Lithium- and Dimethylaluminium-di-2-pyridyl-phosphides: the First Metal Diorganophosphides without a Metal–Phosphorus Bond within a Contact Ion Pair

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$[Li\{(2-NC_5H_4)_2P\}\{thf\}]$ **2** (thf = tetrahydrofuran) and $[AlMe_2\{(2-NC_5H_4)_2P\}]$ **3** are obtained in high yield by treating $(2-NC_5H_4)_2PH$ **1**, with Bu^nLi and Me_3Al, respectively; the X-ray-structure determination confirms that **2** is the first contact ion pair of a lithium diorganophosphide without Li–P contact, which makes the $(2-NC_5H_4)_2P^-$ ion a versatile ligand for III/V precursors (already established in **3**).

Lithium diorganophosphides, namely $LiPPh_2$, have long been key reagents in introducing a metal-bridging phosphido centre[1] as well as a diorganophosphide transfer agent.[2] In all known structures[3–5] of $LiPPh_2$ with the exception of $[Li(12\text{-}crown\text{-}4)_2][PPh_2]$, which adopts the structure of a solvent separated ion pair,[3] the lithium atom is attached to the phosphorus atom (average separation 258 pm). Here, we report the novel structure of lithium-di-2-pyridyl-phosphide **1**, which owing to anion solvation *via* the nitrogen atoms of the pyridyl rings, lacks a Li–P contact within the contact ion pair. The P–C bond in the average $LiPPh_2$ structure is 183.4 pm while the C–P–C angle is 104.3°. In aryl-, alkyl- and/or silyl-substituted lithium phosphines[6–12] that angle varies from 103.2[10] to 114.0°.[11] Dimethyl-aluminium-di-2-pyridyl-phosphide **2** is a very promising precursor for III/V semiconducting films.

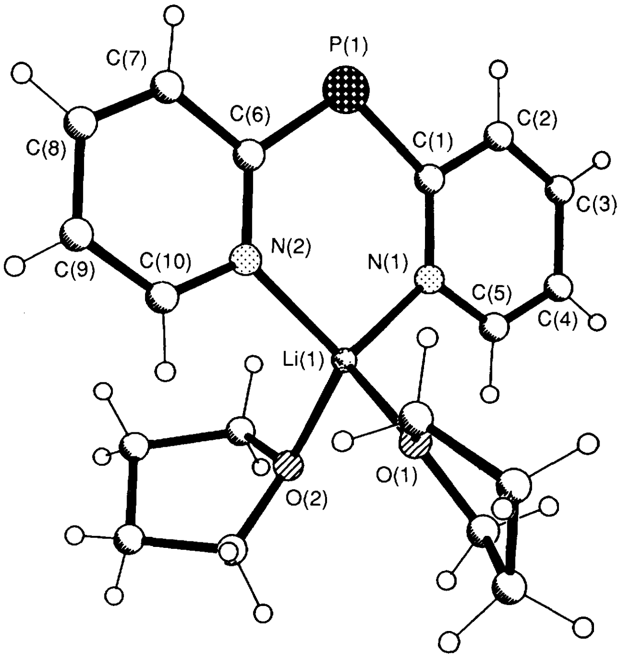

Fig. 1 The X-ray structure of **2**. Selected distances (pm) and angles (°): P(1)–C(1) 179.4(4); P(1)–C(6) 179.8(4); Li(1)–N(1) 196.9(8); Li(1)–N(2) 196.9(7); C(1)–P(1)–C(6) 110.4(2); N(1)–L(1)–N(2) 102.1(3); O(1)–Li(1)–O(2) 99.9(3).

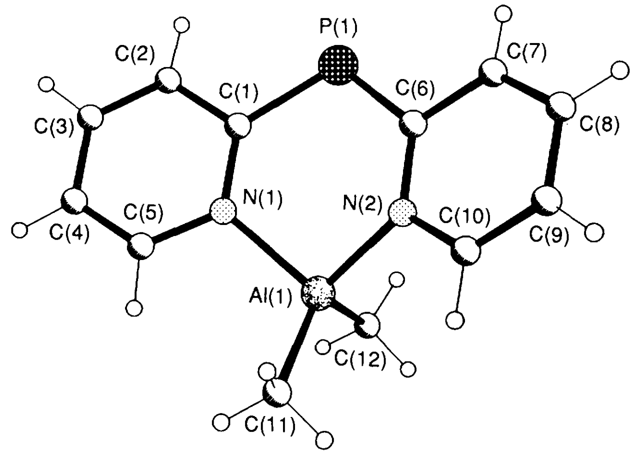

Fig. 2 The X-ray structure of **3**. Selected distances (pm) and angles (°): P(1)–C(1) 178.6(2); P(1)–C(6) 178.2(2); Al(1)–N(1) 192.4(1); Al(1)–N(2) 192.9(1); C(1)–P(1)–C(6) 106.6(1); N(1)–Al(1)–N(2) 99.0(1); C(11)–Al(1)–C(12) 119.5(1).

We aimed to synthesize a diorganophosphide in which the organic substituents at the phosphorus atom could donate concomitantly electrons to the lithium atom. This should inhibit polymerization without the use of chelating amines such as $(Me_2NCH_2CH_2)_2NMe$ or $Me_2NCH_2CH_2NMe_2$. Therefore, we chose the di-2-pyridyl-phosphide ligand, predicting that the two nitrogen atoms in each substituent at the phosphorus atom would chelate the lithium atom. In the reaction of tri-(2-pyridyl)-phosphine[13] with lithium metal a cleavage of one P–aryl bond occurs. The hydrolysis shown in Scheme 1 yields di-(2-pyridyl)-phosphine **1** as a dark-red oil.[†]

$$(2\text{-NC}_5\text{H}_4)_3\text{P} + 2\,\text{Li} \xrightarrow{\text{i, ii}} (2\text{-NC}_5\text{H}_4)_2\text{PH}$$

Scheme 1 *Reagents and conditions*: i, 2Li, thf, 25 °C; ii 2H_2O; $-C_5H_5N$ $-2LiOH$

Reaction of **1** with n-butyllithium in thf leads to *N,N'*-di-(2-pyridyl)-phosphidolithium-bis(tetrahydrofuranate) **2**, Scheme 2. Crystals of **2** suitable for X-ray analysis were obtained after cooling a solution to −3 °C for 3 days; **2** is monomeric in the solid state (Fig. 1).[†] The lithium atom is coordinated by the nitrogen atoms and by two thf molecules and is within the plane of the anion, whereas the thf is located above and below that plane.

$$\mathbf{1} + \text{Bu}^{\text{n}}\text{Li} \xrightarrow{\text{i}} [\text{Li}\{(2\text{-NC}_5\text{H}_4)_2\text{P}\}\{\text{thf}\}_2]$$

Scheme 2 i, thf, n-hexane, 25 °C; $-Bu^nH$

2 Adopts almost the same structure as $[HC(2\text{-}NC_5H_4)_2\text{-}Li(thf)_2]$.[14] The Li–N bond lengths are in the normal range[15,16] and as long as in $[Ph_2C(2\text{-}NC_5H_4)Li(Et_2O_2]$.[17] Whereas the C–P–C angle in the $LiPPh_2$ derivatives is 104.3° on average, it is 110.4° in **2**. The P–C bond length is 179.6 ppm, *i.e.* 4.1 pm shorter than in the average $LiPPh_2$ structure. While a P–C single bond is 185 pm, a P–C double bond is 167 pm (ranging from 161 to 171 pm) long.[18] Thus, the P–C bond in **2** is almost in agreement with a bond order of 1.5 and comparable with the P–C bond in 2,6-dimethyl-4-phenylphosphabenzene.[19] The relatively large C–P–C angle illustrates as well the partial delocalization of the negative charge throughout the whole anion. In the Ph_2P^- anion[3] the two phenyl rings are almost coplanar and the P–C bond length is 180.8 pm. The almost perfect planarity of the anion in **2** facilitates the delocalization. The two ring planes intersect at an angle of 173°.

The complexation of the metal by the two nitrogen atoms leaves the phosphorus atom two coordinated. This arrangement makes the di-(2-pyridyl)-phosphine a versatile reagent for the synthesis of III/V precursors. The resulting materials should be volatile because they are monomers and the leaving groups (pyridine or picoline) in the MOCVD (metal organic chemical vapour deposition) process are both volatile and thermally stable. Therefore, we replaced the lithium atom in **2** for an aluminium atom. *N,N'*-Di-(2-pyridyl)-phosphido-dimethylaluminium is obtained *via* two different routes:[‡] first, in the reaction of **2** with dimethylaluminium chloride where LiCl is eliminated Scheme 3(*a*) and secondly in the reaction of **1** with trimethylaluminium where methane is formed Scheme 3(*b*).

(*a*) $\mathbf{2} + \text{Me}_2\text{AlCl} \rightarrow \text{AlMe}_2\{(2\text{-NC}_5\text{H}_4)_2\text{P}\} + \text{LiCl}$

(*b*) $\mathbf{1} + \text{AlMe}_3 \rightarrow \text{AlMe}_2\{(2\text{-NC}_5\text{H}_4)_2\text{P}\} + \text{CH}_4$

Scheme 3 *Reagents*: (*a*) n-hexane, Et_2O, −40 °C; (*b*) n-hexane, −40 °C

Suitable crystals of **3** were obtained after storage of a Et_2O–hexane solution at +3 °C for 5 days. The structure of **3** is almost identical with that of **2**, except that the $Li(thf)_2$ unit is replaced by an $AlMe_2$ unit (Fig. 2).[†] The aluminium atom is coordinated by the nitrogen atoms within the pyridyl rings leaving the phosphorus atom uncomplexed. The most striking difference compared with **2** is the non-planarity of the anion in **3** (Fig. 3). The two pyridyl ring planes intersect at an angle of 155°. Whereas the lithium atom in **2** is only 14 pm out of the plane of the anion, the aluminium atom in **3** is 72 pm out of it [best least-squares plane of the $P(2\text{-}NC_5H_4)_2$-moiety in both structures]. The C–P–C angle in **3** is 106.6° and the average P–C bond length is 178.4 pm, indicating that the coordination geometry of the phosphorus atom is not too rigid. Although the relatively short P–C bond shows partial double-bond character, the butterfly arrangement of **3** [Fig. 3(*b*)] proves that the $(2\text{-}NC_5H_4)$ ligands can be rotated about the P–C bond. The smaller angle at the phosphorus forces the nitrogen atoms into close contact [N(1)···N(2) 292.2 pm in **3**, 306.4 pm in **2**]. To avoid repulsion the pyridyl ligands are twisted along the P–C bond and the aluminium atom is displaced from the anion plane (Fig. 3). The Al–N distances of **3** (av. 192.2 pm)

[†] *Crystal data* for **2** (−120 °C): $C_{18}H_{24}LiN_2O_2P$, $M = 338.3$, orthorhombic, space group $Pna2_1$, $a = 1791.8(1)$, $b = 935.7(1)$, $c = 1085.0(1)$ pm, $U = 1.8191(3)$ nm³, $Z = 4$, $D_c = 1.235$ Mg m^{-3}, $\mu = 0.162$ mm^{-1}, 2628 measured reflections, 2386 independent, which were all employed in the refinement, $2\theta_{max.} = 45°$, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.045$ ($F > 4\sigma F$) and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.100$ (all data) of $w^{-1} = \sigma^2(F_o^2) + (g_1 \cdot P)^2 + g_2 \cdot P$ with $P = (F_o^2 + 2F_c^2)/3$ and $g_1 = 0.022$, $g_2 = 1.959$, max. residual density: 1.7×10^2 e nm^{-3}.

3 (−120 °C): $C_{12}H_{14}AlN_2P$, $M = 244.2$, monoclinic, space group $P2_1/c$, $a = 1060.1(1)$, $b = 864.4(1)$, $c = 1414.9(1)$ pm, $\beta = 104.97(1)°$, $U = 1.2526(1)$ nm³, $Z = 4$, $D_c = 1.295$ Mg m^{-3}, $\mu = 0.263$ mm^{-1}, 6370 measured reflections, 3677 independent, 3676 employed in the refinement, $2\theta_{max.} = 60°$, $R1 = 0.040$ and $wR2 = 0.111$ (all data, $g_1 = 0.059$, $g_2 = 0.175$; as defined above), max. residual density: 4.7×10^2 e nm^{-3}.

Data of both discussed structures were collected on a Stoe-Siemens diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 71.073$ pm). The structures were solved by direct methods.[23] All non-hydrogen atoms were refined anisotropically on (F^2).[24] Refinement of an inversion twin parameter[25] [$x = -0.09(18)$ where $x = 0$ for the correct absolute structure and +1 for the inverted structure] confirmed the absolute structure of **3**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No.1 .

[‡] *Syntheses*: **1**: To a solution of 12.8 g (50 mmol) tri-(2-pyridyl)-phosphine in 70 ml tetrahydrofuran 0.7 g (100 mmol) lithium wire were added at room temp. The reaction solution was stirred for 3 h, resulting in a dark-red solution, which was worked-up. Yield: 6.2 g (66%) as a dark-red oil b.p. 110 °C at 0.01 Torr. ^1H NMR (250 MHz, $CDCl_3$) δ 5.44 (d, $^1J_{PH}$ 225 Hz, 1H, PH). 7.0–8.6 (m, 8H, ArH). ^{31}P NMR (101 MHz, $CDCl_3$) δ −34.1. IR (NaCl) ν/cm^{-1} 3040, 2930, 2312 (P–H), 1572, 1450, 1419, 1151, 1045, 988, 752, 619, 513. MS (FI) 188 (M^+; 100%).

2: A solution of 2.2 ml 2.3 mol dm^{-3} (5 mmol) n-butyllithium in n-hexane was dropped into 0.94 g (5 mmol) of **1** in 15 ml tetrahydrofuran. Slow evaporation of the solvent gave red crystals. Yield: 1.11 g (66%), decomposition >50 °C, ^1H NMR (250 MHz, C_6D_6) δ 1.36 (8H, thf), 3.52 (8H, thf), 6.0–8.0 (m, 8H, ArH). ^7Li (97 MHz, C_6D_6) δ 2.5, ^{31}P NMR (101 MHz, C_6D_6) δ 13.0.

3: First route: 1.13 g (6 mmol) of **1** were dissolved in 10 ml diethyl ether. A solution of 2.6 ml 2.3 mol dm^{-3} (6 mmol) n-butyllithium in n-hexane was added at room temp. over a period of 30 min. After stirring for 2 h the dark-red reaction mixture was cooled to −40 °C and a solution of 6 ml 1 mol dm^{-3} (6 mmol) dimethylaluminium chloride in n-hexane was added over a period of 1 h. The reaction mixture was warmed to room temp. and stirred over night. Lithium chloride was filtered off and 3 days storage of the clear solution at 3 °C yielded dark-red crystals.

Second route: 3.76 g (20 mmol) **1** were suspended in 30 ml n-hexane. After cooling to −40 °C a solution of 10 ml 2 mol dm^{-3} trimethylaluminium in n-hexane (20 mmol) was added over a period of 30 min. The reaction mixture was warmed to room temp. and stirred over night. After evaporation of the organic solvent **3** was obtained as a crude product in a yield of 90% , which can be purified by recrystallisation from a solution of n-hexane–diethyl ether at 3 °C, m.p. 105 °C, MS (EI) 244 (M^+, 85%) ^1H NMR (250 MHz, C_6D_6): δ −0.36 (s, 6H, CH_3), 5.94 (dddd, $^3J_{5,4}$ 7.0, $^3J_{5,6}$ 6.1, $^4J_{5,3}$ 1.3, $^5J_{5,P}$ 0.5 Hz, 2H, 5-H), 6.37 (dddd, $^3J_{4,3}$ 8.6, $^3J_{4,5}$ 7.0, $^4J_{4,6}$ 1.6, $^4J_{4,P}$ 1.0 Hz, 2H, 4-H), 7.30 (dddd, $^3J_{3,P}$ 10.0, $^3J_{3,4}$ 8.6, $^4J_{3,5}$ 1.3, $^5J_{3,6}$ 1.0 Hz, 2H, 3-H), 7.49 (dddd, $^3J_{6,5}$ 6.1, $^4J_{6,4}$ 1.6, $^4J_{6,P}$ 1.0, $^5J_{6,3}$ 1.0 Hz, 2H, 6-H), ^{31}P NMR (101 MHz, C_6D_6) δ 25.7.

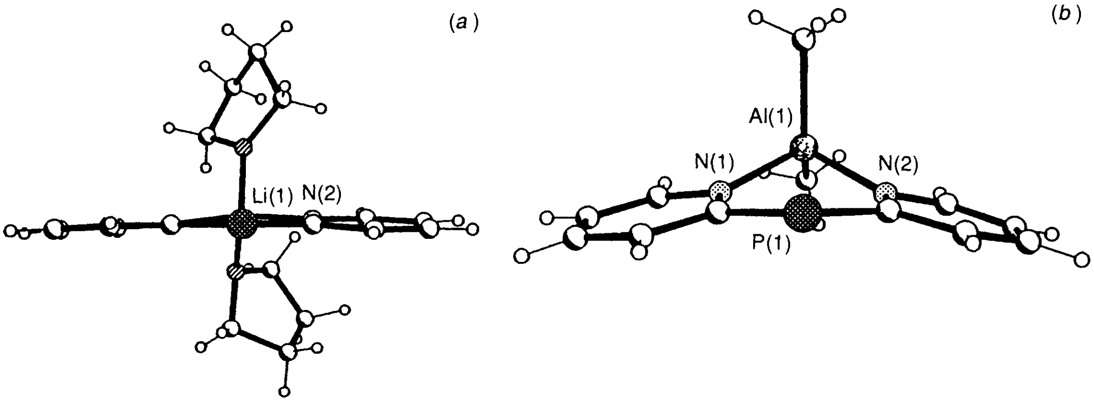

Fig. 3 The basic structural difference between **2** and **3**: (*a*) the planar arrangement of **2**; (*b*) the butterfly arrangement of **3**

range between Al–N-distances in amides $[(Me_3Si)_2NAlH_3\text{-}Li\cdot(OEt_2)_2]$ and $[\{Me_3Si)_2N\}_2AlH_2Li\cdot(OEt_2)_2$ (av. 186 pm)][20] and in aluminium complexes with uncharged *N*-donating ligands such as trichloro-tris(pyridine)-aluminium[21] (av. 207 pm). Thus, they are comparable with the Al–N-distance in bis[(2-pyridyl)-bis(trimethylsilyl)methyl)]aluminium[22] (av. 192 pm) and with those in $AlMe_2\{(2\text{-}NC_5H_4)_2CH\}$.[14]

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