

Synthesis, Structure, and Reactivity of Novel Intramolecularly Coordinated Organolead(II) Compounds^[‡]

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Dedicated to Professor Jaroslav Holeček on the occasion of his 70th birthday

Keywords: Lead / Chain structures / Carbene homologues / Phosphorus / Hypervalent compounds

The intramolecularly coordinated heteroleptic organolead(II) compounds {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}PbX (**2**, X = Cl; **3**, X = SPh) have been synthesized. Single-crystal X-ray analyses reveal that both compounds adopt polymeric chain structures by intermolecular Pb–X···Pb bridges, a structural motif previously unknown for organolead(II) derivatives. Compound **2** reacts with lithium diisopropylamide, *i*Pr₂NLi, and lithium bis(trimethylsilyl)methane, (Me₃Si)₂CHLi, respectively, to provide in situ the corresponding organolead(II) compounds {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}PbX (**4**, X = *i*Pr₂N; **5**, X = (Me₃Si)₂CH), which were identified by NMR spectroscopy but could not be obtained as analytically pure sub-

stances. Attempts to isolate the intramolecularly coordinated organolead(II) hexafluorophosphate {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}Pb⁺PF₆[–] from the reaction of **2** with TlPF₆ also failed. Instead, the unprecedented salt [{5-*t*Bu-1,3-[P(O)(OEt)₂]₂C₆H₃]₄·(Pb₂F)] [PF₆]₃·4THF (**6**) was obtained, in which the [(Pb–F–Pb)]³⁺ cation is stabilized by eight intermolecular P=O→Pb interactions. Compound **6** was characterized by single-crystal X-ray analysis and electrospray mass spectrometry.

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Introduction

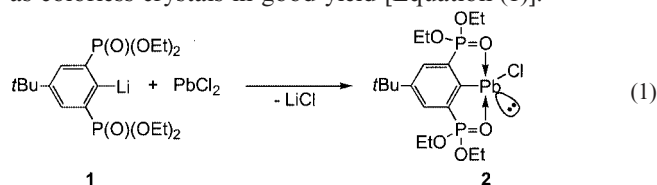
Most of the extensive research on the chemistry of the heavier group-14 element carbene analogues ER₂ (E = Si, Ge, Sn, Pb; R = alkyl, aryl, alkoxide, thiolate, diorganamide)^[1] has focused on divalent tin^[1] and germanium^[1] compounds, with fewer studies on low-valent silicon^[2–7] and organolead compounds.^[1,4,8,9] Of the latter, compounds containing π-bonded ligands^[10–17] and Pb–C σ-bonds have been investigated. Divalent lead compounds can be stabilized by bulky^[18–33] intramolecularly coordinating substituents.^[33–43] Unlike diorganolead compounds^[18–31,34–41] there are few examples of RPbX heteroleptic plumbynes {R = 2,6-[2,4,6-(*i*Pr)₃C₆H₂]₂C₆H₃, C(SiMe₃)₃, C(SiMe₃)₂(SiMe₂OMe), N(SiMe₃)C(Ph)C(SiMe₃)₂, C(SiMe₃)₂(SiMe₂C₅H₄N-2), C(SiMe₂Ph)₃, X = Br, Cl},^[31–33,42,43] which

are particularly interesting as they allow further derivatizations at the Pb–X function.

Recently, we reported the arylbis(phosphonic) esters 5-*t*Bu-1,3-[P(O)(OR)₂]₂C₆H₃ (**A**, R = Et; **B**, R = *i*Pr) and the application of their deprotonated monoanions to the synthesis of intramolecularly coordinated organosilicon(IV),^[44–46] organotin(IV),^[47–49] and organolead(IV)^[50] compounds, and of intramolecularly coordinated heteroleptic stannylenes.^[51] The latter, owing to intramolecular P=O→Sn coordination, show notably enhanced stability towards oxidation and thermal decomposition. We present here the synthesis and structure of the corresponding heteroleptic plumbylene and describe its reactivity towards nucleophiles.

Results and Discussion

The organolithium compound {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}Li (**1**)^[47] reacts with PbCl₂ to give the heteroleptic plumbylene {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}PbCl (**2**) as colorless crystals in good yield [Equation (1)].



[‡] Some of these results were first presented at the 10th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead, ICCOC-GTL-10, 8–12 July 2001, Bordeaux, France (Book of Abstracts 2P26). This work includes parts of the intended PhD thesis of K. Peveling.

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On contact with air and moisture, it slowly decomposes to give the protonated ligand **A** ($\delta^{31}\text{P} = 18.5$ ppm) and unidentified products (10% decomposition after 4 d, 99% decomposition after 41 d). Under inert conditions and dissolved in C_6D_6 , **2** is rather stable. No decomposition was observed after storage at 65 °C for 41 d.

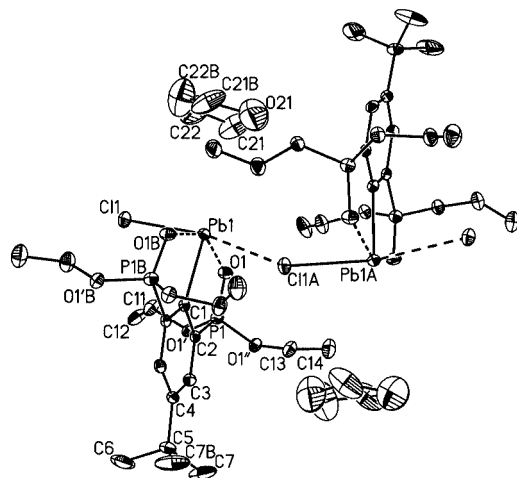


Figure 1. General view (SHELXTL) of two molecular units of **2**·THF showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -0.5 + x, y, -0.5 - z$; $b = x, 0.5 - y, z$; $c = 0.5 + x, y, -0.5 - z$)

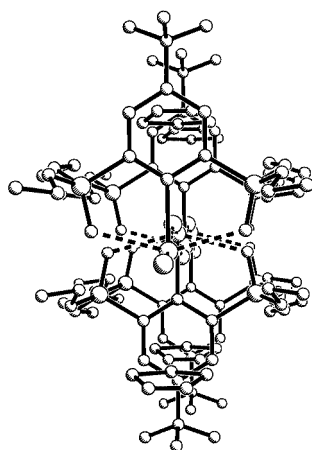


Figure 2. View along the Pb–Cl axis of **2**·THF

The molecular structure of **2**·THF (Figures 1 and 2), selected geometrical data (Table 1) and relevant crystallographic parameters (Table 2) are given here.

Unlike related heteroleptic plumblyenes $[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)]\text{PbCl}$,^[43] $[\{2,6-[2,4,6-(i\text{Pr})_3\text{C}_6\text{H}_2]_2\text{C}_6\text{H}_3\}\text{PbBr}]_2$,^[31] $[(\text{PhMe}_2\text{Si})_3\text{CPbCl}]_2$,^[32,33] $\{[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{OMe})]\text{PbCl}\}_2$,^[33] $[\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2]\text{PbCl}\}_2$,^[42] and $[(\text{Me}_3\text{Si})_3\text{CPbCl}]_3$ ^[33] being monomers, dimers and trimers, respectively, in the solid state, compound **2** forms an infinite zigzag chain via intermolecular, almost symmetrical Pb–Cl–Pb bridges ($\Delta\text{Pb–Cl}$ 0.106 Å, $\text{Pb}(1)–\text{Cl}(1)–\text{Pb}(1\text{A})$ 155.96(6)°). The $\text{Pb}(1)–\text{Cl}(1)$ and $\text{Pb}(1)\cdots\text{Cl}(1\text{A})$ distances of 2.795(1) and 2.901(1) Å, respectively, are in the range found in other monoorganoplumbyl-

Table 1. Selected bond lengths [Å], bond angles [°], and torsion angles [°] for **2**·THF and **3**

	2 ·THF	3
Pb(1)–C(1)	2.305(5)	2.327(3)
Pb(1)–O(1)	2.518(2)	2.671(2)
Pb(1)–O(2)		2.520(2)
Pb(1)–Cl(1)	2.795(1)	
Pb(1)–Cl(1A)	2.901(1)	
Pb(1)–S(1)		2.7090(9)
Pb(1)–S(1A)		3.2958(9)
S(1)–C(21)		1.755(4)
P(1)–O(1)	1.480(2)	1.483(2)
P(1)–O(1')	1.577(2)	1.570(2)
P(1)–O(1'')	1.574(2)	1.584(2)
P(2)–O(2)		1.488(2)
P(2)–O(2')		1.578(2)
P(2)–O(2'')		1.563(2)
P(1)–C(2)	1.788(3)	1.755(3)
P(2)–C(6)		1.783(3)
O(1)–Pb(1)–C(1)	74.78(5)	72.5(1)
O(2)–Pb(1)–C(1)		76.2(1)
O(1)–Pb(1)–O(2)		148.70(6)
O(1)–Pb(1)–O(1B)	149.5(1)	
O(1)–P(1)–C(2)	110.0(1)	111.5(1)
O(2)–P(2)–C(6)		111.8(1)
P(1)–O(1)–Pb(1)	116.4(1)	114.1(1)
P(2)–O(2)–Pb(1)		113.7(1)
P(1)–C(2)–C(3)	121.3(2)	122.6(3)
P(2)–C(6)–C(5)		119.2(3)
C(2)–C(1)–Pb(1)	121.5(2)	124.1(2)
C(6)–C(1)–Pb(1)		119.6(2)
Pb(1A)–Cl(1A)–Pb(1)	155.96(6)	
Cl(1)–Pb(1)–Cl(1A)	169.60(1)	
C(1)–Pb(1)–Cl(1)	89.1(1)	
C(1)–Pb(1)–Cl(1A)	80.5(1)	
O(1)–Pb(1)–Cl(1)	89.23(5)	
O(1)–Pb(1)–Cl(1A)	88.04(5)	
Pb(1)–S(1)–Pb(1A)		18.72(1)
S(1)–Pb(1)–S(1A)		158.533(8)
C(1)–Pb(1)–S(1)		84.96(8)
O(1)–Pb(1)–S(1)		91.44(5)
Pb(1)–S(1)–C(21)		104.2(1)
Pb(1)–C(1)–C(2)–C(3)	169.3(2)	172.0(2)
P(1)–C(2)–C(3)–C(4)	177.5(3)	–177.8(3)
O(1)–P(1)–C(2)–C(3)	–170.9(2)	–170.2(3)
C(1)–Pb(1)–Cl(1)–Pb(1C)	0.0	
O(1)–Pb(1)–Cl(1)–Pb(1A)	74.79(5)	
Cl(1A)–Pb(1)–Cl(1)–Pb(1C)	0.0	
C(1)–Pb(1)–S(1)–C(21)		–149.6(1)
C(1)–Pb(1)–S(1)–Pb(1A)		–114.00(9)
O(1)–Pb(1)–S(1)–Pb(1A)		173.68(6)
S(1)–Pb(1)–S(1A)–Pb(1A)		101.18(6)

enes such as $[(\text{PhMe}_2\text{Si})_3\text{CPbCl}]_2$ [$\text{Pb–Cl} = 2.729(3)$ Å, $\text{Pb}\cdots\text{Cl}' = 2.962(3)$ Å],^[32,33] $[(\text{Me}_3\text{Si})_3\text{CPbCl}]_3$ [$\text{Pb–Cl} = 2.71(2)$ Å, $\text{Pb}\cdots\text{Cl}' = 2.73(1)$ Å, $\text{Pb}\cdots\text{Cl}'' = 2.74(1)$ Å],^[33] $\{[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{OMe})]\text{PbCl}\}_2$ [$\text{Pb–Cl} = 2.680(5)$ Å, $\text{Pb}\cdots\text{Cl}' = 2.868(5)$ Å],^[33] $[\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2]\text{PbCl}_2$ [$\text{Pb–Cl} = 2.609(3)$ Å, $\text{Pb}\cdots\text{Cl}' = 3.276(3)$ Å],^[42] and $[\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)]\text{PbCl}$ [$\text{Pb–Cl} = 2.647(3)$ Å].^[43] The organic substituents at adjacent lead atoms in the heteroleptic plumbylene **2** are staggered with $\text{C}(1)–\text{Pb}(1)\cdots\text{Pb}(1\text{A})–\text{C}(1\text{A}) = 180.0^\circ$.

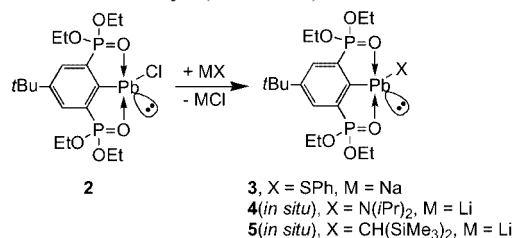
Table 2. Crystallographic data for **2**·THF, **3**, and **6**·THF

	2 ·THF	3	6
Empirical formula	C ₂₂ H ₃₉ ClO ₇ P ₂ Pb	C ₂₄ H ₃₆ O ₆ P ₂ PbS	C ₈₈ H ₁₆₀ F ₁₉ O ₂₈ P ₁₁ Pb ₂
Formula mass	720.11	721.72	2782.21
Crystal system	orthorhombic	monoclinic	monoclinic
Crystal size [mm]	0.17 × 0.15 × 0.15	0.15 × 0.15 × 0.13	0.15 × 0.15 × 0.13
Space group	<i>Pnma</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> [Å]	11.0907(2)	14.0353(3)	36.1419(5)
<i>b</i> [Å]	16.3289(4)	10.5415(2)	18.3134(3)
<i>c</i> [Å]	15.6283(4)	19.6993(5)	26.1390(5)
β [°]	90	99.9054(8)	127.2822(7)
<i>V</i> [Å ³]	2830.3(1)	2871.1(1)	13765.7(4)
<i>Z</i>	4	4	4
ρ_{calcd} [g/cm ³]	1.690	1.670	1.342
ρ_{found} [g/cm ³]	1.620 ± 0.05	1.518 ± 0.003	not measured
μ [mm ⁻¹]	6.205	6.095	2.653
<i>F</i> (000)	1424	1424	5648
θ range [°]	3.19 to 27.47	2.95 to 27.45	2.96 to 27.46
Index ranges	−14 ≤ <i>h</i> ≤ 14 −21 ≤ <i>k</i> ≤ 21 −20 ≤ <i>l</i> ≤ 20	−18 ≤ <i>h</i> ≤ 18 −13 ≤ <i>k</i> ≤ 13 −25 ≤ <i>l</i> ≤ 25	−46 ≤ <i>h</i> ≤ 46 −23 ≤ <i>k</i> ≤ 23 −33 ≤ <i>l</i> ≤ 26
No. of reflns. collected	21665	27814	55752
Completeness to θ_{max}	99.8%	99.6%	98.6%
No. of independent reflns./ <i>R</i> _{int}	3349/0.042	6531/0.053	15542/0.043
No. of reflns. obsd. with [<i>I</i> > 2 σ (<i>I</i>)]	1996	3517	6078
No. of refined parameters	160	316	704
GooF (<i>F</i> ²)	0.915	0.598	0.812
<i>R</i> 1 (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.0232	0.0248	0.0489
<i>wR</i> 2 (<i>F</i> ²) (all data)	0.0455	0.0353	0.1273
(Δ/σ) _{max}	0.001	0.001	0.001
Largest diff. peak/hole [e/Å ³]	0.830/−0.966	0.862/−0.971	0.731/−0.488

The lead atom exhibits a ψ -octahedral configuration with O(1), O(1B), Cl(1) and Cl(1A) occupying the equatorial positions and C(1) being almost perpendicular to these atoms and *trans* to the lone pair. The stereochemical influence of the lone pair is mainly manifested by the Cl(1)–Pb(1)–Cl(1A), C(1)–Pb(1)–Cl(1), and C(1)–Pb(1)–Cl(1A) angles of 169.60(1), 89.1(1), and 80.5(1)°, respectively. The O(1)–Pb(1)–O(1B) angle of 149.5(1)° is close to the corresponding angle in the related heteroleptic stannylene {4-*t*Bu-2,6-[P(O)(OiPr)₂]₂-C₆H₂}/SnCl [O(1)–Sn(1)–O(2) 152.00(5)°]^[52] but much bigger than the O(1)–Pb(1)–O(2) of 119.36(5)° in the intramolecularly [4+2]-coordinated tetraorganolead(IV) derivative {4-*t*Bu-2,6-[P(O)(OEt)₂]₂-C₆H₂}/PbPh₃.^[50] In contrast to related organosilicon(IV),^[44–46] organotin(IV),^[47–49] and organolead(IV)^[50] compounds containing the O,C,O-coordinating ligand {4-*t*Bu-2,6-[P(O)(OR)₂]₂-C₆H₂}[−] (R = Et, *i*Pr), in the organoplumbylene **2** the P(O)(OEt)₂ groups and the lead atom are slightly displaced in the same direction from the plane defined by the aromatic ring [P(1)–C(2)–C(3)–C(4) = 177.5(3)°, Pb(1)–C(1)–C(2)–C(3) = 169.3(2)°]. The intramolecular Pb(1)–O(1) and Pb(1)–O(1B) distances of 2.518(2) Å are close to the intramolecular Pb–O [2.52(2) Å] reported for {2-[Ph₂P(O)CH₂]₂-C₆H₄S₂}/Pb.^[53] The IR spectrum of **2** shows a band at $\tilde{\nu}(\text{P}=\text{O}) = 1201 \text{ cm}^{-1}$ which is similar to that for the related stannylene {4-*t*Bu-2,6-[P(O)(OEt)₂]₂-C₆H₂}/SnCl [$\tilde{\nu}(\text{P}=\text{O}) = 1192 \text{ cm}^{-1}$].^[51]

The singlet at $\delta = 52.0$ [$J(^{207}\text{Pb} - ^{31}\text{P}) = 127 \text{ Hz}$] ppm in the ³¹P NMR (C₆D₆) spectrum of organolead(II) chloride **2** is at a higher frequency than for the corresponding organotin(II) compound {4-*t*Bu-2,6-[P(O)(OEt)₂]₂-C₆H₂}/SnCl (in [D₈]toluene: $\delta = 39.1 \text{ ppm}$).^[51] The solid-state ³¹P NMR spectrum shows a broad resonance at $\delta = 54.5 \text{ ppm}$. No ²⁰⁷Pb NMR chemical shift could be obtained, which accords with reported problems in recording ²⁰⁷Pb NMR spectra of [(PhMe₂Si)₃CPbCl]₂,^[32,33] [(Me₃Si)₃CPbCl]₃,^[33] [{2,6-[2,4,6-(*i*Pr)₃C₆H₂]₂-C₆H₃}/PbBr]₂,^[31] and [{2,6-[2,4,6-(*i*Pr)₃C₆H₂]₂-C₆H₃}/PbBr·py].^[31]

Compound **2** reacts with sodium thiophenolate under nucleophilic substitution at the Pb–Cl function to give the corresponding organolead(II) thiophenolate **3** as a colorless crystalline solid that is stable at 20 °C under aerobic conditions for several days (Scheme 1).



Scheme 1

The molecular structure of compound **3** (Figures 3 and 4), selected geometrical data (Table 1), and relevant crystal-

lographic parameters (Table 2) are detailed here. As with organolead(II) chloride **2**, the organolead(II) thiophenolate **3** forms a polymeric zigzag chain with, however, a less symmetric intermolecular Pb–S···Pb bridge [$\Delta\text{Pb–S}$ 0.5868 Å, Pb(1)–S(1)–Pb(1A) 18.72(1)°]. The torsion angle C(1)–Pb(1)···Pb(1a)–C(1a) is 170.9(1)°. The related organolead(II) thiophenolate derivative {2,4,6-[(Me₃Si)₂CH]₃C₆H₂}Pb{2,4,6-[(Me₃Si)₂CH]₃C₆H₂S},^[54,55] however, is a monomer. As with compound **2**, the lead atom in the organolead(II) thiophenolate **3** shows a distorted ψ -octahedral configuration with O(1), O(2), S(1) and S(1A) occupying the equatorial positions and C(1) being almost perpendicular to these atoms. The stereochemical influence of the lone pair is shown by the S(1)–Pb(1)–S(1A) angle of 158.533(8)°. In contrast to the related organolead(II) chloride **2**, in **3** the intramolecular Pb(1)–O(1) and Pb(1)–O(2) distances differ [2.671(2) and 2.520(2) Å, respectively]. The non-equivalence of the two phosphorus atoms is also shown in the solid-state ³¹P NMR spectrum by two resonances at δ = 50.4 and 45.0 ppm. The IR spectrum, however, is not sensitive enough to distinguish the two phosphoryl groups and shows only one band at $\tilde{\nu}(\text{P=O})$ = 1208 cm^{−1}. The O(1)–Pb(1)–O(2) angle of 148.70(6)° is again rather similar to the 152.48(7)° found in the related stannylene {4-*t*Bu-2,6-[P(O)(*Oi*Pr)₂]₂C₆H₂}SnSPh.^[52] The Pb(1)–S(1) distance of 2.7090(9) Å lies in the range of Pb–S distances found in [{2,6-(*i*Pr)₂C₆H₂}S]₂Pb₃ [Pb–S = 2.554(4)–2.896(3) Å].^[56] The Pb(1)···S(1A) distance [3.2958(9) Å] is in the range of lead–sulfur secondary bond lengths found in ∞ [(S₂PPh₂)₂Pb] (Pb···S = 3.270–3.448 Å).^[57] Compounds **2** and **3** appear to be the first organolead(II) derivatives to exhibit polymeric chain structures.

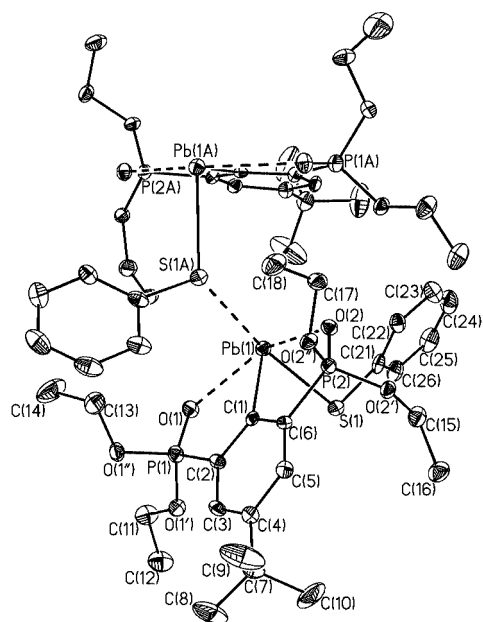


Figure 3. General view (SHELXTL) of two molecular units of **3** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -0.5 - x$, $-0.5 + y$, $0.5 - z$)

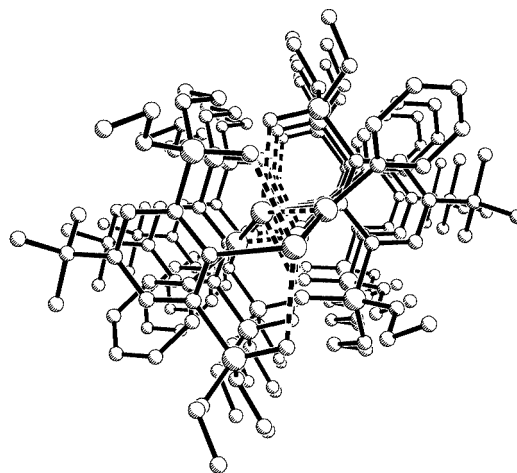


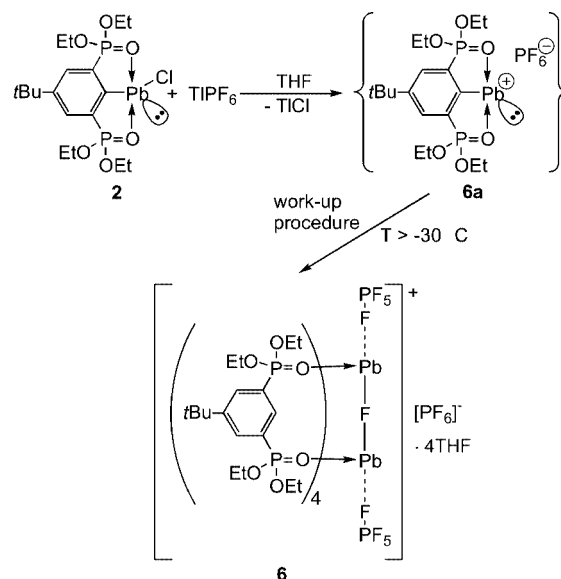
Figure 4. View along the Pb–S axis of **3**

Osmometric molecular weight determinations in THF showed that plumbynes **2** and **3** are monomeric in solution.

Compound **2** also reacts with lithium diisopropylamide and lithium bis(trimethylsilyl)methane by nucleophilic substitution at the Pb–Cl function to give, in situ, moderate yields of the heteroleptic plumbynes {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}PbNi/Pr₂ (**4**) and {4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}PbCH(SiMe₃)₂ (**5**) (Scheme 1). Neither **4** nor **5** could be obtained analytically pure but their identity was confirmed by NMR spectroscopy (see Exp. Sect. and Supporting Information). Remarkably, the ²⁰⁷Pb NMR chemical shift of **5** could be determined { δ = 6874 [$J(^{207}\text{Pb-}^{31}\text{P})$ = 129 Hz] ppm}.

The reactions shown in Scheme 1 are always accompanied by Pb–C bond cleavage. No reaction between **2** and sulfur was observed even at 60 °C.

In an attempt to prepare the intramolecularly coordinated organolead(II) hexafluorophosphate [{4-*t*Bu-2,6-[P(O)(OEt)₂]₂C₆H₂}Pb]⁺PF₆[−] (**6a**), compound **2** was treated with TIPF₆ in THF at −78 °C (Scheme 2). The ³¹P



Scheme 2

NMR spectrum of the crude reaction mixture showed signals (a) at $\delta = 18.0$ (integral 27%, assigned to 5-*t*Bu-1,3-[P(O)(OEt)₂]₂C₆H₃) ppm and (b) at $\delta = 54.1$ [$J(^{31}\text{P}-^{207}\text{Pb}) = 150$ Hz, integral 73%] ppm. The latter signal is assigned with caution to the phosphonyl phosphorus atom in the salt **6a**.

After filtration under inert conditions through a diatomaceous earth filter, in the filtrate, the ratio of the ^{31}P NMR signals (a) to (b) changed to 88:12. From this filtrate, air- and moisture-sensitive single crystals of [$\{5\text{-}t\text{Bu-1,3-[P(O)(OEt)}_2\text{]}_2\text{C}_6\text{H}_3\}_4\cdot(\text{Pb}_2\text{F})\} [\text{PF}_6]_3\cdot 4\text{THF}$ (**6**) were obtained.

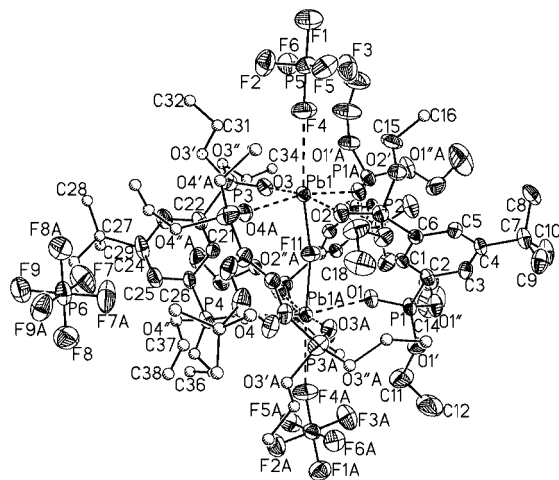


Figure 5. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $-x, y, 0.5 - z$)

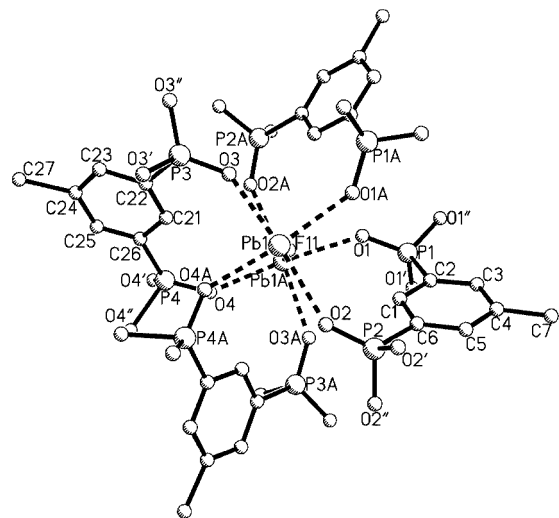


Figure 6. View along the Pb-F-Pb axis of **6**; methyl and ethyl groups, as well as THF and PF_6^- , are omitted for clarity

The molecular structure of **6** (Figures 5 and 6), selected geometrical data (Table 3), and relevant crystallographic parameters (Table 2) are given below.

The salt **6** consists of a $[(\text{Pb}-\text{F}-\text{Pb})]^{3+}$ cation stabilized by eight intermolecular $\text{P}=\text{O} \rightarrow \text{Pb}$ coordinations of four 5-*t*Bu-1,3-[P(O)(OEt)₂]₂C₆H₃ molecules, three $[\text{PF}_6]^-$ anions,

Table 3. Selected bond lengths [$\text{\AA}$], bond angles [$^\circ$], and torsion angles [$^\circ$] of **6**

	6
Pb(1)–F(11)	2.2762(7)
Pb(1A)–F(11)	2.2762(7)
Pb(1)–O(2)	2.536(4)
Pb(1)–O(3)	2.479(4)
Pb(1)–O(1A)	2.550(4)
Pb(1)–O(4A)	2.426(4)
Pb(1)–F(4)	3.075(5)
Pb(1A)–O(1)	2.550(4)
P(5)–F(5)	1.601(5)
P(5)–F(4)	1.578(5)
P(5)–F(2)	1.574(5)
P(1)–O(1)	1.479(4)
P(1)–O(1')	1.547(5)
P(1)–O(1'')	1.529(5)
P(2)–O(2)	1.485(4)
P(2)–O(2')	1.559(5)
P(2)–O(2'')	1.559(5)
P(1)–C(2)	1.786(6)
P(2)–C(6)	1.789(6)
Pb(1)–F(11)–Pb(1A)	167.4(3)
F(4)–Pb(1)–F(11)	172.8(2)
O(1A)–Pb(1)–O(2)	95.6(1)
O(1A)–Pb(1)–O(3)	87.7(1)
O(3)–Pb(1)–O(4A)	84.4(1)
O(4A)–Pb(1)–O(2)	90.1(1)
O(2)–Pb(1)–O(3)	170.2(1)
O(1A)–Pb(1)–O(4A)	163.3(1)
P(1)–O(1)–Pb(1A)	140.2(3)
P(2)–O(2)–Pb(1)	146.1(3)
P(4)–O(4)–Pb(1A)	137.0(3)
F(11)–Pb(1)–O(2)	85.6(1)
F(11)–Pb(1)–O(3)	86.2(1)
F(11)–Pb(1)–O(1A)	76.5(2)
P(1)–C(2)–C(3)–C(4)	–177.9(5)
O(1)–P(1)–C(2)–C(3)	–155.5(5)
F(11)–Pb(1)–O(4A)	88.3(2)
O(4A)–Pb(1)–F(4)	97.8(2)
O(1)–P(1)–O(1')	115.7(3)
O(1)–P(1)–O(1'')	113.6(3)
O(1')–P(1)–O(2'')	102.0(3)
C(6)–P(2)–O(2)	112.7(3)
C(2)–P(1)–O(1)	112.3(3)
C(1)–C(6)–P(2)	118.2(5)
C(1)–C(2)–P(1)	118.5(5)
C(3)–C(4)–C(7)	122.4(6)
C(2)–C(3)–C(4)	120.8(6)
C(4)–C(5)–C(6)	121.1(6)
F(4)–P(5)–F(6)	88.9(3)
F(2)–P(5)–F(4)	91.5(3)
C(6)–C(2)–Pb(1A)–Pb(1)	37.5(2)
C(4)–C(5)–C(6)–P(2)	–177.7(5)
O(2)–P(2)–C(6)–C(5)	159.6(5)

and four THF molecules. The cationic part of the structure has an axis of improper rotation. The three $[\text{PF}_6]^-$ anions are crystallographically non-equivalent. Two symmetry-related ones (P5/P5A) show a $\text{Pb}(1) \cdots \text{F}(4)$ distance of 3.075(5) $\text{\AA}$ whereas the third one (P6) is far from the lead atoms [$\text{Pb}(1) \cdots \text{F}(7)$ 8.437(6) $\text{\AA}$]. The $\text{Pb}(1) \cdots \text{F}(11)$ distance of 2.2762(7) $\text{\AA}$ is rather short compared with $\text{Pb}-\text{F}$ in $\alpha\text{-PbF}_2$ [2.418(2), 2.439(8) $\text{\AA}$]^[58] and $\beta\text{-PbF}_2$ (2.573 $\text{\AA}$).^[59] Lead–fluorine distances of 3.04(6) and 3.30 $\text{\AA}$ have been

reported for $\text{Pb}(\text{hdhfa})_2$ [$\text{Hdhfa} = 1,5\text{-bis}(\text{undecafluorocyclohexyl})\text{pentane-2,4-dione}$]^[60] and $\text{bis}(2,2\text{-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionato})\text{lead}$,^[61] respectively. The lead atom exhibits a distorted octahedral configuration with four $\text{P}=\text{O}$ oxygen atoms equatorial and F(4), F(11) in axial positions. Distortion from the ideal geometry is manifested by F(4)–Pb(1)–F(11), O(2)–Pb(1)–O(3), and O(1A)–Pb(1)–O(4A) angles of 172.8(2), 170.2(1), and 163.3(1)°, respectively. The Pb–O distances lie between 2.426(4) [Pb(1)–O(4A)] and 2.550(4) Å [Pb(1)–O(1A)]. They are up to 0.245 Å shorter than the Pb–O distance in the intramolecularly coordinated organolead(II) chloride and thiophenolate **2** and **3**, respectively. The Pb(1)–F(11)–Pb(1A) angle amounts to 167.4(3)°. The electrospray mass spectrum of **6** in CH_3CN shows a cluster pattern at $m/z = 1039$, which is assigned to $\{(\text{Pb} + \text{F} + 2(5\text{-}t\text{Bu-1,3-[P(O)(OEt)}_2\text{C}_6\text{H}_3)]^+ \}^+$. The IR spectrum (KBr pellet) of **6** shows a band at $\tilde{\nu}(\text{P}=\text{O}) = 1197\text{ cm}^{-1}$, indicating strong $\text{P}=\text{O} \rightarrow \text{Pb}$ coordination. The ^1H and ^{31}P NMR spectra of **6** exclusively show signals corresponding to the protonated ligand $5\text{-}t\text{Bu-1,3-[P(O)(OEt)}_2\text{C}_6\text{H}_3]$ (**A**), THF , and PF_6^- anion.

Conclusion

We have demonstrated the capacity of the phosphorus-containing O,C,O-coordinating ligand $4\text{-}t\text{Bu-2,6-[P(O)(OEt)}_2\text{C}_6\text{H}_4]$ for the synthesis of stable heteroleptic organolead(II) compounds. This ligand or a modified version (replacement of ethyl groups by more bulky substituents) is also, probably, suitable to stabilize the corresponding germanium(II) and silicon(II) compounds. Although no rational synthesis for compound **6** has been developed yet, its serendipitous formation might help in developing concepts for the stabilization of di- and oligonuclear metal cations. Notably, Mews et al. have isolated and structurally characterized a compound that contains an $[(\text{Sn}-\text{F}-\text{Sn})\cdot 4\text{Ph}_3\text{PO}]^{3+}$ cation.^[62]

Experimental Section

General Remarks: All solvents were dried and purified by standard procedures. All reactions were carried out under argon using Schlenk techniques. Bruker DPX-300 and DRX-400 spectrometers were used to obtain ^1H , ^{13}C , ^{31}P , and ^{207}Pb NMR spectra. ^{31}P MAS NMR spectra were recorded with a Bruker MSL 400 spectrometer using cross-polarisation and high-energy proton decoupling. Two rotation frequencies (6000–9000 Hz) have been used to identify the isotropic shift. A repetition delay of 4.0 s and a 90.0° pulse of 5.0 μs were employed. ^1H , ^{13}C , ^{31}P , and ^{207}Pb NMR chemical shifts (δ) are given in ppm and referenced to Me_4Si , H_3PO_4 (85%), and PbNO_3 (saturated in D_2O) as appropriate. NMR spectra were recorded at room temperature unless otherwise stated. IR spectra were recorded with a Bruker IFS 28 spectrometer. UV measurements were performed with a Varian Cary 100. Elemental analyses were obtained with a LECO-CHNS-932 analyser. Molecular weight determinations were performed with a Knauer Osmometer K7000 in freshly distilled solvent and were referenced against ben-

zil. Electrospray mass spectra were recorded in the positive mode with a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The relevant compound was dissolved in CH_3CN to give an approximate solution concentration of $1\cdot 10^{-4}\text{ mol}\cdot\text{L}^{-1}$. The sample was then introduced via a syringe pump operating at $10\text{ }\mu\text{L min}^{-1}$. The capillary voltage was varied between 7.0 and 8.7 V, while the cone-skimmer voltage was varied between 33.7 and 83.5 V. Identification of the inspected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The m/z values reported correspond to the most intense peaks in the corresponding isotope pattern. $\{4\text{-}t\text{Bu-2,6-[P(O)(OEt)}_2\text{C}_6\text{H}_3]\text{Li}$ (**1**) was prepared as previously reported.^[47]

[4-tert-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (2): PbCl_2 (3.32 g, 11.94 mmol) was added portionwise, at -78°C , to a solution of [4-tert-butyl-2,6-bis(diethoxyphosphonyl)phenyl]lithium (**1**) (3.12 g, 7.57 mmol) in THF (150 mL). The reaction mixture was then stirred for 16 h (-78°C to room temperature) and, after filtration, the solvent (50 mL) was evaporated. Crystallization at -6°C afforded 4.42 g (81%) of **2**·THF as colorless crystals, m.p. 185°C . After removal of THF by reduced pressure (11 Torr), **2** was characterized. ^1H NMR (400.13 MHz, C_6D_6): $\delta = 1.08$ (t, 12 H, CH_3), 1.13 (s, 9 H, CH_3), 4.02–4.17 ($\nu_{1/2} = 32\text{ Hz}$, 4 H, CH_2), 4.17–4.33 ($\nu_{1/2} = 36\text{ Hz}$, 4 H, CH_2), 8.29 (complex pattern, 2 H, aromatics) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, C_6D_6): $\delta = 16.4$ (d, $^3J_{\text{C,P}} = 6\text{ Hz}$, 4 C, CH_3), 31.0 (s, 3 C, CH_3), 34.9 (s, 1 C, C), 63.3 ($\nu_{1/2} = 23\text{ Hz}$, 4 C, CH_2), 135.1 (dd, $^1J_{\text{C,P}} = 196$, $^3J_{\text{C,P}} = 24\text{ Hz}$, 2 C, C-2,6), 135.7 (dd, $^2J_{\text{C,P}} = 16$, $^4J_{\text{C,P}} = 5\text{ Hz}$, 2 C, C-3,5), 150.1 (t, $^3J_{\text{C,P}} = 12\text{ Hz}$, 1 C, C-4), 250.7 (t, $^2J_{\text{C,P}} = 35\text{ Hz}$, 1 C, C-1) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6): $\delta = 52.0$ (s, $J_{\text{P,Pb}} = 127$, $^1J_{\text{C,P}} = 196\text{ Hz}$ ppm. $^{31}\text{P}\{^1\text{H}\}$ MAS NMR (161.98 MHz): $\delta = 54.6$ ppm. IR (KBr): $\tilde{\nu}(\text{P}=\text{O}) = 1201$, 1179 cm^{-1} . UV/Vis (CH_3CN): $\lambda = 217\text{ nm}$, $\epsilon = 25309\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; $\lambda = 279\text{ nm}$, $\epsilon = 3122\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; $\lambda = 286\text{ nm}$, $\epsilon = 3039\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Molecular weight determination (THF, 28°C , $c = 0.0147\text{ mol}\cdot\text{L}^{-1}$): 602.0 g mol^{-1} . $\text{C}_{18}\text{H}_{31}\text{ClO}_6\text{P}_2\text{Pb}$ (648.0): calcd. C 33.4, H 4.8; found C 33.4, H 4.8. MS: m/z (%) = 647 (45) [$\text{M} - \text{H}$], 612 (88) [$\text{M} - \text{Cl} - \text{H}$], 539 (52) [$\text{M} - \text{Cl} - \text{OEt} - \text{Et}$].

Investigations on the Stability of [4-tert-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (2). **A:** [4-tert-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) was exposed to light and atmospheric moisture on a watch glass. After $t_1 = 4\text{ d}$ and $t_2 = 41\text{ d}$, respectively, representative portions were dissolved in C_6D_6 and analysed by NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6 , t_1): $\delta = 19.0$ [s, 1-tert-butyl-3,5-bis(diethoxyphosphonyl)benzene, 10%], 52.5 (s, $J_{\text{P,Pb}} = 128\text{ Hz}$, 2, 90%) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6 , t_2): $\delta = 19.0$ [s, 1-tert-butyl-3,5-bis(diethoxyphosphonyl)benzene, 99%], 52.5 (s, $J_{\text{P,Pb}} = 128\text{ Hz}$, **2**, 1%) ppm. **B:** [4-tert-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (10 mg, $1.5\cdot 10^{-5}\text{ mol}$) in C_6D_6 (0.4 mL) was sealed under inert conditions in an NMR tube at 65°C for $t_3 = 41\text{ d}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, C_6D_6 , t_3): $\delta = 19.0$ [s, 1-tert-butyl-3,5-bis(diethoxyphosphonyl)benzene, 6%], 52.5 (s, $J_{\text{P,Pb}} = 128\text{ Hz}$, **2**, 94%) ppm.

[4-tert-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]thiophenolato-plumbylene (3): NaSC_6H_5 (0.16 g, 1.21 mmol) was added portionwise, at -78°C , to a suspension of [4-tert-butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (0.41 g, 0.63 mmol) in THF (100 mL). After the reaction mixture had been stirred for 16 h (-78°C to room temperature), it was decanted from an insoluble residue. The solution was then kept at -6°C to afford **3** [0.15 g (33%)] as colorless crystals, m.p. 86°C . ^1H NMR (400.13 MHz, $[\text{D}_8]\text{thf}$): $\delta = 1.26$ (t, 6 H, CH_3), 1.31 (t, 6 H, CH_3), 1.36 (s, 9 H,

CH₃), 4.02–4.23 (complex pattern, 6 H, CH₂), 4.28–4.40 (complex pattern, 2 H, CH₂), 6.86 (t, 1 H, aromatics), 7.04 (t, 2 H, aromatics), 7.33 (d, 2 H, aromatics), 8.05 (complex pattern, 2 H, aromatics) ppm. ¹³C{¹H} NMR (100.61 MHz, [D₈]thf): δ = 17.7 (d, ³J_{C,P} = 6 Hz, 2 C, CH₃), 17.8 (d, ³J_{C,P} = 6 Hz, 2 C, CH₃), 32.4 (s, 3 C, CH₃), 36.6 (s, 1 C, C), 63.9 (d, ²J_{C,P} = 6 Hz, 2 C, CH₂), 65.0 (d, ²J_{C,P} = 4 Hz, 2 C, CH₂), 124.8 (s, 2 C, C_p), 129.2 (s, 2 C, C_m), 135.2 (s, 2 C, C_o), 136.9 (dd, ²J_{C,P} = 17, ⁴J_{C,P} = 4 Hz, 2 C, C-3,5), 137.2 (dd, ¹J_{C,P} = 195, ³J_{C,P} = 25 Hz, 2 C, C-2,6), 145.3 (s, 1 C, C_i), 151.4 (t, ³J_{C,P} = 13 Hz, 1 C, C-4), 239.4 (t, ²J_{C,P} = 35 Hz, 1 C, C-1) ppm. ³¹P{¹H} NMR (161.98 MHz, [D₈]thf): δ = 47.8 (s, J_{P,Pb} = 123 Hz) ppm. ³¹P{¹H} MAS NMR (161.98 MHz): δ = 45.5, 50.4 ppm. IR (KBr): ν̄(P=O) = 1208, 1183 cm⁻¹. UV/Vis (CH₃CN): λ = 215 nm, ε = 28695 L·mol⁻¹·cm⁻¹; λ = 259 nm, ε = 13211 L·mol⁻¹·cm⁻¹. Molecular weight determination (THF, 28 °C, c = 0.0069 mol·L⁻¹): 727.7 g mol⁻¹. C₂₄H₃₀O₆P₂PbS (721.8): calcd. C 39.9, H 5.0; found C 40.0, H 5.1. MS: m/z (%) = 613 (100) [M – SPh], 391 (65) [M – SPh – 3 OEt – Et – tBu], FAB-MS: m/z (%) = 613 (100) [M – SPh].

[4-*tert*-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]diisopropylamino-plumbylene (4). **Method A:** A solution of *i*Pr₂NLi in hexane/diethyl ether (3:1) (37 mL, 0.75 M) was added, at –78 °C, to a solution of 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene (7.5 g, 18.5 mmol) in THF (120 mL) and the reaction mixture was stirred at this temperature for 5 h. PbCl₂ (3.85 g, 13.8 mmol) was added portionwise and the suspension stirred for 16 h (–78 to –30 °C). After filtration some of the solvent (75 mL) was evaporated. Crystallization at –6 °C afforded **2**·THF [1.98 g (20%)]. The solvent was then evaporated, and the residue dissolved in hexane (50 mL). After decantation from insoluble **2** and 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, the solvent was removed in vacuo to give 4.18 g of a yellow oil containing **4** (yield 45%, purity 83%) and residues of **2** (δ³¹P = 52.0 ppm, 5%) and 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene (δ³¹P = 18.4 ppm, 12%). ¹H NMR (400.13 MHz, C₆D₆): δ = 0.98 (t, 6 H, CH₃), 1.13 (s, 9 H, CH₃), 1.22 (t, 6 H, CH₃), 1.53 [s, 6 H, C(H)(CH₃)₂], 1.55 [s, 6 H, C(H)(CH₃)₂], 3.68–3.79 (complex pattern, 2 H, CH₂), 3.86–3.97 (complex pattern, 2 H, CH₂), 4.17–4.34 (complex pattern, 4 H, CH₂), 5.12–5.28 (sept, 2 H, CH), 8.20 (complex pattern, 2 H, aromatics) ppm. ¹³C{¹H} NMR (100.61 MHz, C₆D₆): δ = 16.4 (complex pattern, ³J_{C,P} = 7 Hz, 4 C, CH₃), 30.1 [s, 3 C, C(CH₃)₃], 31.0 [s, 4 C, C(H)(CH₃)₂], 34.7 (s, 1 C, C), 53.7 (s, 2 C, CH), 62.1 (d, 2 C, ²J_{C,P} = 5 Hz, CH₂), 62.3 (d, 2 C, ²J_{C,P} = 6 Hz, CH₂), 134.8 (dd, ²J_{C,P} = 17, ⁴J_{C,P} = 4 Hz, 2 C, C-3,5), 136.1 (dd, ¹J_{C,P} = 197, ³J_{C,P} = 26 Hz, 2 C, C-2,6), 148.9 (t, ³J_{C,P} = 13 Hz, 1 C, C-4), 236.8 (t, ²J_{C,P} = 38 Hz, 1 C, C-1) ppm. ³¹P{¹H} NMR (161.98 MHz, C₆D₆): δ = 41.7 (s, J_{P,Pb} = 116 Hz) ppm. IR (KBr): ν̄(P=O) = 1203 cm⁻¹. **Method B:** A solution of LDA in hexane/diethyl ether (3:1) (0.4 mL, 0.75 M) was added, at –78 °C, to a suspension of [4-*tert*-butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (0.187 g, 0.289 mmol) in THF (15 mL). After the reaction mixture had been stirred for 4 h at this temperature, it was characterized by ³¹P NMR spectroscopy. ³¹P{¹H} NMR (81.02 MHz, D₂O capillary): δ = 18.4 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 5%], 41.7 (s, J_{P,Pb} = 122 Hz, **4**, 83%), 52.0 (s, **2**, 12%).

[4-*tert*-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]bis(trimethylsilyl)methylplumbylene (5): LiCH(SiMe₃)₂ (0.181 g, 1.09 mmol) was added portionwise, at –78 °C, to a suspension of [4-*tert*-butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (0.679 g, 1.05 mmol) in THF (50 mL). After the reaction mixture had been stirred for 16 h (–78 to –30 °C), it was filtered. Evaporation of the solvent then afforded 0.20 g (25%) of **5** as a pale yellow oil. ¹H

NMR (400.13 MHz, C₆D₆): δ = –0.60 [s, 1 H, CH(SiMe₃)₂], 0.39 (s, 18 H, SiMe₃), 0.95 (t, 6 H, CH₃), 1.16 (s, 9 H, CH₃), 1.20 (t, 6 H, CH₃), 3.66–3.76 (complex pattern, 2 H, CH₂), 3.83–3.93 (complex pattern, 2 H, CH₂), 4.07–4.24 (complex pattern, 4 H, CH₂), 8.10 (complex pattern, 2 H, aromatics) ppm. ¹³C{¹H} NMR (100.61 MHz, C₆D₆): δ = 5.4 (s, 6 C, SiMe₃), 16.3 (complex pattern, 2 C, CH₃), 16.5 (complex pattern, 2 C, CH₃), 31.1 (s, 3 C, CH₃), 34.7 (s, 1 C, C), 62.3 (complex pattern, CH₂), 62.9 [s, 1 C, C(H)(SiMe₃)₂], 134.4 (dd, ²J_{C,P} = 17, ⁴J_{C,P} = 5 Hz, 2 C, C-3,5), 135.8 (dd, ¹J_{C,P} = 198, ³J_{C,P} = 25 Hz, 2 C, C-2,6), 149.0 (t, ³J_{C,P} = 13 Hz, 1 C, C-4), 231.8 (t, ²J_{C,P} = 37 Hz, 1 C, C-1) ppm. ³¹P{¹H} NMR (161.98 MHz, C₆D₆): δ = 42.1 (s, J_{P,Pb} = 125 Hz) ppm. ²⁰⁷Pb{¹H} NMR (83.72 MHz, C₆D₆): δ = 6874 (t, J_{P,Pb} = 129 Hz) ppm. IR (KBr): ν̄(P=O) = 1208 cm⁻¹. MS: m/z (%) = 613 (48) [M – C(H)(SiMe₃)₂], 406 (39) [M – C(H)(SiMe₃)₂ – Pb].

[[5-*t*-Bu-1,3-[P(O)(OEt)₂]₂C₆H₃]₄(Pb₂F)] [PF₆]₃·4THF (6): [4-*tert*-butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (0.107 g, 0.165 mmol) was added portionwise, at –78 °C, to a solution of TIPF₆ (0.055 g, 0.157 mmol) in THF (20 mL). The reaction mixture was then stirred at –78 °C under exclusion of light for 140 min. After storage at –35 °C for 5 d, the suspension was characterized by ³¹P NMR spectroscopy. ³¹P{¹H} NMR (81.02 MHz, D₂O capillary): δ = 18.0 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 27%], 54.1 (s, 73%). After the suspension had been filtered through a diatomaceous earth filter, the solution was once more characterized by ³¹P NMR spectroscopy. ³¹P{¹H} NMR (161.98 MHz, D₂O capillary): δ = 17.9 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 88%], 54.0 (s, 12%). Crystallization at –35 °C afforded 0.13 g (29%) of **6** as colorless crystals. ¹H NMR (400.13 MHz, C₆D₆): δ = 1.14 (s, 9 H, CH₃), 1.17 (t, 12 H, CH₃), 1.45 (m, 4 H, THF), 3.61 (m, 4 H, THF), 4.10–4.26 (complex pattern, 8 H, CH₂), 8.20 (d, 2 H, aromatics), 8.81 (t, 1 H, aromatics) ppm. ³¹P{¹H} NMR (161.98 MHz, C₆D₆): δ = 18.8 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene], –142.3 (PF₆[–]) ppm. IR (KBr, inert): ν̄(P=O) = 1197 cm⁻¹, ν̄(OH) not observed. ESMS: m/z = 1039 [Pb + F + 2 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene]⁺; 713 [Pb + 3 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene]²⁺; 510 [2 Pb + 4 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene]⁴⁺; 407 [1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene + H]⁺. Elemental analysis and the melting point of **6** were obtained after THF had been removed under reduced pressure (11 Torr). C₇₂H₁₂₈F₁₉O₂₄P₁₁Pb₂ (2493.9): calcd. C 34.6, H 5.2; found C 34.2, H 5.0.

The ¹H, ¹³C, and ³¹P NMR spectra of compound **4** and the ¹H, ¹³C, ³¹P, and ²⁰⁷Pb NMR spectra of compound **5** are available.^[2]

X-ray Crystallographic Study: Intensity data for the colorless crystals were collected with a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α (0.71073 Å) radiation at 173(1) K. The data collection covered almost the whole sphere of the reciprocal space with 3 collections at different *k* angles with 244 (2), 305 (3), and 260 (6) frames via *w* rotation (Δ/ω = 1°) at two times 15 s (2), 20 s (3), and 30 s (6) per frame. The crystal-to-detector distance was 3.4 cm. Crystal decay was monitored by repeating the initial frames at the end of the data collection. Analysis of the duplicate reflections revealed no indication of any decay. The structure was solved by direct methods SHELXS-97^[63] and successive difference Fourier syntheses. Refinement was applied with full-matrix least-squares methods SHELXL-97.^[64] H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 for non-methyl and at 1.5 for methyl groups times U_{eq} of the carrier C atom. In **3** a disordered ethoxy group was found with occupancies of 0.6 [C(14)] and 0.4 [C(14')]. In **6**

the *tert*-butyl and the ethoxy groups are disordered over two sites with occupancies of 0.4 [C(27'), C(28'), C(29')], 0.5 [O(3'), O(3''), O(4'), O(4''), C(34), C(35), C(36), C(37), C(38), O(3'A), O(3''A), O(4'A), O(4''A), C(34'), C(35'), C(36'), C(37'), C(38')] and 0.6 [C(27), C(28), C(29)]. The disordered groups, one solvent molecule [O(71) to C(75)], C(16), C(30), C(31), C(32) and C(33) were refined isotropically whereas C(73), C(74), C(73'), C(73'') are disordered over two positions with an occupancy of 0.5. All solvent molecules were refined with an occupancy of 0.5 except for the disordered atoms. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the International Tables for X-ray Crystallography.^[65] The figures were created by SHELXTL.^[66] Crystallographic data are given in Table 2, selected bond lengths and angles for **2** and **3** in Table 1, and for **6** in Table 3. CCDC-205058 (**2**), -205059 (**3**), and -205060 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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