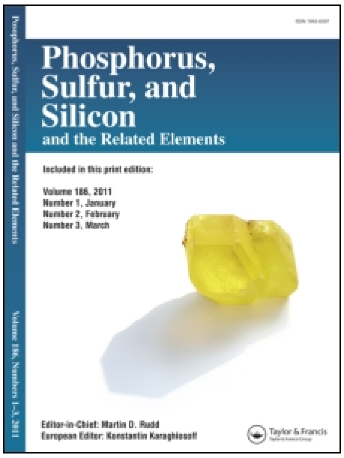

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Inorganic Chelate Rings in Organolead(IV) Derivatives of Organophosphorus Ligands from 6-Membered to 16-Membered Rings

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New organolead(IV) complexes of the type $R_3Pb[(OPPh_2)(XPPh_2)N]$, $R_2Pb[(OPPh_2)(XPPh_2)N]_2$ (R = Me, Ph; X = O, S) and $Me_3Pb(O_2PPh_2)$ have been prepared and characterized by IR and multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy. The X-ray molecular structure of the $Me_2Pb[(OPPh_2)_2N]_2$ and $Me_3Pb(O_2PPh_2)$ is discussed.

Keywords: dichalcogenoimidodiphosphinato ligands; inorganic rings; organoPb(IV) complexes

INTRODUCTION

Interesting structural patterns in solid state have been reported for organolead(IV) derivatives of dithiophosphorus ligands, *i.e.* monomeric $Ph_3PbS_2P(OEt)_2$ (tetrahedral PbS_4 core)[1] or $Ph_2Pb(S_2PPh_2)_2$ (octahedral PbS_6 core)[2], but chain polymeric $[Ph_3PbS_2PMe_2]_n$ (trigonal bipyramidal PbS_5 core)[3]. On the other hand, only inorganic lead(II) derivatives, $Pb[(XPPh_2)(YPPh_2)N]_2$ (X = Y = S[4], Se[5]; X = O, Y = S[6]), but no organolead(IV) complexes containing organophosphorus ligands of the type $[O_2PR_2]^-$ and $[(XPR'_2)(YPR''_2)N]^-$ have been characterized so far.

Here we report on the synthesis and characterization of various $R_{4-n}Pb[(OPPh_2)(XPPh_2)N]_n$ and $Me_3Pb(O_2PPh_2)$ derivatives.

RESULTS AND DISCUSSION

Organolead(IV) compounds were prepared by reacting $R_{4-n}PbCl_n$ and the alkaline salt of the appropriate ligand (Table 1):

$$R_{4-n}PbCl_n + n\,M[(OPPh_2)(XPPh_2)N] \longrightarrow R_{4-n}Pb[(OPPh_2)(XPPh_2)N]_n + n\,MCl$$

$$Me_3PbCl + NaO_2PPh_2 \longrightarrow Me_3Pb(O_2PPh_2) + NaCl$$

The IR spectra as well as the ^{31}P chemical shifts of organolead(IV) complexes are consistent with the presence of the deprotonated form of the ligand. The magnitude of the ^{207}Pb-proton and ^{207}Pb-carbon coupling constants [$^2J(PbH)$ / $^1J(PbC)$ 79.3 / 341.4 Hz for **1**, 85.7 / 391.7 Hz for **5**, and $^3J(PbH)$ / $^2J(PbC)$ 113.0 / 87.5 Hz for **2**, 216.5 / 131.0 Hz for **3**, 186.5 / - (not obsd.) for **4**] are indicativ for the presence of two or three organic groups attached to the metal atom.

Attempts to grow crystals of $Me_3Pb[(OPPh_2)_2N]$ (**1**) for X-ray diffraction studies resulted in isolation of $Me_2Pb[(OPPh_2)_2N]_2$ (**6**), due to a decomposition process with migration of a methyl group from

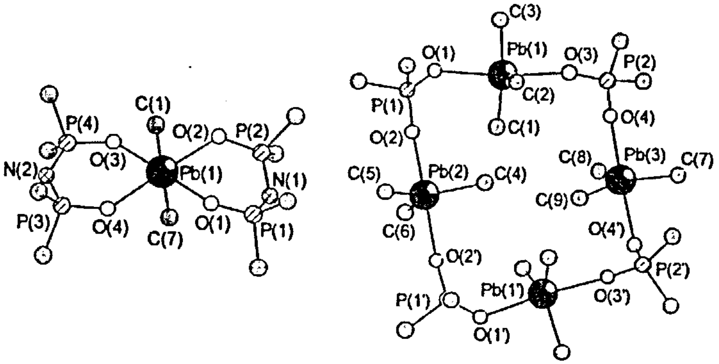
Table 1. Synthesis and NMR data for organolead(IV) derivatives.

Compounds	Yield (%)	M.p. (°C)	$\delta(^{31}P)$ (ppm)[c]
$Me_3Pb[(OPPh_2)_2N]$,[a] 1	95	147-149	13.8s,br
$Ph_3Pb[(OPPh_2)(SPPh_2)N]$,[b] 2	82	114-116	31.8s (PS) 14.3 (PO)
$Ph_2Pb[(OPPh_2)_2N]_2$,[a] 3	88	228-229 (dec.)	19.7s
$Ph_2Pb[(OPPh_2)(SPPh_2)N]_2$,[b] 4	89	190 (dec.)	31.8s (PS) 21.8 (PO)
$Me_3Pb(O_2PPh_2)$,[a] 5	88	217-219	16.8s[d]

[a] Using the Na salt of the ligand; [b] Using the K salt of the ligand;
[c] Abbreviations: s = singlet, br = broad; [c] $^1J(PC)$ 134.0 Hz.

The Pb atom to the ligand. The crystal contains two similar independent molecules; the imidodiphosphinato ligands act as monometallic biconnective units, leading to a spiro-bicyclic system with *six-membered* PbO_2P_2N rings (range Pb-O 2.35-2.47 Å, for molecule **6a**) of a distorted boat conformation (Fig. 1a). The coordination geometry at lead is slightly distorted octahedral [O-Pb-O (*trans*) 172.6, 174.1°, C-Pb-C 172.8°].

The crystal of the trimethyllead(IV) phosphinate (**5**) contains discrete tetrameric units, $[Me_3Pb(O_2PPh_2)]_4$, with bridging phosphinato ligands (range: Pb-O 2.37-2.44, P-O 1.47-1.52 Å), thus resulting in a *sixteen-membered* $Pb_4O_8P_4$ inorganic ring (Fig. 1b). The coordination geometry at lead atoms is distorted trigonal bipyramidal [range: O-Pb-O (*trans*) 174.4, 177.5°, C-Pb-C 114-130°].



(a) **(b)**

Figure 1. View of the structure of **(a)** $Me_2Pb[(OPPh_2)_2N]_2$, and **(b)** $[Me_3Pb(O_2PPh_2)]_4$ (for clarity only *ipso* carbons of the phenyl groups are shown.).

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