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From Neutral to Ionic Species: Syntheses, X-ray Crystallographic and Multinuclear NMR Spectroscopic Studies of Li···P($SiMe_3$)–P*t*Bu_2 and its Solvent Complexes

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Abstract

$Li(THF)_3P(SiMe_3)$–P*t*Bu_2 (**1**) prepared by the reaction of $(Me_3Si)_2P$–P*t*Bu_2 with *n*-butyllithium in THF has been isolated in good yields. Compound **1** eliminates THF on drying *in vacuo* yielding the dimeric [Li(THF)P($SiMe_3$)–P*t*Bu_2]$_2$ (**2**). By metallation of H($SiMe_3$)P–P*t*Bu_2 with *n*-butyllithium in hexane, the solvent-free derivative [Li(Me_3Si)P–P*t*Bu_2]$_4$ (**3**) has been prepared. Compounds **1**–**3** form the ionic species $[Li(TMEDA)_2]^+$[(Me_3Si)P−P*t*Bu_2]$^-$ (**4**) or $[Li(12\text{-crown-}4)_2]^+$[($SiMe_3$)P−P*t*$Bu_2$]$^-$ (**5**) with TMEDA (TMEDA = $Me_2N(CH_2)_2NMe_2$) or 12-crown-4, respectively, in solution. The molecular structures of **1**–**5** were established by single crystal X-ray diffraction. Compound **3** forms a cyclic tetramer with a flat butterfly geometry. Extensive solution NMR spectroscopic investigations have shown that all species except of **3** exist in the same form in solution as in the solid state. Moreover, multinuclear variable-temperature NMR studies showed that **2** is involved in a rapid conversion between conformers at 298 K, which can be slowed down on the NMR time scale at 183 K.

Introduction

The alkali and alkaline earth phosphanides are intensively studied. Many examples were synthesized, structurally characterized in the solid state, and used as starting materials for the synthesis of main group element and transition metal element compounds.[1] This is quite contrary to the alkali metal diphosphanides. There are only few reports on their synthetic use as building blocks for the synthesis of phosphorus-rich compounds[2] and, in particular, transition metal complexes.[3] The use of lithium diphosphanides in transition metal chemistry promises a variety of interesting compounds with regard to their structure and reactivity. The R_2P–PR'-group may not only act as a terminal phosphanylphosphido ligand but also as a bidentate ligand forming dinuclear complexes. The phosphanylphosphinidene substituent, generated in the course of the complex forming reaction may be terminal or side-on bound depending on the substituents R or R'. Some of these motives could meanwhile be realized.[3]

To the best of our knowledge, only three papers report on molecular structure determinations of lithium diphosphanides of the general type $Li(L)_n[RP{-}PR_2]$ {R = H, Ph, *i*Pr, N*i*Pr_2, $SiMe_3$ or $SiIs_2F$ (Is = 2,4,6-*i*$Pr_3C_6H_2$); L = THF or DME (DME = $MeOCH_2$-CH_2OMe)}.[4a–c] In one paper the potassium diphosphanide $[\{(tBuP)_2H\}K\cdot PMDETA]_2$ (PMDETA = $(Me_2NCH_2CH_2)_2NMe$) has been described,[4d] but nothing about the structures of these compounds in solution has been mentioned.

As we assume that the course of the reaction with different substrate molecules depends on the structures of the lithium diphosphanides in solution, it is our intention to get this structural information. We further want to elucidate in which way the terminal R_2P group may determine the molecular structure depending on its sterical requirement. Moreover, our focus is directed to the influence of donor molecules such as THF, Et_2O, dioxane, DME, TMEDA (TMEDA = $Me_2N(CH_2)_2NMe_2$), PMDETA or 12-crown-4 on these structures. Emphasis is also given to whether such structural motives as in alkali phosphanides or alkali amides of the general formula MPR_2 or MNR_2 can be observed, or whether new structural arrangements occur.

Alkali metal phosphanides (and alkali metal amides as well) usually crystallize as solvated monomers **A**, as donor-stabilized or solvent-free dimers with a central $[(\mu\text{-}P)_2Li_2]$ ring **B**, as oligomers with ladder-like annellated $[(\mu\text{-}P)_2Li_2]$ rings **C**, **D**, or as chain-like polymers **E** (Scheme 1).[1] The formation of an eight-membered ring system **F** was observed only once so far. The tetrameric compound

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$[Li_4\{P(SiiPr_3)_2\}_3\{P(H)SiiPr_3\}]$[5] is composed from three $LiP(SiiPr_3)_2$ moieties and one $LiHP(SiiPr_3)$ unit which together form a P_4Li_4 ring. Furthermore, $[Li(PhN–PPh_2)(OEt_2)]_2$ is reported to form a $[(\mu\text{-}N)_2Li_2]$ core, in which the phosphorus atoms using their free electron pairs coordinate to the neighboring Li atoms forming three-membered rings.[6] This structure may arise if either the available donor molecules fail to complete the coordination sphere around the cation, or no donor molecule (ether or amine) is present. In such a way, the bidentate ligand $[t\mathrm{BuP–P(H)}t\mathrm{Bu}]^-$ in $[K(PMDETA)\{(t\mathrm{BuP–P(H)}t\mathrm{Bu}\}]_2$ forms a central K_2P_2 ring with the anionic P centers. The neutral P centers coordinate to the potassium ions, which are incompletely solvated by PMDETA, yielding peripheral three-membered rings.[4d] Such a three-membered ring structure was also described for the monomeric lithium bis(diphenylphosphino)amide $Li(THF)_3N(PPh_2)_2$.[7] Driess *et al.* report on $Li(THF)(Is_2(F)Si)P–P(NiPr_2)_2$, finding a covalent interaction between Li and P in this compound. The coordination sphere of Li is completed by chelatization (fluorine, nitrogen), and one additional molecule of THF.[4c] As a final structural motive, the dimerization is also possible by formation of a six-membered ring assisted by the interaction of the lithium atom with the terminal phosphorus donor. As far as we are aware, $[Li(THF)\{PhP–P(H)Ph\}]_4$ is the only example where such rings dimerize to give a cage-like structure.[4a]

Scheme 1. Structure motives of lithium phosphanides (L = monodentate ligand).

In this work we describe the synthesis and single crystal X-ray structural determination of $Li(L)_n(Me_3Si)P–Pt\mathrm{Bu}_2$ (L = THF, n = 3, 1, 0; L = TMEDA, n = 2; L = 12-crown-4, n = 2). All compounds were investigated at various temperatures by multinuclear NMR spectroscopy in order to elucidate the structures in solution. In the case of **3**, NMR diffusion measurements were carried out.

Results and Discussion

Synthesis of Diphosphanides

$Li(THF)_3(Me_3Si)P–Pt\mathrm{Bu}_2$ (**1**) is accessible in good yields by cleaving one Si–P bond in $(Me_3Si)_2P–Pt\mathrm{Bu}_2$ with *n*BuLi in THF (Scheme 2).[2b] The stoichiometric ratio of lithium diphosphanide to THF is 1 : 3 in the crystals collected directly from this solution. After drying at 10^{-3} mbar/298 K, the crystals still contain 1.7 to 2.9 moles of THF, depending on the time of treatment. When $Li(THF)_3(Me_3Si)P–Pt\mathrm{Bu}_2$ is desiccated in a high vacuum ($1.2\cdot10^{-6}$ mbar) for about 15 hours at 298 K, the THF content of the product is degraded until a ratio of lithium diphosphanide to THF of 1 : 1 is reached. The obtained powdery substance can be dissolved in lukewarm hexane and crystallized at 238 K. The product was found to be $[Li(THF)(Me_3Si)P–Pt\mathrm{Bu}_2]_2 \cdot C_6H_{14}$ (**2**).

As it is well known that solvent-free lithium phosphanides, $LiPR_2$ (R = Et,[8] *t*Bu,[9] $SiMe_3$[10]) are available by metallation of $H–PR_2$ with *n*BuLi in nonpolar solvents as toluene or hexane, the preparation of the corresponding $Li(Me_3Si)P–Pt\mathrm{Bu}_2$ was anticipated, provided that $H(Me_3Si)P–Pt\mathrm{Bu}_2$ is available as starting material. However, our attempts to prepare $H(Me_3Si)P–Pt\mathrm{Bu}_2$ by partial hydrolysis or methanolysis of $(Me_3Si)_2P–Pt\mathrm{Bu}_2$ led differently from $[(Me_3Si)t\mathrm{BuP}]_2$ or $t\mathrm{Bu}(Me_3Si)P–Pt\mathrm{Bu}_2$[2b] always under cleavage of the P–P bond to mixtures of $HPt\mathrm{Bu}_2$ and polyphosphorus compounds of uncertain composition. Finally the diphosphane $H(Me_3Si)P–Pt\mathrm{Bu}_2$ was prepared by partial methanolysis of $Li(THF)_3(Me_3Si)P–Pt\mathrm{Bu}_2$ (**1**). By metallation of this diphosphane with *n*BuLi in hexane the solvent-free lithium diphosphanide **3** is accessible in good yields. Crystals grown from hexane at 298 K have the structure of $[Li(Me_3Si)P–Pt\mathrm{Bu}_2]_4$ (**3**). TMEDA or 12-crown-4 replace the THF ligand in the THF rich diphosphanide **1** yielding $[Li(TMEDA)_2]^+[(Me_3Si)P–Pt\mathrm{Bu}_2]^-$ (**4**) or $[Li(12\text{-crown-}4)_2]^+[(Me_3Si)P–Pt\mathrm{Bu}_2]^-$ (**5**), respectively. As expected the same compounds also result from **2** and **3**.

Scheme 2. Syntheses of compounds **1–5**.

X-ray Studies

The structures of **1**–**5** were determined by single-crystal X-ray diffraction (Figures 1–5). Selected bond lengths and angles are given in Table 1. The data for a comparative structure discussion are summarized in Table 2 and Table S1. The coordination number of Li ranges from six (**6**) to two (**21**).

In the monomer $Li(THF)_3(Me_3Si)P–Pt\mathrm{Bu}_2$ (**1**), the lithium atom adopts a distorted tetrahedral environment of three THF molecules and the P1 atom of the diphosphanide moiety (Figure 1). The phosphorus atom P1 in **1** has pyramidal coordination geometry. The Li–P distance of 2.555(9) Å exceeds only slightly the sum of the covalent radii of Li (1.33 Å), and P (1.11 Å).[11] This distance favorably compares with those determined for the monomeric lithium phosphanides **8**[12] and **9**[13] (Table 2). In comparison with the recently described lithium diphosphanides **10**[4b] and **11**[4b], the Li–P distance in **1** is slightly longer, however the P–P distance of 2.178(2) Å is in the range of values found for these compounds. The P–P distance in **1** is however significantly shorter than in some typical diphosphanes[14] (Table S2), and it is located near the lower limit of the range of 2.17 to 2.24 Å given by Corbridge[15] for P–P single bonds. On the other hand, the P–P distance is in the range of values found in transition metal complexes with the η^2-RP=PR ligand (about 2.10 Å),[16a] but significantly longer than the distances determined in free diphosphenes (about 2.02 Å).[16b,c]

Table 1. Selected bond lengths [Å] and angles [°] for **1**–**5**.

	1	**4**	**5**
P1–P2	2.178(2)	2.1886(9)	2.1657(9)
P1–Li1	2.555(9)	no bond[a]	no bond[a]
P1–Si1	2.198(2)	2.191(1)	2.1720(9)

P2–C4	1.906(5)	1.910(3)	1.902(2)
P2–C8	1.899(4)	1.909(3)	1.907(2)
P2–P1–Si1	94.32(7)	94.97(4)	97.40(3)
P2–P1–Li1	132.7(2)		
Si1–P1–Li1	108.3(2)		
	2		
P1–P2	2.1866(7)	Li1–P1	2.485(3)
P1–Si1	2.2117(8)	Li1–P1A	2.490(3)
Li1–P1–Li1A	77.2(1)	P2–P1–Li1	119.57(7)
P1–Li1–P1A	102.8(1)	Si1–P1–Li1	118.78(7)
P2–P1–Si1	99.03(3)	P2–P1–Li1A	123.80(7)
Si1–P1–Li1A	119.71(7)		
	3		
P1–P2	2.199(2)	P1–Li1	2.398(8)
P3–P4	2.198(2)	P3–Li1	2.400(8)
P1–Si1	2.225(2)	P3–Li2	2.421(9)
P3–Si2	2.222(2)	P1–Li2A	2.422(9)
Li1–P1–Li2A	110.3(4)	Si1–P1–Li1	109.9(3)
Li1–P3–Li2	112.5(4)	P2–P1–Li2A	115.2(2)
P1–Li1–P3	153.4(5)	Si1–P1–Li2A	99.7(2)
P3–Li2–P1A	159.4(5)	P4–P3–Li1	112.7(3)
P2–P1–Si1	100.63(6)	Si2–P3–Li1	105.5(3)
P4–P3–Si2	98.84(7)	P4–P3–Li2	120.2(3)
P2–P1–Li1	118.7(3)	Si2–P3–Li2	104.6(2)

[a] The atomic distances are 5.037 Å for **4** and 5.788 Å for **5**.

Table 2. Selected bond lengths [Å] for lithium phosphanides.

Compound	No.	Li–P	Ref.
$[\mathrm{Li(DME)_3}][(\mathrm{SiMe_3})\mathrm{P{-}PPh_2}]$	**6**	no bond[a]	[4b]
$[\mathrm{Li(TMEDA)_2}][\mathrm{P(SiH_3)_2}]$	**7**	no bond[a]	[23]
$\mathrm{Li(PMDETA)PPh_2}$	**8**	2.567(6)	[12]
$\mathrm{Li(THF)_3P(H)Mes}$	**9**	2.533(9)	[13]
$\mathrm{Li(THF)_3(SiMe_3)P{-}P}i\mathrm{Pr_2}$	**10**	2.536(7)	[4b]
$\mathrm{Li(THF)_3(SiMe_3)P{-}P(N}i\mathrm{Pr_2)_2}$	**11**	2.539(9)	[4b]
$[\mathrm{Li(THF)_2P(SiMe_3)_2}]_2$	**12**	2.62(2)	[17]
$[\mathrm{Li(DME)P(SiMe_3)_2}]_2$	**13**	2.559(4)	[18]
$[\mathrm{Li(TMEDA)PPh(SiMe_3)}]_2$	**14**	2.60(2)–2.63(2)	[19]
$[\mathrm{Li(TMEDA)PPh_2}]_2$	**15**	2.57(2)–2.67(2)	[12]
$[\mathrm{Li(OEt_2)PMes_2}]_2$	**16**	2.48(1)–2.517(2)	[13]
$[\mathrm{Li(THF)_{0.5}P(SiMe_3)_2}]_4$	**17**	2.44(2)–2.64(2)	[17]
$[\mathrm{Li(THF)_{0.5}P}t\mathrm{Bu_2}]_4$	**18**	2.466(5)–2.652(5)	[20]
$[\mathrm{Li\{P(CH(SiMe_3)_2)\}}]_2$	**19**	2.456(9)–2.48(1)	[21]
$[\mathrm{Li\{P(SiPh_3)_2\}}]_2$	**20**	2.449(6)–2.495(6)	[5]
$[\mathrm{Li_4\{P(Si}i\mathrm{Pr_3)\}_3\{P(H)(Si}i\mathrm{Pr_3)\}}]$	**21**	2.40(2)–2.50(1)	[5]

[a] The atomic distances are 5.564 Å for **6** and 4.908 Å for **7**.

$[\mathrm{Li(THF)P(SiMe_3){-}P}t\mathrm{Bu_2}]_2$ (**2**) forms a dimer with a planar $\mathrm{P_2Li_2}$ heterocycle on a special crystallographic position (Figure 2). The characteristic four-membered structural element $\mathrm{P_2Li_2}$ in **2** has been reported already for a series of lithium phosphanides (**12**–**16**).[12,13,17,18,19] The substituents at the ring P atoms are in *trans* position to each other. The P–P distance of 2.1866(7) Å is slightly larger compared to that in the monomer **1**. The lithium atoms accomplish a coordination number of only 3 with the two neighboring ring P atoms and one THF molecule. The Li–P distances (2.485(3) and 2.490(3) Å) are comparable with values that have been determined in the above examples with a planar $\mathrm{P_2Li_2}$ ring and a threefold coordinated lithium. The coordination number 3 of the lithium atom in **2** may be caused by the relatively large steric demand of the $t\mathrm{Bu_2P}$ ligand compared to the trimethylsilyl groups in $[\mathrm{Li(THF)_2P(SiMe_3)_2}]_2$ (**12**),[17] preventing a further association of two four-membered rings to a ladder-like tetramer as observed in **17**[17] and **18**.[20] The phosphorus atoms positioned in the direct neighborhood to the lithium atoms are in a distorted tetrahedral environment of two lithium atoms, one phosphanyl, and one trimethylsilyl group. The spatial arrangement of the ligands around the lithium atom in **2** is similar to the one in the tetramers **17**[17] and **18**[20].

Figure 1. ORTEP representation of molecule **1** at the probability level of 50%. The hydrogen atoms are omitted for clarity.

Figure 2. ORTEP representation of molecule **2** at the probability level of 50%. The hydrogen atoms are omitted for clarity. The symmetry generated atoms are labelled with 'A'.

The THF ligand-free tetrameric diphosphanide $[Li(Me_3Si)P–PtBu_2]_4$ (**3**) has a cyclic structure of type **F** in the solid state. The compounds **19**[21] and **20**[5] (Table 2), which also contain no donor ligands, exist as dimers of type **B** (Scheme 1), while $[LiP(SiMe_3)_2]_6$[22] forms a ladder-like structure of type **D** with Li_2P_2 subunits. The structure of **3** (Figure 3a) is analogous to that observed for **21**[5], however **3** is the first example of a diphosphanide derivative existing as an eight-membered ring in which all phosphorus atoms bear the same ligands. The asymmetric unit contains half of a molecule; the complete molecule has crystallographic twofold rotational symmetry. Due to a slight folding along P3···P3A (152.03°) the ring has a butterfly-like form (Figure 3b). In the less folded **21** this angle is 172.36°. In **3**, the phosphanyl substituents are in almost equatorial positions to the ring, whereas the $SiMe_3$ groups are nearly axially aligned. The only twofold coordinated lithium atoms form relatively large endocyclic bond angles of 153.4(5)° and 159.4(5)° to their neighboring phosphorus atoms, whereas in the mixed substituted tetramer **21** angles are reported up to 164.5(6)°. In contrast to **21**, where the bulky Si*i*Pr_3 groups are positioned both sides outwards the ring and thus force large Si–P–Si angles (113.8° and 116.7°), the sterically less demanding P*t*Bu_2 groups (favored by the short P–P distances of 2.198(2) and 2.199(2) Å) allow for considerably smaller P–P–Si angles of 98.84(7)° and 100.63(6)°. In **3** the Li–P distances vary from 2.398(8) to 2.422(9)Å, and are comparable to the distances in **21**.

Figure 3a.

Figure 3b.

Figure 3. a) ORTEP representation of molecule **3** at the probability level of 50%. The hydrogen atoms are omitted for clarity. b) The butterfly-like conformation of the tetrameric ring in compound **3**. The symmetry generated atoms are labelled with 'A'.

Because of the result of the NMR spectroscopic investigations on **3** in solution (see NMR discussion below) a powder diffractogram was measured to check the bulk of the solid. The measured and the calculated powder diffractogram of **3** are in very good accordance. It confirms the phase uniformity of the sample, and shows that the powder contains exclusively compound **3** (Figure S1).

The crystalline $[Li(TMEDA)_2]^+[(Me_3Si)P{-}PtBu_2]^-$ (**4**) contains isolated ions (Figure 4). The tetrahedrally coordinated lithium atom is distortedly surrounded by the nitrogen atoms of two chelate ligands. The carbon atoms of one of the TMEDA ligands are disordered over two positions. The distance of 5.037 Å between lithium and phosphorus is out of the range of a Li–P chemical bond (around 2.6 Å). Therefore an interaction of Li with the diphosphanide anion can be excluded just as in **7**,[23] which also exists as an ionic compound. On the other hand, TMEDA is not strong enough to isolate the chelated lithium as a separate cation in $Li(TMEDA)[\eta^2\text{-}(tBu_2P)_2P]$,[2e] **14**,[19] and **15**.[12] The Si–P bond in **4** is arranged in *anti* position to the *t*Bu groups. The P–P distances as well as those observed in **1**–**3** differ only slightly.

Figure 4. ORTEP representation of the ionic structure **4** at the probability level of 50%. The hydrogen atoms are omitted for clarity. One TMEDA ligand (including N1 and N2) is disordered over two equal positions.

Isolated ions are present in $[Li(12\text{-crown-}4)_2]^+$ $[(SiMe_3)P{-}\,PtBu_2]^-$ (**5**) in the solid state (Figure 5) as in the case of **4** and **6**.[4b] Li1 and P1 do not get closer than 5.788 Å in **5.** Thus their interaction can be excluded in this complex, too. The Si–P bond is *transoid* oriented to the bisect of the C4–P2–C8 plane in **5,** as it is also in **4.** The P–P distance of 2.1657(9) Å is slightly shorter than in **1** and **4**, respectively. The increase of the P2–P1–Si1 angle by 2.43° compared to **4**, or by 3.08° compared to **1**, as well as the decrease of the angle between the P1–P2 bond and the C4–P2–C8 plane is in correspondence with the shorter P–P distance. The superimposed structures of **4** and **5** (Figure S2) show that both anions are nearly identical, the root mean square of the overlay of the anions is 0.064 Å, the largest difference between atom positions is 0.137 Å. In the $[Li(12\text{-crown-}4)_2]^+$ ion of **5** the lithium is surrounded by a quadratic antiprism of oxygen atoms.

Summarizing we have shown that there is a clear correlation between the Li–P distance and the coordination number of Li. The higher the coordination number of Li (2, 3 and 4), the longer the Li–P distance is. The coordination number of Li is 2 in compounds **3** and **19**–**21**,[21,5] it is 3 in **2** and in **16**–**18**,[13,17,20] while compound **1** as well as the dimeric compounds **12**–**15**[12,17–19] contain a tetra- coordinated lithium. Coordination numbers of 4 or higher lead to ionic structures as in **4** and **5** as well as in **6**[4b] and **7**.[23] The influence of the space requirement of the phosphorus substituents on the

Figure 5. ORTEP representation of the ionic structure **5** at the probability level of 50%. The hydrogen atoms are omitted for clarity.

Li–P bond length should also be taken into account especially in the case of coordination number 2. The dimer $[Li\{P(SiPh_3)_2\}]_2$ (**20**)[5] holds an intermediate position. As a result of the bulky phosphorus substituents the lithium is solvent-free, but there is a stabilizing interaction of lithium with the phenyl groups of the neighboring $SiPh_3$ substituents. However the formation of tetrameric aggregates has not been observed in **20** in contrast to **3**. Eight-membered ring structures as in **3** or **21**[5] are realized when the formation of four-membered rings is prevented by steric demanding substituents.

NMR Spectroscopic Investigations

The ^1H and $^{31}P\{^1H\}$ NMR data of compounds **1**–**5** are collected in Table 3, atoms are numbered according to Figures 1–5. For comparison issues, data of $HP(SiMe_3)$–P*t*Bu$_2$ (**E1**) and $(Me_3Si)_2P$–P*t*Bu$_2$ (**E2**) are included as well. The ^7Li, $^{29}Si\{^1H\}$, and $^{13}C\{^1H\}$ NMR data are given in the Experimental Section. The ^1H, $^{31}P\{^1H\}$, and ^7Li NMR spectra of the THF complexes **1** and **2** were measured in the temperature range from 183 to 343 K in order to test for exchange or dissociation-association processes in solution. The lower limit of the temperature range is due to the increasing viscosity of the solutions and the onset of crystallization, both causing a strong line broadening especially in the ^1H spectra. Above 343 K no further change of the signal patterns was observed, with growing decomposition of the compounds. In this temperature range a considerable drift of the chemical shift values of **1**–**5** was observed, however, this occurred for $HP(SiMe_3)$–P*t*Bu$_2$ and other compounds to a similar extent and therefore cannot be used as evidence for changes in structures or binding conditions of **1**–**5**.

Crystals of **1** easily lose THF when dried at 298 K/10^{-3} mbar. In solutions of such crystals always a THF content of less than 3 is detected by integration of the ^1H NMR spectra. A sample with a THF content of n = 2.8 was used for the investigations. At 298 K in the ^1H NMR spectrum the signal of the $SiMe_3$ group of **1** appears as a doublet ($^3J_{HP} = 0.3$ Hz), the two equivalent *t*Bu groups as a doublet with $^3J_{HP} = 10.5$ Hz. The $^{31}P\{^1H\}$ NMR spectra show the two expected doublets (AX spin system; Figure 6). No splitting of the P1 signal by scalar ^7Li–^{31}P coupling occurs; however, its lines are considerably broadened ($W_{1/2} \approx 125$ Hz). The difference of the

Table 3. ^{1}H and ^{31}P{^{1}H} NMR data of Li(L)$_n$P(SiMe$_3$)–P*t*Bu$_2$ **1**–**5** and related compounds; numbering of the phosphorus atoms according to X-ray structures.[a]

	^{1}H		^{31}P		
	*t*Bu	SiMe$_3$	P1	P2	
	δ($^{3}J_{HP}$) ($^{4}J_{HP}$)	δ ($^{3}J_{HP}$) ($^{4}J_{HP}$)	δ	δ	($^{1}J_{PP}$)
1	1.39 (10.5)	0.51 (0.3)	–246.3	47.5	(–278.6)
2	1.36 (10.6)	0.49 (2.6)	–246.9	47.6	(–274.5)
3A	1.30 (10.8)	0.47 (3.9)	–244.3	43.7	(–267.5)
3B	1.41 (13.1)	0.51 (5.7)	–247.5	38.1	(–455)
4	1.47 (10.2)	0.56 (3.8) (0.8)	–242.5	44.5	(–272.5)
5	1.72 (10.0)	0.79 (3.4) (0.8)	–238.5	46.9	(–277.0)
E1[b]	1.18 (11.3) (0.6)	0.29 (4.2) (0.8)	–197.3	18.9	(–190.2)
E2[c]	1.29 (11.9)	0.38 (5.2)	–200.8	44.5	(–400.0)

[a] Temperature 298 K; solvent toluene-*d*$_8$; δ [ppm]; *J* [Hz]. [b] **E1** : HP(SiMe$_3$)–P*t*Bu$_2$. [c] **E2** : (Me$_3$Si)$_2$P–P*t*Bu$_2$.

chemical shifts between P1 and P2 increases by *ca*. 48 ppm compared to (Me$_3$Si)$_2$P–P*t*Bu$_2$ (**E2**), and by *ca*. 77 ppm compared to HP(SiMe$_3$)–P*t*Bu$_2$ (**E1**) (see Table 3). A similar change of chemical shifts was reported by Pikies *et al.* for Li(THF)$_3$P(SiMe$_3$)–P*i*Pr$_2$ (**10**) and Li(THF)$_3$P(SiMe$_3$)–P(N*i*Pr$_2$)$_2$ (**11**).[4b] In the ^{7}Li spectrum only a broad singlet without fine structure is observed at 2.48 ppm ($W_{1/2} \approx$ 30 Hz). In the ^{29}Si{^{1}H} spectrum, a doublet (δ = 0.67 ppm, $^{1}J_{SiP}$ = 29.4 Hz) at 298 K is observed, which splits into a doublet of doublets ($^{1}J_{SiP}$ = 38.1 Hz; $^{2}J_{SiP}$ = 31.4 Hz) at 203 K. Considering that a contact species is proven for **1** in the solid state, one could expect to detect scalar ^{7}Li–^{31}P couplings both in the ^{31}P{^{1}H} as well as in the ^{7}Li NMR spectra. The lack of any coupling at 298 K may either suggest the existence of a solvent-separated ion pair in solution or an exchange process which proceeds fast on the NMR time scale. At lower temperatures, the resonance lines become broader with the ^{31}P signals undergoing a stepwise upfield shift. In the ^{7}Li spectrum, the room temperature signal splits at 253 K into two signals (Figure 6). At 243 K the signal located at lower frequency gets sharper, and the scalar ^{7}Li–^{31}P coupling becomes observable and is fully present at 203 K. The same situation occurs at 203 K in the ^{31}P NMR spectra, where P2 shows a doublet caused by P1, and P1 exhibits a doublet of quadruplets arising from the coupling to P2 and to one quadrupolar ^{7}Li (I = 3/2). At this temperature compound **1** can best be described as a contact ion pair species.

Figure 6. ^{31}P{^{1}H} and ^{7}Li NMR spectra of **1** as a function of temperature.

If **1** is dissolved in THF-*d*$_8$ (i.e. a large excess of the neutral ligand THF is present), no splitting of the P1 signal by ^{7}Li is observed from 298 K down to 183 K. Obviously even at 183 K the lithium exchange between the monomeric species among each other proceeds so fast on the NMR time scale that no scalar ^{7}Li–^{31}P coupling can be observed.

The ^{1}H NMR spectrum of the dimeric compound **2** at 298 K shows a doublet for the SiMe$_3$ and the *t*Bu groups due to the coupling with the directly linked P atom. The THF content, via ^{1}H NMR integration, matches the value determined in the solid state. Up to 343 K there is nearly no change in the ^{1}H NMR resonances, whereas on cooling to 213 K the signals of the SiMe$_3$ and *t*Bu groups are slightly downfield shifted, and simultaneously the SiMe$_3$ peak loses its doublet structure. In the ^{31}P{^{1}H} NMR spectrum, P2 appears as the AA' part of an AA'XX' spin system, where P1 shows a complex multiplet due to the additional splitting of the XX' part by scalar coupling to ^{7}Li. In the ^{7}Li NMR spectrum a triplet appears at 2.83 ppm ($^{1}J_{LiP}$ = 57.2 Hz) due to coupling with two equivalent neighboring ^{31}P nuclei. The ^{29}Si{^{1}H} signal appears at 0.85 ppm (dd, $^{1}J_{SiP1}$ = 30.3, $^{2}J_{SiP2}$ = 11.6 Hz). At 298 K the NMR spectra prove undoubtedly that **2** exists in solution as a dimer just as in the solid state. This structure was confirmed by optimising the ^{31}P{^{1}H} NMR data set of **2** by simulating the ^{31}P NMR spectra[24] based on the cyclic solid state P$_2$Li$_2$ structure (Figure S3). Remarkably, despite of changing from monomer **1** to dimer **2** the chemical shifts δ_{P1} and δ_{P2} as well as the coupling constant $^{1}J_{PP}$ remain nearly unaffected.

When increasing the temperature up to 343 K the multiplet patterns of P1 and P2 observed at 298 K fade into broad poorly resolved doublets ($^{1}J_{PP} = -278$ Hz) (Figure 7). This observation and the fact, that in the ^{7}Li NMR spectrum at 343 K a broad singlet (2.7 ppm; $W_{1/2} \approx$ 50 Hz) is found instead of a triplet, may be explained by fast exchange or dissociation-association processes. In the ^{31}P{^{1}H} NMR spectrum at 223 K P2 gives rise to a broad doublet

Figure 7. ^{31}P{^{1}H} and ^{7}Li NMR spectra of **2** at selected temperatures.

which is converted on further cooling to 183 K to two superimposed AA' multiplets (44.43 and 42.59 ppm) of two AA'XX' spin systems. At 223 K the peak of P1 is very broad ($W_{1/2} \approx 490$ Hz), but at 183 K a fine structure (doublet of $I = 3/2$ septets) appears due to scalar ^{7}Li–^{31}P coupling. In the ^{7}Li NMR spectrum at 183 K two almost overlapped triplet peaks (2.95 ppm; $^1J_{LiP} = 54.2$ and 55.8 Hz) could be resolved (Figure S4). In the ^{29}Si{^{1}H} NMR spectrum at this temperature only a minor broadening of the lines in the doublet of doublets is observed. It is worth mentioning that this dynamic process is fully reversible and it may be concluded that the conversion of two structurally very similar isomers is more and more hindered with decreasing temperature, until the transformation is frozen at 183 K. In this sense the patterns observed at room temperature are averaged values from two rapidly rearranging dimers.

When samples of Li(THF)$_n$P(SiMe$_3$)–P*t*Bu$_2$ with different contents of THF ($1.3 < n < 3$) were measured at 298 K, the spectra showed doublets for the P atoms and a singlet for the Li atom. When a sample with a THF content of n = 2 was measured stepwise down to 183 K, at 223 K two separate spectra were observed which can be assigned to compounds **1** and **2**. At 183 K their superimposed signals can clearly be distinguished (Figure S4). At this low temperature the relative intensities of **1** and **2** remain constant in a given sample, however, the intensity of the signals of monomer **1** increases relative to dimer **2** with increasing content of THF. This means that more and more of compound **1** is formed by redistribution of the ligand THF which is present in excess related to **2**.

In the ^{1}H NMR spectrum of a freshly prepared sample of crystals of **3** in toluene-*d*$_8$ two different species **3A** and **3B** appear in a ratio of 10:1 at room temperature. The doublets observed for the SiMe$_3$ groups of **3A** and **3B** are superimposed whereas the doublets of the *t*Bu groups are nicely separated. In the ^{31}P{^{1}H} NMR spectrum two doublets ($\delta_{P1} = -244.3$; $\delta_{P2} = 43.7$ ppm) can be assigned to **3A**, and two further doublets ($\delta_{P1} = -247.5$; $\delta_{P2} = 38.1$ ppm) to **3B**. In the ^{7}Li NMR spectrum three signals are clearly observed. A strong unstructured signal at 3.54 ppm ($W_{1/2} \approx 25$ Hz) can be assigned to **3A**, and a broad triplet of triplets at 2.83 ppm to **3B**. Neither in the ^{31}P{^{1}H} nor in the ^{7}Li NMR spectra of **3A** any signal splitting due to Li–P coupling appears although this could be expected to result from the ring structure found in the solid state. Similarly, Driess *et al.* did not observe a Li–P coupling in [Li$_4${P(Si^{i}Pr$_3$)$_2$}$_3$ {P(H)Si^{i}Pr$_3$}].[5] A third very broad unstructured signal ($W_{1/2} \approx 200$ Hz) of low intensity appearing simultaneously with **3B** at *ca.* 1.5 ppm could not be assigned. In the ^{29}Si{^{1}H} NMR spectrum, **3A** is represented by a doublet of doublets at 1.37 ppm, and **3B** by a doublet of doublets at –1.89 ppm. It is worth mentioning the remarkably large absolute values of the coupling constants in **3B** ($^1J_{PP} = -455$ Hz, $^1J_{SiP} = 56.6$ Hz) compared to **3A** ($^1J_{PP} = -267.5$ Hz, $^1J_{SiP} = 26.8$ Hz). In this case, measurements as a function of temperature did not give any further information.

In a long-term NMR investigation (Figure S5) performed at 298 K with several samples, a continuous decrease of the intensity of the signals of **3A** was observed. After 19 weeks only the signals of **3B** were present in the NMR spectra. Due to the broad signals observed in the ^{7}Li spectrum and especially in the ^{31}P{^{1}H} spectrum of **3B**, a series of simulated model spin systems did not lead to a decision on the structure of compound **3B**.[24] Anyway, the low resolved P1 and Li multiplets in the NMR spectra of **3B** may give evidence for the presence of a Li–P contact species, whereas the spectra don't clarify at all the structure of **3A** in solution. Our experimental NMR spectroscopic investigations, too, did not permit a decisive conclusion on the molecular structure of the dissolved crystals of **3**. As a parallel experiment, an excess of Me$_3$SiCl was added to a solution containing **3B** as the main constituent. The exclusive formation of (Me$_3$Si)$_2$P–P*t*Bu$_2$ indicates that **3B** must be an oligomer of {LiP(SiMe$_3$)–P*t*Bu$_2$}.

The complete assignment of the ^{31}P and ^{7}Li NMR signals was carried out through a 2D ^{7}Li,^{31}P gHMQC spectrum performed with ^{1}H decoupling during the whole sequence (Figure S6). The indirect ^{31}P detection of ^{7}Li has already been applied previously.[25] On a sample where both **3A** and **3B** coexisted in solution, only **3B** gave the desired correlations, thus establishing the connectivity between the lithium and the two phosphorus atoms. Interestingly, only P1 could nicely resolve the coupling with the Li atom in the 2D map. No cross peaks were detected for **3A** probably due to a complete loss of transverse magnetization (fast T$_2$ relaxation) during the delays included in the pulse sequence. The broad signals observed for **3A** in the ^{7}Li and ^{31}P{^{1}H} NMR spectra confirm this statement.

Additional insights into the solution structure of species **3A** and **3B** were obtained via diffusion studies. The measurement of diffusion constants via pulsed gradient spin-echo (PGSE) NMR methods[26] has recently attracted increasing interest as this technique provides data on molecular volumes, and thus indirectly on structural characteristics.[27] In addition, the sequences needed are available in a standard NMR spectrometer facilitating the performance of the experiment. The calculated r_H values (via Stokes-Einstein equation) assume spherical shapes; hence, they do not represent the real shape of the molecules. Nevertheless their use is well established for comparisons, since they offer a rapid and easy method to recognize ion pairing and/or aggregation.

Table 4 shows PGSE diffusion data for **3A** and **3B** in toluene solution. In the traditional Stejskal-Tanner plots[28] (Figure S7), the less the attenuation, the lower the diffusion coefficient, the larger the molecular size. Although the viscosity of the toluene solutions varies with concentration, we have used pure solvent viscosity for radii calculation via the Stokes-Einstein equation.

Table 4. Diffusion coefficient (D) and hydrodynamic radius (r_H) values for species **3A** and **3B** in *ca*. 60 mmol toluene-*d*$_8$ samples at ambient temperature.

Species	$D \times 10^{-10}$ [m^2 s^{-1}][a]	r_H [Å][b]	$r_{X\text{-Ray}}$ [Å][c]
3	–	–	7.4
3A	6.317	5.9	–
3B	3.589	10.3	–

[a] Experimental error in D values is ± 2 %. [b] The viscosity, η, used in the Stokes-Einstein equation is 0.5819×10^{-3} kg m^{-1} s^{-1}. Viscosity was taken from www.knovel.com. [c] Deduced from the X-ray structure of **3** by considering the volume of the crystallographic cell divided by *Z*.

No information could be derived from ^{7}Li PGSE NMR since in every condition essayed no magnetization was detected after the execution of the stimulated echo (or Stejskal-Tanner) sequence, even when employing very short diffusion times Δ.

From the measured D values at *ca*. 60 mmol samples for **3A** and **3B**, we estimate the hydrodynamic radii r_H to be 5.9 and 10.3 Å, respectively, which are not in agreement with the value derived from the crystallographic data of **3** (7.4 Å, see Table 4). We can therefore conclude that when crystals of **3** are dissolved in toluene, a new species of smaller size than **3** is obtained which is eventually transformed into a much larger aggregate within time. In fact, for two spherical molecules, in which one has five times the volume of the other, one expects the ratio of the slopes (or D-values) to be $5^{1/3} \approx 1.71$. The experimental ratio of D-values of 1.74 (Table 4) is consistent with **3B** having about five or six times the volume of **3A**. An exchange between both species cannot be excluded, what could represent a source of uncertainty. Diffusion NMR measurements could not be conducted at low temperature because of too low solubility. In addition the cooling of the sample causes the formation of convection currents within the sample, which can be mistaken for faster diffusion, or even completely distort the shape of the ln(I/Io) vs. G^2 plot.

The behavior of **4** and **5** in solution is very similar. In their ^1H NMR spectra the $SiMe_3$ group is observed as a doublet of doublets due to scalar ^1H–^{31}P coupling with the two phosphorus nuclei, whereas the protons of the two *t*Bu groups appear just as a doublet. The ^1H NMR signals of NCH_2 and NCH_3 in TMEDA for **4** (NCH_2 : δ = 1.91 ppm, NCH_3 : δ = 1.95 ppm) appear in reverse order of the signal sequence for the free TMEDA (NCH_2 2.28 ppm, NCH_3 2.09 ppm). The relative positions of the TMEDA signals were discussed on lithium phosphanides as an indication for a coordinative bonding of TMEDA to lithium.[29] But this reversal remains without any significant effect on the chemical shift of the nuclei in **4** other than ^1H. Heteronuclear NOE methods, while inherently very insensitive, have received attention for structural elucidation in many cases providing the clue for structure identification.[30] In species **4**, a ^1H,^7Li HOESY spectrum was acquired and indicates a contact between the NCH_3 protons and the lithium atom. In the ^{31}P NMR spectra of **4** and **5** appear two doublets, respectively. The chemical shift difference of the two ^{31}P signals is nearly the same in **4** and **5** but considerably smaller than in **1**. In the ^7Li NMR spectra of **4** and **5** only a sharp singlet ($W_{1/2} \approx 6$ Hz) is observed, respectively, which establishes in solution a rather symmetric environment around the lithium as the one observed in the solid state. The lack of any ^7Li–^{31}P coupling even at temperatures near the freezing point of the solvent indicates that both compounds exist, as expected, as solvent-separated ion pairs also in solution.

Conclusions

This work extends the so far small family of fully characterized lithium diphosphanides by the series of $Li(L)_nP(SiMe_3)$–P*t*Bu_2 (L = THF, n = 0–3; L = TMEDA, 12-crown-4, n = 2). It is a contribution to the fine tuning of structures by donor molecules and substituents. We have proven the correlation between the Li–P distance and the coordination number of Li, as well as the influence of donor molecules on the Li–P distance in these compounds. Starting from the monomeric $Li(THF)_3P(SiMe_3)$–P*t*Bu_2 (**1**) the dimeric $[Li(THF)P(SiMe_3)$–P*t*$Bu_2]_2$ (**2**) containing a $[(\mu\text{-}P)_2Li_2]$ core can be obtained by elimination of THF *in vacuo*. A further degradation is not possible by this method. The appearance of a second set of NMR signals on cooling the solution of **2** below 200 K suggests that there exist two structurally very similar conformers which quickly rearrange into each other at higher temperatures. If the THF content exceeds the stoichiometric value of n = 1, compound **1** is formed in the corresponding amount besides of **2** with decreasing temperature. $[LiP(SiMe_3)$–P*t*$Bu_2]_4$ (**3**) is available by lithiation of $HP(SiMe_3)$–P*t*Bu_2 with *n*BuLi in hexane. The tetrameric **3** exists in the solid state with a butterfly-shaped Li_4P_4 ring structure. Compound **3** is the first fully characterized example of such a structure where all skeleton P atoms bear the same substituents. The combined steric requirements of the P*t*Bu_2 and the $SiMe_3$ group prevent an analogous ladder structure as in $[LiP(SiMe_3)_2]_6$.[22] Noteworthy is the slow conversion of **3A** in solution at 293 K into a new, and hitherto unknown species **3B,** which shows ^7Li–^{31}P coupling. PGSE NMR diffusion measurements have also shown that the size of the newly formed species **3B** is at least five times larger than **3A**, suggesting an aggregation process. Compounds **1**–**3** react with TMEDA or 12-crown-4 resulting in the ion pairs $[Li(TMEDA)_2]^+$ $[(Me_3Si)P$–P*t*$Bu_2]^-$ (**4**), or $[Li(12\text{-crown-}4)_2]^+[(SiMe_3)P$–P*t*$Bu_2]^-$ (**5**), respectively.

By extensive multinuclear NMR studies we could show that all compounds with the exception of **3** exist in solution in the same molecular structure as in the solid state.

Experimental Section

General: All manipulations were carried out under a dry nitrogen atmosphere with exclusion of air and moisture using standard Schlenk techniques. The appropriate solvents were dried according to standard procedures (toluene, THF, TMEDA, C_6D_6, and toluene-d_8 over sodium/benzophenone; 12-crown-4 over potassium, hexane, and pentane over $LiAlH_4$) and freshly distilled prior to use. *n*BuLi (1.6 M in hexane) was purchased from Sigma-Aldrich and used as received. $(Me_3Si)_2P$–P*t*Bu_2 was prepared according to a literature procedure.[2b] The ^1H, ^{13}C, ^{31}P, ^7Li, ^{29}Si, and ^{15}N NMR spectra were recorded on Bruker AMX 300 and Av 400 spectrometers, using the deuterated solvent (C_6D_6, or toluene-d_8 for low temperature experiments) as internal lock, and TMS (^1H, ^{13}C, ^{29}Si), 85% H_3PO_4 (^{31}P), 1M LiCl (^7Li), and $MeNO_2$ (^{15}N) as external standards. The ^1H, and $^{31}P\{^1H\}$ NMR data of $Li(L)_nP(SiMe_3)$–P*t*Bu_2 (**1**–**5**) are collected in Table 3. $^7Li,^{31}P\{^1H\}$ HMQC 2D experiments were performed using spectral widths of 31055 Hz (^{31}P) and 2170 Hz (^7Li), a final matrix after zero filling of 1024×256, and an evolution delay of $^nJ_{PLi}$ = 17 ms. Unless otherwise stated, standard Bruker software routines (TOPSPIN) were used for the 1D and 2D NMR measurements. Temperature calibration of the NMR measurements was carried out using Bruker standard samples.

Diffusion measurements were performed using the Stimulated Echo Pulse Sequence[26a] without spinning. The shape of the gradient pulse was rectangular, and its strength varied automatically in the course of the experiments. The *D* values were determined from the slope of the regression line ln(I/I_0) versus G^2, according to Equation 1. I/I_0 = observed spin echo intensity/intensity without gradients, *G* = gradient strength, Δ = delay between the mid-points of the gradients, *D* = diffusion coefficient, δ = gradient length.

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2\left(\Delta - \frac{\delta}{3}\right)DG^2 \qquad \text{(Eq. 1)}$$

The calibration of the gradients was carried out via a diffusion measurement of HDO in D_2O, which afforded a slope of $2.022 \cdot 10^{-4}$. All of the data leading to the reported *D* values afforded lines whose correlation coefficients were > 0.999. To check reproducibility, three different measurements with different diffusion parameters (δ and/or Δ) were always carried out. The gradient strength was incremented in 8% steps from 10% to 98% and the recovery delay set to 5 times T_1.

Elemental analysis determination was performed with an Elementar vario EL analyser. High resolution mass spectra were measured on a Varian MAT 8200 mass spectrometer.

Crystal data, data collection and refinement parameters are summarized in Table S3. Suitable crystals of compounds **1**–**4** were selected in inert oil (KEL-F) and mounted on a glass pin, compound **5** was selected in a glove box and mounted in a glass capillary. The moisture sensitive crystals were immediately brought into a cooled dry N_2 stream. Crystallographic data were collected for **1** on a STOE stadi IV, while for **2**–**5** on a STOE IPDS II image plate diffractometer. Numerical absorption corrections were applied to the data. The structures were solved by direct methods (SHELXS-97),[31] and anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms was performed using the software SHELXL-97.[31] Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. The molecular graphics were prepared using the software Mercury[32] of CSD.

CCDC 679341–679344 (**1**–**4**) and CCDC 935977 (**5**) contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The powder diffractogram was measured on a STOE STADI-P instrument equipped with a Germanium monochromator using Cu-Kα radiation.

$Li(THF)_n(Me_3Si)P–PtBu_2$ (n = 1.7 – 3), (1): Compound **1** was synthesized according to an optimized literature method.[2b] Over a 3 h period *n*BuLi (1.6 M in hexane, 34.4 mL, 55.0 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2P{-}PtBu_2$ (17.72 g, 55.0 mmol) in THF (100 mL) at 253 K. The reaction mixture was allowed to warm slowly to room temperature. After stirring overnight, half of the solvent was removed under reduced pressure. Meanwhile a crystalline precipitate separated which was dissolved by adding pentane (200 mL) and warming moderately. Colorless crystals grew from this solution at 238 K. The isolated product had the composition $Li(THF)_{2.8}(Me_3Si)P–PtBu_2$ after drying. A second crystal fraction had the composition $Li(THF)_{1.8}(Me_3Si)P–PtBu_2$. Overall yield: 44.6 mmol (81%). $C_{11}H_{27}LiP_2Si \cdot 2.8\ C_4H_8O$ (458.21): calcd. C 58.19, H 10.87; found C 58.24, H 10.90. $^{13}C\{^1H\}$ NMR (toluene-d_8): δ = 5.9 (d, $^2J_{CP}$ = 6.9 Hz, $Si(CH_3)_3$), 32.4 (d, $^2J_{CP}$ = 15.0 Hz, $C(CH_3)_3$), 32.6 (d, $^1J_{CP}$ = 33.9 Hz, $C(CH_3)_3$). ^7Li NMR (toluene-d_8): δ = 2.48 (s) ppm. ^{29}Si NMR (toluene-d_8): δ = 0.67 (d, $^1J_{SiP}$ = 29.4 Hz) ppm.

$[Li(THF)(Me_3Si)P{-}PtBu_2]_2$ (2): The diphosphanide $Li(THF)_{2.8}(Me_3Si)P–PtBu_2$ (0.50 g, 1.1 mmol) was evacuated for 15 h at 298 K / 1.2 $\cdot$ 10^{-3} mbar. Any solvents were thoroughly removed *in vacuo* from the material used for elemental analysis and NMR spectra. The yellowish powder-like residue was dissolved in hexane (5 mL) and warmed moderately. Colorless crystals of **2** suitable for X-ray studies grew at 238 K. Yield: 0.30 g (83%). $C_{22}H_{54}Li_2P_4Si_2 \cdot 2C_4H_8O$ (656.84): calcd. C 54.86, H 10.74; found C 54.50, H 10.75. $^{13}C\{^1H\}$ NMR (toluene-d_8): δ = 5.8 (A part of AXX', $^2J_{CP} + {}^4J_{CP}$ = 15.7 Hz, $Si(CH_3)_3$), 32.4 (d, $^2J_{CP}$ = 14.6 Hz, $C(CH_3)_3$), 32.6 (d, $^1J_{CP}$ = 33.4 Hz, $C(CH_3)_3$). ^7Li NMR (toluene-d_8): δ = 2.83 (d, $^1J_{LiP}$ = 57.1 Hz) ppm. ^{29}Si NMR (toluene-d_8): δ = 0.85 (dd, $^1J_{SiP}$ = 30.3 Hz, $^2J_{CP}$ = 11.6 Hz) ppm.

$[Li(Me_3Si)P{-}PtBu_2]_4$ (3). Step 1: Methanolysis of $Li(THF)_{2.8}(Me_3Si)P–PtBu_2$. A mixture of MeOH (0.40 g, 12.5 mmol) and pentane (10 mL) at 293 K was added dropwise to a rigorously stirred solution of $Li(THF)_{2.8}P(SiMe_3){-}PtBu_2$ (5.71 g, 12.5 mmol) in pentane (80 mL). The bright yellow precipitate of LiOMe was filtered off after a reaction time of 2 h at 293 K. The volatile components were removed *in vacuo* at 293 K. The residue was the desired product $H(Me_3Si)P{-}PtBu_2$ confirmed by NMR spectra.[2b] Yield: 2.97 g (95%). MS (EI): *m/z* (%) = 250.14370 (37.6) (calcd. for $C_{11}H_{28}P_2Si$ 250.14356) [M^+], 235.116 (6.1) [$M^+{-}CH_3$]. $^{13}C\{H\}$ NMR (toluene-d_8, 343 K, unresolved multiplet at 298 K): δ = 1.7 (dd, $^2J_{CP}$ = 10.5 Hz, $^3J_{CP}$ = 5.1 Hz, $Si(CH_3)_3$), 30.9 (dd, $^2J_{CP}$ = 15.0 Hz, $^3J_{CP}$ = 5.5 Hz, $C(CH_3)_3$), 32.8 (dd, $^1J_{CP}$ = 32.8 Hz, $^2J_{CP}$ = 5.6 Hz $C(CH_3)_3$). ^{29}Si NMR (toluene-d_8): δ = 3.80 (dd, $^1J_{SiP}$ = 20.2 Hz, $^2J_{CP}$ = 18.7 Hz) ppm.

Step 2: Metallation **of $H(Me_3Si)P{-}PtBu_2$**. A solution of *n*BuLi (1.6 M in hexane, 7.4 mL, 11.8 mmol, diluted with 10 mL hexane) was added dropwise to a solution of $H(Me_3Si)P{-}PtBu_2$ (2.95 g, 11.8 mmol) in hexane (150 mL) at 273 K. After 12 h at 273 K the reaction mixture was stirred for another 48 h at 293 K and concentrated to about 60% of its starting volume. The precipitating solid was again dissolved by moderate warming. Shiny colorless crystals suitable for X-ray studies grew already at 293 K. This compound is pyrophoric. Yield: 1.55 g (51%). $C_{44}H_{108}Li_4P_8Si_4$ (1025.24): calcd. C 51.55, H 10.62; found C 51.07, H 10.25. $^{13}C\{^1H\}$ NMR (toluene-d_8): **3A**: δ = 5.6 (dd, $^2J_{CP}$ = 11.0 Hz, $^3J_{CP}$ = 6.3 Hz, $Si(CH_3)_3$), 32.4 (d, $^2J_{CP}$ = 32.2 Hz, $C(CH_3)_3$), 32.5 (dd, $^1J_{CP}$ = 14.5 Hz, $^2J_{CP}$ = 4.7 Hz, $C(CH_3)_3$). ^7Li NMR (toluene-d_8): δ = 3.54 (s) ppm. ^{29}Si NMR (toluene-d_8): δ = 1.37 (dd, $^1J_{SiP}$ = 26.8 Hz, $^2J_{CP}$ = 16.9 Hz) ppm. **3B**:δ = 3.3 (dd, $^2J_{CP}$ = 14.2 Hz, $^3J_{CP}$ = 1.7 Hz, $Si(CH_3)_3$), 32. 8 (dd, $^2J_{CP}$ = 10.6 Hz, $^3J_{CP}$ = 2.9 Hz, $C(CH_3)_3$), 34.5 (dd, $^1J_{CP}$ = 16.3 Hz, $^2J_{CP}$ = 2.4 Hz $C(CH_3)_3$). ^7Li NMR (toluene-d_8): δ = 2.83 (dd, $^1J_{LiP}$ = 37.5 Hz, $^2J_{LiP}$ = 22.0 Hz) ppm. ^{29}Si NMR (toluene-d_8): δ = –1.89 (d, $^1J_{SiP}$ = 56.6 Hz) ppm.

$[Li(TMEDA)_2]^+[(Me_3Si)P{-}PtBu_2]^-$ (4): A solution of TMEDA (0.3 mL, 2 mmol) in toluene (2 mL)) was added dropwise to a solution of $Li(THF)_{2.8}P(SiMe_3){-}PtBu_2$ (0.66 g, 1.45 mmol) in toluene (5 mL) at 273 K. The turbid pale yellow solution was stirred for 2 h at 293 K, filtered and concentrated to dryness. Some residual free TMEDA was removed at 293 K/1.2 $\cdot$ 10^{-3} mbar. The yellow-brown solid residue was recrystallized from hexane/toluene at 238 K. Yield: 0.60 g (58%). $C_{11}H_{27}LiP_2Si \cdot 2C_6H_{16}N_2$ (488.72): calcd. C 56.53, H 12.17, N 11.46; found C 56.03, H 12.04, N 11.18. $^{13}C\{^1H\}$ NMR (toluene-d_8): δ = 6.5 (dd, $^2J_{CP}$ = 12.5 Hz, $^3J_{CP}$ = 7.3 Hz, $Si(CH_3)_3$), 32.4 (dd, $^2J_{CP}$ = 14.7 Hz, $^3J_{CP}$ = 5.2 Hz, $C(CH_3)_3$), 32.5 (dd, $^1J_{CP}$ = 34.1 Hz, $^2J_{CP}$ = 4.6 Hz, $C(CH_3)_3$), 45.7 (s, $N(CH_3)$), 57.4 (s, $N(CH_2)$). ^7Li NMR (toluene-d_8): δ = 2.27 (s) ppm. ^{29}Si NMR (toluene-d_8): δ = 0.25 (dd, $^1J_{SiP}$ = 36.6 Hz, $^2J_{CP}$ = 31.1 Hz) ppm. ^{15}N NMR (toluene-d_8): δ = 19.7 (s) ppm.

$[Li(12\text{-}crown\text{-}4)_2]^+[(SiMe_3)P{-}PtBu_2]^-$ (5): A solution of 12-crown-4 (0.62 g, 3.5 mmol) in hexane (25 mL) was added dropwise to a solution of $Li(THF)_{2.8}P(SiMe_3){-}PtBu_2$ (0.64 g, 1.4 mmol) in hexane (25 mL) at 293 K. A white solid precipitated immediately. This mixture was cooled and filtered at 238 K. Colorless needles of **5** suitable for X-ray analysis grew from a solution of the isolated solid in toluene/THF at 273 K. Yield: 0.55 g (64%). $C_{11}H_{27}LiP_2Si \cdot 2C_8H_{16}O_4$ (608.73): calcd. C 53.27, H 9.77; found C 52.93, H 9.71. $^{13}C\{^1H\}$ NMR (THF-d_8, the solubility in toluene is too low): δ = 5.7 (dd, $^2J_{CP}$ = 11.2 Hz, $^3J_{CP}$ = 9.5 Hz, $Si(CH_3)_3$), 31.5 (dd, $^2J_{CP}$ = 14.7 Hz, $^3J_{CP}$ = 5.2 Hz $C(CH_3)_3$), 31.7 (dd, $^1J_{CP}$ = 34.5 Hz, $^2J_{CP}$ = 7.8 Hz $C(CH_3)_3$), 69.5 (s, 12-crown-4). ^7Li NMR (toluene-d_8): δ = –0.02 (s) ppm. ^{29}Si NMR (toluene-d_8): δ = –1.24 (dd, $^1J_{SiP}$ = 61.7 Hz, $^2J_{CP}$ = 31.1 Hz) ppm.

Supporting Information (see footnote on the first page of this article): Details of the structural and NMR investigations, table of crystallographic data.

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