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Synthesis and structural characterisation of an unusual phosphine-borane-substituted organoplumbate

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ABSTRACT

Treatment of $(n\text{-Pr}_2P)_2CH_2$ with $BH_3 \cdot SMe_2$ yields the phosphine-borane $\{n\text{-Pr}_2P(BH_3)\}_2CH_2$ (**1**) as an air-stable colourless oil. Treatment of **1** with *n*-BuLi affords $[\{n\text{-Pr}_2P(BH_3)\}_2CH]Li$ (**2**). The reaction of **2** with PbI_2 gives the highly insoluble phosphine-borane-substituted plumbate $[\{n\text{-Pr}_2P(BH_3)\}_2CHPbI_2]_2[Li(THF)_4]_2 \cdot THF$ (**3**). The solid-state structure of **3** contains an unusual dimeric organoplumbate dianion.

1. Introduction

Over the last two decades there has been significant progress in the isolation of stable heavier group 14 carbene analogues [diorganotetrylenes, R_2E (E = Si, Ge, Sn, Pb)] [1]. However, the number of such compounds with alkyl substituents remains rather limited, in part due to their reactivity and their tendency to oligomerise to the corresponding alkene analogues $R_2Sn = SnR_2$ or polystannanes $(R_2Sn)_n$. The successful synthesis of monomeric dialkyltetrylenes usually depends on the alkyl substituents possessing sufficient steric bulk to prevent these oligomerisation processes and to protect the electron-deficient Sn(II) centres from attack by nucleophiles [2].

In this regard, we recently reported a new method for the stabilisation of dialkyltetrylenes which relies on the delocalisation of electron density from remote B–H bonds in the molecule into the vacant *p*-orbital at the Sn(II) centre [3–6]. We have shown that such agostic-type B–H…E interactions (E = Sn, Pb) stabilise both cyclic and acyclic stannylenes and plumbylenes and have reported several examples of this type of compound, including the acyclic species *rac*-$[(Me_2RSi)\{Me_2P(BH_3)\}CH]_2E$ (E = Sn, Pb; R = Me, Ph) [6]. In all of the compounds we have isolated so far each alkyl ligand possesses a single borane group which is able to interact with the Sn(II) centre. Where both *rac*- and *meso*-diastereomers may be isolated, for example in the cyclic species $[CH_2C(SiMe_3)\{PiPr(BH_3)\}]_2Sn$ (**A**), we have found that the corresponding stannylene or plumbylene exhibits either two (*rac*) or one (*meso*) B–H…E interaction (Chart 1). The *meso* diastereomers of these compounds are subject to dynamic equilibria in solution involving rapid exchange of the two phosphine-borane groups.

We were interested to observe whether the incorporation of further phosphine-borane groups into these molecules would reveal new ligand coordination modes or dynamic behaviour. In this contribution we report the synthesis of a new bis(phosphine-borane), its metallation, and the reactions of the resulting phosphine-borane-stabilised carbanion with lead(II) halides.

2. Results and discussion

Treatment of the symmetrical diphosphine $(n\text{-Pr}_2P)_2CH_2$ [7] with 2 equiv. of $BH_3 \cdot SMe_2$ yields the phosphine-borane $\{n\text{-Pr}_2P(BH_3)\}_2CH_2$ (**1**) as an air-stable, colourless oil (Scheme 1). The reaction between **1** and one equiv. of *n*-BuLi in THF gives the phosphine-borane-stabilised carbanion complex $[\{n\text{-Pr}_2P(BH_3)\}_2CH]Li(THF)_2$ (**2**), which was isolated as a colourless oil. Unfortunately, despite repeated attempts, we were unable to crystallise this material; metallation was, however, confirmed by NMR spectroscopy. The $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of **2** in C_6D_6 exhibit a broad quartet at 6.4 ppm and a broad doublet at −37.5 ppm, respectively, with a $^{11}B–^{31}P$ coupling constant of 78 Hz [*cf.* $^{31}P\{^1H\}$ 17.2 ppm, $^{11}B\{^1H\}$ −40.3 ppm, $J_{PB} = 59$ Hz for **1** in $CDCl_3$]. This is consistent with our previous observations that α-metallation of phosphine-boranes leads to an increase in the $^{11}B–^{31}P$ coupling constant of between 20 and 50 Hz [8].

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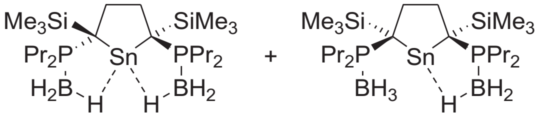


rac-**A** *meso*-**A**

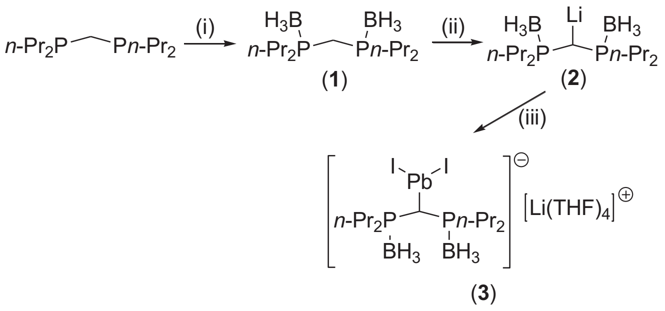
Chart 1.

Unexpectedly, the reaction of PbI_2 with two equivalents of **2** in THF did not yield the corresponding dialkylplumbylene $[\{n\text{-}Pr_2P(BH_3)\}_2CH]_2Pb$, but gave the extremely insoluble organoplumbate complex $[[\{n\text{-}Pr_2P(BH_3)\}_2CH]PbI_2]_2[Li(THF)_4]_2\cdot THF$ (**3**) as a pale yellow solid, which precipitated immediately from the reaction solution. Compound **3** appears to be the sole phosphorus-containing product, irrespective of the reaction stoichiometry, but is most efficiently synthesised by the reaction of PbI_2 with one equiv. of **2** in THF. Attempts to force the reaction to completion were unsuccessful: heating a mixture of PbI_2 and two equivalents of **2** in either THF or DME under reflux for several hours once again yielded **3** as the only phosphorus-containing product. The extremely low solubility of **3**, even in the strong donor solvent THF, prevented characterisation of this compound by NMR spectroscopy; however, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture exhibits a broad signal at 22.0 ppm, which we attribute to **3**.

The reactions of $PbCl_2$, $SnCl_2$ or SnI_2 with one equiv. of **2** in THF similarly led to the precipitation of a pale yellow solid which proved insoluble in common organic solvents and which we were therefore unable to crystallise or characterise further. However, the crude reaction mixtures from the reactions of $PbCl_2$ or SnI_2 with **2** each exhibited a single peak in their $^{31}P\{^1H\}$ NMR spectra at 22.5 and 25.3 ppm, respectively, similar to that observed for **3**, suggesting that similar plumbate and stannate species are formed in these reactions.

A small number of single crystals of **3** suitable for X-ray crystallography were obtained by cooling the supernatant solution, after removal of the solid material by filtration, to 5 °C for 12 h. The structure of **3** is shown in Fig. 1 and details of selected bond lengths and angles are given in Table 1. Compound **3** crystallises as an unusual separated ion pair containing a weakly-bonded dimeric organoplumbate dianion and two $[Li(THF)_4]^+$ counterions, along with a molecule of THF of crystallisation; the asymmetric unit contains one half of each of two crystallographically independent centrosymmetric organoplumbate dianions together with two independent cations, and the uncoordinated THF molecules are disordered around inversion centres.

The $Li(THF)_4{}^+$ cations in **3** are typical of such species and require no further comment. Each lead(II) centre in the dianion fragment is bound by three iodide ions and one carbanion to give a distorted pseudo-trigonal bipyramidal geometry at the metal centres, where one of the equatorial sites is nominally occupied by a stereochemically active lone pair. The two $RPbI_2^-$ units thus form a centrosymmetric iodide-bridged dimer containing a central Pb_2I_2 parallelogram. In contrast to our previous reports of phosphine-borane-substituted dialkylstannylenes and plumbylenes, there are no short B–H…Pb contacts in **3**; indeed, the lead atoms in **3** may be considered electron-precise. The dimeric organoplumbate dianion in **3** appears to be a unique structural motif, which has not been observed previously for organolead(II) compounds.



Scheme 1. Reagents and conditions: (i) $BH_3\cdot SMe_2$, Et_2O; (ii) *n*-BuLi, THF; (iii) PbI_2, THF.

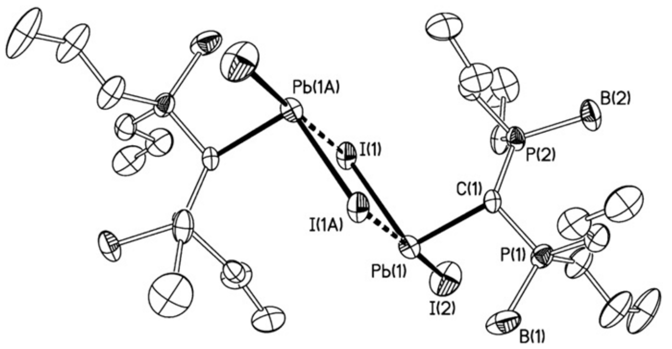


Fig. 1. Structure of one of the weakly bonded dianions of **3** with H atoms omitted for clarity. The other dianion has essentially the same structure.

The Pb–I distances within the two $RPbI_2$ units range from 3.0171(13) to 3.0840(8) Å, whereas the Pb…I distances between the $RPbI_2$ units are substantially longer [Pb(1)…I(1A) 3.5409(10), Pb(2)…I(3B) 3.5360(8) Å; A and B denote inversion-generated atoms], although these are still significantly shorter than the sum of the van der Waals radii of lead and iodine [4.00 Å] [9]. The structure of the $R_2Pb_2I_4$ core of the organoplumbate dianion in **3** is similar to that of the anionic unit of $(Ph_4P)_2[Pb_2I_6]$ in which the Pb–I distances within the Pb_2I_2 core are 3.0359(9) and 3.5707(8) Å [10]. A similar dimeric structure is observed in $[Pb_2(2\text{-aminomethylpyridine})_2(\mu\text{-}I)_2I_2]$, which has Pb–I distances within the Pb_2I_2 core of 3.2584(7) and 3.4152(8) Å; [11]. The Pb–C distances of 2.435(11) and 2.449(10) Å in **3** are similar to the Pb–C distances in previously reported mono- and dialkylplumbylenes; for example, the Pb–C distance in $[\{(Me_2PhSi)_3C\}PbCl]_2$ is 2.435(1) Å [12], while the Pb–C distances in *rac*-$[(Me_3Si)\{Me_2P(BH_3)\}CH]_2Pb$ are 2.363(2) and 2.424(2) Å [6].

The hemidirected arrangement of atoms around the Pb(II) centre in **3** is evidence for a stereochemically active lone pair of electrons. The I(2)–Pb(1)–I(1A) and I(4)–Pb(2)–I(3B) bond angles of 178.46(4) and 177.55(2) Å, respectively, are much larger than the remaining angles around Pb(1) and Pb(2), which range from 81.5(3) to 105.3(2)°.

3. Experimental

3.1. General comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether and THF were distilled from sodium/potassium alloy and potassium, respectively, under an atmosphere of dry nitrogen and were stored over a potassium film or activated 4 Å molecular sieves, respectively. Deuterated chloroform was distilled from CaH_2 and deuterated benzene was distilled from potassium; both solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4 Å molecular sieves. The diphosphine $(n\text{-}Pr_2P)_2CH_2$ was prepared according to previously published procedure [7], *n*-BuLi was supplied by Aldrich as a 2.5 M solution in hexane,