Crystal and Molecular Structure of Pentaphenyl[tris(trimethylsilyl)methyl]diplumbane†

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The reaction of $PbPh_2Cl_2$ with two equivalents of $Li[C(SiMe_3)_3]$ gave the diplumbane, $Ph_3Pb-Pb[C(SiMe_3)_3]Ph_2$ instead of the expected $Pb[C(SiMe_3)_3]_2Ph_2$. A crystal-structure determination confirmed the presence of a Pb–Pb bond and the arrangement of the six substituents suggested that considerable steric strain between the $C(SiMe_3)_3$ group and the phenyls is present. Force-field calculations indicate that the structure of the expected product, $Pb[C(SiMe_3)_3]_2Ph_2$, may be severely distorted due to the presence of the two bulky groups. Possible steps in the formation pathway leading to the observed product, involving a phenyl group migration and radical coupling to give a Pb–Pb bond are discussed.

A recent report on the reaction of diphenyllead(IV) dichloride with two equivalents of $Li[Si(SiMe_3)_3](thf)_3$ (thf = tetrahydrofuran) showed that both the expected disubstituted plumbane, $Pb[Si(SiMe_3)_3]_2Ph_2$, and the diplumbane, $[\{Pb[Si(SiMe_3)_3]Ph_2\}_2]$, were isolated.[1] NMR spectroscopic experiments on solutions of the individual compounds showed the former to be stable in solution while the latter decomposed over a period of hours. In the solid state, $[\{Pb[Si(SiMe_3)_3]Ph_2\}_2]$ was sufficiently stable to permit a crystal-structure determination that confirmed the presence of the Pb–Pb bond and revealed structural parameters resembling those of Pb_2Ph_6. A pathway to the diplumbane structure involving reduction of the probable intermediate $Pb[Si(SiMe_3)_3]Ph_2Cl$ to give $^{\bullet}Pb[Si(SiMe_3)_3]Ph_2$ radicals which could couple to form the Pb–Pb link was proposed.

The outcome of the aforementioned reaction and our interest in the effects of very bulky substituents on the stability of main group compounds[2,3] led us to investigate the reaction of $PbPh_2Cl_2$ with $Li[C(SiMe_3)_3]$.

Experimental

Materials.—Diphenyllead(IV) dichloride was obtained from Organometallics and tris(trimethylsilyl)methane from Aldrich. Tris(trimethylsilyl)methyllithium was prepared as described in the literature.[4] Diethyl ether and tetrahydrofuran were dried by distillation from $LiAlH_4$; benzene was distilled from CaH_2.

Procedures.—All reactions were conducted using Schlenk techniques under dry argon as described elsewhere.[1]

Preparation of 1,1,1,2,2-*Pentaphenyl*-2-[*tris*(*trimethylsilyl*)*methyl*]*diplumbane.*—A solution of $Li[C(SiMe_3)_3]$ was prepared[4] from $CH(SiMe_3)_3$ (2.5 g, 10.74 mmol) in thf (20 cm^3) and LiMe (9.0 cm^3, 1.56 mol dm^{-3}; 14.0 mmol in diethyl ether). After reflux, volatiles were removed *in vacuo* and diethyl ether (75 cm^3) was added to the residue, forming the lithium reagent solution upon stirring. This solution was added dropwise to a diethyl ether suspension of $PbPh_2Cl_2$ (2.320 g, 5.366 mmol) held at −78 °C. The reaction mixture, which became yellow during the addition, was stirred for 6 h at −78 °C, allowed to warm to ambient temperature and stirred for another 18 h. The final orange-yellow mixture was filtered, the filtrate concentrated and stored at 4 °C for two weeks. Yellow crude product was isolated from the mother-liquor, washed three times with small volumes of benzene and dried *in vacuo* overnight. The product used for the structure determination and elemental analysis was purified by recrystallization from benzene (three times) giving yellow crystals (0.82 g, 29%), m.p. 143 °C (turns green at 134 °C) (Found: C, 46.45; H, 5.00. Calc. for $C_{40}H_{52}Pb_2Si_3$: C, 46.55; H, 5.05%). NMR (C_6D_6): ^1H, δ 0.294 (s, 27 H, $SiMe_3$) and 7.03–8.15 (m, 25 H, C_6H_5); ^{13}C, δ 6.263 ($SiMe_3$), 129.77, 129.93, 138.48, 138.71, 156.17 and 160.61 (C_6H_5). UV/VIS (C_6H_6): λ 331 nm (ε 3.41 × 10^5 dm^3 mol^{-1} cm^{-1}). IR (Nujol): 3000w, 2620vw, 1910w, 1840w, 1785w, 1555m, 1430s, 1330w, 1295m, 1260s, 1195w, 1165w, 1065m, 1026vs, 1010s, 860vs (br), 796(sh), 746vs, 720s, 675m, 630w, 600m and 470vs cm^{-1}. The ^1H NMR spectrum (C_6D_6) of the reaction mixture after crystallization of the product exhibited two notable resonances at δ 0.135, identified as $CH(SiMe_3)_3$ by comparison with an authentic sample, and 0.265 (discussed in the following) along with smaller signals at δ 0.274, 0.228 {probably $C(SiMe_3)_4$ [δ($CDCl_3$) 0.24]}, 0.116 and 0.091.

Structure of 1,1,1,2,2-*Pentaphenyl*-2-[*tris*(*trimethylsilyl*)*methyl*]*diplumbane.*—Pale yellow plates of $C_{40}H_{52}Pb_2Si_3$ (M = 1031.52) crystallize in the primitive, triclinic space group $P\bar{1}$ (no. 2), a = 10.749(2), b = 11.644(2), c = 19.103(10) Å, α = 76.32(3), β = 84.37(3), γ = 63.65(1)°, U = 2081.52 Å^3, Z = 2, D_c = 1.646 g cm^{-3}, $F(000)$ = 996, T = 289 K. A total of 4037 data were collected with an Enraf-Nonius CAD4 diffractometer [λ(Mo-Kα)] in the interval $4.0 \leqslant 2\theta \leqslant 50.0°$ of which 2750 were unique and had intensities greater than $3\sigma(I)$. The data were corrected for absorption using empirical psi-scan curves (six reflections, μ = 82.466 cm^{-1}); the relative transmission coefficients ranged from 0.1529 to 0.9999. All data processing was carried out using the standard Enraf-Nonius software package. Final $R(F)$ and $R'(F)$ factors were, respectively, 0.0497 and 0.0509, at which point shift/error was less than 0.1 and the residual density was *ca.* 1 e Å^{-3} or less. Atomic coordinates are in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

The monosubstituted triphenylplumbane, $Pb[C(SiMe_3)_3]Ph_3$, has been prepared by other investigators from $PbPh_3Cl$ and $Li[C(SiMe_3)_3]$[5,6] but the more crowded $Pb[C(SiMe_3)_3]_2Ph_2$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Positional parameters and their estimated standard deviations (e.s.d.s) in parentheses for $Ph_3Pb–Pb[C(SiMe_3)_3]Ph_2$

Atom	*x*	*y*	*z*
Pb(1)	0.275 49(7)	0.195 76(7)	0.249 76(5)
Pb(2)	0.010 94(7)	0.428 36(7)	0.228 57(5)
Si(1)	0.119 3(7)	−0.003 5(7)	0.264 7(5)
Si(2)	0.277 8(7)	−0.028 3(7)	0.400 0(4)
Si(3)	0.441 0(7)	−0.137 1(7)	0.268 1(5)
C(1)	0.276(2)	−0.003(2)	0.300(1)
C(2)	−0.042(2)	0.094(2)	0.316(2)
C(3)	0.072(2)	0.073(2)	0.172(1)
C(4)	0.128(2)	−0.171(2)	0.278(1)
C(5)	0.165(2)	0.122(2)	0.431(1)
C(6)	0.211(2)	−0.153(2)	0.449(1)
C(7)	0.466(2)	−0.087(2)	0.434(1)
C(8)	0.416(3)	−0.151(2)	0.170(1)
C(9)	0.482(2)	−0.306(2)	0.327(2)
C(10)	0.600(2)	−0.115(3)	0.267(2)
C(11)	0.391(2)	0.261(2)	0.315(1)
C(12)	0.534(2)	0.196(2)	0.329(1)
C(13)	0.589(2)	0.251(2)	0.369(1)
C(14)	0.511(2)	0.366(2)	0.389(2)
C(15)	0.374(2)	0.427(2)	0.378(1)
C(16)	0.315(2)	0.369(2)	0.337(1)
C(17)	0.379(2)	0.198(2)	0.142(1)
C(18)	0.510(2)	0.196(2)	0.137(1)
C(19)	0.587(2)	0.194(3)	0.077(2)
C(20)	0.537(2)	0.182(2)	0.019(2)
C(21)	0.403(3)	0.196(3)	0.017(1)
C(22)	0.320(2)	0.203(2)	0.080(1)
C(23)	−0.076(2)	0.502(2)	0.329(1)
C(24)	−0.060(2)	0.609(2)	0.341(1)
C(25)	−0.099(2)	0.654(2)	0.401(1)
C(26)	−0.166(2)	0.598(3)	0.450(1)
C(27)	−0.186(2)	0.493(2)	0.442(1)
C(28)	−0.136(2)	0.440(2)	0.382(1)
C(29)	−0.166(2)	0.437(2)	0.172(1)
C(30)	−0.284(2)	0.439(2)	0.212(1)
C(31)	−0.397(2)	0.454(2)	0.174(1)
C(32)	−0.388(2)	0.459(2)	0.102(2)
C(33)	−0.280(2)	0.461(2)	0.063(1)
C(34)	−0.162(2)	0.445(2)	0.097(1)
C(35)	0.052(2)	0.591(2)	0.159(1)
C(36)	0.182(2)	0.585(2)	0.144(1)
C(37)	0.200(2)	0.690(2)	0.101(2)
C(38)	0.096(2)	0.795(2)	0.069(1)
C(39)	−0.034(2)	0.807(2)	0.083(2)
C(40)	−0.054(2)	0.700(2)	0.128(2)

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $Ph_3Pb–Pb[C(SiMe_3)_3]Ph_2$

Pb(1)–Pb(2)	2.908(1)	Pb(2)–C(23)	2.232(11)	Si(1)–C(1)	1.880(10)	Si(1)–C(1)	1.880(10)
Pb(1)–C(1)	2.280(10)	Pb(2)–C(29)	2.233(11)	Si(2)–C(1)	1.864(11)	Si(1)–C(2)	1.923(14)
Pb(1)–C(11)	2.296(11)	Pb(2)–C(35)	2.240(11)	Si(3)–C(1)	1.934(11)	Si(1)–C(3)	1.797(14)
Pb(1)–C(17)	2.249(11)					Si(1)–C(4)	1.869(12)
Pb(2)–Pb(1)–C(1)	118.6(2)	Pb(1)–Pb(2)–C(23)	114.1(3)	Pb(1)–C(1)–Si(3)	108.0(4)	C(1)–Si(1)–C(3)	117.6(5)
Pb(2)–Pb(1)–C(11)	99.6(3)	Pb(1)–Pb(2)–C(29)	121.2(3)	Si(1)–C(1)–Si(2)	113.0(5)	C(1)–Si(1)–C(4)	113.7(5)
Pb(2)–Pb(1)–C(17)	105.5(3)	Pb(1)–Pb(2)–C(35)	106.7(4)	Si(1)–C(1)–Si(3)	108.7(6)	C(2)–Si(1)–C(3)	103.4(6)
C(1)–Pb(1)–C(11)	115.0(4)	C(23)–Pb(2)–C(29)	106.6(5)	Si(2)–C(1)–Si(3)	110.1(5)	C(2)–Si(1)–C(4)	106.5(6)
C(1)–Pb(1)–C(17)	112.3(4)	C(23)–Pb(2)–C(35)	103.5(5)	C(1)–Si(1)–C(2)	108.8(6)	C(3)–Si(1)–C(4)	105.8(6)
C(11)–Pb(1)–C(17)	104.1(4)	Pb(1)–C(1)–Si(1)	107.7(4)	Si(2)–C(1)–Si(3)	110.1(5)		

has not yet been reported in the literature. In this investigation, the reaction of a suspension of $PbPh_2Cl_2$ in diethyl ether with two equivalents of $Li[C(SiMe_3)_3]$ was found to give a yellow thermochromic solid with the composition $Pb_2[C(SiMe_3)_3]Ph_5$ instead of the expected $Pb[C(SiMe_3)_3]_2Ph_2$. Although the yield was low (29%), the product was found to be reasonably stable in the solid state and in solution. A differential scanning calorimetry scan of the solid failed to show any appreciable enthalpy change on passing the yellow-to-green transition temperature of 134 °C. NMR spectra were consistent with an unsymmetrical diplumbane structure, $Ph_3Pb–Pb[C(SiMe_3)_3]Ph_2$ for the compound. Our earlier studies[1,3] of the reactions of MR_2Cl_2 (M = Ge, R = Me, Ph or Cl; M = Pb, R = Ph) with two equivalents of $Li[Si(SiMe_3)_3]$ identified symmetrical digermane and diplumbane products of the form $[(Me_3Si)_3Si]R_2M–MR_2[SiMe_3)_3]$; no unsymmetrical derivatives were detected among the products in those investigations. Unsymmetrical diplumbanes appear to be rare in the literature so an X-ray crystal-structure determination was carried out.

Crystal Structure of the Product.—The molecule (Fig. 1) consists of a central pair of lead atoms, of which one is bonded to three phenyl rings while the other contains two phenyl rings and a $C(SiMe_3)_3$ substituent. The Pb–Pb distance is 2.908(1) Å (Table 2) which is notably greater than that in Pb_2Ph_6 [2.844(4) Å].[7] Other elongated bonds include Pb–C(1) [2.280(10) Å], which is appreciably longer than that in $PbMe_4$ [2.238(9) Å],[8] and the Pb–C(phenyl) distances which average 2.250 Å, slightly exceeding those in Pb_2Ph_6 [2.22(2) Å].[7] In addition to elongated bonds, the diplumbane exhibited distortions in the bond angles including large Pb(2)–Pb(1)–C(1) and Pb(1)–Pb(2)–C(29) [118.6(2) and 121.2(3)°] and small Pb(2)–Pb(1)–C(11) and Pb(2)–Pb(1)–C(17) [99.6(3) and 105.5(3)°] angles. These distortions and others in the diplumbane structure

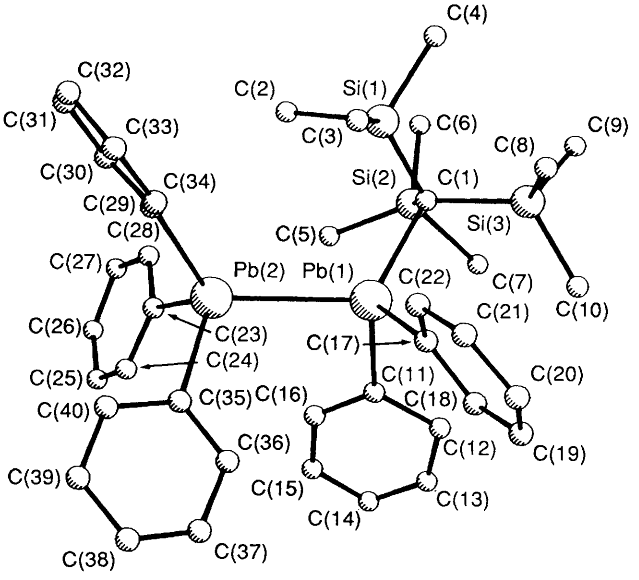

Fig. 1 Molecular structure of $Ph_3Pb–Pb[C(SiMe_3)_3]Ph_2$

are consistent with the presence of considerable steric interactions between the $C(SiMe_3)_3$ group and the phenyl rings on both lead atoms. The fact that the Pb–Pb and Pb–C(phenyl) distances are nearly as large as those in $[\{Pb[Si(SiMe_3)_3]Ph_2\}_2]$ [where there are bulky $Si(SiMe_3)_3$ groups on both lead atoms] suggests that the steric influence of the $C(SiMe_3)_3$ group is greater than that of its silyl analogue, as would be expected from cone angle considerations.[9]

Some insight into why $Pb[C(SiMe_3)_3]_2Ph_2$ was not obtained in this reaction comes from a molecular-mechanics calculation using CHEM3D+[10] on the plumbane (dihedral angles for which no literature values could be found were set to zero). Fig. 2 shows the minimized structure; the large C–Pb–C angle (134°) suggests that marked steric strain is unavoidable in the molecule. Although the MMX force field is not ideally suited for use with strained molecules, in our experience it usually *underestimates* the size of bond angles around crowded atoms. For example, CHEM3D+ predicted an Si–Sn–Si bond angle of *ca.* 123° for the highly strained molecule $Sn[Si(SiMe_3)_3]_2Cl_2$, whereas the measured[2] angle by X-ray diffraction was 142.5°. Thus, the substantial distortion of the central bond angles in the energy-minimized structure may indicate that the actual molecule is *even more distorted* and perhaps unstable owing to steric strain. In this regard, Glocking and Gowda[11] attempted to prepare $Pb[C(SiMe_3)_3]_2Me_2$ *via* the reaction of $PbMe_2Cl_2$ with excess $Li[C(SiMe_3)_3]$ but were only able to isolate the monosubstituted product, $Pb[C(SiMe_3)_3]Me_2Cl$.

The question of how $Ph_3Pb–Pb[C(SiMe_3)_3]Ph_2$ originates from the reactants used in our study has not been completely resolved. We have established that no $PbPh_3Cl$ was present in the starting materials from which the $PbPh_3$ portion of its structure might have formed, so some type of phenyl transfer step is indicated. A similar reaction [equation (1)] was recently

$$2PbPh_2Cl_2 + Na_2X(thf) \longrightarrow (PbPh_3)_2X \text{ (major product)} \qquad (1)$$

reported by Bahr and Boudjouk[12] who proposed that a phenyl migration, initiated by nucleophilic attack by X (S or Se) on the halide-bridged, solid-state structure of $PbPh_2Cl_2$ (heterogeneous reaction conditions), was responsible for the presence of the $PbPh_3$ group in their product. Since our reaction is also heterogeneous and involves a potential nucleophile, it is possible that the same type of phenyl migration takes place here but we have no direct evidence of this route.

It is probable that the Pb–Pb link in the product originates in the same way as that in $[(Me_3Si)_3Si]Ph_2Pb–PbPh_2[Si(SiMe_3)_3]$, which is one product of the reaction of $PbPh_2Cl_2$ with two equivalents of $Li[SiSiMe_3)_3](thf)_3$.[1] This M–M bond formation in reactions of MR_2Cl_2 (M = Group 14 element) with two equivalents of $Li[E(SiMe_3)_3]$ (E = C or Si) is no longer considered to be surprising since this is the third case where it has been observed,[13] as compared to just one case (M = Sn) where only the disubstituted product was obtained.[2] In the $PbPh_2Cl_2$ reaction, a pathway to the diplumbane was proposed involving a one-electron reduction of the intermediate $Pb[C(SiMe_3)_3]Ph_2Cl$ by the lithium silyl reagent, forming the plumbyl radical, $^{\bullet}Pb[C(SiMe_3)_3]Ph_2$, coupling of which could give the diplumbane product. Since $Li[C(SiMe_3)_3]$ is a strong reductant, this pathway may be operative in the reaction described here. Support for this suggestion comes from the observation of an ^1H NMR signal in the reaction mixture at $\delta(C_6D_6)$ 0.265 which we assign to $Pb[C(Si\mathit{Me}_3)_3]Ph_2Cl$ based on the literature[11] value of $\delta(CDCl_3)$ 0.255 for Pb[C(Si-

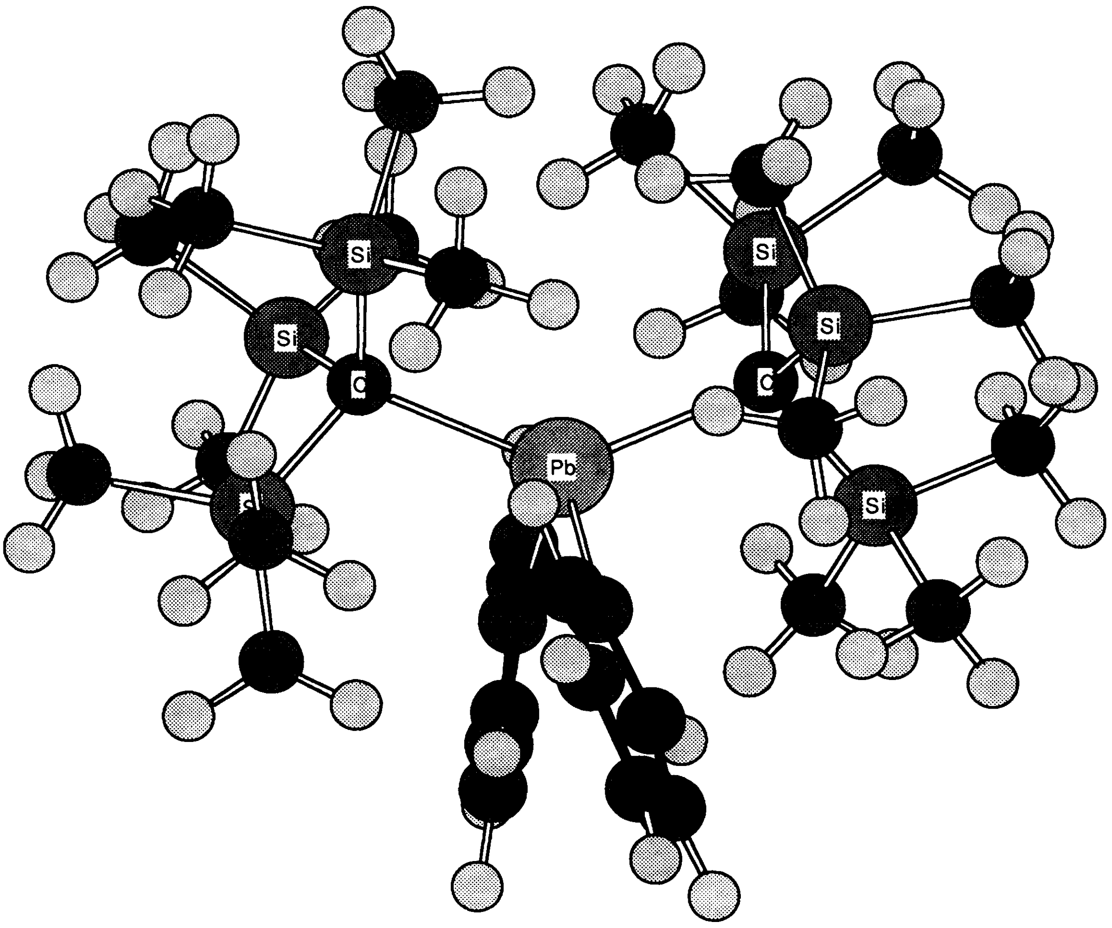

Fig. 2 Molecular structure of $Pb[C(SiMe_3)_3]_2Ph_2$ as predicted by force-field calculations

Me$_3$)$_3$]Me$_2$. The Pb–H coupling observed for the latter compound, however, was not present in our spectrum.

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