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Some Reactions of the Ethylenebis(phenylphosphido)dilithium Reagent [{Li(THF)$_2$}$_2$(PhPCH$_2$CH$_2$PPh)]$_2$, and its X-ray Structure*

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The title compound **1a**, first described by Issleib and Böttcher [1], is of some importance in synthesis as a 1,2-ethylenebis(phenylposphido) transfer reagent (see, for example, ref. 2). It is also a rare example of a metal bis(organo)phosphide and therefore its structure and reactivity are of relevance to the current interest in lithium di(organo)phosphides [Li(PR$_2$)L$_m$]$_n$. X-ray data have become available on a number of such compounds [3], some of which show structures at variance with those postulated on the basis of studies of these reagents in solutions. For example, LiPPh$_2$ has been proposed on the basis of its multinuclear NMR spectra to be a dimer [4] in Et$_2$O or a tetramer [5] in THF. However, it has recently been suggested that the ^{7}Li{^{1}H} and ^{31}P{^{1}H} NMR data for Et$_2$O solutions are consistent with the polymer found for the solid state [3b].

We now report (i) the X-ray structure of [{Li(THF)$_2$}$_2$(PhPCH$_2$CH$_2$PPh)]$_2$ (THF = tetrahydrofuran) (**1a**), and (ii) its role as a precursor of some synthetically useful derivatives; see also ref. 6.

Experimental

The compound [{Li(THF)$_2$}$_2$(PhPCH$_2$CH$_2$PPh)]$_2$ (**1a**) was prepared from Ph$_2$PCH$_2$CH$_2$PPh$_2$ (35.0 g, 0.09 mol) and Li powder (2.4 g, 0.35 mol), which were stirred in THF (500 cm^3) at *ca.* 25 °C for 6 h. Residual Li powder was removed by filtration and the solution was concentrated to afford a bright orange solid; the yield of recrystallised product (bright yellow crystals from THF at −25 °C) was 22.0 g, 45.5%.

The complex [{Li(TMEDA)}$_2$(PhPCH$_2$CH$_2$PPh)]$_2$ (**1b**) was precipitated (1.6 g, 80%) from a benzene solution (120 cm^3) of compound **1a** (2.2 g, 2.0 mmol) upon the addition of TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) (1.8 cm^3, 12.0 mmol) at *ca.* 25 °C. The neutral ligand-free bis(phosphido)dilithium compound [Li$_2$(PhPCH$_2$CH$_2$PPh)]$_n$ (**1c**) was obtained in near quantitative yield (4.10 g, 92%) by the addition of a stoichiometric amount of LiBu^n in n-hexane to a hexane solution of PhHPCH$_2$CH$_2$PHPh (**2**) (4.27 g, 17.4 mmol) at *ca.* 25 °C [1].

The diphosphine (**2**) was prepared from compound **1a** (18.0 g, 16.5 mmol) suspended in diethyl ether (100 cm^3), by cautious dropwise addition of water (5 cm^3) with stirring at 0 °C. The reaction mixture was quenched with more water (100 cm^3). The organic layer was separated, dried (MgSO$_4$, 24 h), and evaporated to leave a residual oil, which upon distillation (88–96 °C at 0.1 Torr) yielded **2** (5.5 g, 68%), as a colourless oil which slowly crystallised at ambient temperature. Acid hydrolysis afforded a similar product, as discussed more fully below.

The compound Ph(Me$_3$Si)PCH$_2$CH$_2$P(SiMe$_3$)Ph (**3**) was prepared by the addition of SiClMe$_3$ (1.2 cm^3, 9.5 mmol) to a THF solution of compound **1a** (2.31 g, 2.10 mmol) at 0 °C; it was recrystallised as colourless needles (0.90 g, 55%) from THF–C$_5$H$_{12}$ at −25 °C.

Single crystals of compound **1a**, suitable for X-ray analysis were mounted in sealed capillaries under argon.

C$_{60}$H$_{42}$Li$_4$O$_8$P$_4$, M 1093.1, space group $P\bar{1}$, triclinic, $a = 10.447(4)$, $b = 12.730(5)$, $c = 13.864(4)$ Å, $\alpha = 63.08(2)$, $\beta = 82.25(3)$, $\gamma = 85.85(3)°$, $V = 1629.0$ Å^3, $Z = 1$, $D_C = 1.11$ g cm^3.

The structure of **1** was solved by routine direct methods and refined to $R = 0.093$, $R' = 0.105$, using 2215 reflections $[I > \sigma(I)]$ measured on an Enraf Nonius CAD-4 diffractometer with Mo Kα radiation.

All manipulations were performed under an argon atmosphere, using Schlenk techniques. Compounds **1a**, **1b**, and **1c** are pyrophoric in air and must be handled with extreme caution. All solvents were freshly distilled immediately prior to use. NMR spectra were recorded on Bruker WP80 or WH360 spectrometers and chemical shifts are reported in ppm to high frequency of the usual references.

Results and Discussion

The reagent [{Li(THF)$_2$}$_2$(PhPCH$_2$CH$_2$PPh)]$_2$ (**1a**) was obtained from four reactions (Scheme 1). In our hands, its most convenient synthesis was from 1,2-bis(diphenylphosphino)ethane and Li powder (i, in Scheme 1); as compound **1a** is a potential diphosphide transfer agent [1, 2], we decided to explore other methods of preparation (see also refs. 6 and 7).

Compound **1a** is only sparingly soluble in aromatic solvents, but much more so in THF; solution NMR results (toluene-d$_8$) have been reported elsewhere [8].

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*No reprints available.

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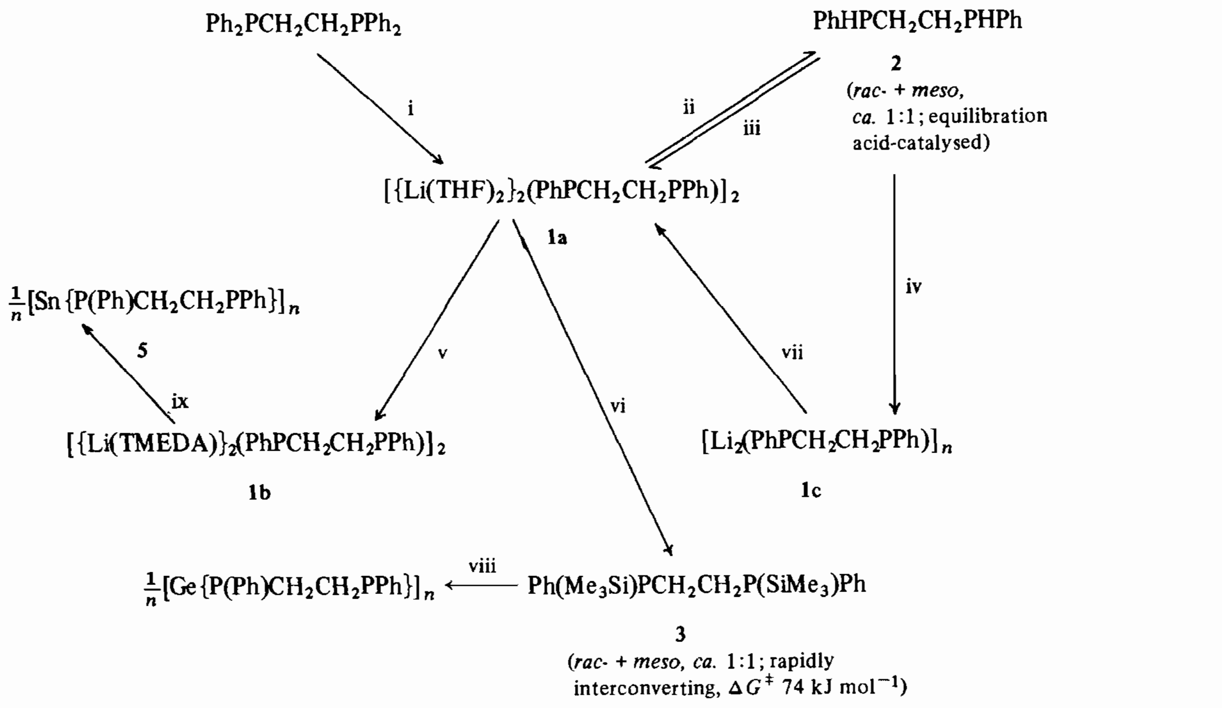

Scheme 1. Reactants and conditions: (i) 4 Li, THF, 6 h, 25 °C; (ii) H_2O, Et_2O, 25 °C, and then distilled *in vacuo*, boiling point 88–96 °C at 0.1 Torr; (iii) 2 LiBu/hexane, THF, 25 °C; (iv) as in iii, but hexane as solvent; (v) 2TMEDA, C_6H_6, 25 °C; (vi) 2SiClMe$_3$, THF, 0 °C; (vii) THF, 25 °C; (viii) $GeCl_2$(dioxane), THF, 25 °C; (ix) $SnCl_2$, THF, −78 °C.

The X-ray structure of crystalline $[\{Li(THF)_2\}_2(PhPCH_2CH_2PPh)]_2$ (**1a**) (Fig. 1, Table I) consists of two symmetry related, five membered rings (LiP_2C_2) linked by bridging $\{Li(THF)_2\}$ moieties [Li(1) and Li(1)′ in Fig. 1] to form an $(LiPC)_4$ macrocycle and as such is unique amongst Li–diorganophosphide structures available for comparison [3, 8]. The only other structurally characterised diphosphide, 1,2-$C_6H_4(PPh)_2\{Li(TMEDA)\}_2$ (**4**) is a monomer, both in the solid and in solution [8]. One possible reason for this difference is that the C_2H_4 backbone of compound **1a** allows for a greater degree of flexibility, so that the Li environment is less distorted [*i.e.* P–Li–P 113.2(7) and 88.7(5)°; *cf.* 72(1)° in **4**]. The differences in the geometry about the atoms P(1) and P(2) are attributed to steric interactions in the macrocycle to accommodate the bulky phenyl and THF ligands.

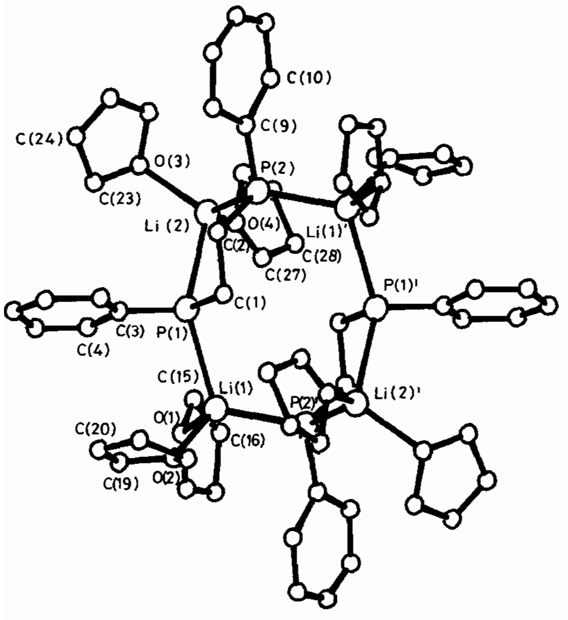

Fig. 1. The molecular structure and atom numbering scheme for $[\{Li(THF)_2\}_2(PhPCH_2CH_2PPh)]_2$ (**1a**).

Treatment of each of the lithium compounds (**1a–c**) with water afforded a diastereomeric mixture of the bis-secondary phosphine (**2**) [9]. The diastereomers were distinguished by (i) two singlets in the $^{31}P\{^1H\}$ NMR (δ −46.10, −46.60 ppm; toluene-d_8); and (ii) the different $(-CH_2-)_2$ coupling patterns (formally *AA′BB′*), at 1.8–1.5 and 1.65–1.6 ppm (^1H NMR). In contrast, the $^{31}P\{^1H\}$ NMR spectrum at 305 K of the product obtained after acid hydrolysis (HCl/H_2O or NH_4Cl/H_2O, followed by Et_2O extraction and distillation *in vacuo*) showed a singlet (iii) at the average chemical shift (−46.35 ppm) of the *rac*- and *meso*-forms, which was resolved into the singlets (i) at 203 K. Conversely, these signals (i)

TABLE I. Selected Bond Distances and Angles for $[\{Li(THF)_2\}_2(PhPCH_2CH_2PPh)]_2$ (**1a**)[a]

Bond lengths (Å)			
Li(1)–P(1)	2.57(1)	Li(2)–P(1)	2.56(2)
Li(1)–P(2)′	2.57(2)	Li(2)–P(2)	2.53(2)
Li(1)–O(1)	2.00(2)	Li(2)–O(3)	2.02(2)
Li(1)–O(2)	1.99(2)	Li(2)–O(4)	1.95(2)
P(1)–C(1)	1.88(1)	P(2)–C(2)	1.88(1)
P(1)–C(3)	1.83(1)	P(2)–C(9)	1.80(1)
Bond angles (°)			
P(1)–Li(1)–P(2)′	113.2(7)	P(2)′–Li(1)–O(1)	114.9(6)
P(1)–Li(1)–O(1)	109.2(6)	P(2)′–Li(1)–O(2)	105.8(6)
P(1)–Li(1)–O(2)	114.0(6)	P(2)–Li(2)–O(3)	113.3(7)
P(1)–Li(2)–P(2)	88.7(5)	P(2)–Li(2)–O(4)	119(1)
P(1)–Li(2)–O(4)	116.8(6)	O(1)–Li(1)–O(2)	99.0(9)
P(1)–Li(2)–O(3)	118.2(9)	O(3)–Li(2)–O(4)	101.7(7)
Li(1)–P(1)–Li(2)	138.6(5)	Li(2)–P(1)–C(1)	96.5(5)
Li(1)–P(1)–C(1)	101.7(4)	Li(2)–P(1)–C(3)	106.9(5)
Li(1)–P(1)–C(3)	104.1(5)	C(1)–P(1)–C(3)	104.4(4)
Li(1)′–P(2)–Li(2)	128.7(5)	Li(1)′–P(2)–C(2)	111.2(4)
Li(1)′–P(2)–C(9)	105.9(5)	Li(2)–P(2)–C(2)	92.3(5)
C(2)–P(2)–C(9)	106.3(4)	Li(2)–P(2)–C(9)	113.5(4)

[a] e.s.d.s given in parentheses.

coalesced to the singlet (iii) at elevated temperatures. A mixture of the two samples or a catalytic amount of HCl/Et_2O added to compound **2**, also yielded the singlet signal (iii). We interpret these observations as implying that the *rac* $\rightleftharpoons$ *meso* equilibration is acid-catalysed.

Reaction of compound **1a** with $SiClMe_3$ afforded the bis-tertiary phosphine (**3**) [9]; we believe this to be a diastereomeric mixture. The $^{31}P\{^1H\}$ NMR (δ −76.1, −77.1 ppm) and the ^1H NMR [δ 0.05, 0.03 ppm; $^3J(^{31}P-{}^1H)$ 4.36 Hz, $P(SiMe_3)$] spectra indicate that this reaction also occurred without diastereoselectivity.

Reaction of compound **3** with $GeCl_2$(dioxane) gave $[Ge\{PhPCH_2CH_2PPh\}]_n$ (**4**) [$^{31}P\{^1H\}$ NMR: −22, −29 ppm], see also ref. 10. Similarly, a stoichiometric mixture of compound **1b** and $SnCl_2$ in THF at −78 °C afforded $[Sn\{PhPCH_2CH_2PPh\}]_n$ (**5**) [NMR: $^{119}Sn\{^1H\}$, 201.4 ppm, $^1J(^{119}Sn-{}^{31}P)$ 1020 Hz; $^{31}P\{^1H\}$, −16.4 ppm], which was unstable at higher temperatures.

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