Lithiated organophosphorus enamines: a new synthetic approach and the first crystal structures

William Clegg,[a] Robert P. Davies,[b] Lorraine Dunbar,[b] Neil Feeder,[b] Stephen T. Liddle,[a] Robert E. Mulvey,[c] Ronald Snaith*[b] and Andrew E. H. Wheatley[b]

[a] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*
[b] *Department of Chemistry, University of Cambridge, Cambridge, UK CB2 1EW. E-mail: rs10003@cam.ac.uk*
[c] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL*

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Made by a nitrile insertion/hydrogen migration process *via* $Ph_2P(O)CH_2Li$ and Bu^tCN, the enamide $Ph_2P(O)CH{=}C(Bu^t)N(H)Li$ and its TMEDA hemisolvate exist as tetrameric and dinuclear arrangements respectively: the novel structure of the starting lithiated phosphane oxide, also in its TMEDA hemisolvated form, is shown to contain Li–C contacts of two distinct types.

Previously we have described the nitrile insertion reaction and subsequent Lewis base-promoted ketimide to azaallyl rearrangement depicted in eqn. (1) (R = H or Pr^n).[1] Here we show

$$RCH_2Li + Bu^tC{\equiv}N \longrightarrow RCH_2(Bu^t)C{=}NLi$$

$$\Big\downarrow \text{HMPA}$$

$$RC(H){=}C(Bu^t)N(H)Li{\cdot}HMPA \quad (1)$$

that this dual process can be extended to a functionalised group, R = $Ph_2P(O)$ in the lithiated phosphane oxide $Ph_2P(O)CH_2Li$, and that it can thereby occur without the aid of an external Lewis base. Such lithiated phosphane oxides are widely used as Horner–Wittig reagents[2] for the stereoselective synthesis of alkenes. As such, their metal–ligand bonding is of particular interest since in rare cases intimate C–Li contacts can contribute to the stability of these generally exclusively Li–O bonded molecules. For this reason we determined first the crystal structure of the starting lithiated phosphane oxide in its partially TMEDA-solvated form, $\{[Ph_2P(O)CH_2Li]_2{\cdot}TMEDA\}_2$ **1**, thereby revealing a unique tetranuclear arrangement which has in fact two distinct types of C–Li contact. The products of the nitrile insertion reactions of $Ph_2P(O)CH_2Li$, $\{Ph_2P(O)CH{=}C(Bu^t)N(H)Li\}_4$ **2** and $\{Ph_2P(O)CH{=}C(Bu^t)N(H)Li\}_2{\cdot}TMEDA$ **3**, have also been crystallographically characterised, so giving the first crystal structures of lithiated organophosphorus enamines. We also report some preliminary reactions of **2** which show that it can behave as either a C-based or a N-based nucleophile.

Although earlier attempts to produce crystals of the solvent-free parent compound $Ph_2P(O)CH_2Li$ failed,[3] we have now successfully crystallised its TMEDA hemisolvate **1**.† Despite a high *R* value, the key features of the solid-state structure of **1**‡ are clear-cut. Thus, although formally tetrameric, the centrosymmetric molecular structure of **1** (Fig. 1) is best regarded as a pseudo-dimer, constructed by the dimerisation of two dinuclear units. 'Dimerisation' operates through a strictly planar $(OLi)_2$ ring, a feature common to purely dinuclear lithiophosphane oxide dimers.[4] Each dinuclear unit accommodates two distinct Li atoms within a puckered (POLiOLiC) ring. With respect to individual monomeric (CPOLi) units, the short C26–Li1 contact [2.171(13) Å] within this six-membered ring is intermolecular. A bidentate TMEDA ligand completes the four-fold coordination of Li1. Fused onto the (POLiOLiC) ring is an (OPCLi) chelate ring, made possible by the C13–Li2 contact [2.340(13) Å]. Here, the carbanionic CH_2^- centre functions as an internal coordinating centre, to the exclusion of TMEDA (note that in the synthesis of **1** a 3 : 2 TMEDA : Li ratio was used). Crystallographic confirmation of Li–C contacts in lithiated phosphane oxides has so far been limited to those within (POCLi) chelates in non-solvated $\{Ph_2P(O)CHLiC(H)MeEt\}_4$[3] and to intermolecular ones in the dimer of fully TMEDA-solvated lithio *P*-isopropyl-1,3,2-dioxaphosphorinane 2-oxide[5] (their mean lengths of 2.230 and 2.228 Å, respectively, lie between those found in **1**). Both types of contact are uniquely combined within the structure of **1**, a fact directly attributable to its *partially* solvated nature (*i.e.* with non-solvated and solvated Li sites).

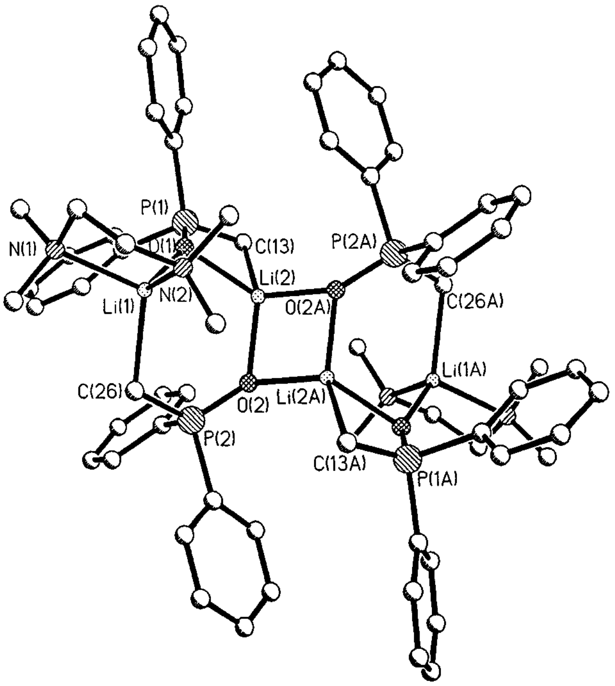

Fig. 1 Molecular structure of **1**. Hydrogen atoms are omitted for clarity.

Having an in-built Lewis base function, $Ph_2P(O)CH_2Li$ does not require the participation of a donor solvent to convert to the enamide **2** on addition of nitrile [eqn. (2)]. Accordingly, a

$$Ph_2P(O)CH_2Li + Bu^tC{\equiv}N \longrightarrow Ph_2P(O)CH{=}C(Bu^t)N(H)Li$$

$$\mathbf{2}$$

$$\Big\downarrow \text{TMEDA}$$

$$\tfrac{1}{2}[\{Ph_2P(O)CH{=}C(Bu^t)N(H)Li\}_2{\cdot}TMEDA] \quad (2)$$

$$\mathbf{3}$$

hexane–toluene solvent system was used.† No ketimide intermediate, as detected in the simple alkyl systems [eqn. (1)], is observable here, nitrile insertion and hydrogen transfer (from

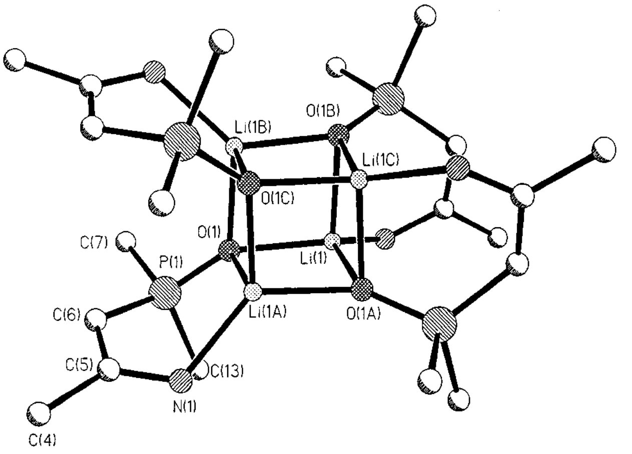

Fig. 2 Molecular structure of **2**. Only the *ipso*-C of Ph and the quaternary C of Bu^t groups are shown. Hydrogen atoms are omitted for clarity.

the CH_2 unit to the N atom) both having occurred. To make the hemisolvated derivative **3**, the same reaction is followed, but TMEDA is added subsequently [eqn. (2)].†

Based on a $(LiO)_4$ pseudocubane core, the molecular structure of **2** (Fig. 2)‡ has N atoms internally donating to the Li ones within (OPCCNLi) chelate rings. The most revealing feature is that relatively long $\mathrm{PC}\underset{\cdots}{-}\mathrm{C}$ [1.399(5) Å] and short $\mathrm{C}\underset{\cdots}{-}\mathrm{N}$ [1.310(4) Å] bond lengths within these rings indicate a delocalised arrangement with a high degree of imidoalkyl $[RC(H)–C(Bu^t)=NH]^-$ character, moreso than in the simple lithium azaallyl $\{Pr^nC(H)=C(Bu^t)N(H)Li{\cdot}HMPA\}_2$ [1] [corresponding lengths: 1.345(3) and 1.390(3) Å]. Accordingly, the Li–N bond in **2** is short [1.958(6) Å; *cf* 2.012 Å (mean) in the latter], reflecting also the relatively strain-free conformation [CNLi angle, 119.2(3)°] of the six-membered chelate ring. No C–Li contacts are therefore necessary, so the *C*(H)*C*(Bu^t) atoms display sp^2 rather than sp^3 hybridisation. The second enamide structure **3** (Fig. 3)‡ is constructed around an asymmetrical, essentially planar $(LiO)_2$ rhomboidal ring. Chelation of Li1 by TMEDA forces the chelating (OPCCN) arms into a *cis* conformation with both N atoms internally donating to Li2: in this way both Li atoms attain (distorted tetrahedral) four coordination. The Li–O bond lengths within the OPCCNLi chelated units are significantly longer [2.075(6) Å] than those involving the TMEDA-solvated Li [1.913(6) Å]. These are counterbalanced by short Li–N(anion) bonds and long Li–N(TMEDA) bonds [1.990(5) and 2.094(7) Å, respectively]. Similarly, the wider bite size of the OPCCN ligand [99.5(1)°; *cf* 88.0(4)° for TMEDA] is offset by narrower O–Li2–O bond angles [94.8(4)° *cf.* 105.9(4)° for OLi1O]. As in **2**, the $\mathrm{PC}\underset{\cdots}{-}\mathrm{C}$ and $\mathrm{C}\underset{\cdots}{-}\mathrm{N}$ bond lengths in **3** [1.408(5) and 1.321(5) Å, respectively] suggest that the imidoalkyl canonical form again makes a substantial contribution to the enamide structure, and show therefore that the resonance delocalisation within the OPCCN anion is largely unaffected by the change in aggregation or the introduction of solvation.

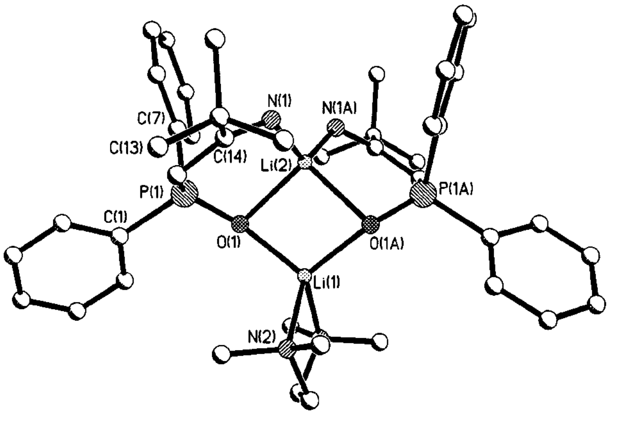

Fig. 3 Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

Finally, quenching the lithium complexes **2** or **3** with suitable electrophiles can give access to new organophosphorus enamines. Related compounds of the type $Ph_2P(O)CH=C(R)N(H)R'$, made by nucleophilic addition of amines to 1-alkynylphosphine oxides,[6] are useful precursors to α,β-unsaturated ketimines and ketones. Interestingly, preliminary studies on **2** indicate that methanolysis affords $Ph_2P(O)CH=C(Bu^t)NH_2$ but that treatment with methyl iodide affords chiral $Ph_2P(O)CH(Me)$-$C(Bu^t)=NH$.† This ambi-(N- or C-) nucleophilic behaviour, and the potential uses of the products as unusual new ligands, are being explored further.

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Notes and references

† Standard inert-atmosphere Schlenk techniques were used for all syntheses. **1**: Bu^{n}Li (6 mmol in hexane) was added to a suspension of $Ph_2P(O)CH_3$ (6 mmol) in toluene (5 ml) containing TMEDA (3 mmol) at −78 °C. Warming to room temperature gave a yellow precipitate. Hexane was removed *in vacuo* and replaced by toluene (2 ml). Dissolution was achieved by heating the mixture following the addition of more TMEDA (6 mmol). Allowing the solution to cool gradually in a water bath afforded yellow rhomboidal crystals of **1** (yield, 36%; mp decomp. from 90 °C). **2**: $Ph_2P(O)CH_3$ (5 mmol) was suspended in toluene and chilled to −78 °C prior to the addition of Bu^{n}Li (5 mmol in hexane). Warmed to room temperature and treated with Bu^{t}CN (5 mmol) the solution changed from pale to dark yellow. It was then stirred for 30 min before being transferred to a 65 °C water bath and allowed to cool slowly. The solution deposited pale yellow cubic crystals of **2** (yield, 52%; mp decomp. from 175 °C). **3** : the synthesis of **2** was followed to the dark yellow solution stage. TMEDA (5 mmol) was subsequently added. Storing this solution at −30 °C for 4 days produced bright yellow crystals of **3** (yield, 48%; mp decomp. from 167 °C). **1**, **2** and **3** were also characterised by elemental analysis and NMR (^{1}H and ^{13}C) spectral data (to be published in a full paper). The quenched products were also characterised by their ^{1}H NMR spectra.

‡ *Crystal data for*: **1**: $C_{32}H_{40}Li_2N_2O_2P_2$, M = 560.48, monoclinic, space group $P2_1/n$, a = 12.683(2), b = 10.290(1), c = 24.527(3) Å, β = 98.782(3)°, U = 3163.5(7) Å^3, Z = 4, D_c = 1.177 g cm^{-3}, μ = 0.167 mm^{-1} (Mo-Kα, λ = 0.71069 Å), T = 160(2) K; R_w = 0.3095 on F^2 values of all 5560 unique data, conventional R = 0.1039 on F values of 3437 reflections with $F_o^2 > 2\sigma(F_o^2)$, 365 parameters; final difference map within ±0.68 e Å^{-3}. **2**: $C_{18.88}H_{22.25}LiNOP$, M = 317.04, tetragonal, space group $P4/n$, a = 16.472(2), c = 13.664(3) Å, U = 3707.4(10) Å^3, Z = 8, D_c = 1.136 g cm^{-3}, μ = 0.150 mm^{-1} (Mo-Kα, λ = 0.71069 Å), T = 180(2) K; R_w = 0.2018 on F^2values of all 3268 unique data, conventional R = 0.0618 on F values of 2390 reflections with $F_o^2 > 2\sigma(F_o^2)$, 206 parameters; final difference map within ±0.63 e Å^{-3}. **3**: $C_{21}H_{29}LiN_2OP$, M = 363.37, monoclinic, space group $C2/c$, a = 27.740(6), b = 9.803(2), c = 20.206(4) Å, β = 130.69(3)°, U = 4166.61(14) Å^3, Z = 8, D_c = 1.159 g cm^{-3}, μ = 0.143 mm^{-1} (Mo-Kα, λ = 0.71069 Å), T = 180(2) K; R_w = 0.1464 on F^2 values of all 3669 unique data, conventional R = 0.0634 on F values of 1998 reflections with $F_o^2 > 2\sigma(F_o^2)$, 245 parameters; final difference map within ±0.26 e Å^{-3}.

CCDC 182/1291. See http://www.rsc.org/suppdata/cc/1999/1401/ for crystallographic files in .cif format.

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