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Phenyllead(IV) Diorganophosphinodithioates, $Ph_nPb(S_2PR_2)_{4-n}$. Synthesis, Spectroscopic Characterization, and NMR Study of the Redistribution/Decomposition of Diphenyllead(IV) Derivatives

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ABSTRACT

Tri- and diphenyllead(IV) diorganophosphinodithioates, $Ph_nPb(S_2PR_2)_{4-n}$ (n = 2 and 3; R = Me, Et, Ph) were prepared by reacting the corresponding organolead(IV) chloride with the sodium or ammonium salt of the phosphinodithioic acid. The title compounds were investigated by infrared, ^1H and ^{31}P NMR, and mass spectroscopy, and possible structures were proposed. The diphenyllead(IV) phosphinodithioates, $Ph_2Pb(S_2PR_2)_2$, undergo decomposition on standing or on moderate heating, the least stable being the ethyl derivative. The process was monitored by using ^1H and ^{31}P NMR spectroscopy, and a reaction pathway leading to $Ph_3PbS_2PR_2$, $Pb(S_2PR_2)_2$, and $R_2P(S)SPh$ was established.

INTRODUCTION

Diorganodithiophosphorus ligands, i.e., phosphinodithioates, $R_2PS_2^-$, and phosphorodithioates, $(RO)_2PS_2^-$ (R = alkyl, aryl), exhibit a broad variety of coordination patterns [1], and, therefore, the synthesis of new metal derivatives containing such ligands presents continuous interest. Heavy metals are particularly attractive due to their tendency to exhibit higher coordination numbers, which often result in unexpected structures. While numerous studies deal with the synthesis and structure of tin dithiophosph(in)ates [2,3], such studies are scarce for lead. Some inorganic lead(II) phosphoro- and phosphinodithioates are known, and X-ray molecular structure determinations have been reported for $Pb[S_2P(OR)_2]_2$ (R = Et [4,5], Pr^i [6], Bu^i [4], Ph [4]), $Pb[S_2P(OEt)_2]_2 \cdot bipy$ [7], $Pb[S_2P(OEt)_2]_2 \cdot en$ [7], $\{Pb[S_2P(OEt)_2]_2\}_2 \cdot en$ [7], and $Pb(S_2PR_2)_2$ (R = Et [8], Ph [9]). By contrast, organolead(IV) derivatives have been less studied. Thus, some di- and triphenyllead(IV) diorganophosphorodithioates, $R_nPb[S_2P(OR')_2]_{4-n}$, have been reported [10], and the molecular structures of $Ph_3PbS_2P(OEt)_2$ and $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ were determined [11]. However, no organolead(IV) phosphinodithioates, $R_nPb(S_2PR_2)_{4-n}$, have been described so far.

We report here the synthesis and spectroscopic properties of the first di- and triphenyllead(IV) diorganophosphinodithioates. Of these, the diphenyllead derivatives, $Ph_2Pb(S_2PR_2)_2$, R = Me, Et, Ph, were found to be thermally unstable, and an NMR investigation of the decomposition was performed to elucidate the process.

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EXPERIMENTAL SECTION

Phenyllead(IV) chlorides were commercial products. Sodium dialkylphosphinodithioates, $NaS_2PMe_2 \cdot 2H_2O$ [12] and $NaS_2PEt_2 \cdot 2H_2O$ [13], were prepared from $R_2P(S)–P(S)R_2$, S_8, and $Na_2S \cdot xH_2O$, using published procedures. Ammonium diphenylphosphinodithioate was prepared by bubbling dried gaseous ammonia into the benzene solution of the free acid (obtained according to the literature [14]). The phenyl esters of phosphinodithioic acids, $R_2P(S)SPh$, were obtained by reacting NaSPh with $R_2P(S)Cl$ in THF/benzene, according to the literature [15]. Infrared spectra were recorded for KBr disks on a PERKIN ELMER 283B spectrometer. ^1H and ^{31}P NMR spectra were obtained in C_6D_6 solutions on a VARIAN GEMINI 300 MHz apparatus, operating at 299.949 and 121.421 MHz for the respective nuclei. The internal deuterated solvent and H_3PO_4 (85%) served as the lock for the spectrometer. Mass spectra were obtained using the DCI(–) method on a FINNIGAN MAT 8222 instrument (for organolead(IV) derivatives) and the EI method on a HEWLETT-PACKARD 5985 GS/MS instrument (for inorganic lead(II) compounds).

Preparation of the Compounds

The quantities of reagents and solvent used, yields, melting points of organolead compounds obtained, and relevant IR data are listed in Table 1. Details of particular syntheses are provided subsequently. Mass spectral characterization of the compounds is provided in Table 2.

$Ph_3PbS_2PR_2$ (R = Me, Et, Ph). Stoichiometric amounts of Ph_3PbCl and a given sodium or ammonium diorganophosphinodithioate (see Table 1) were suspended in benzene and then stirred under reflux for 4 hours. The hot reaction mixture was filtered to remove the resulting NaCl or NH_4Cl. The clear filtrate was allowed to cool to room temperature, when small amounts of unreacted Ph_3PbCl deposited and were removed by filtration. After the removal of the solvent on a rotary evaporator in vacuum, the recrystallization of the remaining white solid product from acetonitrile led to each desired triphenyllead(IV) diorganophosphinodithioate, as colorless crystals (Table 1).

$Ph_3PbS_2PMe_2$. ^1H (δ, C_6D_6, TMS): 1.61d (6H, $^2J(PH) = 12.9$ Hz), P–CH_3; 7.06t (3H, $^3J(HH) = 7.3$ Hz), Pb–C_6H_5 (para); 7.20t (6H, $^3J(HH) = 7.3$ Hz, $^4J(^{207}PbH) = 37$ Hz), Pb–C_6H_5 (meta); 7.89d (6H, $^3J(HH) = 7.5$ Hz, $^3J(^{207}PbH) = 105.4$ Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 53.8.

$Ph_3PbS_2PEt_2$. ^1H (δ, C_6D_6, TMS): 1.03dt (6H, $^3J(HH) = 7.4$ Hz, $^3J(PH) = 21.1$ Hz), P–CH_2CH_3; 1.73dq (4H, $^3J(HH) = 7.6$ Hz, $^2J(PH) = 10.8$ Hz), P–CH_2CH_3; 7.06t (3H, $^3J(HH) = 7.6$ Hz), Pb–C_6H_5 (para); 7.21t (6H, $^3J(HH) = 7.8$ Hz, $^4J(^{207}PbH = 37.2$ Hz), Pb–C_6H_5 (meta); 7.90d (6H, $^3J(HH) = 8.1$ Hz, $^3J(^{207}PbH) = 105$ Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 75.8.

$Ph_3PbS_2PPh_2$. ^1H (δ, C_6D_6, TMS): 6.90m (6H) P–C_6H_5 (meta + para); 8.09dm (4H, $^3J(PH) = 14.4$ Hz), P–C_6H_5 (ortho); 7.01t (3H, $^3J(HH) = 7.5$ Hz), Pb–C_6H_5 (para); 7.12t (6H, $^3J(HH) = 7.6$ Hz, $^4J(^{207}PbH) = 37.9$ Hz), Pb–C_6H_5 (meta); 7.76d (6H, $^3J(HH) = 7.4$ Hz, $^3J(^{207}PbH) = 105.4$ Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 59.4.

$Ph_2Pb(S_2PMe_2)_2$. The reaction mixture obtained from Ph_2PbCl_2 and $NaS_2PMe_2 \cdot 2H_2O$ (1:2 molar ratio) in benzene was filtered after 2 hours of stirring at room temperature. The clear filtrate

TABLE 1 Preparation and Properties of Phenyllead(IV) Diorganophosphinodithioates

Starting Materials[a]				*Infrared Data*		
Ph_nPbCl_{4-n} g (mmol)	*$MS_2PR_2 \cdot xH_2O$ g (mmol)*	*Product*[b] *Yield (%)*	*Mp (°C)*	*ν_{as} (PS_2)*	*ν_s (PS_2)*	*Δ*[c]
Ph_3PbCl 1.18 (2.5)	$NaS_2PMe_2 \cdot 2H_2O$ 0.46 (2.5)	$Ph_3PbS_2PMe_2$ 1.20 g (86)	122–124	596m	451s	145
Ph_3PbCl 1.18 (2.5)	$NaS_2PEt_2 \cdot 2H_2O$ 0.53 (2.5)	$Ph_3PbS_2PEt_2$ 0.90 g (61)	85–86	590s	474m	116
Ph_3PbCl 0.95 (2.0)	$NH_4S_2PPh_2$ 0.54 (2.0)	$Ph_3PbS_2PPh_2$ 1.03 g (75)	108–110	667s	535vs	132
Ph_2PbCl_2 0.62 (1.44)	$NaS_2PMe_2 \cdot 2H_2O$ 0.53 (2.88)	$Ph_2Pb(S_2PMe_2)_2$ 0.65 g (75)	140–142	593vs	491s	102
Ph_2PbCl_2 0.54 (1.25)	$NH_4S_2PPh_2$ 0.67 (2.5)	$Ph_2Pb(S_2PPh_2)_2$ 0.90 g (84)	198–200	635s 609m	555vs 546s	80

[a] All reactions were performed in 25 mL benzene.

[b] Recrystallization performed from acetonitrile.

[c] $\Delta\nu = \nu_{as}$ (PS_2) $- \nu_s(PS_2)$.

TABLE 2 DCI(−) Mass Spectra of $Ph_3PbS_2PR_2$ and $Ph_2Pb(S_2PR_2)_2$ (*m/e*, %)

	Ph₃PbS₂PR₂			*Ph₂Pb(S₂PR₂)₂*	
	R = Me	*R = Et*	*R = Ph*	*R = Me*	*R = Ph*
$[Ph_2Pb(S_2PR_2)_2\text{–}H]^+$	—	—	—	611 (<1)	—
$[Ph_3PbS_2PR_2\text{–}H]^+$	—	591 (4)	687 (1)	—	—
$PhPb(S_2PR_2)_2^+$	—	—	—	535 (11)	783 (1)
$Ph_2PbS(S_2PR_2)^+$	—	—	—	519 (<1)	643 (<1)
$Ph_2PbS_2PR_2^+$	487 (64)	515 (56)	611 (31)	487 (35)	611 (9)
$Pb(S_2PR_2)_2^+$	—	—	—	458 (37)	706 (5)
Ph_3PbS^+	471 (<1)	471 (11)	471 (4)	—	—
Ph_3Pb^+	439 (41)	439 (100)	439 (100)	—	—
$S_2PR_2^+$	125 (100)	153 (34)	249 (47)	125 (100)	249 (75)
SPR_2^+	93 (1)	121 (<1)	217 (17)	93 (<1)	217 (68)
PhS^+	—	—	—	—	109 (100)

was evaporated in vacuum and the remaining solid was recrystallized from acetonitrile, resulting in colorless crystals of the title compound. ^1H (δ, C_6D_6, TMS): 1.35d (12H, $^2J(PH)$ = 13.2 Hz), P–CH_3: 7.02t (2H, $^3J(HH)$ = 7.3 Hz), Pb–C_6H_5 (para); 7.25t (4H, $^3J(HH)$ = 7.3 Hz, $^4J(^{207}PbH)$ = 71.6 Hz), Pb–C_6H_5 (meta); 8.50d (4H, $^3J(HH)$ = 7.3 Hz, $^3J(^{207}PbH)$ = 179.8 Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 58.5.

The compound is relatively unstable and attempts to recrystallize it after ca. 1 month storage led to isolation of the lead(II) derivative, $Pb(S_2PMe_2)_2$, formed as a result of decomposition.

Reaction of Ph_2PbCl_2 with $NaS_2PEt_2 \cdot 2H_2O$. A mixture of Ph_2PbCl_2 (0.62 g, 1.43 mmol) and $NaS_2PEt_2 \cdot 2H_2O$ (0.61 g, 2.88 mmol) in 25 mL of anhydrous benzene was stirred at reflux for 2 hours and then filtered hot. The clear filtrate was evaporated in vacuum, leading to a yellowish oil. Its treatment with hot acetonitrile allowed the isolation of 0.3 g of yellowish crystals of $Pb(S_2PEt_2)_2$ (mp 115–117°C). The total removal of the acetonitrile resulted in an oily product, partially crystallized, whose ^1H NMR spectrum showed a resonance characteristic of triphenyllead diethyldithiophosphinate ($^3J(^{207}PbH)$ of ca. 100 Hz). The target compound, $Ph_2Pb(S_2PEt_2)_2$, could not be isolated [NMR spectra indicate decomposition in less than 5 hours (Table 4)]. However, data obtained with freshly prepared reaction mixtures, directly in an NMR tube, are indicative of the compound's formation: ^1H (δ, C_6D_6, TMS): 0.84dt (12H, $^3J(HH)$ = 7.5 Hz, $^3J(PH)$ = 21.5 Hz), P–CH_2CH_3; 1.42dq (8H, $^3J(HH)$ = 7.5 Hz, $^2J(PH)$ = 10.8 Hz), P–CH_2CH_3; 7.01t (2H, $^3J(HH)$ = 7.3 Hz), Pb–C_6H_5 (para); 7.24t (4H, $^3J(HH)$ = 7.5 Hz, $^4J(^{207}PbH)$ = 70.8 Hz), Pb–C_6H_5 (meta); 8.47d (4H, $^3J(HH)$ = 7.5 Hz, $^3J(^{207}PbH)$ = 178.7 Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 79.1.

$Ph_2Pb(S_2PPh_2)_2$. Ph_2PbCl_2 and $NH_4S_2PPh_2$ (1:2 molar ratio) in benzene were stirred at room temperature for 2 hours, and the reaction mixture was filtered to remove the resulting NH_4Cl and the unreacted starting materials. After concentration in vacuum, the clear filtrate deposited white crystals of $Ph_2Pb(S_2PPh_2)_2$, which were filtered off and recrystallized from methylene chloride or acetonitrile. ^1H (δ, C_6D_6, TMS): 6.94–6.84m (14H), P–C_6H_5 (meta + para) + Pb–C_6H_5 (para); 7.88dm (8H, $^3J(HH)$ = 7.6 Hz), P–C_6H_5 (ortho); 7.02t (4H, $^3J(HH)$ = 7.6 Hz), Pb–C_6H_5 (meta); 8.36d (4H, $^3J(HH)$ = 7.2 Hz, $^3J(^{207}PbH)$ = 177.2 Hz), Pb–C_6H_5 (ortho); $^{31}P\{^1H\}$ (δ, C_6D_6): 61.

If the clear solution obtained after filtration of a refluxed reaction mixture is allowed to evaporate in the open atmosphere, well-formed crystals of the decomposition product $Pb(S_2PPh_2)_2$ can be isolated.

$Pb(S_2PMe_2)_2$. Clear aqueous solutions of $Pb(OCOCH_3)_2 \cdot 3H_2O$ (0.76 g, 2 mmol, in 50 mL H_2O) and $NaS_2PMe_2 \cdot 2H_2O$ (0.74 g, 4 mmol, in 50 mL H_2O) were mixed, resulting in an immediate precipitation of a white solid. The reaction mixture was stirred at room temperature for 15 minutes and then filtered. The solid product was washed several times with distilled water, then with ethanol and diethyl ether, and was dried in vacuum. Recrystallization from isopropyl alcohol produced colorless needles of $Pb(S_2PMe_2)_2$, mp 232–234°C. Yield: 0.70 g (76%). IR (cm^{-1}, KBr): ν_{as} (PS_2) = 574vs, ν_s (PS_2) = 487vs; ^1H (δ, C_6D_6): 1.57d ($^2J(PH)$ = 13.2 Hz); $^{31}P\{^1H\}$ (δ, C_6D_6): 59.4; MS-EI (*m/e*, %): 458 (8), $M^{+\cdot}$; 365 (2), $PbS(S_2PMe_2)^+$; 333 (100), $PbS_2PMe_2^+$; 301 (6), $PbSPMe_2^+$; 240 (4), PbS^+; 208 (15), Pb^+; 125 (2), $Me_2PS_2^+$; 93 (58), Me_2PS^+.

Similarly, we obtained the following.

$Pb(S_2PEt_2)_2$. Colorless crystals (90% yield), mp 116–117°C (from Pr^iOH) (lit. mp 114.5°C [16]); IR (cm^{-1}, KBr): $\nu_{as}(PS_2)$ = 583vs, $\nu_s(PS_2)$ = 480vs; ^1H (δ, C_6D_6): 1.72dq (8H, $^3J(HH)$ = 7.7 Hz, $^2J(PH)$ = 11

Hz), P–CH_2CH$_3$; 1.17dt (12H, ^3J(HH) = 7.4 Hz, ^3J(PH) = 21.3 Hz), P–CH$_2$CH_3; ^{31}P{^{1}H} (δ, C_6D_6): 79.2; MS–EI (*m/e*, %): 514 (7), $M^{+\cdot}$; 393 (1), $PbS(S_2PEt_2)^+$; 361 (100), $PbS_2PEt_2^+$; 329 (2), $PbSPEt_2^+$; 240 (3), PbS^+; 208 (7), Pb^+; 153 (2), $Et_2PS_2^+$; 121 (13), Et_2PS^+.

Pb(S_2PPh_2)$_2$. White-yellowish crystals (98% yield), mp 194–196°C (from benzene); IR (cm^{-1}, KBr): $\nu_{as}(PS_2) = 636s$, $\nu_s(PS_2) = 557vs$; ^{1}H (δ, C_6D_6): 8.13dm (8H, ^3J(PH) = 14.2 Hz), P–C$_6H_5$ (ortho); 7.20m (12H), P–C$_6H_5$ (meta + para); ^{31}P{^{1}H} (δ, C_6D_6): 60.1; MS–EI (*m/e*, %): 706 (1), M^+; 489 (2), $PbS(S_2PPh_2)^+$; 457 (94), $PbS_2PPh_2^+$; 425 (4), PbSPPh$_2$; 249 (2), $Ph_2PS_2^+$; 240 (1), PbS^+; 217 (100), Ph_2PS^+; 208 (10), Pb^+; 185 (22), Ph_2P^+; 140 (79), $PhPS^+$.

RESULTS AND DISCUSSION

Triphenyl- and diphenyllead(IV) diorganophosphinodithioates were prepared by reacting stoichiometric amounts of the corresponding organolead(IV) chloride and the appropriate sodium or ammonium salt of the phosphinodithioic acid, in anhydrous benzene (Equation 1):

$$\begin{aligned} &\mathrm{Ph_nPbCl_{4-n}} + (4-n)\,\mathrm{MS_2PR_2\cdot xH_2O} \\ &\quad\rightarrow \mathrm{Ph_nPb(S_2PR_2)_{4-n}} \\ &\quad + (4-n)\,\mathrm{MCl} + (4-n)\,\mathrm{xH_2O} \qquad [1] \end{aligned}$$

$$\begin{aligned} n = 2 \text{ or } 3\text{: } & R = \mathrm{Me, Et}; \quad M = \mathrm{Na};\ x = 2 \\ & R = \mathrm{Ph}; \quad M = \mathrm{NH_4};\ x = 0 \end{aligned}$$

The compounds were isolated as colorless, crystalline solids, after recrystallization from acetonitrile (Table 1). They are readily soluble in organic solvents, e.g., benzene, chloroform.

The diphenyllead(IV) derivatives, $Ph_2Pb(S_2PR_2)_2$, underwent decomposition when stored for more than 10 days, or during repeated recrystallizations. Thus, for R = Me or Ph, successive attempts to grow crystals suitable for X-ray structure determination resulted in the isolation of inorganic lead(II) derivatives, as established by NMR (for R = Me) spectroscopy and X-ray diffraction (for R = Ph [9]). For R = Et, it was even impossible to obtain a pure sample of $Ph_2Pb(S_2PEt_2)_2$, although the mass spectrum of the fresh solid, separated from the initial reaction mixture, showed an ion fragment, i.e., *m/e* 667, corresponding to the molecular mass of this compound. Moreover, the ^{1}H and ^{31}P NMR spectra recorded for a reaction mixture obtained from Ph_2PbCl_2 and $NaS_2PEt_2 \cdot 2H_2O$, directly in an NMR tube (see subsequent discussion), indicated the presence of a mixture of diphenyllead(IV), triphenyllead(IV), and inorganic lead(II) diethylphosphinodithioates. All attempts to separate the components of this mixture led only to pure samples of solid triphenyllead(IV) and lead(II) derivatives.

Two pathways for the decomposition process of $Ph_2Pb(S_2PR_2)_2$ derivatives, described by the following equations, might be considered:

$$\begin{array}{c} 2\,\mathrm{Ph_2Pb(S_2PR_2)_2} \rightarrow \mathrm{Ph_3PbS_2PR_2} + \\ \mathrm{[PhPb(S_2PR_2)_3]} \\ \text{(unstable)} \\ \downarrow \\ \mathrm{Pb(S_2PR_2)_2} + \mathrm{R_2P(S)SPh} \end{array} \qquad [2]$$

or

$$\begin{array}{c} 3\,\mathrm{Ph_2Pb(S_2PR_2)_2} \rightarrow 2\,\mathrm{Ph_3PbS_2PR_2} + \\ \mathrm{[Pb(S_2PR_2)_4]} \\ \text{(unstable)} \\ \downarrow \\ \mathrm{Pb(S_2PR_2)_2} + \mathrm{[R_2P(S)S]_2} \end{array} \qquad [3]$$

The NMR investigation of the process (discussed subsequently) supports the first alternative (Equation 2), which is similar to the previously reported behavior of Me_2PbX_2 [17]:

$$\begin{array}{lll} \mathrm{Me_2PbX_2} \longrightarrow \mathrm{Me_3PbX} + & \mathrm{[MePbX_3]} & \\ & \text{(unstable)} & [4] \\ & \downarrow & \\ & \mathrm{PbX_2 + MeX} & \end{array}$$

The second alternative (Equation 3), which is the common route of decomposition of other metal phosphinodithioates, e.g., $Tl(S_2PR_2)_3$ to TlS_2PR_2 and $[R_2P(S)S]_2$ [18], is ruled out since the ^{31}P NMR spectra of reaction mixtures do not contain any resonance with a chemical shift corresponding to the bis(diorganothiophosphinyl)disulfanes.

To confirm the assignments of the ^{1}H and ^{31}P chemical shifts, inorganic lead(II) diorganophosphinodithioates were prepared directly from $Pb(OCOCH_3)_2 \cdot 3H_2O$ and the appropriate salt of the dithioacid (Equation 5):

$$\begin{aligned} &\mathrm{Pb(OCOCH_3)_2\cdot 3H_2O} + 2\,\mathrm{MS_2PR_2\cdot xH_2O} \\ &\quad\rightarrow \mathrm{Pb(S_2PR_2)_2} + 2\,\mathrm{MOCOCH_3} \\ &\quad + (2x+3)\,\mathrm{H_2O} \qquad [5] \end{aligned}$$

The corresponding phenyl esters of the diorganophosphinodithioic acids, $R_2P(S)SPh$, were prepared for comparison by reacting $R_2P(S)Cl$ with NaSPh (as described in the literature [15]), and their ^{31}P NMR spectra were recorded to assist in the assignment of resonances observed in the experiments done directly in NMR tubes.

Details on the synthesis of phenyllead(IV) phosphinodithioates are given in the Experimental section and in Table 1, which also contains the yields, the melting points, and relevant infrared data. The compounds synthesized during this work were characterized by infrared, ^{1}H and ^{31}P NMR, and mass spectroscopy.

TABLE 3 Comparative Selected ^1H NMR Data for $Ph_2Pb(S_2PR_2)_2$ (at Different Time Intervals after Mixing the Starting Materials Directly in an NMR Tube) and for $Ph_3PbS_2PR_2$, $Pb(S_2PR_2)_2$, and $R_2P(S)SPh$

Compound	*Time (Hours)*	*^1H Chemical Shifts (in ppm)*^{a,b}						
$Ph_2Pb(S_2PMe_2)_2$	0.5	8.50d (179.8)	—	—	—	—	1.35d (13.2)	
	192	no changes						
	192^{c}	8.53d^{d} (180.4)	7.90d (104.7)	7.50d^{e}	1.54d^{e} (13.4)	1.40d (12.6)	1.37d (12.9)	
	390^{c}	8.53d^{f} (180.5)	7.90d (104.7)	7.50d	1.54d (13.2)	1.42d (13.2)	1.40d (12.9)	
	416^{g}	—	7.90d (104.7)		1.55d (13.5)	1.38d (12.9)		
Compare with:								
$Ph_3PbS_2PMe_2$		—	7.89d (105.4)	— —	1.61d (12.9)	— —	— —	
$Pb(S_2PMe_2)_2$		—	—	—	1.57d (13.2)	—	—	
$Me_2P(S)SPh$		—	—	7.40d	—	1.42d (13.2)	—	
$Ph_2Pb(S_2PEt_2)_2$	0.5	8.47d (178.7)	—	—	—	—	—	0.84dt (21.5)
	5	8.46d (178.7)	7.92d^{e}	7.60d^{e}		1.2–0.8^{h}		
	22	8.50d (179.0)	7.92d (105.3)	7.58d		1.2–0.8^{h}		
	195	—	7.90d (104.2)	7.54d	1.18dt (21.3)	1.033dt (21.0)	1.03dt (21.0)	—
Compare with:								
$Ph_3PbS_2PEt_2$		—	7.90d (105.0)	—	—	—	1.03dt (21.1)	—
$Pb(S_2PEt_2)_2$		—	—	—	1.17dt (21.3)	—	—	—
$Et_2P(S)SPh$		—	—	7.50d	—	1.05dt (21.3)	—	—
$Ph_2Pb(S_2PPh_2)_2$	0.5	8.36d (177.2)	—	7.88dm (14.5)	—			
	24	8.36d (177.2)	8.04dm^{e}	7.88dm (14.8)	7.50d^{e}			
	192^{c}	8.35d^{e}	8.1–8.0^{h}	7.70d	7.50d			
	200^{c}	—	8.1–8.0^{h}	7.70d	7.50d			
Compare with:								
$Ph_3PbS_2PPh_2$		—	8.09dm (14.4)	7.76d (105.4)	— —			
$Pb(S_2PPh_2)_2$		—	8.13dm (14.2)	—	—			
$Ph_2P(S)SPh$		—	8.03dm (14.3)	—	7.42d			

[a] Only the representative chemical shifts are given, i.e., is, for the doublet resonances of ortho protons of phenyl groups bound to lead, sulfur (in esters), and phosphorus (for Ph_2PS_2 derivatives), and, respectively, the resonances for the methyl protons (for Me_2PS_2 and Et_2PS_2 derivatives).

[b] The 207-lead-proton and 31-phosphorus-proton coupling constants are listed in parentheses.

[c] After 1 additional hour of heating at 70°C.

[d] The intensity ratio between the *ortho* proton resonances of Ph_2Pb and Ph_3Pb derivatives was 3.3:1.

[e] Low intensity resonance.

[f] Intensity ratio 1.6:1 (see footnote *d*).

[g] After an additional 4 hours of heating at 70°C.

[h] Complex signal.

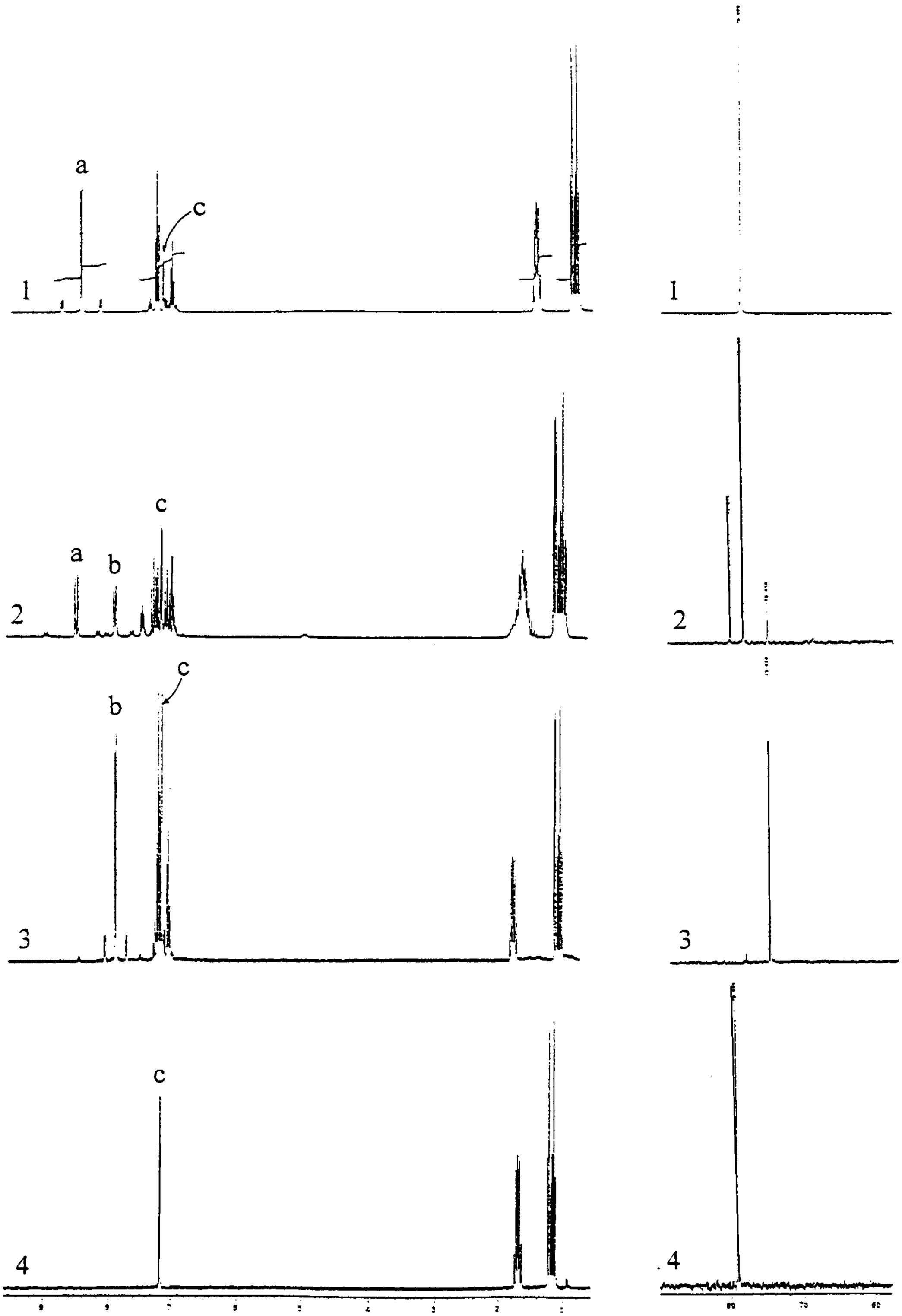


FIGURE 1 (A) ^1H and (B) $^{31}P\{^1H\}$ NMR spectra of $Ph_2Pb(S_2PEt_2)_2$. NMR tube reaction: (1) at initial stage and (2) after 120 hours [(a) *ortho* protons of Ph_2Pb derivative, (b) *ortho* protons of Ph_3Pb derivatives, and (c) benzene], compared with those of (3) $Ph_3PbS_2PEt_2$ and (4) $Pb(S_2PEt_2)_2$.

TABLE 4 Comparative $^{31}P\{^1H\}$ NMR Data for $Ph_2Pb(S_2PR_2)_2$ (at Different Time Intervals after Mixing the Starting Materials Directly in an NMR Tube) and for $Ph_3PbS_2PR_2$, $Pb(S_2PR_2)_2$, $R_2P(S)SPh$, and $[R_2P(S)S]_2$

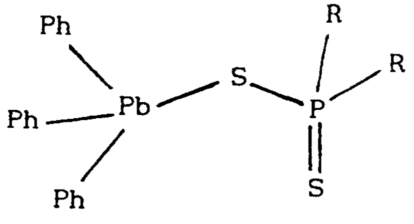
Compound	*Time (Hours)*	*$^{31}P\{^1H\}$ chemical shifts (in ppm)*				
$Ph_2Pb(S_2PMe_2)_2$	0.5	—	—	58.5	—	—
	192	no changes				
	192[a]	—	—	58.5	58.1[b]	—
	390[a]	—	59.2[b]	58.5	58.0	53.8
	416[c]	—	59.2	—	57.9	53.2
Compare with:						
$Ph_3PbS_2PMe_2$		—	—	—	—	53.8
$Pb(S_2PMe_2)_2$		—	59.4	—	—	—
$Me_2P(S)SPh$		—	—	—	58.1	—
$[Me_2P(S)S]_2$		65.2[d]	—	—	—	—
$Ph_2Pb(S_2PEt_2)_2$	0.5	—	—	79.1	—	
	5	—	81.1[b]	79.1	75.9[b]	
	22	—	81.1	79.1	75.8	
	195	—	81.1	79.1	75.8	
Compare with:						
$Ph_3PbS_2PEt_2$		—	—	—	75.8	
$Pb(S_2PEt_2)_2$		—	—	79.2	—	
$Et_2P(S)SPh$		—	81.8	—	—	
$[Et_2P(S)S]_2$		88.7[d]	—	—	—	
$Ph_2Pb(S_2PPh_2)_2$	0.5	—	—	61.0		
	24	—	65.1[b]	61.0		
	192[a]	—	65.1	59.8		
	200[a]	—	65.1	59.6		
Compare with:						
$Ph_3PbS_2PPh_2$		—	—	59.4		
$Pb(S_2PPh_2)_2$		—	—	60.1		
$Ph_2P(S)SPh$		—	65.4	—		
$[Ph_2P(S)S]_2$		69.7[d]	—	—		

[a] After 1 additional hour of heating at 70°C.
[b] Low intensity resonance.
[c] After 4 hours of heating at 70°C.
[d] Note the absence of signals due to disulfanes in the decomposition products.

Infrared Spectra

In addition to the expected strong absorptions due to the phenyl groups bonded to lead, the spectra of $Ph_nPb(S_2PR_2)_{4-n}$ exhibited strong bands in the 650–450 cm^{-1} region, which were assigned to PS_2 stretching vibrations (Table 1). Only for $Ph_2Pb(S_2PPh_2)_2$, these bands are split into two components, a pattern which is also common for other metal diphenylphosphinodithioates [19,20].

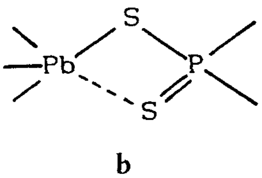
In the case of triphenyllead derivatives, $Ph_3PbS_2PR_2$, the difference $\Delta\nu = \nu_{as}(PS_2) - \nu_s(PS_2)$ is larger than 100 cm^{-1}, thus suggesting a monodentate coordination pattern of the dithiophosphinato ligand [21] (structure **a**). A similar structure was established by X-ray diffraction for a triphenyllead(IV) dithiophosphate, $Ph_3PbS_2P(OEt)_2$ [11].

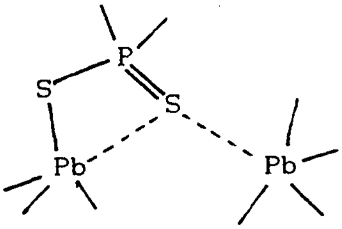


a

For $Ph_2Pb(S_2PMe_2)_2$, a $\Delta\nu$ value of ca. 100 cm^{-1} was measured, which is considered indicative of monodentate coordination of the phosphinodithioato ligand [21]. The magnitude of the $\Delta\nu$ value (ca. 80 cm^{-1}) observed for $Ph_2Pb(S_2PPh_2)_2$ is consistent with anisobidentate coordination of phosphinodithioato groups.

Weak metal-sulfur contacts are well documented by several previous structural data reports concerning metal dithiophosphorus derivatives. For example, in the case of the related $Me_2Sn(S_2PR_2)_2$ (R = Me [22], Et [23]), the $\Delta\nu$ values (larger than 110 cm^{-1}) would suggest monodentate coordination of the dithioligand, but the single-crystal X-ray diffraction (R = Me [24], Et [23]) established the presence of additional weak, intramolecular secondary interactions between the tin and the second sulfur, doubly bonded to phosphorus, leading to chelate formation. Moreover, it was shown by X-ray diffraction that, in a diphenyllead(IV) phosphorodithioate, $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$ [11], the sulfur atoms exhibit not only intramolecular, but also intermolecular secondary Pb . . . S interactions, leading to dimeric associations. Similar coordination patterns, **b** or **c**, might also be expected for the analogous diphenyllead(IV) phosphinodithioates.


b


c

Mass Spectra

The fragments observed in the DCI(−) mass spectra of $Ph_3PbS_2PR_2$ (R = Me, Et, Ph) and $Ph_2Pb(S_2PR_2)_2$ (R = Me, Ph) are listed in Table 2. The molecular ion $[M\text{-}H]^+$, when observed ($Ph_3PS_2PR_2$, R = Et and Ph, and $Ph_2Pb(S_2PMe_2)_2$), is of low intensity.

For triphenyllead(IV), two ions of the first fragmentation are observed, i.e., $Ph_2PbS_2PR_2^+$ (resulting from the splitting off of a phenyl group) and Ph_3Pb^+ (resulting from cleavage of the lead–sulfur bond). The Ph_3Pb^+ is the base peak for R = Et and Ph, whereas for R = Me, the base peak is $Me_2PS_2^+$. Similar $R_2PS_2^+$ ions of rather high intensity are also observed for the other two compounds. A Ph_3PbS^+ fragment of low intensity is present in the mass spectra of all three triphenyllead(IV) derivatives, indicating that cleavage of the sulfur–phosphorus bond can also occur.

For diphenyllead(IV) derivatives, various lead-containing fragments are observed, but generally they are of medium or low intensity. In both cases, the base peak is a lead-free ion, *i.e.*, $Me_2PS_2^+$ for R = Me and PhS^+ for R = Ph. Fragments containing two phosphinodithioato groups, e.g., $PhPb(S_2PR_2)_2$ or $Pb(S_2PR_2)_2$, are also present.

NMR Spectra

^1H and ^{31}P NMR spectra of phenyllead(IV) phosphinodithioates exhibit the expected resonances for organic groups attached to lead and phosphorus. The observed chemical shifts and coupling constants are listed in the Experimental section.

The proton resonances for methyl and ethyl groups bound to phosphorus are always split into two components of the same intensity as a result of the phosphorus-proton couplings. The patterns of these signals indicate the equivalence of the organic groups bound to phosphorus.

In the range of δ = 7–8.6, all the organolead(IV) compounds exhibit a resonance for the ortho protons of the phenyl groups bound to lead, which is split into two components of the same intensity (due to the proton-proton coupling) and surrounded by 207-lead-proton satellites. The magnitude of the ^{207}Pb-H coupling constants for diphenyllead(IV) derivatives (ca. 180 Hz) is much larger than for triphenyllead(IV) compounds (ca. 105 Hz) and, therefore, can serve as diagnostic in the identification of the resulting reaction products [25].

The proton-decoupled ^{31}P resonances appear as singlets both for triphenyl- and diphenyllead(IV) derivatives. This is consistent with the presence of equivalent phosphorus atoms in the diorganolead compounds and suggests that intra- and/or intermolecular sulfur–lead interactions, if present in the solid state, are broken in solution. As a result, the phosphinodithioato ligands behave as true monodentate units, which are allowed to rotate freely around the primary lead–sulfur bond.

All diphenyllead(IV) diorganophosphinodithioates, $Ph_2Pb(S_2PR_2)_2$, decompose on standing at room temperature or on heating, thus complicating the NMR spectra. The results of the NMR monitoring of this decomposition are summarized in Tables 3 and 4. The assignment of ^1H and $^{31}P\{^1H\}$ NMR resonances, observed in the spectra of the diphenyllead(IV) compounds as a result of the decomposition, was assisted by a comparison with the spectra of inorganic lead(II) derivatives, $Pb(S_2PR_2)_2$, and those of phosphinodithioic acid phenyl esters, $R_2P(S)SPh$.

For R = Me and Ph, the compounds are reasonably stable at room temperature. Experiments carried out directly in an NMR tube show that significant changes of the spectra of diphenyllead(IV) derivatives appear at room temperature ca. 8 days after reaction of stoichiometric amounts of Ph_2PbCl_2 and MS_2PR_2 in C_6D_6 (Tables 3 and 4). However, when the reaction mixtures are heated even for a short time (e.g. ca. 1 hour), the ^1H NMR spectra become more complicated. After prolonged heating, the resonance of the aromatic ortho protons of diphenyllead(IV) derivatives disappears completely, and only two other doublet resonances are observed: one (surrounded by satellites, $^3J(^{207}PbH)$ ca. 100 Hz) corresponding to the ortho protons of the triphenyllead(IV) derivative and the other due to the ortho protons of the S-phenyl group in the ester $R_2P(S)SPh$, both compounds being formed in the decomposition process. For R = Me, this process is accompanied by modifications in the high field region (characteristic of alkyl protons); i.e., four doublet resonances could be observed in an intermediate phase of the decomposition and only three at the end of the process. For R = Ph, the proton NMR spectra are much more complicated because of the overlap of resonances due to the phenyl groups bonded to lead and phosphorus.

The decomposition of the ethyl derivative, $Ph_2Pb(S_2PEt_2)_2$, is much more rapid, and significant changes in the ^1H and ^{31}P NMR spectra are noticed at room temperature even after 5 hours following the mixing of the reagents in the NMR tube (Tables 3 and 4, and Figure 1). After 22 hours, doublet resonances surrounded by satellites, at $\delta = 8.50$ ($^3J(^{207}PbH) = 179$ Hz) and 7.92 ($^3J(^{207}PbH) = 105.3$ Hz), were observed, thus indicating the existence of both di- and triphenyllead(IV) phosphinodithioates in the reaction mixture. Simultaneously, the alkyl region became more and more complicated.

After 195 hours, the doublet at $\delta = 8.50$ disappeared and only the new doublets at 7.9 and 7.54 (belonging to the $Et_2P(S)SPh$ ester) were observed. The alkyl region now became much clearer and contained three new doublets of triplets.

The decomposition process was also followed using $^{31}P\{^1H\}$ NMR spectroscopy. All the freshly prepared reaction mixtures of $Ph_2Pb(S_2PR_2)_2$ contained only one resonance, as expected for the presence of only one phosphorus-containing compound. In time or after heating, in parallel with the complication of the ^1H NMR spectra, the number of phosphorus resonances increased (Table 4) due to the appearance of the decomposition products in the reaction mixture. The presence of less than four resonances at the intermediate phase is the result of almost identical chemical shifts assigned to $Ph_2Pb(S_2PEt_2)_2$ and $Pb(S_2PEt_2)_2$ and $Ph_2Pb(S_2PPh_2)_2$, $Ph_3PbS_2PPh_2$, and $Pb(S_2PPh_2)_2$, respectively.

Additional proof for the redistribution/decomposition process of $Ph_2Pb(S_2PR_2)_2$, described by Equation (2), is provided by the isolation from their reaction mixtures of pure samples of $Pb(S_2PR_2)_2$ (R = Me, Et, Ph), which exhibit the same melting points and infrared and NMR spectra as the compounds obtained directly by reacting lead(II) acetate with the appropriate phosphinodithioate.

SUMMARY

New triphenyl- and diphenyllead(IV) diorganophosphinodithioates, $Ph_3PbS_2PR_2$ and $Ph_2Pb(S_2PR_2)_2$ (R = Me, Et, Ph), were obtained from organolead(IV) chlorides and sodium or ammonium phosphinodithioates and were characterized by infrared, mass, and NMR spectroscopy. A redistribution/decomposition reaction pathway involving the formation of $Ph_3PbS_2PR_2$, $Pb(S_2PR_2)_2$, and $R_2P(S)SPh$, was established for the observed degradation of the diphenyllead(IV) diorganophosphinodithioates. This process was monitored by ^1H and ^{31}P NMR spectroscopy and was proved by isolation of $Pb(S_2PR_2)_2$ from the decomposed reaction mixture.

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