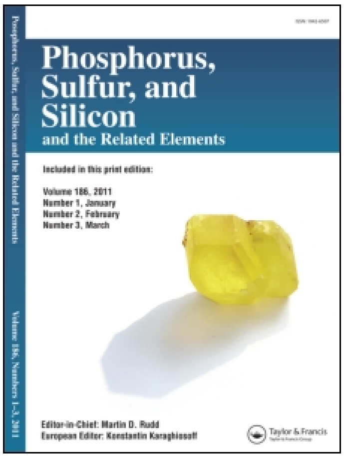

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Imido Analogues of Group 15 Oxoanions

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Reactions of binary group 15 halides with primary amines in the presence of base and subsequent by metallation with *n*-butyllithium produces imido anions of the group 15 elements. Applications of this methodology to a range of group 15 halides are described along with the syntheses and X-ray crystal structures of three complexes which are the imido analogues of the orthophosphate anion, the phosphite anion and the arsenate anion respectively.

Keywords: phosphorus; arsenic; imido; lithium; X-ray structures

The development of new ligands based on imido complexes of the p block elements has been a subject which has excited considerable recent interest. Chivers and Stalke have investigated imido chalcogenide anions which have been found to act both as ligands to other metals or as imido transfer reagents.[1-3] An alternative synthetic route to both imido- and related phosphinidene-ligands of the heavier congeners of groups 14 and 15 elements have been investigated by Wright *et al.*, utilising transmetallation of primary(amido)lithium (or phosphidolithium) with dimethylamido complexes of main group elements.[4] Niecke *et al.* have perhaps been most instrumental in addressing the unequivocal characterisation of imido and amido phosphorus complexes. They reported a stable iminophosphane, RN=PR', and have subsequently reported the structures of imido analogues of kinetically unstable phosphorus oxoanions.[5] The planar tris(imido)metaphosphate anion, $[P(NR)_3]^-$ and the $[P(NR)_2]^-$ anions are isoelectronic with the kinetically unstable $[PO_3]^-$ and $[PO_2]^-$ anions respectively, and more importantly, with the nitrate $[NO_3]^-$ and nitrite $[NO_2]^-$ anions.[6,7]

Our own interest in this area has focussed on the study of imido analogues on the group 15 oxoanions. We have found that these can be made from the reaction between phosphorus halides and amines in the presence of a base (typically NEt_3) followed by metallation of the remaining amido proton with *n*-butyllithium. Herein are reported the applications of this preparative route using a range of phosphorus halides and primary amines together with the structures of the imido group 15 anions that result. All products have been characterised by elemental analyses, IR and NMR spectroscopy and low temperature single crystal X-ray diffraction.

The reaction of P_2I_4 with RNH_2 (1:4 equiv.) in THF/NEt_3 solution followed by metallation using *n*BuLi (4 equiv.) results in the formation of complexes of formula $Li_3P(NR)_4$. The $[P(NR)_4]^{3-}$ trianion present in these complexes is isolectronic with the orthophosphate anion, $[PO_4]^{3-}$.[8] Single crystal X-ray crystallographic experiments reveal these complexes exist as either ion-contacted or ion-separated structures in the solid state. These structures are dependent on the amine employed and the nature of the donor molecules which solvate the lithium centres. One example of an ion-contacted lithium salt of an imidophosphate anion is shown in Figure 1. In this dimeric species, six lithium cations bind two $P(NR)_4$ trianions, with four of these lithium centres holding the two trianions together and a further lithium complexing the pendant imido arm of each phosphorus atom. The P–N distances in the $P(NR_4)^{3-}$ anion (av. 1.64 Å) are considerably shorter than that expected for a formal single bond (cf. 1.77Å),[9] being at the upper limit for that observed in formally double bonded P=N species (cf. 1.56-1.62Å).[9] The core is organised so as to maximise the contacts between the hard lithium centres and the hard nitrogen and oxygen centres.

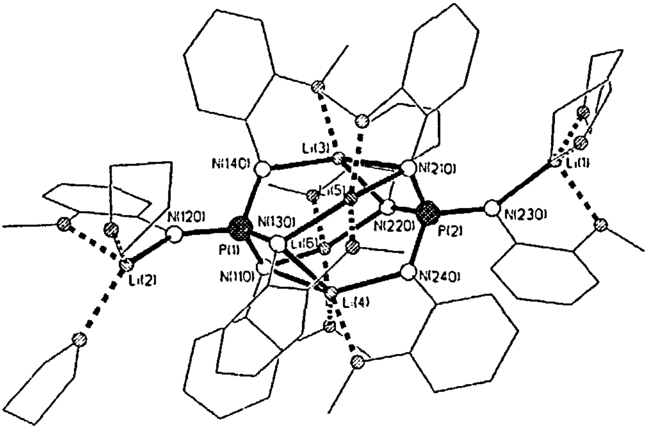

FIGURE 1 Crystal structure of $[Li_3P(NR)_4]_2$ (R = 2-methoxyphenyl)

The route by which these complexes are formed is somewhat unclear, although the most likely precusor to such imidophosphate anions is $[P\{N(H)R\}_4I]$, which would readily form imido phosphate anion upon metallation.

In contrast to the above, the reaction of PCl_3 with 2-methoxyaniline (1:3 equiv.) in THF/NEt_3 solution, followed by metallation with *n*BuLi (2 or 3 equiv.) yields a complex $[Li_2P(H)(NR)_3]_2$, whose tris imido phosphonate anion is the imido analogue of the phosphite anion, $[HPO_3]^{2-}$ (see Figure 2).

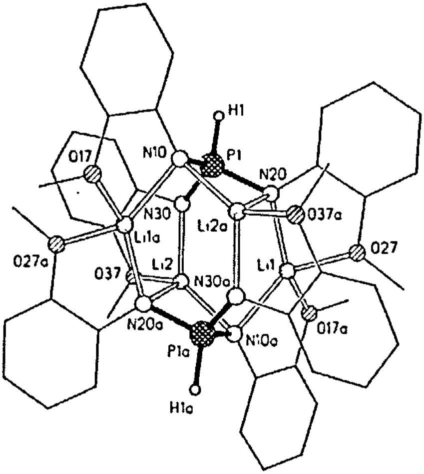

FIGURE 2 Crystal structure of $[Li_2HP(NR)_3]_2$ (R = 2-methoxyphenyl)

Within this complex, P–N bond lengths range from 1.613(2) Å to 1.630(2) Å. The shorter bond distances observed compared with those in the related imidophosphate anion, $[P(NR)_4]^{3-}$ {1.64 Å}[8] are perhaps due to the enhanced double bond character in $[HP(NR)_3]^{2-}$ where formally, one P=N bond and two P–N bonds form a resonance hybrid, in contrast to the anion $[P(NR)_4]^{3-}$ where the ratio is one P=N bonds to three P–N bonds.

It seems reasonable to postulate that the $[HP(NR)_3]^{2-}$ anion has resulted from 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, R_2P–N(H)R' have shown that the P–H tautomer is stabilised by both electron withdrawing amide groups (R') and bulky substituents on the P and N centres (R and R'). 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]

The similar reaction used to form the imidophosphite anion by using $AsCl_3$ in place of PCl_3 gives a quite different result. Hence, the reaction of $AsCl_3$ with benzylamine (1:3 equiv.) in THF/NEt_3 solution, followed by metallation with *n*BuLi (3 equiv.) yields a complex $[Li_3As(NR)_3]_2$ (see Figure 3).

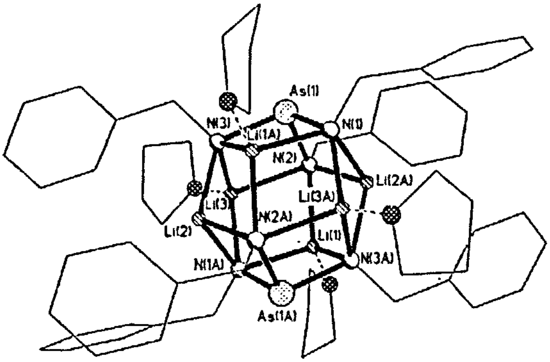

FIGURE 3 Crystal structure of $[Li_3As(NR)_3]_2$ (R = benzyl)

The crystal structure shows two $As(NR)_3$ trianions bound by six lithium cations. The As–N bond lengths (av. 1.88 Å) are very much in the realm of commonly accepted values for As–N single bonds. It is interesting that, whereas comparable imido phosphorus complexes possess P–N bond lengths intermediate in length between commonly accepted values for single and double bonds, the corresponding As–N distances are typical of commonly accepted values for single bonds.

The different products observed in the reactions of ECl_3 / amine / *n*BuLi for E= As and P can be rationalised by the weaker As=N bonds and the preference for the +3 oxidation state for As. Hence, the proposed As{N(H)R}$_3$ intermediate following amination of the halide shows no desire for an amido proton shift to the As centre, and all three protons are subsequently metallated to give the $[As(NR)_3]^{3-}$ anion.

We are continuing to investigate the extent to which the imido anions mimic the chemistry of their oxo counterparts and are probing the mechanisms by which these anions are formed.

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