Lithium Bis(triisopropylsilyl)phosphanide and its Pentacarbonyltungsten Adduct: Synthesis and Crystal Structures of the Dimer $[(thf)Li\text{-}P(SiiPr_3)_2]_2$ and the Solvent-Separated Ion Pair $[(thf)_4Li]^+ [(OC)_5W\text{-}P(SiiPr_3)_2]^-$

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The lithiation of bis(triisopropylsilyl)phosphane with *n*-butyllithium in THF gave quantitatively dimeric (thf)LiP(Si*i*Pr$_3$)$_2$ (**1**) with three-coordinate lithium atoms. The molecular structure of **1** shows Li-P bond lengths of 253.3(6) pm. In order to obtain the pentacarbonyltungsten complex of the sterically demanding phosphanide, (thf)W(CO)$_5$ was reacted with (thf)LiP(Si*i*Pr$_3$)$_2$ in THF. The resulting solvent-separated complex $[(thf)_4Li]^+$ $[(OC)_5WP(SiiPr_3)_2]^-$ (**2**) was structurally characterized and shows a very large W-P distance of 266.65(7) pm.

Key words: Phosphanes, Bis(triisopropylsilyl)phosphanides, Solvent-Separated Complex, Lithium Phosphanides, Pentacarbonyltungsten Complexes

Introduction

Trialkylsilyl substituted lithium phosphanides are valuable synthons for a wide variety of redox reactions as well as for the formation of multiple bonds between phosphorus and carbon or metal atoms. LiP(SiMe$_3$)$_2$ was investigated intensively in adducts with varying amounts of different Lewis-bases. Regardless of the degree of aggregation or the number of coordinated neutral Lewis-bases the structural motif is the Li_2P_2-cycle. With decreasing amount of coligands the oligomerization degree grows. The solvent-free LiP(SiMe$_3$)$_2$ crystallizes as a hexamer with a ladder-like structure [1], whereas the ether-adducts (dme)LiP(SiMe$_3$)$_2$ [2] and (thf)$_2$LiP(SiMe$_3$)$_2$ [3] precipitate as dimers. After loss of THF molecules a tetrameric compound of the type $(thf)_2Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2$ has been isolated and characterized by X-ray crystallography. The coordination of the tridentate 2,5,8-trimethyl-2,5,8-triazanonane (PMDETA) leads to monomeric (pmdeta)LiP(SiMe$_3$)$_2$ [3]. The extensive review articles of Fritz *et al.* summarize the synthesis of phosphanes and phosphanides as well as the reactivity studies [4].

The bulkier lithium bis(triisopropylsilyl)phosphanides have not been investigated in such depth. The synthesis and crystallization of LiP(Si*i*Pr$_3$)$_2$ led to an eight-membered Li_4P_4 ring, one of the triisopropylsilyl groups being substituted by a hydrogen atom thus yielding the complex $Li_4[\mu\text{-}P(SiiPr_3)_2]_3[\mu\text{-}P(H)SiiPr_3]$ [5]. The enhancement of the steric strain by substitution of the trimethylsilyl group by the triisopropylsilyl substituent is best shown for the tris(trialkylsilyl)phosphanes: whereas P(SiMe$_3$)$_3$ has a phosphorus atom in a trigonal pyramidal skeleton [6], P(Si*i*Pr$_3$)$_3$ is nearly planar [7]. On the other hand, the tri(*tert*-butyl)silylphosphanides of the alkali metals show a wide variety of structures depending on the size of the metal [8].

Results and Discussion

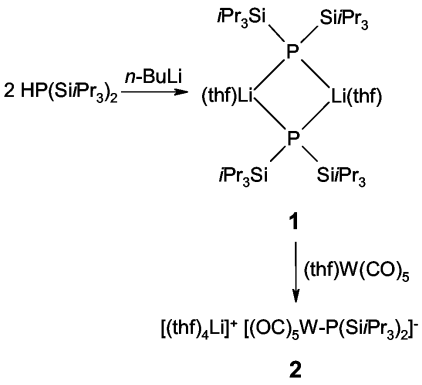
Synthesis

The lithiation of bis(triisopropylsilyl)phosphane with *n*-butyllithium in THF gave quantitatively dimeric

Table 1. Comparison of selected NMR data of HP(Si*i*Pr$_3$)$_2$ [12], **1** and **2**.

Compound	**HP(Si*i*Pr$_3$)$_2$**	**1**	**2**
^{1}H NMR:			
δ(SiCH)	1.15	1.15	1.48
δ(Me)	1.17	1.21	1.67
^3J(H,H)	–	6.4	6.6
^{13}C{^{1}H} NMR:			
δ(SiCH)	14.8	16.5	19.4
δ(Me)	19.6	29.4	24.7
δ(*trans*-CO)	–	–	202.4
^1J(W,C$_{trans}$)	–	–	157.8
^2J(P,C$_{trans}$)	9.1	9.3	11.8
δ(*cis*-CO)	–	–	202.6
^1J(W,C$_{cis}$)	–	–	125.3
^2J(P,C$_{cis}$)	9.1	9.3	2.3
^{29}Si{^{1}H} NMR:			
δ(Si*i*Pr$_3$)	20.9	21.6	21.1
^1J(P,Si)	41.0	49.7	40.8
^{31}P{^{1}H} NMR:			
δ(P)	−286.2	−374.7	−409.2
^{7}Li{^{1}H} NMR:			
δ(Li)	–	3.29	3.27

(thf)LiP(Si*i*Pr$_3$)$_2$ (**1**) with three-coordinate lithium atoms. In the course of our investigations concerning the pentacarbonyltungsten complexes of sterically demanding phosphanides we reacted (thf)W(CO)$_5$ with (thf)LiP(Si*i*Pr$_3$)$_2$ in THF which not only led to a monomerization of the dimer but the formation of the solvent-separated complex [(thf)$_4$Li]$^+$ [(OC)$_5$WP(Si*i*Pr$_3$)$_2$]$^-$ (**2**) according to eq. (1) [9].



(1)

Previous investigations were performed by the research group of Mathey [10]. Starting from (OC)$_5$W-PH$_3$, lithiation and metathesis reactions allowed the synthesis of pentacarbonyltungsten complexes of lithium phosphanides and trialkylsilylphosphanes. Multiply lithiated species are extremely reactive and decompose immediately at room temperature [10]. Therefore, the synthesis according to eq. (1) is preferred in comparison to the multi-step synthesis starting from (OC)$_5$W-PH$_3$. Scheer and coworkers described a bis(pentacarbonyltungsten) complex of the phosphanide anion [11].

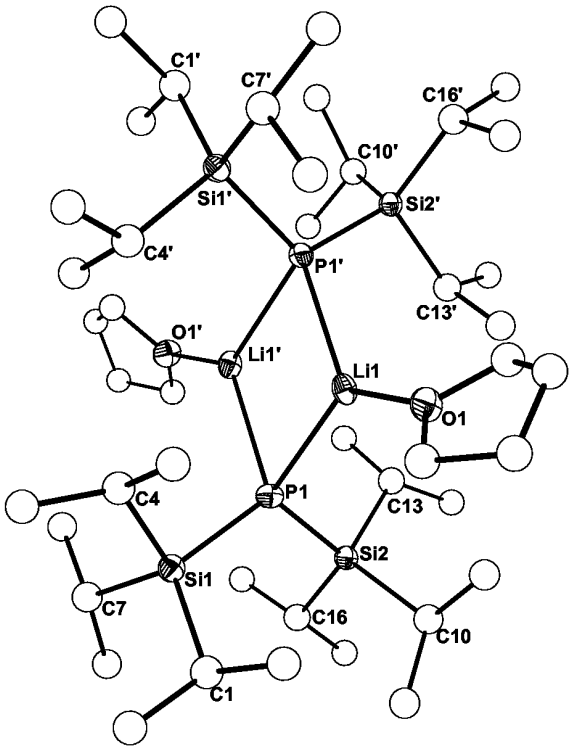


Fig. 1. Molecular structure of **1**. The ellipsoids represent a probability of 25%. For clarity reasons the H atoms are neglected and the C atoms drawn with arbitrary radii. Selected bond lengths [pm]: Li1-P1 253.3(6), Li1-P1' 253.3(6), Li1-O1 192.0(6), Li1···Li1' 304.3(11), P1-Si1 220.3(2), P1-Si2 220.7(2); angles [°]: P1-Li1-P1' 106.1(2), O1-Li1-P1 128.0(3), O1-Li1-P1' 125.9(3), Li1-P1-Li1' 73.8(2), Si1-P1-Si2 117.76(6), Si1-P1-Li1 113.3(2), Si1-P1-Li1' 115.5(2).

NMR spectroscopy

In Table 1 the NMR parameters of **1** and **2** are summarized together with those of HP(Si*i*Pr$_3$)$_2$ [12]. The increasing shielding of the ^{31}P nuclei correlates with the build-up of negative charge on the phosphorus atom. The ^1J(P,Si) coupling constants show a value of approximately 41 Hz for HP(Si*i*Pr$_3$)$_2$ and **2** whereas 50 Hz is measured for the lithium derivative **1**. This suggests a coordination number of three at all the phosphorus atoms and therefore **1** should be dissociated in THF solution. However, the influence of the third substituent (H, W or Li) of the P(Si*i*Pr$_3$)$_2$ moiety on the chemical shift of the silicon nuclei is negligible.

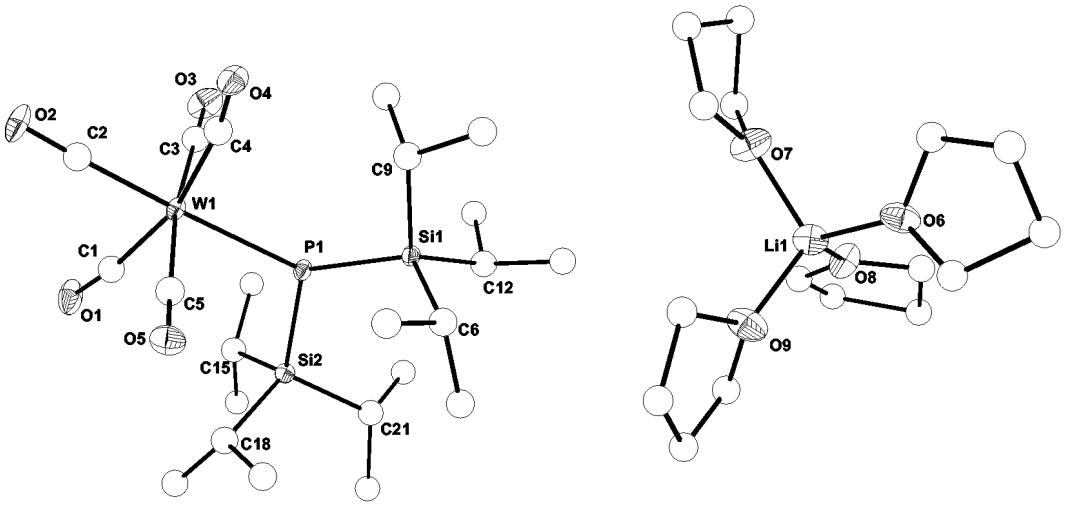


Fig. 2. Molecular structure of **2**. The ellipsoids represent a probability of 25%. The H atoms are neglected for clarity reasons and the carbon atoms drawn with arbitrary radii. Selected bond lengths [pm]: W1-C1 203.7(3), W1-C2 195.4(3), W1-C3 203.5(3), W1-C4 203.3(3), W1-C5 204.0(3), W1-P1 266.65(7), P1-Si1 223.4(1), P1-Si2 223.4(1), Si1-C6 190.7(3), Si1-C9 190.4(3), Si1-C12 190.6(3), Li-O8 191.0(7); angles [°]: Si1-P1-Si2 116.9(4), Si1-P1-W1 120.5(3), Si2-P1-W1 113.0(4), C2-W1-C3 91.8(1), C2-W1-C4 81.2(1), P1-W1-C4 99.5(8), P1-Si1-C12 109.3(9).

The pentacarbonyltungsten fragment shows two sets of carbonyl ligands with characteristic NMR parameters. While the CO groups display very similar chemical shifts, the coupling constants of the carbonyl in *trans* position to the phosphanide ligand shows larger coupling constants to the phosphorus and the tungsten nuclei.

X-ray crystallographic investigations

A comparison of the structures of the compounds $HP(Si\mathit{i}Pr_3)_2$ [12], $P(Si\mathit{i}Pr_3)_3$ [7], $(thf)LiP(Si\mathit{i}Pr_3)_2$ (**1**), and $[(thf)_4Li]^+$ $[(OC)_5WP(Si\mathit{i}Pr_3)_2]^-$ (**2**) can allow the evaluation of the influence of the steric demand on the one hand and the enhancement of the anionic charge on the phosphorus atom on the other. Therefore, the crystal structures of **1** and **2** were determined by X-ray crystallography (Figs 1 and 2).

Selected structural parameters are summarized in Table 2. The P-Si bond lengths decrease with increasing charge on the phosphorus atom. The phosphanes $HP(Si\mathit{i}Pr_3)_2$ [12] and $P(Si\mathit{i}Pr_3)_3$ [7] show values of $\sim$ 226.5 pm regardless of the geometry at the phosphorus atom. The bulkiness of the triisopropylsilyl groups leads to a trigonally planar coordination of the P atom for $P(Si\mathit{i}Pr_3)_3$ [7] whereas the Si-P-Si angle for $HP(Si\mathit{i}Pr_3)_2$ [12] lies at 116.7°. The intramolecular steric strain mainly affects the bond angles but not the P-Si distances. However, the increase of the anionic charge on the phosphorus atom in **2** and **1** leads to a shortening of the P-Si bonds due to additional electrostatic attractions between the negative phosphorus and the positively charged silicon atoms. Assuming that the bulkiness of the triisopropylsilyl groups enforces vander-Waals contacts between these substituents and consequently a shortening of the P-Si bond, a widening of the Si-P-Si bond angle may be induced. This correlation between negative charge on the phosphorus atom, P-Si bond lengths and Si-P-Si bond angles is reflected by the data for this series of related compounds.

Table 2. Comparison of selected structural parameters of $HP(Si\mathit{i}Pr_3)_2$ [12] (M = H), $P(Si\mathit{i}Pr_3)_3$ [7], **1** (M = Li) and **2** (M = W).

Compound	**$HP(Si\mathit{i}Pr_3)_2$**	**$P(Si\mathit{i}Pr_3)_3$**	**1**	**2**
M-P	125(3)	–	253.3(6)	266.7(7)
P-Si	226.0(1)	226.5(6)	220.3(2)	223.4(1)
Si-C	190.4(2)	190.7(2)	187.1(4)	190.6(3)
M-P-Si1	94(1)	–	113.3(2)	120.5(3)
M-P-Si2	97(1)	–	113.7(2)	113.0(4)
Si1-P-Si2	116.7(3)	120.0(2)	117.8(6)	116.9(4)
M-P-M'	–	–	73.8(2)	–

The W-P bond distance of **2** with 266.6 pm is longer than in comparable compounds. Tungsten phosphanides such as $[\{(Me_3Si)_2HCPC(H)H\text{-}C(H)Ph\}W(CO_5)]$ and $[(2\text{-pyridyl})\ P(NMe_2)_2][W(CO)_5]$ display W-P distances of 250.6 [13] and 254.0 pm [14],

	Li-P	Li'-P	P-Li-P	Li-P-Li	Si-P-Si	Lit.
$[LiP(SiMe_3)_2]_6$	252(1)	256(1)	104.5(4)	73.8(3)	107.8(1)	[1]
$Li_4(\mu_2\text{-}PR_2)_2(\mu_3\text{-}PR_2)_2(THF)_2$	255(3)	264(2)	105.4(9)	72.9(8)	106.5(3)	[3]
$[LiP(SiMe_3)_2]_2$ 2DME	255.9(4)	255.9(4)	104.3(2)	75.7(2)	105.9(1)	[2]
$[LiP(SiMe_3)_2]_2$ 4THF	262(2)	262(2)	100.0(8)	80.0(7)	104.7(2)	[3]
$[LiP(SiPh_3)_2]_2$	249.5(6)	244.9(6)	106.5(2)	72.9(2)	119.62(6)	[5]
$[LiP(Si\mathit{i}Pr_3)_2]_2$ 2THF	253.3(6)	253.3(6)	106.1(2)	73.8(2)	117.76(6)	

Table 3. Comparison of selected structural parameters of lithium phosphanides with a $[LiP(SiR_3)_2]_2$ fragment [bond lengths (pm) and angles (°)].

respectively. In Cp'CpTa(CO)(μ-PMe_2)W(CO)$_4$PMe Ph(o-anisyl) (Cp' = 1-*t*Bu-3,4-Me_2-C_5H_2) a larger value of 262.8 pm was observed due to a steric repulsion between the two organometallic fragments [15].

In agreement with the very large P-W distance of 266.7 pm and the non-planar environment of the phosphorus atom (angle sum at P1: 350.4°) the *trans* CO stretching vibration is shifted towards smaller wavenumbers (1904 cm^{-1}). Coordinated phosphanes and phosphanides are strong σ-donors but weak π-acceptors. Therefore, the π-backbonding from tungsten to the *trans*-carbonyl ligand is strengthened which consequently leads to a weakening of this CO bond. Comparable values (1872 cm^{-1}) were observed for the ion pair PPh_4^+ $[H_2P(W(CO)_5)_2]^-$ [11].

For comparison a series of silylated phoshanides are summarized in Table 3. The steric demand of the triisopropylsilyl groups leads to a lower coordination number of three and a planar environment for the alkali metal atoms. As a consequence the Li-P distances lie in the same range as observed for the trimethylsilyl substituted phosphanides. Even for $[(dme)LiPH_2]_\infty$ similar Li-P distances were published [16]. The bulkiness of the Si*i*Pr$_3$ groups strongly widens the Si-P-Si bond angle by more than 10° compared to the bis(trimethylsilyl)phosphanides. Similar results were obtained for alkyl and aryl substituted phosphanides [17].

Experimental Section

General remarks

All reactions were performed in an argon atmosphere using standard Schlenk techniques. All solvents were dried with Na/benzophenone und distilled prior to use. NMR spectra were recorded on a Jeol Eclipse-400 spectrometer operating at 400.18 MHz for ^{1}H, at 100.63 MHz for ^{13}C, at 141.99 MHz for ^{31}P, at 79.50 MHz for ^{29}Si, and at 155.37 MHz for ^{7}Li. Chemical shifts are given with respect to $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si) and 85% H_3PO_4 (^{31}P). $HP(Si\mathit{i}Pr_3)_2$ [12] and (thf)W(CO)$_5$ [10] were prepared according to literature procedures.

Table 4. Crystallographic parameters, details of data collection and refinement procedures of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{22}H_{50}LiOPSi_2$	$C_{39}H_{74}LiO_9PSi_2W$
Formula weight (g·mol^{-1})	424.71	964.92
Temperature T (K)	193(2)	183(2) K
Space group	$C2/c$	$P2_1/n$
a (Å)	12.637(2)	11.0661(1)
b (Å)	18.023(2)	23.5290(3)
c (Å)	22.834(3)	19.2191(2)
β (deg)	98.989(2)	105.771(1)
V (Å^3)	5136(1)	4815.78(9)
Z	8	4
ρ_{calcd} (g·cm^3)	1.098	1.331
μ (mm^{-1})	0.210	2.527
Collected reflections	11255	50889
Independent reflections	3476	11022
Observed reflections ($i > 2\sigma(i)$)	2352	9443
Absorption correction	SADABS	none
Max/min transmission	0.9807/0.6096	0.8679/0.9875
wR_2[a] (on F^2)	0.1715	0.0708
R_1[a] ($i > 2\sigma(i)$)	0.0611	0.028
Goodness-of-fit s[b] on F^2	1.030	1.004
CCDC number	CCDC-268234	CCDC-268233

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

*[(thf)LiP(SiiPr$_3$)$_2$]$_2$ (**1**):* Bis(triisopropylsilyl)phosphane (2.0 ml, 5.2 mmol) was dissolved in 1 ml of THF and 7 ml of toluene and then lithiated with a 2.5 M *n*BuLi solution in hexane at r.t. After complete addition the reaction mixture was stirred for 12 h. In order to obtain single crystals, the reaction mixture was cooled to 4 °C. Colorless crystals of **1** (3.65 g, 4.3 mmol) precipitated. Yield. 83%. – M.p. 151 °C. – IR: 2301, 1473, 1449, 1430, 1384, 1374, 1360, 1294, 1243, 1225, 1207, 1160, 1083, 1070, 1037, 1016, 990. – $C_{36}H_{84}Li_2P_2Si_4$ (706.23) (THF-free complex): calcd. C 61.31, H 12.01; found C 59.55, H 12.01.

*[(thf)$_4$Li]$^+$ [(OC)$_5$WP(SiiPr$_3$)$_2$]$^-$ (**2**):* The synthesis is straight forward by addition of a solution of (thf)W(CO)$_5$ (10 mmol) in 20 ml THF to a solution of **1** (3.40 g, 4.0 mmol) in 10 ml THF. In order to obtain single crystals, the volume of the reaction mixture was reduced to 10 ml. After storage for one day at −30 °C the solution was decanted and stored at −30 °C. After several days red crystals of **2** precipitated. Yield: 52%. – M.p. 82 °C. – IR: 2946, 2887, 2863, 2065, 2049, 1935, 1904, 1782, 1463, 1044, 1015, 918,

880. – $C_{35}H_{66}O_8LiPSi_2W$ (892.87) (calculated with 3 THF molecules): calcd. C 47.08, H 7.45; found C 46.74, H 7.54.

Crystal structure determination of **1** *and* **2***:* The data sets for the compounds were collected on a Nonius KappaCCD diffractometer (2) and on a Siemens P4 diffractometer equipped with a Bruker "Smart" CCD-camera system at fixed 2θ, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Data was corrected for Lorentz polarization and absorption effects [18 – 21].

The structures were solved by direct methods (SHELXS [22]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [23]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Supporting information available: Crystallographic data (excluding structure factors) for the structures of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-268234 for **1** and CCDC-268233 for **2**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

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