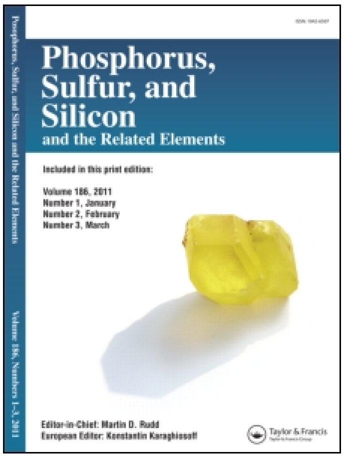

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TRIMESITYLLEAD DERIVATIVES, Mes_3PbR, R = Me, CH_2Ph, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, Me_3Ge INCLUDING STRUCTURAL ANALYSIS OF MONOMERIC Mes_3PbCl AND ATTEMPTED FORMATION OF $Mes_3PbSnMe_3$

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Trimesityllead-R derivatives (R = methyl, benzyl, allyl, propargyl, and trimethylgermyl) have been synthesized from the salt elimination reaction between trimesitylleadlithium and RX. The germanium derivative is the first alkylgermanium derivative of lead. The spectroscopic properties of the compounds are reported, along with the single crystal structure of trimesityllead chloride which reveals that the Pb atom has a distorted tetrahedral coördination with an average Pb-C bond length of 2.234Å, and C-Pb-Cl bond angles much smaller than the C-Pb-C angles. This is the first structurally characterized monomeric organolead halide. The Pb-Cl bond length of 2.61Å is considerably shorter than the Pb-Cl bond length found in other oligomeric or polymeric organolead chlorides and significantly longer than recent theoretical estimations. Attempts to synthesize the trimethyltin derivative resulted in migration of a mesityl group to form mesityltrimethyltin as the only isolated compound.

Key words: Trimesitylleadlithium; group 14 derivatives; chloride structure.

INTRODUCTION

The mesityl group (Mes) has been well used in silicon and germanium chemistry to stabilize and isolate new types of compounds, e.g. disilenes and digermenes.[1,2,3] In contrast there are few reports of mesityl derivatives of lead. Gilman and co-workers briefly mentioned tetramesityllead in 1939, and much later Glockling and coworkers reported the formation of trimesitylleadbromide and

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Happy 60th birthday Alan.

dimesityleaddibromide;[4,5] hexamesityldilead has been synthesized and recently its solid-state ^{207}Pb NMR was studied.[6] The utility of the mesityl group in lead may be illustrated by our recent isolation of the first acylplumbanes, Mes_3PbCOR, R = Me, Ph.[7] We now report the use of the trimesityllead group to form standard organolead compounds, including the first alkylgermyl derivative of lead, $Mes_3PbGeMe_3$, the first monomeric chlorolead compound, Mes_3PbCl, and attempts to prepare an alkyltin derivative, $Mes_3PbSnMe_3$.

RESULTS AND DISCUSSION

Hexamesityldilead was readily cleaved by lithium in a THF solution to provide a charcoal-grey slurry of $[(Mes)_3Pb]^-Li^+$ that was used for derivatization via addition of organic and organometallic halides, eq 1, 2.

$$Mes_3PbPbMes_3 + 2\ Li \longrightarrow 2\ [Mes_3Pb]^-Li^+ \qquad (1)$$

$$Mes_3PbLi + R\text{-}X \xrightarrow[THF]{-78^\circ C} Mes_3PbR \qquad (2)$$

$$(R = -CH_3,\ -CH_2C_6H_5, -CH_2\text{-}CH{=}CH_2, -CH_2C{\equiv}CH,\ -GeMe_3);\ (X = Cl,\ Br)$$

When organic iodides were used in place of the chlorides or bromides, a significant halogen metal exchange occurred that resulted in a mixture of halogenation and alkylation reactions. In the case of MeI the two products were observed in a 3:1 ratio, eq 3.

$$2\ Mes_3PbLi + 2\ MeI \xrightarrow{-78^\circ C} Mes_3PbI\ (75\%) + Mes_3PbMe\ (25\%) \qquad (3)$$

The organolead derivatives are stable to air and moisture; however, while the germyl derivative $Mes_3Pb\text{-}GeMe_3$ was stable indefinitely at -25°C in the solid state, or in hydrocarbon solution for short periods of time, at room temperature it slowly decomposed to a yellow material insoluble in common organic solvents. Due to this limited stability we were unable to obtain satisfactory elemental analyses on this material; however, all the spectroscopic data are in accord with the proposed structure and the compound represents the first Pb-Ge bonded compound having alkyl substituents at germanium. In general lead compounds of both Ge and Sn are only reported with aryl substituents on both the lead and other group 14 metal(loid).[8]

Attempts to synthesize the tin analog, $Mes_3PbSnMe_3$, were not successful; the reaction between Mes_3PbLi and Me_3SnCl led to the high yield formation of mesityltrimethyltin, eq 4.

$$[Mes_3Pb]^-Li^+ + Me_3SnCl \longrightarrow MesSnMe_3 \quad (4)$$

This chemistry is reminiscent of the decomposition of trialkyl- and triaryllead derivatives of the transition metals. In these systems a 1,2-alkyl(aryl) shift from lead to the transition metal resulted in the formation of transition metal alkyl or aryl complexes, e.g. eq 5.[9]

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2PbMe_3 \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)Fe(CO)_2Me + PbMe_2 \quad (5)$$

The spectroscopic data of the new compounds, recorded in Table 1, confirm their structural assignments. The ^{207}Pb NMR of the organic compounds of $(Mes)_3Pb$ exhibited a resonance in the range -278 to -227 ppm. Changing the organic substituent from methyl to benzyl, allyl or propargyl did not produce significant changes in the chemical shift. Replacement of the organic groups by the Me_3Ge substituent resulted in a high frequency shift to -381 ppm. Dräger et al have reported ^{207}Pb chemical shifts -271 ppm ($Ph_3Pb\text{-}GePh_3$) and at -265 ppm ($o\text{-}Tol_3Pb\text{-}GePh_3$).[8b,d]

Structure of Trimesitylleadchloride

There has been some recent interest in establishing a sound basis set for Pb that would permit *ab initio* calculations on lead compounds to become as routine, and reliable, as those for C, Si etc.[10] A recent study made predictions concerning the Pb-Cl bond length, however, there were no monomeric Pb-Cl structures reported in the literature for comparison, most examples being oligomeric with chlorine bridges betweeen lead atoms of adjacent molecules.[11] Hoping that the sterically encumbered $(Mes)_3PbCl$ might not be able to exhibit such interactions we have determined the single crystal structure of this compound. The molecule does indeed exhibit monomeric behaviour, and the structure is illustrated in Fig. 1. Selected bond lengths and angles are presented in Table 2.

The structure, with a molecule of solvent of crystallization, contains two independent molecules in the asymmetric unit which are identical in bond lengths and angles but have different conformations. In one of the molecules, the chlorine atom is pointing towards one of the mesityl groups while in the other molecule, the chlorine atom is directed away from one of the mesityl groups. The lead atom has distorted tetrahedral coördination, and is sterically protected by the large mesityl groups with an average Pb-C bond length of 2.234Å. These Pb-C bonds are significantly longer than the Pb-C bonds observed in Ph_3PbCl, Ph_3PbBr, and Ph_3PbOH which average 2.111Å.[11] Such elongation of bond lengths is to be expected on the basis of the steric demand of the mesityl group. For example the Si-C(*ipso*) bond lengths in mesitylsilicon compounds are also significantly longer than the corresponding bond in phenyl analogs.[12]

A stereoview of the unit cell is presented in Figure 2. The C-Pb-C bond angles (average 116°) are much wider than the C-Pb-Cl bond angles (average 100°). Recently, in the *ab initio* study noted above, Kaupp and Schleyer reported that the bond angles in the compounds with different groups, R_nPbX_{4-n} (n = 1-3) deviated widely from 109.5°, and the angle between the electronegative substituents were smaller, and those between more electropositive groups were larger than, the tetrahedral angle. The Pb-Cl bond length of 2.612(5)Å is significantly shorter than the bond lengths found in oligomeric Ph_3PbCl and Ph_2PbCl_2, 2.706(1)Å and 2.795(6)Å.[11b,c] The value is however significantly **longer** than those predicted by the *ab initio* calculation for a series of simple hydridolead chloride systems, $H_{4-n}PbCl_n$, which were in the range of 2.381Å to 2.466Å.

EXPERIMENTAL

All manipulations were carried out in dry, oxygen-free solvents. Hexamesityldilead was prepared according to published procedure.[6] Trimesityllead chloride was prepared from hexamesityldilead and ammonium hexachloroplumbate in THF by the reported method.[13] All organic halides were purchased from Aldrich Chemicals;

trimethylbromogermane was purchased from Gelest Inc.; and elemental analyses were performed by Galbraith Laboratories. Typical syntheses are provided to illustrate the general procedure for all compounds reported.

Synthesis of trimesitylleadlithium

A Schlenk flask was charged with 50 mL of a THF solution of hexamesityldilead, 2g (1.77 mmol), and 0.5 g of finely cut lithium. The mixture was magnetically stirred for 15 h at room temperature after which time the color of the mixture had changed from light yellow to a characteristic dark grey slurry.

Synthesis of $(Mes)_3PbCH_2Ph$.

A 250 mL three-necked flask equipped with magnetic stirring bar and addition funnel was charged with 0.44 g (3.54 mmol) of benzyl chloride and 30 mL of THF. The solution was cooled to -78°C with a liquid N_2/acetone slurry. The trimesitylleadlithium solution prepared above was transferred via a cannula to the addition funnel and added dropwise. Upon complete addition, the mixture was stirred at low temperature for 30 min and then the solution was slowly permitted to warm to room temperature and stirred for 15 h. The solvent was removed on a rotary evaporator and 50 mL of hexane was added to dissolve the product. The hexane solution was filtered, and the solvent removed *in vacuo* to yield a white solid which was recrystallized from ethanol, 1.04 g (1.58 mmole, 45%). Analytical and spectral data are recorded in Table 1.

Attempted synthesis of $Mes_3PbSnMe_3$

The reaction between Mes_3PbLi and Me_3SnCl was performed in the manner described above. Subsequent to removal of the hexane solvent, after extraction to remove salts, a white solid residue was obtained. Recrystallization from hexane resulted in a 50% yield of $MesSnMe_3$, ^{119}Sn NMR ($CDCl_3$) -47.6 ppm (lit. -50.0 ppm in CH_2Cl_2).[14]

Structure determination and refinement of Mes_3PbCl

Crystals suitable for X-ray diffraction were grown by the slowevaporation of the solvent from a saturated solution of $(Mes)_3PbCl$

in chloroform. A colorless crystal (approximate size 0.24 x 0.16 x 0.30) was mounted on a R3m/V Nicolet four circle diffractometer. Unit cell parameters were determined from 22 reflections ($15 < 2\Theta < 30^{o}$) and refined by the least squares method. Intensities were measured with graphite monochromatized MoK_{α} radiation using the ω-scan technique with α scan width of 1.20^{o} and variable scan speed between 3 and 20 ^{o}/min. 5953 reflections were measured of which 5350 were independent reflections and 3931 were considered observed [$F > 2.0\sigma(F)$]. Three standard reflections were measured every 97 reflections and showed no significant decay. Lorentz polarization corrections were made and a face indexed numerical adsorption correction was applied using the following faces and corresponding distances between them: 100, 100, d = 0.30 mm; 010, 010, d = 0.16 mm; 001, 001, d = 0.08 mm. This gave a Min/Max transmission ratio of 0.379/0.620.

The structure was solved and refined using the SHELXTL-PLUS software package on a Microvax II computer. The function minimized was $\Sigma\omega(F_o-F_c)^2$ with $\omega^{-1} = \sigma^2(F) + 0.0028F^2$. The final R value was 7.41% and the weighted value was 8.79. No effort was made to improve the weighting scheme to get wR < R. Complete bond lengths, bond angles, atomic coördinates, anisotropic displacement coefficients, observed and calculated structure factors are available from the authors.

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TABLE 1

Analytical and NMR spectral data ($CDCl_3$) of new compounds

Compd.	C Fnd(Calcd);H Fnd(Calcd)	m.pt. °C	% Yld
Mes_3PbCH_3	56.55(58.10);6.24(6.27)	149-150	48
^{1}H	1.61 (s, 3H, ^{2}J = 56Hz, $PbCH_3$); 2.57, 2.55 (s, 27H, o, p-CH_3); 7.18 (s, 6H, ^{4}J = 33Hz)		
^{13}C	11.5 (CH_3); 20.9 (p-CH_3); 26.0 (o-CH_3); 128.3, 137.4, 144.3, 154.2 (Ph) ^{207}Pb -278.6		
$Mes_3PbCH_2C_6H_5$	61.83(62.36);5.77(6.15)	119	45
^{1}H	2.31, 2.50 (s, 27H, o, p-CH_3); 3.57 (s, 2H, ^{2}J = 58Hz, CH_2); 6.92 (s, 6H, C_6H_2); 7.05 (m, 5H, C_6H_5) ^{207}Pb -227.3		
$Mes_3PbCH_2CH{=}CH_2$	58.79(59.57);5.81(6.33)	123-124	56
^{1}H	2.37, 2.48 (s, 27H, o, p-CH_3); 3.06 (d, 2H, J=8Hz, CH_2); 5.04 (dd) 4.99 (s), 4.81 (dd, J = 8Hz, CH_2); 6.05 - 6.18 (m, 1H, J= 8 Hz, CH); 7.09 (s, 6H, ^{4}J = 32Hz, C_6H_2)		
^{13}C	21.2 (p-CH_3); 26.5 (o-CH_3); 36.9 (CH_2); 113.8 ($CH{=}\underline{CH_2}$); 128.8, 137.8, 144.5, 156.5 (C_6H_2); 137.3 ($\underline{CH}{=}CH_2$) ^{207}Pb -237.1		
$MesPbCH_2C{\equiv}CH$	59.28(59.77);6.15(6.02)	138(d)	52
^{1}H	1.79 (t, 2H, J = 6Hz, CH_2); 2.31 (s, 27H, o-, p-CH_3); 2.47 (d, 1H, J = 6Hz, C≡CH); 6.96 (s, 6H, ^{4}J = 35 Hz, C_6H_2)		
^{13}C	13.8 (CH_2); 20.9 (p-CH_3); 25.9 (o-CH_3); 69.1, 85.6 (C≡C); 128.6, 137.7, 144.1, 155.8 (C_6H_2) ^{207}Pb -230.5		
$Mes_3Pb{-}GeMe_3$ (C_6D_6)		196-200	36
^{1}H	0.83 (s, 9H, ^{3}J=48 Hz, CH_3); 2.38, 2.61 (s, 27H, o, p-CH_3); 7.11 (s, 6H, C_6H_2)		
^{13}C	4.0 (CH_3); 20.9 (p-CH_3); 27.4 (o-CH_3); 128.8, 137.2, 144.7, 154.9 (C_6H_2) ^{207}Pb -381.5		
Mes_3PbCl			
^{1}H	2.25, 2.38 (s, 27H, o, p-CH_3); 6.97 (s, 6H, ^{4}J = 49 Hz)		
^{13}C	21.0 (p-CH_3); 25.0 (o-CH_3); 129.9, 139.2, 143.5, 160.8 (C_6H_2)		
^{207}Pb	-41.3; [-61.3 (C_6D_6)]		

TABLE 2

Selected bond angles (°) and lengths (Å) for Mes_3PbCl

Pb-Cl	2.612(5)	Pb'-Cl'	2.619(5)
Pb-C(10)	2.254(23)	Pb'-C(10')	2.163(26)
Pb-C(1)	2.226(23)	Pb'-C(1')	2.242(25)
Pb-C(19)	2.223(22)	Pb'-C(19')	2.221(20)
Cl-Pb-C(1)	101.3(7)	Cl'-Pb'-C(1')	102.8(7)
Cl-Pb-C(19)	97.0(6)	Cl'-Pb'-C(19')	97.5(6)
C(1)-Pb-(C10)	115.1(9)	C(1')-Pb-C(10')	116.3(10)
C(1)-Pb-C(19)	120.7(8)	C(1')-Pb-C(19')	115.5(9)

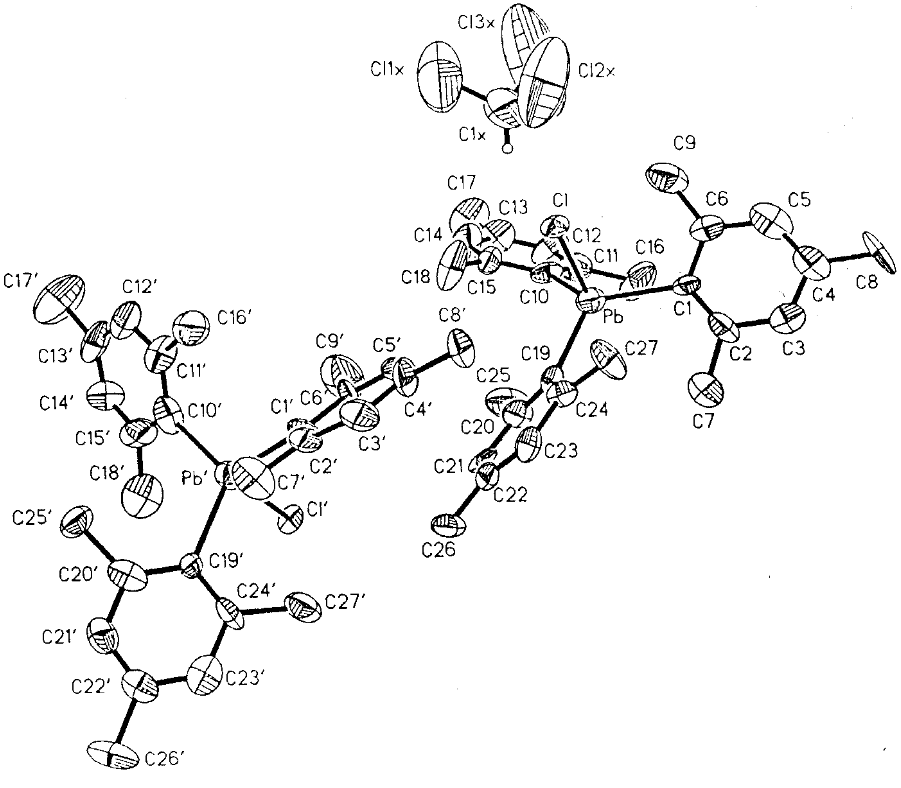

FIGURE 1 Crystal structure of Mes_3PbCl, space group $P\bar{1}$, a = 8.339(3)Å, b = 16.993(7)Å, c = 19.685(7)Å, α = 94.82(3)°, β = 96.74(3)°, γ = 91.63(3)°, Z = 2.

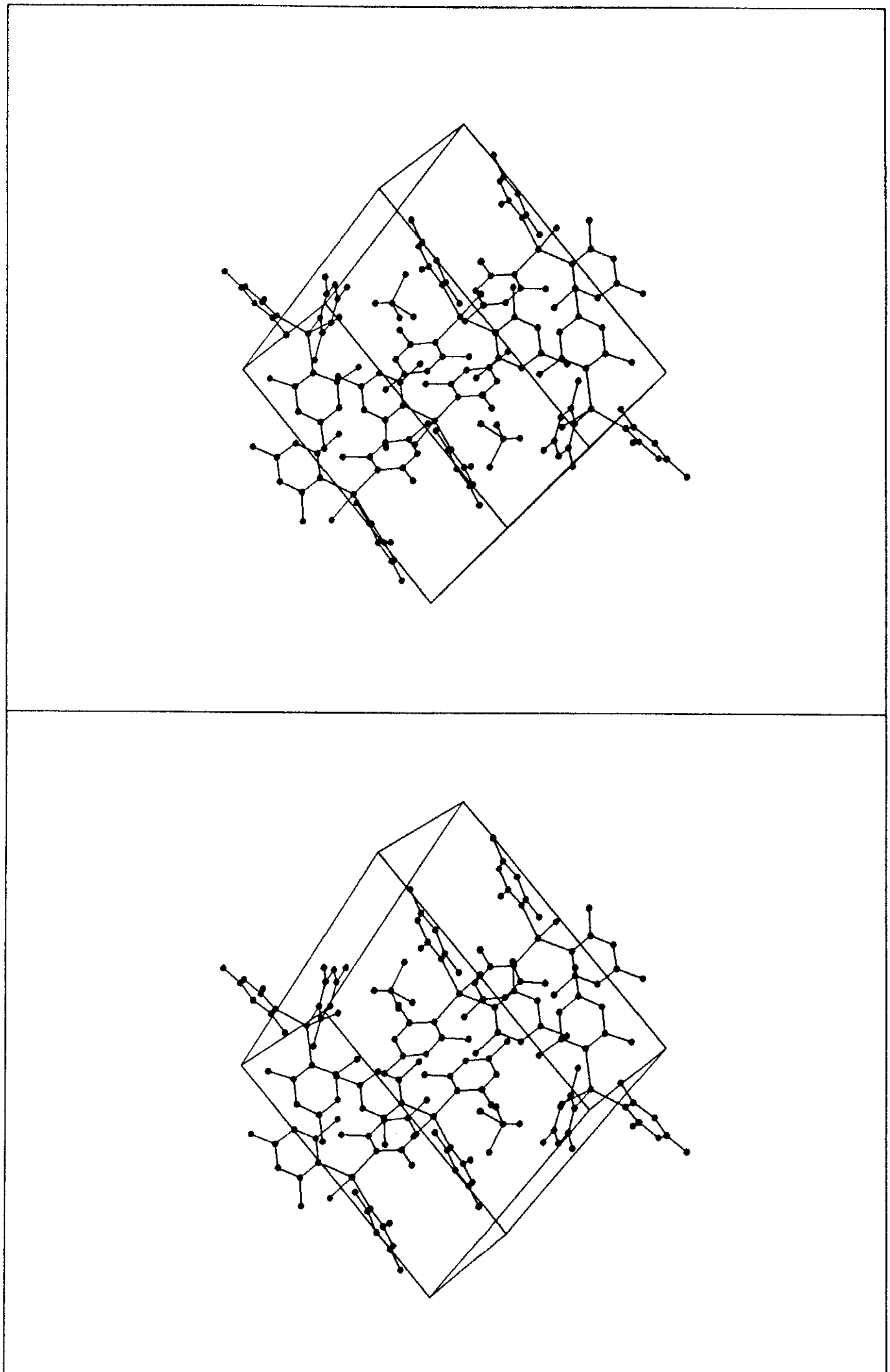

FIGURE 2 Stereoview of Mes_3PbCl