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Synthesis and structure of the extended phosphazane ligand $[(1,4\text{-C}_6\text{H}_4)\{\text{N}(\mu\text{-PN}^t\text{Bu})_2\text{N}^t\text{Bu}\}_2]^{4-}$

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The reaction of the phenylene-bridged precursor $(1,4\text{-C}_6\text{H}_4)[\text{N}(\text{PCl}_2)_2]_2$ with $^t\text{BuNH}_2$ in the presence of Et_3N gives the new ligand precursor $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PNH}^t\text{Bu})_2]_2$, deprotonation of which with Bu_2Mg gives the novel tetraanion $[(1,4\text{-C}_6\text{H}_4)\{\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2\}_2]^{4-}$.

The applications of organic macrocycles (based on carbon frameworks) as hosts for a broad range of guest molecules, cations and anions is a central area of modern coordination chemistry.¹ The high thermodynamic stability of carbon-bonded frameworks underpins their stability as hosts. In contrast, macromolecular inorganic systems have been far less explored, largely due to the significantly less selective synthetic routes to these species and the lower thermodynamic and kinetic stability of non-carbon frameworks. Nonetheless, a few inorganic bonding systems which combine high bond energy and low bond polarity offer the potential to develop macromolecular chemistry which parallels that in the organic arena. In particular, since the $\text{P}^{\text{III}}\text{-N}$ bond energy (290 kJ mol^{-1}) is competitive with that of the C-C bond (346 kJ mol^{-1}) there have been significant developments in the area of macrocyclic phosphazanes in the past ten years.

We have found that dimers of the type $[\text{ClP}(\mu\text{-NR})_2]_2$ are good building blocks for the formation of a series of phosphazane-based macrocycles. Two sorts of macrocycles can be obtained using inorganic or organic linkers, $[\{\text{P}(\mu\text{-NR})_2(\mu\text{-X})\}_n]$ ($\text{X} = \text{NH}, \text{O}, \text{Se}$) (Figure 1A) and $[\{\text{P}(\mu\text{-NR})_2(\mu\text{-LL}')\}_n]$ (where LL' is an organic linker) (Figure 1B).³ Apart from their host-guest behaviour, a particular interest in these species is their potential in gas storage, by virtue of their tubular or bowl-shaped cavities which results in large free volume and low density. A possible advantage over organic calixarenes (which have also shown potential in gas storage) is the polar nature of the $\text{P}^{\delta+}\text{-N}^{\delta-}$ bonds which could facilitate chemisorption of gases like H_2 .⁴

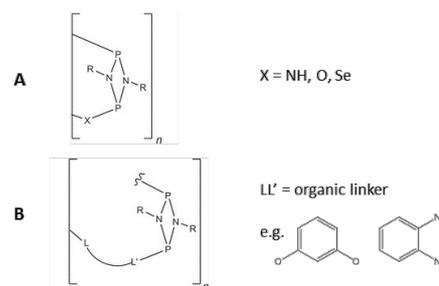
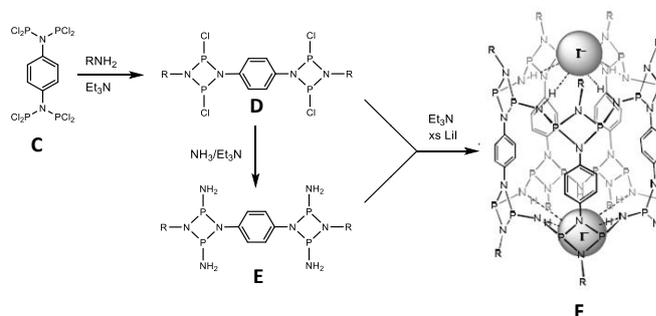


Figure 1. Two types of phosph(III)azane macrocycle formed by linking of P_2N_2 units with inorganic (X) or organic (LL') linkers.



Scheme 1. A potential route to supramolecular tubular phosph(III)azanes.

Our major interest in this area is the further expansion of the supramolecular chemistry of phosphazanes, and the challenges involved in the development of robust synthetic strategies to complex inorganic molecules of this type. One interesting target is tubular macrocycles like **F** (Scheme 1), for which a simple anion-templating strategy (analogous to that used in the synthesis of the previous macrocycles **A** and **B**) may also be possible using the key new bridged precursors **D** and **E**. During studies aimed at the synthesis of **F** we found that the condensation reaction of $^t\text{BuNH}_2$ with the previously reported precursor **C**⁵ cannot be controlled to give a chloro-species of type **D** (Scheme 2). Instead, the fully substituted bridged phosph(III)azane $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2]_2$ was formed.

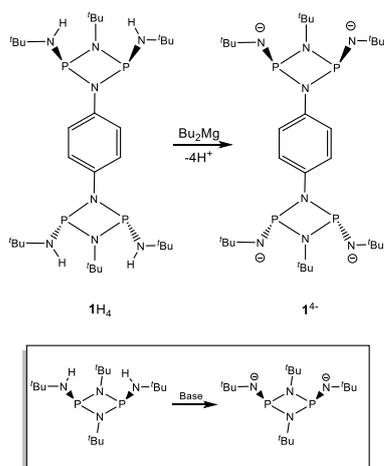
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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: ³¹P, ¹H, ¹³C NMR and X-ray data on **1H4** and **1[Mg·(THF)2]**. See DOI: 10.1039/x0xx00000x

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$\text{N}^t\text{Bu}_2(\text{PNH}^t\text{Bu})_2$ ($\mathbf{1H}_4$) is obtained (Scheme 2). This species is closely related to the



Scheme 2. Deprotonation of $\mathbf{1H}_4$ to give the tetraanion $[(1,4\text{-C}_6\text{H}_4)\{\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2\}_2]^{4-}$ and (insert) the analogous deprotonation of the unbridged counterpart.

unbridged ligand species $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]$, which is a source of the $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]^{2-}$ ligand (Scheme 2, insert).⁶ Like the latter precursor,⁷ $\mathbf{1H}_4$ can be deprotonated by organometallic bases to give the tetraanion $[(1,4\text{-C}_6\text{H}_4)\{\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2\}_2]^{4-}$ ($\mathbf{1}^{4-}$) (Scheme 2), providing an approach to extended phosphazane ligands of this type. Apart from its potential as new ligand system, this reaction is a rare example the poly-deprotonated of a relatively small molecule.⁸

The slow, dropwise addition of $^t\text{BuNH}_2$ (2 equivalents) to a solution of \mathbf{C} (1 equivalent) in toluene in the presence of excess Et_3N (as a Brønsted base) was carried out with the purpose of obtaining the tetrachloride bridged species \mathbf{D} . However, an *in situ* ^{31}P NMR study shows that the only phosphorus-containing product formed is the bridged phosph(III)azane $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PNH}^t\text{Bu})_2]_2$ ($\mathbf{1H}_4$). Repeating the reaction using the correct stoichiometry of \mathbf{C} : $^t\text{BuNH}_2$ (1 : 4 equivalents) gives $\mathbf{1H}_4$ in 84% yield as an amorphous powder after filtration of the $\text{Et}_3\text{N}\cdot\text{HCl}$ produced and removal of the solvent. † Satisfactory elemental analysis could not be obtained on this powder or on the crystalline material, however, unambiguous characterisation of $\mathbf{1H}_4$ was made based on NMR spectroscopic and single-crystal X-ray studies. According to NMR studies, no more than 1.5% impurities are present in samples of $\mathbf{1H}_4$ (see Figure 3).

The room-temperature ^{31}P NMR spectrum of $\mathbf{1H}_4$ shows a singlet at δ 96.6 ppm (ESI, Fig. S1), not dissimilar to that of the unbridged counterpart $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]$ (δ 88.5 ppm). This spectrum remained unchanged down to -60°C , suggesting that only one conformational isomer is present in solution. The room-temperature ^1H NMR spectrum displays a singlet at δ 7.48 ppm corresponding to the protons of the bridging phenylene group, and two singlets at δ 1.44 and 1.21 ppm, corresponding to the N^tBu and NH^tBu groups (ESI, Fig. S2).

Crystallisation of the crude powder of $\mathbf{1H}_4$ from n-hexane gave the unsolvated ligand ($\mathbf{1H}_4$), while crystallisation from cyclohexane gives the solvate ($\mathbf{1H}_4\cdot\text{cyclohexane}$). Data for unsolvated $\mathbf{1H}_4$ are discussed here, while the details of the structure and refinement of $\mathbf{1H}_4\cdot\text{cyclohexane}$ are provided in the ESI.

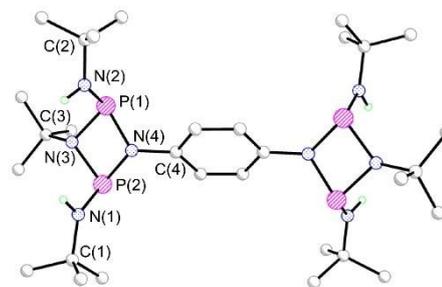


Figure 2 Molecular structure of the hetero-functional, bridged compound $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-PNH}^t\text{Bu})_2\text{N}^t\text{Bu}]_2$ ($\mathbf{1H}_4$). H-atoms (except those attached to N) have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): P(1)-N(2) 1.654(6), P(1)-N(3) 1.734(5), P(1)-N(4) 1.738(5), P(1)⋯P(2) 2.636(2), P(2)-N(1) 1.658(6), P(2)-N(4) 1.725(5), P(2)-N(3) 1.734(5), N(3)-P(1)-N(4) 79.5(2), N(4)-P(2)-N(3) 79.9(2), P(2)-N(3)-P(1) 98.9(3), P(2)-N(4)-P(1) 99.7(3).

The molecular structure of $\mathbf{1H}_4$ consists of two P_2N_2 ring units which are linked together by a *para*-phenylene bridge (Figure 2). Like the phosphazane dimer $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]$, both of the P_2N_2 ring units of $\mathbf{1H}_4$ are puckered (with a hinge-angle of *ca.* 19.5° about the P⋯P vector). Looking along the major axis of the molecule (i.e., along the C_2 -axis of the C_6H_4 ring), the P_2N_2 ring units are eclipsed with respect to each other and their mean planes are twisted at an angle 44° to the plane of the bridging C_6H_4 unit. The P-N bonds ($\mu\text{-N}$ mean 1.733 Å, terminal mean 1.656 Å), P-N-P (mean 99°) and N-P-N ($\mu\text{-N}$ mean 79.7° , terminal mean 104.8°) angles in $\mathbf{1H}_4$ are similar to those observed previously in the structure of $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]$.⁶

The deprotonation of $\mathbf{1H}_4$ was investigated using a number of organometallic bases, i.e., $\text{Sn}(\text{NMe}_2)_2$, AlMe_3 , $^t\text{BuLi}$ and Bu_2Mg . No products were observed in reactions with $\text{Sn}(\text{NMe}_2)_2$ and AlMe_3 , even after reflux the only signal observed by NMR spectroscopy corresponded to the starting material. However, in the ^{31}P NMR spectrum of the product isolated from a 1 : 4 stoichiometric mixture of $\mathbf{1H}_4$ and $^t\text{BuLi}$ (respectively) in THF, after reflux, a major peak at δ 89 ppm is observed. This corresponds to the previously reported dimer $[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]$ (lit. δ 88.5 ppm),⁵ resulting from apparent extensive fragmentation of the framework of $\mathbf{1H}_4$ under these conditions. Only in the case of reaction of $\mathbf{1H}_4$ with Bu_2Mg at room temperature (1 : 2 equivalents, respectively) was clean formation of a single new species observed in the *in situ* ^{31}P NMR spectrum (singlet, δ 132.7 ppm) (Figure 3) (ESI, Fig S4). The product, $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2]_2[\text{Mg}\cdot(\text{THF})_2]_2$ [$\mathbf{1}\{\text{Mg}\cdot(\text{THF})_2\}_2$], is formed in high yield according to extensive *in situ* ^1H , ^{13}C and ^{31}P NMR spectroscopic studies (showing around 4% impurities, Fig. S4-S10, ESI), and could be isolated as crystals upon storage of the reaction solution at -20°C .

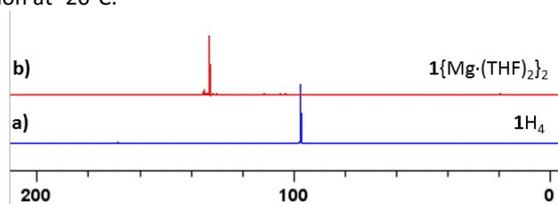


Figure 3. ^{31}P NMR spectrum of a) $\mathbf{1H}_4$ and b) the 2 : 1 reaction of Bu_2Mg with $\mathbf{1H}_4$ at room temperature.

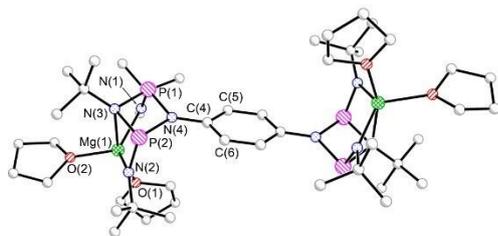


Figure 4. Molecular structure $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-N}^t\text{Bu})_2(\text{PN}^t\text{Bu})_2]_2[\text{Mg}\cdot(\text{THF})_2]_2$ $[\text{1}\{\text{Mg}\cdot(\text{TH})_2\}_2]$. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Mg(1)-N(1,2) mean 2.062, Mg-N(3) 2.337(3), Mg(1)-O mean 2.07, P-N N(1,2) range 1.647(3)-1.648(3), P-N(3,4) range 1.745(3)-1.778(3), ($\mu\text{-N}$)-P-($\mu\text{-N}$) 79.3(1), ($\mu\text{-N}$)-P-N(1,2) range 96.3(1)-106.9(1), P(1)-N(3)-P(2) 99.9(1), P(1)-N(4)-P(2) 101.6(2), C(4)-N(4)-P(1) 129.7(2), C(4)-N(4)-P(2) 128.7(2).

Unfortunately, $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$ is not stable at room temperature in the solid state. Upon removal of the reaction solvent the complex was observed to decompose in to a number of species in repeated attempts to isolate it, the ^{31}P NMR spectrum showing four peaks at δ 94, 102, 106 and 110 ppm. These resonances do not correspond to hydrolysis products, as shown by a separate study of the controlled addition of water to $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$ which produces mainly 1H_4 . The same four resonances are observed when the reaction of 1H_4 with Bu_2Mg is performed at 50°C overnight, indicating that we are observing genuine decomposition rather than simply THF-desolvation. This conclusion is supported by elemental analysis of the dry solid (see ESI).

Low-temperature (180(2) K) X-ray data on $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$ was obtained by mounting the crystals directly from solution at -20°C , to avoid the solid-state decomposition which was noted earlier. The structure of the complex (Figure 4) is related to the previously reported Mg-complex $\{[(^t\text{BuN})\text{P}(\mu\text{-N}^t\text{Bu})_2]\text{Mg}\cdot(\text{THF})_2\}$, obtained from the deprotonation of $\{[(^t\text{BuNH})\text{P}(\mu\text{-N}^t\text{Bu})_2]\}$ with Bu_2Mg in THF and consisting of a $\text{P}_2\text{N}_4\text{Mg}$ -secocubane unit.⁷ In the case of $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$, two such secocubane units are located at either end of the molecule in the solid-state structure (Figure 4). Like the previously reported secocubane $\{[(^t\text{BuN})\text{P}(\mu\text{-N}^t\text{Bu})_2]\text{Mg}\cdot(\text{THF})_2\}$, the Mg^{2+} ions of $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$ have distorted trigonal bipyramidal geometries ($\tau = 0.67^9$), being coordinated by two THF molecules and by the two terminal N-atoms and one $\mu\text{-N}$ -atom of the phosphazane unit of the $[\text{1}]^{4-}$ tetra-anion. The P-N bond lengths ($\mu\text{-N}$ range 1.745(3)-1.778(3) mean 1.647, terminal-N range 1.647(3)-1.648(3) Å) and P_2N_2 -ring P-N-P [range 99.9(1)-101.6(2) $^\circ$] and N-P-N [79.3(1) $^\circ$] angles are similar to those in $\{[(^t\text{BuN})\text{P}(\mu\text{-N}^t\text{Bu})_2]\text{Mg}\cdot(\text{THF})_2\}$ ($\mu\text{-N}$ mean 1.77, terminal-N mean 1.66 Å, P_2N_2 -ring P-N-P mean 99.4, N-P-N mean 80.5 $^\circ$).⁶

In summary, we have reported the synthesis of the first bridged phosph(III)azane ligand of its class, which is related to the chelating nitrogen donor bis(amido)cyclo diphosph(III)azanes $[(\text{RNH})\text{P}(\mu\text{-NR})_2]$ ligands. Complete deprotonation was possible using Bu_2Mg to give the tetraanion 1^{4-} , providing an *in situ* source of this anion. This opens up a new area of supramolecular chemistry. In particular, in preliminary work we have now shown that the reactions of **C** (Scheme 1) with more sterically demanding amines than $^t\text{BuNH}_2$ does lead to the formation of the key precursors **D**. For example, using DippNH_2 ($\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4$) in place of $^t\text{BuNH}_2$ results in clean

formation of this type of framework according to *in situ* ^{31}P NMR spectroscopy (ESI, Fig S11). Further work in this area will explore the coordination chemistry of the new bridged tetraanion **1** with a range of metals (a particular area of interest being magneto-chemistry) and move forward with the functionalisation and cyclisation of species **D**.

Acknowledgements: We thank the ERC: Advanced Investigator Award for D.S.W (R.S., R.J.L., R.G).

Notes and references

\ddagger **Synthesis of 1H_4 :** $^t\text{BuNH}_2$ (0.6 ml, 5.8 mmol) was added to a solution of $p\text{-C}_6\text{H}_4[\text{N}(\text{PCl}_2)_2]_2$ **C** (500 mg, 0.97 mmol) and Et_3N (1ml, 7.8 mmol) in toluene (40 ml) at -78°C . The mixture was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was filtered (Celite, P4) and the solvent was removed under vacuum to give the product as a white powder (419 mg, 84%). Addition of hexane and storage at room temperature afforded colourless crystals of $(1,4\text{-C}_6\text{H}_4)[\text{N}(\mu\text{-PNH}^t\text{Bu})_2\text{N}^t\text{Bu}]_2$ (1H_4). ^1H NMR (400 MHz, C_6D_6 , 25°C) δ 7.48 (s, Ph, 4H), 2.90 (m,br, NH, 4H), 1.44 (s, 18H, N^tBu), 1.21 (s, 36H, N^tBu). ^{13}C NMR (100.62 MHz, C_6D_6 , 25°C) δ 139.1 (t, $J_{\text{PC}} = 13.38$), 118.5 (t, $J_{\text{PC}} = 9.56$), 52.3 (t, $J_{\text{PC}} = 14.34$), 51.5 (d, $J_{\text{PC}} = 12.02$), 33.1 (d, $J_{\text{PC}} = 8.79$), 31.8 (t, $J_{\text{PC}} = 7.26$). ^{31}P NMR (161.97 MHz, C_6D_6 , 25°C , rel. to 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$) δ 96.6 (s) (^{31}P NMR suggests no more than ca. 1% impurities).

Synthesis of $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$: 0.3 ml of 0.5 M dibutylmagnesium (in *n*-heptane) was added to a solution of 1H_4 (0.05 g, 0.07 mmol) in THF (5 ml) at 0°C . The mixture was allowed to warm to room temperature and stirred at room temperature for 24 h. Addition of hexane and storage at -20°C for 2 days afforded colourless crystals of $[\text{1}\{\text{Mg}\cdot(\text{THF})_2\}_2]$. ^1H NMR (500 MHz, $d_8\text{-THF}$, 25°C) δ 6.93 (s, Ph, 4H), 1.33 (s, 18H, N^tBu), 1.28 (s, 36H, N^tBu). ^{13}C NMR (100.62 MHz, $d_8\text{-THF}$, 25°C) δ 138.8 (t), 116.1 (t, $J_{\text{PC}} = 8.20$), 52.5 (t, $J_{\text{PC}} = 14.65$), 51.9 (d, $J_{\text{PC}} = 20.51$), 36.3 (d, $J_{\text{PC}} = 12.88$), 31.7 (t, $J_{\text{PC}} = 8.11$). ^{31}P NMR (202.48 MHz, $d_8\text{-THF}$ 25°C , rel. to 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$) δ 132.7 (s).

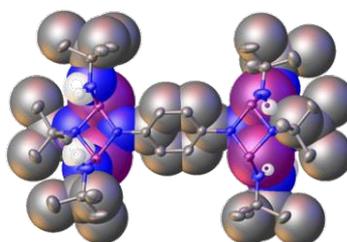
CCDC reference numbers 1435095-1435098. See <http://www.rsc.org/xxx> for crystallographic data in CIF or other electronic format.

- (a) *Comprehensive Coordination Chemistry II*, ed. J. McCleverty and T. J. Meyer, Elsevier Pergamon, Oxford, 1995; (b) M. S. Balakrishna, D. J. Eisler and T. Chivers, *Chem. Soc. Rev.*, 2007, **36**, 650; (c) *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. W. Steed, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Elsevier Pergamon, Oxford, 1996.
- J. E. Huyee, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Ed., Pearson Ed., 2006.
- S. G. Calera and D. S. Wright, *Dalton Trans.*, 2010, **39**, 5055, and references therein.
- J. L. Atwood, L. J. Barbour, A. Jerga, and B. L. Schottel, *Science*, 2002, **298**, 1000.
- C. Ganesamoorthy, M. S. Balakrishna, J. T. Mague and H. M. Tuononen, *Inorg. Chem.*, 2008, **47**, 7035.
- I. Schranz and L. Stahl, *Inorg. Chem.*, 1998, **37**, 1493.
- L. Stahl, *Coordination Chemistry Reviews*, 2000, **210**, 203.
- F. Rivals, G. T. Lawson, M. A. Benson, P. I. Richards, S. Zacchini and A. Steiner, *Inorg. Chim. Acta*, 2011, **372**, 304; W. Clegg, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings and D. M. Tooke, *Angew. Chem. Int. Ed.*, 2001, **40**, 3902; W. Clegg, E. Crosbie, S. H. Dale-Black, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, D. L. Ramsay and S. D. Robertson, *Organometallics*, 2015, **34**, 2580.
- N. T. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1439.

Graphical Abstract

Synthesis and structure of the extended phosphazane ligand (1,4-C₆H₄)[N(μ-PN^tBu)₂N^tBu]₂⁴⁻

R. Sevilla, R. J. Less, R. García-Rodríguez, A. D. Bond and D. S. Wright



Reaction of (1,4-C₆H₄)[N(PCl₂)₂]₂ with ^tBuNH₂ in the presence of Et₃N gives the bridged phosph(III)azane (1,4-C₆H₄)[N(μ-PNH^tBu)₂N^tBu]₂ (**1H**₄), which can be deprotonated to give the tetraanion (1,4-C₆H₄)[N(μ-PN^tBu)₂N^tBu]₂⁴⁻ (**1**⁴⁻). The latter represents a new type of phosphazane ligand.