

# Metalated diphosphanylsiloxanes with polycyclic and polymeric structures

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## Abstract

The reactions of the diphosphanylsiloxane  $O(SiPr_2PH_2)_2$  (**1**) with  $MiPr_3$  ( $M = Ga, In$ ) produced the polycyclic compounds  $[O\{SiPr_2(PH)MiPr_2\}\{SiPr_2(P)MiPr\}]_2$  (**2**, **3**). Compounds **2** and **3** are composed of three  $M_2P_2$  rings forming a ladder structure and two  $OSi_2P_2M$  rings. By reactions of **1** with  $n$ -BuLi the polymeric compound  $[O(SiPr_2PHLi)_2(THF)(TMEDA)] \cdot THF$  (**4**) was obtained. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Silicon; Phosphorus; Gallium; Indium; Polycyclic compounds

## 1. Introduction

During the last decade several groups have investigated metalation reactions of primary silylphosphines ( $R_3SiPH_2$ ) [1,2]. These reactions yield ring or cage compounds. We are engaged in metalation reactions of diphosphanylsilanes ( $R_2Si(PH_2)_2$ ) as well as diphosphanylsiloxanes ( $O(SiR_2PH_2)_2$ ). From such reactions some unusual polycyclic compounds can be obtained [3,4]. Recently, we synthesized for example the compounds  $[O(SiPr_2PHMe_2)_2]_4$  by the reaction of  $O(SiPr_2PH_2)_2$  (**1**) with  $MEt_3$  ( $M = Al, Ga$ ). These compounds show a 16-membered  $M_8P_8$  ring as structural motif (see Scheme 1) [4].

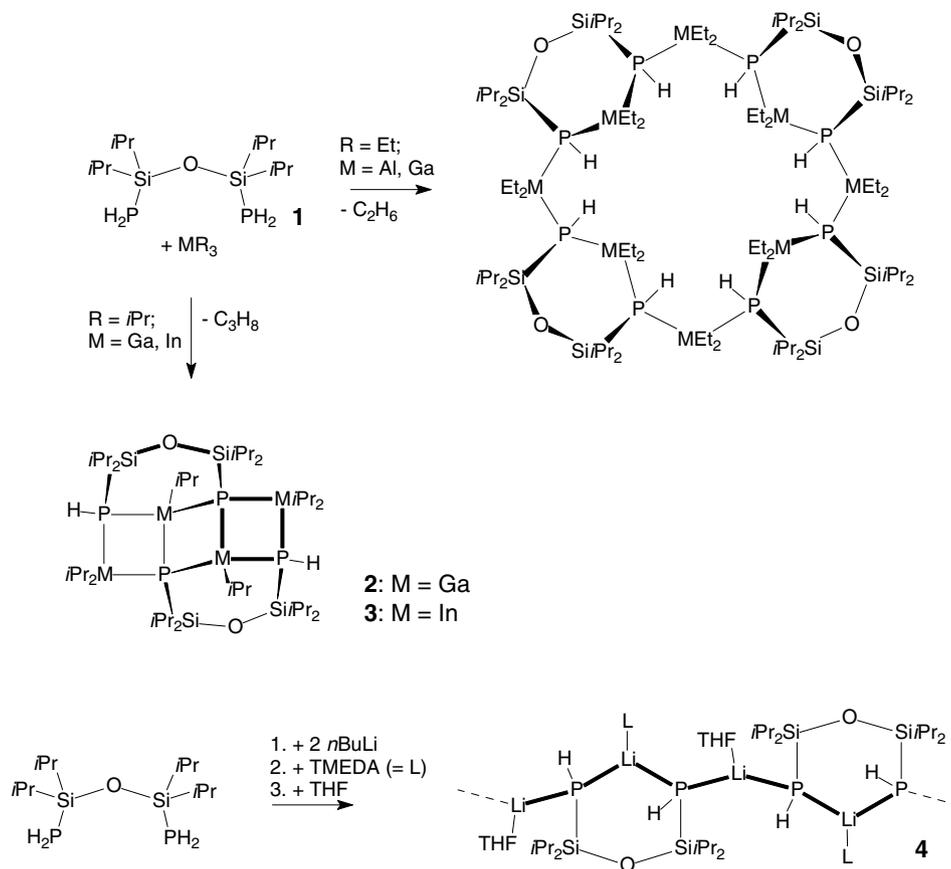
The sterically more demanding  $Ga_iPr_3$  instead of  $GaEt_3$  reacts with **1** at 70 °C to form the polycyclic compound **2**. Single crystals of **2** can be obtained by recrystallization of the crude product from heptane. The analogous indium compound **3** can be synthesized by the reaction of **1** with  $IniPr_3$ . The product of the reaction of **1** with  $n$ -BuLi is the polymeric Li–P chain compound  $[O(SiPr_2PHLi)_2(THF)(TMEDA)] \cdot THF$  (**4**).

## 2. Results and discussion

The centrosymmetric compound **2** crystallizes in the monoclinic space group  $P2_1/n$  [5]. The molecule consists of a  $Ga_4P_4$ -ladder arrangement. Adjacent phosphorus atoms are bridged by  $SiPr_2-O-SiPr_2$  units resulting in a pentacyclic core structure composed of three  $Ga_2P_2$  rings and two  $OSi_2P_2Ga$  rings. The three  $Ga_2P_2$  rings are in chair-conformation with the  $SiPr_2-O-SiPr_2$  bridges located above and under this moiety. On the Ga atoms of the central  $Ga_2P_2$  ring (Ga(1) and Ga(1')) one isopropyl group is retained, whereas on Ga(2) and Ga(2') two unreacted isopropyl groups remain. Consequently each one hydrogen substituent is retained at the outer P atoms. These hydrogen atoms were located in the fourier map. In the infra-red spectrum of **2** a band observed at  $2324\text{ cm}^{-1}$  can be assigned to the P–H stretch vibration. The  $^{31}P\{^1H\}$  NMR spectrum consists of two multiplet resonances for the two different phosphorus positions in **2** at  $-216.9$  and  $-244.2$  ppm (AA'XX' spin system). In the  $^{31}P$  NMR spectrum the signal at  $\delta = -244.2$  shows a  $^1J_{PH}$  coupling (260 Hz). Therefore, this signal can be assigned to the outer P atoms (P(1) and P(1')) in Fig. 1. The Ga–P bond lengths within **2** are in the range of 238.4–249.6 pm. The longest Ga–P bond can be observed at the outer end of

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Scheme 1. Metalation reactions of the diphosphanylsiloxane  $O(SiPr_2PH_2)_2$  (**1**).

the ladder structure (Ga(2)–P(1)), whereas the Ga(1)–P(2) bond is considerably shorter (238.4 pm). Other cyclic or polycyclic Ga/P compounds exhibit Ga–P bond lengths in the range of 234–250 pm [6].

The molecular structure of the indium compound **3** is almost identical with the structure of **2**. Compound **3** crystallizes in the triclinic space group  $P\bar{1}$  [5]. The In–P bond distances observed in **3** are between 255.9(2) and 269.4(2) pm.

The reaction of **1** with 2 equiv. of  $n$ -BuLi in heptane yields a colourless microcrystalline precipitate. A clear solution can be obtained by subsequent addition of TMEDA and THF. Colourless needle-shaped crystals precipitate from this solution at 6 °C. The X-ray analysis of these crystals revealed the composition  $[O(SiPr_2PHLi)_2(THF)(TMEDA)] \cdot THF$  (**4**) [5] (see Fig. 2). Compound **4** crystallizes in the tetragonal space group  $Ibca$  and exists as a polymer in the solid state. The phosphanyl groups of the starting material are lithiated. One of the lithium ions is coordinated by both phosphorus atoms of one diphosphanylsiloxane fragment. A six-membered, slightly twisted heterocycle of the element combination  $OSi_2P_2Li$  is formed. This lithium ion is further coordinated by a TMEDA ligand resulting in a distorted tetrahedral coordination environment. The second lithium ion in **4** has a bridging position between two rings resulting in a poly-

meric Li–P chain. The bridging Li ion is coordinated by an additional THF ligand, resulting in a distorted trigonal planar coordination geometry. Pairs of phosphorus atoms of the Li–P chain are bridged by  $SiPr_2O$ – $SiPr_2$  groups above and below the chain in alternating fashion. The Li–P bonds are 248.8 and 253.1 pm long. These values are almost in the range of Li–P bond lengths observed in other chain like  $LiPR_2$  compounds (249–266 pm) [7].

Currently, we investigate reactions of **1** with metal amides, metal alkoxides and metal alkyl compounds. Moreover, we study the synthetic potential of compound **4**, in particular the incorporation of  $O(SiR_2PH)_2$  fragments in cyclic ligands.

### 3. Experimental

All manipulations were carried out under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use.  $[O(SiPr_2PH_2)_2]$  (**1**) was prepared according to a published procedure [4].  $n$ -BuLi (1.6 M solution in hexane) was obtained from Aldrich.  $GaIPr_3$  and  $IniPr_3$  were prepared by Grignard reactions starting from  $MCl_3$  ( $M = Ga, In$ ) and  $iPrMgCl$  as described in the literature [8]. The  $^{31}P$  NMR spectra were recorded on a Bruker Avance 300 spectrometer. A summary of the crystallo-

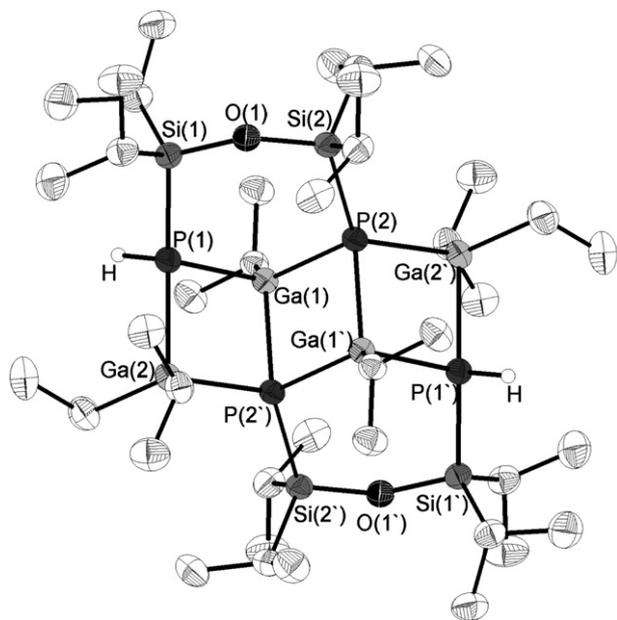


Fig. 1. Molecular structure of **2** (ORTEP, thermal ellipsoids set at the 50% probability level). Hydrogen atoms of the organic groups are omitted for clarity. Selected bond lengths (pm) and angles ( $^{\circ}$ ): Ga(1)–P(1) 240.09(8), Ga(1)–P(2) 238.36(11), Ga(1)–P(2') 243.84(8), Ga(2)–P(1) 249.64(8), Ga(2)–P(2') 243.32(8), Si(1)–P(1) 225.89(12), Si(2)–P(2) 225.66(11); P(1)–Ga(1)–P(2) 103.98(3), P(1)–Ga(1)–P(2') 89.01(3), P(2)–Ga(1)–P(2') 93.37(3), P(1)–Ga(2)–P(2') 86.96(3), Ga(1)–P(1)–Ga(2) 91.49(3), Ga(1)–P(2)–Ga(2') 108.98(3), Ga(1)–P(2)–Ga(1') 86.63(3), Ga(1')–P(2)–Ga(2') 92.14(3), Si(1)–O(1)–Si(2) 158.20(4).

graphic data for the compounds **2–4** can be found in Table 1 and Ref. [5]

Compound **2**: 0.25 g  $\text{GaIPr}_3$  (1.26 mmol) were added to 0.20 g  $[\text{O}(\text{Si}i\text{Pr}_2\text{PH}_2)_2]$  (0.65 mmol). The reaction mixture was stirred and heated to 70  $^{\circ}\text{C}$  for one hour. During that time, gas evolution can be observed. Subsequently, the obtained colourless solid was dissolved in 15 ml of heptane. Cooling this solution to 6  $^{\circ}\text{C}$  yields colourless rhombic

crystals of **2**. Yield: 0.25 g (68.9%), elemental analysis: calculated for  $\text{C}_{42}\text{H}_{100}\text{Ga}_4\text{O}_2\text{P}_4\text{Si}_4$  (1152.4): C, 43.78; H 8.75. Found: C, 43.83; H 8.91%.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.44$  (d, m,  $\text{PH}$ ,  $^1J_{\text{PH}} = 260$  Hz, 2H), 0.9–1.9 (superposition of the isopropyl groups, 98H);  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta = 10.6$  (m), 15.2 (m);  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -244$  (m,  $\text{PH}$ ,  $^1J_{\text{P,H}} = 260$  Hz),  $-217$  (m,  $\text{P}$ ); IR (KBr): 2926 (vs), 2891 (vs), 2867 (vs), 2747 (w), 2710 (w), 2362 (w), 2324 (m), 1459(vs), 1384 (s), 1363 (m), 1286 (w), 1248 (m), 1196 (s), 1151 (w), 1076 (vs), 1043 (vs), 1016 (w), 992 (s), 918 (m), 879 (vs), 807 (w), 732 (w), 673 (vs), 595 (vs), 567 (vs), 508 (vs), 407 (m).

Compound **3**: 0.33 g  $\text{In}i\text{Pr}_3$  (1.35 mmol) were added to a solution of 0.21 g  $[\text{O}(\text{Si}i\text{Pr}_2\text{PH}_2)_2]$  (0.67 mmol) in 10 ml toluene. The reaction mixture was stirred for 1 h and subsequently cooled to  $-35$   $^{\circ}\text{C}$ . Colourless crystals of **3** appear within five days. Yield: 0.28 g (62.2%), elemental analysis: calc. for  $\text{C}_{42}\text{H}_{100}\text{In}_4\text{O}_2\text{P}_4\text{Si}_4$  (1332.8): C, 37.85; H, 7.56. Found: C, 37.91; H 7.55%.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 1.95$  (d, m,  $\text{PH}$ ,  $^1J_{\text{PH}} = 254$  Hz, 2H), 0.9–1.9 (superposition of the isopropyl groups, 98H);  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -268$  (m,  $\text{PH}$ ,  $^1J_{\text{P,H}} = 254$  Hz),  $-251$  (m,  $\text{P}$ ); IR (KBr): 2944 (vs), 2844 (vs), 2746 (w), 2709 (m), 2320 (m), 1460 (vs), 1384 (s), 1362 (m), 1286 (w), 1261 (m), 1237 (m), 1180 (s), 1141 (s), 1080 (vs), 1044 (vs), 987 (s), 967 (s), 919 (s), 880 (vs), 806 (m), 663 (s), 598 (vs), 566 (vs), 513 (s), 461 (s), 421 (m).

Compound **4**: 1.05 ml 1.6 M *n*-butyllithium solution (1.68 mmol) were added to a solution of 0.26 g  $[\text{O}(\text{Si}i\text{Pr}_2\text{PH}_2)_2]$  (0.84 mmol) in 10 ml heptane at 0  $^{\circ}\text{C}$ . The reaction mixture was stirred for 30 min and then heated up to 22  $^{\circ}\text{C}$ . Subsequently, 1 ml of TMEDA and then 10 ml of THF were added. The clear solution obtained was cooled down to 6  $^{\circ}\text{C}$ . Colourless needle-shaped crystals of **4** appear within five days. Yield: 0.20 g (47.3% calc. for  $\text{C}_{22}\text{H}_{46}\text{Li}_2\text{N}_2\text{O}_2\text{P}_2\text{Si}_2$  (502.6 g/mol)). No satisfying elemental analysis can be obtained due to partially loss of solvent molecules.

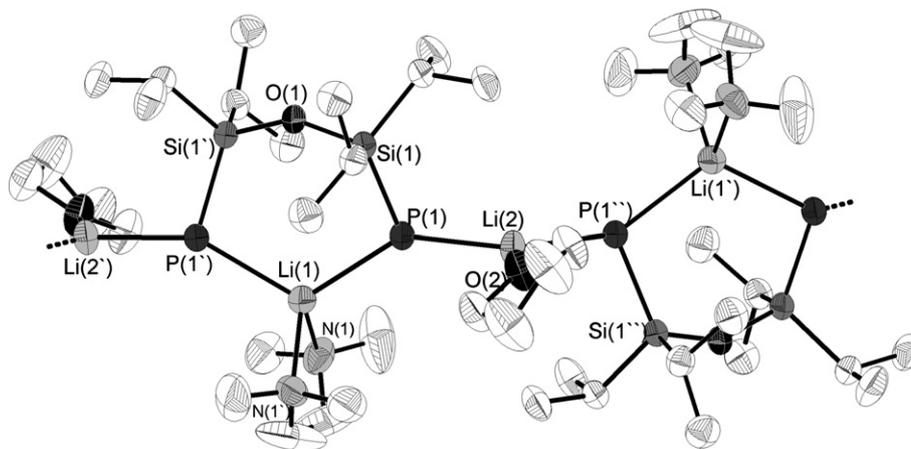


Fig. 2. Structure of **4** (ORTEP, thermal ellipsoids set at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles ( $^{\circ}$ ): Si(1)–O(1) 165.38(11), Si(1)–P(1) 221.15(12), P(1)–Li(1) 253.1(4), P(1)–Li(2) 248.8(4), Li(1)–N(1) 215.6(6), Li(2)–O(1) 191.2(10); P(1)–Li(1)–P(1') 116.1(3), P(1)–Li(2)–P(1') 125.6(4), Li(1)–P(1)–Li(2) 142.43(15), Si(1)–O(1)–Si(1') 148.9(2).

Table 1  
Crystallographic data of 2–4 [5]

Compound	2	3	4
Formula	C <sub>42</sub> H <sub>100</sub> Ga <sub>4</sub> O <sub>2</sub> P <sub>4</sub> Si <sub>4</sub>	C <sub>42</sub> H <sub>100</sub> In <sub>4</sub> O <sub>2</sub> P <sub>4</sub> Si <sub>4</sub>	C <sub>26</sub> H <sub>52</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>I</i> <i>bca</i>
Formula units	2	2	8
Temperature (K)	180	180	200
Lattice constants			
<i>a</i> (Å)	11.385(2)	11.740(2)	17.233(3)
<i>b</i> (Å)	17.931(4)	12.674(3)	19.417(4)
<i>c</i> (Å)	14.905(3)	22.488(5)	21.932(4)
$\alpha$ (°)	90	103.06(3)	90
$\beta$ (°)	103.55(3)	94.02(3)	90
$\gamma$ (°)	90	107.78(3)	90
Volume (Å <sup>3</sup> )	2958.3(10)	3065.5(11)	7339(3)
Density (g/cm <sup>3</sup> )	1.294	1.442	1.037
2 $\theta$ Range (°)	4–52	4–48	4–48
Reflections measured	17 685	17 188	11 119
Independent reflections ( <i>R</i> <sub>int</sub> )	5271 (0.0564)	8702 (0.0845)	2824 (0.0395)
Ind. reflections with <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> )	5016	7586	2483
Parameter	257	505	161
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	2.021	1.679	0.209
<i>R</i> <sub>1</sub>	0.0478	0.0612	0.0664
<i>wR</i> <sub>2</sub> (all data)	0.1349	0.1564	0.2012
Residual electron density (min/max)	–0.732/0.489	–1.454/1.174	–0.511/0.945

<sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  = –1.90 (d, <sup>1</sup>*J*<sub>P,H</sub> = 150 Hz, PH, 2H), 0.80 (sep., <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>, 4H), 1.03 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>, 12H), 1.06 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>, 12H), 2.19 (s, N(CH<sub>3</sub>)<sub>2</sub>, 12H), 2.34 (s, C<sub>2</sub>H<sub>4</sub>(NMe<sub>2</sub>)<sub>2</sub>, 4H); <sup>7</sup>Li{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>):  $\delta$  = 1.46 (s); <sup>29</sup>Si{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>):  $\delta$  = 25.0 (d, <sup>1</sup>*J*<sub>PH</sub> = 57.9 Hz); <sup>31</sup>P NMR (THF-*d*<sub>8</sub>):  $\delta$  = –314 (d, <sup>1</sup>*J*<sub>P,H</sub> = 150 Hz); IR (KBr): 2944 (vs), 2891 (m), 2866 (vs), 2299 (s), 14634 (s), 1385 (m), 1365 (w), 1260 (w), 1214 (w), 1159 (w), 1082 (s), 1051 (vs), 989 (s), 919 (w), 882 (s), 801 (w), 644 (s), 604 (s), 500 (s), 453 (m).

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## Appendix A. Supplementary data

CCDC 615858, 615859 and 615860 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.12.005](https://doi.org/10.1016/j.jorganchem.2006.12.005).

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