Synthesis and *X*-Ray Structure of [$\{Li(thf)_2PHMes\}_n$] (thf = tetrahydrofuran; Mes = 2,4,6-$Me_3C_6H_2$)

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The reaction between PH_2Mes (Mes = 2,4,6-$Me_3C_6H_2$) and $LiBu^n$ in tetrahydrofuran (thf) at ambient temperature affords the crystalline polymeric lithium phosphide [$\{Li(thf)_2PHMes\}_n$], whose *X*-ray structure shows a helical arrangement of four-co-ordinate P and Li atoms and the presence of both helical enantiomers (*P* and *M*), which are related by two crystallographic glide planes.

As part of our continuing studies of *P*-functionalised phosphido metal complexes[1,2] we have become interested in compounds in which the functionality at phosphorus is H; *e.g.* [$Mg(tmeda)(PHPh)_2$] (tmeda = $Me_2NCH_2CH_2NMe_2$).[3] More recently, we have investigated the metallation of PH_2Mes (Mes = 2,4,6-$Me_3C_6H_2$). PH_2Mes was treated with 1 equiv. of $LiBu^n$ in tetrahydrofuran (thf). After removal of the solvent *in vacuo* (10^{-2} Torr) and recrystallisation of the residue from pentane we obtained the pale yellow, crystalline lithium phosphide (**1**) in 78% yield, for which n.m.r. and analytical data were in agreement with the empirical formula [$Li(thf)_2PHMes$].† Therefore, we believe that the complex [$Li(thf)_3PHMes$] (**2**),[4] which was also obtained from $LiBu^n$ and PH_2Mes in thf, readily loses one equivalent of thf to give the observed product (**1**). A single crystal *X*-ray diffraction study showed that (**1**) is an infinite polymer [*cf.* the monomeric (**2**)[4]].

The structure (Figures 1 and 2)‡ consists of a helix of four-co-ordinate lithium and phosphorus atoms. The glide planes of the space group $Pna2_1$ generate the two enantiomeric helical forms (*P* and *M*). The lithium atoms in the helices are coplanar, as are the phosphorus atoms. Both lithium and phosphorus have distorted tetrahedral geometries with ∠LiPLi′ 130.0(2) and PLiP′ 122.3(2)°, respectively. The Li–P bond lengths of 2.640(6) and 2.656(6) Å are typical of lithium phosphides,[5,6] in which both lithium and phosphorus are four-co-ordinate. Structures containing three-co-ordinate lithium typically exhibit shorter LiP distances.[6]

Four other, structurally characterised polymeric lithium phosphides have been reported.[6,7] Of these, [$\{Li(thf)PCy_2\}_n$][6] (Cy = cyclohexyl) also exhibits a helical structure but differs from (**1**) in being composed of four-co-ordinate tetrahedral phosphorus and three-co-ordinate, almost planar, lithium atoms. The other polymers, namely [$\{Li(OEt_2)PPh_2\}_n$],[6] [$\{Li(thf)_2PPh_2\}_n$],[6] and [$\{Li(dme)PH_2\}_n$][7] (dme = 1,2-dimethoxyethane), can be described as infinite chains having mutually coplanar lithium and phosphorus atoms. For none of the above were the enantiomers detected in the solid state.

We had hoped to obtain information on the structure of (**1**) in solution from ^{31}P and ^7Li n.m.r. data, since ^7Li–^{31}P couplings in the range of 36—120 Hz have been observed for other lithium phosphides.[8,9] However, in the temperature range 180—293 K in $CD_3C_6D_5$, no ^7Li–^{31}P coupling was observed in the ^7Li and ^{31}P n.m.r. spectra. In the weakly co-ordinating solvent toluene it is unlikely that a dissociation into ion pairs would occur. Issleib *et al.*[9] prepared LiPHMes in Et_2O or thf and recorded its ^7Li and ^{31}P n.m.r. spectra. ^7Li–^{31}P coupling was observed in Et_2O at low temperature but not in thf. The absence of coupling in the latter case has been attributed to a rapid intermolecular lithium exchange process, which occurs without formation of separated ion pairs. Such a

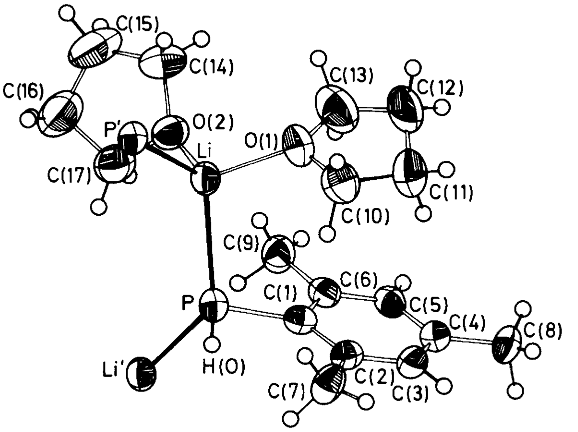

Figure 1. Detail of the asymmetric unit of [$\{Li(thf)_2PHMes\}_n$] (**1**) showing the atom numbering scheme employed. The atoms are drawn as 50% thermal motion ellipsoids. Selected bond lengths and angles are as follows: Li–P 2.640(6), Li–P′ 2.656(6), P–H(0) 1.39(3), Li–O(1) 1.978(6), Li–O(2) 1.973(6), P–C(1) 1.825(3) Å, P–Li–P′ 122.3(2), Li–P–Li′ 130.0(2), Li–P–H(0) 109.7(12), Li–P–C(1) 105.9(2)°.

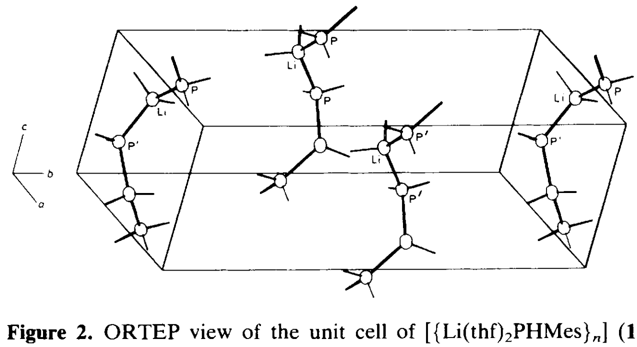

Figure 2. ORTEP view of the unit cell of [$\{Li(thf)_2PHMes\}_n$] (**1**) showing both enantiomeric forms.

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† *N.m.r. chemical shift* (δ) *data* (C_7D_8), 25 °C: ^1H (300 MHz): 6.77 (s, 2,4,6-$Me_3C_6H_2$), 2.56 (d, PH) [^1J ($^{31}P^1H$) 187 Hz], 2.54 (s, *o*-Me in 2,4,6-$Me_3C_6H_2$), 2.19 (s, *p*-Me in 2,4,6-$Me_3C_6H_2$), and 3.16—3.47 and 1.21—1.30 (each m, thf); ^{31}P (121.5 MHz, ref. ext. 85% H_3PO_4): −163.2 (d, PH) [$^1J(^{31}P^1H)$ 187 Hz]; ^7Li (116.6 MHz, ref. ext. 1 M LiBr/H_2O, C_7D_8): 2.17 (s); ^{13}C (75.5 MHz): 147.46 (d, P-C_{Mes}) [$^1J(^{31}P^{13}C)$ 34.9 Hz], 136.58 (d, *o*-C in Mes) [$^2J(^{31}P^{13}C)$ 8.5 Hz], 127.32 (s, *p*-C in Mes), 68.35 and 25.65 (each s, thf), 25.38 (d, *o*-Me in Mes) [$^3J(^{31}P^{13}C)$ 12.4 Hz], 21.20 (s, *p*-Me in Mes). I.r. (Nujol, CsI): 2308s (νPH), 1050vs and 920s (thf), 308s and 282s cm^{-1} (νLiP). Satisfactory analytical data were obtained.

‡ *Crystal data*: (**1**) $C_{17}H_{28}LiO_2P$, M_r = 302.33, orthorhombic, space group $Pna2_1$, a = 9.511(1), b = 23.636(2), c = 8.146(1) Å, U = 1831 Å^3, Z = 4, D_c = 1.096 g cm^{-3}, μ = 12.3 cm^{-1}, 1981 observed, independent reflections, $2\theta_{max.}$ = 55°, $F(000)$ = 652, R = 0.038, R_w = 0.036 (Cu-K_α radiation, λ = 1.5418 Å, T = −50 °C). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

process would account for the non-observance of coupling in (**1**).

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