DALTON
FULL PAPER

Lead(IV) complexes with phosphinoyldithioformates, $R_2P(O)CS_2^-$ ($R = Ph$ or $PhCH_2$). Syntheses and characterization. Crystal structures of $[PPh_4][S_2CP(O)Ph_2]\cdot0.5H_2O$, $[PbPh_2\{S_2CP(O)Ph_2\}_2]$ and $[PbPh_2Cl\{S_2CP(O)Ph_2\}]$

Sigurjón Norberg Ólafsson,[a] **Claus Flensburg**[b] **and Peter Andersen** *[b]

[a] *Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland*
[b] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*

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Lead(IV) complexes with phosphinoyl substituted dithioformate, $L = R_2P(O)CS_2^-$ ($R = Ph$ or $PhCH_2$), have been synthesized and characterized by UV/vis, IR and NMR (^1H, ^{13}C and ^{31}P). The following types of compounds are described: $(PPh_4)L$, $PbPh_2L_2$, $PbPh_2X(L)$ ($X = Cl$, Br or I) and $PbPh_3L$. Among these compounds the structure has been determined from single crystal X-ray diffraction data (122 K) of $[PPh_4][Ph_2P(O)CS_2]\cdot0.5\ H_2O$, $[PbPh_2\{S_2CP(O)Ph_2\}_2]$ and $[PbPh_2Cl\{S_2CP(O)Ph_2\}]$. The preferred co-ordination mode for L is bidentate through S and O. The crystal structures of the two complexes show them both to be mononuclear, one octahedral with the phenyl ligands *trans* to each other and the other five-co-ordinated. The complexes are buckled to form nearly planar five-membered chelate rings. The magnitude of the NMR coupling constants between lead and atoms in the phenyl ligands close to lead, especially the *ipso* carbon atom, reflects the co-ordination number in a remarkable way. On that basis the $PbPh_3L$ complex with $R = PhCH_2$ is found to be four-co-ordinated in non-co-ordinating organic solvents. Variable-temperature NMR measurements reveal a fluxional behaviour of the six- and five-co-ordinated complexes, and different molecular symmetries are observed at low temperature.

Introduction

The co-ordination chemistry of substituted dithioformates, XCS_2^- ($X = R$, NR_2, OR or SR), has been studied extensively over many decades. They form stable complexes with most metal ions as described in several review articles.[1] The ligands bind in a mono- or bi-dentate manner and in all cases through the dithioformate sulfur atoms, and in accordance with this many have X–C bonds shorter than a single bond.[1]

In recent years the chemistry of the analogous phosphinodithioformates, $R_2PCS_2^-$, and their complexes has found considerable attention.[2] These ligands are, like the above mentioned, potentially ambibidentate and should be able to bind to metal centres through S or P in a monodentate fashion as well as through S,S′ or S,P in a bidentate mode. The P–C bond distance in the "free" ligand indicates a single bond, and all bonding modes[2] have been found except the monodentate one through S.

There are only a few studies on the related phosphinoyldithioformates, $R_2P(O)CS_2^-$, and their phosphinothioyl analogues, $R_2P(S)CS_2^-$, and their complexes.[3] Compared to the phosphinothioyl compounds the phosphinoyl compounds are more stable and easy to handle, and we present here the first results of a more systematic study of organometallic complexes of Group 14 metals incorporating the ligands $R_2P(O)CS_2^-$ ($R = Ph$ or $PhCH_2$). The main topic will be the ligand and some of its lead(IV) complexes with emphasis on synthesis, characterization and structural behaviour as determined from spectroscopic data (primarily NMR) and X-ray diffraction.

Results and discussion

Three types of complexes with $R_2P(O)CS_2^-$ ($R = Ph$ or $PhCH_2$) are described in the following: $[PbPh_2\{S_2CP(O)R_2\}_2]$ **1**, $[PbPh_2X\{S_2CP(O)R_2\}]$ **2** ($X = Cl$, Br or I) and $[PbPh_3\{S_2CP(O)R_2\}]$ **3**.

The potassium salts of the "free" ligands (L) were prepared by treating an equimolar solution of $R_2P(O)H$ and CS_2 in tetrahydrofuran in the presence of potassium hydroxide. A double exchange reaction between the potassium salts and PPh_4Br yielded the tetraphenylphosphonium salts of the ligands, $[PPh_4][S_2CP(O)R_2]$. Reaction in acetone between $KS_2CP(O)R_2$ and, respectively, $PbPh_2Cl_2$ (molar ratio 2:1), $PbPh_2X_2$ ($X = Cl$, Br or I; molar ratio 1:1) and $PbPh_3Cl$ (molar ratio 1:1) produced compounds **1**, **2** and **3** in moderate to high yields.

All the compounds are air stable crystalline solids, moderately soluble in chlorinated organic solvents, but insoluble in hydrocarbons and alcohols. They were identified from elemental analysis and infrared spectra. They are all coloured. The UV/vis spectral data (CH_2Cl_2 solutions) are given in Table 1, where the intense ($\log \varepsilon = 4$) band around 350–370 nm is assigned to a $\pi \longrightarrow \pi^*$ transition in the dithiocarboxylate group.[4] The "free" ligands, $R_2P(O)CS_2^-$ (and $R_2PCS_2^-$),[3b] show two less intense bands in the region 470–560 nm in contrast to XCS_2^- ($X = NR_2$, OR or SR) which only exhibit one band in this region, assigned to an $n \longrightarrow \pi^*$ transition.[4] However, on complexation to the lead atom one of these bands disappears, and it is always the one at lower wavelength.

The phosphinoyldithioformate anion is an ambidentate ligand with three donor atoms, the sulfur atoms of the CS_2 group and the oxygen atom of the phosphinoyl group. Several bonding modes to lead are therefore possible including monodentate, bidentate (with the possibility of one weaker bond)[5,6] forming four- or five-membered rings and bridging co-ordination. IR spectral data of the compounds are given in Table 1 and ^1H, ^{13}C and ^{31}P NMR data in Tables 2, 3 and 4; in the following these data for L, **1**, **2** and **3** are discussed in relation to structural properties. Structural information based on X-ray diffraction data for compounds of type L, **1** and **2** is given as well.

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Table 1 Selected IR (KBr pellets) and UV/vis (CH_2Cl_2 solution) data

						UV/vis transitions			
	IR stretching vibrations[a]/cm^{-1}					$\pi \longrightarrow \pi^*$		$\pi \longrightarrow \pi^*$	
Compound	ν(P=O)	$\Delta\nu$(P=O)[b]	ν_1(CS_2)	ν_2(CS_2)	ν(Pb–S)	λ/nm	log ε	λ/nm	log ε
[PPh_4][S_2CP(O)Ph_2]	1176 (vs)	0	1032 (vs)	915 (w)		368	4.09	483 555	1.79 1.40
[PPh_4][S_2CP(O)($CH_2Ph)_2$]	1200 (vs)	0	1030 (vs)	910 (w)		364	4.00	472 555	1.85 1.25
1a	1133 (vs)	−43	1035 (vs)	900 (s)	370 (m)	362	4.42	544	1.84
1b	1110 (s)	−90	1039 (vs)	918 (m)	386 (m)	368	4.44	550	1.87
2a1	1137 (vs)	−39	1049 (s)	910 (s)	379 (m)	360	4.04	562	1.47
2a2	1134 (vs)	−42	1044 (s)	908 (m)	380 (m)	361	4.01	567	1.46
2a3	1130 (vs)	−46	1050 (s)	897 (m)	379 (m)	360	4.06	567[c]	1.81[c]
2b1	1108 (vs)	−92	1048 (vs)	920 (m)	386 (m)	355	4.06	553	1.48
2b2	1110 (vs)	−90	1050 (vs)	919 (m)	389 (m)	358	4.05	556	1.50
2b3	1102 (s)	−98	1047 (s)	914 (m)	391 (m)	356	4.06	556	1.60
3a	1150 (vs)	−26	1057 (s)	880 (m)	360 (m)	351	3.86		
3b	1170 (vs)	−30	1049 (vs)	886 (m)	386 (m)	348	3.85	529	1.47

[a] vs, very strong; s, strong; m, mediuim; w, weak. [b] $\nu(P{=}O)_{complex} - \nu(P{=}O)_{ligand}$. [c] Shoulder.

Table 2 ^1H NMR data[a] in $CDCl_3$ or CD_2Cl_2

	Chemical shifts (δ) and coupling constants (J/Hz)		
Compound	PCH_aH_b	PC_6H_5 or PCC_6H_5	PbC_6H_5 or $P(C_6H_5)_4^+$
(PPh_4) **L1**[b]		7.96 (m, 4H$_o$), 7.19 (m, 4H$_m$), 7.28 (m, 2H$_p$), ^3J(PH$_o$) 10.7, ^4J(PH$_m$) 2.7	7.53 (m, 8H$_o$), 7.69 (m, 8H$_m$), 7.80 (m, 4H$_p$), ^3J(PbH$_o$) 12.9, ^4J(PbH$_m$) 3.7, ^5J(PH$_p$)
(PPh_4) **L2**[c]	3.66 (t, 2H$_a$), 3.36 (dd, 2H$_b$), ^2J (PH$_a$) 14.1, ^2J (PH$_b$) 12.4, ^2J(H$_a$H$_b$) 14.0	7.24 (m, 4H$_o$), 7.15 (m, 4H$_m$), 7.08 (m, 2H$_p$)	7.62 (m, 8H$_o$), 7.75 (m, 8H$_m$), 7.90 (m, 4H$_p$), ^3J(PbH$_o$) 13.0, ^4J(PbH$_m$) 3.7
1a[c]		7.42 (m, 8H$_o$), 7.26 (m, 8H$_m$), H$_p$ obscd., ^3J(PH$_o$) 7.8, ^4J(PH$_m$) 3.6	8.05 (m, 4H$_o$), 7.40 (m, 4H$_m$), H$_p$ obscd., ^3J(PbH$_o$) 187, ^4J(PbH$_m$) 73
1b[c]	3.09 (dd, 4H$_a$), 2.95 (t, 4H$_b$), ^2J (PH$_a$) 12.3, ^2J (PH$_b$) 14.2, ^2J(H$_a$H$_b$) 14.2	6.85 (m, 8H$_o$), 7.12 (m, 8H$_m$), 7.18 (m, 4H$_p$)	7.82 (m, 4H$_o$), 7.46 (m, 4H$_m$), 7.36 (m, 2H$_p$), ^3J(PbH$_o$) 187, ^4J(PbH$_m$) 75, ^5J(PbH$_p$) 29
2a1[b]		7.57 (m, 4H$_o$), 7.31 (m, 4H$_m$), H$_p$ obscd.	8.08 (m, 4H$_o$), 7.47 (m, 4H$_m$), 7.40 (m, 2H$_p$), ^3J(PbH$_o$) 170, ^4J(PbH$_m$) 68
2a2[b]		7.59 (m, 4H$_o$), 7.33 (m, 4H$_m$), H$_p$ obscd.	8.11 (m, 4H$_o$), 7.51 (m, 4H$_m$), 7.39 (m, 2H$_p$), ^3J(PbH$_o$) 169, ^4J(PbH$_m$) 68
2a3[b]		7.55 (m, 4H$_o$), 7.32 (m, 4H$_m$), H$_p$ obscd.	8.09 (m, 4H$_o$), 7.50 (m, 4H$_m$), 7.38 (m, 2H$_p$), ^3J(PbH$_o$) 169, ^4J(PbH$_m$) 65
2b1[b]	3.35 (t, 2H$_a$), 3.28 (t, 2H$_b$), ^2J (PH$_a$) 13.3, ^2J (PH$_b$) 12.5, ^2J(H$_a$H$_b$) 14.6	6.98 (m, 4H$_o$), 7.13 (m, 4H$_m$), 7.19 (m, 2H$_p$)	7.91 (m, 4H$_o$), 7.53 (m, 4H$_m$), 7.41 (m, 2H$_p$), ^3J(PbH$_o$) 168, ^4J(PbH$_m$) 70
2b2[b]	3.22–3.36 (m, 4H)	6.95 (m, 4H$_o$), 7.12 (m, 4H$_m$), 7.19 (m, 2H$_p$)	7.91 (m, 4H$_o$), 7.52 (m, 4H$_m$), 7.39 (m, 2H$_p$), ^3J(PbH$_o$) 165, ^4J(PbH$_m$) 67
2b3[b]	3.18–3.34 (m, 4H)	6.94 (m, 4H$_o$), 7.12 (m, 4H$_m$), 7.19 (m, 2H$_p$)	7.93 (m, 4H$_o$), 7.52 (m, 4H$_m$), 7.39 (m, 2H$_p$), ^3J(PbH$_o$) 166, ^4J(PbH$_m$) 66
3a[c]		7.43–7.22 (m, 10H)	7.70 (m, 6H$_o$) , 7.50 (m, 6H$_m$) , H$_p$ obscd., ^3J(PbH$_o$) 106, ^4J(PbH$_m$) 38
3b[c]	3.46 (dd, 2H$_a$), 3.35 (t, 2H$_b$), ^2J (PH$_a$) 12.8, ^2J (PH$_b$) 13.5, ^2J(H$_a$H$_b$) 14.2	7.06 (m, 4H$_o$), 7.20 (m, 4H$_m$), 7.25 (m, 2H$_p$)	7.67 (m, 6H$_o$), 7.51 (m, 6H$_m$), 7.41 (m, 3H$_p$), ^3J(PbH$_o$) 106, ^4J(PbH$_m$) 38

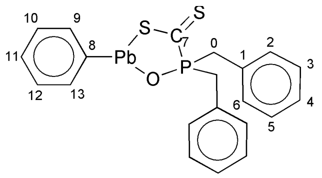
[a] t = triplet, dd = doublet of doublets, m = multiplet, obscd. = obscured. [b] In $CDCl_3$. [c] In CD_2Cl_2.

The ligands $R_2P(O)CS_2^-$ (R = Ph, L1; $PhCH_2$, L2)

IR and NMR. The infrared spectra of L show as expected many intense absorption bands due to the phenyl and benzyl groups attached to phosphorus. In addition the spectra exhibit intense bands assigned to the stretching modes of the P=O and CS_2 groups, which are relevant in determining the co-ordination behaviour of the ligands. The very intense band in the 1200 cm^{-1} region can with confidence be assigned to the ν(P=O) stretching mode. For the starting materials, $R_2P(O)H$, this vibration is also found near 1200 cm^{-1}.[7,8] The intense bands at *ca.*1030 cm^{-1} and those of medium intensity at *ca.* 910 cm^{-1} are assigned to the CS_2^- antisymmetric and symmetric stretching vibrations, respectively.[2h,3c]

The ^1H and ^{13}C NMR spectra of compounds **L1** and **L2** exhibit the expected resonances for the organic groups attached to phosphorus. The signals are split into two components as a result of phosphorus coupling to the proton and carbon nuclei. The assignments are given in Tables 2 and 3. The methylene protons on each benzyl group in **L2** are chemically non-equivalent giving rise to two proton signals. The proton spectra of **L2** at different temperatures show that the chemical shift difference, $\Delta\delta = \delta(H_a) - \delta(H_b)$, between the two methylene protons increases on lowering the temperature (0.26 ppm at 298 K, 0.31 ppm at 277 K, 0.34 at 248 K, 0.36 ppm at 226 K). This difference, $\Delta\delta$, also varies with the solvent [0.34 ppm in $(CD_3)_2CO$ down to 0.26 ppm in CD_3OD]. These variations are probably due to changes in the population of the different staggered conformations of the benzyl groups. The ^{13}C resonances for the CS_2 carbon appear at very low field (δ 254 and

Table 3 ^{13}C-{^{1}H} NMR data[a] in $CDCl_3$ or CD_2Cl_2



	Chemical shifts (δ) and coupling constants (J/Hz)									
Compound	δC^0 $^1J(PC^0)$	δC^1 $^{n+1}J(PC^1)$[b]	δC^2 $^{n+2}J(PC^2)$[b]	δC^3 $^{n+3}J(PC^3)$[b]	δC^4 $^{n+4}J(PC^4)$[b]	δC^7 $^1J(PC^7)$	δC^8 $^1J(PbC^8)$	δC^9 $^2J(PbC^9)$	δC^{10} $^3J(PbC^{10})$	δC^{11} $^4J(PbC^{11})$
(PPh_4)**L1**[c]		135.2 (d) 99.1	132.6 (d) 8.4	127.1 (d) 11.4	130.0 (d) 2.5	253.8 (d) 71.6	117.2 (d) 92.5[d]	134.2 (d) 10.4[d]	130.7 (d) 12.8[d]	135.7 (d) 3.0[d]
(PPh_4)**L2**[e]	36.3 (d) 60.5	134.7 (d) 7	130.2 (d) 4.9	127.9 (d) 2.1	125.8 (d) 2.5	257.7 (d) 62.1	117.6 (d) 89.5[d]	134.5 (d) 10.3[d]	130.7 (d) 12.9[d]	135.8 (d) 3.0[d]
1a[c]		130.0 (d) 105.7	132.7 (d) 9.6	128.5 (d) 12.6	132.6 (d) 2.5	249.2 (d) 69.8	168.3 (ss) 1210	134.3 (ss) 120.7	130.6 (ss) 180.0	130.2 (ss) 38.0
1b[e]	36.0 (d) 63.4	130.6 (d) 8.4	130.3 (d) 5.4	128.8 (d) 2.6	127.4 (d) 3.0	248.0 (d) 57.8	168.6 (ss) 1188	134.2 (ss) 120.8	131.1 (ss) 179.0	130.3 (ss) 37.3
2a1[c]		127.9 (d) 107.4	132.6 (d) 9.8	128.5 (d) 13.0	134.0 (s)	240.6 (d) 66.1	161.7 (ss) 924	135.0 (ss) 120.0	130.5 (ss) 161.7	130.6 (ss) 33.2
2a2[c]		127.9 (d) 108.2	132.6 (d) 9.8	128.5 (d) 13.0	132.9 (s)	240.6 (d) 70.3	161.5 (ss) 898	135.1 (ss) 118.6	130.4 (ss) 159.1	130.5 (ss) 34.0
2a3[c]		128 (d) 108	132.6 (d) 9.8	128.4 (d) 12.8	132.8 (s)	—[f]	—[f]	134.9 (ss) 117.7	130.3 (ss) 155	130.4 (s)
2b1[c]	35.6 (d) 64.0	128.9 (d) 8	129.9 (d) 5.5	128.8 (d) 2.7	127.6 (d) 3.0	242.4 (d) 53.4	161.9 (ss) 908	135.0 (ss) 120.2	130.6 (ss) 161.0	130.5 (ss) 34.9
2b2[c]	35.6 (d) 64.2	128.9 (d) 9	129.9 (d) 5.5	128.7 (d) 2.4	127.6 (s)	242.3 (d) 55.0	161.7 (s)	135.0 (ss) 118.2	130.5 (ss) 160.1	130.5 (ss) 35.1
2b3[c]	35.7 (d) 64.0	129.0 (d) 9	129.9 (d) 5.4	128.7 (d) 2.6	127.5 (d) 2.8	242.1 (d) 57.2	161.0 (ss) 844	135.0 (ss) 115.1	130.4 (ss) 154.3	130.4 (ss) 34.2
3b[e]	37.0 (d) 63.0	131.7 (d) 8.3	130.4 (d) 5.0	128.7 (d) 2.5	127.1 (d) 3.0	247.1 (d) 55.1	156.9 (ss) 562	137.2 (ss) 83.7	130.4 (ss) 130.4	129.8 (ss) 23.3

[a] s = singlet, ss = singlet accompanied by spin–spin coupling satellites, d = doublet. [b] $n = 0$ with **L1**, $n = 1$ with **L2**. [c] In $CDCl_3$. [d] $J(PC)$ in the PPh_4^+ ion. [e] In CD_2Cl_2. [f] Insufficient signal-to-noise ratio.

Table 4 ^{31}P-{^{1}H} NMR data in $CDCl_3$–CH_2Cl_2 (1 : 2) at 298 K

Compound	$\delta(^{31}P)$[a]	$\Delta\delta$[b]	$^2J(PbP)$ /Hz
$[PPh_4][S_2CP(O)Ph_2]$[c]	15.1 (s)		
$[PPh_4][S_2CP(O)(CH_2Ph)_2]$[c]	30.3 (s)		
1a	28.9 (ss)	13.8	90.0
1b	46.8 (s, sh)	16.5	
	48.7 (s)[d,e]	18.4	
	47.8 (ss)[e]	17.5	97.2
2a1	26.7 (ss)	11.6	109.1
2a2	26.7 (ss)	11.6	108.0
2a3	26.0 (ss)	10.9	100.3
2b1	44.3 (ss)	14.0	107.9
2b3	44.3 (ss)	14.0	106.8
2b3	44.2 (ss)	13.9	101.6
3b	40.6 (s)	10.3	

[a] s = singlet, (s,sh) = broad singlet with unresolved shoulders, (ss) = singlet accompanied by spin–spin coupling satellites. [b] $\Delta\delta = \delta(^{31}P)_{complex} - \delta(^{31}P)_{ligand}$. [c] $\delta(PPh_4)$, s at 22.3. [d] Minor peak with signal-to-noise ratio too small for determination of satellites. [e] 230 K.

258) because of the magnetic anisotropy of the C–S multiple bond and the relatively high electronegativity of the three atoms bound to this carbon atom. The ^{31}P NMR resonances (Table 4) appear as singlets shifted to higher magnetic field by *ca.* 30 ppm compared with those of the phosphinothioyl analogues, $R_2P(S)CS_2^-$ (R = Ph or $PhCH_2$).[3b]

Crystal structure of $[PPh_4][Ph_2P(O)CS_2]\cdot 0.5H_2O$. The monoclinic unit cells of this red-brown salt contain two different pairs of cations and anions. The tetraphenylphosphonium ions are as expected,[9] and the two tetrahedral anions are very much alike as can be seen from Table 5 and Fig. 1. All C–S bonds are approximately of equal length, 1.666(2)–1.678(2) Å, intermediate between a single and a double bond, and comparable to those in similar compounds, *e.g.* $[PPh_4][S_2CP(C_6H_{11})_2]$;[11] 1.685 Å, and $K(S_2COEt)$;[12] 1.680 Å. The P–O distances, 1.492(1) and 1.488(1) Å, are close to what is characterized as a P–O double bond (typically 1.46–1.48 Å, *e.g.* 1.483 Å in Ph_3PO[13]). The P–CS_2 bonds, 1.839(2) and 1.847(2) Å, are equal to a P–C sp^2 single bond (typically 1.84–1.85 Å). A water of crystallization (from the solvents) forms a hydrogen bond to an oxygen atom in one of the anions [O(3)···O(1A): 2.675(2) Å].

$[PbPh_2\{S_2CP(O)R_2\}_2]$ (R = Ph, 1a; CH_2Ph, 1b)

IR and NMR. The infrared spectra show the intense band for the stretching vibration of the phosphinoyl group to be shifted by 43 (compound **1a**) and 90 cm^{-1} (**1b**) to lower wavenumbers compared with the tetraphenylphosphonium salts of the ligands, **L1** and **L2**. This shift indicates co-ordination through the oxygen atom of the phosphinoyl group. Lead(IV) complexes with R_3PO ligands show similar co-ordination shifts for the P=O stretching mode. The appearance of the ν(C=S) vibration at 1035 and 1039 cm^{-1}, shifted to higher wavenumbers compared with $\nu_1(CS_2)$ of the unco-ordinated ligand, indicates S-co-ordination as well. Bands at 370 cm^{-1} for **1a** and 386 cm^{-1} for **1b**, not observed for the "free" ligands or in the spectrum of $PbPh_2Cl_2$, are assigned to the Pb–S stretching mode. Comparative values of ν(Pb–S) are 360 cm^{-1} for $[PbPh_2(S_2CNEt_2)_2]$[14] and 372 cm^{-1} for $[PbPh_3\{SC(O)OEt\}]$.[15] Therefore, among mononuclear species, the most likely co-ordination mode in these bis complexes is O,S bidentate, according to the IR spectra.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of complexes **1a** and **1b** in CH_2Cl_2 solution at 297 K show only one set of signals for the

Table 5 Selected bond lengths (in Å) for the two complexes and the "free" ligand. The more important bond angles and torsion angles are given in the text

Complex **1a**		Complex **2a1**		"Free" ligand	
		Pb–Cl	2.619(1)		
Pb–S(1)	2.714(1)	Pb–S(1)	2.645(1)		
Pb–S(3)	2.704(1)				
Pb–O(1)	2.443(3)	Pb–O	2.421(2)		
Pb–O(2)	2.471(3)				
Pb–C(11)	2.185(4)	Pb–C(11)	2.183(3)		
Pb–C(21)	2.163(4)	Pb–C(21)	2.175(3)		
P(1)–O(1)	1.504(3)	P–O	1.505(2)	P(1A)–O(1A)	1.492(1)
P(2)–O(2)	1.505(3)			P(1B)–O(1B)	1.488(1)
P(1)–C(31)	1.789(4)	P–C(31)	1.802(3)	P(1A)–C(11A)	1.819(2)
P(2)–C(51)	1.791(4)			P(1B)–C(21B)	1.811(2)
P(1)–C(41)	1.783(4)	P–C(41)	1.794(3)	P(1A)–C(21A)	1.809(2)
P(2)–C(61)	1.786(4)			P(1B)–C(11B)	1.820(2)
P(1)–C(1)	1.841(4)	P–C(1)	1.838(4)	P(1A)–C(1A)	1.839(2)
P(2)–C(2)	1.836(4)			P(1B)–C(1B)	1.847(2)
C(1)–S(1)	1.707(4)	C(1) –S(1)	1.703(3)	C(1A)–S(1A)	1.670(2)
C(2)–S(3)	1.706(5)			C(1B)–S(2B)	1.678(2)
C(1)–S(2)	1.648(4)	C(1) –S(2)	1.642(3)	C(1A)–S(2A)	1.678(2)
C(2)–S(4)	1.649(5)			C(1B)–S(1B)	1.666(2)
C–C	1.360(9)	C–C	1.367(6)	C–C	1.378(3)
	−1.408(6)		−1.398(5)	incl. PPh_4^+	−1.405(3)
				P–C	1.787(2)
				in PPh_4^+	−1.797(2)

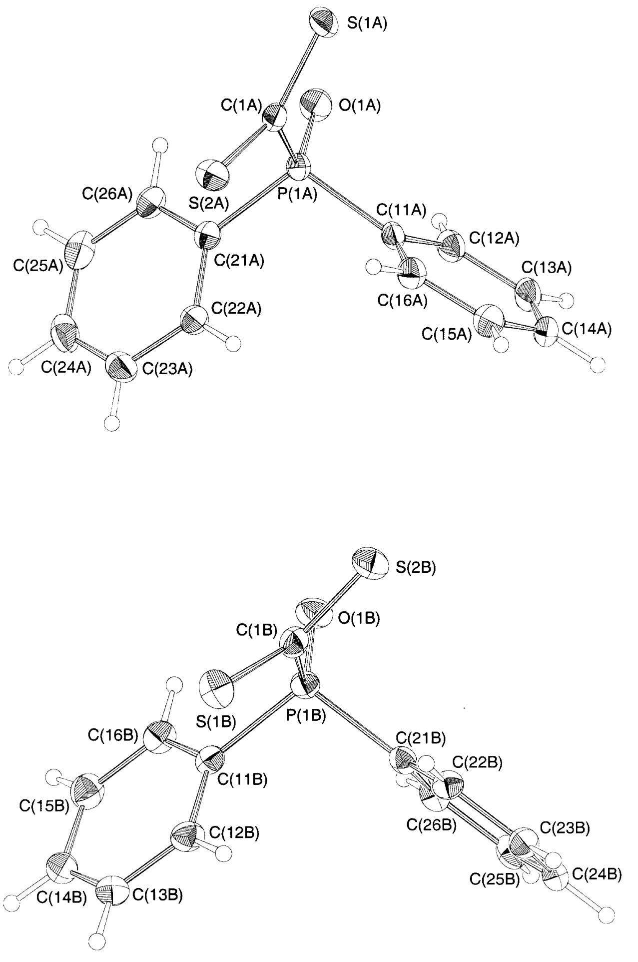


Fig. 1 An ORTEP[10] drawing of the two independent anions in $[PPh_4][Ph_2P(O)CS_2]\cdot 0.5\ H_2O$ with ellipsoids at the 50% probability level (as in all cases shown). The hydrogen atoms have arbitrary radii.

two phenyl ligands and one set for the two phosphinoyldithioformate ligands. This provides evidence for their structural equivalence on the NMR timescale and for an arrangement with relatively high symmetry. The ^1H and ^{13}C signals for the phenyl ligands and the ^{31}P signal are all accompanied by ^{207}Pb satellites.

The co-ordination of the phosphinoyldithioformate ligand is further confirmed by a marked upfield shift of the *ipso*-carbon atoms in its phenyl rings as well as of the CS_2 carbon atom (C^1 and C^7, respectively, in Table 3).

The magnitude of the coupling constants $^3J(^{207}Pb,^1H)$ and $^1J(^{207}Pb,^{13}C)$ to the phenyl ligands in diphenyl- and triphenyllead(IV) complexes provides information on the co-ordination number of the lead atom,[16,17] and the values 187 Hz for $^3J(^{207}Pb,^1H)$ and *ca.* 1200 Hz for $^1J(^{207}Pb,^{13}C)$ found for **1a** and **1b** can be considered as characteristic for a co-ordination number of six, as is found in crystals of **1a** (see the structure of **1a** and compounds with lower co-ordination numbers below).

The bis complexes are non-rigid at room temperature in chlorinated solvents as judged from the considerable line broadening in the NMR spectra. In **1b** the $(PhCH_2)_2P$ moiety is suitable for studying the dynamic stereochemistry of the molecule and distinguishing between some of the possible stereoisomers. Fig. 2 shows the ^1H NMR spectra of **1b** in the methylene region in the temperature range 239–326 K in $CDCl_3$. The slow exchange limit spectrum ($T = 239$ K) displays two $(PhCH_2)_2P$ spectra in the approximate intensity ratio 1 : 5 [$\delta(H_{a1})$ 3.34, $\delta(H_{b1})$ 3.28 and $\delta(H_{a2})$ 2.98, $\delta(H_{b2})$ 2.81]. This suggests the presence of two stereoisomers with molecular symmetries high enough to render all benzyl groups in both isomers equivalent. As the temperature of the NMR sample is raised the signals of both isomers broaden, then coalesce and finally appear in the fast exchange limit spectra at 326 K as one $(PhCH_2)_2P$ spectrum [two overlapping triplets, $\delta(H_a)$ 3.14, $\delta(H_b)$ 3.06]. Provided that the molecule is of the type $M(AB)_2X_2$ with the possibilities of two *trans*(X,X) isomers (C_{2v} and C_{2h}) and three *cis*(X,X) isomers (C_2, C_2 and C_1), then this dynamic process could involve the *cis–trans*(A,A) isomerization of the chelate rings in the equatorial plane ($C_{2v} \longleftrightarrow C_{2h}$) with the phenyl ligands keeping their axial position. This conclusion is supported by both ^{31}P and ^{13}C spectra in the slow exchange region at 230 K. The ^{31}P spectrum exhibits two singlets at δ 46.8 and 48.7 in approximately the same intensity ratio as the signals in the proton spectra. The ^{13}C spectrum displays two sets of signals as well. The more populated isomer shows signals for (see the labelling in Table 3) C^7, C^8 and C^0 at 246.7(d), 166.9 (ss) and 34.52(d) with $^1J(P,C^7) = 54.0$, $^1J(Pb,C^8) = 1162$ and $^1J(P,C^0) = 63.5$ Hz and the less populated one the signals for C^7, C^8 and C^0 at 241.8(d), 161.3 (s) and 34.78(d) with

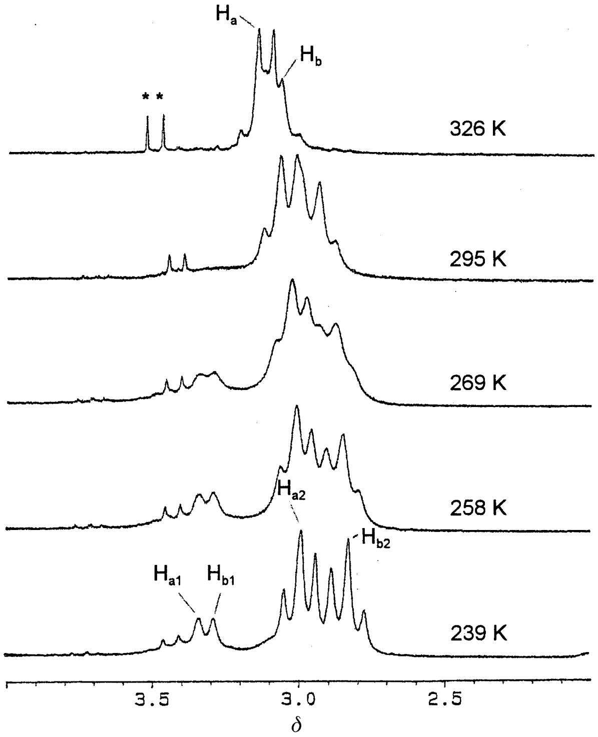


Fig. 2 Variable-temperature ^{1}H NMR spectra of the methylene region of complex **1b** in $CDCl_3$ (* impurity).

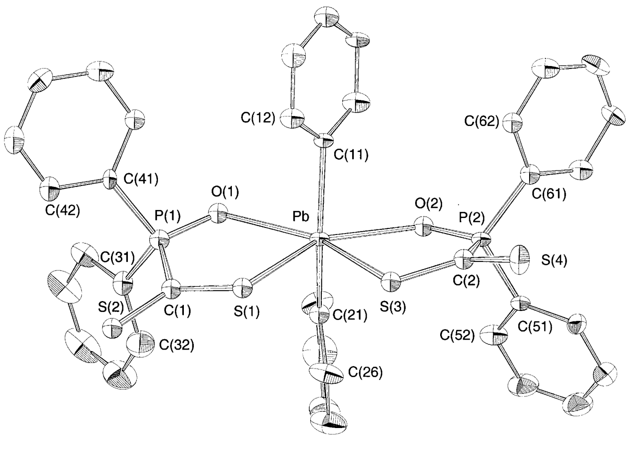


Fig. 3 An ORTEP drawing of $[PbPh_2\{S_2CP(O)Ph_2\}_2]$. For clarity hydrogen atoms are omitted and only the first two of the six sequential labels of the carbon atoms in the phenyl rings are shown.

^1J(P,C^7) = 52.6 and ^1J(P,C^0) = 63.9 Hz. As the C^0 signals for both isomers appear as one doublet, the molecular symmetry C_2 as well as C_1 are ruled out.

Crystal structure of $[PbPh_2\{S_2CP(O)Ph_2\}_2]$ 1a. This molecule is shown in Fig. 3, and selected bond distances are given in Table 5. The complex has a distorted octahedral structure with nearly C_2 symmetry, the pseudo twofold axis bisecting the O1–Pb–O2 angle [133.96(10)°]. The two phenyl ligands are *trans* to each other, and the $Ph_2P(O)CS_2^-$ ligands bind in a bidentate manner through oxygen and sulfur with the sulfur atoms *cis* to each other. The Pb–S distance is comparable to the short Pb–S distance in six-co-ordinated *trans*-$[PbPh_2(S_2PPh_2)_2]$ [2.6556(7) Å] which, however, also has a significantly longer Pb–S distance [3.0171(6) Å].[6] In this complex the bonding of $Ph_2PS_2^-$ was therefore characterized as anisobidentate. In the present complex the Pb–O bonds are also rather long compared to the Pb–S bonds, and accordingly the P–O distances are only slightly longer than in the "free" ligand. The O–Pb–S angles are small (76°) with a large separation between O1 and O2 (4.524 Å) and a small one between S1 and S3 (3.269 Å, with S1–Pb–S3 being 74.29°), and the two *trans*-phenyl ligands are tilted into the O–Pb–O gap [C11–Pb–C21 is 151.3(2)°], much in the same manner as in the above mentioned $Ph_2PS_2^-$ complex. The two O–P–C–S torsion angles in the five-membered chelate rings are 10.5(3) and 18.5(3)°. While the P–C distances in these rings are the same as in the "free" ligand, the C–S distances differ as expected: 1.707(4) Å for the one with S binding to lead against 1.648(4) Å for the other, compared to 1.67–1.68 Å for both bonds in the "free" ligand. Compared to the planar 5d^8 complex, $[Pt\{S_2CP(S)(C_6H_{11})_2\}_2]$,[3e] where the ligand binds in a similar way, the most striking difference is that the two Pt–S distances are as short as 2.29 and 2.31 Å and the S–Pt–S chelate angle is 93.5°. The P–S distance (2.01 Å) is accordingly significantly longer than in the free S-methyl ester of this ligand[3d] (1.95 Å).

$[PbPh_2X\{S_2CP(O)R_2\}]$ (R = Ph, X = Cl, 2a1; Br, 2a2; or I, 2a3. R = CH_2Ph, X = Cl, 2b1; Br, 2b2; or I, 2b3)

IR and NMR. The infrared spectra show for all compounds of type **2** the same major features as already discussed for **1**. Especially the co-ordination shift, $\Delta\nu$(P=O), to lower wavenumbers (*ca.* 40 cm^{-1} for **2a** and *ca.* 90 cm^{-1} for **2b**) accompanied by an opposite shift of $\nu_1(CS_2)$ (15–20 cm^{-1}) support the bidentate S,O-co-ordination mode of the phosphinoyldithioformate ligand in all complexes of type **2**.

The ^{13}C NMR spectra at 298 K in $CDCl_3$ show for all the $[PbPh_2X\{S_2CP(O)R_2\}]$ complexes all the resonances expected for two equivalent phenyl ligands co-ordinated to lead and one phosphinoyldithioformate ligand. The coupling constants between ^{207}Pb and the *ipso*-carbon atoms in the $PbPh_2$ part are in the range 844–924 Hz, decreasing in the order Cl > Br > I, and are thereby approximately 300 Hz smaller than for the six-co-ordinated bis complexes **1**, indicating the co-ordination number five in the type **2** in solution (*cf.* the crystal structure of **2a1** below). The observed values for the coupling constants ^3J(^{207}Pb,^{1}H) and ^4J(^{207}Pb,^{1}H), 165–170 and 65–70 Hz, respectively, are significantly smaller than those found for the type **1** complexes and thus confirm the co-ordination number five. The ^{31}P NMR spectra for all type **2** complexes show singlets accompanied by ^{207}Pb spin satellites. The coupling constants ^2J(^{207}Pb,^{31}P) are in the range 100–109 Hz, decreasing in the order Cl > Br > I.

The complexes of type **2**, like those of type **1**, show fluxional behaviour in chloroform. The variable-temperature ^{1}H NMR spectra of **2b1** display in the slow exchange region (237 K) two spectra in the intensity ratio 1 : 4. Analysis of the methylene part of the spectra shows the more populated isomer to have molecular symmetry C_s and the less populated the symmetry C_1.

Crystal structure of $[PbPh_2Cl\{S_2CP(O)Ph_2\}]$ 2a1. The asymmetric unit in the centrosymmetric unit cell is shown in Fig. 4 and selected bond lengths in Table 5. The complex may be described (see below) as a distorted five-co-ordinate square pyramid with a dithioformate sulfur atom as apex. $Ph_2P(O)CS_2^-$ co-ordinates in the same way as in the above described $[PbPh_2\{S_2CP(O)Ph_2\}_2]$ **1a**, except that the Pb–O and Pb–S distances now are a little, but significantly, shorter probably because of the lower co-ordination number. The O–Pb–S angle is 76.83(6)°, and the O–P–C–S torsion angle in the chelate ring is 8.6(2)°. Other bond lengths and angles in the bidentate ligand are similar in the two complexes.

While one chlorine atom has a normal bond [2.6186(9) Å] to lead, another chlorine atom (Cl′) from the centrosymmetrically related unit forms a very weak bond [3.1944(11) Å]. This "octahedral dimer" is shown in Fig. 5, from which it can also be seen that the *trans*-phenyl groups are tilted into the large O–Cl′ gap, the C11–Pb–C21 angle being 150.22(13)°, nearly the same as in

1a. However, the crystal structure is in accordance with the conclusions drawn from the NMR and IR spectra, that the complex is five-co-ordinated and that the phosphinoyldithioformate ligand co-ordinates through the O and one S atom.

X-Ray powder diffraction data of the three **2a** compounds show that **2a1** and **2a2** are isomorphous. The corresponding three **2b** compounds are not isomorphous and not isomorphous with the **2a** series.

[PbPh$_3${S$_2$CP(O)R$_2$}] (R = Ph, 3a; or CH$_2$Ph, 3b)

IR and NMR. The IR spectra resemble those for the compounds of type **1** and **2**, indicating the phosphinoyldithioformate ligands to be S,O-co-ordinated in the solid. The co-ordination shift for ν(P=O) is, however, significantly smaller than for **1** or **2** suggesting the Pb–O bond in **3** to be even weaker than in solid **1** and **2**.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of compound **3b** are all compatible with four-co-ordinated lead. The ^{31}P spectra at room temperature show the expected singlets, but without the ^{207}Pb coupling satellites in contrast to all type **1** and **2** compounds where the magnitude of the coupling $^2J(^{207}\text{Pb},^{31}\text{P})$ is found to be 90–109 Hz. This indicates a more than two bond distance between Pb and P and therefore co-ordination only through S atoms. On cooling a solution of **3b** only small chemical shift differences are observed, and the ^{31}P spectrum remains as one singlet. Therefore exchange phenomena are hardly responsible for the lack of coupling. ^{1}H and ^{13}C NMR measurements show well behaved spectra with signals and couplings showing the same picture. The coupling constant $^1J(\text{Pb},\text{C}^8)$ for **3b**, 562 Hz, is *ca.* 300 Hz smaller than for the five-co-ordinated compounds **2** and *ca.* 600 Hz smaller than for the six-co-ordinated compounds **1** consistent with the co-ordination number of four and thus no chelate co-ordination of the phosphinoyldithioformate ligand in solution. The coupling constants $^3J(\text{Pb},\text{H}_o)$ and $^4J(\text{Pb},\text{H}_m)$ confirm this conclusion.[16,17] The analogous triphenyllead(IV) compound [PbPh$_3$(S$_2$CNC$_4$H$_8$)] exhibits distorted T_d symmetry with a monodentate tetramethylenedithiocarbamate ligand.[18]

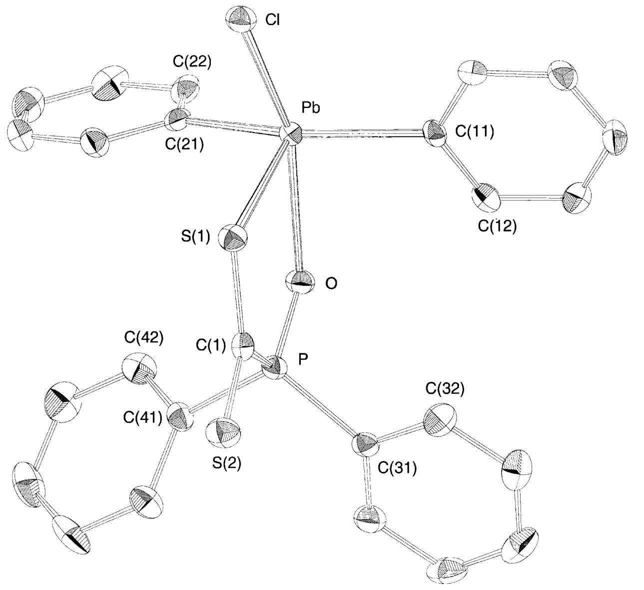


Fig. 4 An ORTEP drawing of [PbPh$_2$Cl{S$_2$CP(O)Ph$_2$}]. Details as in Fig. 3.

It has not been possible to grow single crystals of the compounds of type **3** suitable for X-ray analysis. Furthermore the solution data available for **3a** are limited because of its low solubility. On the basis of the crystal structure of **1a** and **2a** and the results derived from the NMR data we expect the complexes of type **1** and **2** to be mononuclear in the crystalline state as well as in the investigated solutions. With the co-ordination number four the same applies to **3b**. However, the low solubility of **3a** may well be associated with a higher nuclearity and accordingly a co-ordination number higher than four for this complex.

Conclusion

Reaction in non-co-ordinating organic solvents between phenylhalogenolead(IV) compounds and diphenyl- or dibenzyl-phosphinoyldithioformate, yields four-, five- or six-co-ordinated complexes. NMR (^{1}H, ^{13}C and ^{31}P) provides valuable information on the structure of the complexes in solution and also reveals a fluxional behaviour of the five- and six-co-ordinated compounds without ligand exchange. The magnitude of the coupling constants between lead and the hydrogen atoms in the positions *ortho* and *meta* to lead in the phenyl ligands, and particularly of the coupling constants between lead and the *ipso*-carbon atom in these ligands, reflects in a remarkable way the co-ordination number of these complexes.

In the solid state IR data give additional structural information. X-Ray analyses show that the preferred co-ordination mode of the phosphinoyldithioformate ligand is bidentate through an S and an O atom buckled to nearly planar five-

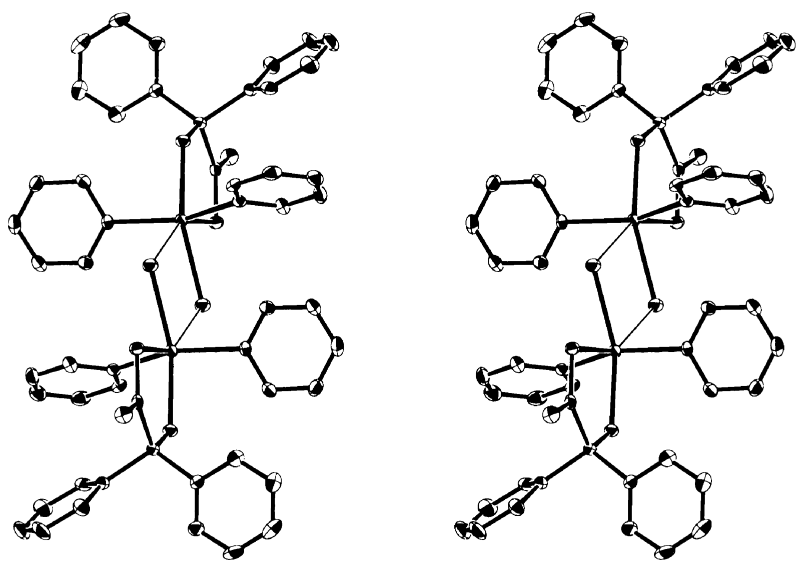


Fig. 5 Stereoscopic ORTEP drawing of [PbPh$_2$Cl{S$_2$CP(O)Ph$_2$}]. Two molecules connected by a centre of inversion are shown with the Pb $\cdots$ Cl contact [3.1944(11) Å] indicated with a thin line unlike the Pb–Cl bond [2.6186(9) Å] with normal linewidth.

membered chelate rings with relatively long Pb–O bonds. In ongoing studies of tin(IV) complexes with this type of ligand[19] the same co-ordination behaviour is observed, and the five-co-ordinate $[Sn(CH_3)_2Br\{S_2CP(O)(CH_2Ph)_2\}]$ even has a completely planar chelate ring (crystallographic mirror plane). The correlation between co-ordination number and the above mentioned magnitudes of the NMR coupling constants to the metal atom is also found in these tin(IV) complexes.

Experimental

NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.133, 101.256 and 62.896 MHz for ^1H, $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ respectively. The deuteriated solvent served as the lock in the ^1H and ^{13}C measurements with tetramethylsilane as internal reference. The ^{31}P NMR spectra were calibrated against an external 85% H_3PO_4 aqueous solution. The high frequency positive convention was used for all chemical shifts. The infrared spectra were obtained with a Perkin-Elmer 283 spectrophotometer in the range 4000–200 cm^{-1} using KBr/CsI pellets, UV/vis spectra on Ultraspec3000 or Perkin-Elmer Lambda17 spectrophotometers. Elemental analyses were carried out on a Carlo Erba Strumentazione model 1106 analyser. A STOE Stadi P X-ray powder diffractometer was used to obtain powder diffraction data with Cu-Kα1 radiation selected by a curved germanium monochromator. Data were collected from 5 to 40° (2θ) in 0.01° intervals using a position sensitive detector covering 7° in 2θ. The software STOE WinXPOW (version 1.05, 1999) supplied with the instrument was used for the data treatment.

$PbPh_2Cl_2$, $PbPh_3Cl$ and $PbPh_4$ were purchased from Ventron Corporation and used as such after vacuum drying. $PbPh_2Br_2$ and $PbPh_2I_2$ were obtained by treating a solution of $PbPh_4$ in chloroform with chloroform solutions of Br_2 and I_2, respectively, in a 1 : 2 molar ratio. $Ph_2P(O)H$[8] and $(PhCH_2)_2P(O)H$[7] were prepared by published methods. Solvents were purified by standard procedures. Anhydrous solvents were purchased from Aldrich and used as received.

Preparations

The following syntheses of the potassium and tetraphenylphosphonium salts of the ligands are modifications of earlier procedures[3b,c] primarily concerning the choice of solvent and time of reaction.

$K[Ph_2P(O)CS_2]\cdot C_4H_8O_2$ (KL1). A stirred solution of $Ph_2P(O)H$ (20.95 g, 0.1036 mol) in thf (200 ml) was cooled to −6 °C and treated with CS_2 (8.68 g, 0.114 mol) and subsequently with an aqueous solution of 14.14 M KOH (7.33 ml, 0.1036 mol). This mixture was stirred vigorously for 45 min, while it changed from colourless to red-brown. The solvent was removed by rotary evaporation and the red-brown oil dissolved in 1,4-dioxane (150 ml). The solution was stirred overnight at room temperature, and a red-orange precipitate was formed. Diethyl ether (120 ml) was added and the mixture cooled to −6 °C after which the precipitate was filtered off in air and dried *in vacuo*. Crude yield: 24.0 g, 57%. The potassium salt was recrystallized by dissolving the solid in acetonitrile (*ca.* 200 ml), filtering the red solution and adding 1,4-dioxane (100 ml) and diethyl ether (200 ml). The resulting red-orange powder was filtered off, washed with 1,4-dioxane–diethyl ether (1 : 1) and dried *in vacuo*. Yield: 19.0 g, 45%. Calc. for $C_{13}H_{10}KOPS_2\cdot C_4H_8O_2$: C, 50.47; H, 4.48. Found: C, 50.50; H, 4.38%.

$K[(PhCH_2)_2P(O)CS_2]$ (KL2). A stirred solution of $(PhCH_2)_2P(O)H$ (25.08 g, 0.1089 mol) in thf (250 ml) was treated with CS_2 (9.12 g, 0.120 mol) and subsequently with an aqueous solution of 14.14 M KOH (8.47 ml, 0.1089 mol). This mixture was stirred vigorously for 20 h, while it changed from colourless to red-brown. KOH pellets (10 g) were added as a drying agent, and the mixture was stirred for 1 h after which the aqueous KOH phase was removed with a syringe. Pyridine (70 ml) was added, the solution filtered and the thf removed by rotary evaporation. The red-brown pyridine solution was treated with diethyl ether (120 ml) and kept overnight at −6 °C. The orange precipitate was filtered off in air, washed with diethyl ether–thf (3 : 1) and dried *in vacuo*. Yield: 19.8 g, 53%. Calc. for $C_{15}H_{14}KOPS_2$: C, 52.30; H, 4.10. Found: C, 52.40; H, 4.17%.

$[PPh_4][Ph_2P(O)CS_2]\cdot 0.5H_2O$. Tetraphenylphosphonium bromide (0.419 g, 1.00 mmol) was added to a stirred suspension of **KL1** (0.405 g, 1.00 mmol) in CH_2Cl_2 (10 ml). The solution changed from colourless to wine-red instantaneously and a white precipitate (KBr) formed. After filtration or centrifugation the solvent was removed at once by rotary evaporation. The oily salmon pink solid was dissolved in acetonitrile (10 ml), and the wine-red solution treated with diethyl ether until turbid and stored at 5 °C for 20 h. The resulting red-brown crystalline product was filtered off in air, washed with diethyl ether and dried *in vacuo*. Yield: 0.323 g, 79%. Calc. for $C_{37}H_{31}O_{1.5}P_2S_2$: C, 71.02; H, 4.99. Found: C, 70.96; H, 5.00%.

$[PPh_4][(PhCH_2)_2P(O)CS_2]$. This compound was isolated in a similar way from **KL2** and PPh_4Br as red-brown crystals. Yield: *ca.* 70%. Calc. for $C_{39}H_{34}OP_2S_2$: C, 72.64; H, 5.32. Found: C, 72.89; H, 5.20%.

$[PbPh_2\{S_2CP(O)Ph_2\}_2]$ 1a. *Method (a).* A solution of **KL1** (0.570 g, 1.41 mmol) in acetone (25 ml) was added dropwise to a stirred suspension of $PbPh_2Cl_2$ (0.300 g, 0.694 mmol) in acetone (10 ml). After the mixture had been stirred for 20 min a violet solid had formed in a wine-red solution. The powder was filtered off in air, washed with acetone, water and methanol and dried *in vacuo*. Yield: 0.340 g, 54%. Recrystallization from dichloromethane–hexane gave crystals suitable for single crystal X-ray diffraction. Calc. for $C_{38}H_{30}O_2P_2PbS_4$: C, 49.82; H, 3.30. Found: C, 49.61; H, 3.26%.

Method (b). $PbPh_2Cl_2$ (0.120 g, 0.278 mmol) was added to a stirred suspension of **KL1** (0.224 g, 0.554 mmol) in CH_2Cl_2 (5 ml). The solution changed from colourless to dark blue instantaneously and a white precipitate (KBr) formed, which was removed by centrifugation. Diethyl ether (5 ml) was added to the solution, and the mixture kept at −5 °C overnight, after which the resulting violet crystalline product was filtered off in air, washed with dichloromethane–diethyl ether (1 : 1) and dried *in vacuo*. Yield: 0.194 g, 76%. All spectroscopic data for complex **1a** prepared in this way are identical with those obtained by method (a).

$[PbPh_2\{S_2CP(O)(CH_2Ph)_2\}_2]$ 1b. *Method (a).* A solution of **KL2** (0.344 g, 1.00 mmol) in acetone (18 ml) was added dropwise over 30 min to a stirred suspension of $PbPh_2Cl_2$ (0.216 g, 0.500 mmol) in acetone (8 ml). After the mixture had been stirred for 10 min a red-brown solid had formed in a red-brown solution. Diethyl ether (10 ml) was added and the mixture stirred for 15 min, after which the product was filtered off in air, washed with acetone–diethyl ether (1 : 1), water and methanol and dried *in vacuo*. Yield: 0.433 g, 89%. Recrystallization from dichloromethane–hexane gave purple-red crystals. Calc. for $C_{42}H_{38}O_2P_2PbS_4$: C, 51.89; H, 3.94. Found: C, 51.38; H, 3.88%.

Method (b). A solution of (PPh_4)**L2** (0.330 g, 0.511 mmol) in dichloromethane (10 ml) was added dropwise over 5 min to a stirred suspension of $PbPh_2Cl_2$ (0.111 g, 0.257 mmol) in dichloromethane (7 ml). Methanol (25 ml) was added to the clear, orange-red solution and the dichloromethane removed by rotary evaporation. The solution turned wine-red and a precipitate started to form. After 20 hours the purple-red crystalline precipitate was collected by filtration, washed with

Table 6 Crystal data and summary of the data collection and structure refinement results

	(PPh_4) **L1**·$0.5H_2O$	**1a**	**2a1**
Formula	$C_{74}H_{62}O_3P_4S_4$	$C_{38}H_{30}O_2P_2PbS_4$	$C_{25}H_{20}ClOPPbS_2$
M	1251.36	915.99	674.14
T/K	122(1)	122(1)	122(1)
Space group	$P2_1$	$P2_1/n$	$P2_1/n$
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
a/Å	9.1216(14)	14.403(3)	14.911(3)
b/Å	41.242(8)	17.634(5)	8.2427(17)
c/Å	9.3324(12)	14.420(4)	20.384(4)
β/°	117.221(11)	90.03(2)	103.468(16)
Z	2	4	4
Wavelength/Å	1.5418	0.71073	0.71073
μ/mm^{-1}	2.755	4.955	7.286
Measured reflections	14683	15143	12040
Unique reflections	12809	10630	5309
R_{int}	0.021	0.0752	0.0308
Refined parameters	772	424	280
$R(F)$ for reflections with $F/\sigma(F) > 4$	0.0294	0.0394	0.0227
$wR(F^2)$ for all reflections	0.0735	0.0964	0.0391

methanol and dried *in vacuo*. Yield: 0.191 g, 77%. All spectroscopic data for complex **1b** prepared in this way are identical with those obtained by method (a).

[PbPh$_2$Cl{S$_2$CP(O)Ph$_2$}] 2a1. A solution of K**L1** (0.276 g, 0.682 mmol) in acetonitrile (15 ml) was added dropwise over 5 min to a stirred suspension of $PbPh_2Cl_2$ (0.296 g, 0.685 mmol) in dichloromethane (10 ml). The red-violet mixture was filtered after 20 min and the dichloromethane removed by rotary evaporation. The resulting violet microcrystalline powder was filtered off in air, washed with acetonitrile, water and finally with acetonitrile and dried *in vacuo*. Yield: 0.337 g, 73%. Recrystallization from chloroform–hexane gave crystals suitable for single crystal X-ray diffraction. Calc. for $C_{25}H_{20}ClOPPbS_2$: C, 44.54; H, 2.99. Found: C, 44.52; H, 3.00%.

[PbPh$_2$Cl{S$_2$CP(O)(CH$_2$Ph)$_2$}] 2b1. Similar procedure as for complex **2a1** using K**L2** (0.265 g, 0.769 mmol) and $PbPh_2Cl_2$ (0.333 g, 0.771 mmol). Yield: 0.330 g, 61%, blue-violet microcrystals. Calc. for $C_{27}H_{24}ClOPPbS_2$: C, 46.18; H, 3.44. Found: C, 46.00; H, 3.44%.

[PbPh$_2$Br{S$_2$CP(O)Ph$_2$}] 2a2. $PbPh_2Br_2$ (0.447 g, 0.857 mmol) was added to a stirred suspension of K**L1** (0.346 g, 0.854 mmol) in acetone (5 ml). The solution changed from colourless to wine-red instantaneously and a white precipitate (KBr) formed. After stirring for 2 min the precipitate was removed by centrifugation, and 2-propanol (10 ml) added to the solution which was kept at −5 °C overnight. The resulting violet, crystalline product was filtered off in air, washed with 2-propanol and dried *in vacuo*. Yield 0.383 g, 62%. Calc. for $C_{25}H_{20}BrOPPbS_2$: C, 41.78; H, 2.81. Found: C, 40.20; H, 2.77%.

[PbPh$_2$Br{S$_2$CP(O)(CH$_2$Ph)$_2$}] 22b2. Similar procedure as for complex **2a2** using K**L2** (0.173 g, 0.502 mmol) and $PbPh_2Br_2$ (0.263 g, 0.504 mmol). Yield: 0.234 g, 62%, blue-violet microcrystals. Calc. for $C_{27}H_{24}BrOPPbS_2$: C, 43.43; H, 3.24. Found: C, 42.70; H, 3.18%.

[PbPh$_2$I{S$_2$CP(O)Ph$_2$}] 2a3. Similar procedure as for complex **2a2** using K**L1** (0.202 g, 0.499 mmol) and $PbPh_2I_2$ (0.306 g, 0.497 mmol). Yield 0.252 g, 66%, brown microcrystals. Calc. for $C_{25}H_{20}IOPPbS_2$: C, 39.22; H, 2.63. Found: C, 39.20; H, 2.66%.

[PbPh$_2$I{S$_2$CP(O)(CH$_2$Ph)$_2$}] 2b3. Similar procedure as for complex **2a2** using K**L2** (0.439 g, 1.27 mmol) and $PbPh_2I_2$ (0.786 g, 1.28 mmol). Yield 0.790 g, 78%, red-brown microcrystals. Calc. for $C_{27}H_{24}IOPPbS_2$: C, 40.86; H, 3.05. Found: C, 40.70; H, 3.08%.

[PbPh$_3${S$_2$CP(O)Ph$_2$}] 3a. K**L1** (0.230 g, 0.569 mmol) was added to a suspension of $PbPh_3Cl$ (0.270 g, 0.569 mmol) in acetone (7 ml), and the mixture stirred for 5 min. The resulting wine-red solution produced a blue-violet precipitate which was filtered off in air, washed with acetone, water and finally with acetone and dried *in vacuo*. The substance shows in the common organic solvents very limited solubility in contrast to all other complexes in this work. Yield 0.306 g, 75%. Calc. for $C_{31}H_{25}OPPbS_2$: C, 52.01; H, 3.52. Found: C, 52.12; H, 3.53%.

[PbPh$_3${S$_2$CP(O)(CH$_2$Ph)$_2$}] 3b. A solution of K**L2** (0.386 g, 1.12 mmol) in acetone (25 ml) was added dropwise over 30 min to a stirred suspension of $PbPh_3Cl$ (0.521 g, 1.10 mmol) in acetone–diethyl ether (1 : 1) (25 ml). After the mixture had been stirred for 10 min a pink solid had formed, which was filtered off in air, washed with acetone–diethyl ether (1 : 1), water and methanol and dried *in vacuo*. Recrystallization from dichloromethane–hexane gave a rose powder. Yield: 0.385 g, 47%. Calc. for $C_{33}H_{29}OPPbS_2$: C, 53.28; H, 3.93. Found: C, 52.80; H, 3.86%.

Crystal structure determinations

Crystal, data collection and refinement parameters for compounds (PPh_4)**L1**, **1a** and **2a** are given in Table 6. Based on profile scans, suitable crystals for single-crystal X-ray diffraction were selected. The data were collected on an Enraf-Nonius CAD4 diffractometer equipped with an Oxford Cryostreams low-temperature device. Data reduction was performed with the DREADD program package[20] and absorption correction with the ABSORB set of programs.[21] The structures were solved by direct methods using SHELXS[22] and completed by subsequent Fourier difference synthesis and refined with SHELXL.[23] All hydrogen atoms were placed at idealized positions except for the two of the water molecule in (PPh_4)**L1**. The isotropic displacement parameters for all the hydrogen atoms were constrained to be 1.2 times the equivalent isotropic displacement parameter of the atom to which a hydrogen atom is covalently bonded.

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See http://www.rsc.org/suppdata/dt/b0/b006672i/ for crystallographic files in .cif format.

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