min, a gray-black precipitate was evident. The reaction mixture was stirred 8 h at –78 °C, allowed to warm to room temperature, and stirred another 16 h, after which solvent was removed *in vacuo*, the residue was stirred with pentane (50 mL) for 1 h, and the mixture was filtered. The filtrate was concentrated and held at 4 °C overnight, affording a white solid, which was isolated and washed with pentane. ^1H NMR (C_6D_6), δ: 0.270 $(Me_3Si)_4C$; 0.101, $(\mathit{Me}_3Si)_3CH$; –0.848, $(Me_3Si)_3C\mathit{H}$ (by comparison with authentic samples); 0.195 (small, unidentified).

Table I. Crystallographic Data for $(Me_3Si)_3Sn\text{-}Sn(SiMe_3)_3$

$C_{18}H_{54}Si_6Sn_2$
*R*32 (rhombohedral)
fw = 676.64
$a = 10.262(1)$ Å
$\alpha = 106.48(1)°$
$V = 912$ Å^3
$Z = 1$

$T = 25$ °C
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.23$ g-cm^{-3}
$\mu = 15.7$ cm^{-1}
$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.035$
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$

Preparation of Hexakis(trimethylsilyl)digermane. An ether solution (50 mL) of $(THF)_{2.5}LiGe(SiMe_3)_3$ (3596.4 mg, 7.50 mmol) was added dropwise to a cold (–78 °C) ether (50 mL) suspension of $PbCl_2$ (1043.2 mg, 3.75 mmol) with vigorous stirring. A white precipitate that formed during addition turned to a grayish black after addition of the germyl reagent was complete. The reaction mixture was stirred 6 h at –78 °C and then at room temperature for 6 h. Ether was removed *in vacuo*, and the residue was stirred with pentane (75 mL) for 1 h. After filtration, the filtrate was concentrated and held at 4 °C overnight. The colorless transparent crystals (crude yield, 2178.5 mg, 99%) obtained were recrystallized from pentane (purified, isolated yield 991.4 mg, 45%). Further purification (for mass spectra) was accomplished by sublimation at 120 °C *in vacuo*. (mp 280 °C dec in a sealed capillary; lit.[6] 280 °C dec). ^1H NMR (C_6D_6), δ: 0.39 (s); lit.[6] 0.32 in $CDCl_3$. $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 4.867. MS (major envelopes): *m/e* 293 $[(Me_3Si)_3Ge^+]$, 278 $[(Me_3Si)_2GeSiMe_2{}^+]$, 219 $[(Me_3Si)_2Ge - H^+]$, 147 $[Me_3SiGe^+]$. IR (Nujol), cm^{-1}: 3345 (m, vbr), 2740 (vw), 1190 (w), 1855 (w), 1655 (w), 1410 (s, sh), 1325 (m), 1260 (vs), 1195 (vw, sh), 1130 (vw, sh), 1080 (vw, sh), 860 (vs, br), 775 (m), 720 (s), 660 (s), 650 (sh), 565 (w, sh), 375 (m), 360 (sh). An X-ray structure determination was attempted, but the digermane was found to be severely disordered, so the determination was discontinued.

Preparation of Hexakis(trimethylsilyl)distannane. To 20.44 g (2.94 mol) of lithium were added 320 mL of dry THF and 165.3 mL (141.52 g, 1.302 mol) of Me_3SiCl. After the mixture was cooled to –78 °C, 34.4 mL (76.57 g, 0.294 mol) of $SnCl_4$ was added over 3 h. [*Caution*! Addition of $SnCl_4$ produces considerable heat, so cooling adequate to maintain the temperature at –78 °C is necessary and addition should be very slow with vigorous stirring.] After $SnCl_4$ addition was complete, the reaction mixture was stirred 3 h at –78 °C, allowed to warm slowly to ambient temperature, and stirred another 48 h. The greenish brown reaction mixture was filtered and the filtrate divided into two equal portions. The first portion was hydrolyzed with 10% HCl(aq) and extracted with ether, but no organotin compounds were isolated. Solvent was removed *in vacuo* from the second portion, and the residue was stirred with pentane (100 mL) for 1 h. The pentane solution was separated from the undissolved solids, concentrated to 30 mL, and kept at ambient temperature, where it yielded colorless crystals. NMR showed that the crystals still contained small amounts of $(Me_3Si)_4Sn$ impurity, which was removed by vacuum sublimation at 90 °C. Pure single crystals of the product for X-ray investigation were obtained by recrystallization (3×) from pentane, washing with a minimum volume of pentane, and drying *in vacuo* (isolated yield 3146.6 mg, 12.7%; mp 290 °C dec). Anal. Calcd for $C_{18}H_{54}Si_6Sn_2$: C, 31.95; H, 8.04. Found: C, 31.36; H, 7.77. ^1H NMR (C_6D_6), δ: 0.440 (s). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 4.97. MS: *m/e* 339 $[(Me_3Si)_3Sn + H^+]$ (envelope pattern matches that expected for normal isotopic distribution of $(Me_3Si)_3Sn$), 193 $[Me_3SiSn + H^+]$, 145 $[Me_3SiSiMe_3 - H^+]$, 131 $[Me_3SiSiMe_2{}^+]$, 73 $[Me_3Si^+]$. IR (Nujol): 3440 (w, sh), 2720 (vw, sh), 1925 (vw), 1860 (vw), 1725 (vw), 1415 (s, sh), 1330 (w), 1265 (vs), 1195 (vw), 1130 (vw), 1075 (vw, sh), 860 (vs, br), 780 (w), 735 (m), 660 (s), 650 (sh), 510 (w), 400 (s), 390 (sh).

X-ray Crystal Structure Determination. A clear colorless block having approximate dimensions 0.40 × 0.35 × 0.30 mm was mounted in a random orientation on a Nicolet R3m/V diffractometer described earlier.[1a] Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. By the usual methods, the space group was determined to be *R*32 and the structure was solved, revealing the positions of most of the non-hydrogen atoms in the asymmetric unit,

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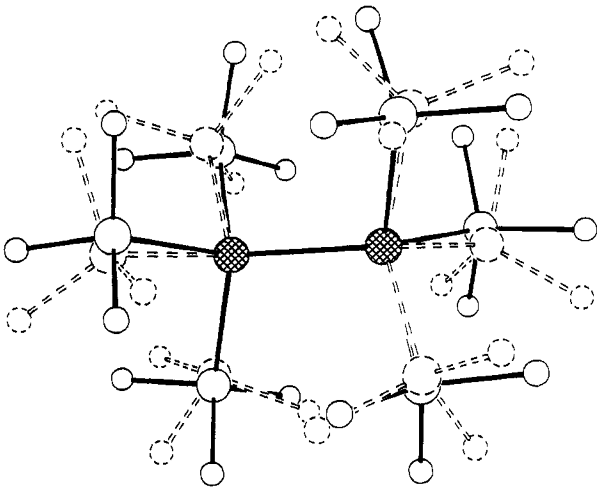

Figure 1. View of the complete disordered model of $(Me_3Si)_3Sn-Sn(SiMe_3)_3$.

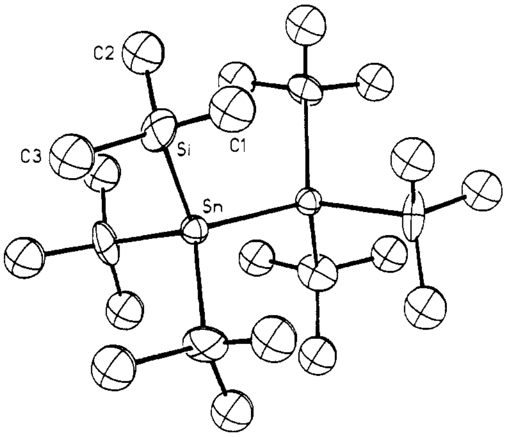

Figure 2. View of the $(Me_3Si)_3Sn-Sn(SiMe_3)_3$ molecule showing the number scheme. Thermal ellipsoids are 30% equiprobability envelopes for Si and Sn, with hydrogens omitted for clarity. Only one disordered orientation is shown.

consisting of one-sixth of a molecule located about a crystallographic 32 site. It was found that the $SiMe_3$ groups are massively disordered, with each one possessing two major orientations. This disorder is so severe that it affects all of the Si sites as well as the C sites. The best way found to model the disorder was by employing two ideal rigid-body $SiMe_3$ units that were allowed to rotate independently, both with population factors of 50%. Due to the severe nature of the disorder, only the Sn and Si atoms could be refined anisotropically. The correct absolute configuration of the molecule was determined by refinement of a coefficient multiplying $\Delta f''$ and this indicated that the reported configuration is definitely preferred over its inverse, although the results were not highly conclusive. After all shift/esd ratios were less than 0.7; convergence was reached at the agreement factors listed in Table I. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.4 e/Å^3.

Results and Discussion

In the series $(Me_3Si)_3E-E(SiMe_3)_3$ (E = C, Si, Ge, Sn), only the E = Si and Ge derivatives have been reported.[6,8] A report that reaction of $LiC(SiMe_3)_3$ with $PbCl_2$ at 0 °C gave metallic lead instead of organolead products led us to reinvestigate the reaction, anticipating that, by analogy to eq 1, it might afford $(Me_3Si)_3C-C(SiMe_3)_3$.[9] Although Pb was observed, no evidence was found in NMR or GC mass spectra for $(Me_3Si)_3C-C(SiMe_3)_3$; instead, $(Me_3Si)_4C$ and $(Me_3Si)_3CH$ were the major products. Since $(Me_3Si)_3Si-Si(SiMe_3)_3$ exhibits structural parameters, including an elongated Si–Si bond, consistent with the presence of appreciable steric strain between the $(Me_3Si)_3Si$ halves of the molecule,[4,5] it is possible that $(Me_3Si)_3C-C(SiMe_3)_3$ is rendered unstable by the increased steric strain expected across the shorter C–C bond.

Table II. Selected Bond Distances (Å) and Angles (deg)

Distances			
Sn–Sn′	2.789(1)	Sn–Si	2.609(14)
Sn–Si′	2.611(14)	Si–C(1)	1.900
Si–C(2)	1.900	Si–C(3)	1.900
Si′–C(1′)	1.900	Si′C(2′)	1.900
Si′–C(3′)	1.900		

Angles			
Si–Sn–Sn′	110.2(2)	Si′–Sn–Sn′	112.7(2)
Si–Sn–Si″	108.8(2)	Si′–Sn–Si″	106.1(2)
Sn–Si–C(1)	110.7(3)	Sn–Si–C(2)	110.8(3)
Sn–Si–C(3)	106.8(2)	Sn–Si′–C(1′)	109.1(2)
Sn–Si′–C(2′)	105.1(3)	Sn–Si′–C(3′)	114.1(3)

Torsion Angles for Type 1 Orientation	
Si–Sn–Sna–Sic	−165.2
Sia–Sn–Sna–Sic	−45.2
Sib–Sn–Sna–Sic	74.8

Torsion Angles for Type 2 Orientation	
Si′c–Sna–Sn–Si′	−178.7
Si′c–Sna–Sn–Si′a	−58.7
Si′c–Sna–Sn–Si′b	61.3

The reaction of $PbCl_2$ with $LiGe(SiMe_3)_3$[6] under conditions similar to those of eq 1 gave $(Me_3Si)_3Ge-Ge(SiMe_3)_3$ in 45% isolated yield. The product was identified by its melting point and NMR spectra, which matched the literature values[6] (shifts closely resembled those of $(Me_3Si)_3Si-Si(SiMe_3)_3$), and by its GC mass spectrum. The latter lacked a parent ion envelope, showing only $(Me_3Si)_3Ge^+$ (*m/e* 293) and smaller fragments in the manner of $(Me_3Si)_3Si-Si(SiMe_3)_3$.[4] The previous report on preparing the digermane[6] by treatment of $LiGe(SiMe_3)_3$ with ethylene dibromide did not mention the yield, but we feel that the $PbCl_2$ method probably represents an improvement because it does not require hydrolysis and does not give appreciable amounts of the byproduct $(Me_3Si)_4Ge$. A structure determination on the digermane was abandoned due to disorder.

Since extending the $PbCl_2$ method to prepare $(Me_3Si)_3Sn-Sn(SiMe_3)_3$ would have required (the as yet unreported) $LiSn(SiMe_3)_3$, we carried out the synthesis of tetrakis(trimethylsilyl)stannane, its expected precursor, by following the procedure of Bürger and Goetze.[10] In that report, 80% of the tin was mentioned as having been recovered in metallic form due to the unwanted reduction of $SnCl_4$ by lithium under the ambient conditions of the procedure, so we decided to perform the reaction at −78 °C in hopes of minimizing the reduction and improving the yield of $(Me_3Si)_4Sn$. After workup of the reaction mixture (hydrolysis omitted), both $(Me_3Si)_4Sn$ and the new distannane $(Me_3Si)_3Sn-Sn(SiMe_3)_3$ were isolated in modest yields. Analytically pure crystals of the distannane were obtained by repeated crystallization from pentane. Elemental analyses, NMR, and GC mass spectra confirmed the identity of the product. Since the distannane was in hand and the yield of $(Me_3Si)_4Sn$ was low, it was decided not to pursue the synthesis of the lithium reagent at that time.

The mechanism of formation of the distannane was not apparent. Bürger and Goetze did not report it as a coproduct in their brief communication on the synthesis of $(Me_3Si)_4Sn$,[10] but since we modified their procedure with a lower initial temperature and omission of the acidic hydrolysis step, these conditions may favor the formation (or survival) of the distannane. Gilman and

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Smith proposed[11] that $(Me_3Si)_3Si$–$Si(SiMe_3)_3$ was a probable intermediate in their synthesis of $(Me_3Si)_4Si$ by the same approach as used here for the tin analogue. Also, reductive coupling of $(Me_3Si)_3SiCl$ gave *both* $(Me_3Si)_3Si$–$Si(SiMe_3)_3$ and $(Me_3Si)_4Si$,[8a] so similar behavior in the tin system might lead to the distannane.

An X-ray structure determination on the distannane exhibited disorder involving the positions of the $SiMe_3$ groups (Figure 1). As a consequence, the trimethylsilyls were treated as rigid bodies and only the tin and silicon atoms refined isotropically (Figure 2). Geometric parameters for the Sn–Si skeleton are listed in Table II. The Sn–Sn distance, 2.789(1) Å, is slightly longer than those in hexaphenyldistannane, 2.77 Å,[12] and $(SnPh_2)_6$, 2.77 Å,[13] but shorter than those in α-Sn, 2.80 Å,[14] and in tetrakis[bis((trimethylsilyl)methyl)tin], 2.839 and 2.834 Å.[15] The coordination about Sn is essentially tetrahedral, with the Si–Sn–Si angles slightly compressed (average 107.5°) and the Sn–Sn–Si angles slightly expanded (average 111.5°). According to the criterion of Bock, Meuret, and Ruppert[5a] for the presence of overcrowding in $(Me_3Si)_3E$–$E(SiMe_3)_3$ structures, $(Me_3Si)_3Sn$–$Sn(SiMe_3)_3$, with an E–E distance of 2.789(1) Å (<333 pm[5a]), would be expected to show evidence for steric interaction, distorting the Si–Sn–Sn–Si dihedral angles away from an ideal D_{3d} symmetry. Unfortunately, the disorder in the structure does not allow us to compare the dihedral angles unequivocally, since there are 64 possible conformations to consider, but the proximity of the methyl groups, as can be seen in the space-filling view of one conformation (Figure 3), supports the contention that there is steric strain between the halves of the molecule, which is relieved by twisting about either the Sn–Sn bond or the Sn–Si bonds, lowering the symmetry from D_{3d}. The absence of appreciable Sn–Sn bond lengthening, in contrast to the enlarged Si–Si distance in $(Me_3Si)_3Si$–$Si(SiMe_3)_3$,[4,5b] indicates that the magnitude of steric strain is smaller in the distannane.

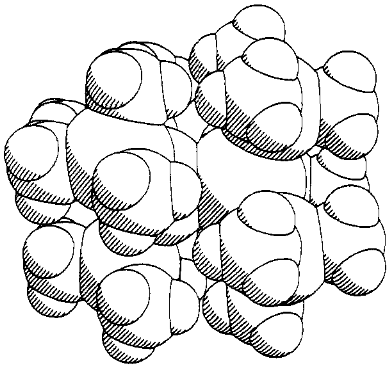

Figure 3. Space-filling view of $(Me_3Si)_3Sn$–$Sn(SiMe_3)_3$ with only one orientation shown.

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Supplementary Material Available: Table listing data collection and processing parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, H atom coordinates, and torsional angles (4 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors (3 pages) are available directly from the corresponding author.

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