

The Observation of a Pb–Li Bond; Synthesis, Structure and Model Molecular Orbital (MO) Calculations on the Monomeric $\text{Ph}_3\text{Pb–Li}(\text{pmdeta})$ Complex [$\text{pmdeta} = (\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$]

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The title compound has been synthesised by the cleavage reaction of $\text{Ph}_3\text{Pb–PbPh}_3$ with Bu^nLi and has been shown to have a monomeric Pb–Li bonded structure in the solid state; *ab initio* calculations have been used to probe the nature of the early main group metal/heavy p block metal bonding involved.

Complexes containing bonds between transition metals and heavy p block metals are well known and have been characterised in the solid state.¹ Recently, we have been interested in the occurrence and the nature of bonds between early main group metals [$\text{M} = \text{Li}, \text{Na}, \text{etc.}$ (group 1); $\text{Mg}, \text{Ca}, \text{etc.}$ (group 2)] and heavy p block metals [$\text{E} = \text{Ga–Tl}$ (group 3); Sn, Pb (group 4); Sb, Bi (group 5)].^{2,3} Previous studies have centred on species which contain non-metallic p block—early main group metal contacts, *e.g.* organometallics (containing C–M), metal amides (N–M), and metal alkoxides (O–M).⁴ Compounds which contain metallic p block elements and alkali or alkaline earth metals, and in which there is a potential for bonding between these, have rarely been studied in their own right though such materials have been known for many years.⁵ More commonly these species have been employed as *in situ* reagents in organic or inorganic syntheses.

A case in point is the early main group metal triorganostannates (commonly formulated as ' R_3SnM ' or ' $\text{R}_3\text{Sn}^-\cdot\text{M}^+$ ') which have been used extensively to promote the formation of Sn–C bonds by their reactions with electrophilic organic substrates such as ketones, epoxides and acid chlorides.⁶

The $\text{Ph}_3\text{Sn–Li}(\text{pmdeta})$ complex [$\text{pmdeta} = (\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$] was recently shown by us to be a Sn–Li bonded monomer in the solid state.² This was the first observation of an alkali or alkaline earth metal–Sn bond in the solid. Our most recent work has centred on extending the syntheses of potentially E–M bonded species and in assessing the occurrence and nature of such bonding.³ Accordingly, we report here the synthesis of the $\text{Ph}_3\text{Pb–Li}(\text{pmdeta})$ complex, **2**. This is the first structurally characterised early main group metal triorganoplumbate (containing Pb–C bonds), and the first compound in which a Pb–Li (or indeed any early main

group metal) Pb bond is observed. *Ab initio* MO calculations have been used to investigate the character of its Pb–Li bonding, which arises from the interaction of the 6s and 6p_z orbitals of Pb with the 2s and 2p_z orbitals of Li. The pyramidal geometry of the Ph₃Pb[−] unit of **2** can be rationalised in terms of the phenyl groups interacting predominantly with the 6p_z orbital of Pb.

The title compound **2** was prepared by the cleavage of hexaphenyldilead (Ph₃Pb–PbPh₃) (1 equiv.) with BuⁿLi (1 equiv.) and pmdeta (1 equiv.) in toluene. The complex was found to be extremely air- and moisture-sensitive and also thermally unstable (only surviving for *ca.* 1 day at 20 °C under N₂).[†] A low-temperature X-ray crystallographic study on a freshly synthesised sample of (**2**),[‡] shows it to be a Pb–Li bonded monomer in the solid state (Fig. 1). It is essentially isostructural with the Ph₃Sn–Li·(pmdeta) complex **1** and contains two crystallographically independent molecules in its asymmetric unit. Complex **2** is the first early main group metal trialkyl- or triaryl-plumbate (containing C–Pb bonds) to be structurally characterised, and the first compound to contain a Pb–Li (or indeed any early main group metal) bond; all other structurally characterised complexes contain bridging P or O centres which hold the metals together, *e.g.* BuⁿP·Pb·(μ₂-PBuⁿ)₂·Li·2thf,⁷ or are ion-separated.⁸ The Pb–Li bond is slightly longer than that expected for a purely covalent interaction [sum of covalent radii of Li and Pb, *ca.* 2.81 Å,⁹ *cf.* av. 2.858(14) Å in **2**]. This situation is similar to the Sn–Li contacted analogue [sum of covalent radii of Sn and Li, *ca.* 2.74 Å,⁹ *cf.* av. 2.817(7) Å in **1**].

The Ph₃Pb[−] anion of **2** is closer to a pyramidal structure than the corresponding Ph₃Sn[−] anion in **1** [av. C–Pb–C, 94.3(3)°, *cf.* C–Sn–C 96.1(2)° in **1**]. These geometries suggest that both metals are using principally p orbitals to bond to their Ph groups and that the interaction with Li is fundamentally with the s orbitals on Sn and Pb. The more compressed (pyramidal) angles in **2** are consistent, in this respect, with the expected increase in energetic separation

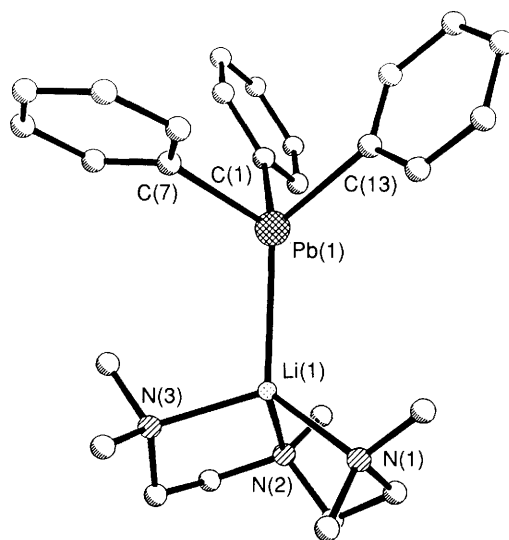


Fig. 1 Molecular structure of one of the monomer molecules in the asymmetric unit of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): molecule 1, Pb(1)–C(1) 2.297(7), Pb(1)–C(7) 2.306(7), Pb(1)–C(13), 2.282(8), Pb(1)–Li(1) 2.852(15); C(1)–Pb(1)–C(7) 95.3(2), C(1)–Pb(1)–C(13) 95.1(3), C(13)–Pb(1)–C(7) 92.6(3); molecule 2, Pb(2)–C(19) 2.306(6), Pb(2)–C(25) 2.295(8), Pb(2)–C(31) 2.293(7), Pb(2)–Li(2) 2.864(13); C(19)–Pb(2)–C(25) 93.9(3), C(19)–Pb(2)–C(31) 96.0(2), C(31)–Pb(2)–C(25) 93.0(3), av. C–Pb–Li (in molecules 1 and 2) 121.9(3).

(inert pair) between the p and s orbitals moving from Sn to Pb. The pyramidal geometry of the Pb centre in **2** contrasts with the more tetrahedral Ph₃Pb[−] units in transition metal complexes, *e.g.* Ph₃PbV(CO)₆ (av. C–Pb–C, *ca.* 106.2°)¹⁰ and *cis*-Pt(PPh₃)₂(PbPh₃)Ph (av. C–Pb–C, *ca.* 106.6°).¹¹

In order to probe the nature of the early main group metal/heavy p block metal bonds found in Ph₃Pb–Li·(pmdeta) **2** and, for comparison, in Ph₃Sn–Li·(pmdeta) **1**, *ab initio* calculations have been performed on a number of solvated and unsolvated models. § Despite differences in the basis sets used, the optimised structures of unsolvated Ph₃Sn–Li **1'** (3-21G¹²) and Ph₃Pb–Li **2'** (double zeta basis set with pseudo-potentials on Pb¹³) [Figs. 2(a) and (b), respectively] both reflect, qualitatively, the observed trends and geometries within the solid-state structures of **1** and **2**. Thus, both calculated models predict the observed compression in the C–Sn–C and C–Pb–C angles (*ca.* 102° in both) and the expansion in the Li–Sn–C and Li–Pb–C angles (*ca.* 116° in both). The Ph₃Sn[−] and Ph₃Pb[−] units in **1'** and **2'** therefore have a geometry significantly distorted from pure tetrahedral (sp³). The major influence, dominating the electron density on the heavy p block metal available for interaction to Li, is the effectiveness of charge

[†] BuⁿLi (0.32 ml, 1.6 mol dm^{−3} in hexanes, 0.5 mmol) was added to a stirred, chilled (*ca.* −20 °C) solution of hexaphenyldilead (Ph₃Pb–PbPh₃) (0.44 g, 0.5 mmol) and pmdeta (0.11 ml, 0.5 mmol) in 35 ml of toluene. A solution colour change from colourless to faint-yellow occurred as the reaction was allowed to heat to 20 °C, with the formation of a white precipitate. This powder was heated gently into solution at *ca.* 50 °C. Slow cooling of the resulting yellow solution to 20 °C gave colourless thermally unstable, air-sensitive crystalline blocks of **2** in 35% yield; decomp. *ca.* 90 °C to black solid (decomp. 1 day at 20 °C under N₂); IR ν/cm^{−1} (Nujol), *ca.* 3100w (C–H aryl), 1563m (m, aryl C=C), bands grouped at 1052, 1033, 1011 ms and 719, 702 (s, *o*-C₆H₅) are particularly characteristic; ¹H NMR (250 MHz; C₆D₆; +25 °C), *ca.* δ 8.6–7.3 (15H, groups of multiplets), 1.84 (23H, br s, pmdeta). Satisfactory analyses (C, H, N) were obtained for all samples of **2**.

[‡] *Crystal data:* C₂₇H₃₈LiN₃Pb, *M* = 618.73, monoclinic, space group *P*2₁, *a* = 12.377(2), *b* = 17.543(2), *c* = 12.663(2) Å, β = 101.801(11)°, *U* = 2691.4(7) Å³, *Z* = 4, *D*_c = 1.527 M gm^{−3}, *F*(000) = 1224, λ = 0.71073 Å, *T* = 153 K, μ(Mo–Kα) = 6.286 mm^{−1}. Data were collected on a Siemens-Stoe AED using an oil-coated rapidly-cooled crystal of dimensions 0.65 × 0.38 × 0.30 mm by the 2θ/ω method (8° ≤ 2θ ≤ 60°). Of a total of 9673 collected reflections, 9233 were unique. The structure was solved by direct methods (SHELX 92) and refined by full-matrix least-squares on *F*² with all data to *R*₁ and *wR*₂ values of 0.037 and 0.086, respectively (SHELX 92); largest difference peak and hole 1.77 and −1.72 eÅ^{−3}. A semi-empirical method from psi-scans was employed for the absorption correction. All hydrogens were located in the difference Fourier map and their positions were refined in a riding model with common refined *U* values for chemically equivalent atoms. The absolute structure was determined by refining the Flack parameter to 0.495(11), implying racemic twinning. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *MO calculations:* **1'**, **1'**·NH₃; the geometries were optimised using the GAUSSIAN 90 suite of programs and a 3-21G basis set (ref. 12). The total energies (in a.u.) calculated for the optimised geometries are: **1'**, −6690.646487; **1'**·NH₃, −6746.58022.

2', **3'**, **3'**·NH₃, **4'**, **4'a** and **4'b**; the geometries were optimised using the GAUSSIAN 90 suite of programs and a double zeta basis set employing pseudo-potentials for Pb (ref. 13). Calculations were performed on an IBM RS6000 system. The total energies (in a.u.) calculated for the optimised geometries are: **2** −700.928846; **3'** −129.558395; **3'**·NH₃ −185.781473; **4'** −5.572736; **4'a** −12.313486; **4'b** −5.0274999.

Ab Initio Program: GAUSSIAN 90 Program (Revision I), M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whitesides, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, *Gaussian Inc.*, Pittsburgh PA, 1990.

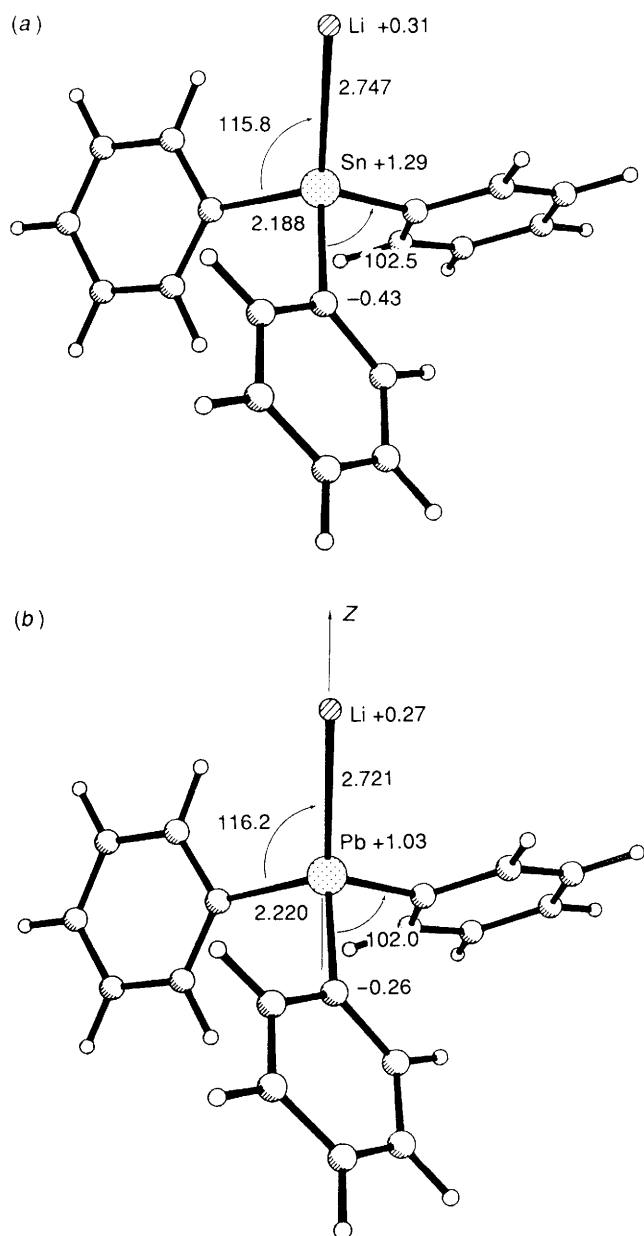


Fig. 2 *Ab initio* optimised geometries of (a) $\text{Ph}_3\text{Sn-Li } 1'$, and (b) $\text{Ph}_3\text{Pb-Li } 2'$. Key bond lengths (Å), angles ($^\circ$) and charges (e).

dispersion from Sn or Pb to their three phenyl rings. The phenyl groups in $1'$ are significantly more negatively charged ($-0.52e$) than those in $2'$ ($-0.44e$). It is interesting to note that, whereas in $2'$ there is a uniform charge distribution within its phenyl rings (*ca.* $-0.25e$ for each C), in $1'$ the bulk of the negative charge is carried by the α -C ($-0.43e$). The outcome of the less effective dispersion of electron density in $2'$, is to leave the Pb more electron rich ($+1.03e$) than Sn in $1'$ ($+1.29e$). There is therefore more electron density on Pb than on Sn to bind to Li^+ .

Some measure of the effects of solvation of the Li is given by model calculations on solvated $\text{Ph}_3\text{Sn-Li-NH}_3$, $1' \cdot \text{NH}_3$. Solvation has the effects of elongating and weakening the Sn-Li bond (now 2.771 \AA , *cf.* 2.747 \AA in $1'$) and further distorting the Ph_3Sn^- anion towards pyramidal geometry (C-Sn-C , 101.2° , *cf.* 102.6° in $1'$). For reasons of their calculational complexity, solvated $\text{Ph}_3\text{Pb-Li}$ models have not been investigated. However, model calculations on unsolvated $\text{Me}_3\text{Pb-Li } 3'$ and

solvated $\text{Me}_3\text{Pb-Li } 3' \cdot \text{NH}_3$, show that a similar elongation of the Pb-Li bond and compression of the Me_3Pb^- anion results from solvation of Li. Further investigations on $\text{H}_3\text{Pb-Li } 4'a$ and isolated PbH_3^- $4'b$ suggest that the geometry about Pb will become even more pyramidal as the Pb and Li centres eventually ion-separate (H-Pb-H in $4'a$ 101.2° , and 93.2° in $4'b$). The latter implies that the Pb-Li bond in $\text{Ph}_3\text{Pb-Li} \cdot (\text{pmdeta})$ 2 [C-Pb-C , $94.3(3)^\circ$] is comparatively weak.

The most surprising result shown by these calculations is the manner in which the heavy p block metals use their orbitals. In $\text{Ph}_3\text{Pb-Li } 2'$ the $6p_z$ orbital is directed towards and, together with the $6s$ orbital, interacts with Li. The Pb-Li bond is therefore a result of s and p, rather than of pure s, interaction. Both the p_x and p_y orbitals are used equivalently in their interaction with the phenyl groups. However, a significant interaction between Pb and these groups is with the $6p_z$ orbital the other lobe of which is directed towards their centre. Such is borne out by examination of the valence orbital populations on Pb ($6s$, 1.395 ; $6p_x$ and $6p_y$, 0.423 ; $6p_z$, 0.727). It is possible that the compression in C-Pb-C angles towards a more pyramidal geometry in $\text{Ph}_3\text{Pb-Li}$ can be rationalised in terms of the phenyl rings maximising their interaction with the $6p_z$ orbital on Pb. The phenyl rings are therefore pulled towards the z-axis. Model calculations on PbH_4 $4'$ (H-Pb-H , 109.0° ; valence orbital populations; $6s$, $1.34e$; $6p_x$, $6p_y$ and $6p_z$, $0.67e$) and on $\text{H}_3\text{Pb-Li } 4'a$ (H-Pb-H , 101.2° ; $6s$, $1.46e$; $6p_x$ and $6p_y$, $0.67e$; $6p_z$, $0.93e$) illustrate this trend most dramatically.

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