Tri(*tert*-butyl)plumbyl-phosphanes, Synthesis and Multinuclear Magnetic Resonance

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Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

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Lead, Phosphorus, Triorganoplumbyl Compounds

The reaction of tri(*tert*-butyl)plumbyl-lithium (1) with various phosphorus chlorides was studied. With diphenyl- and amino(phenyl)phosphorus chlorides the formation of hexa(*tert*-butyl)diplumbane (2) and tetraphenyldiphosphane (3) or the respective 1,2-bis(amino)-1,2-diphenyl-diphosphanes [e. g. 5: amino = PhCH₂(^{*T*}Bu)N] was dominant. The presence of at least one *tert*-butyl group at the phosphorus atom gave access to tri(*tert*-butyl)plumbyl-di(*tert*-butyl)phosphanes (4) and to tri(*tert*-butyl)plumbyl-amino(*tert*-butyl)phosphanes [amino = ^{*T*}Bu(H)N (6), Me(Ph)N (7), PhCH₂(Me)N (8), PhCH₂(^{*T*}Bu)N (9)] via the reaction of 1 with the corresponding phosphorus chlorides. Side products were again 2 and the corresponding diphosphanes [*nu*(H)N(^{*T*}Bu)P (10), Me(Ph)N(^{*T*}Bu)P (11)]. Trimethylplumbyl-benzyl(methyl)-amino(*tert*-butyl)phosphane (12) was prepared for comparison. All compounds were characterized by their ¹H, ¹³C, ¹⁵N (9), ³¹P and ²⁰⁷Pb NMR data. The coupling constants ¹J(²⁰⁷Pb,³¹P) are large and negative, whereas the coupling constants ¹J(²⁰⁷Pb,¹³C) are small and can be of either sign. The coupling constants ²J(³¹P-N-¹³C) of **6** - **12** indicate a preferred conformation of the substituents at phosphorus and nitrogen.

Introduction

Results and Discussion

Lead-phosphorus compounds are of interest because of their labile Pb-P bond which may readily be cleaved either homo- or heterolytically, depending on the reaction conditions. However, only very few plumbyl-phosphanes, $R_3Pb-PR_2^1$ (e. g., R =Me, Ph; $R^1 = Ph$) are known. They have been prepared either by the reaction of triphenyllead chloride with diphenylphosphane in the presence of triethylamine [1], by treatment of triorganolead chlorides with lithium phosphides [2], or by the reaction of trimethylplumbyl-diethylamine with diphenylphosphane [3, 4]. We now report on the reaction of trialkylplumbyl-lithium with phosphorus halides, focusing mainly on tri(tert-butyl)plumbyl-lithium (1) [5], as a new route to plumbyl-phosphanes. Attempts were also made to prepare hitherto unknown trialkylplumbyl-amino(organo)phosphanes. This work continues a systematic study of tri(tertbutyl)plumbyl-element compounds with respect to their synthesis and NMR spectroscopic properties [5 - 7].

Syntheses

Trialkylplumbyl-diorganophosphanes

The reaction of tri(tert-butyl)plumbyl-lithium (1) with diphenylphosphorus chloride did not lead to the desired lead-phosphorus compound but gave hexa(tert-butyl)diplumbane (2) and tetraphenyldiphosphane (3) instead (Scheme 1(a)). A similar result was obtained when tri(tertbutyl)plumbyl iodide was reacted with lithium diphenylphosphide (Scheme 1(b)). In the case of the latter reaction, *tert*-butyl(diphenyl)phosphane was detected as a further product. Therefore, it appears that the diplumbane and the diphosphane are more stable than the corresponding plumbylphosphane. However, in the presence of bulky tertbutyl groups at the phosphorus atom, tri(tert-butyl)plumbyl-di(tert-butyl)phosphane (4) was obtained (Scheme 1(c)), whereas 2 and tetra(tert-butyl)diphosphane were only formed as minor products (5 - 20%).

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Scheme 1.

In order to compare NMR data, we tried to prepare trimethylplumbyl-di(*tert*-butyl)phosphane, Me₃Pb-P'Bu₂. These experiments were not successful, neither by reacting Me₃PbLi [8] with Cl-P'Bu₂ nor by treating Me₃PbBr with 'Bu₂PH/NEt₃ or LiP'Bu₂.

Trialkylplumbyl-amino(organo)phosphanes

As shown for diphenylphosphorus chloride (Scheme 1(a)), the reaction of amino(phenyl)phosphorus chlorides with tri(tert-butyl)plumbyllithium (1) did not afford the desired plumbylphosphanes. Instead, formation of the diplumbane 2 and of 1,2-bis(amino)diphenyldiphosphanes was observed, even in the presence of fairly bulky substituents at the nitrogen atom (Scheme 2). In most cases, mixtures containing numerous phosphorus compounds were formed (as monitored by ³¹P NMR). However, the reaction according to Scheme 2 gave 2 and the diphosphane 5 without an appreciable amount of other products. The ¹H, ¹³C and ³¹P NMR spectra indicate that the formation of the diphosphane 5 takes place in a diastereoselective way. Comparable diphosphanes, but in each case as the expected 1:1 mixture of diastereomers, have been prepared by reduction of the amino(organo)phosphorus chlorides with alkali metals [9].



Scheme 2.



Scheme 3.

 Me_{Ph} $h_{N} \rightarrow h_{N} \rightarrow h_$

Scheme 4.

By using amino(*tert*-butyl)phosphorus chlorides, the corresponding plumbyl-phosphanes 6 - 9 were obtained which are sufficiently stable in order to allow for their NMR spectroscopic characterisation. In the presence of less bulky substituents at the nitrogen atom, e.g. *tert*-butyl together with H, Me and Ph, or Me and CH₂Ph, other reactions dominate. Thus, **6** and **7** are formed together with the bis(phosphanyl)plumbane **10** and **11**, respectively, and also together with considerable amounts of **2** and the 1,2-bis(amino)-1,2-di(*tert*-butyl)diphosphanes. Some of these results are summarized in Scheme 3.

The trimethylplumbyl derivative **12**, the analogue of **8**, was prepared from Me_3PbLi and the corresponding phosphorus halide (Scheme 4). A small amount of tetramethyllead was found as a side product. Obviously, this reaction proceeds more cleanly than in the case of ${}^{t}Bu_3PbLi$, and formation of the diphosphane was not observed. Thus, it is primar-

T	able 1.	¹³ C,	³¹ P and	²⁰⁷ Pb NMI	λ data ^[a,b]	of tri(te	rt-butyl)p	olumbyl-pl	hosphanes 4	, 6 - 9 , bis	(phosphany	l)di(tert-but	tyl)-
p	lumbar	ne 11,	, and of	a trimethy	plumbyl-	phospha	ne 12 for	r comparis	son.				

Comp.	δ^{207} Pb [¹ <i>J</i> (²⁹⁷ Pb, ³¹ P)]	$\delta^{31} P$	$\delta^{13}C$ N(R)R ¹	δ^{13} CPC(CH ₃) ₃	δ^{13} C Pb[C(CH ₃) ₃] ₃
4	165.6 [-1951]	117.8	_	34.8 (-43.8),	56.3 [+42.5] (< 1),
6	47.0 [-1796]	112.4	53.5 (15.3), 33.1 (5.9) ^{<i>t</i>} Bu	35.4 (+13.6) 47.5 (2.0), 30.5 (17.4)	34.9 [+15.3] (1.5) 54.3 [+13.1], 24.5 [+12.6]
7	99.6 [-2029]	130.2	39.5 (+43.4) Me, 151.6 (< 2) Ph, 116.6 (6.5) <i>ortho</i> , 128.7 <i>meta</i> , 118.1 (1.9) <i>para</i>	48.9 (-11.4), 32.1 (+17.1)	54.3 [+12.0] 54.1 [+62.7] (1.5), 34.3 [+15.3] (1.1)
8 9 ^[c]	89.5 [–1983] 145.6 [–1971]	156.2 168.1	n.a. 58.7 (20.9), 29.5 (13.2) ^{t}Bu , 69.6 [11.4] (6.0) 144.7 ($<$ 1) CH ₂ Ph ^[d]	n.a. 47.8 (11.8), 31.5 (17.5)	n.a. 55.3 [-14.2], 34.7 [+17.4]
11 ^[e]	145.5 [–2070], 122.0 [–2061]	140.4, 139.8	40.4 (44.2), 40.4 (44.2) Me, n.a. Ph	48.0 (11.0), 31.9 (17.0), 47.5 (11.0), 32.3 (17.0)	57.1, 34.7 ^[f]
12	-99.3 [-1736]	124.8	45.0 (2.0) Me, 65.6 [27.1], 140.1 (6.4) CH ₂ Ph ^[g]	39.3 [35.0] (2.0), 30.0 [44.3] (17.2)	-0.3 Me ₃ Pb [+24.1] (3.5)

^[a] Measured in C₆D₆ at 25 ± 1 °C; coupling constants $J(^{207}\text{Pb}, ^{13}\text{C})$ (± 1 Hz) and $^{1}J(^{207}\text{Pb}, ^{31}\text{P})$ (± 2 Hz) are given in square brackets, and $J(^{31}\text{P}, ^{13}\text{C})$ (± 1 Hz) in parentheses; n.a. means not assigned due to overlap with signals of other compounds in the mixture; for ³¹P NMR data of **10** see Fig. 1. ^[b] If the sign of a coupling constant is given, it was experimentally determined at least for one example, and in the case of $^{1}J(^{207}\text{Pb}, ^{31}\text{P})$, all signs are alike because of the similar magnitude of all these coupling constants. ^[c] $\delta^{15}\text{N} - 326.5$; $^{1}J(^{31}\text{P}, ^{15}\text{N}) = 81.4$ Hz. ^[d] Other δ^{13} C data: 128.3 *ortho*, 128.6 *meta*, 126.7 *para*. ^[e] Mixture (1:1) of diastereomers. ^[f] ¹³C resonances are broadened; satellites corresponding to $J(^{207}\text{Pb}, ^{13}\text{C})$ cannot be assigned with certainty. ^[g] Other δ^{13} C data: 128.3 (1.3) *ortho*, 128.6 *meta*, 127.4 *para*.



Fig. 1. Part of the 101.3 MHz ³¹P{¹H} MMR spectrum of the reaction mixture containing 'Bu₃Pb-P('Bu)N(H)'Bu (6) $[\delta^{31}P \ 112.4, \ ^1J(^{207}Pb,^{31}P) = 1796$ Hz; satellites are marked by asterisks], the mixture of diastereomers 'Bu₂Pb[P('Bu)N(H)'Bu]₂ (10) $[\delta^{31}P \ 118.5, \ ^1J(^{207}Pb,^{31}P) = 1828$ Hz, and 106.9, $\ ^1J(^{207}Pb,^{31}P) = 1751$ Hz; satellites are marked by arrows], and 1,2bis(*tert*-butylamino)-1,2-di(*tert*-butyl)diphosphane ($\delta^{31}P$ 31.1; the signal is outside of the range shown here).

ily the bulkiness of the amino group which helps to stabilize the respective plumbyl-amino(organo)-

phosphane and not the presence of three *tert*-butyl groups at the lead atom as in **8**.

NMR spectroscopic results

¹³C, ³¹P and ²⁰⁷Pb NMR data are given in Table 1, ¹H NMR data are listed in the experimental section. Although it was not possible to isolate the plumbyl-phosphanes as pure compounds, their molecular structure in solution follows unambiguously from the consistent set of NMR data. The progress of the reactions was monitored by ³¹ P NMR, the formation of Pb-P bonds being indicated by the appearance of ²⁰⁷Pb satellites (Fig. 1). Complementary information was obtained from the signal for ${}^{t}Bu_{3}Pb-Pb^{t}Bu_{3}$ (2) $(\delta^{207}\text{Pb} = 335.1 \text{ [5]})$ and the splitting of other ²⁰⁷Pb NMR signals into the expected doublets due to ${}^{1}J({}^{207}\text{Pb}, {}^{31}\text{P})$ or, e. g. in the case of 7 and 10, into doublets and triplets, since the bis(phosphanyl)plumbane 10 is present as a 1:1 mixture of two diastereomers. The assignment of the ${}^{1}H$ and ${}^{13}C$ NMR signals was straightforward in most cases, except for 8 because of the numerous side products which could not be identified.

The δ^{207} Pb values of **4** and of **6** - **9** cover a range of about 120 ppm. Even the change of substituents

Table 2. Comparison of δ^{31} P values for plumbyl-phosphanes and corresponding phosphorus chlorides.

	6	7	8	9	12
δ^{31} P	112.4	130.2	156.2	168.1	124.8
δ^{31} P(P-Cl)	136.8	159.2	163.3	161.0	163.3
$\Delta^{31} \mathbf{P}^{[a]}$	-22.4	-29.0	-7.1	+7.1	-38.5
[a] $\Lambda^{31}\mathbf{P} = \delta^3$	${}^{31}P - \delta^{31}F$	P(P-C1)			

at the nitrogen atom, three bonds away from the lead atom, gives rise to a range of δ^{207} Pb data of about 100 ppm. This indicates that steric effects exerted by the bulky substituents at the phosphorus atom cause changes in the bond angles at the lead atom. It appears that smaller substituents at the nitrogen atom induce less ²⁹⁷Pb nuclear deshielding [e.g., compare δ^{207} Pb for **6** (47.0) with δ^{207} Pb for **9** (145.6)]. This is not necessarily reflected by the coupling constants ${}^{1}J({}^{207}\text{Pb},{}^{31}\text{P})$ since they are already large and negative, as expected for the influence of the lone pair of electrons at the phosphorus atom [10] and the readily polarisable Pb-P bonds [4]. This argument is supported by the small difference between the magnitude of ${}^{1}J({}^{207}\text{Pb},{}^{31}\text{P})$ of 8 (-1983 Hz) and the corresponding trimethylplumbyl derivative 12 (-1736 Hz), although the trend is in line with other examples of tri(tert-butyl)plumbyl and trimethylplumbyl-element compounds [5 - 7].

In principle, the effects which influence the δ^{207} Pb values should also affect the ³¹P chemical shifts. By comparison (Table 2) of the δ^{31} P data for the plumbyl-phosphanes with those of the corresponding phosphorus chlorides [δ^{31} P(P-Cl)], a marked shielding effect upon substituting the Cl-P by the Pb-P bond becomes apparent only for the less bulky P-amino groups or if the Me₃Pb group (**12**) is present instead of the 'Bu₃Pb group.

The coupling constant ${}^{1}J({}^{207}\text{Pb},{}^{13}\text{C})$ of ${}^{\prime}\text{Bu_3}\text{Pb}$ groups can become small, depending on the nature of the fourth substituent. So far, the only substituent which induces a change of the sign from positive to negative was the ${}^{\prime}\text{Bu_3}\text{Pb}$ group itself in 2 [5]. Here, we have determined a positive sign for this coupling constant in 4 (Fig. 2), 6 and 7. However in 9, where steric repulsion is at a maximum in this series, the sign of ${}^{1}J({}^{207}\text{Pb}, {}^{13}\text{C})$ changes to negative (Fig 3). Clearly, the simple model of rehybridisation [11] cannot be applied here in order to explain the trends of the ${}^{1}J({}^{207}\text{Pb}, {}^{13}\text{C})$ values. It should be noted that the information on the coupling sign is crucial, since



Fig. 2. Contour plot of the 62.9 MHz 2D ${}^{13}C/{}^{1}H$ HETCOR experiment for ${}^{7}Bu_{3}Pb-P'Bu_{2}$ (4), based on ${}^{2}J({}^{13}C,{}^{1}H) = 6.5$ Hz, showing the range of the Pb- ${}^{13}C({}^{7}Bu)$ resonance. The positive tilt of the cross peaks for the ${}^{207}Pb$ satellites indicates that ${}^{1}J({}^{207}Pb,{}^{13}C)$ and ${}^{3}J({}^{207}Pb,{}^{1}H)$ (> 0) have alike signs.



Fig. 3. Contour plot of the 62.9 MHz 2D ¹³C/¹H HETCOR experiment for ^{*t*}Bu₃Pb-P(^{*t*}Bu)N(^{*t*}Bu)CH₂Ph (**9**), based on ²J(¹³C, ¹H) = 6.5 Hz, showing the range of the Pb-C(^{*t*}Bu) resonance. The negative tilt of the cross peaks for the ²⁰⁷Pb satellites indicates that ¹J(²⁰⁷Pb, ¹³C) and ³J(²⁰⁷Pb, ¹H) (> 0) have opposite signs.

the values ${}^{1}J({}^{207}\text{Pb}, {}^{13}\text{C})$ of **6** and **9** are numerically almost identical but their sign is different. The positive sign of ${}^{1}J({}^{207}\text{Pb}, {}^{13}\text{C})$ of the Me₃Pb group in **12** is in agreement with the linear correlation between ${}^{2}J({}^{207}\text{Pb}, {}^{14}\text{M}_{\text{Me}})$ and ${}^{1}J({}^{207}\text{Pb}, {}^{13}\text{C}_{\text{Me}})$ [12].

Both sign and magnitude of the geminal coupling constants ${}^{2}J({}^{31}P-N-{}^{13}C)$ in aminophosphanes reveal the preferred conformation of the amino group with

Table 3. Comparison of coupling constants ${}^{2}J({}^{31}P-N-{}^{13}C)$ of plumbyl-phosphanes and ${}^{2}J({}^{31}P_{P-CI}-N-{}^{13}C)$ of the corresponding phosphorus chlorides^[a].

	6	7	11	9	12
${}^{2}J({}^{31}P-N-{}^{13}C)$ ${}^{2}J({}^{31}P_{P-Cl}-N-{}^{13}C)$	15.3 (^t BuN) +10.4 (^r BuN)	43.4 (MeN) < 1 (MeN) 18.5 (PhN)	44.2 (MeN) < 1 (MeN) 18.5 (PhN)	20.9 (^t BuN), 6.0 (-CH ₂ N) +20.2 (^t BuN) -7.0 (-CH ₂ N)	2.0 (MeN), 27.1 (-CH ₂ N) < 1 (MeN) +32.8 (-CH ₂ N)

^[a] The signs of the coupling constants ${}^{2}J({}^{31}P-N-{}^{13}C)$ of the phosphorus chlorides were experimentally determined [14].



Scheme 5.

respect to an axis representing the assumed orientation of the lone pair of electrons at the phosphorus atom (Scheme 5). Thus, a *syn*-orientation of the N-C bond with respect to the lone pair of electrons is reflected by a large and positive coupling constant ${}^{2}J({}^{31}\text{P-N-}{}^{13}\text{C})$, whereas this coupling constant is small and of either sign for the *anti*-orientation [13].

The amino(tert-butyl)phosphorus chlorides used in this work prefer a certain conformation as a result of steric crowding, indicated by the relative magnitude of the geminal coupling constants. Table 3 shows the comparison of ${}^{2}J({}^{31}P-N-{}^{13}C)$ for 6, 7, 9, 11, and 12 with those of the corresponding phosphorus chlorides $({}^{2}J({}^{31}P_{P-Cl}-N-{}^{13}C))$. With the exception of 7 and 11, the preferred conformation of the plumbyl-phosphanes can be assumed to be similar to that of the phosphorus chlorides. In the case of benzyl(tert-butyl)amino(tert-butyl)phosphorus chloride the molecular structure in the solid state [14] confirms the favoured conformation in which the tert-butyl groups at nitrogen and phosphorus avoid any contact and the N-^{*t*}Bu group is approximately in syn-position.

Experimental

All reactions were carried out in an inert atmosphere of Ar or N₂, using carefully dried solvents and ovendried glassware, and generally observing all necessary precautions to exclude moisture and oxygen. Starting materials such as the hexa(*tert*-butyl)diplumbane (2) and ^{1 Bu₃PbI [15] for the synthesis of ^{1 Bu₃PbLi [5],}}

Me₃PbLi [8] and the phosphorus halides, ¹Bu₂PCl [16], amino(phenyl)- and amino(tert-butyl)phosphorus chlorides [14] were prepared as described or obtained and used as commercial products [Ph2PCl, Ph2PH, BuLi (1.6 M in hexane)]. NMR spectra were recorded with Bruker ARX 250, AC 300 and DRX 500 spectrometers equipped with multinuclear units. The DRX 500, with three independent frequency channels, served for heteronuclear ${}^{13}C{}^{1}H, {}^{31}P{}$ triple resonance experiments in order to assign relevant ¹³C NMR signals in mixtures. Chemical shifts are given with respect to Me₄Si $[\delta^{1}H = 7.15 (C_{6}D_{5}H); 7.24 (CHCl_{3}/CDCl_{3}), \delta^{13}C =$ 128.0 (C₆D₆); 77.0 (CDCl₃)], external neat MeNO₂ [δ^{15} N = 0 for Ξ (¹⁵N) = 10.136767 MHz], external H₃PO₄ (85%, aq.) $[\delta^{31}P = 0 \text{ for } \Xi(^{31}P) = 40.480747 \text{ MHz}],$ and external neat Me₄Pb [δ^{207} Pb = 0 for Ξ (²⁰⁷Pb) = 20.920597 MHz].

Reaction of tri(tert-butyl)plumbyl-lithium (1) with diphenylphosphorus chloride

Tri(*tert*-butyl)plumbyl-lithium (1 mmol) was prepared from tri(*tert*-butyl)plumbyl iodide (0.505 g; 1 mmol) in THF [5], and diphenylphosphorus chloride (0.22 g, 1 mmol) was added in one portion at -50 °C. After warming to r. t., the ³¹P NMR spectra of the reaction mixture indicated the presence of tetraphenyldiphosphane (**3**) and of *tert*-butyl-diphenylphosphane, and the ²⁰⁷Pb NMR spectrum showed one signal at δ^{207} Pb = 335.1 for hexa-(*tert*-butyl)diplumbane (**2**). After removing all volatile material the residue was dissolved in 5 ml of hexane and filtered. Then hexane was removed *in vacuo* and C₆D₆ was added in order to record ¹³C NMR spectra.

3: ${}^{13}C{}^{1}H$ NMR (75.5 MHz, C₆D₆): δ ($J({}^{31}P, {}^{13}C)$) = 136.5 (10.6) (pseudo-t, C-*ipso*); 134.8 (26.0) (pseudo-t, C-*ortho*); 128.4 (22.0) (pseudo-t, C-*meta*); 128.4 (C-*para*). – ${}^{31}P{}^{1}H$ NMR (121.5 MHz, C₆D₆): δ = –13.7.

tert-Butyl-diphenylphosphane: ${}^{13}C{}^{1}H$ NMR (75.5 MHz, C₆D₆): δ ($J({}^{31}P, {}^{13}C)$) = 137.9 (20.0) (d, C-*ipso*); 135.0 (19.7) (d, C-*ortho*); 128.7(16.5) (d, C-*meta*); 128.4 (C-*para*); 30.8 (15.7) (d, CP); 28.9 (14.8) (d, CH₃-CP). – ${}^{31}P{}^{1}H$ NMR (121.5 MHz, C₆D₆): δ = 17.1.

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Reaction of tri(tert-butyl)plumbyl iodide with lithium diphenylphosphide

A suspension of lithium diphenylphosphide (0.19 g, 1 mmol) was freshly prepared from diphenylphosphane and *n*-butyl-lithium (1.6 M in hexane), and tri(*tert*-butyl)plumbyl iodide (0.505 g; 1 mmol) was added in one portion at -50 °C. After warming to r. t. and stirring for 3 h, the ³¹P- and ²⁰⁷Pb NMR spectra of the reaction mixture showed that tetraphenyldiphosphane (**3**) and hexa(*tert*-butyl)diplumbane (**2**) were present.

Tri(tert-butyl)plumbvl-di(tert-butyl)phosphane (4)

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra). 207 Pb and 31 P NMR spectra showed the presence of **2** and **3** as minor products (*ca.* 20%) in addition to tri(*tert*-butyl)plumbyl-di(*tert*-butyl)phosphane (**4**) (see Table 1 for 13 C, 31 P and 207 Pb NMR data).

4: ¹H NMR (300.13 MHz, C₆D₆): δ [J(²⁰⁷Pb, ¹H)] (J(³¹P, ¹H)) = 1.74 [96.3] (s, 27H, tBu₃Pb); 1.45(10.9) (d, 18H, ^tBu₂P).

Tetra(*tert*-butyl)diphosphane: ¹H NMR (300.13 MHz, C₆D₆): δ (*J*(³¹P, ¹H)) = 1.40 (12.3) (pseudo-t). – ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 41.0.

Reaction of tri(tert-butyl)plumbyl-lithium (1) with benzyl(tert-butyl)amino-(phenyl)phosphorus chloride

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra), and according to ²⁰⁷Pb and ³¹P NMR spectra of the reaction mixture the diplumbane (**2**) together with 1,2-bis[benzyl-(*tert*-butyl)amino]-1,2-diphenyldiphosphane (**5**) were the sole products.

5: ¹H NMR (300.13 MHz, C₆D₆): δ (J(³¹P, ¹H)) = 1.02 (s, 18H, ¹BuN); 3.65 (s, 4H, CH₂) 7.1 (m, 2H, H-para), 7.18 (m, 4H, H-meta); 7.34 (m, 4H, H-ortho). – ¹³C{¹H} NMR: δ (J(³¹P,¹³C)) = 56.3 (21.0) (pseudo-d, CN); 29.4 (s, CH₃-CN); 47.4 (s, CH₂N); Ph-C not assigned. – ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 16.4.

Tri(tert-butyl)plumbyl-tert-butylamino(tert-butyl)-phosphane (6)

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra), and led to a mixture of compounds containing **6**, **10** (see Figure 1), **2** and 1,2-bis(*tert*-butylamino)-1,2-di(*tert*-butyl)-diphosphane.

6: ¹H NMR (300.13 MHz, C₆D₆): δ [J(²⁰⁷Pb, ¹H)] (J(³¹P, ¹H)) = 1.69 [89.4] (s, 27H, ^{*t*}Bu₃Pb); 1.22 (13.0) (d, 9H, ^{*t*}BuP); 1.76(s, 9H, ^{*t*}BuN). 1,2-Bis(*tert*-butylamino)-1,2-di(*tert*-butyl)diphosphane: ¹H NMR (250.13 MHz, C₆D₆): δ (J(³¹P, ¹H)) = 1.108 (11.7) (pseudo-t, 18H, ¹BuP); 1.47 (s, 18H ¹BuN); - ¹³C{¹H} NMR (62.9 MHz, C₆D₆): δ (J(³¹P, ¹³C)) = 51.0 (15.1) (pseudo-t, CN); 32.7 (s, CH₃-CN); 31.6 (s, CP); 22.3(24.5) (pseudo-t, CH₃-CP). - ³¹P{¹H} NMR (101.25 MHz, C₆D₆) δ = 31.1.

Tri(tert-butyl)plumbyl-methyl(phenyl)amino(tert-butyl)phosphane (7)

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra), and led to a mixture of compounds containing **7**, **11**, **2** and 1,2-bis[methyl(phenyl)amino]-1,2-di(*tert*-butyl)diphosphane.

7: ¹H NMR (300.13 MHz, C₆D₆): δ [$J(^{207}$ Pb, ¹H)] ($J(^{31}$ P, ¹H)) = 3.21 [6.9] (< 1) (s, 3H, MeN); 1.62 [99.2] (< 1) (s, 27H, 'Bu₃Pb); 1.27 [< 2] (13.5) (d, 9H, 'BuP); not assigned: PhN.

1,2-Bis[methyl(phenyl)amino]-1,2-di(*tert*-butyl)diphosphane: ¹H NMR (300.13 MHz, C₆D₆): δ (J(³¹P, ¹H)) = 3.27 (s, broad, MeN); 1.07 (13.5) (pseudo-t, ^{*t*}BuP); not assigned PhN. – ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ (J(³¹P, ¹³C)) = 39.9 (8.0) (pseudo-t, MeN); 36.4 (17.1) (pseudo-t, CP); 29.1(19.6) (pseudo-t, CH₃-CP), not assigned PhN. – ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 57.0.

Tri(tert-butyl)plumbyl-benzyl(methyl)amino(tert-butyl)-phosphane (8)

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra), and led to a mixture of compounds containing **8** (see Table 1 for ³¹P and ²⁰⁷Pb NMR data) and a large number of other phosphorus containing compounds which were not identified.

Tri(tert-butyl)plumbyl-benzyl(tert-butyl)amino(tert-butyl)phosphane (9)

The reaction was carried out in the same way as described for diphenylphosphorus chloride (vide supra), and led to a mixture of compounds containing 9, 2 and 1,2-bis[benzyl(*tert*-butyl)amino]-1,2-di(*tert*-butyl)diphosphane ($\delta^{31}P = 53.0$), in addition to a small amount of other unidentified phosphorus compounds ($\delta^{31}P = 83.0,144.0, 180.3$).

9: ¹H NMR (300 MHz, C₆D₆): δ [J(²⁰⁷Pb, ¹H)] (J(³¹P, ¹H)) = 1.37 (13.3) (d, 9H, ^{*t*}BuP); 1.34 (s, 9H, ^{*t*}BuN); 5.28 (d, ²J(H,H) = 16.6 Hz, 1H, HCN), 4.29 (d, ²J(H,H) = 16.6 Hz, 1H, HCN); 1.74 [89.0] (s, 27 H, ^{*t*}Bu₃Pb); 7.5 - 7.0 (m, PhN).

Trimethylplumbyl-benzyl(methyl))amino(tert-butyl)phosphane (12)

Benzyl(methyl)amino(*tert*-butyl)phosphorus chloride (0.23 g; 1 mmol) was added in one portion at -50 °C to a freshly prepared solution of trimethylplumbyl-lithium (1 mmol) [8] in THF (20 ml). The mixture was warmed to r. t. and kept stirring for 3 h. The ²⁰⁷Pb NMR spectrum of the reaction mixture showed the presence of a small amount of tetramethyllead in addition to **12**, whereas the ³¹P NMR spectrum showed that **12** was the dominating species containing phosphorus. After removing the THF *in vacuo*, 10 ml of hexane were added, insoluble material

was filtered off, and all volatile material was removed *in* vacuo to leave 0.29 g (64%) of **12** as a yellow oil.

12: ¹H NMR (300 MHz, C₆D₆): δ [J(²⁰⁷Pb, ¹H)] (J(³¹P, ¹H)) = 0.94 [-39.9] (1.3) (d, 9H, Me₃Pb); 1.23 [7.0] (13.5) (d, 9H, ¹BuP); 2.57 [7.8] (5.1) (d, 3H, MeN); 4.16 [11.5] (<1) (d, ²J(H,H) = 16.7 Hz, 1H, CH-N), 4.13 [11.6] (<1) (d, ²J(H,H) = 16.7 Hz, 1H, CH-N) 7.15 - 7.24 (m, 5 H, Ph).

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