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Synthesis and structure of $[An(RO)PS_2]^-$ complexes

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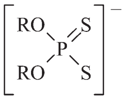
Reaction of $An(S)PS_2P(S)An$ with NaOR [R = Me, Et, ^{i}Pr] gives the non-symmetric phosphonodithioato anions $[An(RO)PS_2]^-$ which can be complexed to a range of metals. The group 10 metals (Ni, Pd and Pt) adopt square planar ML_2 complexes. The zinc and cadmium complexes adopt isostructural dimeric M_2L_4 structures whilst mercury complexes adopt a subtly different dimeric motif. Two distinctly different lead complexes are reported, one consisting of PbL_2 units joined by Pb···S interactions to form distinct dimeric pairs, the other being a completely new structural motif for complexes of this type, PbL_2 units held together by covalently bonded bridging ligands to form an infinite polymeric chain structure. All new compounds have been characterised spectroscopically and nine demonstrative X-ray structures are reported.

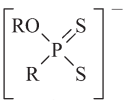
Introduction

Organodithio derivatives of phosphorus have been widely studied for many years.[1] Phosphodithioates, their corresponding acids and metal complexes have been shown to have many industrial and agricultural applications *e.g.* as additives to lubricant oils,[2] floatation reagents for the recovery of metals from their solutions,[3] pesticides and for chemical warfare.[4] More recently research has been conducted on attempts to use these compounds to form liquid transition metal complexes, for use in the preparation of thin layers by chemical vapour deposition (CVD) or of polymer–inorganic nanocomposites.[5] Other recent papers have looked at the biological and potential medicinal uses of dithiophosphate metal complexes and their adducts,[6,7] for example, it has been shown that tin diphenyldithiophosphinato complexes exhibit considerable antiproliferation activity towards certain leukaemia cells.[6] Literature detailing the synthesis, chemistry and structural behaviour of the complexes of phosphorodithioate (**1**) and dithiophosphinodithioate (**3**) ligands is plentiful and widely available.[5,6,8]

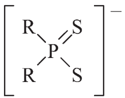
Due to synthetic difficulties,[9] compounds containing phosphonodithioate (**2**) substituents have received little attention.



1
Phosph**oro**dithioate



2
Phosph**ono**dithioate



3
Phosph**ino**dithioate

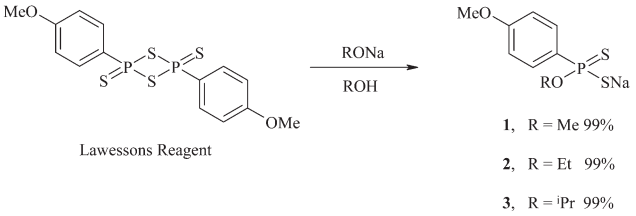
Interest in phosphonodithioate (**2**) derivatives has increased in recent years. Aragoni *et al.* have reported the synthesis and characterisation of several monomeric structures involving two alkoxy(4-methoxyphenyl)dithiophosphonate ligands attached to a group 10 metal centre (Ni^{2+}, $Pd^{2+}$and Pt^{2+}) in a square planar conformation.[10] They achieved this *via* a ring opening reaction of the well known and well studied[11] thionation compound Lawessons Reagent. A similiar method was employed by Özcan *et al.* in the formation of bis[*O*-2,4-di-*tert*-butylphenyl(4-methoxyphenyl)dithiophosphoato] nickel(II), an analogous compound containing a bulky sterically protecting substituent.[12] In both cases X-ray studies unambiguously identified the compounds though there is very little spectroscopic information available.

We recently described the synthesis, full characterisation and crystallographic structural study of alkoxy(ferrocenyl)dithiophosphato compounds.[13] These were formed from Ferrocenyl Lawessons Reagent, a less extensively studied analogue of Lawessons Reagent.[14] Stable complexes were formed with a range of metals (Ni, Pd, Pt, Zn, Cd, Hg, Sn and Pb) and were shown to exhibit several different structural motifs.

Here we report further work on new and some of the few existing alkoxy(4-methoxyphenyl)dithiophosphato compounds, including novel complexes of group 12 (Zn, Cd and Hg) and group 14 (Sn and Pb) metals. Their full characterisation both spectroscopically and structurally provide an excellent comparison to previous work as well as providing a more comprehensive study in a potentially important area of chemistry.

Results and discussion

The phosphonodithioate salt **1** was prepared using an adaption of the literature procedure,[10] Lawessons Reagent was refluxed with 2 molar equivalents of NaOMe in methanol. Phosphonodithioate salts **2** and **3** were also formed from the reaction of Lawessons Reagent with the corresponding sodium alkoxide, but in these cases the sodium alkoxide was prepared from the reaction of sodium metal and the corresponding alcohol and used directly in the alcohol solution, [eqn. (1)].



(1)

Cleavage of the Lawessons Reagent dimeric ring generates the sodium phosphonodithioate salts **1–3** as white powders in almost quantitative yield. Salts **1–3** are soluble in polar solvents such as alcohols and acetone but are insoluble in less polar solvents *e.g.* dichloromethane, chloroform, hexane, *etc*. All of the above salts were found to be air stable both as solids and in solution. The ^{31}P NMR spectra of **1–3** displayed sharp singlets at δ(P) 110.8, 107.7 and 105.7 ppm respectively. The ^{1}H NMR and ^{13}C NMR spectra of these compounds were as expected confirming the presence of both the anisyl and alkoxy moieties. The IR spectra show distinct bands at 1185–1179 cm^{-1}, 1028–1025 cm^{-1}, 678–674 cm^{-1} and 559–557 cm^{-1}, corresponding to ν[(P)–O–C], ν[P–O–(C)], $\nu(PS)_{asym}$ and $\nu(PS)_{sym}$ absorptions respectively.[15] Mass spectrometry showed the expected parent ions as $(M–Na)^+$ at *m*/*z* 233, 248 and 261. The microanalysis of **1–3** was only average, however the purity of the salts was deemed satisfactory for use in further reactions.

Group 10 metals (Ni, Pd, and Pt) in the oxidation state 2+ were refluxed in the corresponding alcohol with two molar equivalents of the phosphonodithioate salts **1–3** to yield complexes of the type ML_2 (L = $[(p\text{-}CH_3O)C_6H_4\{OR\}PS_2]$), **(4–6)** [eqn. (2)], with the exception of **6p** which required the addition of H_2O, to dissolve the

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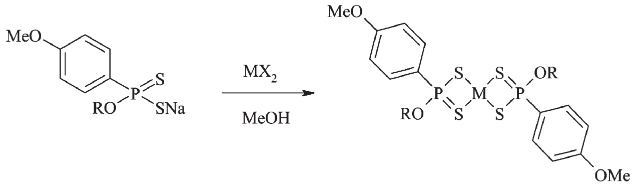
K_2PtCl_4 starting material, before further reflux to yield the desired product.



MX_2 = $NiCl_2$, $Pd(PhCN)_2Cl_2$, $Pt(PhCN)_2Cl_2$, K_2PtCl_4

M =	Ni	R =	Me, **4m**	R =	Et, **4e**	R =	^{i}Pr, **4p**
	Pd		Me, **5m**		Et, **5e**		^{i}Pr, **5p**
	Pt		Me, **6m**		Et, **6e**		^{i}Pr, **6p**

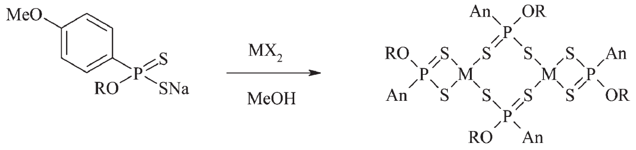
(2)

The metal complexes were prepared in high yields, giving solids exhibiting a range of colours from bright purple to yellow. All are soluble in both chloroform and dichloromethane and found to be air stable as solids and in solution. The ^{31}P NMR of **4m, 4e** and **4p** gave sharp singlets in the range $\delta(P)$ 99.1–105.7 ppm, showing no significant deviation from the signals attributed to the sodium salts **1–3**; consistent with the ferrocenyl analogues of these compounds.[13]

In the cases of complexes **5** and **6** each spectrum contains a pair of sharp singlets of varying intensity, usually close to equal, in the range $\delta(P)$ 104.8–118.4 ppm. This result indicates the presence of two distinct isomeric forms, we believe these to be *cis* and *trans* isomers *i.e.* anisyl groups on the same side of the molecule—*cis*, on the opposite—*trans*. The ^1H and ^{13}C NMR also provide good evidence for these isomers, in each case the expected shifts are present with coupling consistent with the proposed products. However these spectra show each set of resonances to be accompanied by a second set of matching peaks of approximately equal intensity indicating that the proposed isomeric forms exist in solution. This hypothesis is also reinforced by X-ray studies conducted on the similar compound, bis[(methoxy)ferrocenylphosphonodithiato] nickel.[13] Crystals of the *trans* isomer were grown from the isolated product and unambiguously identified. Upon attempts to form a pyridine adduct of this complex, decomposition occurred and crystals obtained were identified as the *cis* isomer. IR spectra showed distinct bands within the expected ranges and in all cases mass spectroscopy found the expected $(M)^+$ ion.

The X-ray structures of **4m** and **4p** (Fig. 1, Table 1) show in each case that the nickel atom resides on a crystallographic inversion centre and is coordinated by four sulfur atoms in a square planar geometry with symmetric NiS_2P rings. The anisyl groups of the two bound ligands are arranged in a *trans* arrangement, *i.e.* above and below the metal coordination plane. The structures of **4e**[10a] and **6m**[10d] are known and are consistent with the above results and other literature examples.[13]

Group 12 metals (Zn, Cd and Hg) in the oxidation state 2+ were refluxed in the corresponding alcohol with two molar equivalents of the phosphonodithioate salts **1–3** for 2 h to yield complexes of the type M_2L_4 (L = $[(p\text{-}CH_3O)C_6H_4\{OR\}PS_2]$), (**7–9**), [eqn. (3)].



MX_2 = $Cd(CH_3COO)_2.2H_2O$, $HgCl_2$ and $ZnCl_2$

M =	Cd	R =	Me, **7m**	R =	Et, **7e**	R =	^{i}Pr, **7p**
	Hg		Me, **8m**		Et, **8e**		^{i}Pr, **8p**
	Zn		Me, **9m**		Et, **9e**		^{i}Pr, **9p**

(3)

Table 1 Selected bond lengths and angles for **4m** and **4p**

	4m	**4p**
M(1)–S(1)	2.2330(6)	2.2298(6)
M(1)–S(2)	2.2413(6)	2.2327(6)
P(1)–S(1)	2.0048(7)	2.0042(8)
P(1)–S(2)	2.0043(8)	2.0082(8)
P(1)–O(1)	1.5856(13)	1.5855(15)
P(1)–C(1)	1.7904(18)	1.792(2)
S(1)–M(1)–S(2)	88.87(2)	88.50(2)
S(1)–P(1)–S(2)	102.77(3)	101.80(3)

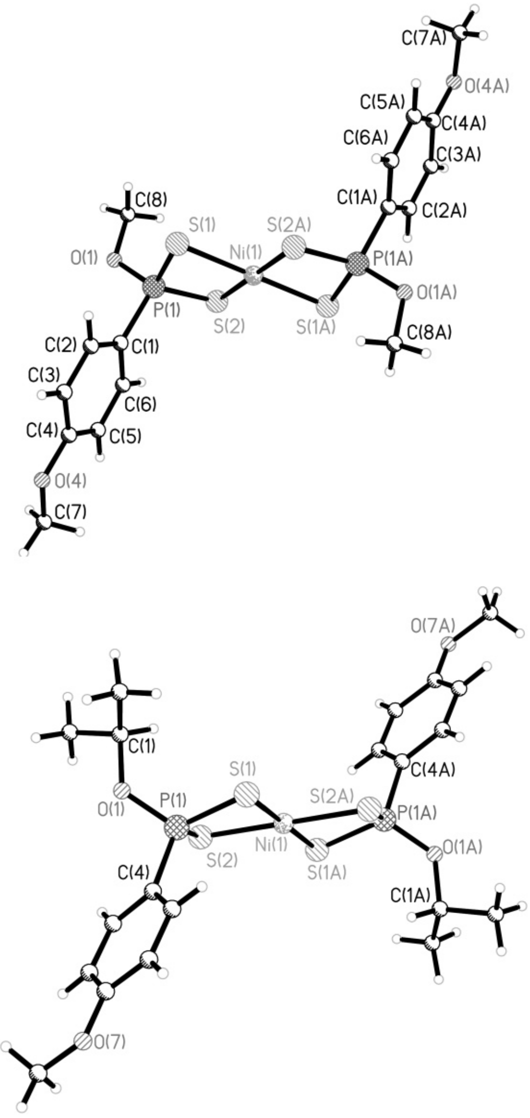


Fig. 1 Upper diagram, the X-ray structure of **4m**; lower diagram, the X-ray structure of **4p**.

Literature examples show that group 12 metal complexes of phosphodithioate ligands exhibit dimeric structures in almost all cases.[8,13] This structural motif consists of an eight membered $M_2P_2S_4$ ring with two terminal bidentate ligands each bound to one metal atom *via* both sulfurs and the other two acting as bridging ligands with their sulfur atoms binding to two different metal atoms.

The metal complexes were isolated as white powders in high yield. All complexes are soluble in chloroform and dichloromethane and air stable as solids and in solution. The ^{31}P spectra of the complexes display sharp singlets with chemical shifts in the range $\delta(P)$ 98.5–109.8 ppm. The ^1H and ^{13}C NMR of all complexes show the same pattern as their corresponding "free phosphonodithioate salts". The above NMR data would suggest that a simple dimer is not the only species present in solution. The two types of ligand present, terminal and bridging, would display two distinct sets of signals, this is not the case and leads us to the conclusion that a more complicated situation exists. Authors of earlier studies conducted on phosphorodithioate and phosphinodithioate complexes of group 12 metals postulated that an equilibrium exists with rapid exchange between a monomeric and a dimeric structure.[16] IR spectra showed distinct bands within the expected ranges, showing similar signals to the free salts and complexes **4–6**. In the mass spectra, the expected (M)$^+$ ions were found for **7m, 7p, 8m** and **8p** only. For all others the most prominent fragments were the loss of one phosphonodithioate ligand, [(p-$CH_3O)C_6H_4\{OR\}PS_2$], and (1/2M)$^+$. The X-ray structures of **9e, 7p** and **9p** (Figs. 2 and 3) were determined and confirmed the dimeric nature of the complexes in the solid state, with the structures being closely related to those of the symmetric $Zn_2[S_2P(OBu)_2]_4$, which we have described previously,[17] and their ferrocenyl analogues,[13] $Cd_2[S_2P(Fc)OMe]_4$ and $Zn_2[S_2P(Fc)OMe]_4$.

The X-ray structures of **8e** and **8p** (Fig. 4, Table 2) were also determined and as was the case for **7p** and **9p** were found to be of a dimeric nature. Unlike **7p** and **9p** in which all M–S distances are approximately equal, **8e** and **8p** exhibit a different pattern. The Hg–S bonds form two distinct pairs of long and short bonds. The bond lengths of Hg(1)–S(1) and Hg(1)–S(11) are approximately equal as are the lengths of Hg(1)–S(2) and Hg(1)–S(12A) with the latter pair being significantly longer (*ca.* 0.3 Å). This pattern forms an axis of symmetry through the molecule with an equal and opposite effect occurring at the other Hg atom. This phenomenon has been noted for similar examples of mercury dithiophosphoroate[18–21] and dithiophosphinoate[22] complexes as well as in mercury xanthate[18] and dithiocarbamate species.[18]

Similar reactions to those described above were carried out with two of the group 14 metals (Sn and Pb), in the oxidation state 2+,

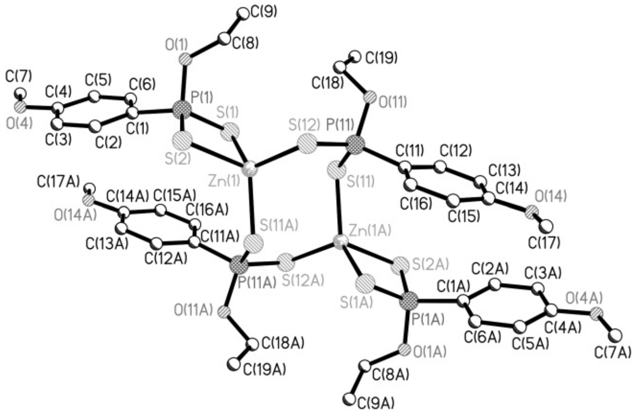


Fig. 2 The X-ray structure of **9e**.

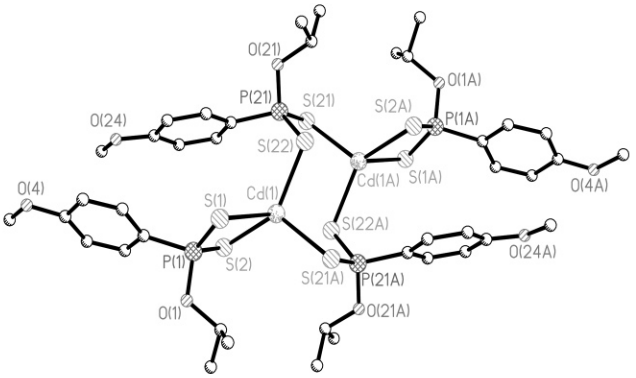


Fig. 3 The X-ray structure of **7p**, the structure of **9p** is isomorphous and is not reproduced.

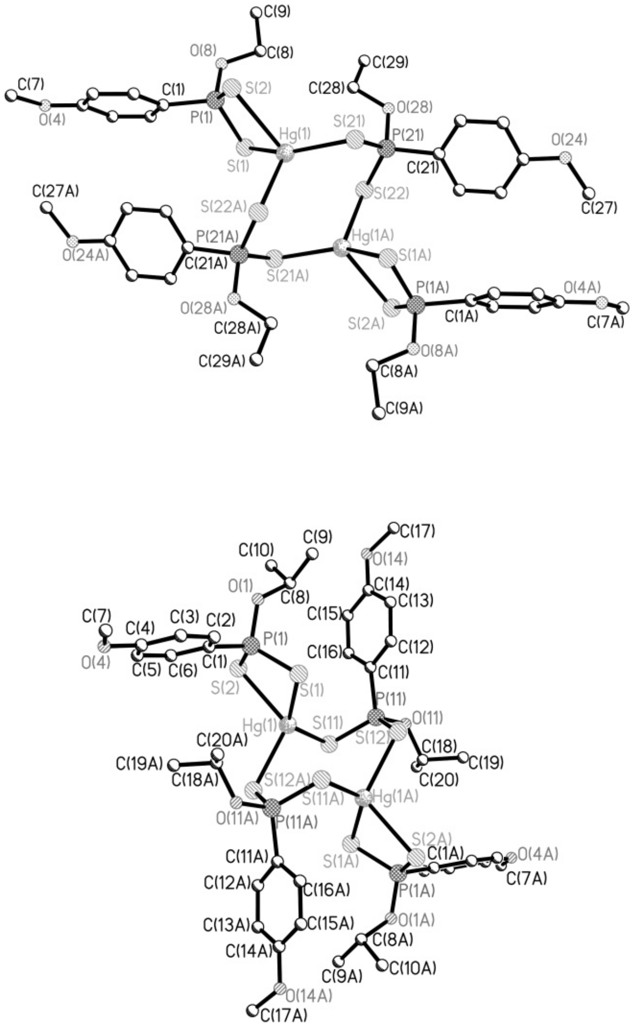
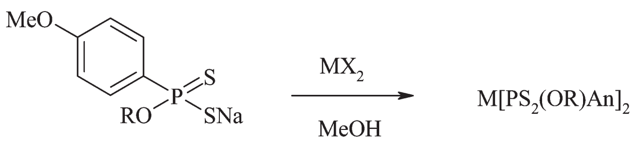


Fig. 4 Upper diagram, the X-ray structure of **8e**; lower diagram, the X-ray structure of **8p**.

Table 2 Selected bond lengths and angles for **7p**, **8e**, **8p**, **9e** and **9p**

	7p	**8e**	**8p**	**9e**	**9p**
M(1)–S(1)	2.6610(8)	2.4656(16)	2.4943(16)	2.3170(12)	2.3382(17)
M(1)–S(2)	2.5249(7)	2.7856(15)	2.7230(17)	2.4377(12)	2.4541(18)
M(1)–S(11)	2.5767(7)	2.4558(16)	2.4978(16)	2.3170(12)	2.3145(18)
M(1)–S(12)	2.5210(7)	2.6239(16)	2.5638(16)	2.3635(12)	2.3610(17)
P(1)–S(1)	1.9964(8)	2.042(2)	2.029(2)	2.0252(14)	2.025(2)
P(1)–S(2)	2.0239(9)	1.986(2)	1.990(2)	2.0006(14)	2.001(2)
P(11)–S(11)	1.9991(9)	2.032(2)	2.013(2)	2.0099(15)	2.018(2)
P(11)–S(12)	2.0409(8)	1.996(2)	2.014(2)	2.0106(14)	2.005(2)
P(1)–O(1)	1.5905(16)	1.591(4)	1.585(4)	1.589(3)	1.589(5)
P(11)–O(11)	1.5842(15)	1.584(4)	1.591(4)	1.588(3)	1.586(5)
P(1)–C(1)	1.796(2)	1.791(6)	1.798(6)	1.788(4)	1.790(6)
P(11)–C(11)	1.786(2)	1.796(6)	1.780(6)	1.783(4)	1.787(6)
S(1)–M(1)–S(2)	79.46(2)	78.17(5)	79.49(5)	86.45(4)	85.93(6)
S(1)–P(1)–S(2)	111.15(4)	111.03(9)	110.63(10)	108.65(6)	108.48(10)
S(11)–M(1)–S(12)	79.49(4)	78.62(3)	78.53(4)	86.44(2)	86.06(6)
S(12)–P(11)–S(11)	111.62(4)	114.87(10)	115.26(9)	113.62(6)	112.88(10)

yielding either white or pale yellow powders in high yield. As was the case for **4–9**, all complexes are soluble in chloroform and dichloromethane and are air stable. ^{31}P, ^{1}H and ^{13}C spectra showed the same pattern to that of complexes **4, 7, 8** and **9**, with ^{31}P chemical shifts in the range δ(P) 89.1–100.9 ppm. IR spectra of compounds **10–11** showed distinct bands in the expected ranges.



$MX_2 = SnCl_2, Pb(CH_3COO)_2.3H_2O$

M = Sn R = Me, **10m** R = Et, **10e** R = ^{i}Pr, **10p**
Pb Me, **11m** Et, **11e** ^{i}Pr, **11p**

(4)

In the mass spectra the most prominent fragments were the loss of one phosphonodithioate ligand, $[(p\text{-}CH_3O)C_6H_4\{OR\}PS_2]$, and $(1/2M)^+$, as was the case for many of the group 12 metal complexes. This result would suggest that compounds **10–11** all exhibit similar covalently bound dimeric structures but this has been found to be incorrect. X-ray studies conducted on **11e** and **11p** (Figs. 5–7, Table 3) show very different structural motifs indicating that for compounds **10–11** a more complicated situation than that proposed for group 12 metal complexes **7–9** may exist.

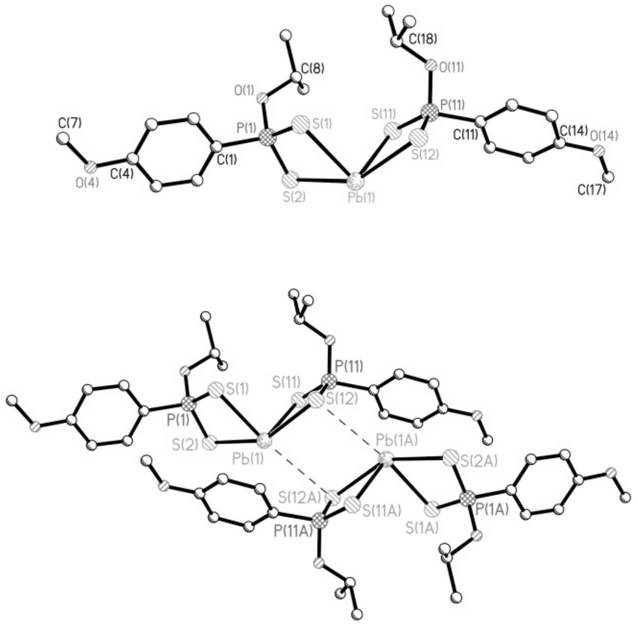


Fig. 5 The X-ray structure of **11p**. Upper diagram, single monomeric unit; lower diagram, pair of units forming dimeric structure.

Very few tin compounds of this type have been investigated, only one complex has been studied by single X-ray crystallography, $[Sn\{(OPh)_2PS_2\}_2]_2$, exhibiting a dimeric structure similar to the complexes of group 12 metals.[15a,23] Several structures of lead phosphorodithioate complexes have been determined, $[Pb\{(OR)_2PS_2\}_2]_n$, with various alkoxy substituents exhibiting a range of structural motifs.[8d,e] Only one example of a lead phosphonodithioate complex has been studied crystallographically, bis[(isopropoxy)ferrocenylphosphonodithioato] lead.[13] The structure of this complex is built up of distorted pyramids, with the apical lead atom 1.41 Å above the basal S_4 plane and the ligands anisobidentate. The molecules are linked by Pb···S interactions (*ca.* 3.9 Å) to form infinite polymeric chains. Despite this complex being the exact ferrocenyl analogue, **11p** was found to adopt a quite different structural motif.

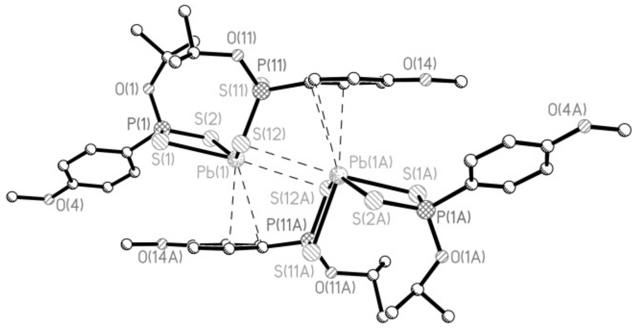


Fig. 6 The X-ray structure of **11p**. Additional Pb···Ar interactions illustrated.

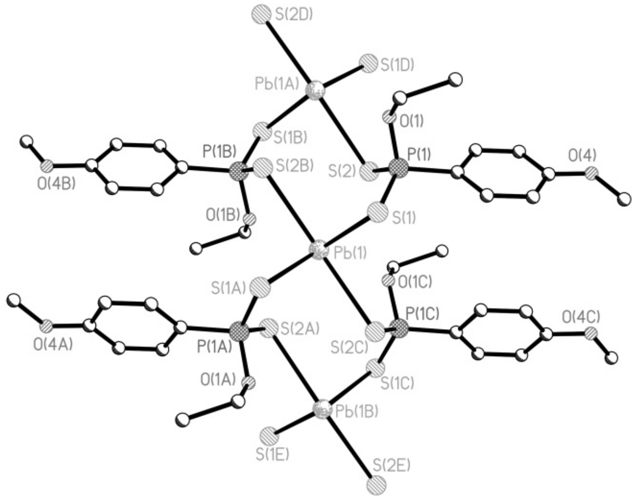


Fig. 7 The X-ray structure of **11e** showing part of the infinite chain structure.

11p adopts a similar molecular unit, the lead resides in the centre of a distorted pyramid, 1.30 Å above the basal S_4 plane and again the ligands are bidentate. But instead of an infinite polymeric chain structure, **11p** adopts a structure consisting of distinct dimeric pairs. In each monomeric building unit one ligand is bidentate chelating (both S atoms bound to one Pb atom only); the other is bimetallic triconnective and participates in the formation of the dimer. The inter-unit secondary Pb···S distance (3.45(1) Å) is significantly longer than the intra-unit Pb···S distances (Pb(1)–S(1) 2.736 Å, Pb(1)–S(2) 2.895 Å), leading to the formation of an eight-membered quasicyclic species. Additional intradimeric interactions occur between a lead atom of one monomeric unit and one of the aromatic rings (Pb(1)–C(11A) 3.28(1) Å, Pb(1)–C(12A) 3.44(1) Å, and Pb(1)–C(16A) 3.32(1) Å) belonging to the other monomer unit. These Pb···Ar interactions seem to stabilize the dimeric structure and may be the reason why the structure is significantly different from that adopted by its ferrocenyl analogue. Bis(diphenylphosphorodithioato) lead has also been shown to adopt a closely related structural motif exhibiting similar Pb···Ar interactions.[24]

Table 3 Selected bond lengths and angles for **11e** and **11p**

	11e	**11p**
M(1)–S(1)	2.8404(11)	2.7363(11)
M(1)–S(2)	—	2.8954(12)
M(1)–S(1A)	2.8404(11)	—
M(1)–S(2B)	3.0706(11)	—
M(1)–S(2C)	3.0706(11)	—
P(1)–S(1)	2.0009(13)	2.0220(15)
P(1)–S(2)	1.9861(14)	1.9881(16)
P(1)–O(1)	1.612(3)	1.589(3)
P(1)–C(1)	1.788(4)	1.794(4)
S(1)–M(1)–S(2)	—	72.44(3)
S(1)–M(1)–S(2B)	79.80(3)	—
S(1)–M(1)–S(2C)	79.80(3)	—
S(1)–P(1)–S(2)	116.63(6)	112.28(7)

The X-ray structure of **11e** was also obtained and was shown to exhibit a completely different motif. There have been several literature examples of these lead complexes showing the formation of infinite polymeric chains,[8d,e] in all cases the monomeric building blocks of the polymers are linked by inter-unit long range Pb···S interactions. Here we report a polymeric structure held together solely by covalent bonding. To the best of our knowledge this type of structural motif has not been seen for lead phosphodithiato complexes. Each lead atom is bound to four sulfur atoms contributed from 4 different phosphonodithioate ligands to form a distorted trigonal bipyramid with a vacant site. Each lead exhibits two long Pb–S bonds (3.0708(11) Å) and 2 short Pb–S (2.8404(11) Å) bonds. All of the ligands within the molecule are bidentate, bridging two lead centres leading to the formation of a continuous array of 8-membered $Pb_2P_2S_4$ rings.

This work clearly demonstrates the versatile coordination of the [(*p*-$CH_3O)C_6H_4\{OR\}PS_2$] ligand towards various metals centres.

Experimental

General

Unless otherwise stated, operations were carried out under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. $Pd(PhCN)_2Cl_2$[25] and $Pt(PhCN)_2Cl_2$[26] were prepared using literature procedures. All other reagents were used as purchased from either Aldrich, Acros or Lancaster and used as received. Infrared spectra were recorded as KBr discs in the range 4000–350 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded using a Jeol GSX Delta 270 or Bruker Avance 300 MHz spectrometer. Microanalyses were performed by the University of St. Andrews microanalysis service. Mass spectra were recorded by both the University of St. Andrews mass spectrometry service and the Swansea mass spectrometry service. We are grateful to Johnson Matthey PLC for the loan of precious metals.

Synthesis

(Methoxy)-4-methoxyphenylphosphonodithioate sodium salt (1). Compound **1** was prepared as detailed in the literature[10a] as a white solid (4.97 g, 98.9%). Found (Calc. For $C_8H_{10}NaO_2PS_2$): C 40.03 (37.50), H 3.67 (3.94), S 25.62 (24.98)%. ^{31}P NMR (methanol D_3) δ: 110.8. ^{1}H NMR (methanol D_3) δ: 8.04 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 13.5 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH, 6.92 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 2.7 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH, 3.79 (s, 3H, ArOMe), 3.54 (d, 3H, $^{2}J(^{1}H–^{1}H)$ 14.7 Hz, CH_3). ^{13}C NMR (methanol D_3) δ: 163.0 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 136.2 (d, ^{1}J ($^{31}P–^{13}C$) 113.9 Hz, Ar C-1), 133.5 (d, ^{3}J ($^{31}P–^{13}C$) 13.6 Hz, *m*-ArC), 114.3 (d, ^{2}J ($^{31}P–^{13}C$) 15.1 Hz, *o*-ArC), 56.6 (s, $ArOCH_3$), 52.0 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1179 (s), 1026 (m), 672 (s), 559 (s). Mass Spec (EI-): $(M - Na)^+$ 233.

(Ethoxy)-4-methoxyphenylphosphonodithioate sodium salt (2). Small pieces of sodium (0.43 g, 18.7 mmol) were stirred in ethanol (30 cm^3) at 0 °C until fully dissolved. To this solution Lawessons Reagent (3.78 g, 9.35 mmol) was added and heated to reflux for 1 h. The reaction mixture was allowed to cool to room temperature and the resulting colourless solution was filtered through a small celite pad. The solvent was removed under reduced pressure to give a white solid (4.98 g, 98.5%). Found (Calc. For $C_9H_{12}NaO_2PS_2$): C 39.58 (40.00), H 3.99 (4.48), S 24.12 (23.68)%. ^{31}P NMR (methanol D_3) δ: 107.7. ^{1}H NMR (methanol D_3) δ: 8.04 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 13.7 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.90 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 2.7 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH, 3.93 (dq = quartet of doublets, 2H, $^{3}J(^{31}P–^{1}H)$ 1.5 Hz, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_2), 3.81 (s, 3H, ArOMe), 1.22 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_3). ^{13}C NMR (methanol D_3) δ: 162.5 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 136.7 (d, ^{1}J ($^{31}P–^{13}C$) 114.6 Hz, Ar C-1), 133.0 (d, ^{3}J ($^{31}P–^{13}C$) 13.2 Hz, *m*-ArC), 113.7 (d, ^{2}J ($^{31}P–^{13}C$) 14.8 Hz, *o*-ArC), 61.1 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH_2), 56.0 (s, $ArOCH_3$), 16.7 (d, ^{3}J ($^{31}P–^{13}C$) 9.1 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1185 (s), 1025 (m), 674 (m), 559 (m). Mass Spec (EI+): $(M - Na)^+$ 248.

(Isopropoxy)-4-methoxyphenylphosphonodithioate sodium salt (3). Small pieces of sodium (0.41 g, 17.9 mmol) were stirred in propan-2-ol (50 cm^3) at 0 °C until fully dissolved. To this solution Lawessons Reagent (3.62 g, 8.96 mmol) was added and heated to reflux for 1 h. The reaction mixture was allowed to cool to room temperature and the resulting colourless solution was filtered through a small celite pad. The solvent was removed under reduced pressure to give a white solid (5.03 g, 98.7%). Found (Calc. For $C_{10}H_{14}NaO_2PS_2$): C 42.46 (42.25), H 5.55 (4.97), S 22.07 (22.51)%. ^{31}P NMR (methanol D_3) δ: 105.7. ^{1}H NMR (methanol D_3) δ: 8.04 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 13.4 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH, 6.88 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH, 4.71 (dsept = septet of doublets, 1H, $^{3}J(^{31}P–^{1}H)$ 2.4 Hz, $^{3}J(^{1}H–^{1}H)$ 6.0 Hz, CH), 3.82 (s, 3H, ArOMe), 1.20 (d, 6H, $^{3}J(^{1}H–^{1}H)$ 6.0 Hz. ^{13}C NMR (methanol D_3) δ: 162.8 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 137.8 (d, ^{1}J ($^{31}P–^{13}C$) 114.7 Hz, Ar C-1), 133.4 (d, ^{3}J ($^{31}P–^{13}C$) 12.8 Hz, *m*-ArC), 114.0 (d, ^{2}J ($^{31}P–^{13}C$) 15.1 Hz, *o*-ArC), 70.3 (d, ^{2}J ($^{31}P–^{13}C$) 7.6 Hz, CH), 56.3 (s, $ArOCH_3$), 25.0 (d, ^{3}J ($^{31}P–^{13}C$) 3.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1180 (s), 1028 (m), 648 (m), 557 (s). Mass Spec (EI+): $(M - Na)^+$ 261.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Ni (4m). A mixture of $NiCl_2$ (0.076 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting purple solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as purple crystals (0.258 g, 84%). Purple crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a dichloromethane solution. Found (Calc. For $C_{16}H_{20}O_4P_2S_4Ni$): C 36.68 (36.65), H 3.80 (3.85), S 24.19 (24.41)%. ^{31}P NMR ($CDCl_3$) δ: 105.7. ^{1}H NMR ($CDCl_3$) δ: 7.92 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.1 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.93 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.3 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH, 3.92 (d, 3H, $^{2}J(^{1}H–^{1}H)$ 14.7 Hz, CH_3), 3.81 (s, 3H, ArOMe). ^{13}C NMR ($CDCl_3$) δ: 163.4 (s, *p*-ArC), 132.0 (d, ^{3}J ($^{31}P–^{13}C$) 15.1 Hz, *m*-ArC), 128.5 (d, ^{1}J ($^{31}P–^{13}C$) 117.0 Hz, Ar C-1), 114.4 (d, ^{2}J ($^{31}P–^{13}C$) 16.6 Hz, *o*-ArC), 55.9 (s, $ArOCH_3$), 52.9 (d, ^{2}J ($^{31}P–^{13}C$) 3.0 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1179 (m), 1027 (s), 667 (m), 550 (s). Mass Spec (EI+): $(M)^+$ 524.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Ni (4e). A mixture of $NiCl_2$ (0.072 g, 0.550 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting brown/purple solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a brown/purple solid (0.205 g, 67%). Found (Calc. For $C_{18}H_{24}O_4P_2S_4Ni$): C 39.17 (39.13), H 4.40 (4.38), S 23.33 (23.18)%. ^{31}P NMR ($CDCl_3$) δ: 102.2. ^{1}H NMR ($CDCl_3$) δ: 7.94 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.1 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.93 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 4.36 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_2), 3.81 (s, 3H, ArOMe), 1.36 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 163.3 (s, *p*-ArC), 132.0 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 128.9 (d, ^{1}J ($^{31}P–^{13}C$) 117.0 Hz, Ar C-1), 114.3 (d, ^{2}J ($^{31}P–^{13}C$) 16.6 Hz, *o*-ArC), 63.1 (d, ^{2}J ($^{31}P–^{13}C$) 7.5 Hz, CH_2), 55.9 (s, $ArOCH_3$), 16.6 (d, $^{3}J(^{31}P–^{13}C)$ 7.5 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1182 (s), 1027 (m), 654 (w), 551 (m). Mass Spec (FAB): $(M)^+$ 552.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Ni (4p). A mixture of $NiCl_2$ (0.076 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting brown/purple solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a purple solid (0.223 g, 73%). Purple crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For $C_{20}H_{28}O_4P_2S_4Ni$): C 41.22 (41.38), H

4.76 (4.87), S 21.79 (22.05)%. ^{31}P NMR (CDCl$_3$) δ: 99.1. ^{1}H NMR (CDCl$_3$) δ: 7.95 (dd, 2H, ^3J(^{31}P–^{1}H) 14.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.93 (dd, 2H, ^4J(^{31}P–^{1}H) 3.6 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 5.15 (dsept, 1H, ^3J(^{31}P–^{1}H) 1.8 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 3.81 (s, 3H, ArOMe), 1.35 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz. ^{13}C NMR (CDCl$_3$) δ: 163.2 (s, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 15.1 Hz, *m*-ArC), 129.2 (d, ^1J (^{31}P–^{13}C) 117.7 Hz, Ar C-1), 114.3 (d, ^2J (^{31}P–^{13}C) 15.9 Hz, *o*-ArC), 72.5 (s, CH), 55.9 (s, ArOCH$_3$), 24.5 (s, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1183 (s), 1026 (m), 663 (m), 553 (s). Mass Spec (FAB): (M)$^+$ 580.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Pd (5m). A mixture of PdCl$_2$(PhCN)$_2$ (0.112 g, 0.293 mmol) and **1** (0.150 g, 0.585 mmol) in methanol (15 cm^3) was refluxed for 20 min. An obvious brown precipitate was observed and collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a brown solid (0.117 g, 70%).

Found (Calc. For C$_{16}$H$_{20}$O$_4$P$_2$S$_4$Pd): C 34.00 (33.57), H 3.84 (3.52), S 22.71 (22.36)%.

Isomer (a): ^{31}P NMR (CDCl$_3$) δ: 118.4. ^{1}H NMR (CDCl$_3$) δ: 7.89 (dd, 2H, ^3J(^{31}P–^{1}H) 14.0 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH, 6.92 (dd, 2H, ^4J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH, 3.88 (d, 3H, ^2J(^{1}H–^{1}H) 14.7 Hz, CH$_3$), 3.80 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.2 (s, *p*-ArC), 131.8 (d, ^3J (^{31}P–^{13}C) 15.8 Hz, *m*-ArC), 128.5 (d, ^1J (^{31}P–^{13}C) 118.3 Hz, Ar C-1), 114.0 (d, ^2J (^{31}P–^{13}C) 18.1 Hz, *o*-ArC), 55.6 (s, ArOCH$_3$), 52.8 (m, CH$_3$).

Isomer (b): ^{31}P NMR (CDCl$_3$) δ: 118.3. ^{1}H NMR (CDCl$_3$) δ: 7.86 (dd, 2H, ^3J(^{31}P–^{1}H) 14.1 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH, 6.90 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH, 3.85 (d, 3H, ^2J(^{1}H–^{1}H) 14.7 Hz, CH$_3$), 3.79 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.2 (s, *p*-ArC), 131.8 (d, ^3J (^{31}P–^{13}C) 15.8 Hz, *m*-ArC), 128.4 (d, ^1J (^{31}P–^{13}C) 119.4 Hz, Ar C-1), 114.0 (d, ^2J (^{31}P–^{13}C) 18.1 Hz, *o*-ArC), 55.6 (s, ArOCH$_3$), 52.8 (m, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1182 (m), 1027 (s), 666 (m), 546 (m). Mass Spec (FAB): (M)$^+$ 572.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Pd (5e). A mixture of PdCl$_2$(PhCN)$_2$ (0.106 g, 0.277 mmol) and **2** (0.150 g, 0.555 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting brown solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a dark orange solid (0.103 g, 62%). Found (Calc. For C$_{18}$H$_{24}$O$_4$P$_2$S$_4$Pd): C 36.28 (36.01), H 3.75 (4.03), S 21.33 (21.32)%.

Isomer (a): ^{31}P NMR (CDCl$_3$) δ: 114.9. ^{1}H NMR (CDCl$_3$) δ: 7.89 (dd, 2H, ^3J(^{31}P–^{1}H) 14.1 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH), 6.91 (dd, 2H, ^4J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 8.9 Hz, *m*-ArH), 4.26 (dq, 2H, ^3J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 7.2 Hz, CH$_2$), 3.80 (s, 3H, ArOMe), 1.37 (t, 3H, ^3J(^{1}H–^{1}H) 6.9 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 163.4 (s, *p*-ArC), 132.2 (d, ^3J (^{31}P–^{13}C) 16.6 Hz, *m*-ArC), 129.0 (d, ^1J (^{31}P–^{13}C) 121.3 Hz, Ar C-1), 114.3 (d, ^2J (^{31}P–^{13}C) 17.3 Hz, *o*-ArC), 63.3 (s, CH$_2$), 55.9 (s, ArOCH$_3$), 16.6 (s, CH$_3$).

Isomer (b): ^{31}P NMR (CDCl$_3$) δ: 114.7. ^{1}H NMR (CDCl$_3$) δ: 7.87 (dd, 2H, ^3J(^{31}P–^{1}H) 14.1 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 4.28 (dq, 2H, ^3J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 7.2 Hz, CH$_2$), 3.78 (s, 3H, ArOMe), 1.35 (t, 3H, ^3J(^{1}H–^{1}H) 6.9 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 163.4 (s, *p*-ArC), 132.2 (d, ^3J (^{31}P–^{13}C) 16.6 Hz, *m*-ArC), 129.0 (d, ^1J (^{31}P–^{13}C) 121.3 Hz, Ar C-1), 114.3 (d, ^2J (^{31}P–^{13}C) 17.3 Hz, *o*-ArC), 63.3 (s, CH$_2$), 55.9 (s, ArOCH$_3$), 16.6 (s, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1181 (s), 1026 (m), 655 (m), 550 (m). Mass Spec (FAB): (M)$^+$ 600.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Pd (5p). A mixture of PdCl$_2$(PhCN)$_2$ (0.101 g, 0.264 mmol) and **1** (0.150 g, 0.528 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting brown solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a brown solid (0.112 g, 67%). Found (Calc. For C$_{20}$H$_{28}$O$_4$P$_2$S$_4$Pd): C 38.06 (38.22), H 4.63 (4.49), S 20.71 (20.37)%.

Isomer (a): ^{31}P NMR (CDCl$_3$) δ: 111.7. ^{1}H NMR (CDCl$_3$) δ: 7.89 (dd, 2H, ^3J(^{31}P–^{1}H) 14.0 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH), 6.91 (dd, 2H, ^4J(^{31}P–^{1}H) 3.6 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *m*-ArH), 5.00 (dsept, 1H, ^3J(^{31}P–^{1}H) 1.8 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 3.80 (s, 3H, ArOMe), 1.34 (d, 6H, ^3J(^{1}H–^{1}H) 6.3 Hz. ^{13}C NMR (CDCl$_3$) δ: 163.2 (d, ^4J (^{31}P–^{13}C) 3.3 Hz, *p*-ArC), 132.2 (d, ^3J (^{31}P–^{13}C) 16.6 Hz, *m*-ArC), 128.5 (d, ^1J (^{31}P–^{13}C) 118.9 Hz, Ar C-1), 114.3 (d, ^2J (^{31}P–^{13}C) 17.4 Hz, *o*-ArC), 72.8 (d, ^2J (^{31}P–^{13}C) 5.5 Hz, CH), 55.9 (s, ArOCH$_3$), 24.8 (d, ^3J (^{31}P–^{13}C) 3.9 Hz, CH$_3$).

Isomer (b): ^{31}P NMR (CDCl$_3$) δ: 111.4. ^{1}H NMR (CDCl$_3$) δ: 7.86 (dd, 2H, ^3J(^{31}P–^{1}H) 14.0 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *m*-ArH), 5.00 (dsept, 1H, ^3J(^{31}P–^{1}H) 1.8 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 3.78 (s, 3H, ArOMe), 1.36(d, 6H, ^3J(^{1}H–^{1}H) 6.3 Hz. ^{13}C NMR (CDCl$_3$) δ: 163.2 (d, ^4J (^{31}P–^{13}C) 3.3 Hz, *p*-ArC), 132.2 (d, ^3J (^{31}P–^{13}C) 16.6 Hz, *m*-ArC), 128.5 (d, ^1J (^{31}P–^{13}C) 118.9 Hz, Ar C-1), 114.3 (d, ^2J (^{31}P–^{13}C) 17.4 Hz, *o*-ArC), 72.8 (d, ^2J (^{31}P–^{13}C) 5.5 Hz, CH), 55.9 (s, ArOCH$_3$), 24.8 (d, ^3J (^{31}P–^{13}C) 3.9 Hz, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1180 (s), 1027 (m), 661 (m), 547 (s). Mass Spec (FAB): (M)$^+$ 628.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Pt (6m). A mixture of PtCl$_2$(PhCN)$_2$ (0.138 g, 0.293 mmol) and **1** (0.150 g, 0.585 mmol) in methanol (15 cm^3) was refluxed for 20 min. An obvious yellow precipitate was observed and collected by suction filtration, washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give a yellow solid (0.114 g, 59%).

Found (Calc. For C$_{16}$H$_{20}$O$_4$P$_2$S$_4$Pt): C 29.51 (29.05), H 2.72 (3.05), S 19.77 (19.35)%.

Isomer (a): ^{31}P NMR (CDCl$_3$) δ: 115.8 (s, ^2J ^{31}P–^{195}Pt 378.5 Hz). ^{1}H NMR (CDCl$_3$) δ: 7.95 (dd, 2H, ^3J(^{31}P–^{1}H) 13.8 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH, 6.91 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH, 3.94 (d, 3H, ^2J(^{1}H–^{1}H) 14.7 Hz, CH$_3$), 3.80 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.4 (s, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 15.8 Hz, *m*-ArC), 129.0 (d, ^1J (^{31}P–^{13}C) 119.0 Hz, Ar C-1), 114.4 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 55.9 (s, ArOCH$_3$), 53.6 (s, CH$_3$).

Isomer (b): ^{31}P NMR (CDCl$_3$) δ: 113.2 (s, ^2J ^{31}P–^{195}Pt 379.3 Hz). ^{1}H NMR (CDCl$_3$) δ: 7.94 (dd, 2H, ^3J(^{31}P–^{1}H) 14.1 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH, 6.90 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH, 3.94 (d, 3H, ^2J(^{1}H–^{1}H) 14.7 Hz, CH$_3$), 3.79 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.4 (s, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 15.8 Hz, *m*-ArC), 128.5 (d, ^1J (^{31}P–^{13}C) 119.4 Hz, Ar C-1), 114.4 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 55.9 (s, ArOCH$_3$), 53.6 (s, CH$_3$).

Selected IR data (KBr) ν/cm^{-1}: 1182 (m), 1027 (s), 666 (m), 546 (s). Mass Spec (FAB): (M)$^+$ 661.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Pt (6e). A mixture of PtCl$_2$(PhCN)$_2$ (0.131 g, 0.277 mmol) and **2** (0.150 g, 0.555 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting pale orange solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a pale orange solid (0.109 g, 57%). Found (Calc. For C$_{18}$H$_{24}$O$_4$P$_2$S$_4$Pt): C 31.67 (31.35), H 3.22 (3.51), S 23.33 (23.18)%.

Isomer (a): ^{31}P NMR (CDCl$_3$) δ: 111.7 (s, ^2J ^{31}P–^{195}Pt 377.8 Hz). ^{1}H NMR (CDCl$_3$) δ: 7.96 (dd, 2H, ^3J(^{31}P–^{1}H) 15.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.92 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 7.5 Hz, *m*-ArH), 4.40 (dq, 2H, ^3J(^{31}P–^{1}H) 1.5 Hz, ^3J(^{1}H–^{1}H) 7.2 Hz, CH$_2$), 3.80 (s, 3H, ArOMe), 1.39 (t, 3H, ^3J(^{1}H–^{1}H) 7.2 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 163.4 (s, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 15.1 Hz, *m*-ArC), 129.4 (d, ^1J (^{31}P–^{13}C) 113.9 Hz, Ar C-1), 114.4 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 63.8 (s, CH$_2$), 55.9 (s, ArOCH$_3$), 16.7 (d, ^3J(^{31}P–^{13}C) 7.5 Hz, CH$_3$).

Isomer (b): ^{31}P NMR (CDCl$_3$) δ: 108.9 (s, ^2J ^{31}P–^{195}Pt 377.9 Hz). ^{1}H NMR (CDCl$_3$) δ: 7.96 (dd, 2H, ^3J(^{31}P–^{1}H) 15.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.89 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 7.5 Hz, *m*-ArH), 4.36 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 1.5 Hz, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_2), 3.79 (s, 3H, ArOMe), 1.38 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 163.4 (s, *p*-ArC), 132.1 (d, ^{3}J ($^{31}P–^{13}C$) 15.1 Hz, *m*-ArC), 129.3 (d, ^{1}J ($^{31}P–^{13}C$) 113.9 Hz, Ar C-1), 114.3 (d, ^{2}J ($^{31}P–^{13}C$) 17.3 Hz, *o*-ArC), 63.8 (s, CH_2), 55.9 (s, $ArOCH_3$), 16.7 (d, $^{3}J(^{31}P–^{13}C)$ 7.5 Hz, CH_3).

Selected IR data (KBr) ν/cm^{-1}: 1180 (s), 1026 (s), 661 (m), 549 (m). Mass Spec (FAB): $(M)^+$ 689.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Pt (6p). A mixture of K_2PtCl_4 (0.219 g, 0.528 mmol) and **1** (0.300 g, 1.055 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. H_2O (15 cm^3) was added and the reaction mixture was refluxed for a further 1 h. An obvious orange precipitate was observed and collected by suction filtration, washed firstly with H_2O (2 × 10 cm^3) then propan-2-ol (2 × 10 cm^3) and dried *in vacuo* to give an orange solid (0.273 g, 72%).

Found (Calc. For $C_{20}H_{28}O_4P_2S_4Pt$): C 33.33 (33.47), H 3.86 (3.94), S 18.31 (17.84)%.

Isomer (a): ^{31}P NMR ($CDCl_3$) δ: 107.7 (s, ^{2}J $^{31}P–^{195}Pt$ 377.8 Hz). ^{1}H NMR ($CDCl_3$) δ: 7.96 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.1 Hz, $^{3}J(^{1}H–^{1}H)$ 9.9 Hz, *o*-ArH), 6.91 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 8.9 Hz, *m*-ArH), 5.16 (dsept, 1H, $^{3}J(^{31}P–^{1}H)$ 2.4 Hz, $^{3}J(^{1}H–^{1}H)$ 6.0 Hz, CH), 3.80 (s, 3H, ArOMe), 1.38 (d, 6H, $^{3}J(^{1}H–^{1}H)$ 6.0 Hz. ^{13}C NMR ($CDCl_3$) δ: 162.7 (s, *p*-ArC), 133.3 (d, ^{3}J ($^{31}P–^{13}C$) 11.4 Hz, *m*-ArC), 120.4 (d, ^{1}J ($^{31}P–^{13}C$) 123.7 Hz, Ar C-1), 114.0 (d, ^{2}J ($^{31}P–^{13}C$) 16.6 Hz, *o*-ArC), 71.0 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH), 55.9 (s, $ArOCH_3$), 24.8 (s, CH_3).

Isomer (b): ^{31}P NMR ($CDCl_3$) δ: 104.8 (s, ^{2}J $^{31}P–^{195}Pt$ 377.3 Hz). ^{1}H NMR ($CDCl_3$) δ: 7.96 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.1 Hz, $^{3}J(^{1}H–^{1}H)$ 9.9 Hz, *o*-ArH), 6.89 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 5.14 (dsept, 1H, $^{3}J(^{31}P–^{1}H)$ 1.8 Hz, $^{3}J(^{1}H–^{1}H)$ 6.6 Hz, CH), 3.79 (s, 3H, ArOMe), 1.37 (d, 6H, $^{3}J(^{1}H–^{1}H)$ 6.2 Hz. ^{13}C NMR ($CDCl_3$) δ: 162.7 (s, *p*-ArC), 131.8 (d, ^{3}J ($^{31}P–^{13}C$) 14.5 Hz, *m*-ArC), 120.4 (d, ^{1}J ($^{31}P–^{13}C$) 123.7 Hz, Ar C-1), 113.8 (d, ^{2}J ($^{31}P–^{13}C$) 16.6 Hz, *o*-ArC), 71.0 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH), 55.7 (s, $ArOCH_3$), 24.3 (s, CH_3).

Selected IR data (KBr) ν/cm^{-1}: 1181 (s), 1025 (m), 661 (m), 546 (m). Mass Spec (FAB): $(M)^+$ 717.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Cd (7m). A mixture of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.156 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.254 g, 75%). Found (Calc. For $C_{32}H_{40}O_8P_4S_8Cd_2$): C 33.02 (33.11), H 3.75 (3.48), S 22.18 (22.05)%. ^{31}P NMR ($CDCl_3$) δ: 109.8. ^{1}H NMR ($CDCl_3$) δ: 8.00 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.7 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.95 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.6 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 3.85 (d, 3H, $^{2}J(^{1}H–^{1}H)$ 15.3 Hz, CH_3), 3.84 (s, 3H, ArOMe). ^{13}C NMR ($CDCl_3$) δ: 163.1 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 132.8 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 128.3 (d, ^{1}J ($^{31}P–^{13}C$) 120.7 Hz, Ar C-1), 114.1 (d, ^{2}J ($^{31}P–^{13}C$) 15.8 Hz, *o*-ArC), 55.9 (s, $ArOCH_3$), 53.1 (d, ^{2}J ($^{31}P–^{13}C$) 7.5 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1179 (m), 1019 (vs), 661 (m), 536 (s). Mass Spec (FAB): $(1/2M)^+$ 580, $(M–PS_2O_2C_8H_{10})^+$ 925, $(M)^+$ 1158.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Cd (7e). A mixture of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.148 g, 0.555 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.311 g, 92%). Found (Calc. For $C_{36}H_{48}O_8P_4S_8Cd_2$): C 35.91 (35.53), H 4.18 (3.98), S 20.87 (21.04)%. ^{31}P NMR ($CDCl_3$) δ: 106.5. ^{1}H NMR ($CDCl_3$) δ: 7.93 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.4 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.87 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.0 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 4.17 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 2.4 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 3.76 (s, 3H, ArOMe), 1.28 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 163.0 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 132.8 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 129.0 (d, ^{1}J ($^{31}P–^{13}C$) 120.7 Hz, Ar C-1), 114.1 (d, ^{2}J ($^{31}P–^{13}C$) 15.8 Hz, *o*-ArC), 63.1 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH_2), 55.9 (s, $ArOCH_3$), 16.5 (d, $^{3}J(^{31}P–^{13}C)$ 9.1 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1179 (s), 1026 (m), 652 (m), 551 (m). Mass Spec (FAB): $(1/2M)^+$ 607, $(M - PS_2O_2C_9H_{12})^+$ 967.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Cd (7p). A mixture of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.141 g, 0.528 mmol) and **2** (0.300 g, 1.06 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.249 g, 74%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For $C_{40}H_{56}O_8P_4S_8Cd_2$): C 37.80 (37.74), H 4.47 (4.44), S 20.35 (20.11)%. ^{31}P NMR ($CDCl_3$) δ: 104.0. ^{1}H NMR ($CDCl_3$) δ: 7.93 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.6 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.85 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.3 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 5.00 (dsept, 1H, $^{3}J(^{31}P–^{1}H)$ 2.4 Hz, $^{3}J(^{1}H–^{1}H)$ 6.3 Hz, CH), 3.76 (s, 3H, ArOMe), 1.29 (d, 6H, $^{3}J(^{1}H–^{1}H)$ 6.3 Hz. ^{13}C NMR ($CDCl_3$) δ: 163.4 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 133.1 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 129.6 (d, ^{1}J ($^{31}P–^{13}C$) 122.2 Hz, Ar C-1), 114.3 (d, ^{2}J ($^{31}P–^{13}C$) 15.8 Hz, *o*-ArC), 73.1 (d, ^{2}J ($^{31}P–^{13}C$) 7.6 Hz, CH), 56.3 (s, $ArOCH_3$), 24.5 (d, ^{3}J ($^{31}P–^{13}C$) 3.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1182 (m), 1029 (m), 663 (m), 539 (s). Mass Spec (FAB): $(M - PS_2O_2C_9H_{12})^+$ 1009, $(M)^+$ 1270.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Hg (8m). A mixture of $HgCl_2$ (0.159 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.306 g, 78%). Found (Calc. For $C_{32}H_{40}O_8P_4S_8Hg_2$): C 28.81 (28.74), H 2.78 (3.02), S 19.42 (19.23)%. ^{31}P NMR ($CDCl_3$) δ: 108.8. ^{1}H NMR ($CDCl_3$) δ: 7.98 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.2 Hz, $^{3}J(^{1}H–^{1}H)$ 8.7 Hz, *o*-ArH), 6.96 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.6 Hz, $^{3}J(^{1}H–^{1}H)$ 8.7 Hz, *m*-ArH), 3.95 (d, 3H, $^{2}J(^{1}H–^{1}H)$ 15.6 Hz, CH_3), 3.85 (s, 3H, ArOMe). ^{13}C NMR ($CDCl_3$) δ: 163.2 (d, ^{4}J ($^{31}P–^{13}C$) 3.8 Hz, *p*-ArC), 132.7 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 128.6 (d, ^{1}J ($^{31}P–^{13}C$) 123.8 Hz, Ar C-1), 114.1 (d, ^{2}J ($^{31}P–^{13}C$) 16.6 Hz, *o*-ArC), 55.9 (s, $ArOCH_3$), 53.1 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1182 (s), 1023 (s), 660 (s), 535 (s). Mass Spec (FAB): $(1/2M)^+$ 667, $(M - PS_2O_2C_8H_{10})^+$ 1101, $(M)^+$ 1333.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Hg (8e). A mixture of $HgCl_2$ (0.151 g, 0.550 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.308 g, 80%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For $C_{36}H_{48}O_8P_4S_8Hg_2$): C 30.95 (31.04), H 3.52 (3.48), S 18.67 (18.38)%. ^{31}P NMR ($CDCl_3$) δ: 105.2. ^{1}H NMR ($CDCl_3$) δ: 7.91 (dd, 2H, $^{3}J(^{31}P–^{1}H)$ 14.6 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *o*-ArH), 6.89 (dd, 2H, $^{4}J(^{31}P–^{1}H)$ 3.3 Hz, $^{3}J(^{1}H–^{1}H)$ 9.0 Hz, *m*-ArH), 4.30 (dq, 2H, $^{3}J(^{31}P–^{1}H)$ 2.7 Hz, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_2), 3.77 (s, 3H, ArOMe), 1.34 (t, 3H, $^{3}J(^{1}H–^{1}H)$ 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 163.1 (d, ^{4}J ($^{31}P–^{13}C$) 3.0 Hz, *p*-ArC), 132.6 (d, ^{3}J ($^{31}P–^{13}C$) 14.3 Hz, *m*-ArC), 129.1 (d, ^{1}J ($^{31}P–^{13}C$) 123.0 Hz, Ar C-1), 114.2 (d, ^{2}J ($^{31}P–^{13}C$) 15.8 Hz, *o*-ArC), 63.2 (d, ^{2}J ($^{31}P–^{13}C$) 6.8 Hz, CH_2), 55.9 (s, $ArOCH_3$), 16.5 (d, $^{3}J(^{31}P–^{13}C)$ 9.1 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1177 (s), 1029 (s), 646 (m), 551 (w). Mass Spec (FAB): $(1/2M)^+$ 685, $(M - PS_2O_2C_9H_{12})^+$ 1143.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Hg (8p). A mixture of HgCl$_2$ (0.143 g, 0.528 mmol) and **2** (0.300 g, 1.06 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.218 g, 57%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For C$_{40}$H$_{56}$O$_8$P$_4$S$_8$Hg$_2$): C 32.90 (33.15), H 3.66 (3.90), S 18.01 (17.66)%. ^{31}P NMR (CDCl$_3$) δ: 102.7. ^{1}H NMR (CDCl$_3$) δ: 7.91 (dd, 2H, ^3J(^{31}P–^{1}H) 14.4 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.6 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 5.13 (dsept, 1H, ^3J(^{31}P–^{1}H) 1.8 Hz, ^3J(^{1}H–^{1}H) 6.6 Hz, CH), 3.78 (s, 3H, ArOMe), 1.35 (d, 6H, ^3J(^{1}H–^{1}H) 6.6 Hz. ^{13}C NMR (CDCl$_3$) δ: 163.1 (d, ^4J (^{31}P–^{13}C) 3.0 Hz, *p*-ArC), 132.7 (d, ^3J (^{31}P–^{13}C) 14.3 Hz, *m*-ArC), 129.5 (d, ^1J (^{31}P–^{13}C) 123.8 Hz, Ar C-1), 114.2 (d, ^2J (^{31}P–^{13}C) 15.9 Hz, *o*-ArC), 73.3 (d, ^2J (^{31}P–^{13}C) 7.6 Hz, CH), 55.9 (s, ArOCH$_3$), 24.5 (d, ^3J (^{31}P–^{13}C) 4.5 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1179 (m), 1025 (m), 663 (m), 539 (s). Mass Spec (FAB): (1/2M)$^+$ 723, (M − PS$_2$O$_2$C$_9$H$_{12}$)$^+$ 1185, (M − C$_2$H$_5$)$^+$ 1417, (M)$^+$ 1446.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Zn (9m). A mixture of ZnCl$_2$ (0.080 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.188 g, 61%). Found (Calc. For C$_{32}$H$_{40}$O$_8$P$_4$S$_8$Zn$_2$): C 36.33 (36.23), H 4.01 (3.80), S 24.54 (24.13)%. ^{31}P NMR (CDCl$_3$) δ: 105.1. ^{1}H NMR (CDCl$_3$) δ: 7.96 (dd, 2H, ^3J(^{31}P–^{1}H) 14.9 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.97 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 3.90 (d, 3H, ^2J(^{1}H–^{1}H) 15.6 Hz, CH$_3$), 3.85 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.2 (d, ^4J (^{31}P–^{13}C) 3.8 Hz, *p*-ArC), 132.6 (d, ^3J (^{31}P–^{13}C) 15.1 Hz, *m*-ArC), 128.4 (d, ^1J (^{31}P–^{13}C) 122.1 Hz, Ar C-1), 114.2 (d, ^2J (^{31}P–^{13}C) 15.8 Hz, *o*-ArC), 55.9 (s, ArOCH$_3$), 52.9 (d, ^2J (^{31}P–^{13}C) 6.8 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1181 (m), 1026 (s), 663 (m), 542 (s). Mass Spec (FAB): (1/2M)$^+$ 531, (M − PS$_2$O$_2$C$_8$H$_{10}$)$^+$ 831.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Zn (9e). A mixture of ZnCl$_2$ (0.076 g, 0.550 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.193 g, 62%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For C$_{36}$H$_{48}$O$_8$P$_4$S$_8$Zn$_2$): C 38.67 (38.71), H 4.02 (4.34), S 22.84 (22.92)%. ^{31}P NMR (CDCl$_3$) δ: 101.3. ^{1}H NMR (CDCl$_3$) δ: 7.89 (dd, 2H, ^3J(^{31}P–^{1}H) 14.6 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 4.24 (dq, 2H, ^3J(^{31}P–^{1}H) 2.7 Hz, ^3J(^{1}H–^{1}H) 6.9 Hz, CH$_2$), 3.77 (s, 3H, ArOMe), 1.31 (t, 3H, ^3J(^{1}H–^{1}H) 6.9 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 163.0 (d, ^4J(^{31}P–^{13}C) 3.0 Hz, *p*-ArC), 132.5 (d, ^3J (^{31}P–^{13}C) 14.3 Hz, *m*-ArC), 128.7 (d, ^1J (^{31}P–^{13}C) 122.6 Hz, Ar C-1), 114.1 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 62.9 (d, ^2J (^{31}P–^{13}C) 6.8 Hz, CH$_2$), 55.9 (s, ArOCH$_3$), 16.4 (d, ^3J(^{31}P–^{13}C) 8.3 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1182 (s), 1026 (s), 654 (m), 543 (s). Mass Spec (FAB): (1/2M)$^+$ 559, (M − PS$_2$O$_2$C$_9$H$_{12}$)$^+$ 873.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Zn (9p). A mixture of ZnCl$_2$ (0.072 g, 0.528 mmol) and **2** (0.300 g, 1.06 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.216 g, 70%) Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For C$_{40}$H$_{56}$O$_8$P$_4$S$_8$Zn$_2$): C 40.98 (40.96), H 4.77 (4.82), S 21.53 (21.81)%. ^{31}P NMR (CDCl$_3$) δ: 98.5. ^{1}H NMR (CDCl$_3$) δ: 7.88 (dd, 2H, ^3J(^{31}P–^{1}H) 14.9 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 8.7 Hz, *m*-ArH), 5.05 (dsept, 1H, ^3J(^{31}P–^{1}H) 2.7 Hz, ^3J(^{1}H–^{1}H) 6.3 Hz, CH), 3.77 (s, 3H, ArOMe), 1.34 (d, 6H, ^3J(^{1}H–^{1}H) 6.3 Hz. ^{13}C NMR (CDCl$_3$) δ: 162.9 (s, *p*-ArC), 132.4 (d, ^3J (^{31}P–^{13}C) 15.1 Hz, *m*-ArC), 129.4 (d, ^1J (^{31}P–^{13}C) 121.0 Hz, Ar C-1), 114.1 (d, ^2J (^{31}P–^{13}C) 15.9 Hz, *o*-ArC), 72.6 (d, ^2J (^{31}P–^{13}C) 6.8 Hz, CH), 55.9 (s, ArOCH$_3$), 24.4 (d, ^3J (^{31}P–^{13}C) 3.8 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1181 (s), 1029 (m), 658 (w), 543 (m). Mass Spec (FAB): (M − PS$_2$O$_2$C$_9$H$_{12}$)$^+$ 915, (M − O$_2$C$_{10}$H$_{13}$)$^+$ 1011.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Sn (10m). A mixture of SnCl$_2$ (0.111 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting pale yellow solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a pale yellow solid (0.277 g, 81%). Found (Calc. For C$_{32}$H$_{40}$O$_8$P$_4$S$_8$Sn$_2$): C 33.09 (32.77), H 3.48 (3.44), S 21.66 (21.83)%. ^{31}P NMR (CDCl$_3$) δ: 95.1. ^{1}H NMR (CDCl$_3$) δ: 7.91 (dd, 2H, ^3J(^{31}P–^{1}H) 15.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.95 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 3.86 (d, 3H, ^2J(^{1}H–^{1}H) 15.6 Hz, CH$_3$), 3.84 (s, 3H, ArOMe). ^{13}C NMR (CDCl$_3$) δ: 163.0 (d, ^4J (^{31}P–^{13}C) 3.8 Hz, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 14.3 Hz, *m*-ArC), 130.7 (d, ^1J (^{31}P–^{13}C) 127.5 Hz, Ar C-1), 114.1 (d, ^2J (^{31}P–^{13}C) 15.8 Hz, *o*-ArC), 56.0 (d, ^2J (^{31}P–^{13}C) 11.3 Hz, CH$_3$), 52.4 (s, ArOCH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1180 (m), 1024 (vs), 663 (m), 539 (s). Mass Spec (FAB): (1/2M)$^+$ 586, (M − PS$_2$O$_2$C$_8$H$_{10}$)$^+$ 939, (M)$^+$ 1172.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Sn (10e). A mixture of SnCl$_2$ (0.076 g, 0.550 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.235 g, 69%). Found (Calc. For C$_{36}$H$_{48}$O$_8$P$_4$S$_8$Sn$_2$): C 35.27 (35.18), H 4.12 (3.94), S 20.34 (20.83)%. ^{31}P NMR (CDCl$_3$) δ: 89.1. ^{1}H NMR (CDCl$_3$) δ: 7.83 (dd, 2H, ^3J(^{31}P–^{1}H) 14.9 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.87 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 4.69 (dq, 2H, ^3J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 7.2 Hz, CH$_2$), 3.78 (s, 3H, ArOMe), 1.29 (t, 3H, ^3J(^{1}H–^{1}H) 6.9 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 163.2 (d, ^4J (^{31}P–^{13}C) 3.0 Hz, *p*-ArC), 132.1 (d, ^3J (^{31}P–^{13}C) 15.3 Hz, *m*-ArC), 129.0 (d, ^1J (^{31}P–^{13}C) 123.1 Hz, Ar C-1), 114.4 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 63.0 (d, ^2J (^{31}P–^{13}C) 6.9 Hz, CH$_2$), 55.9 (s, ArOCH$_3$), 16.5 (d, ^3J(^{31}P–^{13}C) 8.0 Hz, CH$_3$). Selected IR data (KBr) ν/cm^{-1}: 1182 (s), 1024 (s), 655 (m), 545 (m). Mass Spec (FAB): (1/2M)$^+$ 614, (M − PS$_2$O$_2$C$_9$H$_{12}$)$^+$ 982.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Sn (10p). A mixture of SnCl$_2$ (0.100 g, 0.528 mmol) and **2** (0.300 g, 1.06 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting pale yellow solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a pale yellow solid (0.219 g, 65%). Found (Calc. For C$_{40}$H$_{56}$O$_8$P$_4$S$_8$Sn$_2$): C 37.62 (37.39), H 3.97 (4.40), S 20.40 (19.92)%. ^{31}P NMR (CDCl$_3$) δ: 98.5. ^{1}H NMR (CDCl$_3$) δ: 7.88 (dd, 2H, ^3J(^{31}P–^{1}H) 14.1 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.89 (dd, 2H, ^4J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 5.09 (dsept, 1H, ^3J(^{31}P–^{1}H) 2.4 Hz, ^3J(^{1}H–^{1}H) 6.2 Hz, CH), 3.77 (s, 3H, ArOMe), 1.34 (d, 6H, ^3J(^{1}H–^{1}H) 6.2 Hz. ^{13}C NMR (CDCl$_3$) δ: 162.7 (s, *p*-ArC), 132.0 (d, ^3J (^{31}P–^{13}C) 15.0 Hz, *m*-ArC), 129.1 (d, ^1J (^{31}P–^{13}C) 125.6 Hz, Ar C-1), 114.1 (d, ^2J (^{31}P–^{13}C) 16.4 Hz, *o*-ArC), 71.8 (d, ^2J (^{31}P–^{13}C) 6.8 Hz, CH), 55.9 (s, ArOCH$_3$), 24.3

Table 4 Details of the X-ray data collections and refinements

Compound	**4m**	**4p**	**7p**	**8e**
Empirical formula	$C_{16}H_{20}NiO_4P_2S_4$	$C_{20}H_{28}NiO_4P_2S_4$	$C_{40}H_{56}Cd_2O_8P_4S_8$	$C_{36}H_{48}Hg_2O_8P_4S_8$
Crystal colour, habit	Purple, prism	Purple, prism	Colourless, block	Colourless, block
Crystal dimensions/mm	0.2 × 0.05 × 0.05	0.18 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
a/Å	11.823(3)	7.8059(13)	11.308(2)	15.301(3)
b/Å	6.5091(15)	8.7446(15)	11.604(3)	14.741(2)
c/Å	14.414(4)	10.8461(18)	12.339(3)	10.5504(17)
a/°	90	99.405(3)	83.965(4)	90
β/°	110.464(7)	96.962(3)	65.562(3)	94.994(3)
γ/°	90	112.419(3)	68.987(3)	90
U/Å^3	1039.2(4)	661.38(19)	1378.5(5)	2370.7(7)
Z	2	1	1	2
M	525.21	581.31	1270.01	1390.28
D_c/g cm^{-3}	1.678	1.460	1.530	1.948
μ/mm^{-1}	1.510	1.194	1.234	7.002
F(000)	540	302	644	1352
Measured reflections	6428	3771	8814	13693
Independent reflections (R_{int})	2001(0.0285)	2369(0.0087)	4936(0.0147)	4241(0.0655)
Final $R1$, $\omega R2$ [$I > 2\sigma(I)$]	0.0240, 0.0567	0.0300, 0.0776	0.0216, 0.0470	0.0338, 0.0621

Table 5 Details of the X-ray data collections and refinements

Compound	**8p**	**9e**	**9p**	**11e**	**11p**
Empirical formula	$C_{40}H_{56}Hg_2O_8P_4S_8$	$C_{36}H_{48}Zn_2O_8P_4S_8$	$C_{40}H_{56}Zn_2O_8P_4S_8$	$C_{18}H_{24}PbO_4P_2S_4$	$C_{40}H_{56}Pb_2O_8P_4S_8$
Crystal colour, habit	Colourless, block	Colourless, prism	Colourless, prism	Colourless, block	Colourless, block
Crystal dimensions/mm	0.1 × 0.1 × 0.1	0.1 × 0.05 × 0.04	0.17 × 0.1 × 0.1	0.2 × 0.04 × 0.01	0.14 × 0.1 × 0.02
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	10.417(3)	10.796(2)	11.240(2)	22.504(6)	11.2492(16)
b/Å	10.925(3)	11.222(2)	11.580(2)	11.582(3)	12.1942(17)
c/Å	12.287(3)	12.495(2)	12.307(3)	9.857(2)	12.4142(17)
a/°	94.419(7)	65.482(18)	85.470(4)	90	90
β/°	96.945(5)	77.56(2)	64.877(3)	114.824(6)	93.228(2)
γ/°	106.225(7)	79.46(2)	68.546(3)	90	90
U/Å^3	1323.7(7)	1337.4(4)	1344.4(5)	2331.8(10)	1499.3(4)
Z	1	1	1	4	1
M	1446.39	1206.02	1175.95	701.74	1545.76
D_c/g cm^{-3}	1.814	1.497	1.452	1.999	1.712
μ/mm^{-1}	6.274	1.376	1.366	7.754	6.038
F(000)	708	626	608	1360	762
Measured reflections	7772	7767	7926	6948	8988
Independent reflections (R_{int})	4459(0.0564)	4501(0.0288)	4755(0.0393)	2102(0.0284)	5390(0.0265)
Final $R1$, $\omega R2$ [$I > 2\sigma(I)$]	0.0410, 0.0761	0.0419, 0.0996	0.0733, 0.2143	0.0237, 0.0474	0.0276, 0.0643

(d, ^3J (^{31}P–^{13}C) 3.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1180 (s), 1027 (s), 674 (w), 534 (m). Mass Spec (FAB): (1/2M)$^+$ 642, $(M - PS_2O_2C_{10}H_{14})^+$ 1021.

Bis[(methoxy)-4-methoxyphenylphosphonodithioato]Pb (11m). A mixture of $Pb(CH_3COO)_2{\cdot}3H_2O$ (0.222 g, 0.585 mmol) and **1** (0.300 g, 1.71 mmol) in methanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting sticky white solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.245 g, 62%). Found (Calc. For $C_{32}H_{40}O_8P_4S_8Pb_2$): C 28.33 (28.49), H 2.91 (2.99), S 19.22 (18.99)%. ^{31}P NMR ($CDCl_3$) δ: 100.9. ^{1}H NMR ($CDCl_3$) δ: 7.86 (dd, 2H, ^3J(^{31}P–^{1}H) 14.7 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.88 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 3.78 (s, 3H, ArOMe), 3.76 (d, 3H, ^2J(^{1}H–^{1}H) 15.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 163.0 (d, ^4J (^{31}P–^{13}C) 3.2 Hz, *p*-ArC), 131.8 (d, ^3J (^{31}P–^{13}C) 15.1 Hz, *m*-ArC), 129.7 (d, ^1J (^{31}P–^{13}C) 125.5 Hz, Ar C-1), 114.1 (d, ^2J (^{31}P–^{13}C) 15.8 Hz, *o*-ArC), 55.9 (s, $ArOCH_3$), 52.2 (d, ^2J (^{31}P–^{13}C) 8.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1177 (s), 1020 (vs), 666 (m), 552 (m). Mass Spec (FAB): $(M - PS_2O_2C_8H_{10})^+$ 1115.

Bis[(ethoxy)-4-methoxyphenylphosphonodithioato]Pb (11e). A mixture of $Pb(CH_3COO)_2{\cdot}3H_2O$ (0.211 g, 0.550 mmol) and **2** (0.300 g, 1.11 mmol) in ethanol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting pale brown solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.261 g, 67%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For $C_{36}H_{48}O_8P_4S_8Pb_2$): C 30.72 (30.77), H 3.36 (3.45), S 17.79 (18.22)%. ^{31}P NMR ($CDCl_3$) δ: 97.7. ^{1}H NMR ($CDCl_3$) δ: 7.86 (dd, 2H, ^3J(^{31}P–^{1}H) 14.6 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *o*-ArH), 6.87 (dd, 2H, ^4J(^{31}P–^{1}H) 3.3 Hz, ^3J(^{1}H–^{1}H) 9.0 Hz, *m*-ArH), 4.16 (dq, 2H, ^3J(^{31}P–^{1}H) 3.0 Hz, ^3J(^{1}H–^{1}H) 6.9 Hz, CH_2), 3.78 (s, 3H, ArOMe), 1.29 (t, 3H, ^3J(^{1}H–^{1}H) 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$) δ: 162.5 (d, ^4J (^{31}P–^{13}C) 3.1 Hz, *p*-ArC), 132.3 (d, ^1J (^{31}P–^{13}C) 124.6 Hz, Ar C-1), 131.5 (d, ^3J (^{31}P–^{13}C) 14.5 Hz, *m*-ArC), 113.7 (d, ^2J (^{31}P–^{13}C) 16.6 Hz, *o*-ArC), 61.7 (d, ^2J (^{31}P–^{13}C) 7.3 Hz, CH_2), 55.5 (s, $ArOCH_3$), 16.3 (d, ^3J(^{31}P–^{13}C) 8.3 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1181 (s), 1027 (m), 654 (m), 551 (m). Mass Spec (FAB): (1/2M)$^+$ 703, $(M - PS_2O_2C_9H_{12})^+$ 1157.

Bis[(isopropoxy)-4-methoxyphenylphosphonodithioato]Pb (11p). A mixture of $Pb(CH_3COO)_2{\cdot}3H_2O$ (0.200 g, 0.528 mmol) and **2** (0.300 g, 1.06 mmol) in propan-2-ol (15 cm^3) was refluxed for 2 h. The solvent was removed under reduced pressure, the resulting brown solid was redissolved in dichloromethane and filtered through a small celite plug. The filtrate was concentrated under vacuum to *ca.* 10 cm^3 and hexane was added to precipitate the product as a white solid (0.223 g, 58%). Colourless crystals suitable for X-ray analysis were grown by vapour diffusion of hexane into a chloroform solution. Found (Calc. For $C_{40}H_{56}O_8P_4S_8Pb_2$): C 32.96 (32.88), H 3.93 (3.87), S 17.99 (17.52)%. ^{31}P NMR ($CDCl_3$) δ: 95.4. ^{1}H NMR ($CDCl_3$) δ: 7.85 (dd, 2H, $^{3}J(^{31}P{-}^{1}H)$ 14.6 Hz, $^{3}J(^{1}H{-}^{1}H)$ 9.0 Hz, *o*-ArH), 6.86 (dd, 2H, $^{4}J(^{31}P{-}^{1}H)$ 3.3 Hz, $^{3}J(^{1}H{-}^{1}H)$ 9.0 Hz, *m*-ArH), 4.97 (dsept, 1H, $^{3}J(^{31}P{-}^{1}H)$ 3.0 Hz, $^{3}J(^{1}H{-}^{1}H)$ 6.0 Hz, CH), 2.01 (s, 3H, ArOMe), 1.27 (d, 6H, $^{3}J(^{1}H{-}^{1}H)$ 6.3 Hz. ^{13}C NMR ($CDCl_3$) δ: 162.7 (d, $^{4}J\,(^{31}P{-}^{13}C)$ 3.8 Hz, *p*-ArC), 133.1 (d, $^{1}J\,(^{31}P{-}^{13}C)$ 126.0 Hz, Ar C-1), 132.1 (d, $^{3}J\,(^{31}P{-}^{13}C)$ 14.3 Hz, *m*-ArC), 114.0 (d, $^{2}J\,(^{31}P{-}^{13}C)$ 16.6 Hz, *o*-ArC), 71.5 (d, $^{2}J\,(^{31}P{-}^{13}C)$ 6.8 Hz, CH), 55.8 (s, $ArOCH_3$), 24.8 (d, $^{3}J\,(^{31}P{-}^{13}C)$ 3.8 Hz, CH_3). Selected IR data (KBr) ν/cm^{-1}: 1179 (s), 1029 (s), 656 (w), 542 (m). Mass Spec (FAB): $(1/2M)^+$ 731, $(M - PS_2O_2C_{10}H_{14})^+$ 1199.

X-ray crystallography. Tables 1–3 contain slected bond lengths and angles. Tables 4 and 5 list details of data collections and refinements. For, **4m, 8p, 9e** and **11e**, data were collected at 93 K using Mo-Kα radiation [MM007 Rotating Anode source with confocal optics] and a Rigaku Mercury system; for **4m, 7p, 8e, 9p** and **11p** at 125 K using a Bruker SMART [sealed tube] system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[27]

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See http://www.rsc.org/suppdata/dt/b4/b406411a/ for crystallographic data in CIF or other electronic format.

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