Isomerisation, Reactivity and Coordination Chemistry of a New Hybrid, Multi-functional Phosphazane

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The unsymmetric P\textsuperscript{III}/P\textsuperscript{V} cyclodiphosphazane framework \([\text{S}=\text{H}]\text{P}(\mu-\text{N}^\text{tBu})\text{P}\text{NH}^\text{tBu}\) (2) provides entry into the mixed chalcogenide dianion \([\text{S}]\text{P}(\mu-\text{N}^\text{tBu})\text{P}(\text{Se})\text{N}^\text{tBu}\)^\text{2−}, and unique insight into the mechanisms of cis/trans isomerism in phosph(III)- and phosph(V)-azanes.

Establishing synthetic rules for the functionalisation and modification of ligand sets is a central subject in organic and inorganic chemistry. Adapting an established ligand allows easy control over the steric and electronic character in respect to coordination to metal centres. Much of our work has focused on the development of synthetic methodologies to inorganic ligand systems, which parallel developments in the organic arena. Phosph(III)azanes dimers have proved to be highly versatile building blocks in this area, being key starting materials for the construction not only of small multidentate ligand systems but also of large inorganic macrocycles.

Highlighted in Figure 1 are two recent examples in which the phosphazane unit is used to construct a) a new type of hybrid carbene ligand,\textsuperscript{1,3} and b) a large macrocyclic arrangement.\textsuperscript{2,3}

Figure 1 Examples of ligands derived from cyclodiphosphazane building blocks, a) a modified carbene ligand and b) a PIII/PV macrocycle.

One area of particular interest has been the uncovering of new synthetic methods for the selective donor-functionalisation of the P\textsubscript{2}N\textsubscript{2} frameworks of cyclodiphosphazanes. A particularly important family in this class are the isoelectronic ligand systems shown in Figure 2, all of which can be readily accessed from nucleophilic substitution and/or oxidation of simple dichloro-phosphazanes [ClP(\mu-NR)]\textsuperscript{2} (e.g., Scheme 1).

In the current study we set out with the simple aim of combining the previously established nucleophilic and oxidation reactions used in P\textsubscript{2}N\textsubscript{2}-functionalisation (illustrated in Scheme 1) to obtain the first examples of unsymmetric hybrid frameworks based on the diprophosph(III/V)azane unit (Scheme 2). With these new arrangements in hand, we are able to observe direct evidence of the type of mechanism involved in cis/trans isomerisation (inter- or intra-molecular), as well as develop new ligand chemistry based on these multifunctional donor systems.

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\textsuperscript{3} Electronic Supplementary Information (ESI) available: Contains synthetic details, \textsuperscript{1}H, \textsuperscript{31}P, \textsuperscript{77}Se NMR and X-ray analysis on all compounds. See DOI: 10.1039/x0xx00000x

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Synthetic studies started with the previously known unsymmetric cyclophosphazane [ClP(μ−N′Bu)₂PNH₂Bu] (1), which can be conveniently prepared on a multigram scale by the reaction of PCl₃ with BuNH₂ in 1:6 stoichiometric ratio (the excess BuNH₂ acting as a Bronsted base to scavenge HCl). 1 was then reacted with a solution of LiSH in THF, prepared by the previously established procedure from the reaction of H₂S gas with BuLi in THF.¹ In situ ³¹P(¹H) spectroscopy showed complete conversion of 1 into the product [(S=)(H)P(μ−N′Bu)₂PNH₂Bu] (2-trans) after 1 h at room temperature in THF, as indicated by the upfield shift of the P°(P−Cl) resonance in 1 (δ, = 201.2 ppm) to the P°(P(H)(=S)) centre in 2-trans (δ, = 51.6 ppm, ²Jp,p = 5.45 Hz), and the retention of the P°−N(H)Bu group [δ, = 136.1 ppm in 1; cf. δ, = 130.0 ppm (br) in 2-trans] (see ESI). In the fully-coupled ³¹P NMR spectrum, the P°(P(H)(=S)) resonance is observed as a double-double (²Jp,p = 5.45 Hz, ²Jsh = 531.5 Hz). Compound 2-trans can be isolated as a crystalline solid in 63% yield after removal of the reaction solvent and crystallisation from toluene (see ESI). Further confirmation of the presence of a P-H proton and the retention of the N-H proton in 2-trans comes from the ¹H NMR spectrum of the isolated material, with the P-H proton appearing as a double-double (³Jp,p = 531 Hz, ³Jsh = 9.8 Hz) and the N-H proton as a broad singlet (δ, = 2.56 ppm) (see ESI).

Figure 3 shows that the solid-state structure of 2-trans obtained under these conditions has a ‘trans’ arrangement, in which the BuNH group and S atom are on opposite faces of the P₃N₃ ring unit. Noteworthy features of this arrangement are the disposition of the BuNH group exo to the P₃N₃ ring fragment (presumably to avoid steric congestion with the μ−N′Bu groups) and the planar conformation of the P₃N₃ ring.

Heating a sample of isolated 2-trans to 50°C in THF for 16 h leads to complete conversion to 2-cis. The isomerisation of 2 is signalled by the upfield shifts in the P°(P(H)(=S)) NMR resonances, to δ, = 104.0 (d, ²Jp,p = 11.1 Hz, P[III]) and 37.2 ppm (d, ²Jp,p = 11.1 Hz, P[IV]) in 2-cis, from those in 2-trans (δ, = 130.0 and 51.6 ppm, respectively). 2-cis can be crystallised from the reaction in 85% yield (see ESI). The solid-state structure is shown in Figure 4. The metric parameters in 2-trans and 2-cis are very similar. Significantly, there is little or no distortion of the P₃N₃ ring units of 2-trans and 2-cis, which are both almost planar. This can be compared to symmetric cyclo-diphosphazanes of the type [R₂P(μ−NR)₂], where the trans isomers have puckered ring units and the cis isomers have planar ring units.⁴ To the best of our knowledge, there is only one other example in which the solid-state structures of both the cis and trans isomers of an individual cyclophosphazane have been reported, [(PhCC)(μ−N′Bu)]₂.¹⁰

Three potential isomerisation mechanisms have been proposed for cyclo-diphosphazanes: (route a) (vertex) lone-pair inversion at the P-centres, (route b) (edge) inversion at the bridging imido-N atoms, and (route c) cyclo-reversion followed by recombination (2+2 cycloaddition) of the monomer units.⁴ While 2-trans was too thermally unstable to investigate the kinetics of its cis/trans isomerisation further (prolonged heating in THF led to a complicated mixture of decomposition products), it is clear from the quantitative conversion of 2-trans to 2-cis in THF at 50°C that the process cannot involve intermolecular cyclo-reversion, otherwise the symmetrical phosphazane products would also be observed (Scheme 3).

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The in situ $^{31}$P($^1$H) NMR spectrum of the reaction of 2-trans with elemental selenium in toluene at room temperature consists of two doublets at $\delta = 36.2 (J_{P,P} = 14.2$ Hz, P(Se)) and 33.5 ppm ($J_{P,P} = 14.0$ Hz, P(S)) (both splitting into a doublet-doublet in the fully-coupled spectrum) (see ESI). This product, [(S=)(H)P(µ-NBu)₂P(Se)NH₂Bu] 3a, can be isolated as a powder in 94% yield after filtration and removal of the solvent under vacuum (see ESI). The $^{77}$Se NMR spectrum of isolated 3a in CDCl₃ shows a doublet ($J_{P,Se} = 560.6$ Hz), consistent with the oxidation of 2-trans at its $^{{{\text{p}}^{{\text{III}}}}}$ centre (see ESI). The solid-state structure of 3a shows that the oxidation of 2-trans is stereoselective, with retention of the trans-configuration of the $^8$BuNi(Se)-group and S-atom (Figure 5). Like 2-cis and 2-trans, the P₃N₂ ring unit in 3a is almost completely planar; however, an interesting difference is found in the endo-orientation of the $^8$BuNi-group with respect to the P₂N₂ ring (cf. the exo disposition in 2-trans and 2-cis). Since there are no intermolecular N-H-S or -Se interactions occurring in the lattice, it appears that this is due to the steric influence of the Se atom now bonded to the P-centre.

Figure 5 The structure of 3a. H-atoms, except N-H and P-H, have been omitted for clarity. Only one of the two independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): $P_{v-P}$ range 1.674(4)-1.678(4), $P_{v-S}$ 1.926(2)-1.930(2), $P_{v-µ-NBu}$ range 1.685(4)-1.698(3), $P_{v-µ-NBu}$ range 1.627(4)-1.630(4), $P_{v-Se}$ 2.090(1)-2.099(1), $N_{Bu-P-N_{Bu}}$ 83.02(2)-84.21(2), $P_{v-P-N_{Bu}-P}$ range 95.82(2)-96.32(2). The P and N atoms of the P₃N₂ ring unit are only deviated ca. 5.7° out of the plane. Unlike 2, 3a is thermally stable in solution for prolonged periods, allowing the investigation of its isomerisation. Figure 6 shows the changes observed in the $^{31}$P($^1$H) NMR spectrum of 3a upon heating a sample in $d_8$-toluene over the temperature range 40-90 °C. Heating to 40 °C for 24 h results in the appearance of two new resonances at $\delta = 29.7$ [d, $J_{P,P} = 9.8$ Hz, P(Se)] and 22.9 ppm [d, $J_{P,P} = 8.4$ Hz, P(Se)] (cf. 3a $\delta = 36.2$ (d, $J_{P,P} = 14.2$ Hz, P(Se)), 33.5 ppm (d, P(S), $J_{P,P} = 14.0$ Hz)]. The $^{31}$P($^1$H) chemical shift in 3b is similar to that reported for cis-[(BuNH)SeP(µ-NBu)]₂ ($\delta = 26.7$ ppm). Additional information comes from the $^1$H NMR spectrum of the solid reaction products in CDCl₃ recovered after 3 h at 60 °C, which shows the appearance of a new set of P-H, N-H and $^1$Bu resonances in the same relative ratio as that found in 3a, identifying this species (3b) as an isomer of 3a, with the S and Se atoms trans rather than cis with respect to the P₂N₂ ring unit (Scheme 4) (see ESI). The $^{31}$P($^1$H) NMR spectrum of the reaction of solid Se with the 2-cis in toluene also shows the formation of 3b. However, unlike the reaction of 2-trans with Se which occurs smoothly at room temperature, a complicated mixture of products is produced at the higher reaction temperature required (at reflux).

In addition to the resonances for 3b, a further singlet resonance is also apparent after 24 h at 40 °C ($\delta = 30.8$ ppm). Further heating of the reaction to 90 °C for 7 days results in the exclusive formation of this species, the consumption of 3a and 3b and the precipitation of a white solid. The new species was identified as the previously reported symmetric cyclodiphosphazane [(BuNH)SeP(µ-NBu)]₂ (4) (Scheme 4) on the basis of spectroscopic analysis (lit. $^{31}$P($^1$H) NMR $\delta = 26.7$ ppm in THF) (see ESI). The formation of 4 supports the view that the isomerisation of 3a to 3b occurs (at least in part) by the intermolecular cyclo-reversion mechanism. Since the other product of this reaction, symmetric [(S=)(H)P(µ-NBu)]₂ (5) (Scheme 4), is known to be thermally unstable, it is not surprising that this component is not observed in the final NMR spectrum (and is presumably the source of the white solid decomposition product).

The kinetics of the conversion of 3a to 3b was followed by further NMR experiments. The relative integrals of the P-H proton resonances were measured at a temperature of 50 °C for a total time of 588 mins, with NMR spectra being recorded every six mins (a total of 99 separate measurements). As can be seen from Figure 7, the isomerisation of 3a to 3b follows first-order kinetics (with $R^2 = 0.994$). Our overall conclusion, drawn from these data and that shown in Figure 6, is that the isomerisation of 3a to 3b is probably largely via cyclo-reversion, in which the dissociation of 3a into two monomer units is rate determining. We cannot, however, exclude a contribution from intramolecular mechanisms (especially at lower temperatures).
3a is readily deprotonated at both the N-H and P-H positions by reaction with benzylsodium (2 equiv.) in THF at room temperature. The Na complex [Na(THF)Na(THF)\textsubscript{3}[(S)P(µ-N\textsubscript{3}Bu\textsubscript{2})\textsubscript{2}P(Se)N\textsubscript{3}Bu\textsubscript{2}]] (6) can be isolated in crystalline form after layering the reaction with \textit{n}-hexane (in 24% yield) (see ESI). A polymeric arrangement is found for 6 in the solid state (Figure 8), in which the \{(S)P(µ-N\textsubscript{3}Bu\textsubscript{2})P(Se)N\textsubscript{3}Bu\textsubscript{2}\}\textsuperscript{2+} dianion units are held together by alternating \textit{mono}-THF solvated (four-coordinate) Na\textsuperscript{+} cations [Na(1)] by side-on N-Se- and S-bonding on either side of the dianion. The other Na\textsuperscript{+} cation [Na(2)] is solvated by three THF ligands, with one of the THF ligands disordered over coordinated and non-coordinated sites (ca. 50:50). This Na\textsuperscript{+} cation is chelated by the S and Se atoms of the dianion (resulting in trigonal bipyramidal geometry). The large reduction in the exo-Bu\textsubscript{3}N-P (P(2)-N(3) 1.574(4) Å) bond length compared to that in 3a [cf. ca. 1.63 Å] reflects the increase in Zwitter-ionic character upon deprotonation. The retention of the original conformation of the Bu\textsubscript{3}N-group and S- and Se-atoms upon deprotonation of 3a at room temperature is a particularly noteworthy feature of 6. Consistent with this conformational rigidity, if a mixture of isomers 3a and 3b (2:1) is deprotonated with benzylsodium in THF both the cis- and the trans-\{(S)P(µ-N\textsubscript{3}Bu\textsubscript{2})P(Se)N\textsubscript{3}Bu\textsubscript{2}\}\textsuperscript{2+} dianions are observed in solution (in the same 2:1 ratio as the starting materials).

![Figure 7](https://example.com/image7.png)

**Figure 7** Graph of the log of the concentration of 3a ([a-x mol\textsuperscript{-1}] at time (t). The straight line is the best fit line, with \textit{R}\textsuperscript{2} = 0.994.

Thermal ellipsoids are drawn at the 50% probability level for the heavy atoms, the THF ligands have been drawn as wire frames. Selected bond lengths (Å) and angles (°): P(1)-N(2) 1.751(4), P(1)-N(3) 1.746(3), P(1)-S(1) 2.068(2), P(2)-N(1) 1.693(3), P(2)-N(2) 1.680(3), P(2)-N(3) 1.574(4), P(2)-Se(1) 2.187(1), Na(1)-S(1) 2.761(3), Na(1)-Se(1) 2.894(2), Na(2)-Se(1) 2.924(2), Na(2)-N(3) 3.274(4), Na(2a)-S(1) 2.790(2), P(1)-µ-N\textsubscript{3}Bu-P(2) 98.4(2)-99.2(2), N(1)-P(1)-N(2) 79.4(2)-83.0(2), Se(1)-P(2)-N(3) 105.7(1).

In conclusion, by combining previously established synthetic approaches we have been able to build an unsymmetrical P\textsuperscript{6}/P\textsuperscript{5} cyclo-phosphazene framework, [(S=)(H)P(µ-N\textsubscript{3}Bu\textsubscript{2})P(Se)N\textsubscript{3}Bu\textsubscript{2}](2). Both the cis and trans isomers of 2 have been structurally characterised, with the thermally-activated cis/trans isomerisation following an intramolecular pathway. Further elaboration of this framework by oxidation of the P\textsuperscript{5} centre with Se gives the new P\textsuperscript{6} species [(S=)(H)P(µ-N\textsubscript{3}Bu\textsubscript{2})P(=Se)NH\textsubscript{3}Bu\textsubscript{2}] (4), which also undergoes cis/trans isomerism in this case largely via a dissociative cyclo-reversion mechanism. Deprotonation of 4 gives the \{(S)P(µ-N\textsubscript{3}Bu\textsubscript{2})P(Se)N\textsubscript{3}Bu\textsubscript{2}\}\textsuperscript{2-} dianion, the sodium salt of which is a potential starting material for transmetalation reactions with other main group and transition metals.

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**Notes and references**