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-NC₅H₄)₂P}{thf}]₂ (thf = tetrahydrofuran) and [AlMe₂{(2-NC₅H₄)₂P}] 3 are obtained in high yield by treating (2-NC₅H₄)₂PH with Bu₂Li and Me₃Al, 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-NC₅H₄)*P⁻ ion a versatile ligand for III/V precursors (already established in 3).

Lithium diorganophosphides, namely LiPPh₂, have long been key reagents in introducing a metal-bridging phosphido centre¹ as well as a diorganophosphide transfer agent.² In all known structures³–⁵ of LiPPh₂ with the exception of [Li(12-crown-4)][PPh₂], 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 LiPPh₂ structure is 183.4 pm while the C–P–C angle is 104.3°. In aryl-, alkyl- and/or silyl-substituted lithium phosphinides⁶–¹² that angle varies from 103.2° to 114.0°.¹¹ Dimethyl-aluminium-di-2-pyridyl-phosphide 2 is a very promising precursor for III/V semiconducting films.

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 (Me₂NCH₂CH₂)₂NMe or Me₂NCH₂CH₂NMe₂. Therefore, we chose the di-2-pyridyl-phosphide ligand, predicting that the two nitrogen atoms in each substituent at the

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Fig. 1 The X-ray structure of 2. Selected distances (pm) and angles (°): P(1)–C(1) 179.4(4); P(1)–C(6) 178.8(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(1)–Al(1)–C(12) 119.5(1).
phosphorus atom would chelate the lithium atom. In the reaction of tri-(2-pyridyl)-phosphine\(^\dagger\) 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.\(^\dagger\)

Scheme 1 Reagents and conditions: i, 2Li(thf), 25°C; ii H\(_2\)O, -C\(_2\)H\(_5\)N\(_2\) LiOH

Reaction of 1 with n-butyllithium in thf leads to N,N'-di-(2-pyridyl)-phosphidalithium-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.

1 + Bu\(_2\)Li \(\rightarrow\) [Li(2-(NC\(_5\)H\(_4\))\(_2\)P)] [thf]\(_2\)

Scheme 2, thf, n-hexane, 25°C; -BuH

2 Adopts almost the same structure as [HC(2-(NC\(_5\)H\(_4\))\(_2\)P)Li(thf)]\(_2\).\(^\dagger\)\(^\dagger\) The Li–N bond lengths are in the normal range (1.6-1.8 nm) and as long as in [P\(_2\)C\(_2\)(2-(NC\(_5\)H\(_4\))\(_2\)Li[Et\(_2\)O]]\(_2\).\(^\dagger\)\(^\dagger\) Whereas the C–P–C angle in the LiP\(_2\) 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 LiP\(_2\) 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.\(^\dagger\)\(^\dagger\) 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.\(^\dagger\)\(^\dagger\) The relatively large C–P–C angle illustrates as well the partial delocalization of the negative charge throughout the whole anion. In the Ph\(_2\)P– anion\(^\dagger\) the two ring planes 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 aluminum atom. N,N'-Di-(2-pyridyl)-phosphido-trimethylaluminium is obtained as a white solid by reaction 1 with trimethylaluminium where methane is formed (Scheme 3).

(a) 2 + Me\(_2\)AlCl \(\rightarrow\) AlMe\(_2\){[2-(NC\(_5\)H\(_4\))\(_2\)P]} + LiCl

(b) 1 + AlMe\(_3\) \(\rightarrow\) AlMe\(_2\){[2-(NC\(_5\)H\(_4\))\(_2\)P]} + CH\(_4\)

Scheme 3 Reagents: (a) n-hexane, Et\(_2\)O, -40°C; (b) n-hexane, -40°C

Suitable crystals of 3 were obtained after storage of an Et\(_2\)O-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).\(^\dagger\) 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 [both cleast-squares planes of the (2-P(2-NC\(_5\)H\(_4\))\(_2\)P)-geometry 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 the (2-NC\(_5\)H\(_4\))\(_2\)P 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)

\(^\dagger\) 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. \(^1\)H NMR (250 MHz, C\(_6\)D\(_6\)) \(\delta\) 2.53 (s, 6H, CH\(_3\)), 5.94 (dddd, 3J5,4 7.0, 4J3,2 1.3, 3J1,2 0.5 Hz, 2H, H, Ph), 3.52 (8H, thf), 6.0-8.0 (m, 8H, ArH). \(^31\)P NMR (101 MHz, CDC\(_6\)) \(\delta\) 71.073 pm). See Notice to Authors, Issue No. 1.

\(^\dagger\) Crystal data for 2 (\(\sim 120°C\)): C\(_{20}\)H\(_{18}\)N\(_{2}\)P\(_{2}\), M = 338.3, orthorhombic, space group Pn\(_{a21}\), a = 1791.8 (1), b = 935.7 (1), c = 1085.0 (1) pm, \(U = 1.8193(3)\) nm\(^3\), \(Z = 4\), \(D_\text{c} = 1.235\) Mg m\(^{-2}\), \(\mu = 0.162\) mm\(^{-1}\), 2628 measured reflections, 2386 independent, which were all employed in the refinement, 20\(_{\text{max}}\) = 45°, R\(_1\) = \(\Sigma F_\text{co} - F_\text{c}\)/\(\Sigma F_\text{co}\) = 0.045 (\(F > 40 F_\text{co}\)) and wR\(_2\) = [\(\Sigma w(F_\text{c}^2 - F_\text{c}^2)^2/\Sigma wF_\text{c}^2\)]\(^{1/2}\) = 0.100 (all data) of \(w = 1 + (0.047 + 0.047\times\sigma)|F_\text{co}|\). Max. residual density: 1.7 \(\times 10^5\) e nm\(^{-3}\).

3 (\(\sim 120°C\)): C\(_{20}\)H\(_{18}\)Al\(_{2}\)N\(_{2}\)P, M = 244.2, monoclinic, space group P2\(_{1}\)/c, a = 1060.1 (1), b = 864.1 (1), c = 1414.9 (1) pm, \(\beta = 104.97(1)^\circ\), \(U = 1.2526(1)\) nm\(^3\), \(Z = 4\), \(D_\text{c} = 1.295\) Mg m\(^{-3}\), \(\mu = 0.263\) mm\(^{-1}\), 6370 measured reflections, 5677 independent, 5676 employed in the refinement, 20\(_{\text{max}}\) = 60°, R\(_1\) = 0.040 and wR\(_2\) = 0.111 (all data, \(g_{\text{iso}} = 0.095\), \(g_{\text{opt}} = 0.175\); as defined above), max. residual density: 4.7 \(\times 10^5\) e nm\(^{-3}\).

Data of both discussed structures were collected on a Soci-Siemens diffractometer using graphite-monochromated Mo-Ka radiation (\(\lambda = 0.71073\) pm). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically on (F\(_2\)).\(^\dagger\)\(^\dagger\) Refinement of an inversion twin parameter\(^\dagger\)\(^\dagger\) [x = 0.09 (18) where x = 0 for the correct absolute structure and x = 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.
range between Al-N-distances in amides [(Me3Si)2NA1H2-Li-(OEt)2] and [(Me3Si)2N]2AlH2-Li-(OEt)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-N\(_2\)C\(_5\)H\(_4\))\(_2\)CH]}\(^{14}\).

The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Received, 2nd November 1992; Com. 2/05864B

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