Authentication of a Sodium Primary Phosphide: Synthesis and Crystal Structure of $[Na\{PH(C_6H_{11})\}(pmdeta)]_2$ (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine)

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The reaction of the primary phosphine $PH_2(C_6H_{11})$ with NaBu^n in the presence of pmdeta gives the first sodium phosphide containing simple organo substituents $[Na\{PH(C_6H_{11})\}(pmdeta)]_2$ **1** (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) to be structurally characterised.

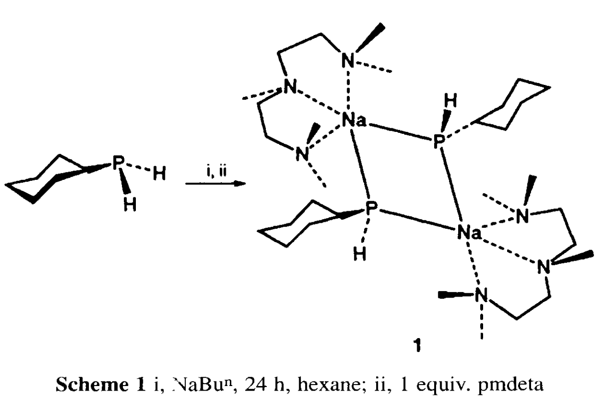
Owing to the synthetic importance of lithium phosphides, $[Li(PR_2)(L)_m]_n$ (R = H, alkyl, aryl), primarily as R_2P^- transfer agents,[1] interest in their solid- and solution-state structures has increased significantly in the recent past.[2] Mostly this has centred on those complexes derived from secondary phosphines despite primary phosphides being synthetically important in their own right.[3] However, in many synthetic procedures, for example in the synthesis of $R_2P(CH_2)_xNR_2$ type ligands,[4,5] the reactive intermediate is a sodium phosphide produced *via* the reaction of the phosphine with sodium metal in liquid ammonia, a common medium for *in situ* reactions. Despite this almost no structural information is available on the heavier alkali metal phosphides.

The structures and hence reactivity of metallated phosphines depend upon the interaction and nature of the phosphido ligand, solvating ligands and the metal itself. Recent comparative metallation studies[6] in amide chemistry have revealed how judicious it is not to simply consider the metal as a counter ion. The structural variety found in alkali metal amide chemistry and the rationale for such structures have been well reviewed[7,8] and as predicted the phosphides adopt similar aggregated structures. Polymers,[9] *e.g.* $[Li(thf)\{P(C_6H_{11})_2\}]_\infty$, ladders,[10] *e.g.* $[Li\{P(SiMe_3)_2\}]_6$, dimers,[11] *e.g.* $[Li(tmen)(PPh_2)]_2$ (tmen = *N,N,N′,N′*-tetramethylenediamine) and monomers[2] *e.g.* $[Li(thf)\{PH(mes)(tmen)\}]$ (mes = $2,4,6\text{-}Me_3C_6H_2$) all have precedents in lithium amide chemistry.

Herein, we report the synthesis and crystal structure† of the first sodium phosphide containing simple organo substituents $[Na\{PH(C_6H_{11})\}(pmdeta)]_2$, **1**, produced *via* the reaction of the primary phosphine $PH_2(C_6H_{11})$ with NaBu^n in the presence of pmdeta (Scheme 1). The structure presented in Fig. 1 is a centrosymmetric dimer with a planar central $(PNa)_2$ ring. The cyclohexyl substituents adopt a transoid position relative to the ring with both Na^+ cations achieving a five-coordinate bonding environment *via* complexation with the tridentate pmdeta ligand. Within the ring P–Na 2.883(8), P′–Na 2.936(7) are comparable to those found in the only other structurally characterised sodium phosphide $[Na(thf)_2\{P(mes)(SiFBu^t{}_2)\}]$,[12] 2.890(1) Å. The ligated pmdeta N–Na distances; Na–N(1) 2.51(2), Na–N(2) 2.61(1), Na–N(3) 2.50(1) Å, are comparable to those found in the analogous sodium dimer,[13] $[Na(\mu\text{-}Ph)(pmdeta)]_2$, 2.609(3), 2.646(3), 2.712(3) Å. It should be noted that there was disorder in the cyclohexyl ligand which contributed to the relatively low precision of the structure determination but was successfully modelled at 50% site occupancy for both conformations of the ligand.

The structure of **1** possesses several interesting features. In **1**, despite the presumably tetrahedral environment at the P centre in the uncomplexed $[Na\{PH(C_6H_{11})\}]_\infty$, **1′**, polymeric ladder, the negligible steric demand of the H substituent allows full incorporation of the pmdeta and subsequent deaggregation to the dimer. This preferred structure allows the Na^+ a coordination number of five, which compares favorably to the four which would be available if the complex was monomeric. For other structurally characterised primary phosphides $[Li(thf)\{PH(mes)\}(tmen)]$ and $[Li(thf)_3\{PH(mes)\}]$[18] the smaller Li^+ centre is coordinatively saturated when offered three potential donor atoms and allows deaggregation to the monomeric state.

In the more widespread chemistry of lithium phosphides and amides, pmdeta usually forces deaggregation to the monomeric species *e.g.* in $[Li(PPh_2)(pmdeta)]$[11] and $[Li\{NPh(naphthyl)\}(pmdeta)]$[14] although the greater coordinative demands of Na^+ can allow dimers to form in only exceptional circumstances. In $[Na\{N(2\text{-}C_5H_4N)Ph\})(pmdeta)]_2$[15] the potentially tridentate ligand acts as only in a bidentate manner similar to that of tmen. However in the sodiumindole derivative[16] $[Na(NC_8H_7)(pmdeta)]_2$ the ligand utilises all available donor atoms, the amido unit is heterocyclic and planar hence leaving a large coordination arc available for the approach of the pmdeta. It is the absence of large steric bulk and the coordinative demands of the metal which determines the manner in which the pmdeta is incorporated, and the subsequent aggregation state. Thus anions with a low three-dimensional



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Scheme 1 i, NaBu^n, 24 h, hexane; ii, 1 equiv. pmdeta

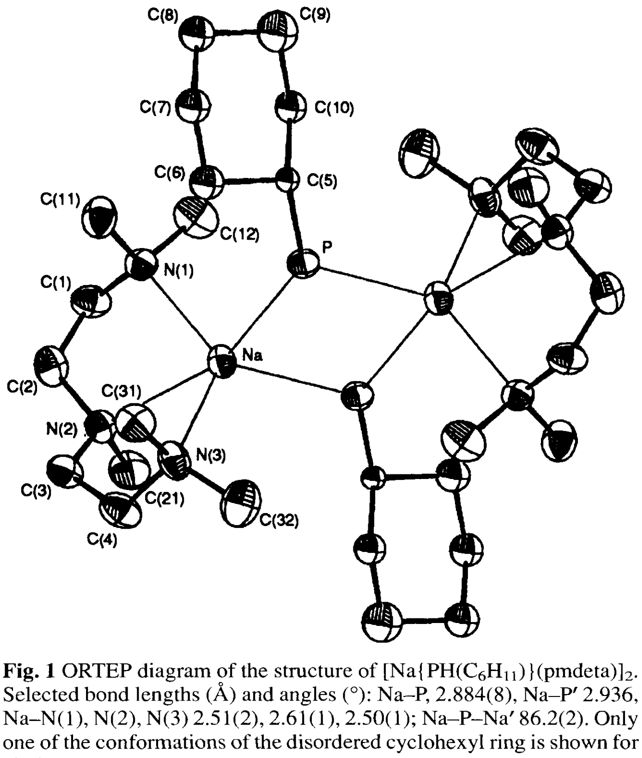

Fig. 1 ORTEP diagram of the structure of $[Na\{PH(C_6H_{11})\}(pmdeta)]_2$. Selected bond lengths (Å) and angles (°): Na–P, 2.884(8), Na–P′ 2.936, Na–N(1), N(2), N(3) 2.51(2), 2.61(1), 2.50(1); Na–P–Na′ 86.2(2). Only one of the conformations of the disordered cyclohexyl ring is shown for clarity.

bulk can allow pmdeta to be fully incorporated into a dimeric system, *e.g.* [Na(NMe$_2$)(pmdeta)]$_2$[16] but it is more likely if the tetrahedral environment around the anion is removed, *e.g.* [Na(μ-Ph)(pmdeta)]$_2$ and [Na(pmdeta)]$_2$.[17] This would also be expected for alkoxides and sulfides.

Increased reactivity occurs when employing Na rather than Li compounds and having the complex in the lowest state of aggregation, *i.e.* monomeric. The fact that for the primary sodium phosphide **1′**, pmdeta is insufficient to ensure monomer formation means more sterically demanding ligands may be required. Primary phosphides may be preferred due to the benefit of retaining the potentially reactive H substituent or when negligible steric resistance is needed but it may be the case that in simple donor systems the metallated secondary phosphides (Li or Na) may be more reactive than their primary analogues.

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Footnote

† *Crystal data* for **1**: single crystal from from hexane $C_{30}H_{72}N_6Na_2P_2$, triclinic, $P\bar{1}$, $Z = 2$, $a = 8.98(1)$, $b = 11.47(1)$, $c = 11.81(1)$ Å, $\alpha = 64.7(1)$, $\beta = 78.9(1)$, $\gamma = 70.0(1)°$, $V = 1031.5$, $D_c = 1.003$ g cm^{-3}, $\mu = 0.15$ mm^{-1} (no abs. correction), $T = 293$ K, $2\theta_{max} = 50°$, 1578 observed reflections [$I > 2.5\sigma(I)$], 175 refined parameters, $R = 0.117$, $R_w = 0.141$ (unit weights); structure solution with direct methods, XTAL3.2 (XTAL 3.2 Reference Manual, ed. S. R. Hall and J. M. Stewart, Lamb, Perth), all H atoms calculated (C–H 0.95 Å), all non-hydrogen atoms were refined with anisotropic temperature factors except the disordered carbons of the cyclohexyl ring which were refined isotropically. (Enraf-Nonius CAD4 diffractometer, crystal mounted in capillaries). The bond lengths and angles of both orientations of this disordered group were restrained to small deviations about the ideal values of 1.54 Å and 109.5°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue 1.

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