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(Tris(trimethylsilyl)silyl)lead(IV) Derivatives

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The reaction of Ph_3PbCl with 1 equiv of $(THF)_3LiSi(SiMe_3)_3$ in ether afforded $Ph_3PbSi(SiMe_3)_3$ in high yield. Our attempts to prepare $Ph_2Pb(Si(SiMe_3)_3)_2$ through a similar reaction of Ph_2PbCl_2 with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ gave a mixture of the expected product, a pale yellow solid, and $[Ph_2PbSi(SiMe_3)_3]_2$, a bright yellow-orange, thermochromic solid. These products were separated by fractional crystallization from the reaction mixture and characterized by their elemental analyses, NMR spectra (^1H, ^{13}C), and infrared and UV–visible spectra. In order to compare $[Ph_2PbSi(SiMe_3)_3]_2$ with its previously reported digermane counterpart, an X-ray structure determination was carried out on the product as a benzene monosolvate. Crystals of $[Ph_2PbSi(SiMe_3)_3]_2$ were monoclinic, $P2_1/n$, with $a = 13.208(2)$ Å, $b = 16.586(3)$ Å, $c = 13.896(3)$ Å, $\beta = 99.29°$, $V = 3004$ Å^3, and $Z = 2$. The molecular structure confirmed that the product is indeed a diplumbane exhibiting a Pb–Pb bond 2.911(1) Å in length. All three products were unreactive toward atmospheric moisture. NMR studies of $Ph_2Pb(Si(SiMe_3)_3)_2$ and $[Ph_2PbSi(SiMe_3)_3]_2$ solutions in ether showed the former to be stable for at least 22 h while the latter decomposed completely within the same period.

Introduction

As a part of a study of the effects of very bulky substituents on the properties of main group compounds, we have prepared selected examples of $(Me_3Si)_3SiER_3$ and $((Me_3Si)_3Si)_2ER_2$ (E = Ge, Sn; R = Cl, alkyl, phenyl) derivatives.[1] The only structurally characterized disubstituted member, $[(Me_3Si)_3Si]_2SnCl_2$, exhibited a significant distortion of the tetrahedral geometry around tin involving a Si–Sn–Si bond angle of over 142°, suggesting that the bulk of the $Si(SiMe_3)_3$ substituent is sufficient to cause pronounced steric strain even with a central atom as large as tin. Molloy and co-workers[2] have also reported that the presence of two tris(trimethylsilyl)methyl, $(Me_3Si)_3C$, substituents on tin also will cause severe steric crowding. Our attempted synthesis of the disubstituted germanium derivative $[(Me_3Si)_3Si]_2GeCl_2$ instead gave the digermane $[(Me_3Si)_3SiGeCl_2]_2$, suggesting that the disubstituted monogermane is unstable owing to steric strain. In order to examine the effect of the central atom on the behavior of tris(trimethylsilyl)–group 14 compounds, we have prepared and studied selected lead(IV) derivatives. We wish to report here the results of that investigation.

Experimental Section

Materials. Triphenyllead chloride was obtained from Organometallics, Inc., while diphenyllead dichloride came from Johnson-Matthey. Their purity was checked using ^1H NMR. The lithium silyl $(THF)_3LiSi(SiMe_3)_3$ was prepared according to the published procedure[3] with the minor modification of using halide-free methyllithium.

Procedures. All manipulations were conducted using Schlenk techniques[4] under an atmosphere of argon unless otherwise noted. Hygroscopic solids were handled in a Vacuum Atmospheres glovebox under dry nitrogen. Solvents were distilled from appropriate drying agents and stored under dry nitrogen or argon. Elemental analyses were performed by Atlantic Microlabs. NMR spectra were obtained using a General Electric QE-300 spectrometer, and mass spectra were obtained using a Hewlett Packard MSD GC mass spectrometer. IR spectra were obtained using a Perkin-Elmer Model 1330 spectrometer with samples either pressed between AgBr windows (Harshaw Chemical) or mulled with Nujol. UV–visible spectra were obtained using a Perkin-Elmer Model 330 spectrophotometer with the sample in benzene solution. The program CHEM 3D+ from Cambridge Scientific Computing Inc. was used for molecular mechanics calculations.

(Tris(trimethylsilyl)silyl)triphenylplumbane, $(Me_3Si)_3SiPb(C_6H_5)_3$ (I). An ether solution (100 mL) of $(THF)_3LiSi(Si(CH_3)_3)_3)$ (2719.6 mg, 5.77 mmol) was added dropwise to a cold (−78 °C) suspension of $(C_6H_5)_3PbCl$ (2736.7 mg, 5.77 mmol) in 100 mL of ether. The reaction mixture was stirred at −78 °C for 8 h and then warmed slowly to ambient temperature, where stirring was continued for 64 h. Ether was removed under reduced pressure; the white solid residue was stirred with 100 mL of pentane for 30 min; then the mixture was filtered and the filtrate concentrated to about 20 mL. After 4 h at ambient temperature, colorless, transparent crystals were isolated, washed three times with pentane, and dried under reduced pressure. The crystals (3200 mg, 80.8% yield) were stable to air and moisture. Mp: 145 °C. Anal. Calcd for $C_{27}H_{42}PbSi_4$: C, 47.26; H, 6.17. Found: C, 47.10; H, 6.15. NMR (C_6D_6): ^1H, δ 0.258 (27H) $[-Si(SiMe_3)_3]$, 7.090–7.834 (mult, 15H) $[-(C_6H_5)_3]$; ^{13}C, δ 3.058 $[-Si(SiMe_3)_3]$, 129.54, 138.32, 152.16 $[-(C_6H_5)_3]$. IR (Nujol, cm^{-1}): 3010 m, 2555 w, 1420 s, 1315 vw, 1285 w, 1250 s, sh, 1235 s, 1045 m, 1005 m, 980 m, 820 vs, 710 vs, 685 s, 615 s, 455 w, 435 s.

1,1,2,2-Tetraphenyl-1,2-bis((trimethylsilyl)silyl)diplumbane, $[(Me_3Si)_3SiPb(C_6H_5)_2]_2$ (II). To a cold (−78 °C) suspension of $(C_6H_5)_2PbCl_2$ (2156 mg, 4.98 mmol) in ether (about 100 mL) was added dropwise 150 mL of an ether solution of $(THF)_3LiSi(Si(CH_3)_3)_3$ (4622.5 mg, 9.81 mmol) while vigorous stirring was maintained. During the addition, a bright yellow color developed in the reaction mixture. After being stirred for 8 h at −78 °C, the mixture was allowed to warm to ambient temperature, where stirring was continued for 16 h. Ether was removed under reduced pressure, and the yellow residue was stirred with pentane (2 × 35 mL, 30 min each). Upon concentration and cooling to 4 °C, the orange pentane solution yielded bright yellow-orange crystals. The product was again crystallized from pentane, isolated, washed three times with small volumes of the same solvent, and dried under reduced pressure (620 mg, 20.7%). High-quality crystals of II for X-ray diffraction were obtained from benzene solution. (The remaining benzene solution was preserved for further use in the isolation of III.) These crystals were not hygroscopic but slowly lost solvent of crystallization (C_6H_6), turning opaque after exposure to air. In a melting point capillary, the crystals were thermochromic, appearing bright yellow at −50 °C, yellow-orange at room temperature, and green at 168 °C and melting at 176 °C. Anal. Calcd for $C_{42}H_{74}Pb_2Si_8$: C, 41.41; H, 6.12. Found: C, 41.84; H, 6.05. NMR (C_6D_6): ^1H, δ 0.116 (54H) $[-Si(SiMe_3)_3]$, 7.149–8.086 (mult, 26H) [two $(C_6H_5)_2$ and one C_6H_6 of crystallization]; ^{13}C, δ 3.25 $[-Si(SiMe_3)_3]$, 129.55, 139.73, 154.52 $[-(C_6H_5)_3]$. UV–vis (C_6H_6): 369 nm ($\epsilon = 5.01 \times 10^5$ M^{-1} cm^{-1}). IR (Nujol, cm^{-1}): 3060 w, 1550 w, 1430 m, 1300 w, 1250 vs, 1260 vw, 1265 m, 1025 m, 1005 m, 855 vs, br, 750 s, 720 m, 650 s, 460 s.

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Table I. Crystallographic Data for $[(Me_3Si)_3SiPb(C_6H_5)_2]_2$ (II)

$C_{42}H_{74}Si_8Pb_2 \cdot C_6H_6$	$P2_1/n$ (monoclinic)
fw = 1296.38	$T = -50$ °C
$a = 13.208(2)$ Å	$\lambda = 0.710\,73$ Å
$b = 16.586(3)$ Å	$\rho_{calcd} = 1.43$ g cm^{-3}
$c = 13.896(3)$ Å	$\mu = 58.2$ cm^{-1}
$\beta = 99.29(1)°$	$R = \sum \lVert F_o\rvert - \lvert F_c\rVert / \sum \lvert F_o\rvert = 0.039$
$V = 3004$ Å^3	$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2} = 0.033$
$Z = 2$	

Diphenylbis(tris(trimethylsilyl)silyl)plumbane, $((Me_3Si)_3Si)_2Pb(C_6H_5)_2$ (III). The benzene solution from the crystallization of II was concentrated, and on standing at ambient temperature, it produced pale yellow, transparent crystals. These were washed three times with small volumes of benzene and dried under reduced pressure, yielding a pale yellow powder, III (880 mg, 20.9%). Mp: 162 °C dec. Anal. Calcd for $C_{30}H_{64}PbSi_8$: C, 42.05; H, 7.53. Found: C, 41.07; H, 7.59. NMR (C_6D_6): ^{1}H, δ 0.268 (54H) [$-Si(SiMe_3)_3$], 7.14–7.98 (mult, 10H) [$-(C_6H_5)_2$]; ^{13}C, δ 3.754 [$-Si(SiMe_3)_3$], 129.07, 139.74, 150.80 [$-(C_6H_5)_2$]. UV–vis (C_6H_6): 299 nm ($\epsilon = 5.76 \times 10^5$ M^{-1} cm^{-1}). IR (Nujol and neat, cm^{-1}): 3095 m, 1890 vw, 1830 vw, 1550 w, 1430 m, 1300 w, 1255 vs, 1070 m, 1025 m, 1015 m, 865 vs, br, 755 m, 715 m, 655 s, 475 s.

X-ray Structure Determination of II

A bright yellow multifaceted block having approximate dimensions 0.50 × 0.48 × 0.32 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. Since the material was known to contain solvent of crystallization, the sample was maintained in a stream of dry nitrogen gas at −50 °C in order to retard any possible decomposition. The crystals appeared bright orange at room temperature but turned bright yellow upon cooling. And after exposure to X-rays at −50 °C, the sample turned a deep amber color. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. During data reduction, Lorentz and polarization corrections were applied, as well as an empirical absorption correction based on ψ scans of 10 reflections having χ values between 70 and 90°. Since there are only two formula units in the cell, the asymmetric unit necessarily consists of one-half dimer and one-half benzene solvent molecule, both located about inversion centers. The Patterson map revealed the location of the unique Pb atom, and remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. 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 1.5 e/Å^3, located near Pb. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Results and Discussion

Reaction of triphenyllead chloride with the lithium silyl according to eq 1, proceeds smoothly to give (tris(trimethylsilyl)silyl)triphenylplumbane (I) as a white crystalline solid in 81%

$$(C_6H_5)_3PbCl + (THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ °C\ to\ room\ temp]{(C_2H_5)_2O} (C_6H_5)_3PbSi(SiMe_3)_3 + LiCl \quad (1)$$

yield. The product is not sensitive to air and is stable up to its melting point of 145 °C, which is lower than that of the analogous tris(trimethylsilyl)methyl derivative $(Me_3Si)_3CPb(C_6H_5)_3$ (mp 195–197 °C).[5] The structure of I should parallel that of $(Me_3Si)_3SiGePh_3$, which has recently been determined by X-ray diffraction.[6] The latter exhibited a slightly elongated Si–Ge bond and deviations of the Si–Si–Si and Si–Si–Ge angles from tetrahedral values, but most of the steric strain along the Si–Ge vector was relieved by twisting distortions. Due to the longer Si–Pb bond, I is expected to exhibit less steric distortions. Although an X-ray structure determination was not carried out for I, we have performed a molecular mechanics calculation on the molecule. Such calculations have been shown to reproduce major aspects of the structures of $(Me_3Si)_3SiGePh_3$[6] and $(Me_3Si)_3SiSi(SiMe_3)_3$[7] with reasonable accuracy. The structure thus predicted for I exhibited a Si–Pb bond distance of 2.6 Å, essentially unchanged from the unstrained distance employed by the program, and average Si–Si–Si and Si–Si–Pb angles of 109.0 and 109.9°, respectively. The similarity of the angles and their nearness to the ideal tetrahedral value, taken along with the absence of Si–Pb bond lengthening, appear to confirm the absence of steric strain along the Si–Pb vector.

The sizable cone angle generated by the $(Me_3Si)_3Si-$ group[8] is expected to cause considerable steric strain in *disubstituted* derivatives of the type $((Me_3Si)_3Si)_2MX_n$, the only exceptions being cases such as $((Me_3Si)_3Si)_2Hg$, where the Si–M–Si bond angle is 180°.[9] As noted in the Introduction, the structure of $((Me_3Si)_3Si)_2SnCl_2$ is markedly distorted from tetrahedral geometry around the tin and $((Me_3Si)_3Si)_2GeCl_2$ appears to be unstable at room temperature. It was thus of interest to attempt the synthesis of a $((Me_3Si)_3Si)_2PbX_2$ compound to ascertain whether the larger radius of Pb would reduce the steric strain sufficiently that the disubstituted Pb(IV) derivative, like that of Sn, would be stable. Since $PbCl_4$ is too strong an oxidizer to use with the lithium silyl reagent, Ph_2PbCl_2 was chosen as the Pb(IV) starting material. The reaction was carried out according to eq 2. After 24 h of stirring, removal of ether under reduced pressure,

$$(C_6H_5)_2PbCl_2 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ °C\ to\ room\ temp]{(C_2H_5)_2O} (C_6H_5)_2Pb(Si(SiMe_3)_3)_2 + 2LiCl \quad (2)$$

extraction of the residue into pentane, concentration, and cooling, bright orange crystals were obtained that were identified as the diplumbane $[(C_6H_5)_2PbSi(SiMe_3)_3]_2$ (II) (30% based on total Pb) by elemental analyses, ^{1}H and ^{13}C NMR spectra, and an X-ray structure determination, the results of which are described below. Upon further concentration and standing at ambient temperature, the remaining solution yielded pale yellow crystals that were identified as the expected (eq 2) disubstituted monoplumbane $(C_6H_5)_2Pb(Si(SiMe_3)_3)_2$ (III) (21% based on total Pb) by elemental analysis and NMR spectra. We were not able to obtain high-quality crystals of III for X-ray analysis, but the chemical shifts of ^{1}H and ^{13}C spectra and the integrated areas of the proton spectra were consistent with the proposed formulation of III.

Description of the Structure of II. Bright yellow crystals of II were grown from benzene; one molecule of benzene of solvation was found to be present in the structure. This benzene was lost under reduced pressure or upon standing at ambient pressure, so the crystals were maintained at low temperature. Crystal and data collection parameters are summarized in Table I; atomic coordinates and geometric parameters for the heavy atoms are presented in Tables II and III, respectively. Figure 1 shows the heavy-atom molecular structure determined for II. The Pb–Pb bond, 2.911(1) Å, is notably longer than that in Ph_6Pb_2, 2.844(4) Å,[10] suggesting that some steric strain exists among the substituents along the Pb–Pb vector. This appears to be confirmed by the average Pb–C distance, 2.255(8) Å, which also exceeds that in Ph_6Pb_2, 2.22(2) Å,[10] and the Pb–Si distance, 2.648(2) Å, which exceeds the sum of the four coordinate, covalent radii of

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Pb	5529(1)	5063(1)	4161(1)	22(1)
Si(1)	5608(2)	6427(1)	3184(2)	24(1)
Si(2)	6004(2)	6127(2)	1629(2)	38(1)
Si(3)	4047(2)	7133(2)	3064(2)	35(1)
Si(4)	6936(2)	7151(2)	4116(2)	36(1)
C(1)	6727(8)	5177(6)	1605(7)	63(5)
C(2)	4801(8)	6039(6)	680(7)	59(5)
C(3)	6802(8)	6955(6)	1250(7)	59(5)
C(4)	2952(7)	6509(5)	2456(7)	45(4)
C(5)	4133(8)	8095(5)	2348(8)	57(5)
C(6)	3781(8)	7379(7)	4293(8)	73(6)
C(7)	7028(9)	8215(5)	3643(8)	69(5)
C(8)	6711(9)	7208(7)	5413(7)	66(5)
C(9)	8232(7)	6639(6)	4122(8)	52(4)
C(10)	4945(7)	4108(5)	3079(7)	29(3)
C(11)	5387(7)	3338(5)	3118(7)	39(4)
C(12)	4976(9)	2746(6)	2402(8)	52(5)
C(13)	4148(8)	2937(7)	1686(8)	53(5)
C(14)	3714(8)	3699(6)	1672(8)	49(4)
C(15)	4104(7)	4272(6)	2348(7)	37(4)
C(16)	7166(7)	4709(5)	4790(7)	30(3)
C(17)	7799(8)	4304(5)	4237(8)	42(4)
C(18)	8806(8)	4140(6)	4680(11)	66(6)
C(19)	9185(9)	4402(6)	5581(11)	67(6)
C(20)	8569(8)	4799(6)	6116(9)	58(5)
C(21)	7549(7)	4963(6)	5720(7)	41(3)
C(22)	4021(32)	214(26)	4510(32)	275(30)
C(23)	4921(56)	485(19)	4212(23)	23413(28)
C(24)	5842(25)	272(34)	4811(64)	276(34)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for II

	A. Bond Lengths		
Pb–Si(1)	2.648(2)	Pb–C(10)	2.235(8)
Pb–C(16)	2.275(8)	Pb–Pb′	2.911(1)
Si(1)–Si(2)	2.357(4)	Si(1)–Si(3)	2.354(4)
Si(1)–Si(4)	2.337(4)	Si(2)–C(1)	1.846(10)
Si(2)–C(2)	1.899(10)	Si(2)–C(3)	1.858(11)
Si(3)–C(4)	1.865(9)	Si(3)–C(5)	1.893(10)
Si(3)–C(6)	1.844(12)	Si(4)–C(7)	1.894(10)
Si(4)–C(8)	1.877(11)	Si(4)–C(9)	1.910(10)
	B. Bond Angles		
Si(1)–Pb–C(10)	107.4(2)	Si(1)–Pb–C(16)	107.7(2)
C(10)–Pb–C(16)	106.2(3)	Si(1)–Pb–Pb′	122.4(1)
C(10)–Pb–Pb′	109.3(2)	C(16)–Pb–Pb′	102.9(3)
Pb–Si(1)–Si(2)	108.8(1)	Pb–Si(1)–Si(3)	110.8(1)
Si(2)–Si(1)–Si(3)	111.2(1)	Pb–Si(1)–Si(4)	104.1(1)
Si(2)–Si(1)–Si(4)	111.0(1)	Si(3)–Si(1)–Si(4)	110.7(1)
Si(1)–Si(2)–C(1)	112.9(3)	Si(1)–Si(2)–C(3)	108.9(3)
Si(1)–Si(2)–C(2)	111.6(4)	Si(1)–Si(3)–C(5)	109.3(4)
Si(1)–Si(3)–C(4)	111.2(3)	Si(1)–Si(3)–C(6)	109.9(4)
Si(1)–Si(4)–C(7)	111.8(3)	Si(1)–Si(4)–C(8)	109.7(4)
Si(1)–Si(4)–C(9)	111.4(3)	Pb–C(10)–C(15)	119.7(6)
Pb–C(10)–C(11)	121.6(6)	Pb–C(16)–C(21)	117.7(7)
Pb–C(16)–C(17)	122.0(7)		
	C. Torsion Angles		
Si(2)–Si(1)–Pb–C(10)	−32.8	C(10)′–Pb′–Pb–C(16)	67.5
Si(2)–Si(1)–Pb–C(16)	81.2	C(16)′–Pb′–Pb–Si(1)	59.1
Si(2)–Si(1)–Pb–Pb′	−160.2	C(10)′–Pb′–Pb–C(10)	−180.0
Si(3)–Si(1)–Pb–C(10)	89.7	C(16)′–Pb′–Pb–C(16)	180.0
Si(3)–Si(1)–Pb–C(16)	−156.3	Si(1)–Pb–C(10)–C(11)	136.6
Si(3)–Si(1)–Pb–Pb′	−37.7	Si(1)–Pb–C(10)–C(15)	−44.5
Si(4)–Si(1)–Pb–C(10)	−151.2	Pb′–Pb–C(10)–C(11)	−88.6
Si(4)–Si(1)–Pb–C(16)	−37.2	Pb′–Pb–C(10)–C(15)	90.2
Si(4)–Si(1)–Pb–Pb′	81.4	Si(1)–Pb–C(16)–C(17)	−82.3
Si(1)′–Pb′–Pb–Si(1)	180.0	Si(1)–Pb–C(16)–C(21)	92.8
Si(1)′–Pb′–Pb–C(10)	53.4	Pb′–Pb–C(16)–C(17)	147.2
Si(1)′–Pb′–Pb–C(16)	−59.1	Pb′–Pb–C(16)–C(21)	−37.7

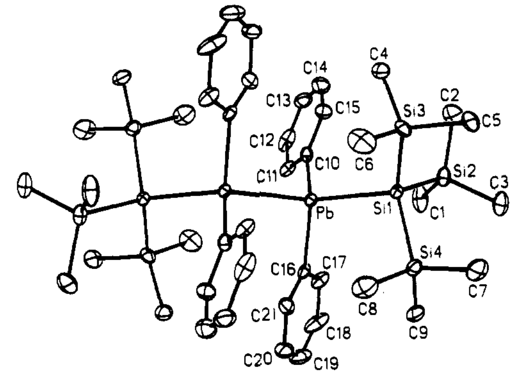
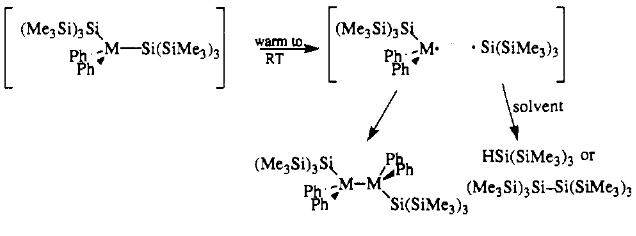


Figure 1. View of the molecule II showing the atom-numbering scheme. The thermal ellipsoids are 30% equiprobability envelopes, with hydrogens omitted for clarity.

Scheme I



the atoms, 2.636 Å,[11] although we are not aware of experimental values with which it might be compared. With the exception of the large Pb–Pb–Si angle, 122.4(1)°, most of the skeletal bond angles fall within about 2° of the expected tetrahedal values but the Si–Si–Si angles (average 111.0°) exceed the Pb–Si–Si angles (average 107.9°) to a degree which compares closely with those in the very strained $((Me_3Si)_3Si)_2SnCl_2$ (average Si–Si–Si = 110.9°, Sn–Si–Si = 108.0°). In the monosubstituted derivative $(Me_3Si)_3SiGe(C_6H_5)_3$, which is presumed to have less steric strain, the relative sizes of the average Si–Si–Si and Ge–Si–Si angles are reversed (108.3° vs 110.7°, respectively).[6] The tris(trimethylsilyl)silyl groups in II are trans to each other across the Pb–Pb bond, as would be expected from steric considerations. There is also an usual torsional twist in the Si(2) group (Pb–Si(1)–Si(2)–C(3)) = −146° compared to Pb–Si(1)–Si(3)–C(5) = −179° and Pb–Si(1)–Si(4)–C(7) = −173°). Since such torsional angles are usually ±180°, this is probably indicative of steric interactions between its methyl groups and the two nearby phenyl rings. These considerations suggest that some steric strain persists in the structure of II.

The fact that both II and III were isolated from the reaction of Ph_2PbCl_2 with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ suggests that *either* one of them is formed initially and subsequently converts to the other *or* they are formed simultaneously via competitive pathways. We initially supposed that the disubstituted derivative, III, was produced first and that, because of steric strain, it underwent Si–Pb bond cleavage, leading to II, as shown in Scheme I. We proposed this type of pathway for the formation of $[(Me_3Si)_3SiGeCl_2]_2$, a Ge counterpart of II, from the reaction of $GeCl_4$ with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$.[1b] The presumed weakness of the Pb–Si bond favored this explanation for the formation of II. In order to determine whether such a conversion of III to II actually takes place under the conditions of our experiment, we prepared solutions of each compound individually in ether, held these for 22 h at ambient temperature, removed the ether, and obtained ^1H spectra of each residue in C_6D_6 solution. The ^1H spectrum of III (δ 0.270) changed minimally over 22 h, and the resonance of II did not appear in the spectrum. (A solution of III stored in the refrigerator several months exhibited a small

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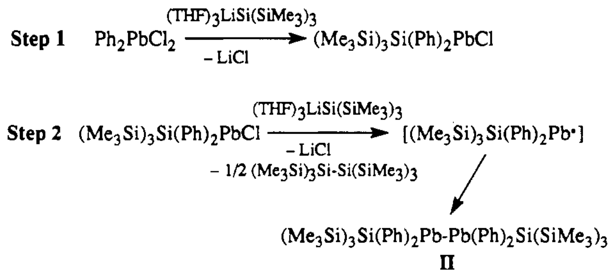
amount of black deposit, presumably Pb.) After 22 h, the resonance of II (δ 0.116) had been essentially completely replaced by a major ^{1}H signal at δ 0.274 (^{13}C, δ 1.338), suggesting a compound with silyl groups similar to, but distinct from, those of III (^{13}c, δ 3.754) but not further identified, and smaller signals at δ 0.189 ($HSi(SiMe_3)_3$, 0.236, 0.180, 0.146 (unidentified), and 0.263 ($Si(SiMe_3)_4$). Although $(Me_3Si)_3SiSi(SiMe_3)_3$ was not detected among the products of the decomposition of II in ether, it was found when the compound was allowed to decompose in C_6D_6. (On standing for several months, a refrigerated benzene solution of II also appeared to form a solid Pb residue.) The facile decomposition of II in solution, probably through disproportionation as proposed[12] for Ph_6Pb_2, explains the low yield of that product. We conclude from these observations that II does not originate from III but rather forms via a different pathway.

A possible route to II involving the reduction of an intermediate is shown in Scheme II. In this route the first equivalent of lithium silyl produces the expected substitution step, forming a monochloro intermediate (step 1) which can either undergo a second substitution to yield III or may be reduced by the second equivalent of lithium silyl (step 2), ultimately forming the dilead derivative. Since the lithium silyl reagent is a fairly strong reducing agent, the known preparation of hexaphenyldilead via the reduction of triphenyllead chloride by an alkali metal serves as a precedent for step 2 of Scheme II.[13] The presence of $(Me_3Si)_3SiSi(SiMe_3)_3$ in the reaction mixture, as required by Scheme II, was indicated by a prominent ^{1}H signal at δ 0.361. We have previously observed that $(Me_3Si)_3SiSi(SiMe_3)_3$ is produced in high yield when $PbCl_2$ is reduced with $(THF)_3LiSi(SiMe_3)_3$.[7]

Scheme II



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Supplementary Material Available: Tables listing data collection and processing parameters, bond lengths, bond angles, anisotropic displacement parameters, hydrogen atomic coordinates and isotropic displacement parameters, and torsion angles (5 pages). Ordering information is given on any current masthead page.

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[12] (a) Willemsens, L. C.; Van der Kerk, G. J. M. *Investigations in the Field of Organolead Chemistry*; Institute for Organic Chemistry TNO: Ultrecht, The Netherlands, 1965; p 9. (b) Zimmer, H.; Homberg, O. H. *J. Org. Chem.* **1966**, *31*, 947. (c) Gilman, H.; Bailie, J. C. *J. Am. Chem. Soc.* **1939**, *61*, 731.

[13] Gilman, H.; Atwell, W. H.; Cartledge, F. K. *Adv. Organomet. Chem.* **1964**, *1*, 90.