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**Preliminary communication**

# THE CLEAVAGE OF P–C BONDS IN DIPHOSPHINES BY LITHIUM: THE CRYSTAL STRUCTURE OF $[Li_4\{PhPCH_2CH_2PPh\}_2(OC_4H_8)_8]$

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## Summary

Reaction of alkane-1,n-diylbisdiphenylphosphines with lithium in tetrahydrofuran gives only the diphosphides resulting from cleavage of a phosphorus–aryl bond at each end of the chain; the course of the reaction is independent of chain length. The X-ray structure of the ethane diphosphide is presented and a possible mechanism discussed.

Cleavage of phosphorus–aryl bonds with lithium in tetrahydrofuran has been used as a source of phosphide ions, particularly diphenylphosphide [1a]. We were interested in the synthesis of a range of di- and poly-phosphorus heterocycles and the commercial availability of the crystalline air-stable diphosphines **1** suggested a simple one-pot route (Scheme 1).

The phosphides, **2**, are well known [1b] having been obtained by Issleib and co-workers by alternative, though less convenient, routes, and using a variety of alkali metals. Further, we expected that the expected intermediate monoanion **4** would be useful in the synthesis of macrocyclic polyphosphines with variable length carbon chains joining the phosphorus atoms. In the event, the route to **3** proved moderately successful [2], but attempts to obtain **4** by cleavage with two equivalents of lithium failed. The diphosphides **2** were the exclusive product (by $^{31}P$ NMR) of the reaction of the diphosphines **1** ($n = 3$–5) with lithium in tetrahydrofuran, regardless of molar ratios. The diphosphine **1** (n = 1) is exceptional in this class of compounds in that it reacts with lithium exclusively with cleavage of the alkyl–phosphorus bond [2,14]. The ethane diphosphine **1** ($n = 2$) gave the diphosphide, together with variable amounts of lithium diphenylphosphide (0–30%), presumably formed as shown in eq. 1 since ethylene was detected after bromination

$$Ph_2PCH_2CH_2PPh_2 \xrightarrow{Li} Ph_2PLi + PH_2PCH_2CH_2Li \rightarrow 2Ph_2PLi + C_2H_4 \qquad (1)$$

(GLC, $^1H$ NMR). In addition, traces (0–5%) of monoanion **4** ($n = 2$), identified by $^{31}P$ NMR ($\delta$ −14.9–40.0, $J(PP)$ 17.6 Hz), were observed. The monoanions could be

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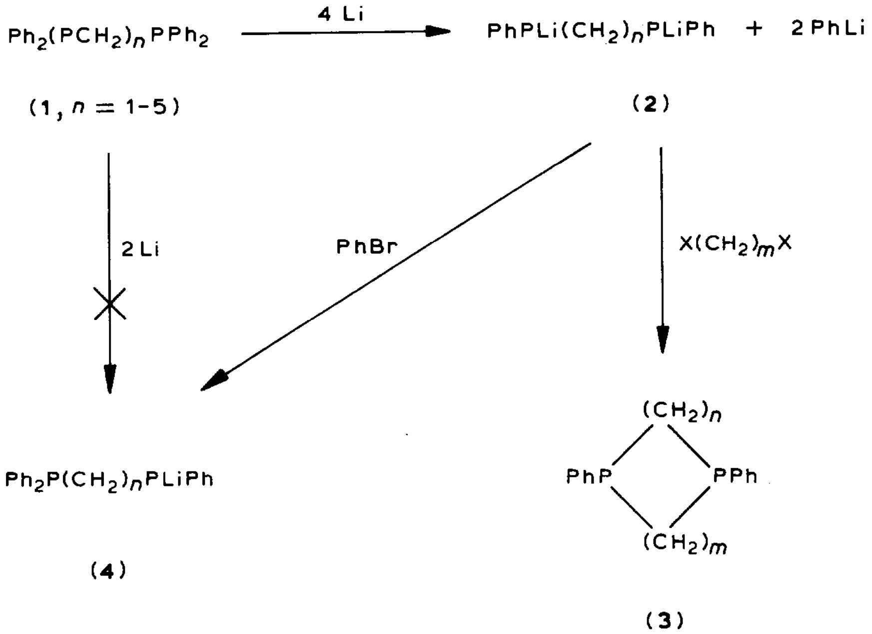

SCHEME 1

readily prepared, however, by treatment of dianions **2** ($n = 2$–5) with bromobenzene. Since nothing is known of the structure of the dianions in solution or the solid state we undertook an X-ray diffraction study on **2** ($n = 2$).

The dilithium compound **2** ($n = 2$), prepared from the diphosphine **1** ($n = 2$) and lithium in tetrahydrofuran with low power sonication at room temperature, was obtained as lemon yellow prisms after recrystallisation from tetrahydrofuran [3]. It is extremely sensitive to moisture and oxygen, and was mounted in a thin-walled glass capillary in an atmosphere of argon saturated with tetrahydrofuran. Data were collected on a CAD-4 diffractometer, Mo-$K_\alpha$ ($\lambda$ 0.71069 Å); graphite monochromator. Crystal data: $C_{30}H_{46}Li_2O_4P_2$, $M = 546.5$, monoclinic, space group $P2_1/c$, $a$ 13.589(2), $b$ 20.569(1), $c$ 13.398(2) Å, $\beta$ 119.29(1), $U$ 3271.0(8) Å$^3$, $D_c$ 1.11 g cm$^{-3}$, $Z = 4$. 3184 reflexions measured ($\theta_{max}$ 25°), including 79 pairs of equivalent $hk0$ (merging $R = 0.017$), giving 3034 unique data. Of these 1406 with $I > 3\sigma(I)$ were considered observed. The structure was solved using MULTAN-80 and Fourier methods. A final value of $R_1 = 0.090$ was obtained.

The structure is shown in Fig. 1 and exhibits several points of considerable interest. The diphosphide exists in the crystal as a centrosymmetric dimer in which the phosphorus and lithium atoms alternate in an eight-membered ring, with no systematic or significant variation in the Li–P(1) bond length (av. 2.573(7) Å); this is considerably larger than the sum of the covalent radii. The molecule contains two types of lithium atom, which differ depending on whether they bridge intramolecularly (PLiP 86.9(3)°) or intermolecularly (PLiP 113.5(2)°). The intramolecular Li bridges lie out of the plane (±1.617 Å) defined by the remaining $P_4Li_2$ system, giving the eight-membered ring the overall appearance of an elongated chair. This

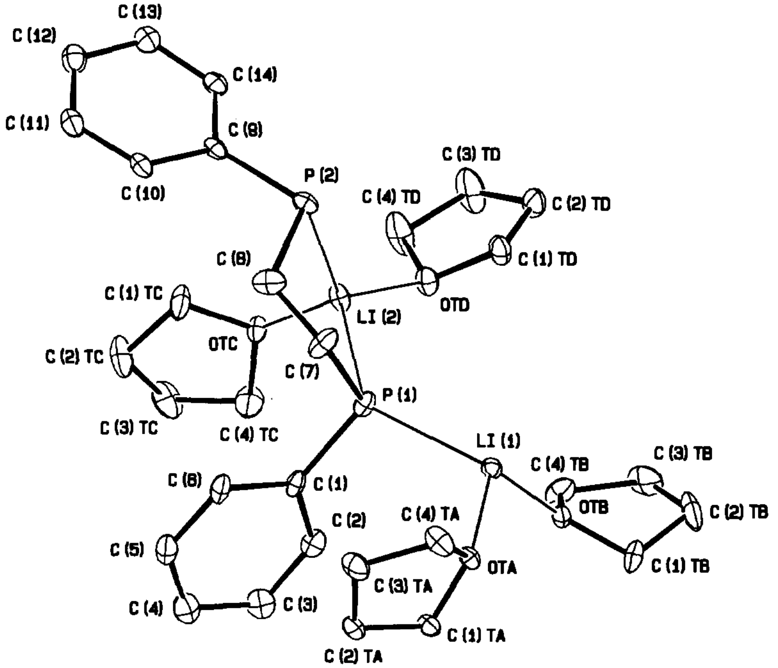

Fig. 1. The crystal structure of $[Li_4\{PhPCH_2CH_2PPh\}_2(OC_4H_8)_8]$ showing only the asymmetric unit.

variation is presumably due to the constraints imposed by the $P_2C_2Li$ ring. There is no Li–Li or P–P bonding. Each lithium is associated with two molecules of tetrahydrofuran, to give a distorted tetrahedral arrangement about the metal atoms.

The structure (Fig. 1) shows a number of points of similarity with lithium di-t-butylphosphide [5] and lithium 2,2,6,6-tetramethylpiperide [6], for which it has been suggested that formation of the eight-membered ring is a consequence of steric crowding due to the bulky alkyl groups, though steric effects are unlikely to be important here, and this is reflected in the large number of molecules of solvent in the unit cell. The compound $\{LiP[CH(SiMe_3)_2]_2\}_2$ has recently been shown to crystallise without solvent and with a planar $Li_2P_2$ ring [7]. There appears to be a difference in the Li–P bond length between **2** ($n = 2$) (2.573(7) Å), $LiPBu^t_2$ (2.488(10) Å) and $LiP[CH(SiMe_3)_2]_2$ (2.473(10) Å) though whether this is due to steric or electronic effects is uncertain.

Another noteworthy feature of the diphosphide structure is the apparent shortening of the $P–C_{aryl}$ bond length (av. 1.804(18) Å) compared with the corresponding bonds (ca. 1.83–1.85 Å) in neutral aryldialkylphosphines [2,8] and triphenylphosphine itself (av. 1.828(3) Å) [9]. A similar shortening was observed in the unassociated diphenylphosphide ion (av. 1.808(4) Å) by Power and his collaborators [10]. If significant, this shortening may reflect partial delocalization of charge from phosphorus into the phenyl ring in the anion, as has been suggested by other spectroscopic studies [11,12]. The opening of the CPC angle (108.7° and 102.7° in **2**, $n = 2$ and 105.2° in diphenylphosphide anion [10]) may be similarly interpreted. However the presence of the poorly defined and strongly vibrating THF molecules in the structure limits the precision of geometrical features.

Nothing in the structure of **2** ($n = 2$) suggests any reason for the preferential formation of diphosphides in the cleavage reaction, it seems reasonable that this occurs because of rapid and strong initial bonding to the metal followed by much slower P–C bond fission and subsequent diffusion away from the surface. Since no cleavage occurs unless at least one aromatic ring is attached to phosphorus [13], the initial point of attachment must be either the aromatic ring or the Ar–P system. A slow second step should ensure that both ends of the diphosphine are adsorbed essentially independently of the chain length separating them [14].

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## References and Notes

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3 $\delta(^{31}P)$: $-62.9$; 2.34, t, $J$ 7.24 Hz, $CH_2$; 5.98, t, J 7.04 Hz, *p*-ArH, 6.38, t, $J$ 7.40 *m* Hz, ArH, 6.74 ppm, *o*-ArH; it began to decompose > 98° but did not melt < 200°; low temperature $^{31}P$ and $^7Li$ NMR studies have proved difficult owing to limited solubility at reduced temperatures. We have no detailed information on solution structures yet.
4 Initial refinement using an ordered atom model produced unrealistic values of bond lengths and angles for the THF molecules and gave large anisotropic thermal parameters. However, it was shown that the data could be fitted to the fully optimised molecular geometry of THF within $C_2$ symmetry constraint obtained by ab initio MO calculations using an STO-3G basis set. The structure was refined (RAELS, A.D. Rae) by modelling two half occupancy molecules at each THF site; bond lengths and angles (other than torsional) were restrained to approach the ideal values.
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13 The failure of trialkylphosphines to react has been noted [1]; we have observed no reaction for tribenzyl-, tris(2-cyanoethyl)-, or tris(dimethylamino)-phosphine.
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15 As this work was being submitted Chou and his collaborators [14] reported that sodium naphthalenide also cleaves these diphosphines, but only the monophosphides **4** are formed.
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