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

Klaus Jurkschat,*[a] Katja Peveling,[a] and Markus Schürmann[a]

Dedicated to Professor Jaroslaw 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)$_2$]$_2$C$_6$H$_2$}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*Pr$_2$NLi, and lithium bis(trimethylsilyl)methane, (Me$_3$Si)$_2$CHLi, respectively, to provide in situ the corresponding organolead(II) compounds {4-*t*Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}PbX (**4**, X = *i*Pr$_2$N; **5**, X = (Me$_3$Si)$_2$CH], which were identified by NMR spectroscopy but could not be obtained as analytically pure substances. Attempts to isolate the intramolecularly coordinated organolead(II) hexafluorophosphate {4-*t*Bu-2,6-[P(O)-(OEt)$_2$]$_2$C$_6$H$_2$}Pb$^+$PF$_6^-$ from the reaction of **2** with TlPF$_6$ also failed. Instead, the unprecedented salt [{5-*t*Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$}$_4$·(Pb$_2$F)] [PF$_6$]$_3$·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.

Introduction

Most of the extensive research on the chemistry of the heavier group-14 element carbene analogues ER$_2$ (E = Si, Ge, Sn, Pb; R = alkyl, aryl, alkoxide, thiolate, diorganoamide)[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 plumbylenes {R = 2,6-[2,4,6-(*i*Pr)$_3$C$_6$H$_2$]$_2$C$_6$H$_3$, C(SiMe$_3$)$_3$, C(SiMe$_3$)$_2$-(SiMe$_2$OMe), N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$, C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), C(SiMe$_2$Ph)$_3$, 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)$_2$]$_2$C$_6$H$_3$ (**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)$_2$]$_2$C$_6$H$_2$}Li (**1**)[47] reacts with PbCl$_2$ to give the heteroleptic plumbylene {4-*t*Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}PbCl (**2**) as colorless crystals in good yield [Equation (1)].

1 **2**

(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.

[a] Lehrstuhl für Anorganische Chemie II der Universität Dortmund,
44221 Dortmund, Germany
Fax: (internat.) + 49-231/7555048
E-mail: kjur@platon.chemie.uni-dortmund.de

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On contact with air and moisture, it slowly decomposes to give the protonated ligand **A** ($\delta^{31}P$ = 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.

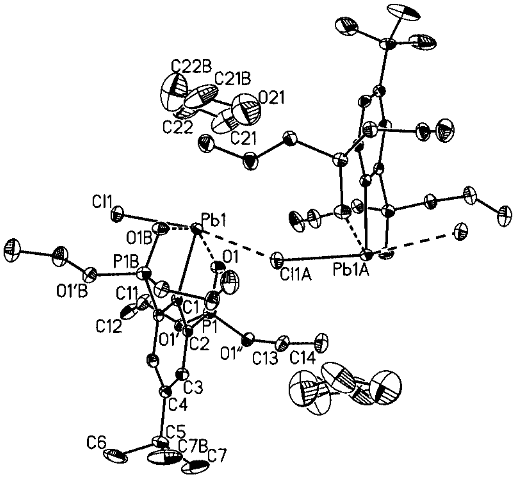


Figure 1. General view (SHELXTL) of two molecular units of **2**·THF showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: *a* = −0.5 + *x*, *y*, −0.5 − *z*; *b* = *x*, 0.5 − *y*, *z*; *c* = 0.5 + *x*, *y*, −0.5 − *z*)

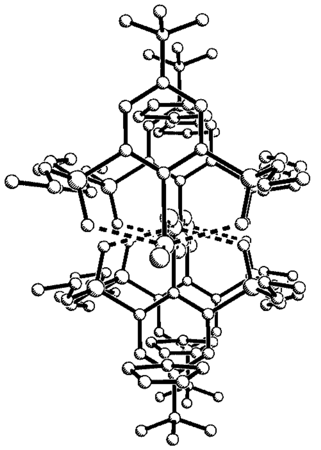


Figure 2. View along the Pb−Cl axis of **2**·THF

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)

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 plumbylenes $[C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2]PbCl$,[43] $[\{2,6\text{-}[2,4,6\text{-}(iPr)_3C_6H_2]_2C_6H_3\}PbBr]_2$,[31] $[(PhMe_2Si)_3CPbCl]_2$,[32,33] $\{[C(SiMe_3)_2(SiMe_2OMe)]PbCl\}_2$,[33] $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]PbCl\}_2$,[42] and $[(Me_3Si)_3CPbCl]_3$[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 (ΔPb−Cl 0.106 Å, Pb(1)−Cl(1)−Pb(1A) 155.96(6)°]. The Pb(1)−Cl(1) and Pb(1)···Cl(1A) distances of 2.795(1) and 2.901(1) Å, respectively, are in the range found in other monoorganoplumbylenes such as $[(PhMe_2Si)_3CPbCl]_2$ [Pb−Cl = 2.729(3) Å, Pb···Cl′ = 2.962(3) Å],[32,33] $[(Me_3Si)_3CPbCl]_3$ [Pb−Cl = 2.71(2) Å, 2.73(1) Å, 2.74(1) Å],[33] $\{[C(SiMe_3)_2(SiMe_2OMe)]PbCl\}_2$ [Pb−Cl = 2.680(5) Å, Pb···Cl′ = 2.868(5) Å],[33] $\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]PbCl\}_2$ [Pb−Cl = 2.609(3) Å, Pb···Cl′ = 3.276(3) Å],[42] and $[C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2]PbCl$ [Pb−Cl = 2.647(3) Å].[43] The organic substituents at adjacent lead atoms in the heteroleptic plumbylene **2** are staggered with C(1)−Pb(1)···Pb(1A)−C(1A) = 180.0°.

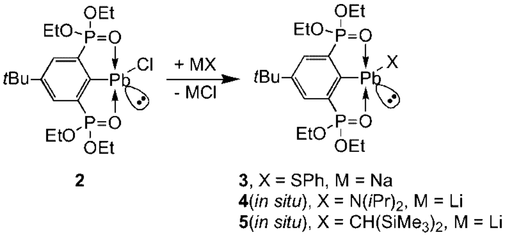
Table 2. Crystallographic data for **2**·THF, **3**, and **6**·THF

	2·THF	**3**	**6**
Empirical formula	$C_{22}H_{39}ClO_7P_2Pb$	$C_{24}H_{36}O_6P_2PbS$	$C_{88}H_{160}F_{19}O_{28}P_{11}Pb_2$
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	*Pnma*	$P2_1/n$	$C2/c$
a [Å]	11.0907(2)	14.0353(3)	36.1419(5)
b [Å]	16.3289(4)	10.5415(2)	18.3134(3)
c, [Å]	15.6283(4)	19.6993(5)	26.1390(5)
β [°]	90	99.9054(8)	127.2822(7)
V [Å^3]	2830.3(1)	2871.1(1)	13765.7(4)
Z	4	4	4
$\rho_{calcd.}$ [g/m^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
F(000)	1424	1424	5648
θ range [°]	3.19 to 27.47	2.95 to 27.45	2.96 to 27.46
Index ranges	$-14 \le h \le 14$ $-21 \le k \le 21$ $-20 \le l \le 20$	$-18 \le h \le 18$ $-13 \le k \le 13$ $-25 \le l \le 25$	$-46 \le h \le 46$ $-23 \le k \le 23$ $-33 \le l \le 26$
No. of reflns. collected	21665	27814	55752
Completeness to θ_{max}	99.8%	99.6%	98.6%
No. of independent reflns./R_{int}	3349/0.042	6531/0.053	15542/0.043
No. of reflns. obsd. with [$I > 2\sigma(I)$]	1996	3517	6078
No. of refined parameters	160	316	704
GooF (F^2)	0.915	0.598	0.812
$R1$ (F) [$I > 2\sigma(I)$]	0.0232	0.0248	0.0489
$wR2$ (F^2) (all data)	0.0455	0.0353	0.1273
$(\Delta/\sigma)_{max}$	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)(O*i*Pr)$_2$]$_2$-C_6H_2}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)$_2$]$_2$C$_6$H$_2$}PbPh$_3$.[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)$_2$]$_2$C$_6$H$_2$}$^-$ (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-[Ph$_2$P(O)CH$_2$]C$_6$H$_4$S}$_2$Pb.[53] The IR spectrum of **2** shows a band at $\tilde{\nu}$(P=O) = 1201 cm^{-1} which is similar to that for the related stannylene {4-*t*Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnCl [$\tilde{\nu}$(P=O) = 1192 cm^{-1}].[51]

The singlet at δ = 52.0 [$J(^{207}Pb-^{31}P)$ = 127 Hz] ppm in the ^{31}P NMR (C$_6$D$_6$) 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)$_2$]$_2$C$_6$H$_2$}SnCl (in [D$_8$]toluene: δ = 39.1 ppm).[51] The solid-state ^{31}P NMR spectrum shows a broad resonance at δ = 54.5 ppm. No ^{207}Pb NMR chemical shift could be obtained, which accords with reported problems in recording ^{207}Pb NMR spectra of [(PhMe$_2$Si)$_3$CPbCl]$_2$,[32,33] [(Me$_3$Si)$_3$CPbCl]$_3$,[33] [{2,6-[2,4,6-(*i*Pr)$_3$C$_6$H$_2$]$_2$C$_6$H$_3$}PbBr]$_2$,[31] and [{2,6-[2,4,6-(*i*Pr)$_3$C$_6$H$_2$]$_2$C$_6$H$_3$}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).



2

3, X = SPh, M = Na
4(*in situ*), X = N(*i*Pr)$_2$, M = Li
5(*in situ*), X = CH(SiMe$_3$)$_2$, M = Li

Scheme 1

The molecular structure of compound **3** (Figures 3 and 4), selected geometrical data (Table 1), and relevant crystallographic 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 [ΔPb−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-[$(Me_3Si)_2CH]_3C_6H_2$}Pb{2,4,6-[$(Me_3Si)_2CH]_3C_6H_2S$},[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 ^{31}P NMR spectrum by two resonances at $\delta = 50.4$ and 45.0 ppm. The IR spectrum, however, is not sensitive enough to distinguish the two phosphonyl groups and shows only one band at $\tilde{\nu}$(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-[$P(O)(OiPr)_2]_2C_6H_2$}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-($iPr)_2C_6H_2$}S]$_2$Pb)$_3$ [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 $_\infty$[$(S_2PPh_2)_2Pb$] (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.

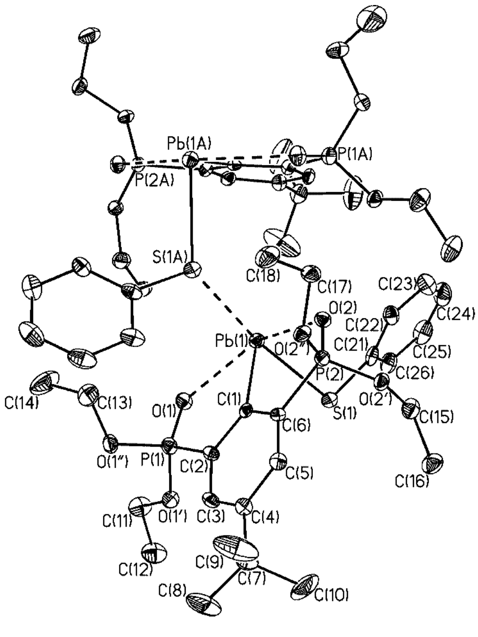


Figure 3. General view (SHELXTL) of two molecular units of **3** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -0.5 - x, -0.5 + y, 0.5 - z$)

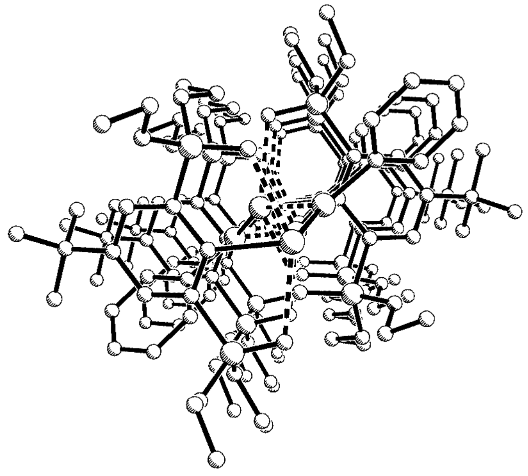


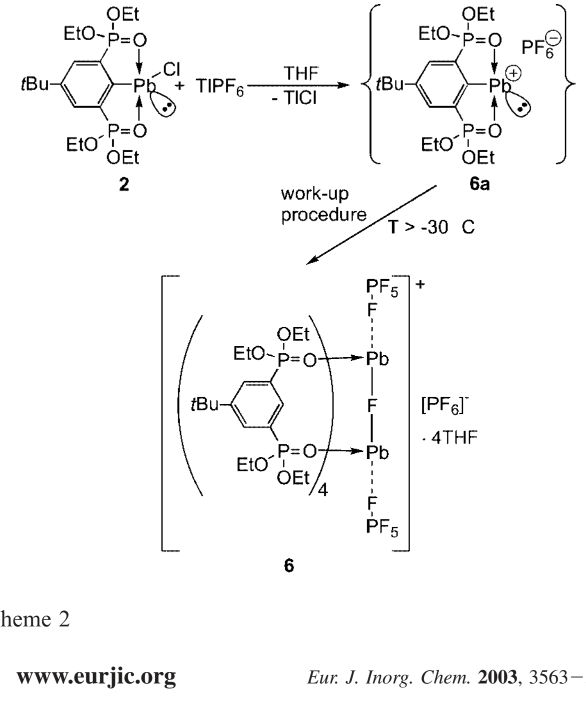
Figure 4. View along the Pb−S axis of **3**

Osmometric molecular weight determinations in THF showed that plumbylenes **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 plumbylenes {4-*t*Bu-2,6-[$P(O)(OEt)_2]_2C_6H_2$}PbN*i*Pr$_2$ (**4**) and {4-*t*Bu-2,6-[$P(O)(OEt)_2]_2C_6H_2$}PbCH$(SiMe_3)_2$ (**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 ^{207}Pb NMR chemical shift of **5** could be determined {δ = 6874 [$J(^{207}Pb-^{31}P)$ = 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-[$P(O)(OEt)_2]_2C_6H_2$}Pb]$^+$ PF_6^- (**6a**), compound **2** was treated with TlPF$_6$ in THF at −78 °C (Scheme 2). The ^{31}P



Scheme 2

NMR spectrum of the crude reaction mixture showed signals (a) at δ = 18.0 (integral 27%, assigned to 5-*t*Bu-1,3-$[P(O)(OEt)_2]_2C_6H_3$) ppm and (b) at δ = 54.1 [$J(^{31}P\text{-}^{207}Pb)$ = 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-*t*Bu-1,3-$[P(O)(OEt)_2]_2C_6H_3\}_4\cdot(Pb_2F)] [PF_6]_3\cdot 4THF$ (**6**) were obtained.

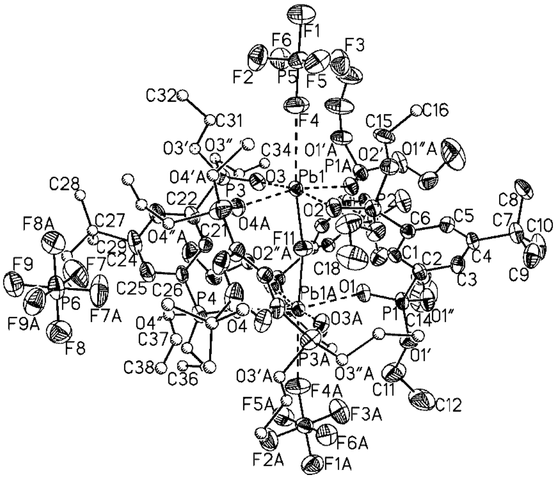


Figure 5. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $-x$, y, $0.5 - z$)

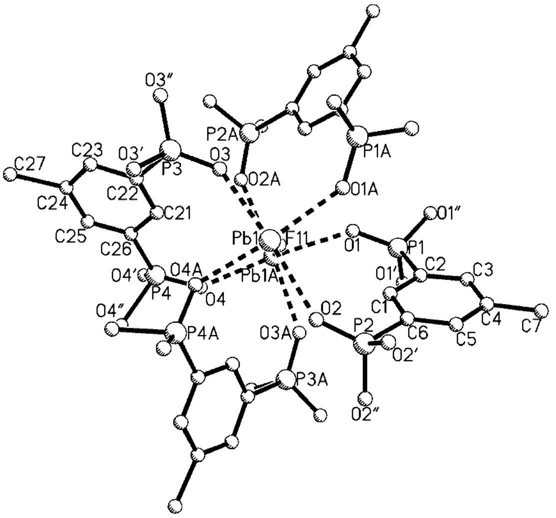


Figure 6. View along the Pb−F−Pb axis of **6**; methyl and ethyl groups, as well as THF and PF_6^-, are omitted for clarity

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 $[(Pb-F-Pb)]^{3+}$ cation stabilized by eight intermolecular P=O→Pb coordinations of four 5-*t*Bu-1,3-$[P(O)(OEt)_2]_2C_6H_3$ molecules, three $[PF_6]^-$ anions, and four THF molecules. The cationic part of the structure has an axis of improper rotation. The three $[PF_6]^-$ anions are crystallographically non-equivalent. Two symmetry-related ones (P5/P5A) show a Pb(1)···F(4) distance of 3.075(5) Å whereas the third one (P6) is far from the lead atoms [Pb(1)···F(7) 8.437(6) Å]. The Pb(1)−F(11) distance of 2.2762(7) Å is rather short compared with Pb−F in α-PbF_2 [2.418(2), 2.439(8) Å][58] and β-PbF_2 (2.573 Å).[59] Lead−fluorine distances of 3.04(6) and 3.30 Å have been

Table 3. Selected bond lengths [Å], bond angles [°], and torsion angles [°] 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)

reported for $Pb(dhfa)_2$ [Hdhfa = 1,5-bis(undecafluorocyclohexyl)pentane-2,4-dione][60] and bis(2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionato)lead,[61] respectively. The lead atom exhibits a distorted octahedral configuration with four P=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 $\{(Pb + F + 2\ (5\text{-}t\text{Bu-1,3-}[P(O)(OEt)_2]_2C_6H_3)\}^+$. The IR spectrum (KBr pellet) of **6** shows a band at $\tilde{\nu}(P{=}O) = 1197\ cm^{-1}$, indicating strong P=O→Pb coordination. The ^1H and ^{31}P NMR spectra of **6** exclusively show signals corresponding to the protonated ligand $5\text{-}t\text{Bu-1,3-}[P(O)(OEt)_2]_2C_6H_3$ (**A**), THF, and PF_6^- anion.

Conclusion

We have demonstrated the capacity of the phosphorus-containing O,C,O-coordinating ligand $4\text{-}t\text{Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2^-$ 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 $[(Sn{-}F{-}Sn)\cdot 4Ph_3PO]^{3+}$ 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 benzil. 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 $1\cdot 10^{-4}\ mol\cdot L^{-1}$. The sample was then introduced via a syringe pump operating at 10 µL 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. $\{4\text{-}t\text{Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}Li$ (**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): δ = 1.08 (t, 12 H, CH_3), 1.13 (s, 9 H, CH_3), 4.02−4.17 ($\nu_{1/2}$ = 32 Hz, 4 H, CH_2), 4.17−4.33 ($\nu_{1/2}$ = 36 Hz, 4 H, CH_2), 8.29 (complex pattern, 2 H, aromatics) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6): δ = 16.4 (d, $^3J_{C,P}$ = 6 Hz, 4 C, CH_3), 31.0 (s, 3 C, CH_3), 34.9 (s, 1 C, C), 63.3 ($\nu_{1/2}$ = 23 Hz, 4 C, CH_2), 135.1 (dd, $^1J_{C,P}$ = 196, $^3J_{C,P}$ = 24 Hz, 2 C, C-2,6), 135.7 (dd, $^2J_{C,P}$ = 16, $^4J_{C,P}$ = 5 Hz, 2 C, C-3,5), 150.1 (t, $^3J_{C,P}$ = 12 Hz, 1 C, C-4), 250.7 (t, $^2J_{C,P}$ = 35 Hz, 1 C, C-1) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ = 52.0 (s, $J_{P,Pb}$ = 127, $^1J_{C,P}$ = 196 Hz ppm. $^{31}P\{^1H\}$ MAS NMR (161.98 MHz): δ = 54.6 ppm. IR (KBr): $\tilde{\nu}(P{=}O)$ = 1201, 1179 cm^{-1}. UV/Vis (CH_3CN): λ = 217 nm, ε = 25309 $L\cdot mol^{-1}\cdot cm^{-1}$; λ = 279 nm, ε = 3122 $L\cdot mol^{-1}\cdot cm^{-1}$; λ = 286 nm, ε = 3039 $L\cdot mol^{-1}\cdot cm^{-1}$. Molecular weight determination (THF, 28 °C, *c* = 0.0147 $mol\cdot L^{-1}$): 602.0 g mol^{-1}. $C_{18}H_{31}ClO_6P_2Pb$ (648.0): calcd. C 33.4, H 4.8; found C 33.4, H 4.8. MS: *m*/*z* (%) = 647 (45) [M − H], 612 (88) [M − Cl − H], 539 (52) [M − Cl − OEt − 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 d and t_2 = 41 d, respectively, representative portions were dissolved in C_6D_6 and analysed by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, t_1): δ = 19.0 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 10%], 52.5 (s, $J_{P,Pb}$ = 128 Hz, **2**, 90%) ppm; $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, t_2): δ = 19.0 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 99%], 52.5 (s, $J_{P,Pb}$ = 128 Hz, **2**, 1%) ppm. **B:** [4-*tert*-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]chloroplumbylene (**2**) (10 mg, $1.5\cdot 10^{-5}$ mol) in C_6D_6 (0.4 mL) was sealed under inert conditions in an NMR tube at 65 °C for t_3 = 41 d. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, t_3): δ = 19.0 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene, 6%], 52.5 (s, $J_{P,Pb}$ = 128 Hz, **2**, 94%) ppm.

[4-*tert*-Butyl-2,6-bis(diethoxyphosphonyl)phenyl]thiophenolatoplumbylene (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, $[D_8]$thf): δ = 1.26 (t, 6 H, CH_3), 1.31 (t, 6 H, CH_3), 1.36 (s, 9 H,

CH_3), 4.02−4.23 (complex pattern, 6 H, CH_2), 4.28−4.40 (complex pattern, 2 H, CH_2), 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. $^{13}C\{^1H\}$ NMR (100.61 MHz, [D$_8$]thf): δ = 17.7 (d, $^3J_{C,P}$ = 6 Hz, 2 C, CH_3), 17.8 (d, $^3J_{C,P}$ = 6 Hz, 2 C, CH_3), 32.4 (s, 3 C, CH_3), 36.6 (s, 1 C, C), 63.9 (d, $^2J_{C,P}$ = 6 Hz, 2 C, CH_2), 65.0 (d, $^2J_{C,P}$ = 4 Hz, 2 C, CH_2), 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. $^{31}P\{^1H\}$ NMR (161.98 MHz, [D$_8$]thf): δ = 47.8 (s, $J_{P,Pb}$ = 123 Hz) ppm. $^{31}P\{^1H\}$ MAS NMR (161.98 MHz): δ = 45.5, 50.4 ppm. IR (KBr): ṽ(P=O) = 1208, 1183 cm^{-1}. UV/Vis (CH_3CN): 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}. $C_{24}H_{36}O_6P_2PbS$ (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 iPr$_2$NLi 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. $PbCl_2$ (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** (δ^{31}P = 52.0 ppm, 5%) and 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene (δ^{31}P = 18.4 ppm, 12%). ^1H NMR (400.13 MHz, C_6D_6): δ = 0.98 (t, 6 H, CH_3), 1.13 (s, 9 H, CH_3), 1.22 (t, 6 H, CH_3), 1.53 [s, 6 H, C(H)$(CH_3)_2$], 1.55 [s, 6 H, C(H)$(CH_3)_2$], 3.68−3.79 (complex pattern, 2 H, CH_2), 3.86−3.97 (complex pattern, 2 H, CH_2), 4.17−4.34 (complex pattern, 4 H, CH_2), 5.12−5.28 (sept, 2 H, CH), 8.20 (complex pattern, 2 H, aromatics) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6): δ = 16.4 (complex pattern, $^3J_{C,P}$ = 7 Hz, 4 C, CH_3), 30.1 [s, 3 C, C$(CH_3)_3$], 31.0 [s, 4 C, C(H)$(CH_3)_2$], 34.7 (s, 1 C, C), 53.7 (s, 2 C, CH), 62.1 (d, 2 C, $^2J_{C,P}$ = 5 Hz, CH_2), 62.3 (d, 2 C, $^2J_{C,P}$ = 6 Hz, CH_2), 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. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ = 41.7 (s, $J_{P,Pb}$ = 116 Hz) ppm. IR (KBr): ṽ(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 ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (81.02 MHz, D_2O 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)]methyl}plumbylene (5): LiCH$(SiMe_3)_2$ (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, C_6D_6): δ = −0.60 [s, 1 H, CH$(SiMe_3)_2$], 0.39 (s, 18 H, $SiMe_3$), 0.95 (t, 6 H, CH_3), 1.16 (s, 9 H, CH_3), 1.20 (t, 6 H, CH_3), 3.66−3.76 (complex pattern, 2 H, CH_2), 3.83−3.93 (complex pattern, 2 H, CH_2), 4.07−4.24 (complex pattern, 4 H, CH_2), 8.10 (complex pattern, 2 H, aromatics) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6): δ = 5.4 (s, 6 C, $SiMe_3$), 16.3 (complex pattern, 2 C, CH_3), 16.5 (complex pattern, 2 C, CH_3), 31.1 (s, 3 C, CH_3), 34.7 (s, 1 C, C), 62.3 (complex pattern, CH_2), 62.9 [s, 1 C, C(H)$(SiMe_3)_2$], 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. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ = 42.1 (s, $J_{P,Pb}$ = 125 Hz) ppm. $^{207}Pb\{^1H\}$ NMR (83.72 MHz, C_6D_6): δ = 6874 (t, $J_{P,Pb}$ = 129 Hz) ppm. IR (KBr): ṽ(P=O) = 1208 cm^{-1}. MS: m/z (%) = 613 (48) [M − C(H)$(SiMe_3)_2$], 406 (39) [M − C(H)$(SiMe_3)_2$ − Pb].

[{5-*t*Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$}$_4$·(Pb$_2$F)] [PF$_6$]$_3$·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 $TlPF_6$ (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 ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (81.02 MHz, D_2O 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 ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR (161.98 MHz, D_2O 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, C_6D_6): δ = 1.14 (s, 9 H, CH_3), 1.17 (t, 12 H, CH_3), 1.45 (m, 4 H, THF), 3.61 (m, 4 H, THF), 4.10−4.26 (complex pattern, 8 H, CH_2), 8.20 (d, 2 H, aromatics), 8.81 (t, 1 H, aromatics) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ = 18.8 [s, 1-*tert*-butyl-3,5-bis(diethoxyphosphonyl)benzene], −142.3 (PF_6^-) ppm. IR (KBr, inert): ṽ(P=O) = 1197 cm^{-1}, ṽ(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). $C_{72}H_{128}F_{19}O_{24}P_{11}Pb_2$ (2493.9): calcd. C 34.6, H 5.2; found C 34.2, H 5.0.

The ^1H, ^{13}C, and ^{31}P NMR spectra of compound **4** and the ^1H, ^{13}C, ^{31}P, and ^{207}Pb 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/conts/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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