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Synthesis, Single-Crystal X-ray Structural Characterization, and Reactivity of a Hexaalkyldiplumbane, $TsiMe_2Pb-PbMe_2Tsi$, Tsi = $(Me_3Si)_3C$

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Introduction

There is a current interest in the synthesis, structural characterization, and chemical properties of molecules containing a Pb–Pb bond.[1–7] Of the group 14 elements lead forms the least stable bonds and the majority of compounds that have been structurally characterized contain aryl substituents, and no methyllead compounds have been characterized. We report the use of the trisyl group, $(Me_3Si)_3C$ (Tsi), to stabilize lead–lead bonds in a system that contains only alkyl groups, $TsiMe_2Pb-PbMe_2Tsi$.

Experimental Section

Preparation of $[\{(Me_3Si)_3C\}Me_2Pb]_2$. A tetrahydrofuran solution (10 mL) of Ph_3SnLi (prepared from 780 mg, 2.02 mmol, of Ph_3SnCl and 47 mg, 6.8 mmol, Li) was added dropwise to a cold (−95 °C) tetrahydrofuran solution (20 mL) of $\{(Me_3Si)_3C\}Me_2PbBr$[8] (1 g, 1.82 mmol) with vigorous stirring. The solution became orange/brown accompanied by the formation of a white precipitate. The reaction mixture was stirred for 1 h at −90 °C and then allowed to warm to room temperature. Solvent was removed *in vacuo* and the yellow residue was stirred with *n*-hexane (50 mL) for 1 h. Filtration, followed by removal of the solvent *in vacuo*, gave an orange/yellow solid. Examination of the crude material by ^1H, ^{119}Sn and ^{207}Pb NMR spectroscopy showed the presence of the title compound, **1**, together with $\{(Me_3Si)_3C\}Me_3Pb$ [^1H (C_6D_6), δ 0.22 (27H, s, $SiMe_3$), 0.91 (9H, s, $PbMe_3$); lit.[8] 0.23, 0.91; ^{207}Pb (C_6D_6), δ 64.4; Ph_3SnMe ^{119}Sn (toluene), δ −90.3] and starting material, $\{(Me_3Si)_3C\}Me_2PbBr$, in the approximate ratio 2:4:2:1.

Crystallization of the crude material from toluene afforded orange crystals of **1** (320 mg, 18%; mp 175 °C dec). Anal. Calcd for $C_{24}H_{66}Si_6Pb_2$: C, 30.74, H, 7.09; Found: C, 30.90, H, 6.95. $^1H(C_6D_6)$: δ 0.29 (s, $SiMe_3$), 1.43 (s, $PbMe_2$). ^{29}Si (C_6D_6): δ 0.16 (s, $SiMe_3$). ^{207}Pb (C_6D_6): δ −48.2. UV/vis (*n*-hexane): $\lambda = 341$ nm, $\epsilon = 1.97 \times 10^4$ M^{-1} cm^{-1}.

Alternative Preparation of $[\{(Me_3Si)_3C\}Me_2Pb]_2$. A tetrahydrofuran solution (10 mL) of $\{(Me_3Si)_3C\}Me_2PbBr$ (514 mg, 0.94 mmol) was stirred with Mg turnings (15 mg, 0.62 mmol) for 18 h. Removal of solvent *in vacuo* gave a yellow residue which was stirred with toluene (30 mL) for 1 h. Filtration followed by removal of solvent *in vacuo* gave a yellow/white solid. Examination by ^1H and ^{207}Pb NMR spectroscopy showed the presence of **1** (7%), $\{(Me_3Si)_3C\}Me_3Pb$ (23%), and unreacted $\{(Me_3Si)_3C\}Me_2PbBr$ (70%).

Photolysis of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ in C_6D_6. A C_6D_6 solution (2 mL) of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ (25 mg, 27 μmol) in a sealed 5 mm NMR tube with a nitrogen atmosphere was set aside under normal laboratory lighting conditions for 3 days. After this time the orange solution had become colorless with the formation of an insoluble pale yellow solid. Examination of the solution by ^1H NMR spectroscopy showed the formation of (a) $(Me_3Si)_3CH$, 59% [^1H, δ 0.14 (27H, s, $SiMe_3$), −0.80 (1H, s, CH)] and (b) $\{(Me_3Si)_3C\}Me_3Pb$, 41%.

A blank experiment involving a similar preparation to that above, but with complete covering of the NMR tube with aluminum foil, resulted in no observable chemistry.

Photolysis of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ in CCl_4. A CCl_4 solution (2 mL) of $[\{Me_3Si)_3C\}Me_2Pb]_2$ (25 mg, 27 μmol) in a sealed 5 mm NMR tube in a nitrogen atmosphere was set aside under normal laboratory lighting conditions for 3 days. After this time the orange solution had become colorless with the formation of an insoluble white solid. Filtration followed by removal of the solvent *in vacuo* gave a white residue. The residue was dissolved in C_6D_6 (1 mL) and examined by ^1H and ^{207}Pb NMR spectroscopy. The main components were identified as (a) $\{(Me_3Si)_3C\}Me_2PbCl$ > 90% [^1H (C_6D_6); δ 0.22 (s, $SiMe_3$), 1.35 (s, $PbMe_2Cl$); lit.[8] 0.23, 1.36; ^{207}Pb (C_6D_6), δ 377.1] and (b) $\{(Me_3Si)_3C\}Me_3Pb$, 5%.

A blank experiment involving a similar preparation to that above, but with complete covering of the NMR tube with aluminum foil, resulted in no observable chemistry.

Photolysis of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ in the Presence of Propargyl Bromide. To a toluene solution (20 mL) of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ (110 mg, 0.12 mmol) was added HC_2CH_2Br (30 mg, 0.25 mmol) and the solution was stirred under normal laboratory lighting conditions for 48 h. After this time the orange solution had become colourless with the formation of an insoluble pale yellow solid. Filtration followed by removal of the solvent *in vacuo* gave a white residue. The residue was dissolved in C_6D_6 (1 mL) and examined by ^1H and ^{207}Pb NMR spectrosopy. The main components were identified as (a) $\{(Me_3Si)_3C\}Me_2PbBr$, 90% [^1H (C_6D_6), δ 0.22 (s, $SiMe_3$), 1.46 (s, $PbMe_2Br$); lit.[8] 0.23, 1.46; ^{207}Pb (C_6D_6), δ 299.5] and (b) $\{(Me_3Si)_3C\}Me_3Pb$, 5%. We found no evidence for the formation of propargyllead derivatives.

Thermolysis of $[\{(Me_3Si)_3C\}Me_2Pb]_2$. A toluene-$d_8$ solution (1 mL) of $[\{(Me_3Si)_3C\}Me_2Pb]_2$ (30 mg, 32 μmol) in a sealed 5 mm NMR tube was heated in an oven maintained at 110 °C. After 45 h the solution had become light yellow with the formation of a slight precipitate. Examination by ^1H NMR showed the presence of three main components: (a) unreacted $[\{(Me_3Si)_3C\}Me_2Pb]_2$, 57%; (b) $\{(Me_3Si)_3C\}Me_3Pb$, 18%; (c) $(Me_3Si)_3CH$, 25%. After 100 h the ratio of the components had changed to a:b:c = 20:32:48, respectively.

Structural Analysis. All the structure determination data are recorded in Table 1, atomic coordinates are in Table 2, and complete bond lengths and angles are in Tables 3 and 4, respectively.

Results and Discussion

We have found two routes to the formation of a stable *hexa*alkyldiplumbane, $[\{(Me_3Si)_3C\}Me_2Pb]_2$ (**1**), eqs 1 and 2.

$$2\{(Me_3Si)_3C\}Me_2PbBr + Mg \rightarrow [\{(Me_3Si)_3C\}Me_2Pb]_2\ (\mathbf{1}) + MgBr_2 \qquad (1)$$

$$\{(Me_3Si)_3C\}Me_2PbBr + [Ph_3Sn]^-Li^+ \rightarrow \mathbf{1} + \{(Me_3Si)_3C\}Me_3Pb + Ph_3MeSn \qquad (2)$$

The yields of the reactions outlined are poor to moderate, 10–20%. Whereas the reaction outlined in eq 1 is an example of a well-established coupling reaction, the mechanism of the tin mediated reaction, eq 2, is not clear. The other products formed in this reaction were $\{(Me_3Si)_3C\}Me_3Pb$ and Ph_3SnMe. The formation of $\{(Me_3Si)_3C\}Me_3Pb$ is understandable in terms of the thermal decomposition of **1** as outlined in eq 3.

$$[\{(Me_3Si)_3C\}Me_2Pb]_2 \rightarrow \{(Me_3Si)_3C\}Me_3Pb \qquad (3)$$

Independent treatment of complex **1** at 110 °C in toluene resulted in the formation of $\{(Me_3Si)_3C\}Me_3Pb$. No evidence

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Table 1. Structure Determination Summary

	Crystal Data
empirical formula	$C_{24}H_{66}Pb_2Si_6$
color; habit	orange plate
cryst size (mm)	0.20 × 0.38 × 0.36
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 8.830(4)$ Å $b = 8.896(5)$ Å $c = 13.734(8)$ Å $\alpha = 92.55(5)°$ $\beta = 104.11(4)°$ $\gamma = 113.65(4)°$
V	946.0(9) Å^3
Z	1
fw	937.7
density (calcd)	1.646 Mg/m^3
abs coeff	9.152 mm^{-1}
F(000)	458
	Data Collection
diffractometer used	Siemens R3m/V
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
temp (K)	298
monochromator	highly oriented graphite cryst
2θ range	3.5–45.0°
scan type	ω
scan speed	variable; 3.00 to 15.00°/min in ω
scan range (ω)	1.20°
bckgd measurement	stationary cryst and stationaryu counter at beginning and end of scan, each for 25.0% of tot. scan time
standard reflcns	3 measd every 97 reflcns
index ranges	$-9 \le h \le 9, -9 \le k \le 9, -14 < l < 14$
reflcns collcd	4762
independent reflcns	2495 ($R_{int} = 2.82\%$)
obsd reflcns	2313 ($F > 3.0\sigma(F)$)
abs corr	semi-empirical
min/max transm	0.1938/1.0000
	Solution and Refinement
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	N/A
extinction corr	$\chi = 0.00027(12)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
H atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0013F^2$
no. of params refined	146
final R indices (obsd data)	$R = 3.88\%$, w$R = 5.03\%$
R indices (all data)	$R = 4.12\%$, w$R = 5.15\%$
goodness-of-fit	1.18
largest and mean Δ/σ	0.068, 0.013
data-to-param ratio	15.8:1
largest diff peak	2.10 e Å^{-3}
largest diff hole	−2.16 e Å^{-3}

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)^a
Pb	596(1)	4733(1)	4113(1)	31(1)
Si(1)	−2435(3)	4311(3)	1890(2)	39(1)
Si(2)	−3057(3)	1226(3)	3033(2)	35(1)
Si(3)	−232(3)	2299(3)	1867(2)	41(1)
C(1)	−1441(11)	3017(10)	2613(6)	32(4)
C(2)	2090(15)	7197(12)	3697(9)	61(5)
C(3)	2553(14)	3717(14)	4589(8)	54(5)
C(4)	−2036(15)	366(13)	4086(8)	55(5)
C(5)	−4452(15)	−580(12)	1983(9)	58(5)
C(6)	−4584(12)	1827(12)	3508(8)	49(5)
C(7)	−1088(18)	5707(14)	1144(9)	63(6)
C(8)	−4548(14)	3025(14)	927(8)	62(6)
C(9)	−2853(16)	5724(13)	2736(9)	56(5)
C(10)	1907(14)	3950(15)	1859(9)	63(6)
C(11)	267(16)	542(14)	2339(10)	64(6)
C(12)	−1521(16)	1474(15)	497(9)	64(6)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Bond Lengths (Å)

Pb−C(1)	2.350(7)	Pb−C(2)	2.243(10)
Pb−C(3)	2.233(14)	Pb−PbA	2.968(2)
Si(1)−C(1)	1.889(10)	Si(1)−C(7)	1.879(13)
Si(1)−C(8)	1.867(10)	Si(1)−C(9)	1.876(15)
Si(2)−C(1)	1.889(9)	Si(2)−C(4)	1.872(13)
Si(2)−C(5)	1.876(10)	Si(2)−C(6)	1.871(13)
Si(3)−C(1)	1.902(11)	Si(3)−C(10)	1.873(11)
Si(3)−C(11)	1.887(14)	Si(3)−C(12)	1.880(11)

Table 4. Bond Angles (deg)

C(1)−Pb−C(2)	107.4(3)	C(1)−Pb−C(3)	107.2(4)
C(2)−Pb−C(3)	103.5(5)	C(1)−Pb−PbA	119.2(3)
C(2)−Pb−PbA	109.5(3)	C(3)−Pb−PbA	108.9(3)
C(1)−Si(1)−C(7)	114.4(6)	C(1)−Si(1)−C(8)	112.9(5)
C(7)−Si(1)−C(8)	104.4(5)	C(1)−Si(1)−C(9)	113.0(5)
C(7)−Si(1)−C(9)	105.1(6)	C(8)−Si(1)−C(9)	106.1(6)
C(1)−Si(2)−C(4)	113.4(5)	C(1)−Si(2)−C(5)	113.1(5)
C(4)−Si(2)−C(5)	105.8(5)	C(1)−Si(2)−C(6)	112.3(5)
C(4)−Si(2)−C(6)	106.1(6)	C(5)−Si(2)−C(6)	105.5(5)
C(1)−Si(3)−C(10)	114.7(5)	C(1)−Si(3)−C(11)	114.3(6)
C(10)−Si(3)−C(11)	104.5(6)	C(1)−Si(3)−C(12)	111.7(6)
C(10)−Si(3)−C(12)	106.4(5)	C(11)−Si(3)−C(12)	104.4(6)
Pb−C(1)−Si(1)	107.3(4)	Pb−C(1)−Si(2)	105.9(4)
Si(1)−C(1)−Si(2)	112.7(5)	Pb−C(1)−Si(3)	107.1(4)
Si(1)−C(1)−Si(3)	111.4(5)	Si(2)−C(1)−Si(3)	112.0(5)

was obtained for the transfer of the trisyl group to tin, i.e. no formation of $\{(Me_3Si)_3C\}Ph_3Sn$. Significant amounts of $(Me_3Si)_3CH$ were also obtained, reminiscent of the thermal decomposition of both germyl and stannyl trisyl derivatives (Tsi)Me_3E, E = Ge, Sn, reported by Glockling et al. from which $(Me_3Si)_3CH$ was the only product isolated.[9]

The formation of Ph_3MeSn, a transmetalation reaction illustrated in eq 2, is more problematical. In reactions designed to form simple Pb−Sn bonds via salt-elimination reactions, e.g. $Ph_3PbSnMe_2Cl$, $(Mes)_3PbSnMe_3$ (Mes = mesityl), we have isolated good to moderate yields of the aryl transfer products $PhMe_2SnCl$ and (Mes)Me_3Sn, respectively, as the sole reaction products, e.g. eq 4.[10]

$$[Ph_3Pb]^-Li^+ + Me_2SnCl_2 \rightarrow PhMe_2SnCl \qquad (4)$$

These observations, coupled with the result described in eq 2, suggest that Pb−Sn bonds, when formed, are very labile with respect to 1,2-aryl (alkyl) migrations from Pb to Sn. Therefore, while we have no direct evidence for the transient presence of $\{(Me_3Si)_3C\}Me_2PbSnPh_3$, we suggest that a 1,2-Me migration occurs subsequent to Pb−Sn bond formation, eq 5.

$$\{(Me_3Si)_3C\}Me_2PbSnPh_3 \rightarrow Ph_3MeSn \qquad (5)$$

This chemistry is reminiscent of the 1,2-aryl- and alkyl-migration reactions that are well-established to occur upon thermal, or photochemical, treatment of transition metal complexes of lead, e.g. eq 6.[11]

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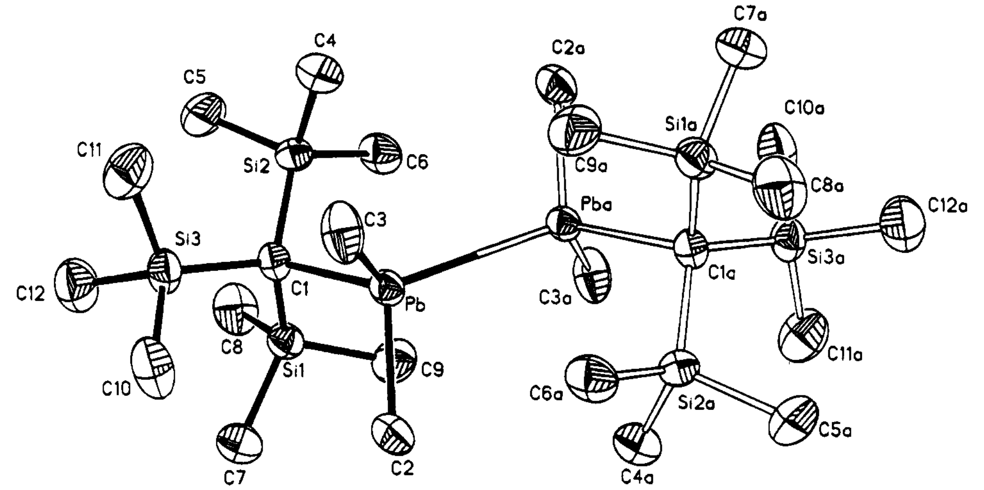

Figure 1. Structure of **1**.

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}PbR_3 \xrightarrow[R = Me, Ph]{\Delta, h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}R + {}^1/_2R_4Pb \quad (6)$$

In general it seems that lead−metal bonds are very prone to such 1,2-group migrations, presumably accompanied by elimination of diaryl(alkyl)lead. Only the hexaaryl systems (Ar_6-SnPb) are reported as stable well-characterized compounds containing lead−tin bonds.[4,6] Furthermore, hexaphenyldiplumbane is reported to be thermally unstable with respect to elimination of Ph_2Pb and formation of Ph_4Pb.[12]

Compound **1** is a bright orange compound, λ_{max} (hexane) = 341 nm, presumably due to a low energy $\sigma \rightarrow \sigma^*$ transition, reminiscent of those observed for transition metal−metal bonds.[13] The chemistry of such bimetallic transition metal complexes is dominated by their tendency to undergo photochemical cleavage of the metal−metal bond. We have subjected **1** to such conditions, irradiating both with a low pressure mercury lamp and with ambient laboratory light since the λ_{max} is close to the visible region. In both cases decoloration of the solutions occurred leading to products that, although we have no direct ESR evidence, clearly suggest radical formation. The fate of these radicals depends upon the environment, and in CCl_4 high yields of $\{(Me_3Si)_3C\}Me_2PbCl$ were obtained, eq 7.

$$\mathbf{1} \xrightarrow{h\nu} [\{(Me_3Si)_3C\}Me_2Pb] \xrightarrow{CCl_4} \{(Me_3Si)_3C\}Me_2PbCl + \text{insoluble material} \quad (7)$$

Other reactions also occur, since as with the thermal treatment of **1**, small yields of $\{(Me_3Si)_3C\}Me_3Pb$ were also obtained from the photochemical treatment, both with ultraviolet irradiation and laboratory lighting. Irradiation in the presence of propargyl bromide led to the formation of $\{(Me_3Si)_3C\}Me_2PbBr$.

Crystal Structure of 1. The structure of **1** is presented in Figure 1, and the bond lengths and angles are reported in Tables 3 and 4. Of note is the Pb−Pb bond length of 2.968(2)Å and Pb−C bond lengths of 2.350(7)Å (Pb−trisyl) and 2.233(14) and 2.243(10) Å (Pb−methyl). These lengths are all longer than those reported in the literature where comparison is possible. There are 6 related organometallic Pb−Pb bonded compounds, $R_3Pb{-}PbR_3$, whose single crystal structures have been determined. The Pb−Pb bond lengths range from 2.839(2), 2.847(2), and 2.846(2) Å for the various forms of $Ph_3PbPbPh_3$[1] to 2.911(1) Å for 1,2-bis{tris(trimethylsilyl)silyl}tetraphenyldilead, $[\{(Me_3Si)_3Si\}Ph_2Pb]_2$,[7] and 2.908 Å for $[\{(Me_3Si)_3C\}Ph_2\text{-}PbPbPh_3$, **2**.[5] Since **1** is the first structure to contain lead−methyl groups the $Pb{-}C_{methyl}$ bond length cannot be compared; however, the $Pb{-}C_{trisyl}$ bond length of 2.350(7) Å in **1** is decidedly longer than that of 2.280(10) Å reported for **2**, although the large standard deviations for both complexes does not permit a detailed comparison. Taken together these data suggest that increasing steric bulk at the Pb atoms significantly contributes to an elongation of the various lead bonds, and our reported Pb−Pb bond length of 2.968(2) Å fits into this trend with the longest reported value by virtue of the two bulky trisyl groups. The bond angles associated with the structure of **1** are in accord with expectation exhibiting a $C_{methyl}{-}Pb{-}C_{methyl}$ angle contraction from the tetrahedral angle to 103.5(5)°, and concomitant increase of the other angles at Pb, especially that of the $C_{trisyl}{-}Pb{-}Pb$ angle of 119.2(3)°.

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Supplementary Material Available: Tables of anisotropic displacement coefficients ($Å^2 \times 10^3$) and H-atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($Å^2 \times 10^3$) (2 pages). Ordering information is given on any current masthead page.

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