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Organolead(IV) derivatives of oxophosphorus ligands. X-ray structures of monomeric $R_2Pb[(OPPh_2)_2N]_2$ (R = Me, Ph) and tetrameric $[Me_3Pb(O_2PPh_2)]_4$

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Abstract

The reaction of $R_{4-n}PbCl_n$ with $Na[(OPPh_2)_2N]$ or $K[(OPPh_2)(SPPh_2)N]$ afforded isolation of $Ph_2Pb[(OPPh_2)_2N]_2$ (**1**), $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$ (**2**), $Me_3Pb[(OPPh_2)_2N]$ (**3**) and $Ph_3Pb[(OPPh_2)(SPPh_2)N]$ (**4**). Attempts to grow crystals of $Me_3Pb[(OPPh_2)_2N]$ (**3**) led to isolation of $Me_2Pb[(OPPh_2)_2N]_2$ (**5**), as a result of decomposition. $Me_3Pb(O_2PPh_2)$ (**6**) was obtained from Me_3PbCl and $Na(O_2PPh_2)$. The compounds were characterized by IR and multinuclear NMR spectroscopy. The molecular structures of **1**, **5** and **6** were determined by single-crystal X-ray diffraction. The crystal of **5** contains two independent molecules in the unit cell. In both compounds the imidodiphosphinato ligands act as monometallic biconnective units, resulting in a *spiro*-bicyclic system with *six-membered* PbO_2P_2N rings of distorted boat conformation. The coordination geometry around the metal atom is distorted octahedral, with C–Pb–C angles close to 180° [178.9(2)° for **1**; 173.4(3)° and 178.7(4)° for molecules **5a** and **5b**, respectively]. The crystal of the trimethyllead(IV) phosphinate (**6**) contains discrete tetrameric units, $[Me_3Pb(O_2PPh_2)]_4$, with bridging phosphinato ligands [range: Pb–O 2.373(3)–2.402(6) Å, P–O 1.495(6)–1.512(6) Å], thus resulting in a *sixteen-membered* $Pb_4O_8P_4$ inorganic ring. The coordination geometry at lead atoms is distorted trigonal bipyramidal, with oxygen atoms in *trans* positions [range: O–Pb–O 174.7(2)–177.6(3)°].
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1. Introduction

The structural investigation of organolead(IV) compounds containing dithiophosphorus ligands has revealed interesting patterns in the solid state (Scheme 1), i.e. monomeric $Ph_3PbS_2P(OEt)_2$ (**a**: monometallic monoconnective dithiophosphato ligand and tetrahedral C_3PbS core) [1], $Ph_2Pb(S_2PR_2)_2$ (R = OCH_2Ph [1], Ph [2]) (**b**: monometallic biconnective dithiophosphorus ligands, distorted octahedral C_2PbS_4 core, bent C_2Pb system), and chain polymeric $[Ph_3PbS_2PMe_2]_n$ (**c**: bime-

tallic biconnective dithiophosphinato ligand, trigonal bipyramidal C_3PbS_2 core, planar C_3Pb system) [3]. By contrast, $Ph_2Pb(O_2PR_2)_2$ (R = Me, Ph) derivatives were recently reported to exhibit a polymeric structure with double-bridged phosphorus ligands between the lead atoms (**d**: bimetallic biconnective phosphinato ligand, octahedral C_2PbO_4 core, linear C_2Pb system) [4]. A similar double-bridging polymeric motif was also reported for inorganic lead(II) diorganophosphinates, $[Pb(O_2PR_2)_2]_n$ (R = Ph [5], Bu^t [6]) (**e**: bimetallic biconnective phosphinato ligands and *pseudo*-trigonal bipyramidal PbO_4 core).

The dichalcogenoimidodiphosphinato anions, $[(XPR_2')(YPR_2')N]^-$, exhibit a significantly larger

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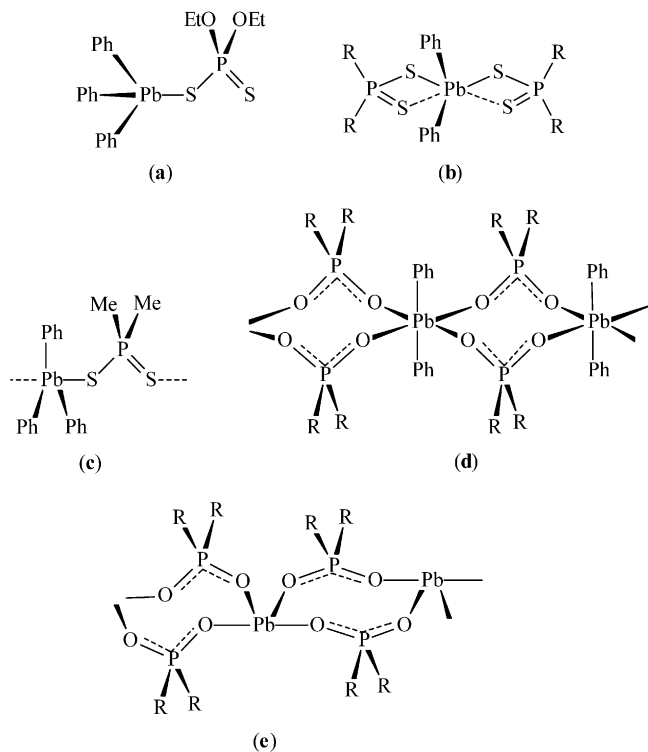
Scheme 1.

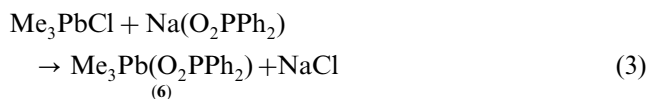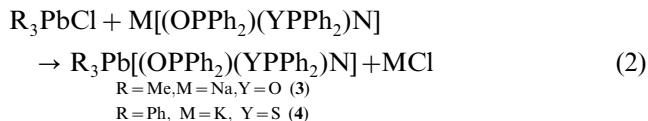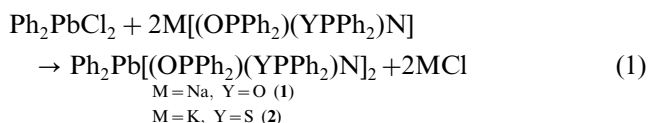X$\cdots$Y bite than the 1,1-dichalcogenophosphorus ligands and are usually found to be coordinated to a metal center through both chalcogen atoms, thus leading to six-membered MXYP$_2$N inorganic chelate (carbon-free) rings [7]. So far, some inorganic lead(II) derivatives, Pb[(XPPh$_2$)(YPPh$_2$)N]$_2$ (X = Y = S [8], Se [9]; X = O, Y = S [10]), have been investigated by single-crystal X-ray diffraction and were found to be basically monomeric regardless of the nature of the chalcogen atoms in the organophosphorus ligand moiety [7]. We have reported some preliminary results on organolead(IV) complexes of the type R$_n$Pb[(OPPh$_2$)-(YPPh$_2$)N]$_{4-n}$ (R = Me, Ph; n = 2, 3; Y = O, S) within an extended abstract for a communication [11] and here we report in detail on the synthesis and spectroscopic characterization of Ph$_2$Pb[(OPPh$_2$)(YPPh$_2$)N]$_2$ [Y = O (1), S (2)], R$_3$Pb[(OPPh$_2$)(YPPh$_2$)N] [R = Me, Y = O (3); R = Ph, Y = S (4)] and Me$_3$Pb(O$_2$PPh$_2$) (6), along with the crystal and molecular structures of 1, Me$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (5) and 6.

2. Results and discussion

2.1. Preparation

New organolead(IV) compounds were prepared as white crystalline solids by reacting Ph$_2$PbCl$_2$ or R$_3$PbCl with the alkali metal salt of the appropriate organopho-

sphorus ligand according to Eqs. (1)–(3):

$$Ph_2PbCl_2 + 2M[(OPPh_2)(YPPh_2)N]$$
$$\rightarrow Ph_2Pb[(OPPh_2)(YPPh_2)N]_2 + 2MCl \quad (1)$$
$$M = Na,\ Y = O\ (1)$$
$$M = K,\ Y = S\ (2)$$

$$R_3PbCl + M[(OPPh_2)(YPPh_2)N]$$
$$\rightarrow R_3Pb[(OPPh_2)(YPPh_2)N] + MCl \quad (2)$$
$$R = Me, M = Na, Y = O\ (3)$$
$$R = Ph,\ M = K,\ Y = S\ (4)$$

$$Me_3PbCl + Na(O_2PPh_2)$$
$$\rightarrow Me_3Pb(O_2PPh_2) + NaCl \quad (3)$$
$$(6)$$

The compounds were characterized by IR and multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P). Although the NMR spectra of a freshly prepared sample of the trimethyllead(IV) complex 3 were consistent with the presence of a PbC$_3$ fragment, attempts to grow single crystals suitable for X-ray diffraction studies led only to isolation of Me$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (5) due to a redistribution process. Similar behavior has already been reported for triorganotin(IV) analogs, thus suggesting a tendency for the ligand moiety to chelate a metal atom and to form a six-membered ring [12,13]. The molecular structures of 1, 5 and 6 have been determined by single-crystal X-ray diffraction.

2.2. IR spectra

The IR spectra of compounds 1–4 exhibit strong bands in the regions 1240–1230 and 1120–1040 cm^{-1}, which were assigned to $v(P_2N)$ and $v(PO)$ vibrations, respectively. In addition, absorptions of medium intensities around 570 cm^{-1} [$v(PS)$] and 770 cm^{-1} [$\rho(CH_3)$], were observed in the spectra of compounds 2 and 4, and the methyl derivative 3, respectively. The assignments for the phosphorus-nitrogen, -oxygen and -sulfur stretching vibrations were made by comparison with the spectra of the free acids and their alkali salts, and suggest bidentate coordination of the phophorus ligand to lead through both chalcogen atoms.

2.3. NMR spectra

The ^{1}H- and ^{13}C-NMR spectra contain characteristic resonance signals for equivalent organic groups bonded to lead and phosphorus atoms and confirm the identity of the compounds obtained. The magnitude of the lead–proton and lead–carbon coupling constants is consistent with the presence of diorganolead(IV) moieties in compounds 1 [^3J(PbH) 216.5 Hz, ^2J(PbC) 131.0 Hz] and 2 [^3J(PbH) 186.5 Hz], and triorganolead(IV) groups in compounds 3 [^2J(PbH) 79.3 Hz, ^1J(PbC) 341.4 Hz] and 4 [^3J(PbH) 113 Hz, ^2J(PbC) 87.5 Hz], respectively.
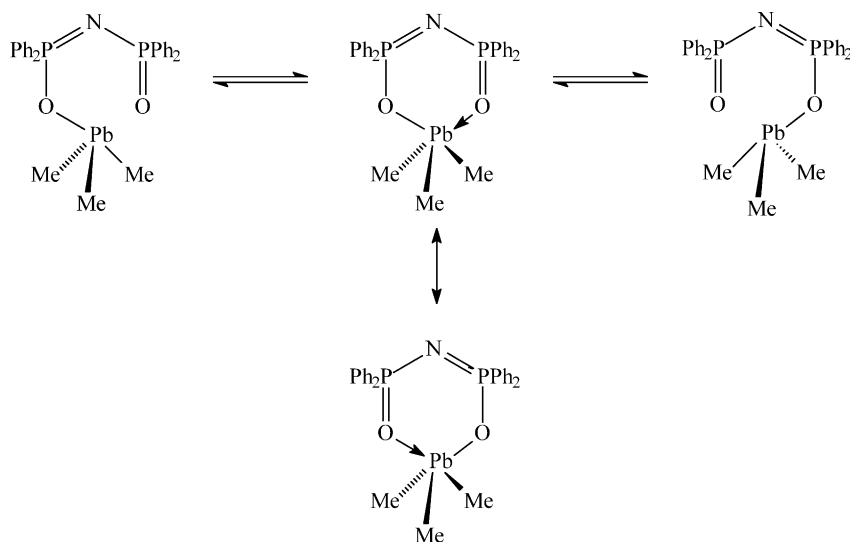
Scheme 2.

For compounds **1** and **3**, which contain a symmetric dioxoimidodiphosphinato ligand, only one ^{31}P resonance is observed, suggesting the equivalence of the phosphorus atoms present in the molecule. In the case of the trimethyllead(IV) derivative **3**, the presence of only one broad ^{31}P resonance suggests a fluxional process in solution, i.e. a fast exchange of the oxygen atom involved in the primary coordination to the metal center (Scheme 2).

The ^{31}P-NMR spectra of the monothioimidodiphosphinato complexes **2** and **4** contain, as expected, two resonance signals for P_O and P_S atoms of a ligand moiety, but the phosphorus–phosphorus couplings could not be observed. The resonance assigned to P_O ($\delta = 14.4$ ppm) in the spectrum of the triphenyllead(IV) derivative, Ph$_3$Pb[(OPPh$_2$)(SPPh$_2$)N] (**4**), is shifted to higher field compared with the diphenyllead(IV) compound **2** ($\delta = 21.8$ ppm) suggesting that the primary coordination of the monothioimidodiphosphinato ligand is achieved through the oxygen atom.

The ^{1}H- and ^{13}C-NMR spectra of the diphenylphosphinato derivative **6** are again consistent with the presence of a Me$_3$Pb moiety [^2J(PbH) 85.7 Hz, ^1J(PC) 391.7 Hz]. Its ^{31}P-NMR spectrum shows a sharp singlet ($\delta = 16.8$ ppm), surrounded by satellites due to the phosphorus–carbon coupling [^1J(PC) 134.0 Hz].

2.4. Molecular structure of Ph$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (1) and Me$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (5)

The crystals of **1** and **5** consist of discrete molecules, of similar structure, separated by normal van der Waals distances. Two independent molecules (designated as **5a** and **5b** in the subsequent discussion) are present in the asymmetric unit of **5**. Selected interatomic distances and

angles are listed in Table 1. Figs. 1 and 2 show the ORTEP-like view of the molecular structures of **1** and **5**, with the atom numbering scheme.

There are some common structural features:

1) the phosphorus ligands act as monometallic biconnective units, leading to a spiro-bicyclic system with *six-membered* PbO$_2$P$_2$N rings, with a planar PbO$_4$ core and similar *endocyclic*-O–Pb–O angles [84.8(1)/87.5(1)° for **1**, 84.1(2)/86.7(2)° for **5a**, and 85.4(2)/87.1(2)° for **5b**],

2) within a coordinated ligand unit the phosphorus–oxygen [1.515(3)–1.520(3) Å for **1**, 1.505(6)–1.519(6) Å for **5a**, and 1.503(6)–1.516(6) Å for **5b**] and the phosphorus–nitrogen [1.584(4)–1.589(4) Å for **1**, 1.583(6)–1.598(7) Å for **5a**, and 1.580(7)–1.600(7) Å for **5b**] bond distances, respectively, are equivalent within experimental error. Their magnitude suggests single phosphorus–oxygen bonds [cf. Ph$_2$P(=O)OH: P–O 1.526(6), P=O 1.486(6) Å] [14] and considerable double bond character for the phosphorus–nitrogen bonds [cf. [(Me$_3$Si)$_2$N–P(=NBu^t)S]$_2$: P–N 1.662(2), P=N 1.529(2) Å] [15].

3) the coordination geometry around the lead atom is distorted octahedral with carbon atoms from the organic groups attached to lead in *trans* positions.

However, there are also significant differences between the molecular structures of **1**, **5a** and **5b**. Different degrees of distortion of the C$_2$PbO$_4$ octahedral core are noticeable. Thus, in the molecule of **1** the lead–oxygen bond distances are similar within a PbO$_2$P$_2$N ring [2.357(3)/2.368(3) and 2.347(3)/2.376(3) Å] and well within the range of those observed in the polymeric Ph$_2$Pb(O$_2$PR$_2$)$_2$ (R = Me, Ph) derivatives [range: 2.307(5)–2.375(5) Å] [4]. The *trans*-C–Pb–C

Table 1
Selected bond lengths (Å) and angles (°) for $Ph_2Pb[(OPPh_2)_2N]_2$ (**1**) and $Me_2Pb[(OPPh_2)_2N]_2$ (**5**)

(**1**)		(**5**)			
		Molecule (**5a**)		Molecule (**5b**)	
Bond lengths					
Pb(1)–C(1)	2.162(5)	Pb(1)–C(1)	2.168(9)	Pb(2)–C(51)	2.124(9)
Pb(1)–C(7)	2.150(5)	Pb(1)–C(2)	2.138(9)	Pb(2)–C(52)	2.13(1)
Pb(1)–O(1)	2.357(3)	Pb(1)–O(1)	2.342(5)	Pb(2)–O(5)	2.432(5)
Pb(1)–O(2)	2.368(3)	Pb(1)–O(2)	2.420(6)	Pb(2)–O(6)	2.363(6)
Pb(1)–O(3)	2.347(3)	Pb(1)–O(3)	2.462(5)	Pb(2)–O(7)	2.382(5)
Pb(1)–O(4)	2.376(3)	Pb(1)–O(4)	2.352(6)	Pb(2)–O(8)	2.407(6)
P(1)–O(1)	1.518(3)	P(1)–O(1)	1.511(6)	P(5)–O(5)	1.516(6)
P(1)–N(1)	1.589(4)	P(1)–N(1)	1.596(7)	P(5)–N(3)	1.600(7)
P(2)–O(2)	1.520(3)	P(2)–O(2)	1.505(6)	P(6)–O(6)	1.512(6)
P(2)–N(1)	1.587(4)	P(2)–N(1)	1.592(6)	P(6)–N(3)	1.594(7)
P(3)–O(3)	1.515(3)	P(3)–O(3)	1.513(6)	P(7)–O(7)	1.513(6)
P(3)–N(2)	1.586(4)	P(3)–N(2)	1.598(7)	P(7)–N(4)	1.581(7)
P(4)–O(4)	1.517(3)	P(4)–O(4)	1.519(6)	P(8)–O(8)	1.503(6)
P(4)–N(2)	1.584(4)	P(4)–N(2)	1.583(6)	P(8)–N(4)	1.580(7)
Bond angles					
C(1)–Pb(1)–C(7)	178.9(2)	C(1)–Pb(1)–C(2)	173.4(3)	C(51)–Pb(2)–C(52)	178.7(4)
O(1)–Pb(1)–O(2)	84.8(1)	O(1)–Pb(1)–O(2)	84.1(2)	O(5)–Pb(2)–O(6)	85.4(2)
O(1)–Pb(1)–O(4)	177.8(1)	O(1)–Pb(1)–O(3)	174.2(2)	O(5)–Pb(2)–O(7)	176.5(2)
O(1)–Pb(1)–O(3)	93.0(1)	O(1)–Pb(1)–O(4)	88.5(2)	O(6)–Pb(2)–O(7)	91.9(2)
O(2)–Pb(1)–O(3)	177.7(1)	O(2)–Pb(1)–O(4)	172.6(2)	O(6)–Pb(2)–O(8)	178.7(2)
O(2)–Pb(1)–O(4)	94.8(1)	O(2)–Pb(1)–O(3)	100.7(2)	O(5)–Pb(2)–O(8)	95.6(2)
O(3)–Pb(1)–O(4)	87.5(1)	O(3)–Pb(1)–O(4)	86.7(2)	O(7)–Pb(2)–O(8)	87.1(2)
C(1)–Pb(1)–O(1)	90.0(2)	C(1)–Pb(1)–O(1)	90.3(3)	C(51)–Pb(2)–O(5)	87.4(3)
C(1)–Pb(1)–O(2)	88.4(1)	C(2)–Pb(1)–O(1)	94.1(3)	C(52)–Pb(2)–O(5)	91.3(3)
C(1)–Pb(1)–O(3)	92.0(2)	C(1)–Pb(1)–O(2)	86.0(3)	C(51)–Pb(2)–O(6)	87.8(3)
C(1)–Pb(1)–O(4)	92.1(2)	C(2)–Pb(1)–O(2)	89.6(3)	C(52)–Pb(2)–O(6)	91.8(3)
C(7)–Pb(1)–O(1)	90.1(2)	C(1)–Pb(1)–O(3)	86.8(3)	C(51)–Pb(2)–O(7)	90.2(3)
C(7)–Pb(1)–O(2)	90.6(2)	C(2)–Pb(1)–O(3)	89.3(3)	C(52)–Pb(2)–O(7)	91.1(3)
C(7)–Pb(1)–O(3)	89.0(2)	C(1)–Pb(1)–O(4)	93.3(3)	C(51)–Pb(2)–O(8)	91.3(3)
C(7)–Pb(1)–O(4)	87.8(2)	C(2)–Pb(1)–O(4)	91.7(3)	C(52)–Pb(2)–O(8)	89.1(3)
O(1)–P(1)–N(1)	116.7(2)	O(1)–P(1)–N(1)	118.4(4)	O(5)–P(5)–N(3)	115.7(3)
O(2)–P(2)–N(1)	117.3(2)	O(2)–P(2)–N(1)	119.2(4)	O(6)–P(6)–N(3)	117.8(4)
O(3)–P(3)–N(2)	118.0(2)	O(3)–P(3)–N(2)	117.2(3)	O(7)–P(7)–N(4)	117.5(4)
O(4)–P(4)–N(2)	118.7(2)	O(4)–P(4)–N(2)	117.4(4)	O(8)–P(8)–N(4)	117.7(4)
P(2)–N(1)–P(1)	127.7(2)	P(1)–N(1)–P(2)	130.8(5)	P(5)–N(3)–P(6)	127.3(5)
P(4)–N(2)–P(3)	135.4(3)	P(3)–N(2)–P(4)	130.8(5)	P(7)–N(4)–P(8)	135.3(5)
Pb(1)–O(1)–P(1)	125.7(2)	Pb(1)–O(1)–P(1)	126.0(3)	Pb(2)–O(5)–P(5)	126.2(3)
Pb(1)–O(2)–P(2)	125.4(2)	Pb(1)–O(2)–P(2)	128.8(3)	Pb(2)–O(6)–P(6)	126.3(3)
Pb(1)–O(3)–P(3)	130.4(2)	Pb(1)–O(3)–P(3)	125.9(3)	Pb(2)–O(7)–P(7)	126.8(3)
Pb(1)–O(4)–P(4)	128.5(2)	Pb(1)–O(4)–P(4)	127.6(3)	Pb(2)–O(8)–P(8)	128.0(3)

[178.9(2)°] and *trans*-O–Pb–O [177.7(1), 177.8(1)°] angles are close to 180°, while the *exocyclic*-O–Pb–O are almost equal [93.0(1), 94.8(1)°]. The C_2PbO_4 core in **5b** also exhibits very similar *trans*-bond angle parameters [*trans*-C–Pb–C 178.7(4)°, *trans*-O–Pb–O 176.5(2), 178.7(2)°]. However, the lead–oxygen bond distances within a PbO_2P_2N ring are significantly different [2.363(6)/2.432(5) and 2.382(5)/2.407(6) Å] and the O–Pb–O angle between the shorter Pb–O bonds [91.9(2)°]

is smaller than that between the longer ones [95.6(2)°]. The distortion of the C_2PbO_4 octahedral core in **5a** towards a bicapped tetrahedraon as observed for C_2PbS_4 in $Ph_2Pb(S_2PR_2)_2$ (R = OCH_2Ph [1], Ph [2]) is even more pronounced. The difference between the Pb–O bond lengths formed by a ligand moiety [2.342(5)/2.420(6) and 2.352(6)/2.462(5) Å] is even greater than in **5b** and the deviation of the *trans*-bond angles at the central metal atom is considerable [*trans*-C–Pb–C
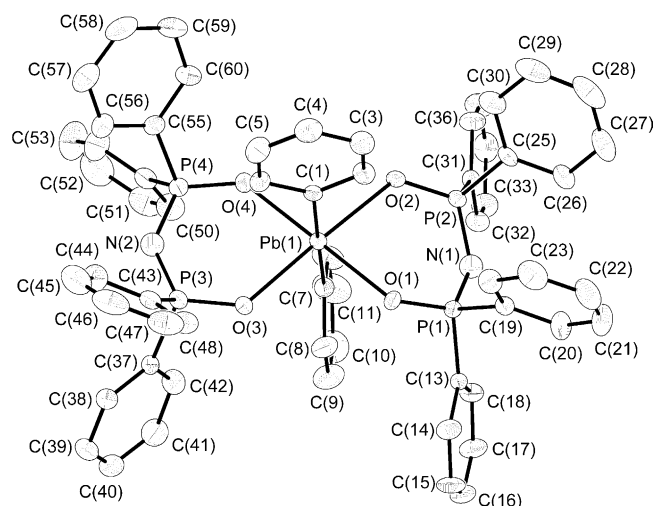
Fig. 1. ORTEP plot of the molecule Ph$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (**1**). The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.
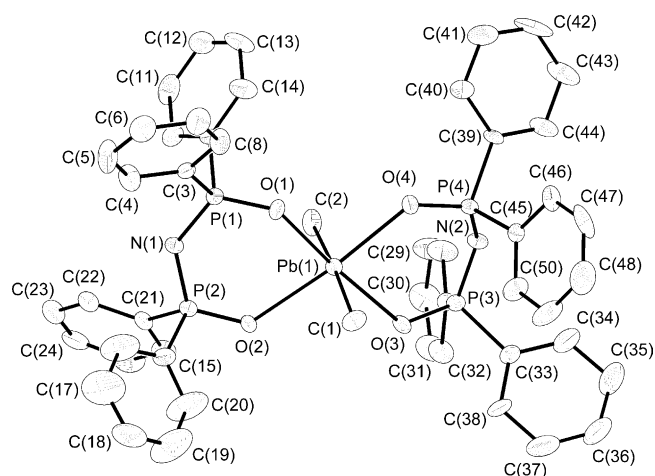

Fig. 2. ORTEP plot of the one of the two molecules in the asymmetric unit of Me$_2$Pb[(OPPh$_2$)$_2$N]$_2$ (**5**). The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

173.4(3)°, *trans*-O–Pb–O 172.6(2), 174.2(2)°]. The C$_2$Pb moiety is bent towards the opened O–Pb–O angle [100.7(2)°] formed by the longer P–O bonds.

Although some delocalization of the p-electrons over the OPNPO systems is suggested by the magnitude of the bonds, the PbO$_2$P$_2$N rings are not planar but exhibit variable conformations. Thus, the six-membered rings in **1** exhibit a chair (almost flattened) and a boat conformation, respectively, both with the metal and the nitrogen atoms in the apices. In **5a** and **5b**, the PbO$_2$P$_2$N rings exhibit boat conformation of variable distortion and with different atom types in the apices: O(1)/P(2) and O(3)/P(4) atoms in **5a**, and Pb(2)/N(3) and O(8)/P(7) atoms in **5b**. The differences in the bond angles within a

PbO$_2$P$_2$N ring (Table 1) and the variable bite of a ligand unit [O···O range: 3.18–3.30 Å] support the high flexibility of the OPNPO skeleton which might account for the differences observed in the PbO$_2$P$_2$N ring conformation.

2.5. Molecular structure of [Me$_3$Pb(O$_2$PPh$_2$)]$_4$ (**6**)

The crystal of the trimethyllead(IV) phosphinate (**6**) contains discrete tetrameric units, [Me$_3$Pb(O$_2$PPh$_2$)]$_4$ (Fig. 3). The tetramer exhibits a crystallographic mirror plane passing through Pb(2) and Pb(3). Selected interatomic distances and angles are listed in Table 2.

The diphenylphosphinato ligands act as a bimetallic biconnective (bridging) moieties between Me$_3$Pb units, thus resulting in a *sixteen-membered* Pb$_4$O$_8$P$_4$ inorganic ring. A similar tetrameric macrocyclic structure was reported previously for the tin analogue, [Me$_3$Sn(O$_2$PPh$_2$)]$_4$ [16]. The Pb$_4$O$_8$P$_4$ ring is not planar, but of chair conformation, with the Pb(1)P$_2$O$_2$ and Pb(3)P$_2$O$_2$ fragments above and below the plane formed by the O(1)Pb(1)O(3)/O(1′)Pb(1′)O(3′) system. Two of the methyl groups at each lead atom protrude into the Pb$_4$O$_8$P$_4$ ring, while the phenyl groups at the phosphorus atoms are orientated outside the ring, thus providing a lipophilic protection to the tetramer.

The lead atoms exhibit a distorted trigonal bipyramidal geometry, with the carbon atoms of the methyl groups in equatorial positions and two oxygen atoms in the axial positions. The C$_3$Pb moieties are planar and the Pb–C [2.16(1)–2.22(1) Å] and Pb–O [2.373(6)–2.402(6) Å] bond lengths are equivalent within experimental error. The differences in the C–Pb–C angles [115.7(6)–130.1(7)°] and the deviation of the O–Pb–O fragment from linearity [O–Pb–O 174.7(2)–177.6(3)°]
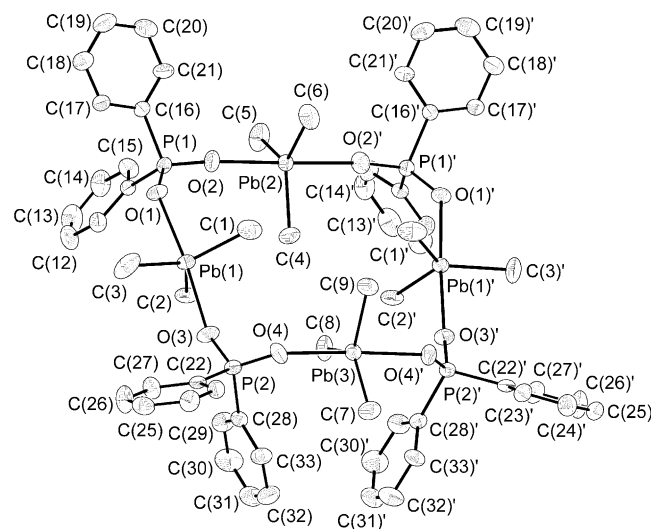

Fig. 3. ORTEP plot of the tetrameric [Me$_3$Pb(OPPh$_2$)$_2$N]$_4$ (**6**). The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for [Me$_3$Pb(OPPh$_2$)$_2$N]$_4$ (**6**) [a]

Bond lengths

Pb(1)–C(1)	2.20(1)	Pb(2)–C(4)	2.18(2)	Pb(3)–C(7)	2.16(1)
Pb(1)–C(2)	2.197(9)	Pb(2)–C(5)	2.17(2)	Pb(3)–C(8)	2.19(2)
Pb(1)–C(3)	2.18(1)	Pb(2)–C(6)	2.22(1)	Pb(3)–C(9)	2.21(1)
Pb(1)–O(1)	2.402(6)	Pb(2)–O(2)	2.373(6)	Pb(3)–O(4)	2.396(5)
Pb(1)–O(3)	2.380(6)	Pb(2)–O(2)′	2.373(6)	Pb(3)–O(4)′	2.396(5)
P(1)–O(1)	1.495(6)	P(2)–O(3)	1.509(7)		
P(1)–O(2)	1.501(6)	P(2)–O(4)	1.512(6)		

Bond angles

O(1)–Pb(1)–O(3)	174.7(2)	O(2)–Pb(2)–O(2)′	177.6(3)	O(4)–Pb(3)–O(4)′	176.5(3)
C(1)–Pb(1)–C(2)	117.1(4)	C(4)–Pb(2)–C(5)	119.7(9)	C(7)–Pb(3)–C(8)	130.1(7)
C(1)–Pb(1)–C(3)	121.6(6)	C(4)–Pb(2)–C(6)	118.4(8)	C(7)–Pb(3)–C(9)	114.2(6)
C(2)–Pb(1)–C(3)	121.2(5)	C(5)–Pb(2)–C(6)	121.8(8)	C(8)–Pb(3)–C(9)	115.7(6)
C(1)–Pb(1)–O(1)	91.7(3)	C(4)–Pb(2)–O(2)	90.4(2)	C(7)–Pb(3)–O(4)	88.3(2)
C(2)–Pb(1)–O(1)	93.4(3)	C(5)–Pb(2)–O(2)	90.8(2)	C(8)–Pb(3)–O(4)	91.2(2)
C(3)–Pb(1)–O(1)	88.6(3)	C(6)–Pb(2)–O(2)	88.8(2)	C(9)–Pb(3)–O(4)	90.6(2)
C(1)–Pb(1)–O(3)	93.4(4)				
C(2)–Pb(1)–O(3)	85.3(3)				
C(3)–Pb(1)–O(3)	87.7(3)				
O(1)–P(1)–O(2)	117.6(4)	O(3)–P(2)–O(4)	117.6(4)		
C(10)–P(1)–C(16)	103.6(4)	C(22)–P(2)–C(28)	106.3(4)		
P(1)–O(1)–Pb(1)	135.6(3)	P(1)–O(2)–Pb(2)	173.4(4)	P(2)–O(4)–Pb(3)	132.3(3)
P(2)–O(3)–Pb(1)	156.8(5)				

[a] Symmetry equivalent atoms (x, $-y+(1/2)$, z) given by a prime.

account for the distortion of the C$_3$PbO$_2$ core from an ideal polyhedron.

Within a phosphinato ligand, the phosphorus–oxygen bonds are equivalent [1.495(6)–1.512(6) Å] and their magnitude suggests intermediate character between single P–O and double P=O bonds [cf. Ph$_2$P(=O)OH: P–O 1.526(6), P=O 1.486(6) Å] [14]. The O–P–O and C–P–C angles (Table 2) are normal for a tetrahedral C$_2$PO$_2$ core, but the bond angles at the oxygen atoms cover a wide range, from angular [P(2)–O(4)–Pb(3) 132.3(3)°] to almost linear [P(1)–O(2)–Pb(2) 173.4(4)°], to allow for the formation of the macrocycle.

3. Conclusions

New R$_2$Pb[(OPPh$_2$)(XPPh$_2$)N]$_2$ and R$_3$Pb[(OPPh$_2$)-(XPPh$_2$)N] (R = Me, Ph; X = O, S) derivatives were prepared and characterized using IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy. The molecular structures of R$_2$Pb[(OPPh$_2$)$_2$N]$_2$ [R = Ph (**1**), Me (**5**)] were investigated by X-ray diffraction. The larger bite of the imidodiphosphinato ligands accounts for the monomeric nature of both compounds. The formation of a *spiro*-bicyclic (NP$_2$O$_2$)PbC$_2$(O$_2$P$_2$N) system is in contrast to the polymeric ring-chain structures with Pb$_2$O$_4$P$_2$ *eight-membered* rings of Ph$_2$Pb(O$_2$PR$_2$)$_2$ (R = Me, Ph) derivatives. The compounds exhibit different degrees of distortion for the octahedral C$_2$PbO$_4$ core

and different conformations of the *six-membered* PbO$_2$P$_2$N inorganic rings. For the trimethyllead(IV) phosphinate (**6**) a tetrameric structure, [Me$_3$Pb(O$_2$PPh$_2$)]$_4$, with a *sixteen-membered* Pb$_4$O$_8$P$_4$ macrocyclic system is established. The bridging nature of the phosphorus ligands results in distorted trigonal bipyramidal C$_3$PbO$_2$ cores.

4. Experimental

4.1. Materials and procedures

Organolead(IV) chlorides were commercial products. Na[O$_2$PPh$_2$] was obtained by reacting Ph$_2$P(O)OH [17] with MeONa, while the other starting materials were prepared according to literature methods: Na[(OPPh$_2$)$_2$N] [18], K[(OPPh$_2$)(SPPh$_2$)N] [12]. Infrared spectra were recorded in the range 4000–400 cm^{-1} in nujol on a SPECORD IR UR 2 (Carl-Zeiss Jena, DDR) instrument. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively, using solutions in dried CDCl$_3$. The chemical shifts are reported in ppm relative to TMS and H$_3$PO$_4$ 85%, respectively.

4.2. Preparation of bis(tetraphenylimidodiphosphinato)-diphenyllead(IV), Ph₂Pb[(OPPh₂)₂N]₂ (1)

Na[(OPPh₂)₂N] (0.5858 g, 1.33 mmol) was added to a solution of Ph₂PbCl₂ (0.2882 g, 0.66 mmol) in 40 ml CH₂Cl₂. The reaction mixture was stirred for 3 h at room temperature and then filtered to remove the resulting NaCl. The filtrate was evaporated under reduced pressure to obtain **1** as a white crystalline product. X-ray quality crystals were grown from CH₂Cl₂–*n*-hexane (1:3) mixture. Yield: 0.70 g (88%), m.p. (dec.) 228–229 °C. Anal. Found: C, 60.2; H, 4.1; N, 2.5. Calc. for C₆₀H₅₀N₂O₄P₄Pb: C, 60.4; H, 4.2; N, 2.4%. IR (nujol, cm⁻¹): 1240vs [ν_{as}(P₂N)], 1120vs, 1080vs, 1060vs [ν(PO)]. ¹H-NMR: δ 6.94dd [4H, Pb–C₆*H*₅-*meta*, ³*J*(HH) 7.1 Hz], 7.08t [2H, Pb–C₆*H*₅-*para*, ³*J*(HH) 7.3 Hz], 7.14ddd [16H, P–C₆*H*₅-*meta*, ³*J*(HH) 7.4, ⁴*J*(PH) 2.5 Hz], 7.27t [8H, P-C₆*H*₅-*para*, ³*J*(HH) 7.4 Hz], 7.49dd [16H, P–C₆*H*₅-*ortho*, ³*J*(HH) 7.5, ³*J*(PH) 12.4 Hz], 7.93d [4H, Pb–C₆*H*₅-*ortho*, ³*J*(PbH) 216.5 Hz]. ¹³C-NMR: δ 127.51d [*C*ₘ, P–*C*₆H₅, ³*J*(PC) 13.3 Hz], 128.76s (*C*ₘ, Pb–*C*₆H₅), 128.93s (*C*ₚ, Pb–*C*₆H₅), 130.02s (*C*ₚ, P–*C*₆H₅), 131.24d [*C*ₒ, P–*C*₆H₅, ²*J*(PC) 10.5 Hz], 134.16s [*C*ₒ, Pb–*C*₆H₅, ²*J*(PbC) 131.0 Hz], 137.27d [*C*ᵢ, P–*C*₆H₅, ¹*J*(PC) 140.0 Hz], 169.96s (*C*ᵢ, Pb–*C*₆H₅). ³¹P-NMR: δ 19.7s.

4.3. Preparation of bis(tetraphenylthioimidodiphosphinato)diphenyllead-(IV), Ph₂Pb[(OPPh₂)(SPPh₂)N]₂ (2)

K[(OPPh₂)(SPPh₂)N] (0.7858 g, 1.66 mmol) was added to a solution of Ph₂PbCl₂ (0.3603 g, 0.83 mmol) in 40 ml anhydrous benzene. The reaction mixture was stirred for 3 h at room temperature and then filtered to remove the resulting KCl. The filtrate was evaporated under reduced pressure to obtain **2** as a white microcrystalline solid. Yield: 0.91 g (89%), m.p. (dec.) 190 °C. Anal. Found: C, 58.7; H, 4.2; N, 2.5. Calc. for C₆₀H₅₀N₂O₂P₄PbS₂: C, 58.8; H, 4.1; N, 2.3%. IR (nujol, cm⁻¹): 1240vs [ν_{as}(P₂N)], 1110vs, 1040s [ν(PO)], 570m [ν(PS)]. ¹H-NMR: δ 7.5m [46H, Pb–C₆*H*₅-*meta*+*para*, P–C₆*H*₅], 8.05d [4H, Pb–C₆*H*₅-*ortho*, ³*J*(HH) 7.6, ³*J*(PbH) 186.5 Hz]. ¹³C-NMR: δ 128.09d [*C*ₘ, (O)P–*C*₆H₅+(S)P–*C*₆H₅, ³*J*(PC) 12.9 Hz], 129.83s,br (*C*ₘ+*C*ₚ, Pb–*C*₆H₅), 131.46s,br [*C*ₒ+*C*ₚ, (O)P–*C*₆H₅+(S)P–*C*₆H₅], 135.02s (*C*ₒ, Pb–*C*₆H₅) (resonance signals for *ipso* carbons could not be observed). ³¹P-NMR: δ 21.8s (*P*ₒ), 31.8s (*P*ₛ).

4.4. Preparation of (tetraphenylimidodiphosphinato)-trimethyllead(VI), Me₃Pb[(OPPh₂)₂N] (3)

Na[(OPPh₂)₂N] (0.7323 g, 1.66 mmol) was added to a solution of Me₃PbCl (0.4796 g, 1.66 mmol) in 40 ml

CH₂Cl₂. The reaction mixture was stirred for 3 h at room temperature and then filtered to remove the resulting NaCl. The filtrate was evaporated under reduced pressure to obtain **3** as a white microcrystalline product. Yield: 0.74 g (95%), m.p. 145–147 °C. Anal. Found: C, 48.2; H, 4.1; N, 2.2. Calc. for C₂₇H₂₉NO₂P₂Pb: C, 48.5; H, 4.4; N, 2.1%. IR (nujol, cm⁻¹): 1240vs [ν_{as}(P₂N)], 1110vs, 1040s [ν(PO)], 770m [ρ(CH₃)]. ¹H-NMR: δ 1.30s [9H, Pb–C*H*₃, ²*J*(PbH) 79.3 Hz], 7.29m (8H, P–C₆*H*₅-*meta*), 7.37t [4H, P–C₆*H*₅-*para*, ³*J*(HH) 7.1 Hz], 7.68dd [8H, P–C₆*H*₅-*ortho*, ³*J*(HH) 7.4, ³*J*(PH) 12.4 Hz]. ¹³C-NMR: δ 19.61s [Pb–*C*H₃, ¹*J*(PbC) 341.4 Hz], 127.95d [*C*ₘ, P–*C*₆H₅, ³*J*(PC) 13.4 Hz], 130.55s (*C*ₚ, P–*C*₆H₅), 131.31d [*C*ₒ, P–*C*₆H₅, ²*J*(PC) 10.7 Hz], 137,23d (*C*ᵢ, P–*C*₆H₅), ¹*J*(PC) 132.3 Hz]. ³¹P-NMR: δ 13.8s,br.

The attempt to obtain suitable crystals for X-ray diffraction from CH₂Cl₂–*n*-hexane (1:3) mixture resulted in isolation of the redistribution product, Me₂Pb[(OPPh₂)₂N]₂ (**5**), following a decomposition process (see Section 2).

4.5. Preparation of (tetraphenylthioimidodiphosphinato)triphenyllead(VI), Ph₃Pb[(OPPh₂)(SPPh₂)N] (4)

K[(OPPh₂)(SPPh₂)N] (0.5239 g, 1.11 mmol) was added to a solution of Ph₃PbCl (0.5267 g, 1.11 mmol) in 40 ml anhydrous benzene. The reaction mixture was stirred for 3 h at room temperature and then filtered to remove the resulting KCl. The filtrate was evaporated under reduced pressure to obtain **4** as a white solid. Yield: 0.81 g (82%), m.p. 112–114 °C. Anal. Found: C, 58.2; H, 4.3; N, 1.4. Calc. for C₄₂H₃₅NOP₂PbS: C, 57.9; H, 4.1; N, 1.6%. IR (nujol, cm⁻¹): 1230s [ν_{as}(P₂N)], 1120s, 1080s, 1060s [ν(PO)], 570m [ν(PS)]. ¹H-NMR: δ 7.3m [25H, Pb–C₆*H*₅-*meta*+*para*, P–C₆*H*₅-*meta*+*para*, (O)P–C₆*H*₅-*ortho*], 7.49m [4H, Pb–C₆*H*₅-*ortho*, ³*J*(PbH) 113 Hz], 7.61dd [4H, (S)P–C₆*H*₅-*ortho*, ³*J*(HH) 7.6, ³*J*(PH) 14.0 Hz]. ¹³C-NMR: δ 127.35d [*C*ₘ, P–*C*₆H₅, ³*J*(PC) 13.2 Hz], 127.69d [*C*ₘ, P–*C*₆H₅, ³*J*(PC) 13.7 Hz], 129.22s (*C*ₚ, Pb–*C*₆H₅), 129.58s (*C*ₚ, P–*C*₆H₅), 129.84s [*C*ₘ, Pb–*C*₆H₅, ³*J*(PbC) 107.1 Hz], 130.28s (*C*ₚ, Pb–*C*₆H₅), 131.32d [*C*ₒ, P–*C*₆H₅, ²*J*(PC) 12.0 Hz], 131.54d [*C*ₒ, P–*C*₆H₅, ²*J*(PC) 11.1 Hz], 136.88s [*C*ₒ, Pb–*C*₆H₅, ²*J*(PbC) 87.5 Hz], 157.16s [*C*ᵢ, Pb–*C*₆H₅] (resonance signals for *ipso* carbons of P–*C*₆H₅ could not be observed). ³¹P-NMR: δ 14.4s (*P*ₒ), 31.6s (*P*ₛ).

4.6. Preparation of (diphenylphosphinato)trimethyllead(VI), Me₃Pb(O₂PPh₂) (6)

Ph₂PO₂Na (0.4803 g, 2 mmol) was added to a solution of Me₃PbCl (0.5755 g, 2 mmol) in 40 ml CH₃Cl. The

reaction mixture was stirred for 3 h at room temperature and then filtered to remove the resulting NaCl. The filtrate was evaporated under reduced pressure to obtain **6** as a white solid. X-ray quality crystals were grown from CH_3Cl–*n*-hexane (1:3) mixture. Yield: 0.83 g (88%), m.p. 216–218 °C. Anal. Found: C, 38.2; H, 4.2. Calc. for $C_{15}H_{19}O_2PPb$: C, 38.4; H, 4.1%. ^{1}H-NMR: δ 1.34s [9H, Pb–C*H*$_3$, [2]*J*(PbH) 85.7 Hz], 7.33m (6H, P–C$_6$*H*$_5$-*meta*+*para*), 7.57dm [4H, P–C$_6$*H*$_5$-*ortho*, [3]*J*(HH) 7.7, [4]*J*(HH) 1.4, [3]*J*(PH) 11.5 Hz]. ^{13}C-NMR: δ 14.37s [Pb–*C*H$_3$, [1]*J*(PC) 391.7 Hz], 122.59d [*C*$_m$, P–C$_6$H$_5$, [3]*J*(PC) 12.2 Hz], 124.79s (*C*$_p$, P–C$_6$H$_5$), 125.81d [*C*$_o$, P–C$_6$H$_5$, [2]*J*(PC) 9.7 Hz], 133.41d [*C*$_i$, P–C$_6$H$_5$, [1]*J*(PC) 134.5 Hz]. ^{31}P-NMR: δ 16.8s [[1]*J*(PC) 134.0 Hz].

4.7. X-ray structure determination

A colourless plate crystal of $Me_2Pb[(OPPh_2)_2N]_2$ (**5**) and block colourless crystals of $Ph_2Pb[(OPPh_2)_2N]_2$ (**1**) and $[Me_3Pb[(O_2Ph_2)]]_4$ (**6**) were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Siemens SMART/CCD system at McMaster University with graphite-monochromated Mo–Kα radiation, operating at 50 kV and 35 mA. Cell constants corresponded to triclinic (**1** and **5**) and orthorhombic (**6**) cells whose dimensions are given in Table 3 along with other experimental parameters and relevant information pertaining to structure solution and refinement. Semiempirical absorption corrections were applied.

The structures were solved by direct methods [19]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [20] was based on 11799 for **1**, 21294 for **5**, and 7762 for **6** [7940 for **1**, 9032 for **5**, and 4521 for **6**, $F^2 > 2\sigma(F^2)$] independent reflections and 630 for **1**, 1103 for **5**, and 364 for **6** variable parameters and converged (largest parameter shift was 0.001 times its estimated S.D.).

5. Supplementary material

Crystallographic data for the structural analysis of compounds **1**, **5** and **6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 182709 (**1**), 182708 (**5**), 182710 (**6**). Copies of the

Table 3
Crystal data and structure refinement for $Ph_2Pb[(OPPh_2)_2N]_2$ (**1**), $Me_2Pb[(OPPh_2)_2N]_2$ (**5**), and $[Me_3Pb(OPPh_2)_2N]_4$ (**6**)

	(**1**)	(**5**)	(**6**)
Empirical formula	$C_{60}H_{50}N_2O_4P_4Pb$	$C_{100}H_{92}N_4O_8P_8Pb_2$	$C_{60}H_{76}O_8P_4Pb_4$
Formula weight	1194.09	2139.92	1877.85
Temperature (°C)	26(2)	26(2)	26(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pnma*
a (Å)	10.689(2)	11.015(1)	15.256(4)
b (Å)	10.824(2)	19.044(1)	29.633(7)
c (Å)	24.782(4)	22.943(2)	14.736(1)
α (°)	86.17(1)	81.86(1)	90
β (°)	79.69(1)	87.75(2)	90
γ (°)	69.54(1)	84.79(1)	90
Volume (Å^3)	2643(3)	4743.0(8)	6661(1)
Z	2	2	4
Density (calculated) (g cm^{-3})	1.500	1.498	1.872
Absorption coefficient (mm^{-1})	3.362	3.737	10.222
$F(0\,0\,0)$	1196	2136	3552
Crystal size (mm^3)	$0.34 \times 0.16 \times 0.18$	$0.19 \times 0.10 \times 0.04$	$0.28 \times 0.25 \times 0.20$
θ range for data collection (°)	2.01–27.52	1.31–27.51	1.37–27.48
Index ranges	$-12 \leq h \leq 13$, $-14 \leq k \leq 13$, $-31 \leq l \leq 32$	$-14 \leq h \leq 13$, $-24 \leq k \leq 24$, $-29 \leq l \leq 29$	$-19 \leq h \leq 19$, $-38 \leq k \leq 16$, $-19 \leq l \leq 18$
Reflections collected	24 163	43 104	46 004
Independent reflections	11 799 [$R_{int} = 0.0538$]	21 294 [$R_{int} = 0.1114$]	7762 [$R_{int} = 0.1071$]
Max./min. transmission	0.6153/0.3944	0.8649/0.5370	0.2343/0.1620
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	11 799/0/630	21 294/0/1103	7762/0/364
Goodness-of-fit on F^2	0.936	0.935	1.001
Final R indices [$F^2 > 2s(F^2)$]	$R_1 = 0.0462$, $wR_2 = 0.0700$	$R_1 = 0.0718$, $wR_2 = 0.0880$	$R_1 = 0.0515$, $wR_2 = 0.0839$
R indices (all data)	$R_1 = 0.0917$, $wR_2 = 0.0802$	$R_1 = 0.2118$, $wR_2 = 0.1169$	$R_1 = 0.1159$, $wR_2 = 0.0998$
Largest difference peak and hole (e Å^3)	1.039 and −0.781	0.758 and −0.765	1.612 and −1.251

information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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