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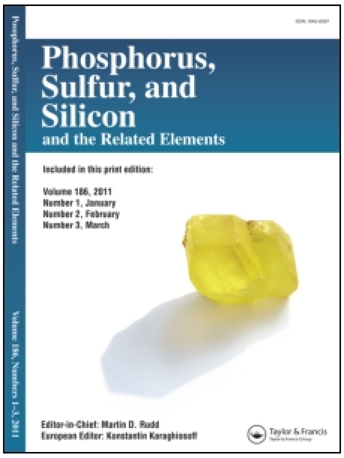

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Crystal Structure of Polymeric Li(thf)PHCy (thf = Tetrahydrofuran, Cy = Cyclohexyl): A Pseudo One-Dimensional Twisted Ladder

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Communication

CRYSTAL STRUCTURE OF POLYMERIC Li(thf)PHCy (thf = TETRAHYDROFURAN, Cy = CYCLOHEXYL): A PSEUDO ONE-DIMENSIONAL TWISTED LADDER

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The crystal structure of Li(thf)PHCy (thf = tetrahydrofuran, Cy = cyclohexyl) shows a polymeric structure with five-coordinate phosphorus atoms and four-coordinate lithium atoms. Three different Li—P distances are observed, which range from 2.608(8) to 2.631(8) Å.

Key words: Lithium cyclohexylphosphide, molecular structure.

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INTRODUCTION

For some time we have been interested in the influence of the substituents R^1, R^2 at the phosphorus atom as well as the nature and number of coordinated donor molecules L (L = ethers, amines) on the solid-state structures of lithium phosphides of type $Li(L)_nPR^1R^2$. Several structural types are already known, including monomeric $Li(thf)_3PHMes$[1] (Mes = 2,4,6-$Me_3C_6H_2$), Li(thf)(tmeda)PHMes[2] (tmeda = $Me_2NCH_2CH_2NMe_2$), and Li(pmdeta)PPh_2[3] (pmdeta = pentamethyldiethylenetriamine), dimeric molecules as in $[Li(thf)_2P(SiMe_3)_2]_2$,[4] $[Li(dme)P(SiMe_3)_2]_2$[5] (dme = 1,2-dimethoxyethane), $[Li(OEt_2)PMes_2]_2$,[1] $[Li(tmeda)PPh(SiMe_3)]_2$,[6] $[Li(tmeda)PPh_2]_2$,[3] $[LiP\{CH(SiMe_3)_2\}_2]_2$[8] and $[Li(dme)PBu^t_2]_2$,[7] the tetrameric compounds $[Li(thf)_{0.5}P(SiMe_3)_2]_4$[4] and $[Li(thf)_{0.5}PBu^t_2]_4$,[9] hexameric $[LiP(SiMe_3)_2]_6$,[10] a polymeric helical arrangement with four-coordinate lithium in $Li(thf)_2PHMes$,[11] a polymeric helical arrangement with three-coordinate lithium in Li(thf)PCy_2[12] and $Li(OEt_2)PPh_2$,[12] infinite chains with mutually coplanar lithium and phosphorus atoms in $Li(thf)_2PPh_2$,[12] Li(dme)PPh_2[7] and Li(dme)PH_2.[5,13] We now report the structure of Li(thf)PHCy, which shows a polymeric arrangement in the solid state. A similar structure was previously proposed for solvent-free $LiPPh_2$.[3] Distorted ladder structures were also observed for the polymeric compounds $[Li(py)SCH_2Ph]$[14] (py = pyridine) and $[NaNC_4Me_4]$.[15]

RESULTS AND DISCUSSION

The lithium phosphide was obtained by reacting equimolar amounts of $CyPH_2$ and BuLi in hexane/thf (20:1) at 0°C. The product precipitates on warming to room temperature. Filtration and cooling of the filtrate to 4°C yields pale yellow crystals of Li(thf)PHCy, which were characterised spectroscopically. The structure (Figures 1 and 2) consists of a polymeric twisted ladder which extends along the a axis. Five-coordinate phosphorus and four-coordinate lithium atoms are present, and the three different Li—P distances observed lie in the range of known Li—P bond lengths:[1-13] P—Li 2.608(8), P—Li′ 2.60(1), P—Li″ 2.631(8) Å (Figure 1, (I)-(III)). The phosphorus atoms show a distorted trigonal bipyramidal environment with the proton and the cyclohexyl ligand occupying equatorial positions, while the environment of the lithium atom is distorted tetrahedral. Accordingly, each Li_2P_2 ring shows a small Li—P—Li′ bond angle of 72.7(3)°, while the P—Li—P′ bond angle is much larger (98.4(3)°).

In the case of hexameric $LiP(SiMe_3)_2$ we assumed that cumulative interaction between the $SiMe_3$ groups of neighbouring phosphorus atoms leads to formation of hexameric units rather than infinite polymeric chains.[10] This assumption seems to be valid in the light of the polymeric structure of Li(thf)PHCy, in which no steric interaction is apparent (Figure 1).

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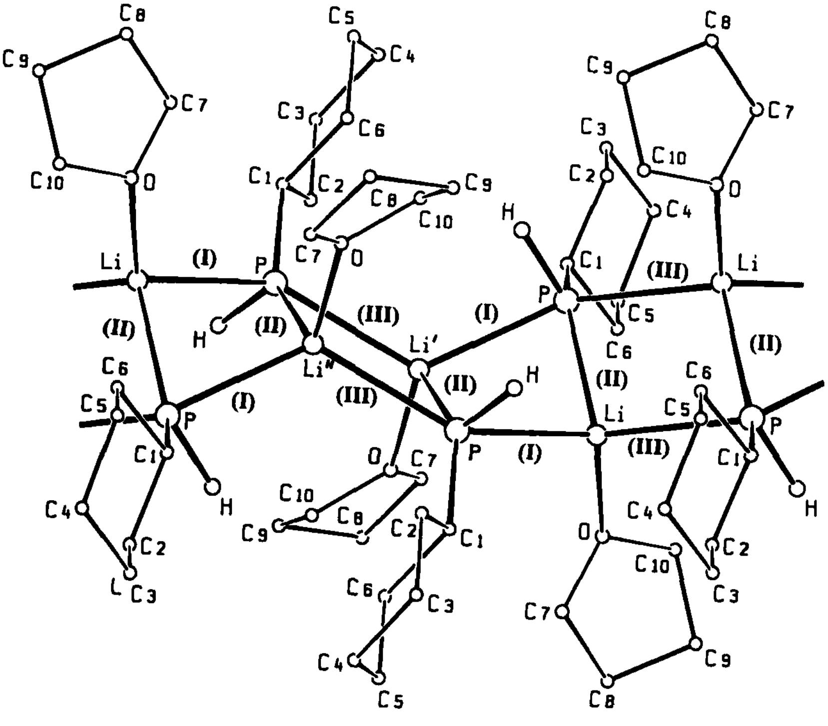

FIGURE 1 Detail of polymeric Li(thf)PHCy showing the atom numbering scheme employed as well as the three different Li—P distances marked (I) through (III). Selected bond lengths and angles are as follows: P—Li 2.608(8) (I), P—Li′ 2.60(1) (II), P—Li″ 2.631(8) (III), P—Cl 1.852(6), Li—O 1.996(7), P—H 1.40(4) Å, Li—P—Li′ 72.7(3), Li—P—Li″ 140.8(4), P—Li—P″ 124.4(4), P—Li—P′ 98.4(3)°. Hydrogen atoms (except P—H) are omitted for clarity.

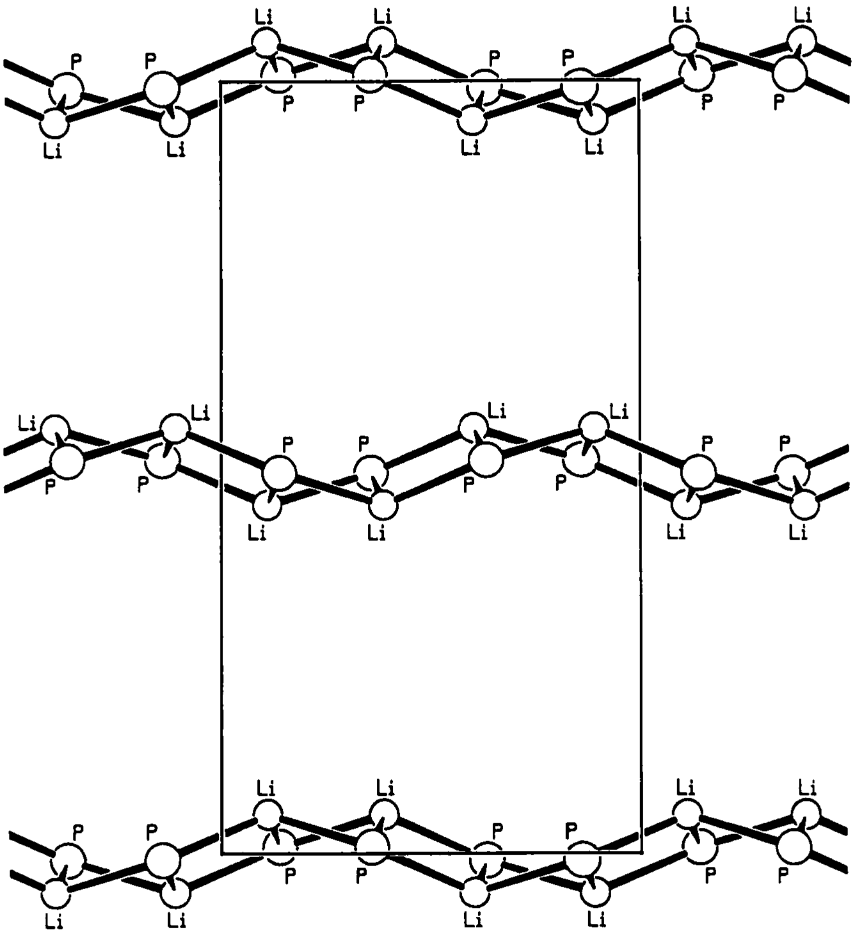

FIGURE 2 View of the unit cell of polymeric Li(thf)PHCy along (010). Only the Li and P atoms are shown.

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EXPERIMENTAL

Li(thf)PHCy: The reaction of equimolar amounts of $CyPH_2$ and BuLi in hexane/thf (20:1) at 0°C yields Li(thf)PHCy in 83% yield. The product precipitates on warming to room temperature. Filtration and cooling of the filtrate to 4°C yields pale yellow crystals of Li(thf)PHCy. Spectroscopic data of Li(thf)PHCy: I.r. (nujol, CsI) 2286 w cm^{-1} (νPH); NMR: (C_7D_8, 25°C): ^{1}H (300 MHz): 2.60 (dd, PH) [$^1J_{PH}$ 187.9 Hz; $^3J_{HH}$ 6.2 Hz], 2.5–1.0 ($C_6\mathit{H}_{11}$), 3.68 and 1.50 (each m, thf); ^{31}P (121.5 MHz, ref. ext. 85% H_3PO_4): −135.4 (s, br, linewidth at half height ca. 51 Hz without proton coupling, ca. 650 Hz with proton coupling); ^{7}Li (116.6 MHz, ref. ext. 1 M $LiBr/H_2O$, C_7D_8): 2.69 (s).

Crystal data of Li(thf)PHCy: $C_{10}H_{20}LiOP$, M_r = 194.19, orthorhombic, space group *P*nna (No. 52), a = 9.252(5), b = 15.228(12), c = 17.024(13) Å, U = 2398 Å^3, Z = 8, D_c = 1.075 g cm^{-3}, μ = 1.53 cm^{-1}, 1658 independent reflections, $F(000)$ 848, R = 0.0848, R_w = 0.0447 (STOE IPDS diffractometer, Mo-Kα radiation, λ = 0.71069, T = −70°C). Further details of the X-ray structure analysis (thermal parameters, H atom coordinates, structure factors) 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 58181.

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