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Inge Sänger, Jens Breunig, Frauke Schödel, Michael Bolte and Hans-Wolfram Lerner*

Activation of P_4 by Li[Si*t*Bu$_3$]: generation of lithium bis(supersilyl)heptaphosphanortricyclanide Li[P_7(Si*t*Bu$_3$)$_2$]

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Abstract: Treatment of P_4 with one equivalent of Li[Si*t*Bu$_3$] leads to the formation of a number of oligo-phosphanes and -phosphides, e.g. the bicyclo[1.1.0]tetraphosphane P_4(Si*t*Bu$_3$)$_2$, the heptaphosphanortricyclane P_7(Si*t*Bu$_3$)$_3$, the tetraphosphides Li$_3$[P(PSi*t*Bu$_3$)$_3$] (Li$_3$**[2a]**), and the pentaphosphacyclopentadienide Li[P_5]. From this reaction we could isolate single crystals of Li$_3$**[2a]**. However, this reaction took another course in the presence of Li[OSi*t*Bu$_3$]. When P_4 was treated with one equivalent of Li[Si*t*Bu$_3$] in the presence of Li[OSi*t*Bu$_3$], the heptaphosphanortricyclanide Li[P_7(Si*t*Bu$_3$)$_2$] (Li**[8a]**) was formed. Single crystals of the cluster {Li$_4$(C_6H_6)(OSi*t*Bu$_3$)**[8a]**$_3$}·C_6H_6 (orthorhombic, space group *Pca*2$_1$) were isolated from the reaction mixture at ambient temperature. This cluster compound consists of three chiral Li[P_7(Si*t*Bu$_3$)$_2$] units, one silanolate Li[OSi*t*Bu$_3$], and one benzene molecule. We further investigated the degradation reaction of the bicyclo[1.1.0]tetraphosphane P_4(Si*t*Bu$_3$)$_2$. After heating a benzene solution to 60 °C for 24 h, we found 100 % conversion of P_4(Si*t*Bu$_3$)$_2$, and P_7(Si*t*Bu$_3$)$_3$ (monoclinic, space group *P*2$_1$/*c*) and *t*Bu$_3$SiPH$_2$ were formed.

Keywords: heptaphosphanortricyclanes; phosphorus; silanides; X-ray structure analysis.

1 Introduction

In the past few decades, the reactivity of P_4 towards nucleophilic agents has been extensively studied [1–6]. Previously we have reported that the products of the reaction between P_4 and the silanides *M*[Si*t*Bu$_3$] (*M* = Li, Na, K) [7–9] depend strongly on the stoichiometry and the solvent [9–17].

Using the reactants in molar ratios from 1:2 to 1:4, different phosphides were formed: (i) the tetraphosphenediides *M*$_2$[*t*Bu$_3$SiPPPPSi*t*Bu$_3$] (*M*$_2$**[1a]**; *M* = Li, Na, K) and Na$_2$[*t*Bu$_2$PhSiPPPPSiPh*t*Bu$_2$] (Na$_2$**[1b]**) were obtained from the reaction of P_4 with *M*[Si*t*Bu$_3$] (*M* = Li, Na, K) [7–9] and Na[SiPh*t*Bu$_2$] [18, 19] in a molar ratio of 1:2 in thf [9–12, 20] (the supersilylated octaphosphides *M*$_4$[P_8(Si*t*Bu$_3$)$_4$] (*M* = Na, K) were also synthesized in a 1:2 stoichiometry but in weakly polar solvents (heptane, *t*BuOMe, etc.); see [9–11, 20]); (ii) the synthesis of the tetraphosphides *M*$_3$[P(PSi*t*Bu$_3$)$_3$] (*M*$_3$**[2a]**; *M* = Li, Na) and Na$_3$[P(PSiPh*t*Bu$_2$)$_3$] (Na$_3$**[2b]**) was achieved by the reaction of P_4 with the silanides *M*[Si*t*Bu$_3$] (*M* = Li, Na) and Na[SiPh*t*Bu$_2$] in a 1:3 stoichiometry in benzene. However, in thf, *M*$_3$**[2a]** (*M* = Li, Na, K) and Na$_3$**[2b]** are unstable and thereby (iii) *M*[*t*Bu$_3$SiPPPSi*t*Bu$_3$] (*M***[3a]**; *M* = Li, Na, K) and Na[*t*Bu$_2$PhSiPPPSiPh*t*Bu$_2$] (Na**[3b]**) were formed [11–13]; (iv) the pentaphosphide Na$_2$[P_5(Si*t*Bu$_3$)$_3$] (Na$_2$**[4a]**) could be synthesized by treating P_4 with four equivalents of Na(thf)$_2$[Si*t*Bu$_3$] in benzene [12, 14, 15]. Recently, we have discovered that white phosphorus reacts with three molar equivalents of Li[Mes] in benzene forming the phosphide Li$_3$[P(PMes)$_3$] [21] that has been produced in analogous 1:3 reactions of P_4 with the silanides *M*[Si*t*Bu$_3$] (*M* = Li, Na) and Na[SiPh*t*Bu$_2$]. In this paper, we present the reaction of P_4 with one equivalent of supersilyllithium Li[Si*t*Bu$_3$] in the presence of Li[OSi*t*Bu$_3$] by which the lithium bis(supersilyl)heptaphosphanortricyclanide Li[P_7(Si*t*Bu$_3$)$_2$] (Li**[8a]**) has been obtained.

2 Results and discussion

When P_4 in benzene was treated with one molar equivalent of Li[Si*t*Bu$_3$], several phosphorus-containing products were formed, as monitored by ^{31}P NMR spectroscopy: e.g. the bicyclo[1.1.0]tetraphosphane P_4(Si*t*Bu$_3$)$_2$ [10], the heptaphosphanortricyclane P_7(Si*t*Bu$_3$)$_3$ [22], the tetraphosphide Li$_3$**[2a]** [13], and the pentaphosphacyclopentadienide

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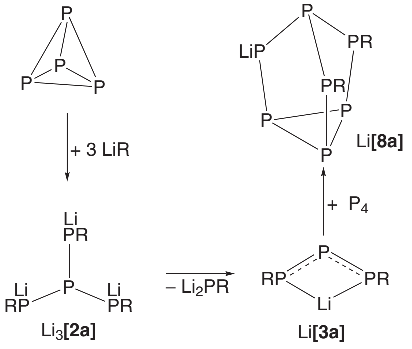
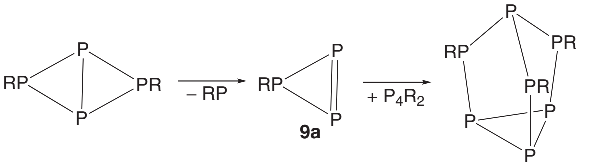
***Corresponding author: Hans-Wolfram Lerner,** Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany, Fax: +49-69-79829260, E-mail: lerner@chemie.uni-frankfurt.de
Inge Sänger, Jens Breunig, Frauke Schödel and Michael Bolte: Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, 60438 Frankfurt am Main, Germany



Scheme 1: Reaction of P$_4$ with supersilyllithium LiR (R = Si*t*Bu$_3$).



Scheme 2: Degradation of the bicyclo[1.1.0]tetraphosphane P$_4$R$_2$ (R = Si*t*Bu$_3$).

Li[P$_5$] [23]. Furthermore, we could isolate single crystals of the tetraphosphide Li$_3$**[2a]** (structural details: CCDC 1426534) from the reaction mixture. However, the reaction of P$_4$ with Li[Si*t*Bu$_3$] took another course in the presence of Li[OSi*t*Bu$_3$] [24, 25]. When P$_4$ was treated with one equivalent of Li[Si*t*Bu$_3$] in the presence of Li[OSi*t*Bu$_3$] [24, 25], the heptaphosphanortricyclanide Li[P$_7$(Si*t*Bu$_3$)$_2$] (Li**[8a]**) was formed. Single crystals of the cluster {Li$_4$(C$_6$H$_6$)(OSi*t*Bu$_3$)**[8a]**$_3$}·C$_6$H$_6$ were isolated from this reaction.

This result suggested a mechanism which is shown in Scheme 1: (i) At first, due to the poor solubility of P$_4$ in benzene, and as consequence thereof, an excess of Li[Si*t*Bu$_3$] being present in solution, Li$_3$**[2a]** was formed. In a second step (ii) Li$_3$**[2a]** releases Li$_2$[PSi*t*Bu$_3$] to give Li**[3a]**, and finally, (iii) Li**[3a]** reacts with P$_4$ to form the heptaphosphanortricyclanide Li**[8a]**. It is worth mentioning that the donor-supported degradation of M_3**[2a]** (M = Li, Na, K) generally leads to the formation of the triphosphallyl compounds M**[3a]**. As alluded to above, in this case, Li[OSi*t*Bu$_3$] was suggested to act as a donor for the degradation of Li$_3$**[2a]**.

Interestingly, cluster build-up also takes place when the bicyclo[1.1.0]tetraphosphane P$_4$(Si*t*Bu$_3$)$_2$ is thermolized. After heating a benzene solution to 60 °C for 24 h, we found 100 % conversion of P$_4$(Si*t*Bu$_3$)$_2$, and the heptaphosphanortricyclane P$_7$(Si*t*Bu$_3$)$_3$ (structural details: CCDC 983799) and the supersilylphosphane *t*Bu$_3$SiPH$_2$ were formed. As shown in Scheme 2, the supersilyl phosphirene **9a** is apparently the key intermediate of this reaction.

The crystals which were obtained from the reaction of P$_4$ with one equivalent of Li[Si*t*Bu$_3$] in the presence of Li[OSi*t*Bu$_3$] are composed of three molecules of the heptaphosphanortricyclanide Li**[8a]**, one molecule of Li[OSi*t*Bu$_3$], and two molecules of benzene. While many examples of heptaphosphanortricyclanes of types **I** [26, 27] and **IV** [22, 27, 28] are known, types **II** [29] and **III** [30] are more elusive (Fig. 1). [PPh$_4$][P$_7$(PhCH$_2$)$_2$] is the only example of a type **III** cluster which has been reported as yet in the literature [30].

The cluster {Li$_4$(C$_6$H$_6$)(OSi*t*Bu$_3$)**[8a]**$_3$} (shown in Figs. 2 and 3; for selected bond lengths and angles see the caption to Fig. 2) crystallizes in the orthorhombic space group *Pca*2$_1$ with an additional benzene molecule in the asymmetric unit (Fig. 2). The cluster consists of three chiral, crystallographically independent, and configurationally identical heptaphosphanortricyclanide Li**[8a]** units, one silanolate Li[OSi*t*Bu$_3$], and one benzene molecule. Within the error of measurement, all three heptaphosphanortricyclanides show identical structural parameters. Therefore, we discuss only the structure of one of those three units. The compound features a Li triangle capped by one [OSi*t*Bu$_3$]$^-$ anion. Each Li cation of this triangle is bonded to two different P atoms of one P$_7$ cluster and to one P atom of another cluster. Two of the seven P atoms are substituted by a supersilyl residue pointing away from the center of the molecule. The three P$_7$ clusters coordinate a fourth Li cation. The coordination sphere of this Li cation is completed by η^6-coordination of a benzene molecule.

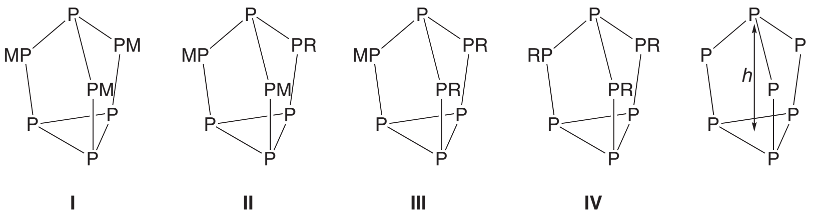


Fig. 1: Heptaphosphanortricyclanides M_3[P$_7$] **(I)**, M_2[RP$_7$] **(II)**, M[R$_2$P$_7$] **(III)**, and heptaphosphanortricyclanes [R$_3$P$_7$] **IV** and definition of the height *h*.

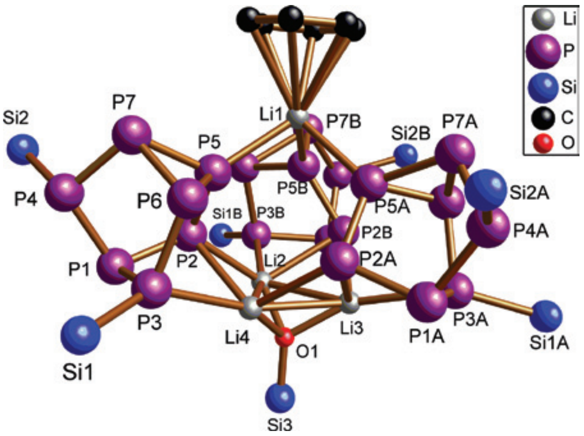


Fig. 2: Molecular structure of {$Li_4(C_6H_6)$(OSi*t*Bu$_3$)**[8a]**$_3$} in the solid state. Hydrogen atoms, carbon atoms on silicon, and cocrystallized C_6H_6 are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Li(1)–P(5) 2.568(8), Li(1)–COG(C_6H_6) 2.258, Li(2)–O(1) 1.922(8), Li(3)–O(1) 1.906(8), Li(4)–O(1) 1.912(9), Li(2)–P(2) 2.656(8), Li(4)–P(2) 2.691(8), Li(4)–P(3) 2.775(8), P(1)–P(2) 2.1598(16), P(1)–P(3) 2.1995(16), P(1)–P(4) 2.1910(16), P(2)–P(5) 2.1434(17), P(3)–P(6) 2.2015(16), P(4)–P(7) 2.1701(16), P(5)–P(6) 2.2188(17), P(5)–P(7) 2.2264(16), P(6)–P(7) 2.2405(16), P(3)–Si(1) 2.3455(17), P(4)–Si(2) 2.3046(16); P(5)–Li(1)–P(5B) 94.0(3), P(2)–Li(2)–P(3B) 102.3(2), P(2)–Li(2)–Li(4) 59.6(2), Li(3)–Li(2)–Li(4) 59.4(3), P(2)–P(1)–P(3) 95.46(6), P(2)–P(1)–P(4) 106.15(6), P(1)–P(3)–P(6) 102.58(6), P(6)–P(5)–P(7) 60.53(5).

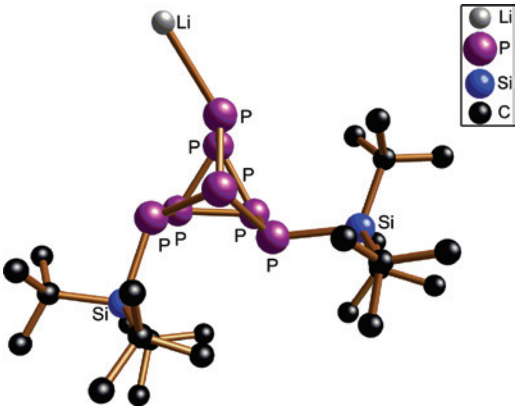


Fig. 3: The structure of the heptaphosphanortricyclanide Li**[8a]** in {$Li_4(C_6H_6)$(OSi*t*Bu$_3$)**[8a]**$_3$}. Only one of the three crystallographically independent and configurationally identical P_7 clusters is shown.

The structural parameters of Li**[8a]** are closer to those of type **IV** clusters (P_7(Si*t*Bu$_3$)$_3$, structural details: CCDC 983799) than to those in [Li(tmeda)]$_3P_7$ [28] (type **I**). The mean length of the P–P bonds in the P_3 ring in Li**[8a]** is 2.228 Å. This is comparable to the value of P_7(Si*t*Bu$_3$)$_3$ (2.224 Å), whereas the length of the related P–P bonds in [Li(tmeda)]$_3P_7$ is 2.255 Å. The distances between the bridgehead P atom and the bridging P atoms of two of these three bonds in Li**[8a]** are comparable to the other two types, but the bond P(1)–P(2) is 0.04 Å shorter than those in type **I** and **IV** clusters.

The distance P(2)–P(5) (2.1434(17) Å) is related to those found in [Li(tmeda)]$_3P_7$ (2.150 Å), whereas the bond lengths P(3)–P(6) and P(4)–P(7) (mean value: 2.186 Å) are like those in P_7(Si*t*Bu$_3$)$_3$ (2.185 Å). A comparison of the heights *h* reveals that the height of Li**[8a]** (*h* = 3.112 Å) is in between the *h* values for [Li(tmeda)]$_3P_7$ (3.02 Å) and P_7(Si*t*Bu$_3$)$_3$ (3.158 Å).

3 Experimental section

The solvents thf, heptane, benzene, and C_6D_6 were stored over sodium/benzophenone and distilled prior to use. Li[Si*t*Bu$_3$] [7] and P_4(Si*t*Bu$_3$)$_2$ [10] were prepared according to the published procedures. All other starting materials were purchased from commercial sources and used without further purification. The NMR spectra were recorded on Bruker AM 250, DPX 250, Avance 400, and Avance 500 spectrometers. NMR chemical shifts (δ) are reported in ppm.

3.1 Reaction of P_4 with Li[Si*t*Bu$_3$]

A solution of Li[Si*t*Bu$_3$] [7] (554 mg, 2.7 mmol) in heptane (10 mL) was added to a mixture of P_4 (300 mg, 2.4 mmol) in benzene (10 mL). In the ^{31}P NMR spectrum of the reaction, mixture signals were observed which are attributable to, e.g. the bicyclo[1.1.0]tetraphosphane P_4(Si*t*Bu$_3$)$_2$ [10], the tetraphosphides Li_3**[2a]** [13], the heptaphosphanortricyclane P_7(Si*t*Bu$_3$)$_3$ [22], and the pentaphosphacyclopentadienide Li[P_5] [23]. Furthermore, we could isolate single crystals of the tetraphosphides Li_3**[2a]** (structural details: CCDC 1426534) from the reaction mixture at ambient temperature.

3.2 Reaction of P_4 with Li[Si*t*Bu$_3$] in the presence of Li[OSi*t*Bu$_3$]

A solution of Li[Si*t*Bu$_3$] [7] (75 mg, 0.36 mmol) and Li[OSi*t*Bu$_3$] [25] (8 mg, 0.04 mmol) in benzene (0.8 mL) was added to a mixture of P_4 (43 mg, 0.35 mmol) in benzene (3 mL). Cocrystals {$Li_4(C_6H_6)$(OSi*t*Bu$_3$)**[8a]**$_3$}·C_6H_6 were obtained from the reaction mixture at ambient temperature (yield: 31 mg, 36 %). {$Li_4(C_6H_6)$(OSi*t*Bu$_3$)**[8a]**$_3$}: – ^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.35 (br, Si*t*Bu$_3$), 1.23 ppm (s, OSi*t*Bu$_3$). – ^{31}P NMR (101.25 MHz, C_6D_6): δ = –177.4 ppm

Table 1: Crystal data and numbers pertinent to data collection and structure refinement of **{**$Li_4(C_6H_6)$(OSi*t*Bu_3)**[8a]**$_3$} · C_6H_6.

	({$Li_4(C_6H_6)$**(OSi*t*Bu**$_3$**)[8a]**$_3$**} · **C_6H_6
Empirical formula	$C_{96}H_{201}Li_4OP_{21}Si_7$
M_r	2246.32
Crystal size, mm^3	0.42 × 0.38 × 0.23
Crystal system	Orthorhombic
Space group	$Pca2_1$
a, Å	29.2281(6)
b, Å	15.0606(3)
c, Å	29.3704(5)
V, Å^3	12928.6(4)
Z	4
$D_{calcd.}$, g cm^{-3}	1.154
μ(MoK_α), mm^{-1}	0.373
F(000), *e*	4840
hkl range	±35, −18/17, ±35
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6171
Refl. measured	124 037
Refl. unique	24 556
R_{int}	0.0510
Param. refined	1163
$R(F)^a/wR(F^2)^b$ (all refls.)	0.0430/0.0916
GoF $(F^2)^c$	1.063
a/b^b	0.035/11.9894
x(Flack)	0.37(8)
$\Delta\rho_{fin}$ (max/min), *e* Å^{-3}	0.674/−0.282

$^aR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$^bwR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.
$^c\mathrm{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

(due to fluxionality arising from Cope rearrangement of the cluster cage at room temperature, only one signal was observed in the ^{31}P NMR spectrum; cf. [31]). – Anal. for $C_{96}H_{201}Li_4OP_{21}Si_7$ (2246.43) calcd. C 51.33, H 9.02; found C 51.75, H 9.25.

3.3 Thermolysis of P_4(Si*t*Bu_3)$_2$

A solution of P_4(Si*t*Bu_3)$_2$ (52 mg, 0.1 mmol) in benzene (1 mL) was heated to 60 °C for 24 h. By cooling to room temperature single crystals of P_7(Si*t*Bu_3)$_3$ (structural details: CCDC 983799) were grown from the solution. The ^{31}P NMR spectrum of the mother liquor revealed solely signals which are attributable to the heptaphosphanortricyclane P_7(Si*t*Bu_3)$_3$ and the supersilylphosphane *t*Bu_3SiPH_2.

3.4 Crystal structure determination

Data of {$Li_4(C_6H_6)$(OSi*t*Bu_3)**[8a]**$_3$} · C_6H_6 were collected on a Stoe IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK_α radiation (λ = 0.71073 Å) and were scaled using the frame scaling procedure in the X-AREA program system [32]. The structure was solved by Direct Methods using the program SHELXS [33, 34] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97 [33, 34]. Details of the crystal structure analysis are summarized in Table 1.

CCDC 983160 ({$Li_4(C_6H_6)$(OSi*t*Bu_3)**[8a]**$_3$} · C_6H_6) contains the 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.

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