Synthesis and X-ray structures of *N*-lithioiminophosphorane·lithium bromide adducts

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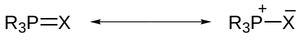
Iminophosphorane anions are shown to be novel and very powerful Lewis-base donors to s-block metals by the isolation and structural characterisation of *N*-lithioiminophosphorane·lithium bromide adducts.

We have recently been interested in the coordination of neutral phosphonium ylides **1a** to lithium compounds.[1] The isoelectronic and isonuclear iminophosphoranes **1b** possess many of the characteristics of phosphorus ylides, with the P–N bond being substantially dipolar in nature[2] which renders them theoretically capable of forming very strong complexes with lithium compounds. Indeed, iminophosphorane–lithium complexes are calculated to be stronger even than complexes between lithium and phosphine oxides **1c**,[1] the third member of this isoelectronic and isonuclear series, and a class of compound commonly used as strong Lewis-base donors to s-block metals.[3] Furthermore, the facile deprotonation (metallation) of ylides or iminophosphoranes[4] (**1a**, **b**, R′ = H) yields species in which the negative charge on the ylidic carbon or iminic nitrogen atom is enhanced, potentially providing Lewis bases of exceptional strength. With the aim of exploring this avenue to provide unusual and potentially useful ligands for s-block metals we now report the syntheses and structural characterisation of *N*-lithoiminophosphorane compounds as their lithium halide complexes. Our results suggest that $R_3P{=}N^-$ ligands offer potential to be developed as new and powerful Lewis-basic ligands in s-block metal coordination chemistry.



$$R_3P{=}X \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{X}$$

1

1a X = CR′$_2$
b X = NR′
c X = O

Until now, the isolation and unambiguous characterisation of a *N*-(s-block-metallated) iminophosphorane has not, to our knowledge, been reported. Even the structural characterisation of a simple iminophosphorane moiety acting as a neutral donor to an s-block metal is limited to one recent example of intramolecular coordination.[5] This is surprising since *N*-lithioiminophosphoranes are well known as reagents in both organic and inorganic synthesis, for example, as synthons for RN^{2-}[6] and as precursors for a wide variety of *N*-substituted iminophosphoranes containing either inorganic, organometallic or organic residues.[7]

N-Lithioiminophosphoranes $[(Ph_3PNLi{\cdot}LiBr)_2{\cdot}4thf]{\cdot}1.5$arene (arene = benzene **3a**, toluene **3b**) were prepared by the reaction of 2 equiv. of BuLi with Ph_3PNH_2Br **2** in arene–thf† and characterised by X-ray crystallography.‡

In the solid state (Fig. 1) **3a** and **3b** are isomorphous and the following discussion will be confined to **3a**, which provided the higher quality X-ray data set. The structure consists of a pseudo-cubane $Li_4N_2Br_2$ core in which each lithium atom is four-coordinate *via* association to three μ_3-bridging anionic centres and one terminal thf molecule. Similar core structures have been found before for C–Li[8] and O–Li[9] species but complexes **3** are unique as mixed-anion tetramers incorporating organic N–Li fragments. The ability of the *N*-lithioiminophosphorane to solvate LiBr and prevent association of the lithium halide into an infinite $(LiX)_\infty$ lattice§ emphasises the powerful Lewis basicity of the iminophosphorane anion that had been anticipated. One face of the cube (Li_2Br_2) is distorted by a fold along the Li(1)···Li(2) axis (angle of fold 30°). This distortion is largely a steric effect due to anion–anion repulsions and has also been seen in other structures containing a $Li_4R_2X_2$ core (X = halogen).[8a,9] Comparison of inter- and intra-ring distances within the core of **3** (average inter- and intra-ring Li–Br distances, 2.738 and 2.603 Å, respectively; average inter- and intra-ring Li–N distances, 1.971 and 2.005 Å, respectively) suggests that the interactions of all four lithium atoms with iminic nitrogen atoms are favoured over those with the bromide anions. While the observed preference for Li–N over Li–Br coordination emphasises the high Lewis basicity of the iminophosphorane anion, such analysis provides no clue as to whether the core is derived from aggregation of two Li_2Br_2 rings or from dimerisation of two LiN·LiBr units.

The structural parameters obtained for the complexes **3** provide a useful guide to the geometry of the unknown isolated $Ph_3P{=}N^-$ anion since the interaction with Li^+ is substantially electrostatic in nature (which contrasts with the largely covalent interactions found for transition metal complexes). For example, the P–N bond in **3** (average P–N distance, 1.541 Å) is significantly shorter than in the dication of the structure of $\{Ph_3P{=}N[Au(PPh_3)]_3\}^{2+}2BF_4^-$ [P–N distance, 1.62(1) Å] in

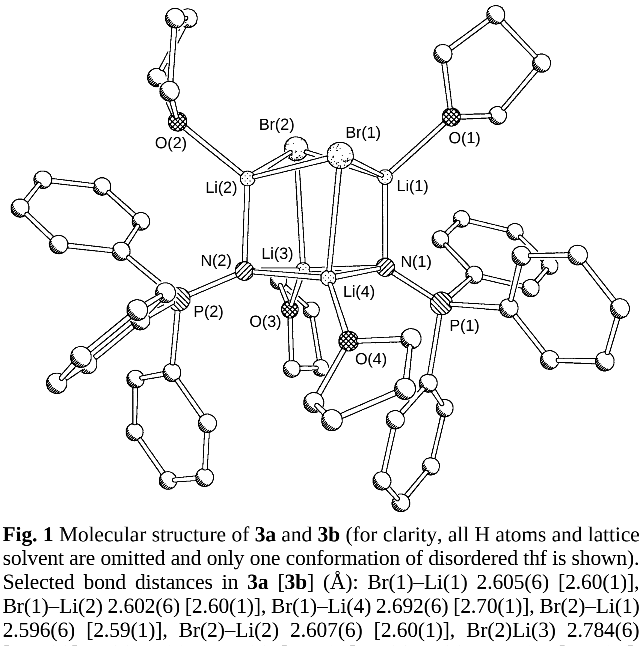


Fig. 1 Molecular structure of **3a** and **3b** (for clarity, all H atoms and lattice solvent are omitted and only one conformation of disordered thf is shown). Selected bond distances in **3a** [**3b**] (Å): Br(1)–Li(1) 2.605(6) [2.60(1)], Br(1)–Li(2) 2.602(6) [2.60(1)], Br(1)–Li(4) 2.692(6) [2.70(1)], Br(2)–Li(1) 2.596(6) [2.59(1)], Br(2)–Li(2) 2.607(6) [2.60(1)], Br(2)Li(3) 2.784(6) [2.74(1)], N(1)–Li(1) 1.962(6) [1.97(1)], N(1)–Li(3) 1.999(6) [2.01(1)], N(1)–Li(4) 2.019(6) [2.03(1)], N(2)–Li(2) 1.979(7) [2.00(1)], N(2)–Li(3) 1.992(6) [2.02(1)], N(2)–Li(4) 2.010(6) [2.00(1)], O(1)–Li(1) 1.960(6) [1.96(1)], O(2)–Li(2) 1.953(7) [1.97(1)], O(3)–Li(3) 1.963(6) [1.95(1)], O(4)–Li(4) 1.993(6) [1.99(1)], N(1)–P(1) 1.541(3) [1.542(6)], N(2)–P(2) 1.541(3) [1.538(6)].

which the $Ph_3P{=}N^-$ unit also μ_3-bridges three metal atoms.[10] Indeed, the P–N bond in **3** is shorter than in all known transition-metal compounds (distances in the range 1.59–1.66 Å).[10,11] It is also slightly shorter than in the parent iminophosphorane, $Ph_3P{=}NH$,¶ which is consistent with an increased electrostatic attraction between $P^{\delta+}$ and a more negative $N^{\delta-}$ after lithiation. As expected, the P–N bond in **3** is longer than the P–O distance in the isoelectronic but neutral $Ph_3P{=}O$ [P–O distance, 1.46(1),[12a] 1.484(1)[12b] Å].

The solution behaviour of **3** is complicated. Again, the discussion here is confined to **3a**, though the general behaviour is common to both complexes. The cryoscopically determined relative molecular mass (RMM) is concentration dependent, as are the relative intensities of resonances in the ^{31}P and ^{7}Li NMR spectra (all in benzene solution), indicating that equilibria operate in solution between two or more species. Even at room temperature, four distinct ^{31}P and three distinct ^{7}Li resonances are observed and one can easily imagine a number of thf-coordinated $(LiN{=}PPh_3)_n$, $(LiBr)_n$ and $[Li_2(Br)(N{=}PPh_3)]_n$ monomers and oligomers that may coexist in solution. Though it is difficult to assign these resonances unambiguously, it is clear from our results that, even in predominantly arene solution, dilithiation of $Ph_3P{=}NH_2Br$ does not give a solution of LiBr-free $(Ph_3P{=}NLi)_n{\cdot}xL$ as has been suggested previously in the protocol for the preparation of primary and secondary amines developed by Cristau *et al.*[6] but instead gives a well defined, stoichiometric 1 : 1 LiBr complex of the *N*-lithioiminophosphorane. Indeed, *N*-lithioiminophosphoranes prepared directly from *N*-unsubstituted iminophosphoranes to give only $R_3P{=}NLi$,[4] followed by reaction with R′X or MX_n (X = halogen) would result in the formation of a mixed organolithium–lithium halide aggregate in solution in any case. These observations are relevant to the use of *N*-lithioiminophosphoranes in synthesis since the nature of the reactive species present in solution is well known to have an effect on the reactivity and/or selectivity of a reagent in solution.[13]

Preliminary results show that LiCl analogues of **3** are accessible, and that **3** may be used in transmetallation reactions. We are currently investigating further the use of highly polar ylidic and iminic ligands as novel complexants in s-block metal chemistry particularly with a view to achieving solvation of LiF in hydrocarbon solvents.

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Footnotes

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† *Syntheses*: All manipulations were carried out under a dry N_2 atmosphere using Schlenk techniques and an inert atmosphere glove box. Solvents were freshly distilled prior to use. Compound **2** was prepared by slight modification of the method reported by Cristau *et al.*[6] *Typical synthetic procedure for* **3**: to a suspension of **2** (2.5 mmol, 0.90 g) in benzene (15 ml), *n*-butyllithium (5 mmol, 3.2 ml of a 1.6 M solution in hexane) was added at 25 °C. The suspension was stirred for 15 min, during which the solution turned yellow and a white precipitate persisted. Addition of 1.5 ml thf followed by warming to *ca.* 70 °C resulted in complete dissolution of the solid into a yellow solution. Upon storage of this solution for 24 h at 25 °C, colourless blocks of **3a** were obtained.

3a: yield 72%, mp 166 °C. ^1H NMR (200 MHz, C_6D_6): δ 8.0 (m, 6 H, *o*-Ph), 6.9–7.7 (m, 9 H, *m,p*-Ph, plus residual C_6H_6), 3.6 (qnt, 8 H, α-thf), 1.3 (qnt, 8 H, β-thf). ^{31}P NMR (101.2 MHz, C_6D_6): (0.01 M), δ 2.0 (s, 1), −1.2 (s, 3.4), −3.9 (s, 1.9), −5.5 (s, 0.4); (0.05 M), δ 1.8 (s, 1), −1.3 (s, 3.5), −4.5 (s, 4.7), −5.5 (s, 0.3); (0.09 M), δ 1.8 (s, 1), −1.3 (s, 4.5), −4.5 (s, 7.8), −5.5 (s, 1.5). ^7Li NMR (194.4 MHz, C_6D_6): δ 3.13 (s), 1.8–2.1 (m), 1.5–1.8 (m); cryoscopy (benzene, K_b = 5.12 K kg mol^{-1}): (0.003 M), ΔT = 0.042 K, RMM 394 ± 42 [degree of association (relative to $Ph_3P{=}NLi{\cdot}LiBr{\cdot}2thf$), n = 0.75]; (0.008 M), ΔT = 0.103 K, RMM = 494 ± 20 (n = 0.95); (0.014 M), ΔT = 0.151 K, RMM = 549 ± 15 (n = 1.05). **3b**: yield 45%, mp 166 °C. ^1H NMR (200 MHz, C_6D_6): δ 7.95 (m, 6 H, *o*-Ph), 6.9–7.7 (m, 9 H, *m*, *p*-Ph), 3.55 (qnt, 8 H, α-thf), 1.25 (qnt, 8 H, β-thf).

‡ *X-Ray structure determinations*: Yellow crystals of $C_{52}H_{62}Br_2Li_4N_2O_4P_2{\cdot}1.5$arene (arene = C_6H_6 **3a**, C_6H_5Me **3b**), are isomorphous, triclinic, space group $P\bar{1}$ (no. 2), M = 1145.7 [1166.8], a = 10.682(1) [10.575(1)], b = 13.758(1) [13.882(1)], c = 22.280(1) [22.398(1)] Å, α = 102.91(1) [100.61(1)], β = 90.85(1) [91.33(1)], γ = 109.74(1) [109.81(1)°], U = 2989.4(4) [3027.5(4) Å^3], Z = 2, D_c = 1.27 [1.28] g cm^{-3}, μ = 14.6[14.4] cm^{-1}, crystal size 0.48 × 0.44 × 0.36 [0.5 × 0.32 × 0.2 mm]. Data collection at T = 150 K, Siemens CCD area detector, graphite-monochromated Mo-Kα radiation, $\bar{\lambda}$ = 0.71073 Å, ω scan mode, $2\theta \leqslant 56°$; Lorentz, polarization and semi-empirical absorption correction[14a] (on Laue equivalents) were applied; min., max. transmission 0.525, 0.638 [0.618, 0.899]; 18255 [14163] total data, 10556 [9818] unique, 8902 [7726] observed [$I \geqslant 2\sigma(I)$]; R_{int} = 0.045 [0.071] before and 0.034 [0.042] after absorption correction. The structures were solved by direct methods and refined by full-matrix least squares against F^2, using SHELXTL (Version 5/VMS) software.[14b] Non-H atoms were refined anisotropically (disordered ones isotropically) with all H atoms, ‘riding’, the disordered solvent in **3b** as rigid bodies; 673 [663] variables *vs.* 10463 [9428] data, R_w (F^2, all data) = 0.127 [0.271], R(F, obs. data) = 0.045 [0.079], max. residual $\Delta\rho$ = 0.85 [0.94] e Å^{-3}. One solvent molecule is in a general position, another at an inversion centre, in **3b** both are disordered. Two thf rings in **3a** and three in **3b** are also disordered. Atomic coordinates, bond lengths and angles, and thermal parameters for **3a** and **3b** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/474.

§ Conceptually similar to the so-called ammonium salt route method of preparing Lewis base-complexed inorganic lithium salts.[15]

¶ We have determined the structure of Ph_3PNH by X-ray (at 153 K) and neutron (at 20 K) diffraction and find the P–N distance to be 1.562(3) and 1.582(2) Å, respectively.[16] Another report of the X-ray structure of Ph_3PNH (at 203 K) gives the P–N distance as 1.524(3) Å.[11b]

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