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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF NEW ORGANOLEAD(IV) COMPLEXES CONTAINING ORGANOPHOSPHORUS LIGANDS

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ABSTRACT

Organolead(IV) derivatives of organophosphorus ligands, $R_nPb[(OPPh_2)(SPPh_2)N]_{4-n}$ (R = Ph; n = 2, 3) and $Me_3Pb[S_2PR_2]$ (X = S, O; R = Me, Et, Ph), were prepared by reacting the corresponding organolead(IV) chloride with the sodium, potassium or ammonium salt of the appropriate organophosphoric acid. The title compounds were investigated by IR and multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy, and possible structures are proposed. All dithiophosphinato complexes exhibited low stability and underwent decomposition on standing. The decomposition process was monitored by using ^1H and ^{31}P NMR spectroscopy, and a decomposition pathway is proposed.

INTRODUCTION

P,P,P',P'-Tetraorganodicalcogenoimidodiphosphinato[1,2] and diorganodithiophosphinato ligands[3,4] exhibit a broad variety of coordination patterns, and only few studies on the synthesis and characterization of organolead(IV) dithiophosphates and -phosphinates were reported so far[7-11], and the structures of $Ph_2Pb[S_2P(OCH_2Ph)_2]_2$, $Ph_3Pb[S_2P(OEt)_2]$[8], $Ph_2Pb[S_2PPh_2]_2$[10] and $^1_\infty[Ph_3Pb\{S_2PMe_2\}]$[11] have been described. The redistribution-decomposition process of bis(diorganodithiophosphinato)diphenyllead(IV), resulting in $Ph_3Pb[S_2PR_2]$, $Pb[S_2PR_2]_2$ and $R_2P(S)SPh$, was monitored using ^1H and ^{31}P NMR.[9] However, only three inorganic lead(II) derivatives with *P,P,P',P'*-tetraphenyldicalcogenoimidodiphosphinato ligands have been described, *i.e.* $Pb[(SPPh_2)_2N]_2$[12], $Pb[(OPPh_2)(SPPh_2)N]_2$[13] and $Pb[(SePPh_2)_2N]_2$[14], but no organolead(IV) complexes have been reported.

We report here on the decomposition process of trimethyllead(IV) diorganodithio-phosphinates monitored by NMR spectroscopy, as well as on the synthesis and spectroscopic properties of the first phenyllead(IV) compounds with the *P,P,P',P'*-tetraphenylthioimidodiphosphinato ligand, $Ph_nPb[(OPPh_2)(SPPh_2)N]_{4-n}$ (n = 2, 3).

RESULTS AND DISCUSSION

We have reported previously on the synthesis of $Ph_3Pb[S_2PR_2]$ (R = Me, Et, Ph) compounds, isolated as stable solids. On the other hand a redistribution-decomposition process of the diorganolead(IV) analogs, $Ph_2Pb[S_2PR_2]_2$, was also discussed.[9] By contrast to the triphenyllead(IV) dithiophosphinates, the trimethyllead(IV) analogs are not stable. From the reaction mixtures obtained in $CHCl_3$ according to equation (*1*) white solid products were isolated, which darkened gradually on standing.

$$Me_3PbCl + M[S_2PR_2].nH_2O \xrightarrow[\substack{-\,MCl \\ -\,nH_2O}]{} Me_3Pb[S_2PR_2] \qquad (1)$$

M = Na   n = 2   R = Me
M = Na   n = 2   R = Et
M = NH_4 n = 0   R = Ph

Attempts to recrystallize the freshly isolated products always led to decomposition and a black solid deposited. For R = Et, X = S, a white, crystalline compound was obtained and identified to be the lead(II) derivative $Pb[S_2PEt_2]_2$, both by NMR (same ^1H, ^{13}C, ^{31}P NMR parameters as reported in ref. 9) studies and a single crystal X-ray diffraction (the crystal and molecular structure of this compound was previously reported[15]). In order to elucidate the decomposition pathway of $Me_3Pb[S_2PR_2]$ compounds, an NMR study of the reaction mixtures prepared in $CHCl_3$ directly in NMR tubes was performed.

Phenyllead(IV) derivatives were prepared by reacting stoichiometric amounts of the corresponding organolead(IV) chloride and potassium *P,P,P',P'*-tetraphenylthioimidodiphosphinate, in anhydrous benzene [equation (*2*)]:

$$Ph_nPbCl_{4-n} + (4\text{-}n)\ K[(OPPh_2)(SPPh_2)N] \longrightarrow$$
$$\longrightarrow Ph_nPb[(OPPh_2)(SPPh_2)N]_{4-n} + (4\text{-}n)\ KCl \qquad (2)$$
$$n = 2, 3$$

In this case, both the diphenyl- and triphenyllead(IV) compounds were isolated as white, crystalline solids. They are readily soluble in organic solvents, *e.g.* benzene, chloroform, dichloromethane, and were characterized by IR and multinuclear NMR spectroscopy.

NMR Studies

The NMR spectra of the reaction mixtures freshly prepared from stoichiometric amounts of Me_3PbCl and $M[S_2PR_2].nH_2O$ are consistent with the formation of the trimethyllead(IV) derivatives of the dithiophosphinato ligands as major products (see Experimental section). Thus, in all cases both the ^1H and ^{13}C NMR spectra contain a singlet for the methyl groups attached to the metal centre, surrounded by lead satellites. The magnitudes of the $^2J(^{207}PbH)$ and $^1J(^{207}PbC)$ coupling constants (ca. 64-75 Hz, and 253-263 Hz, respectively) are consistent with the presence of a Me_3Pb moiety. The resonance signals for the organic groups attached to phosphorus exhibit the expected multiplicity pattern due to the proton-proton and proton-phosphorus couplings. It should be noted that the sodium or ammonium salts of the organophosphinic acids used as starting materials are not soluble in $CDCl_3$.

In addition to the resonance signals expected for $Me_3Pb[S_2PR_2]$, in all cases the ^1H spectra of the freshly prepared reaction mixtures contain a second singlet of very low intensity, also surrounded by lead satellites [$^2J(^{207}PbH)$ 62 Hz], which was assigned to Me_4Pb formed as result of the decomposition process. In addition to the $Me_3Pb[S_2PR_2]$ compound the ^{31}P NMR spectra also indicate the presence of a minor phosphorus-containing product.

To investigate the decomposition pathway of $Me_3Pb[S_2PR_2]$ a reaction mixture was prepared directly from Me_3PbCl and $Na[S_2PEt_2].2H_2O$ in an NMR tube and the ^1H and ^{31}P NMR spectra were recorded immediately after preparation and after 8 days. The results are summarized in Table I and Figures 1 and 2. For the fresh mixture the spectra (Table I) indicate the presence of $Me_3Pb[S_2PEt_2]$ as the major product only slightly impurified by Me_4Pb [Fig. 1(1)] and $Et_2P(S)SMe$ [Fig. 2(1)]; an intensity ratio of 14:1 for the singlets of the methyl groups bound to the lead atoms in these two compounds has been determined [Fig. 1(1)]. After 8 days significant changes were noted. Thus, the ^1H NMR spectrum in $CDCl_3$ [Fig. 1(2)] showed a considerable decomposition of $Me_3Pb[S_2PEt_2]$: the intensity of the resonance signal of the Me_3Pb protons (δ 1.57 ppm) decreased significantly, while that corresponding to Me_4Pb (δ 0.7 ppm) increased to an intensity ratio 1:2.3. Moreover, a doublet at 2.31 ppm, due to the S-methyl protons in $Et_2P(S)SMe$, is observed. The resonance signals of the CH_2 and CH_3 protons of the ethyl groups also became more complicated, consistent with overlapping signals due to ethyl groups of different compounds.

Taking into account the ^1H NMR data and the isolation of $Pb[S_2PEt_2]_2$ from the corresponding reaction mixture, the following decomposition/redistribution

Table I. NMR data [δ (ppm), J (Hz)] of the ($Me_3PbCl + Na[S_2PEt_2].2H_2O$) reaction mixture.

	^{1}H NMR			^{31}P NMR	
	$Me_3Pb[S_2PEt_2]$	Me_4Pb	$Et_2P(S)SMe$	$Me_3Pb[S_2PEt_2]$	$Et_2P(S)SMe$
	$PbCH_3$; $^2J(PbH)$	$PbCH_3$; $^2J(PbH)$	$PSCH_3$; $^3J(PH)$		
Freshly prepared	1.54 s; 64.9	0.70 s; 61.8	-	78.1	82.2
After 8 days	1.57 s; 66.5	0.71 s; 61.6	2.31 d; 13.2	79.7[a]	82.2

[a] ^{31}P resonance of $Pb[S_2PEt_2]_2$ is at 79.6 ppm.

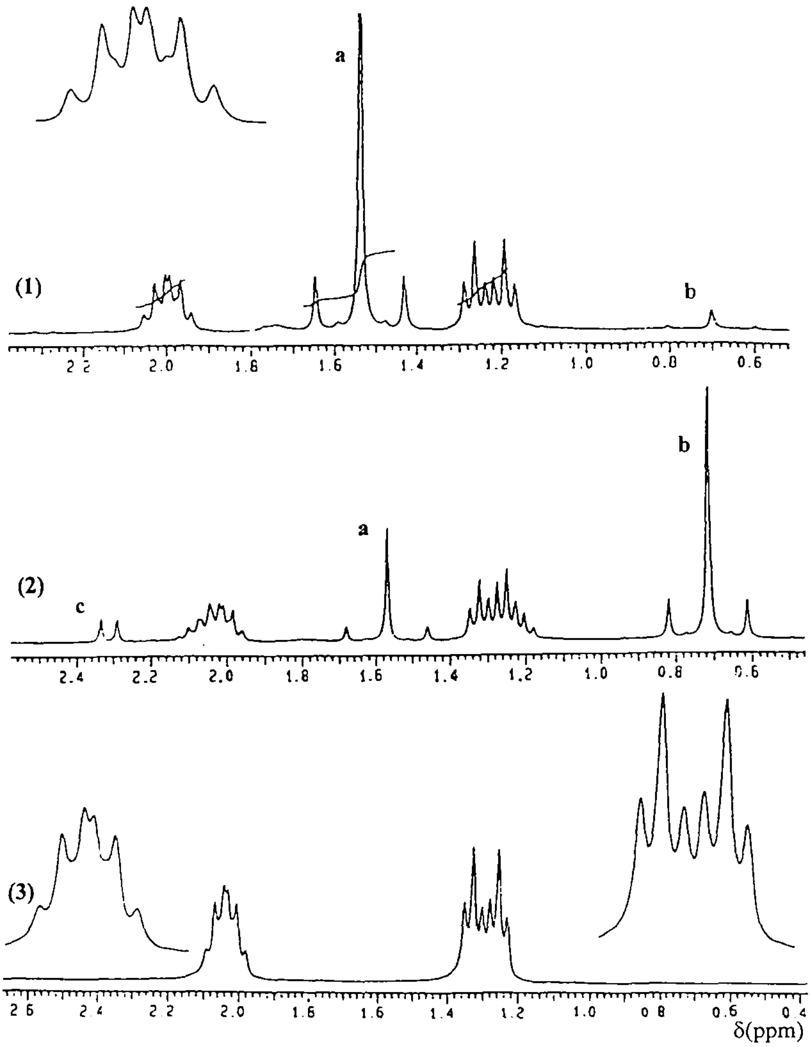

Fig. 1. ^1H NMR spectra of the (Me_3PbCl + $Na[S_2PEt_2].2H_2O$) system - NMR tube reaction: (1) freshly prepared reaction mixture; (2) after 8 days [Me-Pb protons of (**a**) $Me_3Pb[S_2PEt_2]$ and (**b**) Me_4Pb, and (**c**) S-Me protons of $Et_2P(S)SMe$]; (3) spectrum of $Pb[S_2PEt_2]_2$ for comparison.

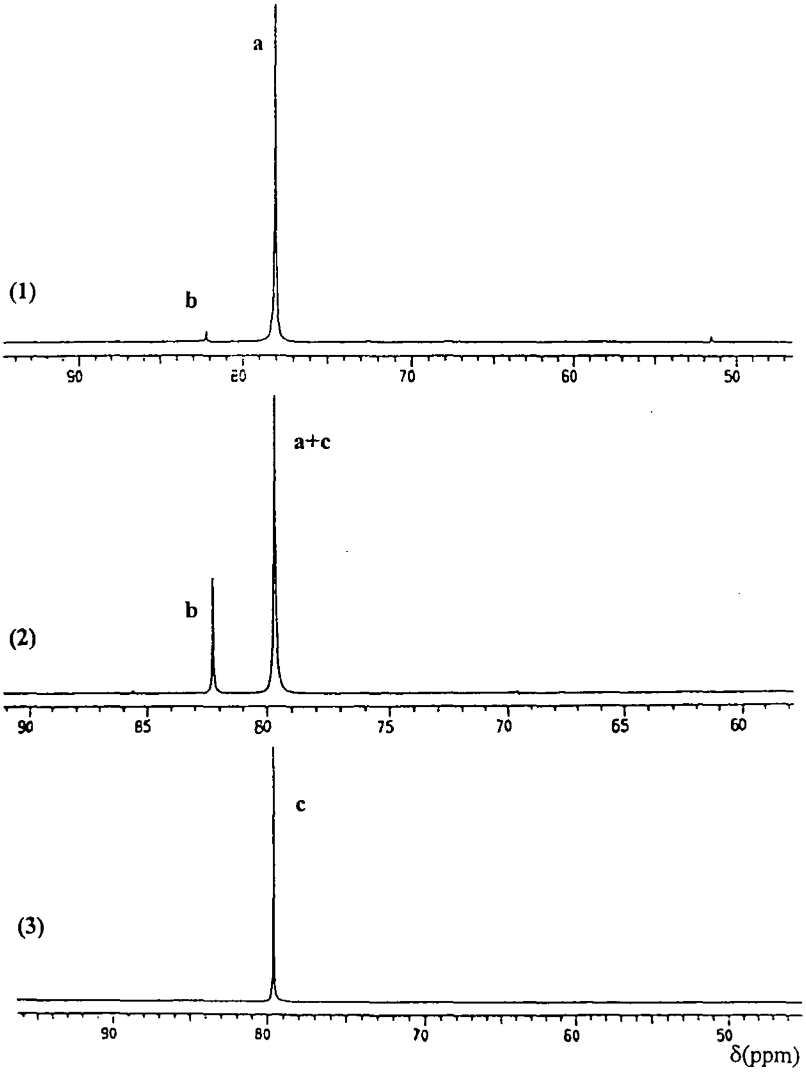

Fig. 2. ^{31}P NMR spectra of the (Me_3PbCl + $Na[S_2PEt_2].2H_2O$) system - NMR tube reaction: (1) freshly prepared reaction mixture; (2) after 8 days [(**a**) $Me_3Pb[S_2PEt_2]$, (**b**) $Et_2P(S)SMe$, and (**c**) $Pb[S_2PEt_2]_2$]; (3) spectrum of $Pb[S_2PEt_2]_2$, for comparison.

pathway has been proposed [equation (*3*)]:

$$3\ Me_3Pb[S_2PEt_2] \longrightarrow 2\ Me_4Pb + Pb[S_2PEt_2]_2 + Et_2P(S)SMe \qquad (3)$$

This pathway is also supported by the ^{31}P NMR spectra of the same reaction mixture (Table I, Fig. 2). Whereas for the freshly prepared reaction mixture two signals can be observed, *i.e.* a very intense one at 78.1 ppm, assigned to $Me_3Pb[S_2PEt_2]$, and one of very low intensity at 82.2 ppm, assigned to $Et_2P(S)SMe$ [Fig. 2(1)], in the spectrum recorded after eight days the intensity of the resonance signal of the S-Me ester has considerably increased. The presence of only two resonance signals [Fig. 2(2)] instead of three as expected for a mixture of $Et_2P(S)SMe$, $Me_3Pb[S_2PEt_2]$ and $Pb[S_2PEt_2]_2$ is due either to the almost identical ^{31}P chemical shifts for the lead-containing compounds (the singlet at 79.7 ppm being the result of the overlap of the corresponding two ^{31}P resonances) or to a fast exchange of the S_2PEt_2 ligands between both lead compounds.

A similar behavior was observed for the (Me_3PbCl + $Na[S_2PMe_2].2H_2O$) and (Me_3PbCl + $NH_4[S_2PPh_2]$) reaction mixtures. In all the cases, the freshly prepared reaction mixture in $CDCl_3$ indicates the presence of $Me_3Pb[S_2PR_2]$ as the main product. However, in addition to the expected ^{31}P signals which are the result of the decomposition process, other resonances of low intensity were also observed, thus suggesting a higher complexity of the decomposition process of both compounds.

In contrast to the $Ph_2Pb[S_2PR_2]_2$ compounds which were proven to undergo decomposition on standing or on heating[9], the corresponding $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$, as well as $Ph_3Pb[(OPPh_2)(SPPh_2)N]$, were isolated as pure, stable solids from benzene. Although the aromatic regions of the ^1H NMR spectra are quite complicated due to presence of different phenyl groups attached to lead and phosphorus, respectively, in both cases the resonances of the equivalent C_6H_5-Pb *ortho*-protons could be identified. The magnitude of the

$^{3}J(^{207}PbH)$ coupling constants (ca. 187 and 113 Hz, respectively) are consistent with the presence of Ph_2Pb and Ph_3Pb moieties. The ^{13}C NMR spectrum of the triphenyllead(IV) derivative in $CDCl_3$ exhibits well resolved doublets for the carbons of the phenyl groups attached to phosphorus, in addition to the singlets surrounded by lead satellites. For both compounds the ^{31}P NMR spectra show two broad resonances as expected for the presence of two different phosphorus atoms in the molecular unit; but a phosphorus-phosphorus coupling was not observed.

Taking into account the previous results reported for related di- and triorganotin(IV) derivatives[16,17], of the two possible isomers for an octahedral structure with a linear Ph_2Pb moiety, *i.e.* (S *trans* S, O *trans* O) and (S *trans* O), the first one (Fig. 3) is proposed for $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$, while in the case of $Ph_3Pb[(OPPh_2)(SPPh_2)N]$ a fluxional behavior in solution might be considered (Fig. 4).

Infrared Spectra

The strong infrared absorptions observed for both phenyllead(IV) complexes in the regions 1240-1230, 1120-1040 and 570 cm^{-1} were assigned to $\nu_{as}(P_2N)$, $\nu(PO)$, and $\nu(PS)$ stretching vibrations, respectively, by comparison with the spectra of the free acid and its potassium salt, thus suggesting bidentate coordination of the deprotonated ligand through both oxygen and sulfur to the metal center.

EXPERIMENTAL

Chemicals

Trimethyllead(IV) chloride and diphenyllead(IV) dichloride were commercially available. The organophosphorus ligands were prepared according

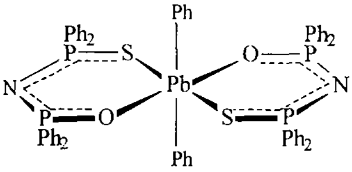

Fig. 3. Proposed Molecular Structure for $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$.

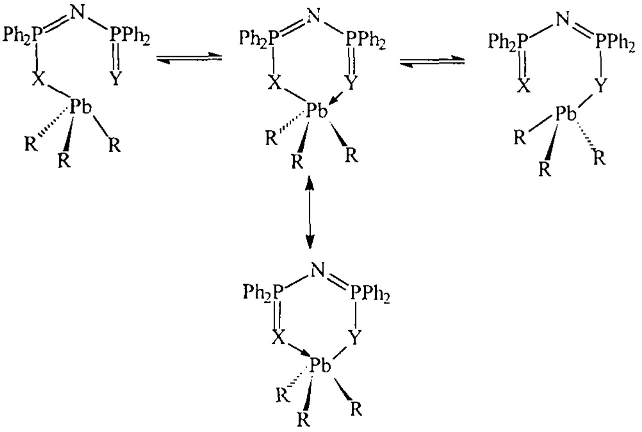

Fig. 4. Fluxional Behavior of $Ph_3Pb[(OPPh_2)(SPPh_2)N]$.

to literature methods: $Na[S_2PMe_2].2H_2O$[18], $Na[S_2PEt_2].2H_2O$[19], $NH_4[S_2PPh_2]$[9], $K[(OPPh_2)(SPPh_2)N]$[16].

Instruments

Infrared spectra were recorded in the range 4000-400 cm^{-1} as KBr pellets on a SPECORD 75 IR Zeiss-Jena (Germany) instrument. ^1H, ^{13}C and ^{31}P NMR spectra were recorded as $CDCl_3$ solutions on a VARIAN GEMINI 300 instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. The chemical shifts (δ) are reported in parts per million (ppm) relative to TMS and 85% H_3PO_4, respectively.

Reaction of Me_3PbCl with $M[S_2PR_2].nH_2O$

A mixture of Me_3PbCl (0.7195 g, 0.0025 moles) and $Na[S_2PEt_2].2H_2O$ (0.5306 g, 0.0025 moles) in 40 mL $CHCl_3$ was stirred at room temperature for 3 hours and then filtered. The clear filtrate was evaporated *in vacuo* leading to a white solid. The target compound, $Me_3Pb[S_2PEt_2]$, could not be isolated, but recrystallization from a $CHCl_3$/n-hexane mixture (1:5) resulted in a crystalline solid identified by NMR spectroscopy as $Pb[S_2PEt_2]_2$: ^1H NMR: 1.29 dt [3H, P-CH_2-CH_3, $^3J(HH)$ 7.4 Hz, $^3J(PH)$ 21.7 Hz]; 2.04 dq [2H, P-CH_2-CH_3, $^3J(HH)$ 7.4 Hz, $^2J(PH)$ 10.7 Hz]. ^{13}C NMR: 6.7 d [P-CH_2-CH_3, $^2J(PC)$ 4.6 Hz]; 34.55 d [P-CH_2-CH_3, $^1J(PC)$ 49.3 Hz]. ^{31}P NMR: 79.6 s.

The NMR data which have been obtained from reaction mixtures freshly prepared in NMR tubes are indicative for the formation of the compounds:

$Me_3Pb[S_2PMe_2]$ [prepared from 0.061 g (0.00021 moles) Me_3PbCl and 0.039 g (0.00021 moles) $Na[S_2PMe_2].2H_2O$, in $CDCl_3$]: ^1H NMR: 1.57 s [9H, Pb-CH_3, $^2J(PbH)$ 64.5Hz]; 2.03 d [6H, P-CH_3, $^2J(PH)$ 12.7 Hz]. ^{13}C NMR: 14.02 s [Pb-CH_3, $^1J(PbC)$ 261.1 Hz]; 31.72 d [P-CH_3, $^1J(PC)$ 56.1Hz]. ^{31}P NMR: 56.3 s.

$Me_3Pb[S_2PEt_2]$ [prepared from 0.057 g (0.00020 moles) Me_3PbCl and 0.045 g (0.00021 moles) $Na[S_2PEt_2].2H_2O$, in $CDCl_3$]: ^1H NMR: 1.54 s [9H, Pb-CH_3, $^2J(PbH)$ 64.9 Hz]; 1.23 dt [6H, P-CH_2-CH_3, $^3J(HH)$ 7.4 Hz, $^3J(PH)$ 21.2 Hz]; 2.00 dq (4H, P-CH_2-CH_3, $^3J(HH)$ 7.5 Hz, $^2J(PH)$ 10.7 Hz]. ^{13}C NMR: 7.41 d [P-CH_2-CH_3, $^2J(PC)$ 4.7 Hz]; 14.81 s [Pb-CH_3, $^1J(PbC)$ 262.7 Hz]; 33.82 d [P-CH_2-CH_3, $^1J(PC)$ 52.5 Hz]. ^{31}P NMR: 78.1 s.

$Me_3Pb[S_2PPh_2]$ [prepared from 0.046 g (0.00016 moles) Me_3PbCl and 0.043 g (0.00016 moles) $NH_4[S_2PPh_2]$, in $CDCl_3$]: ^1H NMR: 1.46 s [9H, Pb-CH_3, $^2J(PbH)$

63.9 Hz]; 7.41 m (6H, P-C_6H_5 - meta+para]; 8.02 dm (4H, P-C_6H_5 - ortho, $^3J(PH)$ 13.9 Hz). ^{13}C NMR: 13.87 s [Pb-CH_3, $^1J(PbC)$ 252.6 Hz]; 128.15 d [C_m, $^3J(PC)$ 13.0 Hz]; 130.73 s (C_p); 130.83 d [C_o, $^2J(PC)$ 7.5 Hz]; 139.60 d [C_i, $^1J(PC)$ 83.9 Hz]. ^{31}P NMR: 61.8 s [$^1J(PC)$ 80.7 Hz].

Synthesis of $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$

A mixture of Ph_2PbCl_2 (0.3603 g, 0.00083 moles) and $K[(OPPh_2)(SPPh_2)N]$ (0.7858 g, 0.00167 moles) in 40 mL anhydrous benzene was stirred at room temperature for 3 hours. The reaction mixture was filtered to remove KCl and the clear filtrate was evaporated *in vacuo* to give $Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$ as a white crystalline solid [yield 0.91 g (89%)], mp 190°C (dec.) [Found: C, 58.56; H, 3.93; N, 2.41; $C_{60}H_{50}N_2O_2P_4S_2Pb$ (1226.28) requires C, 58.77; H, 4.11; N, 2.28%]. IR (cm^{-1}): $\nu_{as}(P_2N)$ 1240 s,br; $\nu(PO)$ 1110 s, 1040 s; $\nu(PS)$ 570 m. ^1H NMR: 8.05 d [4H, Pb-C_6H_5 - ortho, $^3J(HH)$ 7.6 Hz, $^3J(PbH)$ 186.5 Hz]; 7.5 m (46H, Pb-C_6H_5 - meta+para, P-C_6H_5). ^{13}C NMR: 128.09 d [C_m, (S)P-C_6H_5 + (O)P-C_6H_5, $^3J(PC)$ 12.9 Hz]; 129.83 s,br (C_m + C_p, Pb-C_6H_5); 131.46 s,br [C_o + C_p, (S)P-C_6H_5 + (O)P-C_6H_5]; 135.02 s (C_o, Pb-C_6H_5); the resonances of the *ipso* carbons were not observed. ^{31}P NMR: 21.8 s [(O)P-C_6H_5]; 31.8 s [(S)P-C_6H_5].

Synthesis of $Ph_3Pb[(OPPh_2)(SPPh_2)N]$

A mixture of Ph_3PbCl (0.5267 g, 0.00111 moles) and $K[(OPPh_2)(SPPh_2)N]$ (0.5239 g, 0.00111 moles) in 40 mL anhydrous benzene was stirred at room temperature for 3 hours. The reaction mixture was filtered to remove KCl and the clear filtrate was evaporated *in vacuo* to give $Ph_3Pb[(OPPh_2)(SPPh_2)N]$ as a white solid [yield 0.81 g (84%)], mp 112-116°C [Found: C, 57.78; H, 3.80; N, 1.72; $C_{42}H_{35}NOP_2SPb$ (870.95) requires C, 57.92; H, 4.05; N, 1.61%]. IR (cm^{-1}): $\nu_{as}(P_2N)$ 1230 s,br; $\nu(PO)$ 1120 s, 1080 s, 1060 s; $\nu(PS)$ 570 m. ^1H NMR: 7.29 m (complex) [25H, P-C_6H_5 - meta+para, (O)P-C_6H_5 - ortho, Pb-C_6H_5 - meta+para]; 7.49 m [6H, Pb-C_6H_5 - ortho, $^3J(PbH)$ ca. 113 Hz]; 7.61 dd [4H, (S)P-C_6H_5 - orto,

$^3J(HH)$ 7.6 Hz, $^3J(PH)$ 14.0 Hz]. ^{13}C NMR: 127.35 d [C_m, P-C_6H_5, $^3J(PC)$ 13.2 Hz]; 127.69 d [C_m, P-C_6H_5, $^3J(PC)$ 13.7 Hz]; 129.22 s (C_p, Pb-C_6H_5); 129.58 s (C_p, P-C_6H_5); 129.84 s [C_m, Pb-C_6H_5, $^3J(PbC)$ 107.1 Hz]; 130.28 s (C_p, P-C_6H_5); 131.32 d [C_o, P-C_6H_5, $^2J(PC)$ ca.. 12 Hz]; 131.54 d [C_o, P-C_6H_5, $^2J(PC)$ 11.1 Hz]; 136.88 s [C_o, Pb-C_6H_5, $^2J(PbC)$ 87.5 Hz]; 157.16 s (C_i, Pb-C_6H_5); the resonances for the P-C_6H_5 *ipso* carbons were not observed. ^{31}P NMR: 14.3 s [(O)P-C_6H_5]; 31.8 s [(S)P-C_6H_5].

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