

Synthesis and structure of a tris imido phosphonate anion; the missing link in imido analogues of phosphorus oxoanions

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The reaction of PCl_3 with 3 equivalents of 2-methoxyaniline in THF/NET_3 , followed by metallation with Bu^nLi (2 equivalents) yields a complex $[\text{Li}_2\text{P}(\text{H})(\text{NR})_3]_2$ **1** ($\text{R} = 2$ -methoxyphenyl), whose tris imido phosphonate anion is the imido analogue of the phosphite anion, $[\text{HPO}_3]^{2-}$.

The chemistry of main group imido complexes is relatively underdeveloped compared to the vast body of knowledge that has been accumulated on the related imido transition metal species.¹ Recently this imbalance has started to be redressed with the discovery of a diverse series of anionic imido complexes of the main group elements.^{2–6} Our own interest in this area has focused on the study of imido analogues of phosphorus oxoanions. Recent studies on related P–N systems have revealed the beginnings of a family of these compounds. Alkali metal salts of the bis(imino)phosphinate anion, $[\text{R}_2\text{P}(\text{NR}')_2]^-$ have been prepared.² Niecke *et al.* have reported several structures that are imido analogues of kinetically unstable phosphorus oxoanions. This group described the planar tris(imino)metaphosphate anion, $[\text{P}(\text{NR})_3]^-$ and the $[\text{P}(\text{NR})_2]^-$ anion, isoelectronic with the kinetically unstable $[\text{PO}_3]^-$ and $[\text{PO}_2]^-$ anions respectively, but more importantly isoelectronic with the corresponding nitrate $[\text{NO}_3]^-$ and nitrite $[\text{NO}_2]^-$ anions.^{3,4} Recently, we succeeded in synthesising the complex $[\text{Li}(\text{THF})_4][(\text{THF})_2\text{Li}(\mu\text{-NR})_2\text{P}(\mu\text{-NR})_2\text{Li}(\text{THF})_2]$ from the reaction of P_2I_4 with 1-aminonaphthalene (1:4 equivalents) in THF/NET_3 , followed by metallation with Bu^nLi (4 equivalents). The $[\text{P}(\text{NR})_4]^{3-}$ trianion of this complex is isoelectronic with the orthophosphate anion, $[\text{PO}_4]^{3-}$.⁵ Related phosphorus–nitrogen complexes have recently found extensive uses as ligands to a range of metals, some of which have found application as polyolefin catalysts. This work has been reported and reviewed in several recent articles.⁶

Herein, we report the synthesis and structure of the imido analogue of the phosphite anion, $[\text{HPO}_3]^{2-}$. Reaction of PCl_3 with 3 equivalents of 2-methoxyaniline in THF/NET_3 , followed by addition of Bu^nLi (2 equivalents) and subsequent crystallisation from toluene gives $[\text{Li}_2\text{P}(\text{H})(\text{NR})_3]_2$ **1** ($\text{R} = 2$ -methoxyphenyl).[†]

A low-temperature single-crystal X-ray diffraction study was performed on complex **1**.[‡] The complex has an ion-contacted dimeric structure with a crystallographically imposed centre of symmetry wherein two $[\text{HP}(\text{NR})_3]^{2-}$ anions sandwich four lithium cations. The $[\text{HP}(\text{NR})_3]^{2-}$ dianion is formally the imido analogue of the phosphite dianion, $[\text{HPO}_3]^{2-}$.⁷ The crystal structure of **1** is illustrated in Fig. 1.

Each of the phosphorus centres has a distorted tetrahedral geometry, being coordinated to three imido nitrogen atoms and one hydrogen atom. The phosphorus atoms are bound approximately equally to each imido nitrogen atom [with P–N distances ranging from 1.613(2) to 1.630(2) Å]. The shorter bond distances in **1** compared to those in the related imido analogue of the orthophosphate anion, $[\text{P}(\text{NR})_4]^{3-}$ [1.645(4) Å]⁵ is perhaps due to the enhanced double bond character in **1** where formally, one P=N bond and two P–N bonds form a

resonance hybrid, whereas in $[\text{P}(\text{NR})_4]^{3-}$ the ratio is one P=N bond to three P–N bonds.

Within the core of **1** there are two distinct lithium environments. In one domain the lithium centre is complexed by one imido nitrogen centre from each $[\text{HP}(\text{NR})_3]^{2-}$ unit and is additionally complexed by two methoxy sidearms of the corresponding methoxyanilido groups. The second lithium environment has the lithium centre complexed by two imido nitrogen atoms from one $[\text{HP}(\text{NR})_3]^{2-}$ unit but by only one imido centre from the other $[\text{HP}(\text{NR})_3]^{2-}$ unit. The methoxy sidearm of the latter unit completes the distorted tetrahedral geometries about these lithium centres.

The P–H proton could not be unequivocally located from the electron difference map, but its presence could be discerned from the ^1H and ^{31}P NMR spectra and from solution IR spectroscopy. Hence, the ^1H spectra in benzene- d_6 , in addition to confirming the presence of 2-methoxyanilido ligands, show a

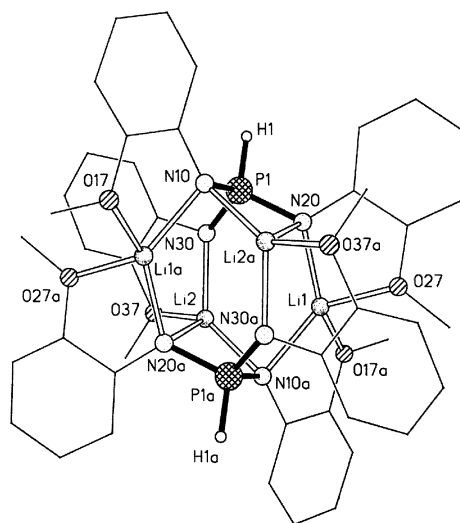


Fig. 1 The crystal structure of **1**. All hydrogen atoms (except P–H hydrogen atoms) have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–N(30) 1.613(2), P(1)–N(20) 1.6194(14), P(1)–N(10) 1.630(2), Li(1)–N(20) 1.991(3), Li(1)–N(10a) 2.063(3), Li(2)–N(30) 1.972(3), Li(2)–N(10a) 2.050(3), Li(2)–N(20a) 2.337(4), Li(1)–O(27) 1.945(3), Li(1)–O(17a) 1.981(3), Li(2)–O(37) 1.925(3), N(30)–P(1)–N(20) 104.60(7), N(30)–P(1)–N(10) 112.77(7), N(20)–P(1)–N(10) 108.91(8), O(27)–Li(1)–O(37a) 99.5(2), O(27)–Li(1)–N(20) 82.68(13), O(17a)–Li(1)–N(20) 141.3(2), O(27)–Li(1)–N(10a) 134.7(2), O(17a)–Li(1)–N(10a) 80.71(12), N(20)–Li(1)–N(10a) 124.6(2), O(37)–Li(2)–N(30) 84.65(13), O(37)–Li(2)–N(10a) 142.0(2), N(30)–Li(2)–N(10a) 130.0(2), O(37)–Li(2)–N(20a) 116.1(2), N(30)–Li(2)–N(20a) 105.74(14), N(10a)–Li(2)–N(20a) 73.78(11), C(11)–N(10)–P(1) 128.33(12), C(11)–N(10)–Li(2a) 124.45(14), P(1)–N(10)–Li(2a) 92.64(11), C(11)–N(10)–Li(1a) 108.32(14), P(1)–N(10)–Li(1a) 109.98(12), Li(2a)–N(10)–Li(1a) 84.54(13), C(21)–N(20)–P(1) 122.86(12), C(21)–N(20)–Li(1) 111.49(14), P(1)–N(20)–Li(1) 125.64(12), C(21)–N(20)–Li(2a) 93.95(12), P(1)–N(20)–Li(2a) 83.05(10), Li(1)–N(20)–Li(2a) 94.68(13), C(31)–N(30)–P(1) 122.67(12), C(31)–N(30)–Li(2) 107.44(14), P(1)–N(30)–Li(2) 122.74(12).

doublet at δ 9.07 with a coupling constant of 436 Hz, consistent with the $^1J_{\text{PH}}$ coupling frequencies observed in related systems.⁸ The corresponding doublet can be observed in the ^{31}P NMR spectra at δ 0.28. This bond can also be observed by IR spectroscopy with a band at 2266 cm^{-1} in THF solution being attributed to the P–H stretching frequency.

Although we have so far been unable to unequivocally identify the intermediates in the steps leading to complex **1**, it seems reasonable to postulate that the $[\text{HP}(\text{NR})_3]^{2-}$ anion of **1** has resulted from a proton exchange from an amido centre to the phosphorus centre in addition to metallation of the remaining amido protons. Similar proton transfer from N to P in iminophosphoranes, $\text{R}_2\text{P}=\text{N}(\text{H})\text{R}'$ has shown that the P–H tautomer is stabilised by both electron withdrawing amide groups (R') and by bulky substituents on the P and N centres (R and R').⁹ Hence, N to P proton transfer accompanying metallation in the postulated $\text{P}\{\text{N}(\text{H})\text{R}\}_3$ intermediate from the first step of our reaction system would yield complex **1**. It is interesting to note that phosphites (or rather phosphorous acid) can be produced by a similar route, *i.e.* hydrolysis of PCl_3 .¹⁰

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Notes and references

† *Preparation of 1*: to an ice-cooled stirred solution of PCl_3 (0.17 ml, 2 mmol) in THF (15 ml) and NEt_3 (4 ml, 28.7 mmol) was added 2-methoxyaniline (0.68 ml, 6 mmol). A white solid was observed in a yellow solution. After stirring for 3 h, the reaction was filtered (porosity 3 sinter with Celite) to give a yellow solution. To this was added Bu^nLi (2.5 ml, 1.6 mol l^{-1} , 4 mmol) which caused the solution to turn brown yellow followed by the precipitation of a white solid after *ca.* 1 min. The solvent was removed *in vacuo* and the solid was redissolved with toluene (8 ml). Storage for 24 h at $-30\text{ }^\circ\text{C}$ yields colourless cubic blocks of **1**. Yield 0.836 g (51%).

No melting or decomposition up to $280\text{ }^\circ\text{C}$; IR (THF solution) $\text{v}/\text{cm}^{-1} = 2266$ (P–H stretch); ^1H NMR ($+25\text{ }^\circ\text{C}$, 300 MHz, benzene- d_6): δ 9.07 (d, 2H, P–H, $^1J_{\text{PH}}$ 436 Hz), 7.25–6.30 (collection of m, 24H, $-\text{NC}_6\text{H}_4\text{OCH}_3$), 2.80 (s, 18H, $-\text{NC}_6\text{H}_4\text{OCH}_3$); ^{31}P NMR ($+25\text{ }^\circ\text{C}$, 121.55 MHz, benzene- d_6): δ 0.28 (d, $^1J_{\text{PH}}$ 436 Hz). Anal. Calc. C, 61.6; H, 5.4; N, 10.3; P, 7.6. Found: C, 61.2; H, 5.4; N, 10.2; P, 7.5%.

‡ *Crystal data for 1*: $\text{C}_{21}\text{H}_{22}\text{Li}_2\text{N}_3\text{O}_3\text{P}$, $M = 409.27$, orthorhombic, space group $Pbca$, $a = 16.026(5)$, $b = 11.410(2)$, $c = 22.560(5)\text{ \AA}$, $U = 4125(2)\text{ \AA}^3$, $Z = 8$, $D_c = 1.318\text{ Mg m}^{-3}$, $T = 173(2)\text{ K}$, $\mu(\text{Mo-K}\alpha) = 0.160\text{ mm}^{-1}$, 24588 reflections measured, 4710 unique ($R_{\text{int}} = 0.0508$) which were used in all calculations. Data were collected on a Bruker SMART CCD area-detector diffractometer¹¹ using a crystal mounted on a glass fibre in a rapidly cooled perfluoropolyether.¹² The structure was solved by direct methods and refined by least squares on F^2 values for all reflections. Absorption corrections were applied, based on multiple and symmetry equivalent measurements.¹³ Final $R1 = 0.0402$ [$I > 2\sigma(I)$] and $wR2 = 0.1042$ (all data).¹⁴

CCDC 182/1739. See <http://www.rsc.org/suppdata/cc/b0/b004192k/> for crystallographic files in .cif format.

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