

Lead(II) complexes with phosphorylthiolato and thiophosphorylthiolato ligands

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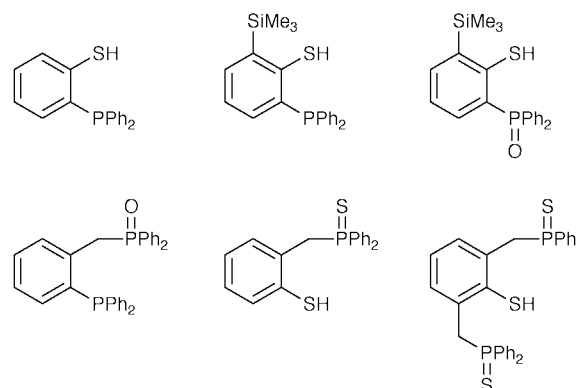
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Neutral lead complexes of a series of phosphorylarenethiol and thiophosphorylarenethiol proligands have been synthesised. Compounds $[\text{Pb}\{2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{S}\}_2]$ **1**, $[\text{Pb}\{2-(\text{Ph}_2\text{P})-6-(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}_2]$ **2** and $[\text{Pb}\{2-(\text{Ph}_2\text{PO})-6-(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}_2]$ **3** were obtained by the electrochemical oxidation of a lead anode in a cell containing an acetonitrile solution of the ligand. $[\text{Pb}\{2-(\text{Ph}_2\text{P}(\text{O})\text{CH}_2)\text{C}_6\text{H}_4\text{S}\}_2]$ **4**, $[\text{Pb}\{2-(\text{Ph}_2\text{P}(\text{S})\text{CH}_2)\text{C}_6\text{H}_4\text{S}\}_2]$ **5** and $[\text{Pb}\{2,6-(\text{Ph}_2\text{P}(\text{S})\text{CH}_2)_2\text{C}_6\text{H}_3\text{S}\}_2]$ **6** were obtained by addition of the appropriate proligand to a methanol solution of lead acetate. The molecular structures of **3**, **4** and **5** show the metal in a five-coordinate geometry with the stereochemically active lone pair on Pb(II) in an equatorial position of a trigonal bipyramid. In **3**, the metal coordination is supplemented by an additional weak Pb–($\eta^6\text{-C}_6\text{H}_6$) intermolecular interaction with a phenyl ring from a neighbouring molecule. Compound **6** consists of monomeric neutral molecules with the lead atom in a pseudo trigonal-bipyramidal geometry and additional weak intramolecular coordination with two sulfur atoms.

Since the interaction of the toxic metal lead with biological systems frequently involves bonding to enzyme sulfhydryl groups, lead–thiolate interactions are of some interest in the design of sequestering agents and several papers have been dedicated to the design of specific complexing agents.¹ Although thiolate complexes of lead(II) that do not involve sterically demanding groups have been known for many years,² structural studies have been hampered by their poor solubility and lack of suitable crystallinity, probably as a result of the tendency of thiolate groups to bridge metal centres to yield polymeric species. Bulky groups close to donor atoms enhance the lipophilicity and the tendency of compounds to form compounds of low molecular weight. This is illustrated by the X-ray structure of $\text{Pb}(\text{SC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2$ which shows the presence of a trinuclear structure with the metal in di- and tri-coordinate environments.³ An alternative route to low molecular weight species involves the saturation of the metal coordination sphere with donor atoms other than thiolate, and X-ray crystal structures of molecular lead(II) complexes with bidentate chelating ligands such as thiohydroxamate,⁴ dithiocarbamate,⁵ thio-benzoate⁶ or dithiophosphinate⁷ have been reported. As a result of our continuous interest in the chemistry of monomeric and low molecular weight thiolate metal complexes of main group elements, we now describe the synthesis and structural characterisation of lead(II) complexes with the phosphorylarenethiol and thiophosphorylarenethiol proligands shown in Scheme 1.

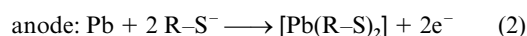
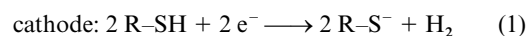
Results and discussion

Lead(II) phosphinothiolato complexes **1**, **2** and **3** were easily prepared in good yield by oxidation of a lead anode in a cell containing an acetonitrile solution of the corresponding proligand and a small amount of tetramethylammonium perchlorate as electrolyte. The compounds are air-stable crystalline yellowish solids, moderately soluble in chloroform, dichloromethane and other common organic solvents.



Scheme 1

The electrochemical efficiency for the process was in all cases close to 0.5 mol F^{−1}. This value and the evolution of hydrogen at the cathode is compatible with the following electrode processes [eqn. (1) and (2)]:



where R–SH represents the phosphorylarenethiol or thiophosphorylarenethiol proligand.

Complexes **4**, **5** and **6** were obtained in reasonable yields by stirring the corresponding proligand and lead acetate in a methanol solution at room temperature for 2 h. Crystalline yellow solids were formed immediately in all cases. The compounds were recrystallised by slow diffusion of either methanol or diethyl ether into a CH₂Cl₂ solution.

The IR spectra of these complexes show no bands attributable to $\nu(\text{S-H})$, which in the free ligands appears at 2500–2400 cm^{−1}. This indicates that the ligands are in the anionic thiolate

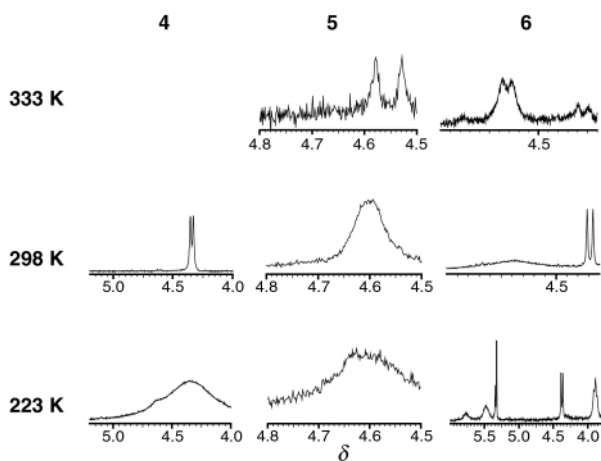


Fig. 1 ^1H NMR of compounds $[\text{Pb}\{2-(\text{Ph}_2\text{P}(\text{O})\text{CH}_2)\text{C}_6\text{H}_4\text{S}\}_2]$ **4**, $[\text{Pb}\{2-(\text{Ph}_2\text{P}(\text{S})\text{CH}_2)\text{C}_6\text{H}_4\text{S}\}_2]$ **5** and $[\text{Pb}\{2,6-(\text{Ph}_2\text{P}(\text{S})\text{CH}_2)_2\text{C}_6\text{H}_3\text{S}\}_2]$ **6** at 233, 298 and 333 K. * resonance of an impurity of CH_2Cl_2 .

form in the complexes. The spectrum also shows bands in the aromatic region characteristic of the coordinated phosphorylthiolate ligand. The compounds containing the trimethylsilyl group show a strong band at $850\text{--}840\text{ cm}^{-1}$ corresponding to $\nu(\text{Si}-\text{C})$ and those with the P=O group another strong band at *ca.* 1130 cm^{-1} .

The main features of the ^1H NMR spectra of these complexes are related to the resonances of the SH and CH_2 protons. The room-temperature ^1H NMR of these complexes show the disappearance of the signal attributable to the SH hydrogen atom (which in the free proligands appears in the range δ 5.1–3.9 as doublets as a result of the coupling with the phosphorus). This again confirms that the ligands are in the anionic thiolate form in the compounds. As for the CH_2 resonances, if the structures of the compounds were rigid in solution, the methylene protons would be diastereotopic, and consequently the appearance of the signal should correspond to an AB system further split by coupling to the phosphorus. However, the behaviour is far more complicated as these resonances are temperature dependent, showing that in solution the compounds are fluxional. This behaviour is summarised in Fig. 1. For compound **4**, at room temperature the signal due to the CH_2 group is a doublet due to two equivalent protons split by phosphorus. The signal broadens at 223 K as the hydrogens become progressively more inequivalent. By contrast for compound **5**, the resonance is broad even at 298 K, broadens further at 223 K and splits into a broad doublet at the higher temperature of 333 K. This suggests a more rigid structure for **5**. For compound **6**, the spectrum shows a broad band due to the CH_2 group of the P=S group bonded to the metal, and a doublet at the same shift value as in the free ligand due to the free P=S group. This latter signal is not temperature dependent. By contrast the other CH_2 signal splits into a broad doublet at 333 K, and at 223 K it appears as two different signals of equal intensity. The signal at lower field is a broad doublet, but the signal at higher field is a triplet, as the result of the overlapping of the splitting due to the hydrogen and phosphorus. This temperature dependence for **6** rules out the possibility of a fluxional mechanism involving alternate coordination of the two P=S groups, as in this case the resonances of both methylene groups would be temperature dependent. In addition, a dissociative mechanism implies that the ^{31}P resonances of **6** should be temperature dependent, and this is not the case (*vide infra*).

A possible mechanism could be a conformational equilibrium, which exchanges the methylene hydrogens between axial and equatorial sites, as shown in Scheme 2.

Another possibility could be a Berry type pseudorotation using the lead atom as the pivotal centre. Obviously, as both

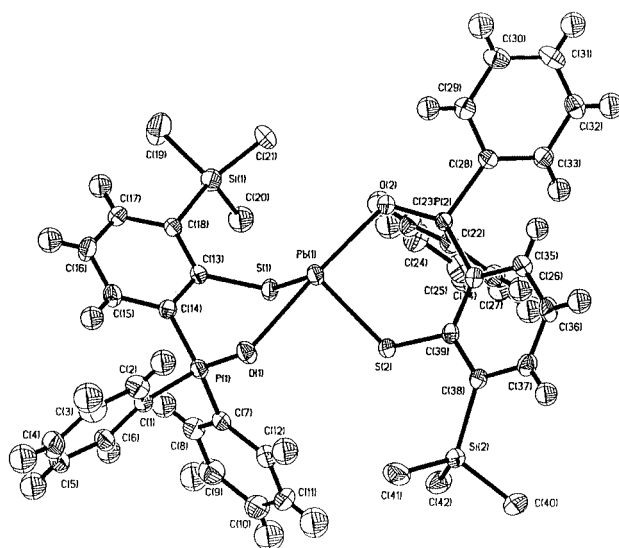
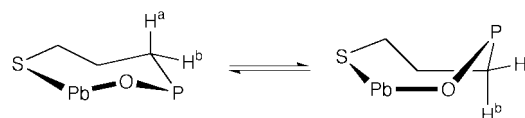


Fig. 2 Molecular structure of $[\text{Pb}\{2-(\text{Ph}_2\text{PO})-6-(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}_2]$ **3**.



Scheme 2

mechanisms operate in the same sense, their concurrent existence cannot be dismissed.

The ^{31}P NMR spectra of complexes **1–3** show a single signal that appear at δ 37.5, 41.6 and 52.8, respectively, and at δ 27.5 and 40.5 for **4** and **5**. For compound **6**, the spectrum shows two resonances at δ 40.2 and 36.6 due to the free and coordinated P=S groups, respectively. The ^{31}P NMR spectrum of compound **6** is temperature independent, showing that the mechanism of exchange does not involve the exchanging of coordinated and free P=S groups.

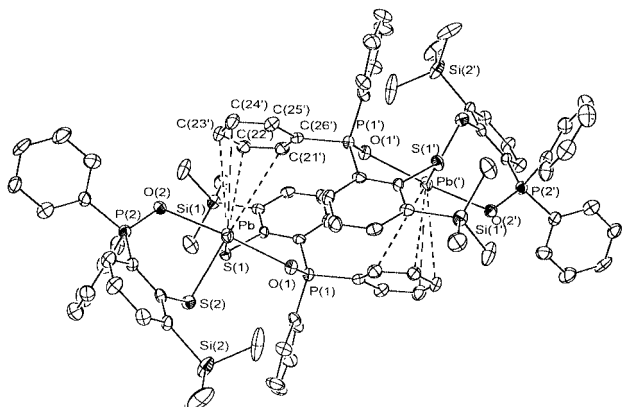
The FAB mass spectra of these compounds show in all cases the molecular ion $[\text{Pb}(\text{R}-\text{S})_2]^+$ (m/z 794, 937, 970, 853, 883 and 1346, respectively, for **1–6**) and also the peak associated with $[\text{Pb}(\text{R}-\text{S})]^+$ formed by loss of one P–S ligand from the initial species. Yellow crystals of **3–6** suitable for X-ray structure determinations were obtained by recrystallisation from CH_2Cl_2 –MeOH. Attempts to obtain crystals of **1** and **2** suitable for X-ray studies were unsuccessful, but analytical and spectroscopic data confirm the presence of lead(II) compounds with two bidentate monoanionic ligands and presumably the complexes have similar structures to that found for complex **3** (*vide infra*).

X-Ray crystal structures

Molecular structure of $[\text{Pb}\{2-(\text{Ph}_2\text{PO})-6-(\text{Me}_3\text{Si})\text{C}_6\text{H}_3\text{S}\}_2]$ **3.** The molecular structure of **3** is shown in Fig. 2 together with the atom-labelling scheme adopted. Selected bond distances and angles appear in Table 1. The structure consists of discrete molecules with the lead atom coordinated by two bidentate anionic 2-diphenylphosphoryl-6-trimethylsilylbenzenethiolate ligands through their oxygen and thiolate sulfur atoms. The overall geometry about the Pb is best described as distorted ψ -trigonal bipyramidal with the oxygen atoms in axial positions, with an O(1)–Pb–O(2) bond angle of $174.38(7)^\circ$, and the sulfur atoms in equatorial sites, with an S(1)–Pb–S(2) bond angle of $81.54(2)^\circ$. The stereochemically active lone pair on the lead atom presumably occupies the third equatorial position. Intermolecular interactions within 5 Å with oxygen or sulfur atoms of any neighbouring molecules do not exist. This contrasts with the behaviour of other Pb(II) complexes with the

Table 1 Selected bond distances (Å) and angles (°) for [Pb(2-(Ph₂PO)-6-(Me₃Si)C₆H₄S)₂]**3**

Pb(1)–O(2)	2.495(2)	Pb(1)–O(1)	2.519(2)
Pb(1)–S(1)	2.6439(8)	Pb(1)–S(2)	2.6462(7)
S(1)–C(13)	1.768(3)	S(2)–C(39)	1.768(3)
P(2)–O(2)	1.501(2)	P(2)–C(22)	1.800(3)
P(1)–O(1)	1.506(2)	P(1)–C(14)	1.808(3)
O(2)–Pb(1)–O(1)	174.38(7)	O(2)–Pb(1)–S(1)	94.50(5)
O(1)–Pb(1)–S(1)	82.14(5)	O(2)–Pb(1)–S(2)	81.34(5)
O(1)–Pb(1)–S(2)	93.68(6)	S(1)–Pb(1)–S(2)	81.54(2)
C(13)–S(1)–Pb(1)	101.41(10)	C(39)–S(2)–Pb(1)	106.13(10)
O(2)–P(2)–C(22)	112.94(13)	O(2)–P(2)–C(34)	116.03(13)

**Fig. 3** Unit cell of **3** showing the η^6 interaction between a phenyl ring and a lead atom.

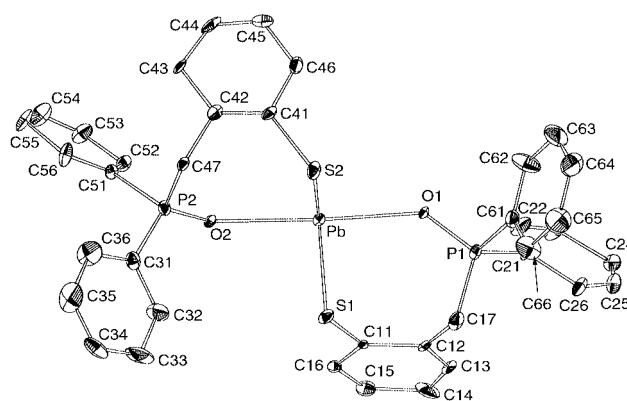
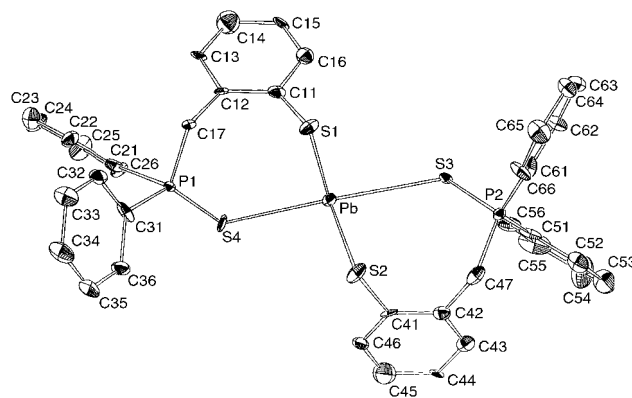
same [PbS₂O₂] core, in which weak intermolecular associations through oxygen or sulfur atoms are observed.^{4–8} Probably the presence of the bulky trimethylsilyl groups in the ligands prevents the metal atom from increasing its coordination number through this type of intermolecular contact. The same situation is found in the bis(*N*-cyclohexylphenylacetothiohydroxamato)-lead(II) complex,⁹ reported as the first monomeric hydroxamato lead complex as a consequence of the bulkiness of the ligands employed. However, for the structure of **3**, Fig. 3, a phenyl ring of one molecule is close to the lead atom of other molecule, leading to a weak Pb–(η^6 -C₆H₅) interaction between the lead electron pair and the phenyl ring. The distances between the lead atom and the carbon atoms of this phenyl group are in the range of 3.50–4.15 Å, average value 3.86 Å, with a value of 3.62 Å for the distance to the centre of the ring. This value is slightly shorter than the sum of the van der Waals radii, 3.70 Å, when the radius of the phenyl group is considered in the direction perpendicular to the phenyl ring.¹⁰ Interactions of the type Pb–(η^6 -C₆H₅) have also been found in [Pb{S(PPh₂)₂N}₂]₂,¹¹ [Pb{S₂P(OPh)₂}]₂¹² and Pb(C₆H₆)(AlCl₄)₄·C₆H₆.¹³

The Pb–S bond distances, 2.6439(8) and 2.6462(7) Å, are in the range 2.55–2.72 Å reported for lead complexes of thiolate ligands where the sulfur donor atom carries a full negative formal charge.^{2,14} The Pb–O bond distances, 2.495(2) and 2.519(2) Å, are also normal and similar to those found in other complexes with the same [PbO₂S₂] environment.^{4,8,9}

Molecular structure of [Pb{2-(Ph₂P(O)CH₂)C₆H₄S}₂]4**.** Fig. 4 shows the molecular structure of **4** and the atomic numbering scheme adopted. Selected bond distances and angles are contained in Table 2. The compound is monomeric with no interactions between neighbouring molecules. The structure is similar to that of **3**, with two anionic ligands coordinated through the thiolate sulfur atoms and the oxygen atoms of the phosphinyl group to the metal. The environment around the lead atom is again a pseudo-trigonal bipyramid with the oxygen atoms in axial positions, and the sulfur atoms and the lone pair in the equatorial positions. This geometry is slightly distorted

Table 2 Selected bond distances (Å) and angles (°) for [Pb{2-(Ph₂P(O)CH₂)C₆H₄S}₂]**4**

Pb–S(1)	2.584(5)	Pb–S(2)	2.617(5)
Pb–O(1)	2.523(16)	Pb–O(2)	2.599(17)
S(1)–C(11)	1.686(18)	S(2)–C(41)	1.879(16)
O(1)–P(1)	1.614(15)	O(2)–P(2)	1.417(15)
P(1)–C(17)	1.77(2)	P(1)–C(21)	1.78(2)
P(1)–C(61)	1.881(13)	P(2)–C(47)	1.822(14)
P(2)–C(31)	1.774(13)	P(2)–C(51)	1.806(15)
S(1)–Pb–S(2)	94.83(8)	S(1)–Pb–O(1)	89.4(3)
S(2)–Pb–O(1)	88.3(3)	C(11)–S(1)–Pb	96.1(5)
C(41)–S(2)–Pb	94.1(5)	P(1)–O(1)–Pb	136.2(7)
O(1)–P(1)–C(17)	114.6(9)	O(1)–P(1)–C(21)	111.0(7)
C(17)–P(1)–C(21)	107.3(10)	O(1)–P(1)–C(61)	106.7(7)
C(17)–P(1)–C(61)	113.5(9)	C(21)–P(1)–C(61)	103.1(9)
O(2)–P(2)–C(47)	112.6(9)	O(2)–P(2)–C(31)	118.1(7)
C(47)–P(2)–C(31)	98.6(7)	O(2)–P(2)–C(51)	111.0(8)
C(47)–P(2)–C(51)	105.6(6)	C(31)–P(2)–C(51)	109.7(8)

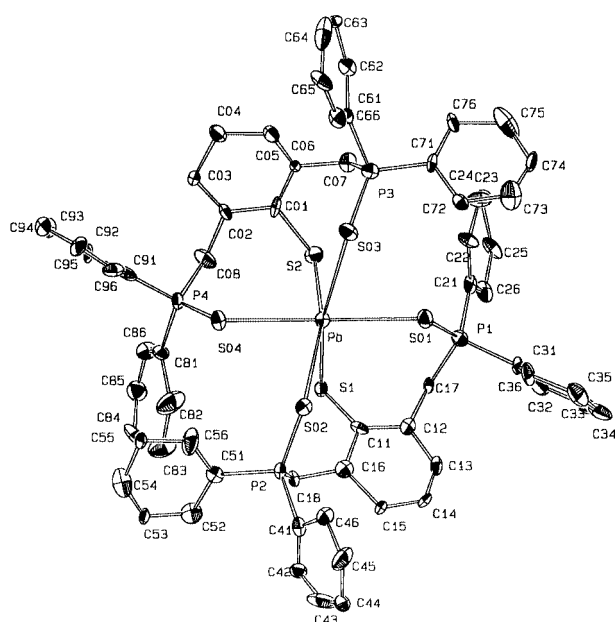
**Fig. 4** Molecular structure of [Pb{2-(Ph₂P(O)CH₂)C₆H₄S}₂]**4**.**Fig. 5** Molecular structure of [Pb{2-(Ph₂P(S)CH₂)C₆H₄S}₂]**5**.

with an O–Pb–O angle of 175.3(5)°, and bond angles between the axial oxygen and sulfur atoms of the equatorial plane in the range 87.2(3)–92.2(3)°, close to the ideal value. The main source of distortion is the value of the equatorial bond angle S–Pb–S (94.83(8)°) as a result of the small bite angle of the ligand and the presence of the lone pair situated in this plane. The Pb–S bond distances of 2.584(5) and 2.617(5) Å are normal. The Pb–O bond distances, 2.523(16) and 2.599(17) Å are in the range, 2.32–2.74 Å, found for bidentate oxygen donor ligands.¹⁵

Molecular structure of [Pb{2-(Ph₂P(S)CH₂)C₆H₄S}₂]5**.** The molecular structure of **5** is shown in Fig. 5, and selected bond distances and angles appear in Table 3. The structure shows disorder within the P=S group with a distinct peak for each of two independent sulfur atoms. The compound is monomeric with the lead atom coordinated to the sulfur atoms of two aniso-

Table 3 Selected bond distances (Å) and angles (°) for [Pb{2-(Ph₂-P(S)CH₂)C₆H₃S₂}₂] **5**

Pb–S(1)	2.550(5)	Pb–S(2)	2.617(6)
Pb–S(4')	2.885(12)	Pb–S(4)	2.950(12)
Pb–S(3')	3.088(14)	Pb–S(3)	3.151(9)
P(1)–C(31)	1.901(11)	P(1)–S(4)	1.973(13)
P(1)–S(4')	1.989(14)	P(2)–C(51)	1.694(12)
P(2)–C(47)	1.74(2)	P(2)–C(61)	1.771(12)
P(2)–S(3')	1.978(17)	P(2)–S(3)	2.003(10)
S(1)–Pb–S(2)	94.90(9)	S(1)–Pb–S(4')	91.2(3)
S(2)–Pb–S(4')	88.8(4)	S(1)–Pb–S(4)	96.1(3)
S(2)–Pb–S(4)	105.8(4)	S(4')–Pb–S(3')	171.7(3)
S(1)–Pb–S(3')	85.5(4)	S(4')–Pb–S(4)	18.3(4)
S(2)–Pb–S(3')	84.0(3)	S(4)–Pb–S(3')	169.9(5)
C(17)–P(1)–C(31)	94.2(6)	C(17)–P(1)–C(21)	106.6(7)
C(31)–P(1)–C(21)	93.7(5)	C(17)–P(1)–S(4)	118.6(7)
C(31)–P(1)–S(4)	131.9(7)	C(21)–P(1)–S(4)	107.7(6)

**Fig. 6** Molecular structure of [Pb{2,6-(Ph₂P(S)CH₂)₂C₆H₃S₂}₂] **6**.

bidentate chelate ligands. The arrangement of the four sulfur atoms around the metal atoms is ψ -trigonal bipyramidal with a vacant equatorial site, and the two sulfur atoms of the P=S groups in axial positions, (S(4')–P–S(3')) 171.7(3)°. The thiolate sulfur atoms are in the equatorial plane (S(1)–Pb–S(2) 94.90(9)°) together with the lone pair of the metal. Two different S–Pb bond lengths are observed in the compound. The shortest length corresponds to the anionic thiolate sulfur atoms and the values, 2.550(5) and 2.617(6) Å, are similar to those observed for **3** and **4**, and in the range for the observed for primary interactions in Pb(II) complexes with terminal mono- or di-thiolate ligands, 2.554(4)–2.696(3) Å.^{14,16}

Molecular structure of [Pb{2,6-(Ph₂P(S)CH₂)₂C₆H₃S₂}₂] **6.** Fig. 6 shows the molecular structure of **6**. Selected bond distances and angles appear in Table 4. The compound consists of monomeric neutral molecules with the metal coordinated by two bidentate monoanionic ligands. The geometry of the primary coordination sphere around the metal is pseudo-bipyramidal with two anionic thiolate sulfur atoms in equatorial positions, bond angle S(2)–Pb–S(1) 85.09(10)° and Pb–S bond distance 2.674(7) Å (average value), and two P=S groups in axial positions, (S(01)–Pb–S(04) 161.60(8)°), Pb–S bond distances 2.986 Å (average). These bond distances are normal and similar to those found in **5**. Significant secondary intramolecular interactions with S(02) and S(03) are observed. These secondary Pb–S bond distances, 3.370(8) and 3.386(7) Å, are

Table 4 Selected bond distances (Å) and angles (°) for [Pb{2,6-(Ph₂-P(S)CH₂)₂C₆H₃S₂}₂] **6**

Pb–S(2)	2.659(7)	Pb–S(1)	2.690(6)
Pb–S(01)	2.953(8)	Pb–S(04)	3.020(6)
Pb–S(02)	3.370(8)	Pb–S(03)	3.386(7)
S(01)–P(1)	1.929(10)	S(02)–P(2)	1.987(9)
S(03)–P(3)	1.909(11)	S(04)–P(4)	1.975(7)
P(1)–C(31)	1.827(18)	P(1)–C(21)	1.84(2)
P(1)–C(17)	1.84(2)	P(2)–C(18)	1.76(2)
P(2)–C(41)	1.81(3)	P(2)–C(51)	1.82(2)
S(1)–C(11)	1.66(2)	S(2)–C(01)	1.889(19)
S(2)–Pb–S(1)	85.09(10)	S(2)–Pb–S(01)	98.1(2)
S(1)–Pb–S(01)	95.0(2)	S(2)–Pb–S(04)	95.4(2)
S(1)–Pb–S(04)	98.55(19)	S(01)–Pb–S(04)	161.60(8)
P(1)–S(01)–Pb	114.6(4)	P(4)–S(04)–Pb	113.8(3)
C(31)–P(1)–C(21)	108.1(10)	C(31)–P(1)–C(17)	106.4(9)
C(21)–P(1)–C(17)	110.9(9)	C(31)–P(1)–S(01)	109.9(7)
C(21)–P(1)–S(01)	108.3(8)	C(17)–P(1)–S(01)	113.1(6)
C(18)–P(2)–C(41)	110.1(11)	C(18)–P(2)–C(51)	104.4(7)
C(11)–S(1)–Pb	98.8(7)	C(01)–S(2)–Pb	98.3(6)

longer than a covalent Pb–S bond but significantly shorter than the sum of van der Waals radii, *ca.* 3.80 Å.¹⁷

Experimental

All manipulations were carried out under an inert atmosphere of dry nitrogen. Lead (Aldrich Chemie) was used in rod form. All other reagents were used as supplied. Syntheses of ligands 2-(Ph₂P)C₆H₄SH, 2-(Ph₂P)-6-(Me₃Si)C₆H₃SH and 2-(Ph₂PO)-6-(Me₃Si)C₆H₃SH were carried out using minor modifications of the standard literature procedures.¹⁸ 2-(Ph₂P(O)CH₂)C₆H₄SH and 2-(Ph₂P(S)CH₂)C₆H₄SH proligands were prepared following a similar method described for the synthesis of 2,6-(Ph₂P(S)CH₂)₂C₆H₃SH.¹⁹

Elemental analyses were performed using a Carlo-Erba EA microanalyser. IR spectra were recorded as KBr mulls on a Bruker IFS-66V. FAB mass spectra were recorded on a Kratos-MS-50T connected to a DS90 data system, using 3-nitrobenzyl alcohol (3-NBA) as matrix material. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX 300 MHz instrument against TMS as internal standard and ³¹P in a Bruker 500 MHz, against H₃PO₄ (85%), using CDCl₃ as a solvent in all cases.

Preparation of the complexes

Complexes **1–3** were obtained using an electrochemical procedure. An acetonitrile solution of the ligand containing about 15 mg of tetramethylammonium perchlorate as a support electrolyte was electrolysed using a platinum wire as the cathode and a metal plate as the sacrificial anode. Applied voltages of 10–15 V allowed sufficient current flow for smooth dissolution of the metal. During electrolysis, nitrogen was bubbled through the solution to provide an inert atmosphere and also to stir the reaction mixture.

[Pb{2-(Ph₂P)C₆H₄S₂}₂] **1.** Electrochemical oxidation of a lead anode in a solution of 2-diphenylphosphinobenzenethiol, 2-(Ph₂P)C₆H₄SH, (0.230 g, 0.782 mmol) in acetonitrile (50 cm³), at 10 V and 10 mA for 2 h caused 75 mg of lead to be dissolved, *E*_r = 0.48 mol F^{–1}. During the electrolysis hydrogen was evolved at the cathode and at the end of the electrolysis a yellow solid appeared at the bottom of the vessel. The solid was filtered off, washed with acetonitrile and diethyl ether and dried *in vacuo* (0.21 g, 73%). Anal. Calc. for C₃₆H₂₈PbP₂S₂: C, 54.5; H, 3.5; S, 8.1. Found: C, 53.4, H, 3.3; S, 8.0%. IR (KBr, cm^{–1}): 1570m, 1482m, 1433s, 1416m, 1241s, 1091m, 738s, 692s; 525s. ¹H NMR (CDCl₃, ppm): δ 7.6–6.5 (m, 28 H). ³¹P NMR (CDCl₃): δ 37.5.

[Pb{2-(Ph₂P)-6-(Me₃Si)C₆H₃S₂}₂] **2.** A similar experiment (12 V, 10 mA, 2 h) with lead as anode and 0.273 g (0.746 mmol) of

Table 5 Summary of crystallographic data for [Pb{2-(Ph₂PO)-6-(Me₃Si)C₆H₃SH}] **3**, [Pb{2-(Ph₂P(O)CH₂)C₆H₄SH}] **4**, [Pb{2-(Ph₂P(S)CH₂)C₆H₄SH}] **5** and [Pb{2,6-(Ph₂P(S)CH₂)₂C₆H₃SH}] **6**

	3	4	5	6
Chemical formula	C ₄₂ H ₄₄ O ₂ P ₂ S ₂ Si ₂ Pb	C ₃₈ H ₃₂ O ₂ P ₂ S ₂ Pb	C ₃₈ H ₃₂ P ₂ S ₄ Pb	C ₆₄ H ₅₄ P ₄ S ₆ Pb
Formula weight	970.20	853.88	886.01	1346.52
<i>T</i> /K	150(2)	150(2)	150(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>
<i>a</i> /Å	11.417(2)	14.6460(10)	15.5560(10)	16.212(3)
<i>b</i> /Å	24.1217(3)	15.5010(10)	15.6120(10)	14.4198(10)
<i>c</i> /Å	15.8139(2)	15.4290(10)	15.0520(10)	25.146(3)
β /°	106.6110(1)	99.583(2)	100.455(2)	92.014(14)
<i>V</i> /Å ³	4173.40(7)	3453.9(4)	3594.8(4)	5874.9(14)
<i>Z</i>	4	4	4	4
μ /mm ⁻¹	4.311	5.131	5.041	3.234
Reflections collected	26969	6487	6712	5678
Independent reflections	9852	3674 (0.0367)	3804 (0.0342)	5678 (0.00)
Data/restraints/parameters	9852/0/455	3674/2/420	3804/68/369	5678/2/676
<i>R</i> ^a	0.0268	0.0337	0.0475	0.0362
<i>wR</i> ₂ ^b	0.0608	0.852	0.1164	0.0849

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $wR_2 = [(\sum w(|F_o| - |F_c|)^2)/\sum w|F_o|^2]^{1/2}$.

2-(Ph₂P)-6-(Me₃Si)C₆H₃SH in 50 cm³ of acetonitrile, dissolved 80 mg of lead, $E_f = 0.52$ mol F⁻¹. As the reaction proceeds the solution changed from colourless to yellow. At the end of the electrolysis the yellow solid deposited in the cell was recovered, washed with cool acetonitrile and diethyl ether and dried *in vacuo* (0.30 g, 86%). Anal. Calc. for C₄₂H₄₄PbP₂S₂Si₂: C, 53.8; H, 4.7; S, 6.8. Found: C, 53.6; H, 4.6; S, 6.4%. IR (KBr, cm⁻¹): 3053m, 2949m, 2893m, 1554m, 1483m, 1434m, 1355s, 1245m, 1086m, 850s, 746s, 692s, 530s. ¹H NMR (CDCl₃): δ 7.7–6.6 (m, 26 H), 0.30 (s, 18H). ³¹P NMR (CDCl₃): δ 41.6.

[Pb{2-(Ph₂PO)-6-(Me₃Si)C₆H₃SH}] **3.** Electrolysis of an acetonitrile solution (50 cm³) containing 2-(Ph₂PO)-6-(Me₃Si)-C₆H₃SH (0.214 g, 0.560 mmol) using a current of 10 mA, (12 V) for 1.5 h caused the dissolution of 58 mg of lead ($E_f = 0.50$ mol F⁻¹) to produce a yellow crystalline solid. The solid was washed with acetonitrile and diethyl ether and dried *in vacuo* (0.22 g, 82%). Anal. Calc. for C₄₂H₄₄PbP₂O₂S₂Si₂: C, 52.0; H, 4.5; S, 6.6. Found: C, 51.2; H, 4.3; S, 6.5%. IR (KBr, cm⁻¹): 3055m, 2952m, 2895m, 1556m, 1438s, 1353s, 1242s, 1130s, 1065m, 845s, 748s, 692s. ¹H NMR (CDCl₃): δ 7.7–6.7 (m, 26H), 0.40 (s, 18H). ³¹P NMR (CDCl₃): δ 52.8. Crystals suitable for X-ray studies were obtained by crystallisation from CH₂Cl₂–MeOH.

[Pb{2-(Ph₂P(O)CH₂)C₆H₄SH}] **4.** To a solution of 2-(Ph₂P(O)CH₂)C₆H₄SH (0.10 g, 0.31 mmol) in 20 ml of methanol was added a solution of lead acetate (0.05 g, 0.154 mmol) in methanol (15 ml). The solution was stirred at room temperature for 2 h to give a bright yellow solid, which was filtered off, washed with methanol, diethyl ether and dried *in vacuo* (0.105 g, 81%). Crystals suitable for X-ray studies were obtained by crystallisation from CH₂Cl₂–diethyl ether and identified by spectroscopy and elemental analysis. Anal. Calc. for C₃₈H₃₂P₂S₂O₂Pb: C, 53.4; H, 3.7; S, 7.5. Found: C, 52.0; H, 3.24; S, 6.7%. IR (KBr, cm⁻¹): 3053m, 2920m, 1582m, 1462m, 1436m, 1383m, 1225w, 1136s, 1094m, 835s, 749m, 722s, 629m, 534s. ¹H NMR (CDCl₃): δ 7.85 (t, 8H), 7.55 (m, 14H), 7.05 (t, 2H), 6.7 (t, 2H), 6.5 (t, 2H), 4.35 (d, $J_{PH} = 12.6$ Hz, CH₂P, 4H). ¹³C NMR (CDCl₃): δ 141–125, 36.6 (d, $J_{PC} = 57.5$ Hz, CH₂P). ³¹P NMR (CDCl₃): δ 27.5.

[Pb{2-(Ph₂P(S)CH₂)C₆H₄SH}] **5.** The same procedure as for **4** was used for the synthesis of this compound. A solution of lead acetate (0.20 g, 0.588 mmol) in 25 ml of methanol was added to 2-(Ph₂P(S)CH₂)C₆H₄SH (0.094 g, 0.290 mmol), in 20 ml of methanol. It was stirred for 2 h to give a yellow solid (0.23 g, 89%). Crystals suitable for X-ray studies were obtained by crystallisation from CH₂Cl₂–MeOH and identified by spectro-

scopy and elemental analysis. Anal. Calc. for C₃₈H₃₂P₂S₄Pb: C, 51.5; H, 3.6; S, 14.5. Found: C, 50.7; H, 3.0; S, 14.2%. IR (KBr, cm⁻¹): 3052m, 2898m, 1582m, 1462w, 1435m, 1104s, 830m, 747m, 699s, 599m. ¹H NMR (CDCl₃): δ 7.9 (complex m, 8H), 7.8 (m, 2H), 7.5 (m, 10H), 7.4 (m, 2H), 7.1 (t, 2H), 6.7 (t, 2H), 6.5 (d, 2H), 4.65 (d, $J_{PH} = 12.4$ Hz, CH₂P, 4H). ¹³C NMR (CDCl₃): δ 142–126, 39.7 (d, $J_{PC} = 51.7$ Hz, CH₂P). ³¹P NMR (CDCl₃): δ 40.5.

[Pb{2,6-(Ph₂P(S)CH₂)₂C₆H₃SH}] **6.** To a methanol solution of 2,6-(Ph₂P(S)CH₂)₂C₆H₃SH (0.33 g, 0.588 mmol) was added 0.1 g (0.29 mmol) of lead acetate. The mixture was stirred for 4 h, the yellow solid formed was filtered off, and washed with methanol and diethyl ether. Yield 0.28 g (72%). Anal. Calc. for C₆₄H₅₄P₄S₆Pb: C, 57.1; H, 4.0; S, 14.3. Found: C, 56.4; H, 4.2; S, 13.6%. ¹H NMR (CDCl₃): δ 7.9–6.8 (m, Ph, 23H), 3.69 (d, $J_{PH} = 13.3$ Hz, CH₂P, 4H). ³¹P NMR (CDCl₃): δ 40.2, 36.6.

X-Ray crystal structure determinations

Data collection. Intensity data were collected on a CAD4 diffractometer for compound **3** and on an Enraf-Nonius DIP2000 image-plate diffractometer for **4–6**, with monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) in all cases. The images were processed with the Denzo and Scalepak programs for the latter compounds.²⁰

Structure analysis and refinement. The structures were solved *via* direct methods²¹ and refined on F_o^2 by full-matrix least-squares methods.²² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealised positions with U_{iso} free to refine. The weighting scheme gave satisfactory agreement analysis. Sources of scattering factors were as in ref. 18. Details of the structure determination are listed in Table 5.

CCDC reference number 186/1802.

See <http://www.rsc.org/suppdata/dt/a9/a908496g/> for crystallographic files in .cif format.

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