The First Imino-lead Complex: Synthesis and X-Ray Characterisation of Pb[μ-N=C(Bu^t)Ph]$_3$Li·thf (thf = tetrahydrofuran)

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The title compound, Pb[N=C(Bu^t)Ph]$_3$Li·thf, has been synthesised by nucleophilic substitution of (C$_5$H$_5$)$_2$Pb (1 equiv.) with LiN=C(Bu^t)(Ph) (2 equiv.) and shown by X-ray crystallography to have a distorted trigonal bipyramidal PbN$_3$Li 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 Ph$_3$E–Li·pmdeta complexes [E = Sn, Pb; pmdeta = (Me$_2$NCH$_2$CH$_2$)$_2$NMe] contain the first structually authenticated early main group metal–heavy p block metal bonds.[1] Such triorganostannates and plumbates are valuable precur-

sors 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$_2$Mg (Cp = C$_5$H$_5$) to Cp$_2$E produces ion-separated and ion-contacted complexes containing unusual Cp$_3$E$^-$ 'paddle

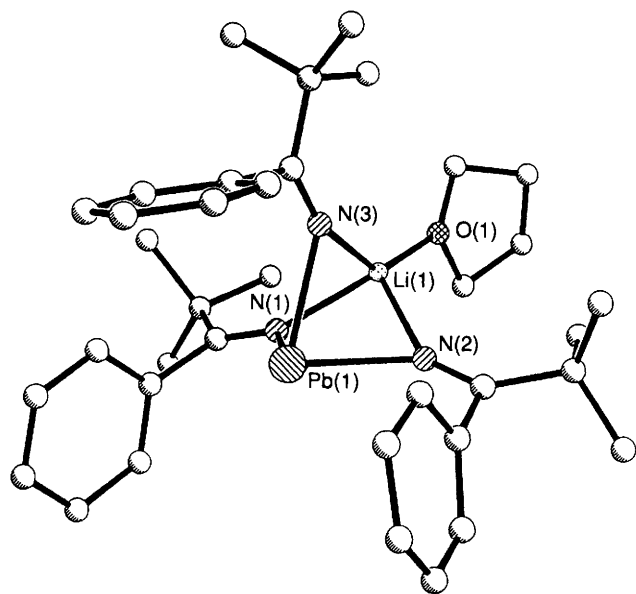Fig. 1 Molecular structure of 1. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–N(1) 2.34(2), Pb(1)–N(2) 2.33(2), Pb(1)–N(3) 2.32(1), Li(1)–N(1) 2.07(3), Li(1)–N(2) 2.07(3), Li(1)–N(3) 2.10(3), Pb(1)···Li(1) 2.85(3), Li(1)–O(1) 1.96(3), N(1)–Pb(1)–N(2) 81.6(5), 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$_2$Sn (1 equiv.) and LiN=C(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 {(η^3-Cp)Sn[μ_2-N=C(NMe$_2$)$_2$]}$_2$.[4] With more potent nucleophiles and Cp$_2$Sn we found that substitution proceeds a stage further, leading to triorganostannates. Hence, the reaction of FlLi (Fl = fluoren-9-yl, C$_{13}$H$_9$; 2 or 3 equiv.) with Cp$_2$Sn (1 equiv.) in thf results in disubstitution followed by addition of a third Fl ligand and in the formation of [(Fl)$_3$Sn]$^-$ [Li(thf)$_4$]$^+$.[5]

We now report the synthesis of the triiminoplumbate complex Pb[μ-N=C(Bu^t)(Ph)]$_3$Li·thf 1, by nucleophilic substitution of Cp$_2$Pb (1 equiv.) with LiN=C(Bu^t)(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 structually characterised triorganoplumbate containing Pb–N bonds.

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$_3$Li 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 Ph$_3$PbLi·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 Sn(dpp)$_3$Li (dpp = 2,6-diphenylphenoxide).[6a] However, there are no structually 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 Å^9).

All three (Bu^t)(Ph)C=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

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$\cdots$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 $(\eta^6\text{-}C_6H_6)Pb(AlCl_4)_2\cdot C_6H_6$ [(centroid)$\eta^6\text{-}C_6H_6\cdots Pb^{II}$, 2.77 Å],[10] but may be an indication of weak π interactions in **1**. However, it should be noted that no $^{13}C\cdots Pb$ coupling could be observed in the room temperature ^{13}C NMR spectrum of **1** in thf. Alternatively, the relatively close arene$\cdots$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)$\cdots$Li(1)–O(1), *ca.* 170°].

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