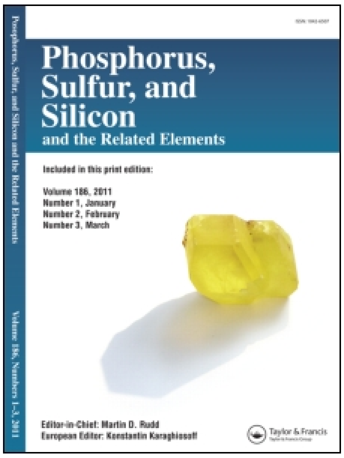

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Aspects of Imido Phosphorus Chemistry

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Phosphorus trichloride and phenyldichlorophosphine were reacted with two equivalents of benzophenone hydrazone and metallated stoichiometrically with *n*butyllithium, to crystallize $Li2(BuP(N_2CPh_2)_2)$ and $Li_2(PhP(N_2CPh_2)_2)$ respectively. An investigation into the synthesis of alternative metal containing imidophosphorus complexes using similar methodology has produced complexes of $((EtZn)PhP(NPhOMe)_2EtZn)_2$ and $PhP(NNCPh_2)_3(PhHg)_3Cl$.

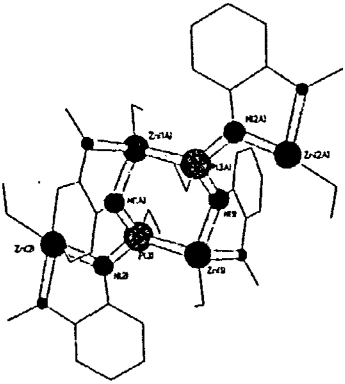
Keywords: phosphorus; imido; lithium

Simple amination reactions of main group halides have been investigated for many years, although only recently definitive results have been realised. Imidochalcogenide anions have been investigated by Chivers and Stalke, who found them to act as both ligands to other metals and as imido transfer reagents to other species.[1,2] Wright extended this work to include imido species of the heavier group 14/15 elements and found applications as precursors to deposition of antimony/alkali metal phases.[3] Imido analogues of kinetically unstable phosphorus oxoanions, $[P(NR)_3]^-$ and $[P(NR)_2]^-$ were discovered by Niecke.[4] Our work has focussed on the synthesis and subsequent examination of imido analogues of pnictide oxoanions. Previously we have reported an imido analogue of the orthophosphate anion $[P(NR)_4]^{3-}$and uncovered an imido analogue of the phosphite anion $[HP(NR)_3]^{2-}$.[5,6] Recent investigations have resulted in the synthesis and characterization by X-ray crystallography of two homologues in the $[R'(NR)_2]^{2-}$ series.

Amination/metallation of phosphorus trichloride with an excess of benzophenone hydrazone and ^{n}BuLi yields $Li_2{}^nBuP(NNCPh_2)_2$. Presumably, the ^{n}BuLi reacts as both a base and a nucleophile, removing the protons from the nitrogen atom but also substituting a ^{n}butyl group onto the phosphorus centre. The reasons this is the preferred reaction pathway are unclear, but may be influenced by steric congestion around the phosphorus centre, hindering the accommodation of three of the more bulkier amine groups. This complex highlights the potential accessibility of other alkyl/aryl imidophosphorus complexes. However, a more elegant and direct synthetic route to this type of product uses phenyldichlorophosphine as the precursor, producing $Li_2PhP(NNCPh_2)_2$.

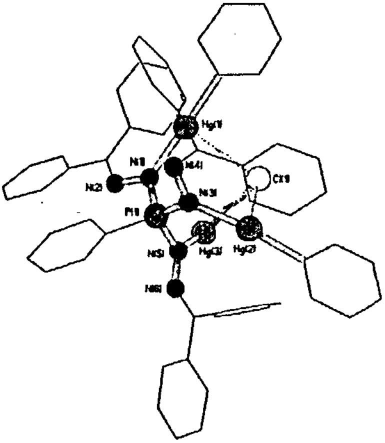
X-ray crystallographic analyses of both structures shows them to remarkably similar. They are ion contacted dimers with two $[RP(NNCPh_2)_2]^{2-}$ anions held together by four lithium centres. The phosphorus atoms have three coordinate, distorted pyramidal geometry, and the P-N bonds are between 1.69 and 1.71Å, indicative of slightly shortened single bonds. The lithium centres occupy two distinct environments; the peripheral lithium centres are in distorted tetrahedral geometry, contacting two nitrogen centres in addition to coordinating two THF molecules, but the central lithium atoms are in rare two coordinate geometry, which is more often a consequence of binding complexes with particular steric bulk.

With the emphasis on potential applications of these lithium imidophosphorus cages, our investigation has broadened to target the inclusion of other metal species within imidophosphorus cages. Two parallel approaches have been used; firstly changing the metallating agent in the primary synthesis and secondly, reacting the isolated imidophosphorus anions with metal halides. Altering the metallating agent from ^{n}butyllithium to diethyl zinc after amination of phosphorus trichloride with ortho-anisidine gives $((EtZn)EtP(NPhOMe)_2EtZn)_2$.



In this complex the ethyl zinc moiety coordinates both the phosphorus and the nitrogen centres, and the ethyl group attaches to the phosphorus centre revealing interesting parallels with the behaviour of the *n*butyl group in the earlier reaction.

Reaction of metal halides with the lithium imidophosphorus products has proved more troublesome. Mercury dichloride was reacted with $Li_2HP(NPhOMe)_3$ and $Li_2PhP(NNCPh_2)_2$. In both cases mercury dropped out of solution and the imidophosphorus moieties oligomerised to form neutral products containing P_2N_2 rings. However, ^{31}P NMR spectra of the reaction mixture indicates the presence of a metal bound phosphorus atom, suggesting there may be a mercury bridged transition state in the reaction, but isolation or further characterisation of these intermediates has proved elusive. Variation of the transmetallating agent to phenylmercury chloride has provided a measure of success. Reaction with $Li_2PhP(NNCPh_2)_2$ yielded a crystalline product where the mercury atoms retained within the imidophosphorus complex $PhP(NNCPh_2)_3(PhHg)_3Cl$.



In this complex the phosphorus atom is four coordinate, with distorted tetrahedral geometry. The mercury centres retain their preferred linear geometry, only slightly distorted by the prescence of a charge balancing chloride anion interacting equally with all three metal centres.

Further work in this exciting area aims to broaden the range of these complexes and improve our understanding of their behaviour.

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