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Novel Synthesis of 1,1,1,4,4,4-Hexamethyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane

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Received September 24, 1991

The reaction of $PbCl_2$ with $(THF)_3Li[Si(SiMe_3)_3]$ in Et_2O at −78 °C produced $(Me_3Si)_3SiSi(SiMe_3)_3$ (I) in quantitative yield. The product was identified by comparison of its physical properties with published values; its structure was established by X-ray crystallography. Two possible mechanisms for the formation of the octasilane are discussed.

During studies of the reaction of $(THF)_3LiSi(SiMe_3)_3$ with group 14 chlorides which have afforded new tris(trimethylsilyl) derivatives of germanium[1] and tin,[2] the reaction of lithium silyl with lead(II) chloride was investigated. The fact that incorporation of bulky substituents into hexaalkyldilead compounds gave dramatically enhanced thermal stabilities[3,4] offered some promise that the anticipated product, $Pb[Si(SiMe_3)_3]_2$, might also be stable. Cowley and co-workers have earlier reported preparation and structural characterization of the tin(II)–silyl derivative $[(Me_3Si)_3Si]_2Sn(\mu\text{-}Cl)Li(THF)_3$[5] and we previously prepared $[(Me_3Si)_3Si]_2Sn{\cdot}THF$[2] so it was of interest to determine whether an analogous lead(II) compound could be synthesized.

Experimental Section

Materials and Procedures. Lead dichloride was obtained from Mallinkrodt. The lithium silyl $(THF)_3LiSi(SiMe_3)_3$ was prepared according to the published procedure[6] with the minor modification of using halide-free methyllithium. All manipulations were conducted using Schlenk techniques[7] under an atmosphere of argon.

Preparation of 1,1,1,4,4,4-Hexamethyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane. To a cold ether suspension of $PbCl_2$ (972.1 mg, 3.495 mmol) was added an ether solution of 2 equiv (3292.7 mg, 6.99 mmol) of $(THF)_3LiSi(SiMe_3)_3$. The reaction mixture was stirred for 2 h at −78 °C and then allowed to warm to ambient temperature and stirred for an additional 8 h. During and after the addition of the silyl reagent a black coloration of the reaction mixture was evident. The solvent was removed in vacuo, the residue was stirred with pentane (2 × 25 mL), and the pentane was separated from the solid residue, concentrated, and held in the refrigerator overnight yielding transparent crystals, which were separated, washed with a small volume of pentane, and dried in vacuo (mp 372 °C in a sealed tube, sublimation observed starting at 240 °C). The yield was 1730 mg (3.495 mmol), quantitative assuming a formula of $C_{18}H_{54}Si_8$ (I). The solid sublimed readily under vacuum at 140 °C leaving no visible residue. The GC–mass spectrum of the product revealed only one component in the total ion chromatogram and that exhibited a parent ion at m/e 494 in agreement with that reported for 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane.[8] The pattern of the parent ion envelope closely matched the isotopic pattern expected for $C_{18}H_{54}Si_8$. This, along with other spectroscopic data, confirmed the identity of the product.[9]

Results and Discussion

The preparative reaction for I can be described as in eq 1. The identity of the product was confirmed by its mass spectrum and a comparison of its spectroscopic properties with those reported earlier for the compound.[8,9]

Table I. Crystallographic Data for I

chem formula $Si_8C_{18}H_{54}{\cdot}(C_5H_{12})$	fw 567.47 g mol^{-1}
	space group $R32$ (hexagonal setting)
a = 16.124 (3) Å	ρ(calc) = 1.101 g cm^{-3}
b = 16.124 (3) Å	μ = 3.183 cm^{-1}
c = 22.806 (3) Å	transm coeff not applied; see μ
V = 5134.99 Å^3	$R(F_o)$ = 0.180
Z = 6 mol/cell	$R_w(F_o)$ = 0.209
T = 25 °C	
λ = 0.71073 Å	

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

Si1–Si1′	2.369 (3)	Si1–C2	1.913 (7)
Si1–Si2	2.358 (1)	Si1–C3	1.691 (10)
Si1–C1	1.917 (6)		
Si1–Si2–C1	113.45 (18)	C1–Si2–C2	111.00 (39)
Si1–Si2–C2	108.35 (18)	C1–Si2–C3	104.37 (35)
Si1–Si2–C3	115.14 (25)		

$$PbCl_2 + 2(THF)_3Li[Si(SiMe_3)_3] \xrightarrow[(C_2H_5)_2O]{-78\text{ to }25\ ^\circ C} \underset{\text{I}}{[(Me_3Si)_3Si]_2} + Pb + 2LiCl \quad (1)$$

An X-ray structure determination was carried out on one of the crystals of I obtained from pentane solution. Examination of the ^1H NMR spectrum of I made up from the same batch of crystals used for the structure determination revealed the presence of a small amount of pentane. Crystal data for the product are listed in Table I, and the structure (hydrogens omitted) is represented in Figure 1. The molecule conforms to D_3 symmetry. As a consequence of the disorder in the structure and the presence of unlocated pentane in the lattice, the degree of refinement achieved was less than usually expected but was sufficient to give acceptable values for the important structural parameters. After completing the structure determination, we became aware that other investigators[10] had also just determined the structure of I prepared by a different route. Starting with a crystal prepared by sublimation, these workers were able to obtain a structure with a lower R factor, but the structural parameters from the two determinations were in good agreement (see supplementary material). Selected bond lengths and angles from our work are listed in Table II. These values also compare reasonably well with those obtained from other structures containing similar fragments. For example, our Si1–Si2 distances are 2.358 (1) Å, which compare well with those (2.356–2.358 Å) published by Geanangel et al.[2] Our Si–C distances are 1.917 (6), 1.913 (7), and 1.691 (10) Å; the first two values are in accord with published values,[2] but the third falls below the normal range, due, we believe, to libration effects (see supplementary material). Similarly, Si–Si–Si and Si–Si–C bond angles closely resemble published results. The

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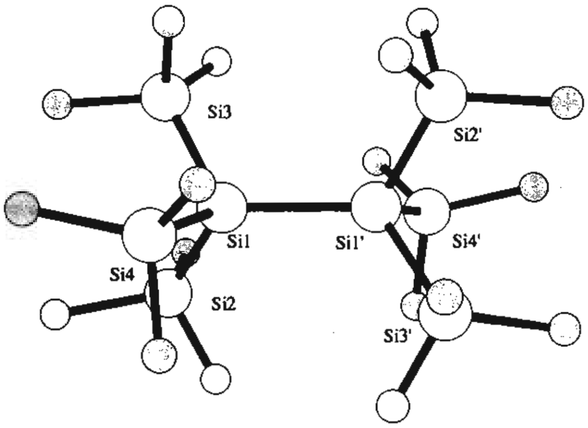

Figure 1. Molecular structure and atom-labeling scheme for I (hydrogens omitted).

Si1–Si1′ distance in I is slightly greater than the literature value for Si–Si bonds (2.332 Å)[11] and the Si1–Si1′–Si angles exceed the tetrahedral value, indicating the presence of some steric strain between the Me_3Si groups in the structure.

In order to assess the effectiveness of molecular mechanics calculations in predicting polysilane structures, we carried out such calculations on the octasilane I using the PCModel and Alchemy II programs. Results from these calculations employing the MMX and TRIPOS force fields are included in Table III. In the former case, polysilane parameters[11] were added to those provided with the programs. The bond distances and angles produced by both the force field calculations match the X-ray values[10] closely.

The high yield of $[(Me_3Si)_3Si]_2$ and the absence of any observed lead-containing products suggest two possible routes for the reaction. First, the expected product, $Pb[Si(SiMe_3)_3]_2$, may form at low temperature but decompose through homolytic cleavage of the Pb–Si bonds. Coupling of the $(Me_3Si)_3Si^{\bullet}$ radicals which result could lead to the observed product. An alternate route involves direct reduction of lead(II) chloride by the lithium silyl reagent giving metallic lead and $(Me_3Si)_3Si^{\bullet}$ radicals, which could then couple as just described. The dark coloration of the residue is consistent with the formation of elemental lead although we did not directly identify the metal. The second step in which the product is formed from $(Me_3Si)_3Si^{\bullet}$ radicals is not in question since the literature procedure for the preparation of $[(Me_3Si)_3Si]_2$ very probably involves the same radicals generated in a more conventional way (eq 2).[8,9] It is notable that the starting material

$$2HSi(SiMe_3)_3 \xrightarrow[130\ ^\circ C,\ C_6H_6]{(t\text{-BuO})_2} [(Me_3Si)_3Si]_2 \qquad (2)$$

in that procedure, $HSi(SiMe_3)_3$, was obtained by the acid hydrolysis of $(THF)_3Li[Si(SiMe_3)_3]$,[12] which means that the direct reaction of that reagent with $PbCl_2$, as described here, is a more efficient method for preparing the octasilane.

Table III. Comparison of Bond Distances (Å) and Angles (deg) from an X-ray Structure Determination and from Molecular Mechanics Calculations

atoms	X-ray results[a]	mol mech A results[b]	mol mech B results[c]
	Distances		
Si1–Si1′	2.403 (2)	2.36	2.4
Si1–Si2	2.3738 (9)	2.40	2.4
Si1–Si3	2.3738 (9)	2.40	2.4
Si1–Si4	2.3738 (9)	2.40	2.4
Si2–C1	1.876 (3)	1.89	1.9
Si2–C2	1.855 (4)	1.88	1.9
Si2–C3	1.858 (3)	1.88	1.9
	Angles		
Si1–Si1′–Si2	113.51 (3)	114.3	113.2
Si1–Si1′–Si3	113.51 (3)	114.3	113.1
Si1–Si1′–Si4	113.51 (3)	114.3	113.0
Si1–Si2–C1	111.1 (1)	110.6	110.6
Si1–Si2–C2	111.87 (9)	110.9	111.9
Si1–Si2–C3	114.9 (1)	111.7	113.5
Si2–Si1–Si3	105.15 (4)	105.8	105.6

[a] Values from ref 10, a more precise structure determination carried out on solvent-free crystals of $C_{18}H_{54}Si_8$. [b] Obtained using PCModel's implementation of the MMX force field, Serena Software, Bloomington, IN. [c] Obtained using Alchemy II incorporating the TRIPOS force field, Tripos Associates, St. Louis, MO. Si–C and Si–Si bond distances of 1.860 and 2.332 Å and stretching constants of 503 and 266 kcal mol^{-1} $Å^{-2}$, respectively, added to minbnd.tab table. Values taken from ref 11.

At present, we cannot distinguish between the pathways involving the homolytic cleavage of the Pb–Si bonds in the lead–silyl species and reduction of $PbCl_2$ by the lithium silyl reagent. Irrespective of the mechanism, however, the increasing availability of lithium silyl reagents[13] suggests that their reaction with $PbCl_2$ may represent an advantageous method of preparing new derivatives. The observation by Glocking and Gowda[14] that $PbCl_2$ reacts with $LiC(SiMe_3)_3$ at 0 °C to deposit metallic lead instead of forming organolead(II) products appears to indicate, in light of our results, that derivatives centered on other group 14 atoms besides silicon may also be formed.

Acknowledgment. We gratefully acknowledge the support of this investigation by the Robert A. Welch Foundation under Grants E-0594 and E-1105. We are also grateful to Professors P. Lickiss and F. Fronczek for providing us with their experimental results prior to publication.

Supplementary Material Available: Text detailing X-ray experimental procedures and results and Tables SI–SVII, listing data collection and processing parameters, atomic coordinates, bond lengths and angles, torsional angles, *U*'s, and *B*'s (14 pages); Table SVIII, listing observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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