

The First Imino-lead Complex: Synthesis and X-Ray Characterisation of $\text{Pb}[\mu\text{-N}=\text{C}(\text{Bu}^t)\text{Ph}]_3\text{Li}\cdot\text{thf}$ (thf = tetrahydrofuran)

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The title compound, $\text{Pb}[\text{N}=\text{C}(\text{Bu}^t)\text{Ph}]_3\text{Li}\cdot\text{thf}$, has been synthesised by nucleophilic substitution of $(\text{C}_5\text{H}_5)_2\text{Pb}$ (1 equiv.) with $\text{LiN}=\text{C}(\text{Bu}^t)(\text{Ph})$ (2 equiv.) and shown by X-ray crystallography to have a distorted trigonal bipyramidal PbN_3Li core structure in which the phenyl groups of the imino ligands face towards, and encircle, the Pb.

We have recently synthesised and structurally characterised compounds of the group 14 heavy p block metals (Sn, Pb).^{1,3-5} The $\text{Ph}_3\text{E-Li}\cdot\text{pmdeta}$ complexes [E = Sn, Pb; *pmdeta* = $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$] contain the first structurally authenticated early main group metal-heavy p block metal bonds.¹ Such triorganostannates and plumbates are valuable precursors

in organic synthesis.² More recently we have been interested in the synthetic utility of heavy p block metal cyclopentadienide complexes as precursors to organometallics and metal 'ate complexes. Nucleophilic addition of CpNa or Cp_2Mg (Cp = C_5H_5) to Cp_2E produces ion-separated and ion-contacted complexes containing unusual Cp_3E^- 'paddle

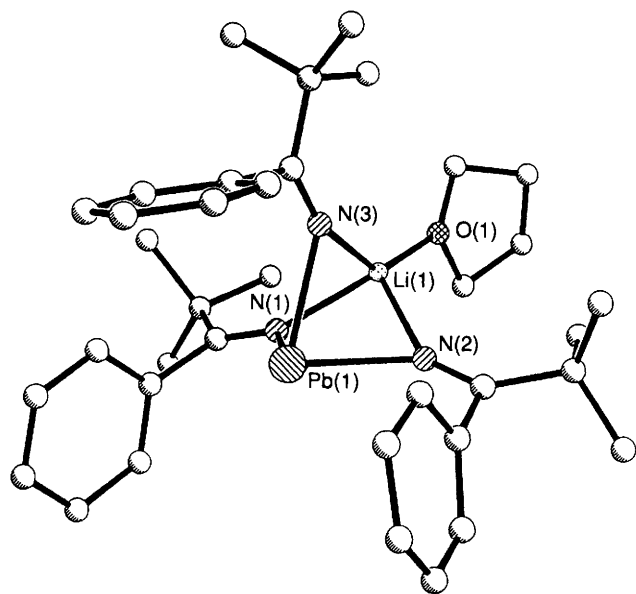


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–N(1) 2.34(2), Pb(1)–N(2) 2.33(2), Pb(1)–N(3) 2.32(1), Li(1)–N(1) 2.07(3), Li(1)–N(2) 2.07(3), Li(1)–N(3) 2.10(3), Pb(1)–Li(1) 2.85(3), Li(1)–O(1) 1.96(3), N(1)–Pb(1)–N(2) 81.6(5), N(2)–Pb(1)–N(3) 74.5(5), N(3)–Pb(1)–N(1) 74.1(5), N(1)–Li(1)–N(2) 95(1), N(2)–Li(1)–N(3) 85(1), N(3)–Li(1)–N(1) 84(1), Li(1)–N(1)–Pb(1) 80.5(9), Li(1)–N(2)–Pb(1) 80.5(9), Li(1)–N(3)–Pb(1) 80.0(8), O(1)–Li(1)–Pb(1) 170(1).

wheel' ions.³ However, the reaction between Cp_2Sn (1 equiv.) and $\text{LiN}=\text{C}(\text{NMe}_2)_2$ (1 equiv.) results in nucleophilic substitution of one of the cyclopentadienide ligands and leads to the formation of the dimeric mixed-ligand complex $\{(\eta^3\text{-Cp})\text{Sn}[\mu_2\text{-N}=\text{C}(\text{NMe}_2)_2]\}_2$.⁴ With more potent nucleophiles and Cp_2Sn we found that substitution proceeds a stage further, leading to triorganostannates. Hence, the reaction of FLi (Fl = fluoren-9-yl, C_{13}H_9 ; 2 or 3 equiv.) with Cp_2Sn (1 equiv.) in thf results in disubstitution followed by addition of a third Fl ligand and in the formation of $[(\text{Fl})_3\text{Sn}]^- [\text{Li}(\text{thf})_4]^+$.⁵

We now report the synthesis of the triiminoplumbate complex $\text{Pb}[\mu\text{-N}=\text{C}(\text{Bu}^t)(\text{Ph})]_3\text{Li}\cdot\text{thf}$ **1**, by nucleophilic substitution of Cp_2Pb (1 equiv.) with $\text{LiN}=\text{C}(\text{Bu}^t)(\text{Ph})$ (2 equiv.) in thf.[†] The solid-state structure of **1** is that of a distorted monomer in which the imino groups bridge the Pb and Li centres. This is the first imino Pb complex and the first structurally characterised triorganoplumbate containing Pb–N bonds.

[†] Synthesis of **1**: a solution of benzonitrile (0.52 ml, 5 mmol) in 10 ml of dry thf was treated at 0 °C with Bu^tLi (2.94 ml, 1.7 mol dm^{-3} in pentane, 5 mmol) under N_2 . To the orange solution produced was added Cp_2Pb (0.84 g, 2.5 mmol, in 5 ml of thf) at –30 °C. The mixture was allowed to warm to 20 °C and then stirred for 10 min. The solution was filtered, through a porosity 4 sinter if necessary, and excess of solvent was removed *in vacuo* until 7 ml of liquid remained whereupon a yellow precipitate developed. This was redissolved by gentle warming, and the solution stored at 5 °C for 24 h. Yellow air-sensitive crystalline rods of **1** were produced in 67% yield (based on imino ligand reacted), m.p. 62 °C, decomp. ca. 70 °C to black solid (Found: C, 56.5; H, 6.3; N, 5.3; Calc for $\text{C}_{37}\text{H}_{50}\text{LiN}_3\text{OPb}$: C, 57.9; H 6.5%; N 5.5%); IR ν/cm^{-1} (Nujol), 3045–3076 (C–H aryl), 1616 [C=N str.; cf. 1637 in $\text{LiN}=\text{C}(\text{Bu}^t)(\text{Ph})$], 1576 (aryl C=C); air-exposed IR spectrum, ν/cm^{-1} 3677 (LiO–H str.), 1623 (C=N str.); ¹H NMR (250 MHz; ²H₈thf; +25 °C), δ ca. 7.26–6.90 (15H, groups of multiplets), 3.60 and 1.70 (8H, coordinated thf), 1.13 (27H, Bu^t); ¹³C NMR (400 MHz; ²H₈thf; +25 °C), δ 175.7 (imino C), 150.0 (aryl C-1), 128.4–126.2 (aryl C-2–C-4), 67.4 and 25.4 (coordinated thf), 45.3 (–CMe₃), 30.1 (–CMe₃).

An X-ray crystallographic study of **1**† shows it to have a monomeric structure in the solid state (Fig. 1). Molecules of **1** contain a trigonal bipyramidal PbN_3Li core in which the bridging imino-N centres link the three-coordinate Pb and four-coordinate (thf-solvated) Li atoms together. It is this bridging which presumably gives rise to the close contact between the two metals rather than there being any significant Pb–Li bonding in **1** [2.85(3) Å in **1**; cf. 2.858(14) Å in the Pb–Li bonded monomer $\text{Ph}_3\text{PbLi}\cdot\text{pmdeta}$;^{1b} sum of covalent radii of Pb and Li, 2.81 Å]. This assertion is confirmed by semi-empirical MO calculations on models of **1** which show no significant Pb···Li interactions.‡ Such a trigonal bipyramidal core motif has been observed in several early main group metal (group 1 and 2) Sn^{II} and Pb^{II} trialkoxide complexes,⁶ e.g. in monomeric $\text{Sn}(\text{dpp})_3\text{Li}$ (dpp = 2,6-diphenylphenoxide).^{6a} However, there are no structurally characterised triorgano derivatives containing Pb–N bonds and **1** is the first imino Pb complex to be structurally characterised.

Within the core of **1**, the Pb–N and Li–N distances fall within the expected ranges [av. Pb–N, 2.332(17) Å; av. Li–N, 2.08(3) Å].^{7,8} However, there are large angular distortions at N(2)–Pb(1)–N(1) [81.6(5)°, cf. av. 74.1(5)° for the other N–Pb–N angles] and at N(1)–Li(1)–N(2) [95(1)°, cf. 85(1)° for the other two N–Li–N angles]. These angular distortions result from the way in which molecules of **1** are associated in the solid state. Two such monomeric units intermesh their phenyl rings at their open Pb(1)N(1)Li(1)N(2) faces and intermolecular aryl (*ortho*)C–H···Pb interactions result (3.26 Å; cf. sum of van der Waals radii of H and Pb, 3.2–3.4 Å⁹).

All three $(\text{Bu}^t)(\text{Ph})\text{C}=\text{N}$ ligands are orientated with their *tert*-butyl groups facing towards the Li·thf⁺ fragment and their phenyl rings facing towards and surrounding the Pb centre in the monomers of **1**. Two of these phenyl groups [associated with the imino ligands at N(1) and N(2)] have centroid···Pb

‡ Crystal data: $\text{C}_{37}\text{H}_{50}\text{LiN}_3\text{OPb}$, $M = 766.94$, orthorhombic, space group $P2_12_12_1$, $a = 16.912(2)$, $b = 19.214(2)$, $c = 11.121(3)$ Å, $U = 3613.7(11)$ Å³, $Z = 4$, $D_c = 1.384$ Mg m^{-3} , $F(000) = 1500$, $\lambda = 0.71073$ Å, $T = 153(1)$ K, $\mu(\text{Mo-K}\alpha) = 4.698$ mm⁻¹. Data were collected on a Siemens-Stoe AED using an oil-coated rapidly-cooled crystal of dimensions 0.35 × 0.31 × 0.30 mm by the $2\theta/\omega$ method ($5.26 \leq 2\theta \leq 44.98^\circ$). Of a total of 5210 collected reflections, 4625 were unique. A semi-empirical absorption correction based on ψ -scans was employed (transmission factors, 0.294–0.665). The structure was solved by direct methods (SHELXLT PLUS) and refined by full-matrix least-squares analysis on F^2 (SHELXL-92; G. M. Sheldrick, Göttingen, 1992) with all data to R and R_w values of 0.0679 and 0.2078, respectively [$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = \sqrt{[\sum w(F_o^2 - F_c^2)^2] / \sum wF_o^4}$]. Largest peak and hole in the final difference map 1.172 and –2.213 e Å⁻³ (located near the Pb centre). The Flack parameter was refined to 0.29(3) (H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **37**, 876); the high estimated standard deviation precludes any comment regarding the absolute structure. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The MNDO program used was VAMP (Dr T. Clark, Erlangen, Germany) based on AMPAC 1.0 and MOPAC 4.0. All calculations were carried out on a CONVEX computer. In the calculational models (a) $\text{Li}(\mu\text{-N}=\text{CH}_2)_3\text{Pb}$ and (b) $\text{Me}_2\text{O}\cdot\text{Li}(\mu\text{-N}=\text{CH}_2)_3\text{Pb}$, the N=CH₂ groups were refined as symmetry-equivalent, giving equal bond lengths and related angles to the Pb and Li atoms and a C_{3v} core geometry. The refined core geometries of both models are similar to that of the solid state structure of **1**, e.g. for (a), N–Li–N, 87.2° (cf. 88.3° in **1**); Li–N–Pb, 78.0° (cf. 80.3° in **1**), Pb···Li, 2.719 Å (cf. 2.85 Å in **1**), although the bond lengths were typically ca. 0.1 Å shorter. The effect of solvation in (b) is to expand the cage, giving a Pb···Li distance closer to that in **1** (2.78 Å). Absolute energies: (a) 13.7; (b) –46.3 kcal mol⁻¹; solvation energy of (a) to (b) –10.0 kcal mol⁻¹ (1 cal = 4.184 J). 10.0 MNDO parameters; C, H, N, O: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4889; Li: taken from MNDOC, W. Thiel, QCPE No. 2, 1988, **2**, 63; Pb: M. J. S. Dewar, M. K. Holloway, G. L. Grady and J. J. P. Stewart, *Organometallics*, 1985, **4**, 1973.

distances (3.86 and 3.83 Å respectively) which approach the sum of the van der Waals radii of Pb and the arene (estimated *ca.* 3.7 Å).⁹ The closest C...Pb contacts (*ca.* 3.21–3.31 Å) are made with the α - and *ortho*-carbon atoms of these rings. Such distances are much longer than have been observed in $(\eta^6\text{-C}_6\text{H}_6)\text{Pb}(\text{AlCl}_4)_2\cdot\text{C}_6\text{H}_6$ [(centroid) $\eta^6\text{-C}_6\text{H}_6\cdots\text{Pb}^{\text{II}}$, 2.77 Å],¹⁰ but may be an indication of weak π interactions in **1**. However, it should be noted that no $^{13}\text{C}\cdots\text{Pb}$ coupling could be observed in the room temperature ^{13}C NMR spectrum of **1** in thf. Alternatively, the relatively close arene...Pb contacts in **1** could also be a consequence of steric repulsion between the Bu^t groups of the imino ligands and the Li-attached thf molecule which forces the imino ligands to pivot toward Pb. Steric repulsion with the Bu^t groups is presumably largely responsible for the bent attachment of the thf ligand to Li [Pb(1)...Li(1)–O(1), *ca.* 170°].

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