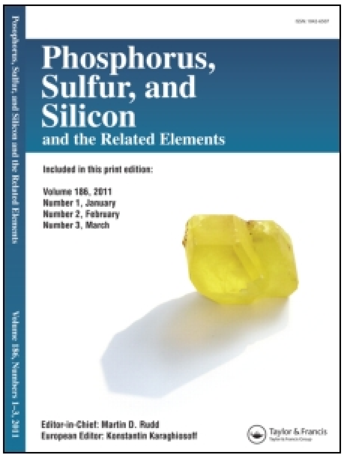

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SYNTHESIS AND CRYSTAL STRUCTURE OF THE LITHIUMPHOSPHAGUANIDINE $Li(THF)NPhC\{N(SiMe_3)Ph\}PC\{N(SiMe_3)Ph\}NP$

Frank Lindenberg[a]; Joachim Sieler[a]; Evamarie Hey-hawkins[a]
[a] Institut für Anorganische Chemie der Universität, Leipzig, Germany

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Communication

SYNTHESIS AND CRYSTAL STRUCTURE OF THE LITHIUMPHOSPHAGUANIDINE Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh

FRANK LINDENBERG, JOACHIM SIELER and EVAMARIE HEY-HAWKINS*

Institut für Anorganische Chemie der Universität, Talstrasse 35,
D-04103 Leipzig, Germany

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The reaction of Li(THF)$_2$P(SiMe$_3$)$_2$ with PhNCNPh yields the N,N′-silylated product

Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh

(**1**), the formation of which can be explained by insertion of one diphenylcarbodiimide molecule into each P—Si bond. **1** was characterised spectroscopically and by X-ray structure analysis. The latter shows the presence of a LiN$_2$C$_2$P six-membered ring with the N—SiMe$_3$ groups having a cis arrangement.

Key words: Lithiumphosphaguanidine, crystal structure.

INTRODUCTION

P-functionalised zirconocene monophosphido complexes Cp$_2$Zr{P(SiMe$_3$)$_2$}(X) (X = Cl, Me) undergo insertion of polar multiply bonded systems (CS$_2$, diazoalkanes, phenylacetylene or carbodiimides)[1,2] into the Zr—P bond, forming novel P-functionalised phosphino ligands that are not accessible from Li(THF)$_2$P(SiMe$_3$)$_2$.[1c,3] Thus, the reaction of (η-C$_5$H$_4$R)$_2$ZrCl{P(SiMe$_3$)$_2$} with R′N=C=NR′ yields the insertion products (η-C$_5$H$_4$R)$_2$Zr(NR′C{P(SiMe$_3$)$_2$}NR′)Cl (R = Me, R′ = Ph[2]; R = H, R′ = Pr^i[4]), while Li(THF)$_2$P(SiMe$_3$)$_2$ reacts with diphenylcarbodiimide to form

Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh

(**1**). We now report the synthesis, spectroscopic studies and structural details of **1**.

SYNTHESIS AND MOLECULAR STRUCTURE OF Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh (1)

Li(THF)$_2$P(SiMe$_3$)$_2$ reacts with PhNCNPh in toluene with formation of the N,N′-silylated product Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh (**1**). Although excess Li(THF)$_2$P(SiMe$_3$)$_2$ was present (100%), only the 1:2 product **1** is formed in ca. 65% yield. Primarily, addition of the P—Si bonds to the C=N bonds of two carbodiimide molecules occurs. A similar result has been reported for the reaction of P(SiMe$_3$)$_3$ with diaryl-substituted carbodiimides, in which initial insertion of the

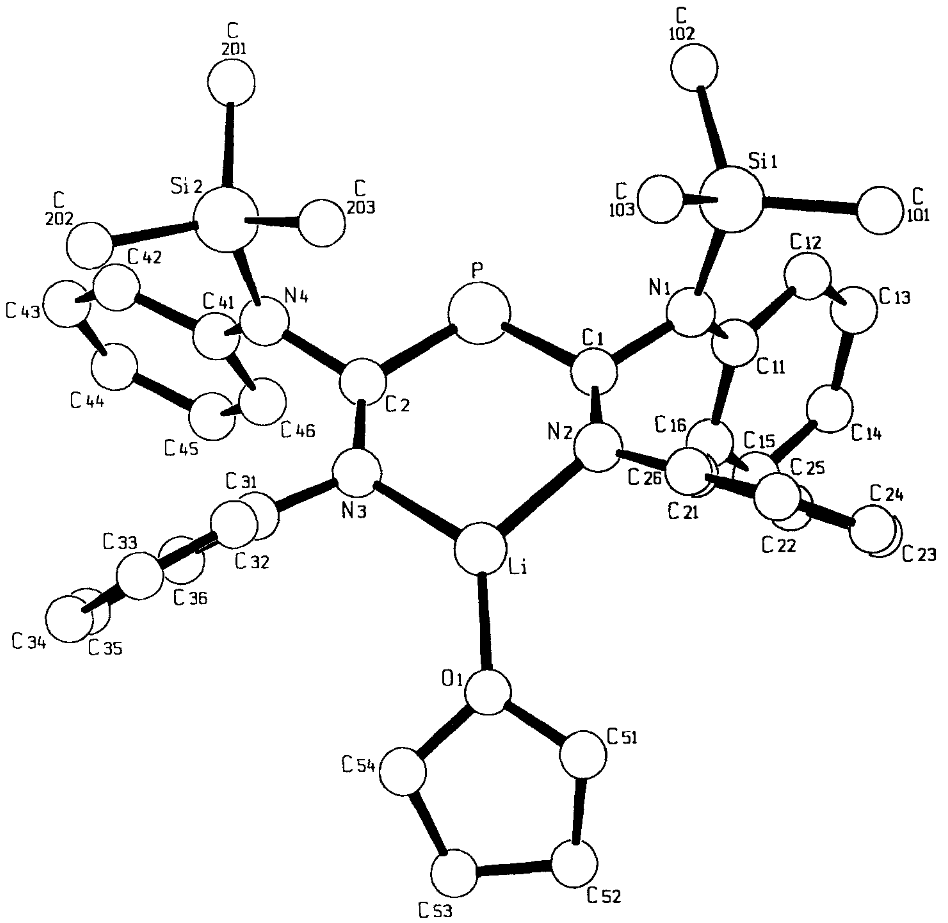


FIGURE 1 Molecular structure of $\overline{\mathrm{Li(THF)NPhC\{N(SiMe_3)Ph\}PC\{N(SiMe_3)Ph\}N}}\mathrm{Ph}$ showing the atom numbering scheme employed. Selected bond lengths (Å) and angles (°) are as follows: P—C1 1.784(6), P—C2 1.783(6), Si1—N1 1.760(5), Si2—N4 1.769(5), O1—Li 1.86(1), N1—C1 1.465(7), N1—C11 1.403(7), N2—C1 1.297(8), N2—C21 1.430(7), N2—Li 1.94(1), N3—C2 1.305(8), N3—C31 1.420(7), N3—Li 1.93(1), N4—C2 1.454(7), N4—C41 1.411(7), C1—P—C2 106.9(4), C51—O1—Li 127.8(5), C54—O1—Li 125.4(5), Si1—N1—C1 119.1(4), Si1—N1—C11 124.9(4), C1—N1—C11 115.4(5), C1—N2—C21 122.8(5), C1—N2—Li 122.6(5), C21—N2—Li 113.8(5), C2—N3—C31 121.5(5), C2—N3—Li 124.2(5), C31—N3—Li 113.9(5), Si2—N4—C2 116.2(4), Si2—N4—C41 124.8(4), C2—N4—C41 118.4(5), P—C1—N1 108.9(5), P—C1—N2 129.6(5), N1—C1—N2 121.1(5), P—C2—N3 129.2(5), P—C2—N4 110.8(5), N3—C2—N4 119.9(5), O1—Li—N2 128.6(6), O1—Li—N3 127.8(6), N2—Li—N3 102.9(6).

heterocumulene into the P—Si bond is observed to give N,P-silylated compounds.[5] These rearrange via P,N-silyl migration into the N,N′,N″-silylated products. The open chain reaction product $\mathrm{N(SiMe_3)PhC\{N(SiMe_3)Ph\}PC\{N(SiMe_3)Ph\}NPh}$, which is comparable to **1**, was characterised spectroscopically.[5] However, disilylated organophosphines $\mathrm{RP(SiMe_3)_2}$ (R = alkyl, aryl) react with diaryl carbodiimides in the stoichiometric ratio 1:1 undergoing insertion without subsequent silyl migration.[6] The reaction of $\mathrm{HP(SiMe_3)_2}$ with diphenylcarbodiimide yields the P-silylated phosphaguanidine $\mathrm{P(SiMe_3)HC\{N(SiMe_3)Ph\}NPh}$.[6]

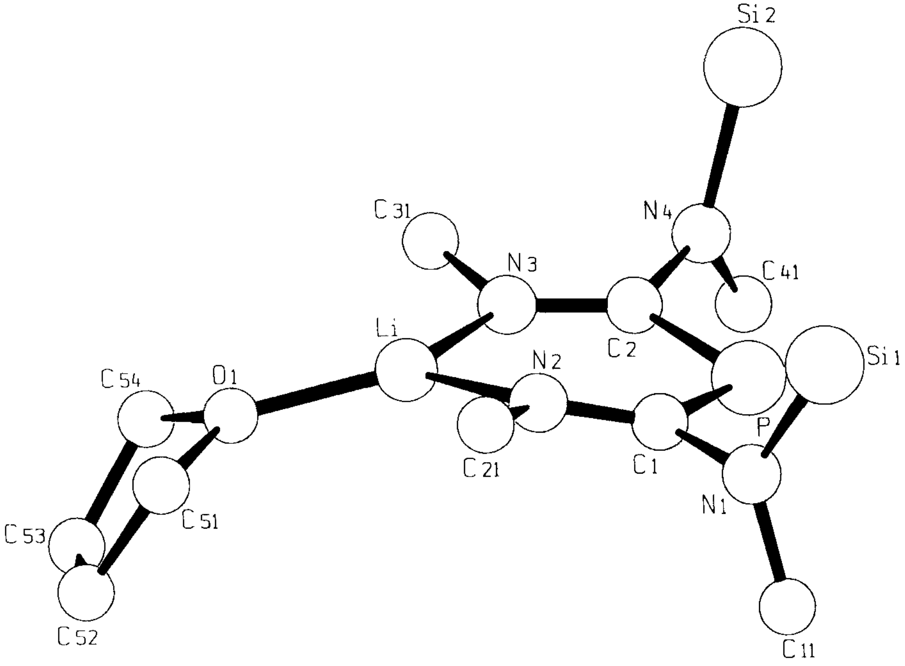
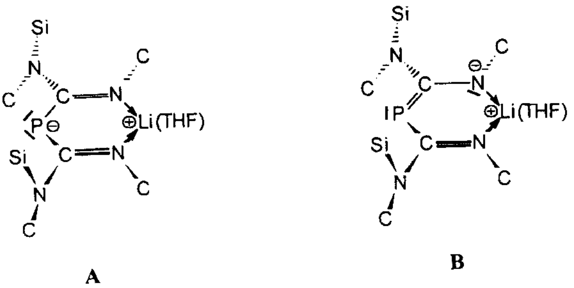


FIGURE 2 Central fragment of Li(THF)NPhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh.



A B

FIGURE 3

The i.r. spectrum of **1** should exhibit the CN vibration at smaller wave numbers (1400 bis 1700 cm^{-1}) compared to the free diphenylcarbodiimide (2140 cm^{-1}). An intense band at 1572 cm^{-1} can be assigned to this mode, although this assignment is complicated by overlap with nujol and phenyl absorptions. In CyP{C(S)NHPh}$_2$, the CN modes are observed at 1552 and 1495 cm^{-1}.[7]

The ^{31}P N.M.R. spectrum of **1** shows a singlet at 28.7 ppm, which broadens on cooling to −80°C (no Li—P coupling can be observed). The signal lies in the range for alkali metal alkylphosphides[8] and is shifted to high field compared to the open chain compound N(SiMe$_3$)PhC{N(SiMe$_3$)Ph}PC{N(SiMe$_3$)Ph}NPh (91 ppm).[5] The X-ray structure determination of **1** shows the presence of molecules with central six-membered LiN$_2$C$_2$P-rings.

1 crystallises triclinic in the space group $P\bar{1}$ with two formula units in the unit cell. The atoms Li, N3, C2, P, C1, N2 form the central fragment of the molecule: a six-membered ring with a conformation between boat and twist-boat (puckering parameters calculated according to Reference 9: Q = 0.247(8) Å, Θ = 74.7(16)°, Φ = 35.1(15)°, Figure 1, Figure 2).

The P atom is coordinated symmetrically by the carbon atoms C1 and C2 (P—C1 1.784(6), P—C2 1.783(6) Å). The P—C bond lengths are only slightly shorter than those observed for P—C single bonds (P—C: ca. 1.85 Å)[10] and are in the same range as those observed for compounds with a partial P—C multiple bond (P—C: ca. 1.74 Å).[11] The C—N bond distances (C1—N2 1.297(8), C2—N3 1.305(8) Å) and the Li—N bond lengths (Li—N2 1.94(1), Li—N3 1.93(1) Å) of the central six-membered ring are equal, within the limits of experimental error. The C—N bond lengths of the central ring are in the range of CN double bonds (expected value 1.28 Å),[12] while the exocyclic CN bonds are in the range of CN single bonds (1.465(7) to 1.454(7)Å). The carbon and nitrogen atoms of the six-membered ring, the lithium atom and the exocyclic nitrogen atoms N1 and N4 exhibit a trigonal planar coordination. There are numerous examples for complexes with silylated amido ligands in which the amido group is planar due to Si—N multiple bond character.[13] The amido groups N1, Si1, C11(Ph) and N4, Si2, C41(Ph) show an almost orthogonal arrangement with the mean plane of the six-membered ring (dihedral angle ca. 88°).

1 can be described as lithium amino imino dialkylphosphide (form **A**) or as phosphaalkenyl lithium (form **B**) (Figure 3). The observed bond lengths of the LiN_2C_2P-ring and the small C1—P—C2 bond angle of 106.9(4)° (corresponds to sp^3 hybridisation) are in agreement with the description shown in **A**. This is also shown in the reactivity of **1** towards protons. When a solution of **1** is reacted with small amounts of water, protonation of the phosphorus atom with formation of $NPhC\{N(SiMe_3)Ph\}PHC\{N(SiMe_3)Ph\}NPh$ (−98.7 ppm, $^1J(PH)$ 235 Hz) can be shown by ^{31}P N.M.R. spectroscopy.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of purified and dried argon. All solvents were rigorously purified and distilled under nitrogen prior to use. N.M.R.: AC 250 and AC 300 (Bruker) (standard ^1H N.M.R.: internal C_7D_8; standard ^{31}P N.M.R.: external 85% H_3PO_4). The i.r. spectrum was recorded with CsI windows in the range 200–4000 cm^{-1} (Perkin-Elmer 883). The melting point was determined on a sample sealed in a capillary under argon. $Li(THF)_2P(SiMe_3)_2$[14] and PhN=C=NPh[15] were prepared according to literature procedures.

$\overline{\mathit{Li(THF)NPhC\{N(SiMe_3)Ph\}PC\{N(SiMe_3)Ph\}NPh}}$ (**1**): 0.24 g (1.24 mmol) diphenylcarbodiimide is added at room temperature to a yellow solution of 0.39 g (1.23 mmol) $Li(THF)_2P(SiMe_3)_2$ in 15 ml toluene. The reaction mixture is stirred for 1 h, then the solvent is removed and the yellow oily residue is dissolved in 10 ml of n-heptane, yielding **1** as bright yellow crystals in 65% yield (0.26 g). M.p. 169–172°C dec. (red).–I.r. (nujol, CsI, cm^{-1}): 1935vw, 1919vw, 1590m, 1572m, 1341m, 1303m, 1248w, 1193m, 1168m, 1092m, 1072m, 1029m, 994m, 940m, 915m, 891w, 843w, 742m, 694m, 639w, 583w, 517w, 479w, 414w, 366w; N.M.R. (C_7D_8, 300 K): ^1H (250 MHz) 0.43 (s, 18 H, $SiMe_3$), 1.05 (m, 4 H, THF), 3.01 (m, 4 H, THF), 7.12–6.65 (m, 20 H, Ph); ^{31}P (121.5 MHz) 28.7 s; ^7Li (116.6 MHz) 1.4 s.

Crystal Data of $\overline{\mathit{Li(THF)NPhC\{N(SiMe_3)Ph\}PC\{N(SiMe_3)Ph\}NPh}}$ (**1**): $C_{36}H_{46}LiN_4OPSi_2$, M_r = 644.87, triclinic, space group $P\bar{1}$ (No. 2), a = 10.008(3), b = 12.854(4), c = 15.196(4) Å, α = 85.17(2), β = 72.78(2), γ = 80.50(2)°, U = 1840.3(10) Å^3, Z = 2, D_c = 1.164 g cm^{-3}, μ = 1.35 cm^{-1}, 5097 independent reflections, F(000) = 688, R = 0.063, R_w = 0.048 (STOE Stadi IV diffractometer, Mo-Kα radiation, λ = 0.71069, T = 200 K, 3° ≤ 2Θ ≤ 50°, ω-Θ scan). Structure solution: direct methods,[16] refinement with

SHELX-76,[17] 289 parameters, Li, P, Si, N and C atoms (THF, $SiMe_3$ ligands and C1, C2) anisotropic, phenyl carbon atoms isotropic, H atoms isotropic in idealised positions. Further details of the X-ray structure analysis (thermal parameters, H atom coordinates) have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen 2, Germany. This material may be requested, quoting the literature reference, the names of the authors, and the deposition number CSD 58858.

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