Syntheses and characterization of cyclodiphosphazanes and macrocyclodiphosphazanes

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES**

SYNTHESES AND CHARACTERIZATION OF CYCLODIPHOSHAZANES AND MACROCYCLODIPHOSHAZANES

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Table of Contents

Acknowledgements.....	i
Table of Contents	ii
Abstract	vi
Abbreviations	viii
Chapter 1: Introduction	1
1.1 Chlorocyclophosphazanes.....	2
1.2 Substitution reactions of dichlorocyclodiphosphazanes and their derivatives.	3
1.2.1 Bis(amido)cyclodiphosphazanes.....	4
1.2.2 Dialkoxycyclodiphosphazanes and disulfidecyclodiphosphazanes	6
1.3 Macrocyclodiphosphazanes formation	8
1.3.1 Inorganic macrocyclodiphosphazanes	9
1.3.2 Hybrid macrocyclodiphosphazanes	15
1.4 Rearrangement and cage formation	18
1.5 Oxidation of phosphorus(III) centres.....	20
1.5.1 Diimides cyclodiphosph(V/V)azanes	21
1.5.2 Dioxides cyclodiphosph(V/V)azanes.....	22
1.5.2 Disulfides cyclodiphosph(V/V)azanes.....	23
1.5.3 Diselenides cyclodiphosph(V/V)azanes	24
1.5.4 Ditellurides cyclodiphosph(V/V)azanes	25
1.6 Bonding, geometry and conformation	25
1.7 Conclusion	28

Chapter 2: General experimental and analytical techniques	30
2.1 Inert-atmosphere techniques	31
2.2. Analytical instruments and procedures	32
2.2.1 Nuclear magnetic resonance spectroscopy (NMR).....	32
2.2.3 FT-IR and elemental analysis	32
2.2.2 Crystallographic analyses	32
2.3. Preparation of starting materials	33
2.4. Syntheses of new compounds	36
Chapter 3: Syntheses and hydrolytic studies on the air-stable [(4-CN-PhO)P(E)(μ -N'Bu)] ₂ (E = O, S and Se) cyclodiphosph(V/V)azanes	71
3.1 Introduction.....	72
3.2 Syntheses of compounds 3.1-3.4	74
3.3 Crystal structures of compounds 3.1-3.4	77
3.4 Air and hydrolytic stability	82
3.5 Theoretical calculations	84
3.6 Comparison with experimental values.....	89
3.7 Conclusion	92
Chapter 4: Metal-free steric C-N bond activation during the oxidation of macrocyclodiphosphazanes [$\{P(\mu-NR)\}_2(\mu-NR)\]_2$ with chalcogen elements.....	93
4.1 Introduction.....	94
4.2 Syntheses of compounds 4.1-4.8	96
4.3 Syntheses of compounds 4.1-4.8 <i>via</i> mechanochemical methods	100

4.4 Crystal structures of compounds 4.2-4.9	101
4.5 Mechanistic studies	104
4.6 Theoretical studies	108
4.7 Conclusion	115
Chapter 5: Mechanochemistry syntheses of cyclodiphosphazanes; substitution and rearrangement	116
5.1 Introduction.....	117
5.2 Syntheses of compounds 5.1-5.4 : acyclic substitution of cyclodiphosphazanes <i>via</i> mechanochemistry method	118
5.3 Crystal structures of compounds 5.1-5.4	120
5.4 Syntheses of compounds 5.5 and 5.6	123
5.5 Crystal structures of compounds 5.5 and 5.6	127
5.6 Conclusion	130
Chapter 6: Novel acyclic trimeric cyclodiphosphazanes $\{P(\mu-N^tBu)\}_2(\mu-E)[\{P(\mu-N^tBu)\}_2N(H)R]_2$	131
6.1 Introduction.....	132
6.2 Syntheses of compounds 6.2-6.5	133
6.3 Crystal structures of compounds 6.2-6.5	135
6.4 Syntheses and crystal structure of <i>O</i> -bridged hexameric macrocyclodiphosphazane $\{(\mu-O)[P(\mu-N^tBu)]_2\}_6$ (compound 6.6)	139
6.5 Conclusion	143
Conclusion and outlook	145

References	147
Publication list	160

Abstract

Organic frameworks have been extensively studied during past decades for a myriad of applications. While inorganic frameworks, composed of non-carbon backbones, remain as mere chemical curiosities due to the much greater kinetic lability of the inorganic bonds. In particular, the instability of cyclodiphosphazane systems containing saturated P-N frameworks, which are of significant interest to our group, has previously undermined the exploration of their use in technological applications.

In this thesis, the author firstly represents a convenient method to enhance the stabilities of these cyclodiphosphazanes by simply oxidizing them with chalcogen elements on the phosphorus centers (chapter 3). In addition, the author also reported the unexpected C-N bond activation occurred during the oxidation process. The experimental and theoretical studies demonstrate that steric factors, most probably steric strain release, play a crucial role in the metal-free activation of the C-N bonds herein described (chapter 4).

Besides, conventionally, syntheses of cyclodiphosphazanes has no tolerance of protic solvents stemming from their high air- and moisture-sensitivities. Therefore, the concept of mechanochemistry has brought the prospect of avoiding the tedious processes associated with the demand of strict anhydrous conditions while synthesizing cyclodiphosphazanes. In chapter 5, the first example of cyclodiphosphazanes synthesized by mechanochemical methodology is reported, further studies on the application of grinding to synthesize a series of new cyclic and acyclic cyclodiphosphazane frameworks is investigated. More importantly, this method enabled the formation of previously reported as inaccessible arrangement adamantoid $P_4(N^tBu)_6$.

Lastly, a family of novel trimeric acyclic poly-cyclodiphosphazanes have been reported in chapter 6. For those structures, their special conformation might enable them as a potential large bite ligand with possible application of stabilizing the low coordination numbers and/or unusual oxidation states transition metal by applying the steric demanding principle. Finally moreover most importantly, inspired by the trimeric structures, as far as we know, the ever big macrocycle with all P(III) centers, *O*-bridged hexamer $\{(\mu\text{-O})[\text{P}(\mu\text{-N}^t\text{Bu})]_2\}_6$, has been synthesized and fully characterized.

Abbreviations

<i>n</i>	Normal
<i>i</i>	Iso
<i>t</i>	Tertiary
Me	Methyl (CH ₃)
Et	Ethyl (C ₂ H ₅)
<i>i</i> Pr	<i>Iso</i> -propyl ((CH ₃) ₂ CH)
<i>n</i> Pr	<i>Normal</i> -propyl (C ₃ H ₇)
<i>t</i> Bu	<i>Tertiary</i> -butyl ((CH ₃) ₃ C)
<i>n</i> Bu	<i>Normal</i> -butyl (C ₄ H ₉)
Ph	Phenyl (C ₆ H ₅)
Py	Pyridyl (NC ₅ H ₄)
Mes*	2,4,6-Tri- <i>t</i> butylphenyl (2,4,6- <i>t</i> Bu ₃ Ph)
Dipp	2,6-Di- <i>i</i> propylphenyl (2,6- <i>i</i> Pr ₂ Ph)
Cy	Cyclohexyl (C ₆ H ₁₁)
THF	Tetrahydrofuran (C ₄ H ₈ O)
Tol	Toluene (C ₇ H ₈)
ACN	Acetonitrile (CH ₃ CN)
DMF	N,N-dimethylformamide
DCM	Dichloromethane (CH ₂ Cl ₂)
CCDC	Cambridge Crystallographic Data Centre
IR	Infra Red
<i>m/z</i>	Mass/charge, units for mass spectrometry
[M+1] ⁺	Parent ion bound to H ⁺
Vppm	Volume parts per million
NMR	Nuclear Magnetic Resonance
δ	Chemical shift
ppm	parts per million
s.	Singlet
d.	Doublet
m.	Multiplet
<i>J</i>	Coupling constant (Hz)

br.	Broad
h.	Hours
min.	Minutes
mmHg	Millimetres of mercury
F_w	Molecular weight of asymmetric unit (g)
ρ_{calc}	Calculated density ($\text{mg}\cdot\text{cm}^{-3}$)
Z	Number of formula units per unit cell
V	Cell volume ($\text{\AA}^3$)
μ	Linear absorption coefficient (mm^{-1})
T	Temperature (K)
R_1	R-factor (unweighted)
wR_2	R-factor (weighted)
λ	Wavelength ($\text{\AA}$)
eV	Electron Volts
e	Electron
$G^\ddagger$	Gibbs Free energy change of transition state
VSEPR	Valence Shell Electron Pair Repulsion
$\Delta\chi$	Difference in electronegativity
esd	Estimated standard deviation

Chapter 1: Introduction

1.1 Chlorocyclophosphazanes

Cyclophosphazane frameworks originated from substitution reaction of chlorocyclophosphazanes with nucleophiles in the presence of Brønsted base, such as triethylamine, is the main topic of this thesis. Chlorocyclophosphazanes, with a common formula of $\{\text{ClP}[\mu\text{-NR}]\}_n$, can be achieved by cyclocondensation reactions between phosphorus trichloride and primary amines or silylamines *via* various synthetic routes as summarized below in *Scheme 1.1*.

Scheme 1.1 Synthetic routes of chlorocyclophosphazanes.

It is well-established that the value of n in $\{\text{ClP}[\mu\text{-NR}]\}_n$ is largely dependent on the steric bulk of the amine substituents within the P_2N_2 ring (*Figure 1.1*).^{6,7} Reactions between PCl_3 and amines containing large substituents, such as *tert*-butyl, give rise to dimeric cyclophosphazane backbones. During this process, traces of monomeric $\text{Cl}_2\text{P}=\text{NR}$ units were detected by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR.⁴ While, the monomeric halo(imino)-phosphines have only been isolated for derivatives involving bulky amines. For instance, the Mes^* (2,4,6-tri-*tert*-butylphenyl) substituent at nitrogen atom increases steric strain within a hypothetical dimer and, hence precludes dimerization.⁸ Primary amines with small substituents, such as methyl group, tend to form larger macrocycles (a tetramer was obtained in this case) on the reaction with R_2PCl_2 due to the less steric demanding.^{9,10} It is noteworthy that the transformation between monomeric, dimeric, and trimeric cyclophosphazane oligomers has been reported.⁷ For example, $\text{Mes}^*\text{N}=\text{PCl}$ (**1.1**) has been isolated as monomer, while, it allows dimerization

when the slightly smaller substituent Dipp (Dipp = 2,6-diisopropylphenyl) was attached to the nitrogen atom. Transformation between dimer and trimer could be found for cyclophosphazanes with ethyl or phenyl substituents on the *endo*-cyclic nitrogen atoms.^{7,11} In general, cyclic $\{CIP[\mu-NR]\}_n$ oligomers with $n > 2$ are rare.

Figure 1.1 Chlorocyclophosphazanes oligomers.

Amongst these oligomers, dichlorocyclodiphosphazane (Figure 1.1, type I) is of considerable interest due to its rigidity and nearly planar backbone, and can serve as excellent building blocks for the design and syntheses of macrocycles and three-dimensional (3D) frameworks.

1.2 Substitution reactions of dichlorocyclodiphosphazanes and their derivatives

Cyclodiphosphazane derivatives $\{R'P[\mu-NR]\}_2$ can be achieved by simple replacement of the chlorine atoms at the phosphorus centers of dichlorocyclodiphosphazanes with nucleophiles. There is a large volume of published studies on the functionalization of cyclodiphosphazanes by substitution reactions of the dichlorocyclodiphosphazanes with primary or secondary amines ($R'NH_2$ or $R'R''NH$), alcohols ($R'OH$) and thiols ($R'SH$) in the presence of Brønsted base (Et_3N is commonly used) as hydrogen chloride scavenger.¹²⁻¹⁴ An alternative approach is the reaction between dichlorocyclodiphosphazanes and silylamines with the formation of silyl chloride as the main driving force; affording amino-substituted cyclodiphosphazanes.¹⁵ Another option is the use of salt metathesis reactions, where metalated

(most commonly lithiated) amines, alcohols or thiols are reacted with dichlorocyclodiphosphazanes to generate MCl (LiCl in most of the cases) and phosphorus substituted products (*Scheme 1.2*).¹⁶⁻¹⁸

Scheme 1.2 Synthetic routes to acyclic cyclodiphosphazane derivatives.

1.2.1 Bis(amido)cyclodiphosphazanes

Homo-substituted bis(amino)cyclodiphosph(III)azanes are cyclodiphosphazanes with identical substituents (*i.e.*, alkyl or aryl) on each *endo*-cyclic and *exo*-cyclic nitrogen atom. One of the most well-known examples is [*t*Bu(H)NP(μ -N'*t*Bu)]₂ (**1.2**) which is best synthesized from the reaction of PCl₃ with a five-fold excess of *tert*-butyl amine.^{19,20} This high yielding procedure is known as the earliest and easiest reported method and, hence, is the most broadly used synthetic protocol for the synthesis of this type of cyclodiphosph(III)azane derivatives (*Scheme 1.3*). The purification of these products can be readily accomplished by crystallization after the removal of the ammonium chloride formed by filtration through celite (P3); however, other methods, such as vacuum distillation, have also been employed. The excess amine functions as the Brønsted base to scavenge the HCl generated during the reaction. The reaction can also be performed in stoichiometric amounts if triethylamine is used as an acid scavenger to reduce the cost.

Scheme 1.3 One-step reaction to synthesize homo-substituted bis(amino)cyclodiphosph(III)azanes. In contrast, the synthesis of hetero-substituted bis(amino)cyclodiphosph(III)azanes is not achievable in single-step reactions. Generally, symmetrically hetero-substituted cyclodiphosph(III)azanes are prepared from $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**)⁴ or $\{\text{ClP}[\mu\text{-NPh}]\}_2$ (**1.4**).^{21,22} The chloro-substituents of these dichloro-derivatives have been confirmed to exhibit a *cis*-configuration, as determined by single-crystal X-ray diffraction (SC-XRD) characterization.

There are two well-established strategies to produce hetero-substituted bis(amino)cyclodiphosph(III)azanes (*Scheme 1.4*). The first and more straightforward - which only works well for acidic amines such as pyrazoles and aniline - is the treatment of dichlorocyclodiphosph(III)azanes (*e.g.*, **1.3**) with two equivalents of a primary amine and two equivalents of triethylamine. The second and more general method of ring substitution is the reaction of **1.3** or **1.4** with two equivalents of the lithium amide for which an additional step needed to generate it *in situ*, commonly by reaction of *n*-BuLi with corresponding amines (*Scheme 1.4*).

Scheme 1.4 Two general pathways to synthesize hetero-substituted bis(amino)cyclodiphosph(III)azanes.

For the synthesis of asymmetrically hetero-substituted bis(amino)cyclodiphosph(III)azanes, $[\text{tBu(H)NP}(\mu\text{-N}^t\text{Bu})_2\text{PCl}]$ (**1.5**) is considered to be an ideal starting material with three *tert*-butyl substituents. It can be easily prepared in a one-step reaction using *tert*-butyl amine, PCl_3 and Brønsted base in 3:2:5 molar ratio. An alternative method for the preparation of the asymmetrically hetero-substituted bis(amino)cyclodiphosph(III)azanes, $[\text{R}'\text{NP}(\mu\text{-NR})\text{PNR}'']$, is shown in *Scheme 1.5*.²³⁻
²⁵ Monochloro species (*Scheme 1.5*, type **II**) with two identical substituents on *endo*-cyclic nitrogen atoms were first prepared from the reaction of dichlorocyclodiphosphazanes, where $\{\text{ClP}[\mu\text{-N}^t\text{Bu}]\}_2$ (**1.3**) or $\{\text{ClP}[\mu\text{-NPh}]\}_2$ (**1.4**) (*Scheme 1.5*, type **I**) were commonly utilized, with nucleophiles ($\text{R}'\text{H}$ and $\text{R}''\text{H}$) added telescopically in a 1:1 ratio forming the desired asymmetric hetero-substituted bis(amino)cyclodiphosph(III)azanes (*Scheme 1.5*, type **III**).

Scheme 1.5 Syntheses of asymmetrically hetero-substituted bis(amino)cyclodiphosph(III/III)azanes.

1.2.2 Dialkoxycyclodiphosphazanes and disulfidecyclodiphosphazanes

The easiest way to produce RO- or RS- substituted cyclodiphosphazanes $[\text{R(E)P}(\mu\text{-NR})]_2$ ($\text{E} = \text{O/S}$) involves the reactions between ROH or RSH with dichlorocyclodiphosphazanes, analogous to the synthesis of bis(amino)cyclodiphosph(III)azanes. The most common starting materials used for their syntheses are $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) and $[\text{ClP}(\mu\text{-NPh})]_2$ (**1.4**).

As previously highlighted, both $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) and $[\text{ClP}(\mu\text{-NPh})]_2$ (**1.4**) adopt a *cis*-configuration. When $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) is reacted with various alcohols, in the presence of a base, the derivatives obtained generally retain their *cis* configuration (as shown in *Scheme 1.6*). However, M. Vijjulatha (1999) highlighted that different synthetic strategies lead to the different isomers in certain cases.²⁶ For example, the reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) with the 2,6-Me₂C₆H₃OH or 4-Me-C₆H₄OH in the presence of triethylamine produces the *cis* isomers, namely *cis*-[(4-Me-C₆H₄OPN^tBu)]₂ (**1.5**) and *cis*-[(2,6-Me₂-C₆H₃OPN^tBu)]₂ (**1.6**) as the only products. However, when the salt metathesis approach is used by reacting **1.3** with the sodium salts 2,6-Me₂C₆H₃ONa or 4-Me-C₆H₄ONa, only the *trans* isomer was obtained. In contrast, a mixture of *cis-trans* products is achieved during the treatment of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) with various substituted lithium phenolate salts. For example, the reaction of 2,6-Me₂C₆H₃OLi with $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) showed a mixture of isomers where the major product displayed a single resonance at 214 ppm in its ³¹P-{¹H} NMR spectrum, which was attributed to the *trans* isomer, *trans*-[(2,6-Me₂-C₆H₃OPN^tBu)]₂ (**1.7**). Unfortunately, this isomer has yet to be isolated and fully characterized.

Unlike in the reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) and 4-Me-C₆H₄OH, where *cis*-[(4-Me-C₆H₄OPN^tBu)]₂ (**1.5**) has been isolated as the sole product, the similar reaction with $[\text{ClP}(\mu\text{-NPh})]_2$ (**1.4**), resulted in the formation of *trans*-[(4-Me-C₆H₄OPNPh)]₂ (**1.8**) as the main product. This suggests that the *cis* isomers may be preferred in the reaction of the more hindered cyclodiphosphazane $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) relative to that of $[\text{ClP}(\mu\text{-NPh})]_2$ (**1.4**).²⁶

Scheme 1.6 Examples for dialkoxycyclodiphosphazanes.

1.3 Macrocyclodiphosphazanes formation

The use of dimers of the type $[\text{ClP}(\mu\text{-NR})]_2$ as building blocks for the synthesis of macrocyclic phosph(III)azane frameworks is largely supported by their *cis* “preorganization”. Previous structural and theoretical studies have shown that the *cis* conformation of these dimers are preferred to *trans* forms both in the solid state and in solution, by a small 4–40 $\text{kJ}\cdot\text{mol}^{-1}$ energy difference (Figure 1.3).²⁷

Two types of macrocycles are commonly generated by reacting the cyclodiphosphazane $[\text{ClP}(\mu\text{-NR})]_2$ with a wide range of inorganic and organic linkers to produce fully inorganic macrocyclodiphosphazanes $[\{\text{P}(\mu\text{-NR})\}_2(\mu\text{-X})]_n$ ($\text{X} = \text{O}, \text{Se}$,

NR; R= H, ⁱPr and ^tBu)) and hybrid-type macrocycles [$\{P(\mu\text{-NR})\}_2(\mu\text{-LL'})\}_n$ (where LL is an organic linker), respectively (Figure 1.3).²⁷

Figure 1.3 Macrocyclodiphosphazanes formation.

1.3.1 Inorganic macrocyclodiphosphazanes

The very first inorganic macrocyclodiphosphazane, a “double decker” molecular cage [$\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ (**1.9**) synthesized with the aforementioned design principle corresponds to that of a cryptand²⁸ was reported by Scherer *et al.* in 1980.²⁹ Compound **1.9** contains two cyclodiphosphazanes units linked by NⁱPr groups. A similar approach was used to synthesize the analogous macrocycle [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-PSiMe}_3)\}_2$ (**1.10**) through a 1:1 reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ with $\text{LiP}(\text{SiMe}_3)_2 \cdot 2\text{THF}$ in hexane at room-temperature with the elimination of 1 equivalent of LiCl and Me_3SiCl , in which the macrocycle formation can be affected by the stoichiometry. In particular, the acyclic symmetrically substituted $[(\text{Me}_3\text{Si})_2\text{PP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.11**) is formed by a 1:2 reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ with $\text{LiP}(\text{SiMe}_3)_2 \cdot 2\text{THF}$.³⁰ Another noteworthy example is the synthesis of the macrocycle [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})\}_2$ (**1.12**) through a

condensation reaction between $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ and $[\text{tBu}(\text{Li})\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ reported by Chivers *et al.* in 1999 (Scheme 1.7).³¹

Scheme 1.7 Synthetic routes of selected inorganic macrocyclodiphosphazanes.

It has been established that the size of macrocyclodiphosphazane systems is dictated by the stoichiometry and the bulkiness of the substituents on the *endo*-cyclic nitrogen atoms. Hence their steric bulkiness has to be taken into consideration while designing and synthesizing macrocyclodiphosphazanes. Indeed, it has been shown that reduction in the steric demands of the bridging NR groups (*i.e.*, NH) results in larger tetrameric macrocyclic systems $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_4$ (**1.13**).³² This tetrameric macrocycle was prepared by the condensation between $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) and the diamino-dimer $[\text{H}_2\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.14**) in the presence of Et_3N as the Brønsted base (Scheme 1.8). In

situ ^{31}P - $\{^1\text{H}\}$ NMR spectroscopic studies revealed the almost exclusive formation of **1.13**, illustrated by a single resonance at 128 ppm. Its tetrameric nature was further confirmed by SC-XRD studies. It is important to note that the exclusive formation of the macrocyclic products in this reaction is attributed to the *cis* pre-organization of both precursors $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.3**) and $[\text{H}_2\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ (**1.14**) in the solid state (and predominantly in solution).

Scheme 1.8 Macrocycles formation of $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_4$ (**1.13**).

Moreover, the use of halide anions as templates has also been a successful strategy to selectively produce pentamers over tetramer during the condensation reactions leading to the formation of macrocyclic arrangements. This effect was first observed during low-temperature studies of the reaction between **1.3** and **1.14** where the ^{31}P - $\{^1\text{H}\}$ NMR spectra showed the formation of a minor secondary product. Subsequent fractional crystallization and X-ray diffraction studies showed that the byproduct was the host-guest complex $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_5\cdot\text{HCl}$ (**1.15**), in which a Cl^- ion is encapsulated at the centre of the cavity *via* interactions with the five N-H protons. Further studies on the condensation reaction of **1.3** $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ and **1.14** $[\text{H}_2\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ in the presence of different lithium halide (LiX) (Scheme 1.9) also revealed that the addition of LiBr to the reaction amplified the formation of the pentameric macrocyclic $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_5$ in the form of $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_5\cdot\text{HBr}$ (**1.16**). Surprisingly, the addition of LiI led to the exclusive formation of the pentamer $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-NH})]_5$.

NH)]₅I⁻·Li⁺(THF)₄ (**1.17**). The solid structures of [{P(μ -N^{*t*}Bu)]₂(μ -NH)]₅·HBr and [{P(μ -N^{*t*}Bu)]₂(μ -NH)]₅I⁻·Li⁺(THF)₄ are distorted compared to [{P(μ -N^{*t*}Bu)]₂(μ -NH)]₅·HCl (*Figure 1.3*); this feature is attributed to the increasing size of the halide, descending down the group.³³

Scheme 1.9 Formation of pentameric host-guest macrocyclodiphosphazanes.

Figure 1.3 Solid state structure of **1.15** (a, top view; b, side view), **1.16** (c, side view), **1.17** (d, side view).³³

In this area of macrocyclodiphosphazanes, a synthetic target has always been crown-ether-like macrocycles containing O-bridges with the common formula of [{P(μ -N^{*t*}Bu)]₂(μ -O)]_n, which were predicted to be capable of selective cation coordination. These macrocycles were prepared through controlled hydrolysis of [ClP(μ -N^{*t*}Bu)]₂ with H₂O, forming [O=(H)P(μ -N^{*t*}Bu)]₂ (**1.18**) at 5 °C, followed by *in situ* reaction with excess *n*-BuLi to form the dianion [O=P(μ -N^{*t*}Bu)]₂²⁻. Subsequently, the dianion reacts with 1 equivalent of [ClP(μ -N^{*t*}Bu)]₂ to afford the tetramer [{P(μ -N^{*t*}Bu)]₂(μ -O)]₄ (**1.19**).

The size of the cavity is reduced compared to that of $[\{P(\mu\text{-}N^t\text{Bu})\}_2(\mu\text{-}NH)]_4$ (**1.13**) due to the presence of shorter P–O bonds.³⁴

An alternative strategy employed to prepare an analogous type of macrocyclic framework - where pre-coordination of $[ClP(\mu\text{-}Npy)]_2$ to CuCl followed by hydrolysis with H_2O in pyridine - results in the formation of the macrocyclic complex $[\{P(\mu\text{-}N^t\text{Bu})\}_2(\mu\text{-}O)]_2[CuCl(\text{pyridine})_2]_4$ (**1.20**), which is the first representative of the series of this type macrocycles (*Scheme 1.10*).³⁵

Scheme 1.10 Formation of O-bridged macrocyclodiphosphazanes.

Inspired by the initial success and determination of the $[\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianion, a potential analogous selenium-based $[(\text{Se}=\text{P}(\mu\text{-N}^t\text{Bu}))_2]^{2-}$ dianion was planned to be synthesized. The bisselenide, $[(\text{Se}=\text{CIP}(\mu\text{-N}^t\text{Bu}))_2]$ (**1.21**) was first prepared through the reaction of elemental selenium with the dimer $[\text{CIP}(\mu\text{-N}^t\text{Bu})]_2$ in the molten state as a mixture of *cis* and *trans* isomers. While, the intended reaction to prepare $[(\text{Se}=\text{P}(\mu\text{-N}^t\text{Bu}))_2]^{2-}$ by refluxing sodium metal in toluene with $[(\text{Se}=\text{CIP}(\mu\text{-N}^t\text{Bu}))_2]$ was not successful, it led instead directly to the formation of hexameric macrocycle $[(\text{Se}=\text{P}(\mu\text{-N}^t\text{Bu})\text{P}(\mu\text{-Se}))_6]$ (**1.22**).³⁶ SC-XRD analysis revealed that the eighteen atoms within the planar macrocyclic arrangement are only slightly distorted from overall planarity. Akin to the report by Wright *et al.*³⁷ The same method has been utilized to synthesize its sulphur derivative, where an excess of sodium metal was reacted with $[(\text{S}=\text{CIP}(\mu\text{-N}^t\text{Bu}))_2]$ (**1.23**) under the identical conditions, and the desired $[(\text{S}=\text{P}(\mu\text{-N}^t\text{Bu})\text{P}(\mu\text{-S}))_6]$ (**1.24**) (*Figure 1.4*) was isolated, albeit at low yields, along with other products, namely $[\{(\text{S}-)\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{PCl}(\text{S})\}\text{Na}(\text{Na}\cdot\text{THF}_2)]_n$ (**1.25**) and $[\{(\text{S}-)\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{PCl}(\text{S})\}(\text{Na}\cdot\text{THF}_2)_2]_n$ (**1.26**).

Figure 1.4 Structures of S/Se-bridged hexameric macrocyclodiphosphazanes.

1.3.2 Hybrid macrocyclodiphosphazanes

Hybrid macrocyclodiphosphazanes with a common formula as $[\{P(\mu\text{-NR})\}_2(\mu\text{-LL}')\}_n]$ could be obtained *via* reacting $[CIP(\mu\text{-NR})]_2$ with bifunctional organic linkers. The most frequently used linkers are aromatic diamines/dialcohols, as well as bifunctional aromatic amines in a form of 1-YH-2-NH-C₆H₄ (Y = O/S), which reacts with $[CIP(\mu\text{-NR})]_2$ in a 1:1 molar ratio in the presence of Et₃N to form their respective desired products.³⁸ The size of the macrocyclodiphosphazanes obtained using this process can be affected by the position of the functional groups within the organic spacer utilized. Dimeric macrocyclodiphosphazanes are the common products when non-linear organic spacers were used. In contrast, the employment of linear organic linkers would mostly lead to the formation of larger macrocycles, along with the formation of a mixture of oligomers.

Figure 1.5 Structures of macrocyclodiphosphazanes **1.27** and **1.28**.

Regardless of the straightforward strategies, the only reported examples prior to 2003 were monomeric species ($n = 1$) with basket-shaped structures in which the LL' spacer spans a P₂N₂ ring.³⁹ Early evidence for the formation of dimeric macrocycles was observed in *via* ³¹P-¹H NMR spectrum of $[\{P(\mu\text{-N}^t\text{Bu})\}_2\{\text{OCH}_2\text{C}(\text{Me})_2\text{CH}_2\text{O}\}]_2$ (**1.27**). NMR studies on the crude of the reaction of **1.27** showed the existence of minor dimer ($n = 2$) in addition to the monomer ($n = 1$).³⁹ Further experimental evidence

was obtained by SC-XRD of the corresponding sixteen-membered P(III)/P(V) or P(V) macrocycle derivatives, achieved by the oxidation of phosphorous atoms within the dimeric framework **1.27** with sulphur or chloranil. Interestingly, addition of two methyl groups at the central carbon on the organic linker $\{\text{O}(\text{CH}_2)_3\text{O}\}$ (*cf.*, $\{\text{OCH}_2\text{C}(\text{Me})_2\text{CH}_2\text{O}\}$), led to the exclusive formation of the monomeric product $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{O}(\text{CH}_2)_3\text{O}]$ (**1.28**).⁴⁰ The formation of the dimeric structure $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\{\text{OCH}_2\text{C}(\text{Me})_2\text{CH}_2\text{O}\}]_2$ (**1.27**) might be due to the increased steric congestion between the methyl groups in the bridge and the *tert*-butyl groups on the *endo*-cyclic nitrogen atoms. This illustrates that even a small variation on the steric bulkiness within the organic linkers can significantly influence the formation of favoured oligomer (*Figure 1.5*).

Figure 1.6 Monomer $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{NHPPhNH}]$ (**1.29**) and dimer $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{NHPPhNH}]_2$ (**1.30**). The formation of either monomer $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{NHPPhNH}]$ (**1.29**) or dimer $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{NHPPhNH}]_2$ (**1.30**) depends largely on the temperature at which the reaction between $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ and 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ was conducted. The exclusive formation of monomeric $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{NHPPhNH}]$ (**1.29**) at higher temperature indicates that the monomer is the most thermodynamically-favoured product. While, room-temperature reaction produces both monomer and dimer, revealing the possibility to fine-tune the

formation of different oligomers by modification of the experimental conditions for a given linker.⁴¹

Larger macrocycles such as trimers and tetramers are still rare in this area. An obvious strategy would be using linear organic linkers, which in some cases result in mixtures of oligomers. Examples are given in *Figure 1.7*, providing an outline of the current state-of-art in this area.

Figure 1.7 Trimeric and tetrameric macrocyclodiphosphazanes.

The first structurally characterized higher oligomer was the trimer, $[\{P(\mu\text{-N}^t\text{Bu})\}_2(1,5\text{-(NH)}_2\text{C}_{10}\text{H}_6)]_3$ (**1.31**),⁴² which is generated from the quantitative condensation of $[\text{CIP}(\mu\text{-N}^t\text{Bu})]_2$ with 1,5-(NH₂)₂C₁₀H₆. It was also observed that a toluene molecule is encapsulated within the cavity of the macrocycle structure $[\{P(\mu\text{-N}^t\text{Bu})\}_2(1,5\text{-(NH)}_2\text{C}_{10}\text{H}_6)]_3$. The Tol molecule interacts with **1.31** *via* C-H---arene interactions, illustrating the ability of this large macrocycle arrangement accommodating guest molecules within its bowl-shaped cavity which resembles that of calixarene compounds.

In addition, both trimeric $[\{P(\mu\text{-NCy})\}_2(1,5\text{-(O)}_2\text{C}_{10}\text{H}_6)]_3$ (**1.32**) and tetrameric $[\{P(\mu\text{-NCy})\}_2(1,5\text{-(O)}_2\text{C}_{10}\text{H}_6)]_4$ (**1.33**) macrocyclodiphosphazanes are generated when precursor $[\text{CIP}(\mu\text{-NCy})]_2$ was reacted with 1,5-(OH)₂C₁₀H₆. The reaction outcomes can be easily explained by the lower steric demands of the Cy group compared to the

^tBu group within the P₂N₂ subunits, combined with the absence of N and presence of the O atoms within the core.

Moreover, the fact that the sole trimer [$\{P(\mu\text{-N}^t\text{Bu})\}_2(1,4\text{-(O)}_2\text{C}_6\text{H}_4)\}_3$ (**1.34**) and tetramer [$\{P(\mu\text{-N}^t\text{Bu})\}_2(1,4\text{-(NH)}_2\text{C}_{10}\text{H}_6)\}_4$ (**1.35**) was obtained by the condensation reaction of $[ClP(\mu\text{-N}^t\text{Bu})]_2$ with 1,4-(O)₂C₆H₄ and 1,4-(NH₂)₂C₆H₄, respectively. It is not unreasonable to suggest that there is a subtle influence of heteroatom on the linkers within the macrocyclic framework can have a selective preference for a specific macrocyclic oligomer.⁴³

1.4 Rearrangement and cage formation

Topological properties of a P–N covalent framework in cyclophosp(III)azanes are imposed by steric and stoichiometric factors. A classic illustration of the strict steric control in cyclophosphazanes are the dimeric $[XP(\mu\text{-NR})]_2$ units, observed largely for sterically demanding groups (*e.g.*, R = ^tBu), whereas trimers $[XP(\mu\text{-NR})]_3$ and larger structures are obtained only with smaller substituents (*e.g.*, R = Me, Et) (*Figure 1.8*). The four-membered P–N ring in a dimeric cyclophosp(III)azane maximizes the available space for sterically demanding groups, which occurs at the expense of increased ring strain. Steric factors also play a crucial role in the oligomerization of cyclic arrangements (**V**, in *Figure 1.8*), as less sterically demanding bridging substituents permit the formation of larger macrocyclic arrangements, such as $[P(\mu\text{-NR})]_2(\mu\text{-NR})_n$ (n = 4, 5).

Figure 1.8 Molecular structures of selected types of phosph(III)azanes.

For different isomers of cyclophosph(III)azane, the steric volume of the substituent on the nitrogen atoms is thought to control the stability and accessibility of the different topologies available. It is possible for topologically different isomers to isomerize under suitable experimental conditions. The conversion between two topological isomers can be rationalized through a concerted twist mechanism. For example, the isomerization of the macrocyclic arrangement **V** was proposed to occur *via* a P-NR-P unit rotation to generate the more thermodynamically stable adamantyl structure **VI**.

Scheme 1.11 Isomerization via twist mechanism between $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})]_2$ (**1.9**) and $P_4(\text{N}^i\text{Pr})_6$ (**1.36**).

The *iso*-propyl ($i\text{Pr}$) substituted macrocyclic structure, $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})]_2$ (**1.9**), is readily converted into the thermodynamically preferred adamantoid form $P_4(\text{N}^i\text{Pr})_6$ (**1.36**) upon prolonged heating (12 days at 160 °C) in a sealed tube.²⁹ Subsequent studies on the more sterically hindered *tert*-butyl analogue, $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})]_2$ (**1.12**), however, revealed no trace of its adamantoid isomer even after prolonged

heating.³¹ Moreover, it was established that the direct syntheses of adamantoid $P_4(NR)_6$ structures, by reacting PCl_3 with RNH_2 , is only successful for less sterically hindered amines (*i.e.*, $R = Me, Et, ^iPr$).^{29,44} With bulkier substituents, such as *tert*-butyl, this solvothermal method was not able to produce the $P_4(NR)_6$ adamantoid topology.

1.5 Oxidation of phosphorus(III) centres

Cyclodiphosph(V/V)azanes are of interest due to their stability and unique coordination properties. Several synthetic routes have been explored to generate bis(amido)cyclodiphosph(V/V)azanes.⁴⁵⁻⁴⁸ Commonly utilized methods are listed in *Scheme 1.12*, and will be explained in detail in the following subsections. Among these, there is a large volume of reported examples involving the oxidation of the corresponding bis(amido)cyclodiphosph(III/III)azanes with chalcogen elements or organic azide derivatives ($E = NR$) (Method A, *Scheme 1.12*). Alternative methods, B and C, involve the direct or *in situ* condensation of $EP(NHR)_3$ units. As early as 1915, Michaelis *et al.* reported the generation of a material with formula $SP(NR)(NHR)$ by simply heating $SP(NHR)_3$ ($R = Et, ^nPr, ^iBu$), with the formation of the corresponding primary amines as a side product. However, the more accurate dimeric structure determination was only achieved in 1966 by Bock and Wiegräber using the molecular weight determinations. Subsequently, tremendous efforts have been dedicated to the studies on the thermolysis of a range of tris(amido)phosphates and tris(amido)thiophosphates.^{45,46} The direct thermal condensation (Method B) showed good yields for the majority R groups studied ($R = ^iPr, ^nBu, etc.$). In contrast, for certain R groups ($R = ^nPr, ^iBu, etc.$), a mixture of the tris(amido)thiophosphate and the corresponding cyclodiphosph(V/V)azane disulfide was obtained through the direct *in situ* route (Method C) at lower temperatures.

Method A **Method B** **Method C**

Scheme 1.12 Synthetic routes of cyclodiphosph(V/V)azanes.

1.5.1 Diimido cyclodiphosph(V/V)azanes

The main procedure used for the synthesis of bis(amido)cyclodiphosph(V/V)azanes *via* the direct oxidation of the phosphorus(III) centres with organic azides has been explored adequately (Method A).^{45,46} The corresponding cyclodiphosph(V/V)azanes **1.37** and **1.38** were obtained by the reaction of $[\text{tBu}(\text{H})\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ with aryl azides in a good yield, and the *cis* confirmation of the phosphorus(III) precursor was retained during these processes.⁴⁷

Less straightforward pathways have also been applied to synthesize such compounds.⁴⁸ For example, through the reaction of SPCl_3 with an excess of $\text{LiN}(\text{H})^t\text{Bu}$, the symmetric *trans*-diimide **1.39** and the dilithium derivative of **1.40** was isolated. The asymmetric *trans*-diimide **1.41** has also been synthesized and structurally characterized; unfortunately, the synthetic details were not reported (*Figure 1.9*).

Figure 1.9 Structures of diimides cyclodiphosph(V/V)azanes.

1.5.2 Bisoxides cyclodiphosph(V/V)azanes

To produce *cis*-dioxide cyclodiphosph(V/V)azanes, such as **1.42**, cumene hydroperoxide⁴⁹ or *tert*-butyl hydroperoxide^{50,51} are the commonly used oxidising agents. Other oxidants, like hydrogen peroxide, dimethyl sulfoxide (DMSO) and *meta*-chloroperoxybenzoic acid (*m*CPBA), have also been explored while approaching the dioxides cyclophosph(V/V)azanes *via* Method A with quantitative transformation.^{46,52-54} Thermolysis of tris(amido)phosphates (Method B) provides alternative methodologies for the synthesis of other derivatives. For instance, the condensation of tris(isobutylamido)phosphate $\text{O}=\text{P}(\text{NH}^i\text{Bu})_3$ at 280-295 °C gives **1.43** with the elimination of *iso*-butylamine. Similar reaction occurs when $\text{O}=\text{P}(\text{NH}^i\text{Pr})_2(\text{NEt}_2)$ is heated to above 250 °C, giving bisoxides cyclophosph(V/V)azanes product **1.44** and releasing diethylamine as the side product.⁵⁵

Examples of indirect syntheses of bisoxides cyclophosph(V/V)azanes formed by rearrangement of alkyloxy substituted cyclodiphosphazanes are shown in *Figure 1.10*. As reported, the oxidation reaction of amine-functionalized cyclodiphosphazane *cis*-

$[\text{Me}_2\text{NCH}_2\text{CH}_2\text{OP}(\mu\text{-N}^t\text{Bu})]_2$ with elemental chalcogen S/Se did not result in the expected disulfides- or diselenides- cyclodiphosphazanes, instead led to the formation of thio- or selenophosphates *trans*- $[\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})\text{ECH}_2\text{CH}_2\text{NMe}_2]_2$ (E = S, **1.45**; Se, **1.46**) through rearrangement.⁵⁶

Figure 1.10 Structures of dioxides cyclodiphosph(V/V)azanes.

1.5.2 Bissulfides cyclodiphosph(V/V)azanes

Well-established synthetic methodologies have enabled successful preparation and structural characterization of a relatively large number of bissulfides cyclodiphosph(V/V)azanes, making them the largest and most abundantly studied category of cyclodiphosph(V/V)azanes.^{46,53,54,57-59} The derivatives **1.47** and **1.50** are prepared by oxidation reactions (Method A) in good yields.⁴⁴ A similar method was also employed to prepare asymmetric bissulfide **1.59**.⁴⁹

For the synthesis of these oxidised cyclodiphosph(V/V)azanes, the most frequently used method is the thermolysis of tris(amido)thiophosphates (Method B). Using this methodology, bissulfides derivatives **1.51** – **1.57** has been isolated and structurally characterized. These reactions were conducted at temperatures ranging from 190 to 240 °C with yields varying from 6 (R = *n*Bu) to 39% (R = Me).⁶⁰⁻⁶²

1.47 , R = R' = Me	1.54 , R = R' = ^s Bu
1.48 , R = R' = Et	1.55 , R = R' = Bz
1.49 , R = R' = ⁱ Pr	1.56 , R = R' = C ₆ H ₉
1.50 , R = R' = ^t Bu	1.57 , R = R' = C ₆ H ₁₁
1.51 , R = R' = ⁿ Pr	1.58 , R = R' = Ph
1.52 , R = R' = ⁿ Bu	1.59 , R = ^t Bu, R' = Ph
1.53 , R = R' = ⁱ Bu	1.60 , R = R' = TMS

Figure 1.11 Structures of disulfides cyclodiphosph(V/V)azanes.

Room-temperature reactions *via* Method C have produced **1.49** and **1.51** – **1.54** in yields ranging from 5 to 22%, and are found to be enhanced by the existence of branched chain amines.^{60,63} An analogue reaction of SPCl₃ with hexamethyl-disilazane, (Me₃Si)₂NH, provides the bis(amido)cyclodiphosph(V/V)azane bissulfide **1.60** and (Me₃Si)NHP(S)Cl₂ as the side product.^{64,65}

1.5.3 biselenides cyclodiphosph(V/V)azanes

So far, the known examples of bis(amido)cyclodiphosph(V/V)azane diselenides **1.61** – **1.68** are all generated *via* Method A by reacting the corresponding P(III)/P(III) systems with elemental selenium, affording good yields of over 60% (*Figure 1.12*).^{46,49,52,58,59,66}

1.61 , R = ^t Bu, R' = N(H) ^t Bu	1.65 , R = Cy, R' = N(H)Cy,
1.62 , R = ^t Bu, R' = N(H)Ph,	1.66 , R = ^t Bu, R' = NC ₄ H ₈ NMe
1.63 , R = ^t Bu, R' = N(H)Cy,	1.67 , R = ^t Bu, R' = NC ₄ H ₈ NMe ₂ I ⁻
1.64 , R = Cy, R' = N(H) ^t Bu,	1.68 , R = ^t Bu, R' = N(H)(CH ₂) ₂ NMe ₃ I ⁻

Figure 1.12 Structures of diselenides cyclodiphosph(V/V)azanes.

1.5.4 Ditellurides cyclodiphosph(V/V)azanes

The synthesis of bis(amido)cyclodiphosph(V/V)azane ditelluride is not as well-established as their bisoxide and bissulfide derivatives. The oxidation reaction of the corresponding P(III)/P(III) system with an excess of tellurium (Method A) only provides the monotelluride.^{67,68} However, initial studies on this system is promising and opens the possibility for the synthesis of related compounds with terminal alkyl substituents (*Figure 1.13*).^{67,69-71}

Figure 1.13 Structures of ditellurides cyclodiphosph(V/V)azanes.

1.6 Bonding, geometry and conformation

For all structurally characterized cyclodiphosph(III)azanes, it has been observed that the nitrogen atoms within the ring exhibit an sp^2 hybridized planar geometry, whereas the phosphorus atoms are pyramidal (sp^3 hybridized). This allows the dimeric cyclodiphosph(III)azane rings to have two different conformers: the phosphorus substituents are arranged on the same side (*cis*) or opposite sides (*trans*) of the P₂N₂ ring plane (*Figure 1.14*). In addition, the P₂N₂ rings in the *cis* isomers are normally slightly puckered; whereas the *trans* isomers tend to be almost planar.⁷²

Figure 1.14 *Cis- and trans- conformation of cyclodiphosph(III)azanes.*

For the preference of *cis*- or *trans*- conformation, some general rules regarding the stability of different isomers were formulated by Norman *et al.*²¹ and simplified by Stahl,⁷³ are summarized below:

- 2,4-Dihalocyclodiphosph(III)azanes, with halide substituents on the phosphorus, are always *cis*, regardless of the nitrogen substituent.
- 1,3-Diaryl-2,4-bis(amino)cyclodiphosph(III)azanes will be *cis* as long as at least one of the phosphorus substituents is a primary amine.
- 1,3-Dialkyl-2,4-bis(amino)cyclodiphosph(III)azanes are always *cis*.

The ring puckering in the *cis* conformation has been rationalized by MO theory and the steric strain associated with the *cis* arrangement of the substituents (*Figure 1.15*). The results indicated that the HOMO is essentially the π^* MO of the naked P_2N_2 ring. Therefore, the antibonding character of the HOMO is enhanced when electron-donating substituents are attached to the phosphorus by increasing the electron density around it, leading to an increase in ring puckering. In contrast, very electron-withdrawing substituents will reduce the antibonding character of the HOMO and result in a nearly planar P_2N_2 ring, which adopts the *trans* conformation to relieve the steric strain. Obviously, this simplified model only concerns the effects of π -donating or accepting substituents. When the phosphorus substituent is a π -donor, like phenylamine, the nitrogen lone pair is generally orthogonal to the HOMO of the ring to pre-

clude any potential interaction between them, as is observed in the solid-state structure of $[\text{Ph}(\text{H})\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ (Figure 1.15).^{73,74}

Figure 1.15 Illustration of HOMO of the naked P_2N_2 ring.

Moreover, it was discovered that the phosphorus-nitrogen bond lengths within the P_2N_2 rings of cyclodiphosph(III)azanes are 1.65-1.75 Å,^{73,74} which is shorter than the standard P-N single bond length of 1.77 Å⁷⁵ in the phosphoramidate anion $\text{NH}_2\text{PO}_3\text{H}^-$. Furthermore, shorter P-N bond lengths are observed within the P_2N_2 rings where the phosphorus are attached by electronegative and δ -withdrawing chlorine substituents compared to those substituted with π -donating amine substituents, suggesting that an electron-deficiency at the phosphorus atoms leads to an increased strength of the P-N bonds. Various theories have been postulated to explain the apparent shortening of the P-N bonds within the cyclodiphosph(III)azane rings, although the results of such studies are debatable and still in its infancy. Specifically, these theories include:

- Ionic contribution to the P-N bond

The presence of electron-withdrawing groups will increase the electron-poor character of phosphorus, which is originally induced by substantial ionic contribution to the P-N bond stemming from the large difference in electronegativity between nitrogen and phosphorus; therefore, further enhancing the ionic character of the P-N bond.⁷⁶

- $d\pi$ - $p\pi$ bonding

Although the energy of d-orbitals on the phosphorus atoms may be too high to interact significantly in any π -bonding with the nitrogen lone pair, it has been established that the attachment of electron-withdrawing groups can decrease the electron-density on

phosphorus, which leads to a contraction of the d-orbitals and a lowering in their energy (*i.e.*, so that they can interact more efficiently). *Ab initio* calculations on related P-N compounds suggest that the d-orbital participation is probably insignificant.⁷⁷

- Negative hyperconjugation between nitrogen lone pairs and σ_{P-X^*} orbitals

The expected favoured conformation in cyclodiphosph(III)azanes, in which the phosphorus and nitrogen lone pairs have a gauche relationship to reduce the repulsion between them, is not observed.⁷⁸ Rather, the formation of the ring results in a deviation from the expected orthogonal relationship between the lone pairs.

It has been postulated that negative hyperconjugation is significant in the bonding of cyclodiphosph(III)azanes thanks to the *ab initio* and Density Functional Theory (DFT) modelling on the compounds $[\text{ClP}(\mu\text{-NMe})]_2$ and $[\text{ClP}(\mu\text{-NSiH}_3)]_2$.⁷⁹ Furthermore, *ab initio* calculations on the related species F_2PNH_2 show that the negative hyperconjugation between the nitrogen lone pair and the P-F σ^* orbital is more important than $d\pi\text{-}p\pi$ interactions.⁸⁰

1.7 Conclusions and scope

So far in this chapter, we have discussed the established methods to synthesize cyclophosphazanes (mainly cyclodiphosphazanes) and macrocyclodiphosphazanes. A conclusion can be made that the synthesis of macrocyclodiphosphazanes and studies on their host-guest chemistry is one of the main research topic in this area. Besides, the air- and moisture- sensitivity of cyclodiphosphazanes handicapped their applications, and the quantitative stabilities remains unexplored. Therefore, in this thesis, the investigation of stabilizing the cyclodiphosphazanes family by oxidation reactions with chalcogens on phosphorus atoms has been carried out, the results show that significant improvement on their stabilities towards air and moisture has been obtained. This al-

allows broader future applications of cyclodiphosphazanes families. In addition, to overcome the challenges in the syntheses of large macrocyclodiphosphazanes and particular size macrocyclodiphosphazanes, new synthetic strategies have been invented and proved to be feasible. Novel cyclodiphosphazane based structures (mainly macrocyclodiphosphazanes) have been synthesized with these new strategies, and therefore providing the potential applications in broader area.

Chapter 2: General experimental and analytical techniques

2.1 Inert-atmosphere techniques

Precautions need to be taken during handling the compounds due to the thermodynamic instability of phosphorus(III)-nitrogen compounds towards air and moisture. Therefore, standard inert atmosphere techniques need to be ensured throughout all practical work. All the reactions were done with the typical vacuum-line techniques to make sure the inert-atmosphere of dry argon and a positive pressure (*Figure 2.1*).

Figure 2.1 Illustration of a vacuum-line.

Reaction products after isolation were kept in the argon-filled glove-box for further handling and storage. Samples entered and left the glove-box through transfer chambers which were evacuated and refilled to ensure that the inert atmosphere environment was maintained inside the box. The atmosphere inside the box was constantly being purified by passing it through two columns, one containing a molecular sieve to remove water while the other includes a copper catalyst which removes oxygen using a circulation pump. Moisture level in the glove-box typically measured 5 volume parts per million (Vppm) when in use, according to a Mitchell moisture meter. Oxygen level

typically measured 5-15 Vppm and was measured using an O₂ meter. The argon pressure inside the box was maintained, above atmospheric, by an automatic pressure regulator coupled with a paraffin-filled lute.

2.2. Analytical instruments and procedures

2.2.1 Nuclear magnetic resonance spectroscopy (NMR)

All ¹H, ¹³C and ³¹P-{¹H} NMR spectra were recorded using either a Bruker AV300 MHz spectrometer or Bruker BBFO 400 MHz spectrometer. The deuterated solvent resonance is used as the internal standard for ¹H and ¹³C NMR and 85% H₃PO₄-D₂O as the external standard for ³¹P NMR. The deuterated solvent used for samples preparation is either directly used upon purchase or with further purification to ensure the water-free and oxygen-free environment according the standard chemical purification procedure from [Purification of Laboratory Chemicals] fifth edition by Wilfred L. F., Armarego Christina L. L. Chai.

2.2.3 FT-IR and elemental analysis

FT-IR spectra were recorded on a Shimadzu IR Prestige-21 FTIR Spectrometer and elemental analysis were performed using Euro Vector Euro EA Elemental Analyzer (CHNS). The sample preparation was made under inert-atmosphere in the glovebox.

2.2.2 Crystallographic analyses

Diffraction-quality crystals were obtained by slow evaporation of solvent from solutions in appropriate temperatures (*i.e.*, either at room-temperature or low-temperature as -7 °C). The crystals were mounted onto quartz fibers, and the X-ray diffraction intensity data were measured at 103 K with a Bruker Kappa diffractometer equipped

with a CCD detector. Either Cu ($\lambda = 1.54178 \text{ \AA}$) or Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was employed depending on the size of the crystals measured, with the APEX 2 suite of programs.⁸¹ All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.⁸² Structural solution and refinement were carried out with the SHELXTL suite of programs.⁸³ The structures were solved by Direct Methods or Patterson maps to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The crystals, which were found to be twinned; of those the twin law and cell parameters were determined using the program CELL_NOW,⁸⁴ and the reflection data were processed and corrections applied using the program TWINABS.⁸⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters.

2.3. Preparation of starting materials

All solvents used [*n*-pentane, acetone, toluene (Tol), tetrahydrofuran (THF), ether, pyridine, dichloromethane (DCM), acetonitrile, *n*-hexane] were freshly distilled over an appropriate drying agent (sodium and benzophenone or calcium hydride) under an atmosphere of dry nitrogen. Starting materials were either synthesized as detailed below or obtained commercially. Phosphorus trichloride, *tert*-butylamine, *iso*-propylamine, and triethylamine were distilled before use and stored under argon over molecular sieves. Phosphorus trichloride was distilled to remove traces of oxidised materials (*e.g.*, $\text{Cl}_3\text{P=O}$). *tert*-butylamine, *iso*-propylamine and triethylamine were distilled over potassium hydroxide.

(I) Preparation of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (**3.0**)

PCl_3 (16.6 ml, 190 mmol) was added dropwise to a solution of $t\text{BuNH}_2$ (60 ml, 571 mmol) in THF (300 ml) at -78°C . The reaction mixture was stirred at -78°C (3 hours),

allowed to warm to room-temperature and then further stirred (1 hour). The resulting suspension was filtered over celite and the solvent removed under vacuum. The residue was distilled at 96 °C, under vacuum (0.2 mmHg), giving a typical yield of 67 % (17.6 g, 64 mmol).

(II) Preparation of $[\text{Cl}(\text{O}=\text{P}(\mu\text{-N}^t\text{Bu})_2)]_2$ (**3.5**)

The method was adopted from the work by Jefferson.⁸⁶ DMSO (0.16 mL, 2.2 mmol) in diethyl ether (2 mL) was added dropwise to stirred solution of **3.0** (0.28 g, 1 mmol) in diethyl ether (10 mL) at -78 °C. The mixture was brought to room-temperature when the addition was completed and the dimethyl sulphide along with the solvent was evaporated under vacuum to yield a white solid.

(III) Preparation of $[\text{Cl}(\text{S}=\text{P}(\mu\text{-N}^t\text{Bu})_2)]_2$ (**3.6**)

The method was adopted from: Gonzalez-Calera S.; Eisler D. J.; Morey J. V.; McPartlin M.; Singh S.; Wright D. S.; *Angew. Chem. Int. Ed.* **2008**, 47, 1111 – 1114.

A mixture of solid **3.0** (5.50 g, 20.0 mmol) and elemental sulphur (1.41 g, 44.0 mmol) was heated to 200 °C for 20 minutes. The mixture turned yellow while heating. The reaction mixture was allowed to cool to room-temperature and subsequently extracted with hexane (100 mL) and filtered through celite (P3). The filtrate was reduced in volume by gradual evaporation under vacuum until precipitation of a colourless solid occurred. The solid was heated back into the solution; storage at -20 °C to afford colourless crystal (desired product) and yellow crystals (S_8). Yield: 2.58 g (38 %). $^{31}\text{P}\{-^1\text{H}\}$ NMR (121 MHz, Acetone- d_6 , δ): 40.96 (s), 40.16 (s). ^1H NMR (300 MHz, Acetone- d_6 , δ): 1.72 (s, ^tBu , 18H). ^{13}C NMR (75 MHz, Acetone- d_6 , δ): 61.74 (s), 30.14 (m), IR (Nujol, NaCl) ν (cm^{-1}): 916 (s, $\text{P}=\text{S}$) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4\text{P}_2$: C, 28.32; H, 5.35; N, 8.26; S, 18.90. Found: C, 28.32; H, 5.59; N, 8.36; S, 19.02.

(IV) Preparation of $[\text{Cl}(\text{Se}=\text{P}(\mu\text{-N}^t\text{Bu})_2)]_2$ (**3.7**)

The method was adopted from: Gonzalez-Calera S.; Eisler D. J.; Morey J. V.; McPartlin M.; Singh S.; Wright D. S.; *Angew. Chem. Int. Ed.* **2008**, 47, 1111 – 1114.

A mixture of solid **3.0** (5.50 g, 20.0 mmol) and elemental selenium (3.47 g, 44.0 mmol) was heated to 200 °C for 30 minutes. The mixture turned yellow while heating. This mixture was allowed to cool to room-temperature and subsequently extracted with hexane (100 mL) and filtered through celite (P3). The filtrate was reduced in volume by gradual evaporation under vacuum until precipitation of a colourless solid occurred. This was heated back into solution and storage at room-temperature. Yield: 3.65 g (42 %).

(V) Synthesis of [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})\}_2$ (**4.1**)

The method was adopted from: Brask, J. K.; Chivers, T.; Krahn, M. L.; Parvez, M. *Inorg. Chem.* **1999**, 38, 290-295. To a solution of $\{\text{Li}[P(\text{N}^t\text{Bu})_2]\}_2 \cdot 2\text{THF}$ (4.89 g, 9.74 mmol) in Tol (50 mL) at 0 °C, a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ (**3.0**) (2.67 g, 9.74 mmol) in Tol (20 mL) was dropwise added. The mixture was then set to reflux at 120 °C for 6 hours. resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of THF. Storage at room-temperature afforded colourless crystals. Yield: 1.96 g (37 %).

(VI) Synthesis of [$\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ (**4.8**)

The method was adopted from the report by Scherer *et al.*²⁹ A solution of crude $\{\text{SiMe}_3(^i\text{Pr})\text{N}\{P(\mu\text{-N}^i\text{Pr})\}_2\}$ (7.25 g, 22.5 mmol) [obtained from 5.56 g (22.5 mmol) $[\text{ClP}(\mu\text{-N}^i\text{Pr})_2]$, and 22.5 mmol $\text{LiN}(^i\text{Pr})\text{SiMe}_3$ in 100 ml ACN was heated under reflux for 15 hours. After cooling to room-temperature was filtered off and washed several times with ACN. Filtrate and washings were again heated under reflux for 15 hours;

was isolated from the solution after cooling to -45 °C, washed, and recrystallized from ACN. Yield: 1.1 g (21%).

2.4. Syntheses of new compounds

2.4.1 Preparation of [(4-CN-PhO)P(μ -N^tBu)]₂ (**3.1**)

4-hydroxybenzonitrile (4.26 g, 36.0 mmol) and Et₃N (5.02 mL, 36.0 mmol) were dissolved in 50 mL of Tol. This solution was added dropwise to a stirred solution of [ClP(μ -N^tBu)]₂ (**3.0**) (4.92 g, 18 mmol) in Tol (50 mL) at -78 °C. The reaction mixture was allowed to warm to room-temperature and was stirred for 12 hours. The precipitate was filtered off through celite (P3) and the white residue obtained was washed with Tol (3 x 10 mL). The combined filtrates were reduced by gradual evaporation under vacuum until precipitation occurred. The solid was heated back into solution. Storage at room-temperature yielded colourless crystals of **3.1**. Yield: 6.66 g (84%). Mp: 139.9 °C. ³¹P-{¹H} NMR (121 MHz, Acetone-d₆, δ): 143.30 (s). ¹H NMR (300 MHz, Acetone-d₆, δ): 7.79 (d, *J* = 11.2 Hz, *m*-Ar, 4H), 7.37 (d, *J* = 8.7 Hz, *o*-Ar, 4H), 1.37 (s, ^tBu, 18H). ¹³C NMR (75 MHz, Acetone-d₆, δ): 157.85 (s), 134.68 (s), 122.70 (t, *J* = 4.2 Hz), 119.25 (s), 107.72 (s), 53.04 (t, *J* = 11.9 Hz), 31.40 (t, *J* = 6.0 Hz). IR (Nujol, NaCl) ν (cm⁻¹): 2220 (s, C $\equiv$ N), 1597 (s, C=C) cm⁻¹. MS (EI) *m/z*: 441.16 [M+1]⁺. Anal. Calcd for C₂₂H₂₆N₄O₂P₂: C, 60.00; H, 5.95; N, 12.72. Found: C, 60.09; H, 5.80; N, 12.69.

Table 2.1. Crystal data and structure refinement for **3.1**.

Empirical formula	C ₂₂ H ₂₆ N ₄ O ₂ P ₂	
Formula weight	440.41	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.1792(4) Å	a = 90°.
	b = 11.1382(5) Å	b = 90°.
	c = 20.0312(10) Å	g = 90°.
Volume	2271.10(18) Å ³	
Z	4	
Density (calculated)	1.288 Mg/m ³	
Absorption coefficient	0.217 mm ⁻¹	
F(000)	928	
Crystal size	0.40 x 0.38 x 0.32 mm ³	
Theta range for data collection	2.03 to 28.48°.	
Index ranges	-9 ≤ h ≤ 13, -14 ≤ k ≤ 13, -26 ≤ l ≤ 26	
Reflections collected	21065	
Independent reflections	5689 [R(int) = 0.0327]	
Completeness to theta = 28.48°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9338 and 0.9182	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5689 / 0 / 277	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0304, wR2 = 0.0714	
R indices (all data)	R1 = 0.0346, wR2 = 0.0773	
Absolute structure parameter	-0.05(6)	
Largest diff. peak and hole	0.279 and -0.303 e.Å ⁻³	

2.4.2 Preparation of [(4-CN-PhO)(O)P(μ -N^tBu)]₂ (**3.2**)

A solution of ^tBuOOH (2.4 mL, 25.0 mmol) in Tol (20 mL) was added dropwise to a stirred Tol (50 mL) solution of [(4-CN-Ph-O)P(μ -N^tBu)]₂ (**3.1**) (2.2 g, 5.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room-temperature and further refluxed for 10 hours. The suspension mixture obtained was filtered through celite (P3) and the residue collected washed with Tol (3 x 10 mL). All volatiles were removed under reduced pressure giving a white solid. Single crystals of **3.2** were collected from an acetone solution stored at room-temperature. Yield: 1.23 g (52%). Mp: 282.2 °C. ³¹P-{¹H} NMR (121 MHz, Acetone-d₆, δ): -7.84 (s). ¹H NMR (300 MHz, Acetone-d₆, δ): 7.10 (d, *J* = 8.8 Hz, *m*-Ar, 4H), 6.91 (d, *J* = 8.8 Hz, *o*-Ar, 4H), 1.22 (s, ^tBu, 18H). ¹³C NMR (75 MHz, Acetone-d₆, δ): 154.39 (s), 134.01 (s), 121.16 (s), 117.93 (s), 109.89 (s), 56.10 (s), 30.22 (t, *J* = 4.9 Hz). IR (Nujol, NaCl) ν (cm⁻¹): 2227 (s, C $\equiv$ N), 1596 (s, C=C) cm⁻¹. MS (EI) *m/z*: 473.15 [M+1]⁺. Anal. Calcd for C₂₂H₂₆N₄O₄P₂: C, 59.93; H, 5.55; N, 11.86. Found: C, 55.98; H, 5.59; N, 12.07.

Table 2.2. Crystal data and structure refinement for **3.2**.

Empirical formula	C ₂₂ H ₂₆ N ₄ O ₄ P ₂	
Formula weight	472.41	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.696(3) Å	α = 90°.

	$b = 15.804(4) \text{ \AA}$	$\beta = 90.520(6)^\circ$.
	$c = 13.043(3) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2410.9(10) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	992	
Crystal size	$0.40 \times 0.34 \times 0.30 \text{ mm}^3$	
Theta range for data collection	$2.02 \text{ to } 27.49^\circ$.	
Index ranges	$-15 \leq h \leq 14, -20 \leq k \leq 20, -16 \leq l \leq 16$	
Reflections collected	19342	
Independent reflections	5489 [R(int) = 0.0639]	
Completeness to $\theta = 27.49^\circ$	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9382 and 0.9188	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5489 / 151 / 335	
Goodness-of-fit on F^2	1.114	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0544, wR2 = 0.1519$	
R indices (all data)	$R1 = 0.0758, wR2 = 0.1782$	
Largest diff. peak and hole	$0.594 \text{ and } -0.564 \text{ e.\AA}^{-3}$	

2.4.3 Preparation of [(4-CN-PhO)(S)P(μ -N'Bu)]₂ (**3.3**)

A suspension of sulphur (0.4 g, 12.5 mmol) and [(4-CN-Ph-O)P(μ -N'Bu)]₂ (**3.1**) (2.2 g, 5.0 mmol) in Tol (50 mL) was refluxed for 96 hours. The resulting suspension was filtered through celite (P3) and the residue obtained washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of acetone (*ca.* 5 mL). Storage at room-temperature afforded colourless crystals. Yield: 0.93 g (37%). Mp: 248.3 °C. ^{31}P -{ ^1H } NMR (121 MHz, Acetone- d_6 , δ): 51.36 (s), 46.17 (s). ^1H NMR (300 MHz, Acetone- d_6 , δ): 7.94 – 7.92 (m, m-Ar, 4H), 7.65 (d, $J = 8.9 \text{ Hz}$, o-Ar, 4H), 1.63 (s, 'Bu, 18H). ^{13}C NMR (75 MHz, Acetone- d_6 , δ): 154.45 (t, $J = 5.0 \text{ Hz}$), 134.17 (s), 123.02 (t, $J = 2.5 \text{ Hz}$), 117.72 (s), 109.57 (s),

58.03 (s), 29.79 (t, $J = 4.8$ Hz). IR (Nujol, NaCl) ν (cm⁻¹): 2227 (s, C $\equiv$ N), 1597 (s, C=C) cm⁻¹, 935 (s, P=S) cm⁻¹. MS (EI) m/z : 505.10 [M+1]⁺. Anal. Calcd for C₂₂H₂₆N₄O₄P₂: C, 52.37; H, 5.19; N, 11.10, S 12.71. Found: C, 52.26; H, 4.93; N, 11.03, S 12.67.

Table 2.3. Sample and crystal data for **3.3cis**.

Chemical formula	C ₂₈ H ₃₈ N ₄ O ₄ P ₂ S ₂	
Formula weight	620.68	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.180 x 0.200 mm	
Crystal habit	yellow block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.2567(9) Å	$\alpha = 89.777(3)^\circ$
	b = 12.8700(11) Å	$\beta = 71.683(3)^\circ$
	c = 14.0384(13) Å	$\gamma = 89.002(3)^\circ$
Volume	1587.5(3) Å ³	
Z	2	
Density (calculated)	1.299 g/cm ³	
Absorption coefficient	0.307 mm ⁻¹	
F(000)	656	
Theta range for data collection	1.53 to 25.45°	
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	
Reflections collected	27320	
Independent reflections	5806 [R(int) = 0.0522]	
Coverage of independent reflections	98.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9520 and 0.9410	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	

Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5806 / 0 / 371
Goodness-of-fit on F2	1.170
$\Delta/\sigma_{\max}$	0.002
Final R indices	4887 data; $I > 2\sigma(I)$ $R1 = 0.0885$, $wR2 = 0.2403$ all data $R1 = 0.1007$, $wR2 = 0.2470$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 16.2066P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.325 and -0.715 $\text{e}\text{\AA}^{-3}$
R.M.S. deviation from mean	0.138 $\text{e}\text{\AA}^{-3}$

Table 2.4. Sample and crystal data for **3.3trans**.

Chemical formula	$\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_2\text{P}_2\text{S}_2$
Formula weight	504.53
Temperature	103(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal size	0.100 x 0.240 x 0.320 mm
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	$a = 8.660(3) \text{\AA}$ $\alpha = 88.330(12)^\circ$ $b = 8.684(3) \text{\AA}$ $\beta = 89.430(11)^\circ$ $c = 17.225(5) \text{\AA}$ $\gamma = 70.346(12)^\circ$
Volume	1219.4(7) $\text{\AA}^3$
Z	2
Density (calculated)	1.374 g/cm^3
Absorption coefficient	0.377 mm^{-1}
F(000)	528
Theta range for data collection	2.37 to 27.16°
Reflections collected	4826
Coverage of independent reflections	94.9%
Max. and min. transmission	0.9630 and 0.8890
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4826 / 24 / 296
Goodness-of-fit on F2	1.168
Final R indices	3872 data; $I > 2\sigma(I)$ $R1 = 0.1340$, $wR2 = 0.3602$ all data $R1 = 0.1532$, $wR2 = 0.3697$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 33.3643P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	2.044 and -0.919 $\text{e}\text{\AA}^{-3}$
R.M.S. deviation from mean	0.237 $\text{e}\text{\AA}^{-3}$

2.4.4 Preparation of [(4-CN-PhO)(Se)P(μ -N^tBu)]₂ (**3.4**)

A suspension of selenium (0.8 g, 10.1 mmol) and [(4-CN-Ph-O)P(μ -N^tBu)]₂ (**3.1**) (2.2 g, 5.0 mmol) in 50 mL of THF was refluxed for 48 hours. The reaction mixture was filtered through celite (P3) and the residue washed with THF (3 x 10 mL). The solvent was removed under vacuo and the solid obtained dissolved in the minimum amount of acetone. Crystallization in acetone afforded colourless crystals of **3.4**. Yield: 2.37 g (79%). Mp: 157.9 °C. ³¹P-{¹H} NMR (121 MHz, Acetone-d₆, δ): 47.04 (s), 39.58 – 39.53 (s). ¹H NMR (300 MHz, Acetone-d₆, δ): 7.93 – 7.90 (m, m-Ar, 4H), 7.64 (d, J = 8.9 Hz, o-Ar, 4H), 1.44 (s, ^tBu, 18H). ¹³C NMR (75 MHz, Acetone-d₆, δ): 155.26 (d, J = 11.0 Hz), 135.11 (d, J = 17.1 Hz), 124.29 – 124.24 (m), 118.65 (s), 110.60 (s), 59.86 (t, J = 26.4 Hz), 30.93 (s). IR (Nujol, NaCl) ν (cm⁻¹): 2226 (s, C $\equiv$ N), 1595 (s, C=C) cm⁻¹, 538 (s, P=Se) cm⁻¹. MS (EI) m/z : 600.99 [M+1]⁺. Anal. Calcd for C₂₂H₂₆N₄O₄P₂: C, 44.16; H, 4.38; N, 9.36. Found: C, 44.63; H, 4.30; N, 9.63.

Table 2.5. Crystal data and structure refinement for **3.4_{cis}**.

Empirical formula	C ₂₂ H ₂₆ N ₄ O ₂ P ₂ Se ₂	
Formula weight	598.33	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 17.3148(9)$ Å	$a = 90^\circ$.
	$b = 16.5674(8)$ Å	$b = 99.046(2)^\circ$.

	$c = 9.0063(5) \text{ \AA}$	$g = 90^\circ$.
Volume	$2551.4(2) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.558 Mg/m^3	
Absorption coefficient	3.050 mm^{-1}	
F(000)	1200	
Crystal size	$0.32 \times 0.24 \times 0.14 \text{ mm}^3$	
Theta range for data collection	1.71 to 31.71° .	
Index ranges	$-25 \leq h \leq 25$, $-23 \leq k \leq 23$, $-13 \leq l \leq 13$	
Reflections collected	28787	
Independent reflections	8473 [R(int) = 0.0573]	
Completeness to $\theta = 28.00^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6748 and 0.4420	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8473 / 0 / 295	
Goodness-of-fit on F^2	0.990	
Final R indices [I > 2 σ (I)]	R1 = 0.0406, wR2 = 0.0937	
R indices (all data)	R1 = 0.0713, wR2 = 0.1164	
Largest diff. peak and hole	0.617 and -0.632 e. $\text{\AA}^{-3}$	

Table 2.6. Crystal data and structure refinement for **3.4trans**.

Chemical formula	$\text{C}_{22}\text{H}_{26.67}\text{N}_4\text{O}_{2.33}\text{P}_2\text{Se}_2$
Formula weight	604.33
Temperature	180(2) K
Wavelength	$0.71073 \text{ \AA}$
Crystal size	$0.070 \times 0.100 \times 0.280 \text{ mm}$
Crystal system	trigonal
Space group	R $\bar{3}$
Unit cell dimensions	$a = 28.9540(10) \text{ \AA}$ $\alpha = 90^\circ$ $b = 28.9540(10) \text{ \AA}$ $\beta = 90^\circ$ $c = 8.8123(4) \text{ \AA}$ $\gamma = 120^\circ$
Volume	$6397.9(4) \text{ \AA}^3$
Z	9
Density (calculated)	1.412 g/cm^3
Absorption coefficient	2.738 mm^{-1}
F(000)	2730
Theta range for data collection	3.72 to 24.95°
Index ranges	$-34 \leq h \leq 34$, $-34 \leq k \leq 32$, $-10 \leq l \leq 10$
Reflections collected	13262
Independent reflections	2483 [R(int) = 0.0542]
Max. and min. transmission	0.8314 and 0.5144

Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 1997)
Function minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$
Data / restraints / parameters	2483 / 18 / 131
Goodness-of-fit on F ²	1.098
$\Delta/\sigma_{\text{max}}$	0.001
Final R indices	1775 data; $I > 2\sigma(I)$ R1 = 0.0681, wR2 = 0.1967 all data R1 = 0.0925, wR2 = 0.2086
Weighting scheme	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0932P)^2 + 46.4840P]$ where $P = (\text{Fo}^2 + 2\text{Fc}^2)/3$
Largest diff. peak and hole	1.210 and -0.546 eÅ ⁻³
R.M.S. deviation from mean	0.094 eÅ ⁻³

2.4.5 Preparation of [(O)P(μ -N^tBu)₂P]₂[μ -N^tBu]₂ (4.2)

A solution of ^tBuOOH (1.0 mL, 10.8 mmol) in Tol (10 mL) was added dropwise to a stirred Tol (20 mL) solution of [{P(μ -N^tBu)₂}]₂(μ -N^tBu)]₂ (**4.1**) (1.0 g, 1.8 mmol) at 0 °C. The reaction mixture was allowed to warm to room-temperature and further re-fluxed for 10 hours. The suspension mixture obtained was filtered through celite (P3) and the residue washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage in fridge at 7 °C afforded colourless crystals. Yield: 0.91 g (87 %). Mp: 244 °C. ³¹P-{¹H} NMR (162 MHz, C₆D₆, δ): 79.87 (d, J = 32.4 Hz), 12.65 (d, J = 32.4 Hz). ¹H NMR (400 MHz, C₆D₆, δ): 1.79 (s, 18H), 1.55 (s, 36H). ¹³C NMR (101 MHz, C₆D₆, δ): 64.26 (s), 64.02 (s), 57.4 (d, J = 20.2 Hz), 34.5 (d, J = 20.2 Hz), 31.1 (dd, J = 8.1 Hz, J = 5.1 Hz), IR (Nujol, NaCl) ν (cm⁻¹): 1267 (s, P=O) cm⁻¹. MS (EI) m/z: 583.33 [M+1]⁺. Anal. Calcd for C₂₄H₅₄N₆P₄O₂: C, 49.48; H, 9.34; N, 14.42. Found: C, 49.44; H, 9.55; N, 14.46 %.

Table 2.7. Sample and crystal data for **4.2**.

Chemical formula	C ₂₄ H ₅₄ N ₆ O ₂ P ₄
Formula weight	582.61 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.160 x 0.200 x 0.300 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	C 1 2/c 1
Unit cell dimensions	$a = 28.850(3) \text{ Å}$ $\alpha = 90^\circ$ $b = 16.8062(15) \text{ Å}$ $\beta = 95.902(5)^\circ$ $c = 19.5072(19) \text{ Å}$ $\gamma = 90^\circ$
Volume	9408.1(16) Å ³
Z	12
Density (calculated)	1.234 g/cm ³
Absorption coefficient	0.272 mm ⁻¹
F(000)	3792
Theta range for data collection	1.40 to 25.47°
Index ranges	-34 ≤ h ≤ 34, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	72830
Independent reflections	8693 [R(int) = 0.1733]
Coverage of independent reflections	99.5%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9580 and 0.9230
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	8693 / 93 / 562
Goodness-of-fit on F ²	1.033
Δ/σ _{max}	0.001
Final R indices	4837 data; I > 2σ(I) R1 = 0.0840, wR2 = 0.2167 all data R1 = 0.1567, wR2 = 0.2690
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.1185P)^2 + 59.4342P]$ where $P = (F_o^2 + 2F_c^2) / 3$

Largest diff. peak and hole	0.617 and -0.758 eÅ ⁻³
R.M.S. deviation from mean	0.151 eÅ ⁻³

2.4.6 Preparation of [(S)P(μ -N^tBu)₂P]₂[μ -N^tBu]₂ (**4.3**)

A suspension of sulphur (0.12 g, 3.8 mmol) and [{P(μ -N^tBu)₂}]₂(μ -N^tBu)₂ (**4.1**) (1.0 g, 1.8 mmol) in Tol (20 mL) was refluxed for 96 hours. The resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage in fridge at 7 °C afforded colourless crystals. Yield: 0.50 g (52 %). Mp: 257 °C. ³¹P-{¹H} NMR (162 MHz, C₆D₆, δ): 57.22 (d, J = 34.0 Hz), 90.08 (d, J = 37.4 Hz). ¹H NMR (400 MHz, C₆D₆, δ): 1.92 (s, 9H), 1.91 (s, 9H), 1.66 (s, 18H). ¹³C NMR (101 MHz, C₆D₆, δ): 66.2 (dd, J = 30.3 Hz, J = 5.0 Hz), 58.7 (s), 58.5 (s), 35.1 (d, J = 23.2 Hz), 30.9 (dd, J = 30.3 Hz, J = 5.0 Hz). IR (Nujol, NaCl) ν (cm⁻¹): 901 (s, P=S) cm⁻¹. MS (EI) m/z : 615.28 [M+1]⁺. Anal. Calcd for C₂₄H₅₄N₆P₄S₂: C, 46.89; H, 8.85; N, 13.67; S, 10.43. Found: C, 47.18; H, 8.75; N, 13.34; S, 10.06 %.

Table 2.8. Sample and crystal data for **4.3**.

Chemical formula	C ₂₄ H ₅₄ N ₆ P ₄ S ₂
Formula weight	614.73 g/mol
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal size	0.220 x 0.300 x 0.380 mm
Crystal habit	colorless block

Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 9.6459(4) Å $\alpha = 105.964(2)^\circ$ b = 10.3589(4) Å $\beta = 113.553(2)^\circ$ c = 10.4150(4) Å $\gamma = 107.650(2)^\circ$
Volume	810.19(6) Å ³
Z	1
Density (calculated)	1.260 g/cm ³
Absorption coefficient	0.386 mm ⁻¹
F(000)	332
Theta range for data collection	2.31 to 31.22°
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	34515
Independent reflections	5227 [R(int) = 0.0856]
Coverage of independent reflections	99.5%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9200 and 0.8670
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5227 / 0 / 172
Goodness-of-fit on F ²	1.040
$\Delta/\sigma_{\max}$	0.001
Final R indices	4224 data; I > 2σ(I) R1 = 0.0376, wR2 = 0.0939 all data R1 = 0.0508, wR2 = 0.1035
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.3000P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.555 and -0.389 eÅ ⁻³
R.M.S. deviation from mean	0.070 eÅ ⁻³

2.4.7 Preparation of [(Se)P(μ -N'Bu)₂P]₂[μ -N'Bu]₂ (4.4)

A suspension of selenium (0.3 g, 3.8 mmol) and [{P(μ -N'Bu)₂}]₂(μ -N'Bu)₂ (**4.1**) (1.0 g, 1.8 mmol) in Tol (20 mL) was refluxed for 96 hours. The resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage in fridge at 7 °C afforded colourless crystals. Yield:

0.50 g (47 %). Mp: 263 °C. ^{31}P - $\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , δ): 45.04 (d, $J = 35.6$ Hz), 101.84 (d, $J = 34.0$ Hz). ^1H NMR (400 MHz, C_6D_6 , δ): 1.98 (s, 9H), 1.96 (s, 9H), 1.71 (s, 18H). ^{13}C NMR (101 MHz, C_6D_6 , δ): 66.9 (dd, $J = 29.3$ Hz, $J = 6.1$ Hz), 59.4 (dd, $J = 22.2$ Hz, $J = 2.0$ Hz), 35.3 (s), 35.0(s), 30.8 (s). IR (Nujol, NaCl) ν (cm^{-1}): 910 (s, $\text{P}=\text{Se}$) cm^{-1} . MS (EI) m/z : 711.18 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{N}_6\text{P}_4\text{Se}_2$: C, 40.68; H, 7.68; N, 11.86. Found: C, 41.00; H, 7.77; N, 11.47 %.

Table 2.9. Sample and crystal data for **4.4**.

Chemical formula	$\text{C}_{24}\text{H}_{54}\text{N}_6\text{P}_4\text{Se}_2$	
Formula weight	708.53 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.220 x 0.360 mm	
Crystal habit	yellow block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 14.4124(17)$ Å	$\alpha = 97.170(3)^\circ$
	$b = 14.8376(18)$ Å	$\beta = 90.358(3)^\circ$
	$c = 15.6745(18)$ Å	$\gamma = 90.076(3)^\circ$
Volume	$3325.6(7)$ Å ³	
Z	4	
Density (calculated)	1.415 g/cm ³	
Absorption coefficient	2.440 mm ⁻¹	
F(000)	1472	
Theta range for data collection	1.38 to 26.18°	
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	
Reflections collected	57280	
Independent reflections	13185 [R(int) = 0.0633]	
Coverage of independent reflections	98.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.6410 and 0.4740	

Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13185 / 350 / 763
Goodness-of-fit on F ²	1.208
$\Delta/\sigma_{\max}$	0.001
Final R indices	10887 data; $I > 2\sigma(I)$ R1 = 0.1199, wR2 = 0.2920 all data R1 = 0.1357, wR2 = 0.2984
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 149.8821P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	2.858 and -1.979 eÅ ⁻³
R.M.S. deviation from mean	0.239 eÅ ⁻³

2.4.8 Preparation of P₄(μ-N^tBu)₄(μ-NH)₂O₄ (4.5)

A solution of *meta*-chloroperoxybenzoic acid (*m*CPBA) (0.15 g, 0.88 mmol) in THF was added dropwise to a stirred THF solution of [{P(μ-N^tBu)}₂(μ-N^tBu)]₂ (**4.1**) (0.11 g, 0.20 mmol) at -78 °C. The reaction mixture was allowed to warm to room-temperature and further stirred for 10 hours. The solvent was removed under vacuum slowly until solid appeared and the suspension obtained was heated to dissolve back. The clear solution was then stored at room-temperature afforded colourless crystals. Yield: 0.50 g (47 %). ³¹P-{¹H} NMR (162 MHz, CDCl₃, δ): -7.18 (s). ¹H NMR (400 MHz, CDCl₃, δ): 1.63 (s, 36H). ¹³C NMR (101 MHz, CDCl₃, δ): 67.95 (s), 30.42(s). IR (CHCl₃, NaCl) ν (cm⁻¹): 3348 (s, N-H), 1621 (s, P=O) cm⁻¹. MS (EI) m/z: 503.20 [M+1]⁺. Anal. Calcd for C₁₆H₃₈N₆P₄O₄: C, 38.25; H, 7.62; N, 16.73. Found: C, 41.00; H, 7.77; N, 11.47 %.

Table 2.10. Sample and crystal data for **4.5**.

Chemical formula	$C_{16}H_{38}N_6O_4P_4$	
Formula weight	502.40 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.160 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 10.2681(17)$ Å	$\alpha = 75.073(2)^\circ$
	$b = 20.274(3)$ Å	$\beta = 81.6278(18)^\circ$
	$c = 35.164(6)$ Å	$\gamma = 89.8588(17)^\circ$
Volume	$6993.(2)$ Å ³	
Z	11	
Density (calculated)	1.312 g/cm ³	
Absorption coefficient	0.330 mm ⁻¹	
F(000)	2948	
Theta range for data collection	3.45 to 29.24°	
Index ranges	-14 ≤ h ≤ 14, -27 ≤ k ≤ 27, -48 ≤ l ≤ 48	
Reflections collected	111730	
Independent reflections	37715 [R(int) = 0.0589]	
Coverage of independent reflections	99.3%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9620 and 0.9370	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	37715 / 342 / 1553	
Goodness-of-fit on F ²	1.029	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	22694 data; I > 2σ(I) R1 = 0.0606, wR2 = 0.1336	
	all data R1 = 0.1143, wR2 = 0.1595	
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 7.1796P]$	

	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.920 and -0.751 eÅ ⁻³
R.M.S. deviation from mean	0.092 eÅ ⁻³

2.4.9 Preparation of P₄(μ-N^tBu)₃(μ-NH)₃S₄ (**4.6**)

A suspension of sulphur (0.24 g, 7.5 mmol) and [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})\}_2$ (**4.1**) (1.0 g, 1.8 mmol) in Tol (20 mL) was refluxed for 96 hours. The resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage in fridge at 7 °C afforded colourless crystals. Yield: 0.50 g (54 %). Mp: 219 °C. ³¹P-¹H NMR (162 MHz, C₆D₆, δ): 34.85 (dd, *J* = 38.9 Hz, *J* = 6.5 Hz), 30.93 (dd, *J* = 38.9 Hz, *J* = 6.5 Hz). ¹H NMR (400 MHz, C₆D₆, δ): 5.16 (s, 2H), 4.12 (s, 1H), 1.59 (s, 9H), 1.56 (s, 9H), 1.23 (s, 9H). ¹³C NMR (101 MHz, C₆D₆, δ): 59.6 (s), 58.7 (s), 58.7 (s), 29.8 (t, *J* = 5.0 Hz), 29.7 (t, *J* = 5.0 Hz), 29.1 (t, *J* = 5.0 Hz). IR (Nujol, NaCl) ν (cm⁻¹): 3346 (s, N-H), 910 (s, P=S) cm⁻¹. MS (EI) *m/z*: 511.03 [M+1]⁺. Anal. Calcd for C₁₂H₃₀N₆P₄S₄: C, 22.90; H, 4.47; N, 11.65. Found: C, 22.96; H, 4.71; N, 11.60 %.

Table 2.11. Sample and crystal data for **4.6**.

Chemical formula	C _{15.50} H ₃₄ N ₆ P ₄ S ₄
Formula weight	556.60
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.040 x 0.200 mm

Crystal habit	colorless needle
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.1732(10) Å $\alpha = 97.047(7)^\circ$ b = 10.5113(13) Å $\beta = 90.836(6)^\circ$ c = 16.519(2) Å $\gamma = 107.053(6)^\circ$
Volume	1344.6(3) Å ³
Z	2
Density (calculated)	1.375 g/cm ³
Absorption coefficient	0.608 mm ⁻¹
F(000)	586
Theta range for data collection	2.25 to 25.23°
Index ranges	-9<=h<=9, -12<=k<=12, -19<=l<=19
Reflections collected	24799
Independent reflections	4853 [R(int) = 0.1597]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9760 and 0.8880
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4853 / 1775 / 534
Goodness-of-fit on F ²	1.015
Final R indices	2139 data; I>2 σ (I) R1 = 0.0756, wR2 = 0.1438 all data R1 = 0.1999, wR2 = 0.2041
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.0355P)^2+6.8457P$] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.537 and -0.610 eÅ ⁻³
R.M.S. deviation from mean	0.091 eÅ ⁻³

2.4.10 Preparation of P₄(μ -N^tBu)₃(μ -NH)₃Se₄ (4.7)

A suspension of Selenium (0.6 g, 7.5 mmol) and [$\{P(\mu$ -N^tBu) $\}_2(\mu$ -N^tBu) $\}_2$ (**4.1**) (1.0 g, 1.8 mmol) in Tol (20 mL) was refluxed for 96 hours. The resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage in fridge at 7 °C afforded colourless crystals. Yield: 0.76 g (60 %). Mp: 246 °C. ³¹P-{¹H} NMR (162 MHz, CDCl₃, δ): 24.86 (dd, *J* = 59.9

Hz, $J = 9.7$ Hz), 22.26 (dd, $J = 59.9$ Hz, $J = 9.7$ Hz). ^1H NMR (400 MHz, C_6D_6 , δ): 5.64 (s, 2H), 4.28 (s, 1H), 1.62 (s, 18H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3 , δ): 60.8 (s), 59.9 (s), 59.8 (s), 30.1 (t, $J = 4.0$ Hz), 29.9 (t, $J = 5.0$ Hz), 29.7 (t, $J = 4.0$ Hz). IR (Nujol, NaCl) ν (cm^{-1}): 3398 (s, N-H), 592 (s, P=Se) cm^{-1} . MS (EI) m/z : 702.82 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{55}\text{H}_{128}\text{N}_{24}\text{P}_{16}\text{Se}_{16}$: C, 22.90; H, 4.47; N, 11.65. Found: C, 22.96; H, 4.71; N, 11.60 %.

Table 2.12. Sample and crystal data for **4.7**.

Chemical formula	$\text{C}_{21}\text{H}_{42}\text{N}_7\text{P}_4\text{Se}_4$	
Formula weight	832.33	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.020 x 0.040 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 10.5460(4)$ Å	$\alpha = 78.264(2)^\circ$
	$b = 12.3897(5)$ Å	$\beta = 70.648(2)^\circ$
	$c = 14.0003(6)$ Å	$\gamma = 75.644(2)^\circ$
Volume	$1657.28(12)$ Å ³	
Z	2	
Density (calculated)	1.668 g/cm ³	
Absorption coefficient	4.644 mm ⁻¹	
F(000)	826	
Theta range for data collection	1.55 to 26.45°	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	
Reflections collected	38958	
Independent reflections	6816 [R(int) = 0.0800]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9550 and 0.8360	

Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6816 / 0 / 337
Goodness-of-fit on F ²	1.064
Final R indices	4998 data; I > 2 σ (I) R1 = 0.0427, wR2 = 0.1152 all data R1 = 0.0727, wR2 = 0.1477
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 0.8079P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.310 and -1.096 eÅ ⁻³
R.M.S. deviation from mean	0.268 eÅ ⁻³

2.4.11 Preparation of P₄(μ-N^{*i*}Pr)₅(μ-NH)Se₄ (**4.9**)

A suspension of selenium (0.7 g, 8.8 mmol) and [$\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ (**4.8**) (1.0 g, 2.1 mmol) in ACN (10 mL) was refluxed for 24 hours. The resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of Tol. Storage at room-temperature afforded colourless crystals. Yield: 0.18 g (12 %). ³¹P- $\{^1\text{H}\}$ NMR (162 MHz, C₆D₆, δ): 55.25 (dd, $J = 247.9$ Hz, $J = 32.4$ Hz), 30.65 (dd, $J = 212.2$ Hz, $J = 32.4$ Hz). ¹H NMR (400 MHz, C₆D₆, δ): 1.68 (d, $J = 4.0$ Hz, 30H), 1.57 (d, $J = 4.0$ Hz, 36H), 1.53 (d, $J = 8.0$ Hz, 24H). ¹³C NMR (101 MHz, C₆D₆, δ): 50.4 (s), 49.2 (s), 46.5 (s), 24.3 (s), 23.1 (s), 22.1 (s). IR (Nujol, NaCl) ν (cm⁻¹): 3454 (s, N-H), 540 (s, P=Se) cm⁻¹. MS (EI) m/z : 741.87 [M+1]⁺.

Table 2.13. Sample and crystal data for **4.9**.

Chemical formula	C ₁₈ H ₄₂ N ₆ P ₄ Se ₄
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Formula weight	782.29 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.060 x 0.080 x 0.120 mm
Crystal habit	colorless block
Crystal system	orthorhombic
Space group	P c c n
Unit cell dimensions	a = 13.8897(11) Å $\alpha = 90^\circ$ b = 15.9187(12) Å $\beta = 90^\circ$ c = 13.2039(11) Å $\gamma = 90^\circ$
Volume	2919.5(4) Å ³
Z	4
Density (calculated)	1.780 g/cm ³
Absorption coefficient	5.265 mm ⁻¹
F(000)	1552
Theta range for data collection	1.95 to 28.31°
Index ranges	-15 ≤ h ≤ 18, -20 ≤ k ≤ 21, -17 ≤ l ≤ 16
Reflections collected	42237
Independent reflections	3638 [R(int) = 0.2097]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.7430 and 0.5710
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3638 / 314 / 241
Goodness-of-fit on F ²	1.045
$\Delta/\sigma_{\max}$	0.001
Final R indices	1832 data; I > 2σ(I) R1 = 0.0652, wR2 = 0.1620 all data R1 = 0.1713, wR2 = 0.2117
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.0800P) ² + 19.2802P] where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	0.811 and -0.941 eÅ ⁻³
R.M.S. deviation from mean	0.196 eÅ ⁻³

2.4.12 Preparation of [Py(H)NP(μ-N'Bu)]₂ (5.1)

To a mixture of [CIP(μ-N'Bu)]₂ (**3.0**) (0.550 g, 2.0 mmol) and 4-aminopyridine (0.376 g, 4.0 mmol), Et₃N (0.56 mL, 4.0 mmol) and 10 mm stainless steel ball are loaded into the miller jar. The mixture is subjected to 30 Hz milling for 9 hours. The product is then extracted with Tol and ammonium salt is filtered off to obtain a clear solution. The filtrate is concentrated and left to crystallize at 5 °C to yield colourless crystals.

The crystals obtained are found to be *cis* isomer. Isolated crystalline yield: 0.061 g (15.7%); Mp: 216°C; $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3 , 162 MHz, δ): 105.11 (s); ^1H NMR (CDCl_3 , 400 MHz, δ): 8.29 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 4H, *m*-ArH), 6.89 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 4H, *o*-ArH), 5.48 (s, 2H, N-H), 1.26 (s, 18H, C(CH₃)₃); ^{13}C NMR (CDCl_3 , 101 MHz, δ): 150.63 (s, *m*-ArC), 111.46 (d, $^3J_{\text{P-C}} = 13.1$ Hz, *o*-ArC), 109.83 (s, N-ArC), 51.93 (t, $^2J_{\text{P-C}} = 13.1$ Hz, C(CH₃)₃), 31.13 (t, $^3J_{\text{P-C}} = 6.1$ Hz, C(CH₃)₃); IR (mineral oil, NaCl) ν (cm⁻¹): 3275 (N-H), 1591 (C=N); MS (EI) *m/z*: 391.22 [M+1]⁺; Despite several attempts satisfactory elemental analysis could not be obtained.^[2]

Table 2.14. Sample and crystal data for **5.1**.

Chemical formula	C ₁₈ H ₂₈ N ₆ P ₂
Formula weight	390.40 g/mol
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal size	0.080 x 0.100 x 0.380 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 13.0009(11) Å α = 90° b = 10.0904(8) Å β = 106.075(3)° c = 16.6209(14) Å γ = 90°
Volume	2095.1(3) Å ³
Z	4
Density (calculated)	1.238 g/cm ³
Absorption coefficient	0.222 mm ⁻¹
F(000)	832
Theta range for data collection	1.63 to 26.00°
Index ranges	-16 ≤ h ≤ 15, -12 ≤ k ≤ 12, -18 ≤ l ≤ 20
Reflections collected	23817
Independent reflections	4129 [R(int) = 0.1095]

Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.9820 and 0.9200
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4129 / 78 / 278
Goodness-of-fit on F ²	1.001
Final R indices	2369 data; I > 2 σ (I) R1 = 0.0483, wR2 = 0.0954 all data R1 = 0.1089, wR2 = 0.1217
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.0432P)^2 + 0.4678P]$ where $P = (F_o^2 + 2F_c^2) / 3$
Largest diff. peak and hole	0.268 and -0.259 e $\text{\AA}^{-3}$
R.M.S. deviation from mean	0.056 e $\text{\AA}^{-3}$

2.4.13 Preparation of [EtO(O=)CPh(H)NP(μ -N'Bu)]₂ (5.2)

To a mixture of [ClP(μ -N'Bu)]₂ (**3.0**) (0.275 g, 1.0 mmol) and ethyl 4-aminobenzoate (0.330 g, 2.0 mmol), Et₃N (0.28 mL, 2.0 mmol) and 10 mm stainless steel ball are added into the miller jar. The mixture is subjected to 30 Hz milling for 6 hours. The product is then extracted with THF and ammonium salt is filtered off to obtain a clear solution. The filtrate is concentrated and left to crystallize at room-temperature. Isolated crystalline yield: 0.237 g (44%); Mp: 166°C; ³¹P-{¹H} NMR (CDCl₃, 162 MHz, δ): 103.74 (s); ¹H NMR (CDCl₃, 400 MHz, δ): 7.91 (d, ³J_{H-H} = 8.8 Hz, 4H, *m*-ArH), 7.04 (d, ³J_{H-H} = 8.4 Hz, 4H, *o*-ArH), 5.26 (br s, 2H, N-H), 4.34 (q, ³J_{H-H} = 7.2 Hz, 4H, CH₂CH₃), 1.37 (t, ³J_{H-H} = 7.2 Hz, 6H, CH₂CH₃), 1.26 (s, 18H, C(CH₃)₃); ¹³C NMR (CDCl₃, 101 MHz, δ): 166.68 (s, C=O), 147.88 (d, ²J_{P-C} = 12.1 Hz, N-ArC), 131.47 (s, *m*-ArC), 122.35 (s, C-C=O), 116.24 (s, *o*-ArC), 60.63 (s, CH₂CH₃), 51.85 (t, ²J_{P-C} = 13.1 Hz, C(CH₃)₃), 31.15 (t, ³J_{P-C} = 6.1 Hz, C(CH₃)₃), 14.57 (s, CH₂CH₃); IR (mineral oil, NaCl) ν (cm⁻¹): 3177 (N-H), 1709 (C=O), 1601 (C=C), 1173 (C-O); MS (EI) *m/z*:

533.27 [M+1]⁺; Anal. Calcd for C₂₆H₃₈N₄O₄P₂: C, 58.64; H, 7.19; N, 10.52. Found: C, 58.43; H, 7.89; N, 10.33%.

Table 2.15. Sample and crystal data for **5.2**.

Chemical formula	C ₅₂ H ₇₂ N ₈ O ₈ P ₄	
Formula weight	1061.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.080 x 0.160 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 20.665(8) Å	α = 90°
	b = 8.996(3) Å	β = 96.153(16)°
	c = 30.851(11) Å	γ = 90°
Volume	5702.(3) Å ³	
Z	4	
Density (calculated)	1.236 g/cm ³	
Absorption coefficient	0.189 mm ⁻¹	
F(000)	2256	
Theta range for data collection	1.98 to 25.38°	
Index ranges	-24 ≤ h ≤ 24, -10 ≤ k ≤ 10, -36 ≤ l ≤ 36	
Reflections collected	35794	
Independent reflections	5143 [R(int) = 0.2754]	
Coverage of independent reflections	98.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9920 and 0.9700	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo ² - Fc ²) ²	
Data / restraints / parameters	5143 / 0 / 333	
Goodness-of-fit on F ²	1.013	
Final R indices	2639 data; I > 2σ(I)	R1 = 0.0836, wR2 = 0.2202
	all data	R1 = 0.1744, wR2 = 0.2893

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1628P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.562 and -0.830 eÅ ⁻³
R.M.S. deviation from mean	0.172 eÅ ⁻³

2.4.14 Preparation of [CNPh (O=COP(μ-N'Bu))₂] (5.3)

To a mixture of [ClP(μ-N'Bu)]₂ (**3.0**) (1.375 g, 5.0 mmol) and 4-cyanobenzoic acid (1.471 g, 10.0 mmol), Et₃N (1.40 mL, 10 mmol) and 10 mm stainless steel ball are added into the miller jar. The mixture is subjected to 30 Hz milling for 6 hours. The product is then extracted with Tol (10 mL) and followed by THF (10 mL). The combined extracts are concentrated and left to crystallize at room-temperature to give colourless block-like crystals. Isolated crystalline yield: 0.953 g (38%); Mp: 169-171°C; ³¹P-{¹H} NMR (CDCl₃, 162 MHz, δ): 172.97 (s); ¹H NMR (CDCl₃, 400 MHz, δ): 8.18 (d, ³J_{H-H} = 8.4 Hz, 4H, *o*-ArH), 7.76 (d, ³J_{H-H} = 8.4 Hz, 4H, *m*-ArH), 1.42 (s, 18H, C(CH₃)₃); ¹³C NMR (CDCl₃, 101 MHz, δ): 164.46 (s, C=O), 134.59 (s, C-C=O), 132.50 (s, *m*-ArC), 130.57 (s, *o*-ArC), 117.89 (s, C≡N), 117.03 (s, C-C≡N), 52.94 (t, ²J_{P-C} = 9.1 Hz, C(CH₃)₃), 31.02 (t, ³J_{P-C} = 6.1 Hz, C(CH₃)₃); IR (mineral oil, NaCl) ν (cm⁻¹): 2228(C≡N), 1699 (C=O), 1688 (C=O); MS (EI) *m/z*: 497.17 [M+1]⁺; Anal. Calcd for C₂₄H₂₆N₄O₄P₂: C, 58.07; H, 5.28; N, 11.29. Found: C, 58.01; H, 5.45; N, 10.86%.

Table 2.16. Sample and crystal data for **5.3**.

Chemical formula	C ₂₄ H ₂₆ N ₄ O ₄ P ₂
Formula weight	496.43
Temperature	103(2) K

Wavelength	0.71073 Å	
Crystal size	0.180 x 0.200 x 0.220 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 21.2150(11) Å	$\alpha = 90^\circ$
	b = 15.9181(8) Å	$\beta = 90^\circ$
	c = 14.9529(7) Å	$\gamma = 90^\circ$
Volume	5049.6(4) Å ³	
Z	8	
Density (calculated)	1.306 g/cm ³	
Absorption coefficient	0.209 mm ⁻¹	
F(000)	2080	
Theta range for data collection	2.10 to 31.72°	
Index ranges	-31 ≤ h ≤ 31, -22 ≤ k ≤ 23, -22 ≤ l ≤ 22	
Reflections collected	74933	
Independent reflections	8537 [R(int) = 0.1032]	
Coverage of independent reflections	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9630 and 0.9550	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8537 / 0 / 313	
Goodness-of-fit on F ²	1.020	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	5468 data; $I > 2\sigma(I)$	R1 = 0.0462, wR2 = 0.1014
	all data	R1 = 0.0940, wR2 = 0.1270
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0490P)^2 + 2.0420P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.439 and -0.472 eÅ ⁻³	
R.M.S. deviation from mean	0.074 eÅ ⁻³	

2.4.15 Preparation of [Pyr(H)NP(μ -N'Bu)]₂ (5.4)

To a mixture of [ClP(μ -N'Bu)]₂ (**3.0**) (1.375 g, 5.0 mmol) and 2-pyrimidinamine (0.950 g, 10.0 mmol), Et₃N (1.40 mL, 10 mmol) and 10 mm stainless steel ball are added into the miller jar. The mixture is subjected to 30 Hz milling for 6 hours. The product is then extracted with THF (10 mL) three times. The combined extracts are concentrated and left to crystallize at room-temperature to give colourless block-like crystals. Isolated crystalline yield: 0.451 g (23%); ³¹P-{¹H} NMR (CDCl₃, 162 MHz,

δ): 110.92 (s). ^1H NMR (C_6D_6 , 400 MHz, δ): 7.98 (d, $^3J_{\text{H-H}} = 4.0$ Hz, 4H, *o*-ArH), 6.07 (t, $^3J_{\text{H-H}} = 6.0$ Hz, 2H, *m*-ArH), 1.31 (s, 18H, $\text{C}(\text{CH}_3)_3$); Other characterization is unsuccessful because of the super sensitivity of **5.4** towards air and moisture.

Table 2.17. Sample and crystal data for **5.4**.

Chemical formula	$\text{C}_{20}\text{H}_{31}\text{N}_{11}\text{P}_2$	
Formula weight	487.50 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.200 x 0.400 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 8.9258(15)$ Å	$\alpha = 91.050(11)^\circ$
	$b = 9.4035(17)$ Å	$\beta = 103.071(9)^\circ$
	$c = 15.634(2)$ Å	$\gamma = 104.914(11)^\circ$
Volume	$1231.1(4)$ Å ³	
Z	2	
Density (calculated)	1.315 g/cm ³	
Absorption coefficient	0.209 mm ⁻¹	
F(000)	516	
Theta range for data collection	3.16 to 28.19°	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20	
Reflections collected	18403	
Independent reflections	5921 [R(int) = 0.1176]	
Coverage of independent reflections	97.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9630 and 0.9210	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$	
Data / restraints / parameters	5921 / 0 / 304	
Goodness-of-fit on F ²	0.999	
Final R indices	3075 data; I > 2σ(I)	R1 = 0.0680, wR2 = 0.1205
	all data	R1 = 0.1563, wR2 = 0.1506

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0513P)^2+0.0334P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.386 and -0.550 eÅ ⁻³
R.M.S. deviation from mean	0.087 eÅ ⁻³

2.4.16 Preparation of P₄(N^{*i*}Pr)₆ (**5.5**)

Before using, the grinding jar was dried at 180 °C for 2 hours. A 10 mm steel ball bearing, [$\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ (**4.8**) (0.1 g, 0.2 mmol) and LiCl (0.02 g, 20%) were loaded into the grinding jar in glove box where the grinder was sealed. Following by 1 hour of milling at a frequency of 30 Hz, compound [$\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ (**4.8**) fully rearranged to P₄(N^{*i*}Pr)₆ (**5.5**) as indicated by *in situ* ³¹P-{¹H} NMR in Tol. Crystallization in Tol yielded colourless crystals. Isolated yield: 0.06 g (60%).

Table 2.18. Sample and crystal data for **5.5**.

Chemical formula	C ₁₆ H _{37.33} N _{5.33} P _{3.56}	
Formula weight	414.63 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.400 x 0.420 mm	
Crystal habit	colorless plate	
Crystal system	orthorhombic	
Space group	P b c m	
Unit cell dimensions	a = 9.6100(3) Å	α = 90°
	b = 35.6117(17) Å	β = 90°
	c = 30.3387(11) Å	γ = 90°
Volume	10382.8(7) Å ³	
Z	18	
Density (calculated)	1.194 g/cm ³	
Absorption coefficient	0.307 mm ⁻¹	
F(000)	4032	

Theta range for data collection	1.14 to 26.42°
Index ranges	-12<=h<=7, -44<=k<=31, -37<=l<=37
Reflections collected	49688
Independent reflections	10836 [R(int) = 0.1691]
Coverage of independent reflections	99.7%
Absorption correction	multi-scan
Max. and min. transmission	0.9640 and 0.8820
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10836 / 1783 / 881
Goodness-of-fit on F ²	1.055
$\Delta/\sigma_{\max}$	0.001
Final R indices	5062 data; $I > 2\sigma(I)$ R1 = 0.1216, wR2 = 0.3083 all data R1 = 0.2440, wR2 = 0.4014
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1818P)^2 + 41.2446P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.751 and -1.334 eÅ ⁻³
R.M.S. deviation from mean	0.290 eÅ ⁻³

2.4.17 Preparation of P₄(N^tBu)₆ (**5.6**)

Before using, the grinder was dried at 180 °C for 2 hours. [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})\}_2$ (**4.1**) (0.1 g, 0.18 mmol) and LiCl (0.02 g, 20%) were added into a grinding jar loaded with a 10 mm ball. The loading and sealing of the grinding jar was performed under inert atmosphere conditions. Following by 1 hour milling at a frequency of 30 Hz, [$\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})\}_2$ (**4.1**) fully rearranged into compound **4** as shown by the in situ ³¹P-¹H} NMR in Tol. Crystals of P₄(N^tBu)₆ (**5.6**) were obtained by slow evaporation of the solvent at room-temperature. Isolated yield: 0.053 g (53%). Mp: 259.7 °C. ³¹P-¹H} NMR (121 MHz, C₆D₆, δ): 54.47 (s). ¹H NMR: (300 MHz, C₆D₆, δ) 1.51 (s, 54H). ¹³C NMR: (75 MHz, C₆D₆, δ) 59.29 (s), 31.38 (s). IR (Nujol, NaCl), ν (cm⁻¹): 800 (s, $\nu(\text{P}-\text{N})$). m/z 551.37 [M+1]⁺. Anal. Calcd for C₂₄H₅₄N₆P₄: C, 52.35; H, 9.88; N, 15.26. Found: C, 52.44; H, 9.82; N, 14.94.

Table 2.19. Sample and crystal data for **5.6**.

Bond precision: N- C = 0.0060 Å Wavelength=1.54184
Cell: a=16.7939(8) b=16.7939(8) c=9.6854(5)
alpha=90 beta=90 gamma=120
Temperature: 173 K
Calculated Reported
Volume 2365.7(3) 2365.7(3)
Space group P -3 m 1 P -3 m 1
Hall group -P 3 2" -P 3 2"
Moiety formula C ₂₄ H ₅₄ N ₆ P ₄ C ₂₄ H ₅₄ N ₆ P ₄
Sum formula C ₂₄ H ₅₄ N ₆ P ₄ C ₂₄ H ₅₄ N ₆ P ₄
Mr 550.61 550.61
Dx, g cm ⁻³ 1.160 1.159
Z 3 3
Mu (mm ⁻¹) 2.378 2.378
F ₀₀₀ 900.0 900.0
F ₀₀₀ ' 905.26
h,k,lmax 20,20,11 20,20,11
Nref 1691 1680
Tmin,Tmax 0.514,0.552 0.707,1.000
Tmin' 0.467
Correction method= MULTI-SCAN
Data completeness= 0.993 Theta(max)= 70.560
R(reflections)= 0.0728(1500) wR2(reflections)= 0.2142(1680)
S = 1.078 Npar= 162

2.4.18 Preparation of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^i\text{Pr})P(\mu\text{-N}^t\text{Bu})_2PN(\text{H})^t\text{Bu}]_2$ (6.3)

A solution of $[\text{}^i\text{Pr}(\text{Li})\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ (1.42 g, 4.29 mmol) in Tol (20 mL) was dropwise added to a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})\text{PN}(\text{H})^t\text{Bu}]_2$ (2.67 g, 8.58 mmol) in Tol at 0 °C which was carried out ice/water bath. The mixture was then set to reflux at 120 °C for 3 hours, resulting suspension mixture was filtered through celite (P3). The residue was washed with Tol (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of hot Tol. Storage at room-

temperature afforded colourless crystals. Yield: 1.38 g (37 %). Mp: 207 °C; $^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz, C_6D_6 , δ): 110.56 (s), 108.35 (d, $J = 90.7$ Hz), 99.22 (d, $J = 95.6$ Hz). ^1H NMR (400 MHz, C_6D_6 , δ): 5.65 (s, 2H, **NH**), 4.61 (m, 2H, **CH**(CH_3)₂), 1.63 (s, 18H, **NHC**(**CH**₃)₃), 1.48 (s, 54H, **NC**(**CH**₃)₃), 1.35 (d, $J = 0.8$ Hz, 12H, **CH**(**CH**₃)₂). ^{13}C NMR (101 MHz, C_6D_6 , δ): 54.8 (s, **NC**(**CH**₃)₃), 51.3 (s, **NHC**(**CH**₃)₃), 44.4 (s, **CH**(**CH**₃)₂), 33.2 (d, $J = 10.0$ Hz, **NC**(**CH**₃)₃), 30.1 (t, $J = 7.0$ Hz, **NC**(**CH**₃)₃), 26.2 (t, $J = 8.0$ Hz, **CH**(**CH**₃)₂). MS (EI) m/z : 871.53 [$\text{M}+1$]⁺. Anal. Calcd for $\text{C}_{38}\text{H}_{88}\text{N}_{10}\text{P}_6$: C, 52.40; H, 10.18; N, 16.08. Found: C, 52.37; H, 10.14; N, 16.07 %.

Table 2.20. Sample and crystal data for **6.3**.

Chemical formula	$\text{C}_{41.50}\text{H}_{92}\text{N}_{10}\text{P}_6$	
Formula weight	917.07 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.280 x 0.360 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	$a = 9.7528(5)$ Å	$\alpha = 90^\circ$
	$b = 31.0754(13)$ Å	$\beta = 99.0455(15)^\circ$
	$c = 18.2261(7)$ Å	$\gamma = 90^\circ$
Volume	$5455.1(4)$ Å ³	
Z	4	
Density (calculated)	1.117 g/cm ³	
Absorption coefficient	0.234 mm ⁻¹	
F(000)	2004	
Theta range for data collection	2.24 to 28.32°	
Index ranges	-13 ≤ h ≤ 7, -41 ≤ k ≤ 40, -24 ≤ l ≤ 24	
Reflections collected	58361	
Independent reflections	13533 [R(int) = 0.0851]	
Max. and min. transmission	0.9950 and 0.9210	
Refinement method	Full-matrix least-squares on F ²	

Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13533 / 1302 / 841
Goodness-of-fit on F2	1.017
$\Delta/\sigma_{\max}$	0.001
Final R indices	8127 data; $I > 2\sigma(I)$ R1 = 0.0562, wR2 = 0.1273 all data R1 = 0.1158, wR2 = 0.1543
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 1.1714P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.594 and -0.443 eÅ ⁻³
R.M.S. deviation from mean	0.081 eÅ ⁻³

2.4.19 Preparation of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-NH})P(\mu\text{-N}^t\text{Bu})_2PN(\text{H})^t\text{Bu}]_2$ (6.4)

A solution of $[\text{H}_2\text{NP}(\mu\text{-N}^t\text{Bu})]_2$ (1.01 g, 4.29 mmol) in THF (20 mL) was dropwise added to a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})PN(\text{H})^t\text{Bu}]_2$ (2.67 g, 8.58 mmol) in THF at 0 °C which was carried out ice/water bath. The mixture was then allowed to warm back to room-temperature stir for overnight, resulting suspension mixture was filtered through celite (P3). The residue was washed with THF (3 x 10 mL). The solvent was removed under vacuum and the white solid obtained was dissolved in the minimum amount of hot THF. Storage at room-temperature afforded colourless crystals. Yield: 2.80 g (83 %). Mp: 162 °C; $^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz, C₆D₆, δ): 113.8 (d, $J = 97.2$ Hz), 104.8 (s), 101.4 (d, $J = 64.8$ Hz). ^1H NMR (400 MHz, C₆D₆, δ): 5.29 (s, 2H, NH^tBu), 3.08 (s, 2H, NH), 1.49 (s, 54H, $\text{NC}(\text{CH}_3)_3$), 1.28 (s, 18H, $\text{NHC}(\text{CH}_3)_3$). ^{13}C NMR (101 MHz, C₆D₆, δ): 53.9 (s, $\text{NC}(\text{CH}_3)_3$), 52.7 (s, $\text{NC}(\text{CH}_3)_3$), 51.7 (s, $\text{NHC}(\text{CH}_3)_3$), 33.4 (t, $J = 10.0$ Hz, $\text{NC}(\text{CH}_3)_3$), 31.9 (t, $J = 7.0$ Hz, $\text{NC}(\text{CH}_3)_3$), 30.6 (t, $J = 8.0$ Hz, $\text{NC}(\text{CH}_3)_3$). MS (EI) m/z : 787.51 $[\text{M}+1]^+$. Anal. Calcd for C₃₂H₇₆N₁₀P₆: C, 48.85; H, 9.74; N, 17.80. Found: C, 48.81; H, 9.79; N, 17.82 %.

2.4.20 Preparation of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})P(\mu\text{-N}^t\text{Bu})_2PN(\text{H})^t\text{Bu}]_2$ (6.5)

A solution of $[\text{LiO}\{P(\mu\text{-N}^t\text{Bu})\}]_2$ (4.29 mmol) in THF (20 mL) was generated *in situ* by controlled hydrolysis of $[\text{ClP}(\mu\text{-N}^t\text{Bu})\text{P}]_2$ (1.18 g, 4.29 mmol) at 0 °C followed by lithiation using *n*-BuLi at room-temperature. Then it was dropwise added to a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})PN(\text{H})^t\text{Bu}]_2$ (2.67 g, 8.58 mmol) in THF at 0 °C which was carried out ice/water bath. The mixture was then allowed to warm back to room-temperature stir for overnight. The solvent was removed under vacuum and the residue was extracted with pentane (10 mL) three times. The solvent of the combined solution was removed under vacuum and obtained white solid was dissolved in the minimum amount of hot hexane. Storage at room-temperature afforded colourless crystals. Yield: 1.89 g (56 %). Mp: 156 °C; $^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz, C_6D_6 , δ): 140.4 (dd, $J = 76.1$ Hz, $J = 147.4$ Hz), 119.2 (s). ^1H NMR (400 MHz, C_6D_6 , δ): 3.37 (s, 2H), 1.56 (s, 18H), 1.50 (s, 36H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, C_6D_6 , δ): 52.4 (s), 51.9 (s), 33.2 (t, $J = 9.0$ Hz), 31.9 (s), 31.7 (t, $J = 8.0$ Hz). MS (EI) m/z : 789.42 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{32}\text{H}_{74}\text{N}_8\text{O}_2\text{P}_6$: C, 48.72; H, 9.46; N, 14.21. Found: C, 48.69; H, 9.43; N, 14.24 %.

Table 2.21. Sample and crystal data for **6.5**.

Chemical formula	$\text{C}_{32}\text{H}_{74}\text{N}_8\text{O}_2\text{P}_6$
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Formula weight	788.81 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.100 x 0.220 mm	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 20.0290(5) Å	$\alpha = 90^\circ$
	b = 23.3627(7) Å	$\beta = 90^\circ$
	c = 9.6838(3) Å	$\gamma = 90^\circ$
Volume	4531.4(2) Å ³	
Z	4	
Density (calculated)	1.156 g/cm ³	
Absorption coefficient	0.273 mm ⁻¹	
F(000)	1712	
Theta range for data collection	1.74 to 27.92°	
Index ranges	-25 ≤ h ≤ 26, -30 ≤ k ≤ 30, -8 ≤ l ≤ 12	
Reflections collected	80110	
Independent reflections	5558 [R(int) = 0.0876]	
Max. and min. transmission	0.9890 and 0.9420	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5558 / 18 / 354	
Goodness-of-fit on F ²	1.066	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	4145 data; I > 2σ(I)	R1 = 0.0513, wR2 = 0.1127
	all data	R1 = 0.0790, wR2 = 0.1274
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 8.8080P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.408 and -0.393 eÅ ⁻³	
R.M.S. deviation from mean	0.065 eÅ ⁻³	

2.4.21 Syntheses of $\{(\mu\text{-O})[\text{P}(\mu\text{-N}^t\text{Bu})]_2\}_6$ (6.6)

First, the trimer $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$ (6.7) was generated *in situ* by following process. A solution of $[\text{LiO}\{\text{P}(\mu\text{-N}^t\text{Bu})\}]_2$ (4.29 mmol) in THF (20 mL) was generated *in situ* by controlled hydrolysis of $[\text{ClP}(\mu\text{-N}^t\text{Bu})\text{P}]_2$ (1.18 g, 4.29 mmol) at 0 °C followed by lithiation using *n*-BuLi at room-temperature. Then it was dropwise added to a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})\text{P}]_2$ (2.36 g, 8.58 mmol) in THF at -78 °C which was allowed to warm back to room-temperature and stir for overnight. This procedure

was duplicated to provide the second batch and same amount of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})P(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$ (**6.7**), further controlled hydrolysis of it was conducted at 0 °C followed by lithiation using *n*-BuLi at room-temperature produced $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})P(\mu\text{-N}^t\text{Bu})_2\text{POLi}]_2$ *in situ* in THF. Then $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})P(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$ was dropwise added to a solution of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})P(\mu\text{-N}^t\text{Bu})_2\text{POLi}]_2$ in THF at -78 °C. The mixture was then allowed to warm back to room-temperature stir for overnight. The solvent was removed under vacuum and extracted with pentane (10 mL) three times. The solvent of the combined solution was removed under vacuum and obtained white solid was dissolved in the minimum amount of hot hexane. Storage at room-temperature afforded colourless crystals. Yield: 1.75 g (31%). $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , δ): 135.9 (s). ^1H NMR (400 MHz, C_6D_6 , δ): 1.38 (s, 108H). ^{13}C NMR (101 MHz, C_6D_6 , δ): 52.7 (s), 32.3 (s). MS (EI) m/z : 1321.57 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{48}\text{H}_{108}\text{N}_{12}\text{O}_6\text{P}_{12}$: C, 43.64; H, 8.24; N, 12.72. Found: C, 43.61; H, 8.19; N, 12.74 %.

Table 2.22. Sample and crystal data for **6.6**.

Chemical formula	$\text{C}_{48}\text{H}_{108}\text{N}_{12}\text{O}_6\text{P}_{12}$
Formula weight	1321.10 g/mol
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.060 x 0.220 mm
Crystal habit	colorless needle
Crystal system	monoclinic
Space group	C 1 2/c 1

Unit cell dimensions	a = 21.7911(18) Å b = 17.0239(18) Å c = 21.1950(19) Å	$\alpha = 90^\circ$ $\beta = 106.148(6)^\circ$ $\gamma = 90^\circ$
Volume	7552.5(12) Å ³	
Z	4	
Density (calculated)	1.162 g/cm ³	
Absorption coefficient	0.316 mm ⁻¹	
F(000)	2832	
Theta range for data collection	1.54 to 25.32°	
Index ranges	-26<=h<=26, -20<=k<=20, -25<=l<=21	
Reflections collected	34579	
Independent reflections	6846 [R(int) = 0.2075]	
Coverage of independent reflections	99.0%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9870 and 0.9340	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6846 / 0 / 370	
Goodness-of-fit on F ²	0.979	
Final R indices	2454 data; I>2σ(I) all data	R1 = 0.0911, wR2 = 0.1949 R1 = 0.2541, wR2 = 0.2670
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1046P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.502 and -0.516 eÅ ⁻³	
R.M.S. deviation from mean	0.088 eÅ ⁻³	

Chapter 3: Syntheses and hydrolytic studies of air-stable [(4-CN-PhO)P(E)(μ -N^tBu)]₂ (E = O, S and Se) cyclodiphosph(V/V)azanes

3.1 Introduction

Organic frameworks have been extensively studied during past decades for a myriad of applications, while inorganic frameworks, composed of non-carbon backbones, still remain as mere chemical curiosities due to the much greater kinetic lability of the inorganic bonds. This is due to their bond polarity, as well as, their variable hybridization and oxidation states.⁸⁷ Besides the major synthetic challenge is posed in the design of robust molecular inorganic frameworks.⁸⁸ The instability of these particular systems containing saturated P-N frameworks, which are of significant interest to our group, has previously undermined the exploration of their use in technological applications.⁸⁹

Cyclodiphosph(III/III)azanes, $[R'P(\mu-NR)]_2$, with a variety of substituents (R or R') have been extensively studied over the past decades.^{13,54,56,90} One of the main reasons, is that they are excellent building blocks for the construction of a myriad of cage^{33,41} and macrocyclic arrangements.^{32,42,43,91} Also, precursors $[CIP(\mu-NR)]_2$ are readily functionalized by nucleophilic substitutions with a variety of nucleophiles,⁹²⁻⁹⁵ which offers them unprecedented versatility as building blocks for the synthesis of a range of multidentate ligands to transition metals.⁹⁶⁻⁹⁸

The general intrinsic bond lability of functionalized cyclodiphosph(III/III)azanes and cyclodiphosph(V/V)azane frameworks (*e.g.*, with nitrile, carboxylic acid, *etc.*) renders these species incapable of tolerating the standard reaction conditions required for many simple organic transformations. Furthermore, a large volume of literature has shown that the cyclodiphosphazane-based compounds are extremely air- and moisture-sensitive. Very few examples have been reported for air-stable cyclodiphosphazane compounds.^{14,46,99} For example, Balakrishna *et al.* reported that the cyclodiphosph(III/III)azane dimers of the type $[RP(\mu-N'Bu)]_2$ (R = morpholine and N-

methyl piperazine)⁹¹ and the acyclic dimer $R[P(\mu\text{-N}^t\text{Bu})]_2\text{PNH}^t\text{Bu}]_2$ (R = resorcinol)¹⁰⁰ are moderately air and moisture stable in both solution and the solid state. Also, the oxidised product of $\{(OCH_2CMe_2CH_2O)[P(\mu\text{-N}^t\text{Bu})]_2\}_2$ with *o*-chloranil reported by Swamy *et al.* exists as an air-stable 16-membered macrocycle, while, the addition products of cyclodiphosph(III/III)azanes with diketones are unstable.¹⁰¹ More surprisingly, Chivers *et al.* reported the synthesis of the mono-telluride $[^t\text{Bu(H)N(Te)P}(\mu\text{-N}^t\text{Bu})_2\text{PN(H)}^t\text{Bu}]$ to be moderately air-stable, which is remarkable for cyclodiphosphazane telluride derivatives.¹⁰²

Figure 3.1 Structures of $\{(OCH_2CMe_2CH_2O)[P(\mu\text{-N}^t\text{Bu})]_2\}_2$ (left) and $[^t\text{Bu(H)N(Te)P}(\mu\text{-N}^t\text{Bu})_2\text{PN(H)}^t\text{Bu}]$ (right).

The chalcogen oxidised cyclodiphosph(V/V)azanes derivatives of the type $[R'(H)N(E)P(\mu\text{-NR})]_2$ (E = O, S and Se) display different sensitivity depending which chalcogen elements was used during the oxidation. Balakrishna *et al.* synthesized series of this type compound (R = Cy, ^tBu and R' = Cy, ^tBu), for those compounds shown in *Scheme 3.1*, the bis(oxo) and bis(sulfide) oxidised products were moderately stable upon exposure to air and moisture; whereas the bis(selenide) derivatives proved to be air and moisture sensitive and, therefore, needed to be handled under strict inert conditions.⁹³

Scheme 3.1 Synthetic routes of $[R'(H)N(E)P(\mu-NR)]_2$ ($E = O, S$ and Se).

In this section, the cyclodiphosph(III/III)azane $[(4\text{-CN-PhO})P(\mu\text{-N'Bu})]_2$ and its oxidised derivatives $[(4\text{-CN-PhO})(E)P(\mu\text{-N'Bu})]_2$ ($E = O, S$ and Se) were synthesized and fully characterized. These newly synthesized derivatives $[(4\text{-CN-PhO})(E)P(\mu\text{-N'Bu})]_2$ ($E = O, S$ and Se) displayed high water and moisture stability. To the best of our knowledge, this is the first example of a series of oxidised derivatives obtained from a single cyclodiphosph(III/III)azane precursor, which are air-stable over prolonged periods of time.

3.2 Syntheses of compounds 3.1-3.4

Scheme 3.2 Synthetic routes of $[(4\text{-CN-PhO})P(\mu\text{-N'Bu})]_2$ (**3.1**).

The air- and moisture-sensitive cyclodiphosph(III/III)azane $[(4\text{-CN-PhO})P(\mu\text{-N'Bu})]_2$ (**3.1**) was prepared by the reaction of $[ClP(\mu\text{-N'Bu})]_2$ with 2 equivalents of 4-CN-

PhOH, 4-hydroxybenzonitrile, in the presence of Et₃N, as a Brønsted base, in 84% isolated yield by crystallization (*Scheme 3.2*).

The presence of only one singlet resonance in the ³¹P-{¹H} NMR spectrum of **3.1** at 143.79 ppm (*cf.*, 207.23 ppm in [ClP(μ-N^tBu)]₂) indicates that there is only one isomer of **3.1** present in solution.^{74,103} The two doublets at 7.79 and 7.37 ppm with a coupling constant of 9 Hz in the room-temperature ¹H NMR spectrum of **3.1** are corresponding to the *meta* and *ortho* protons on the *para*-substituted benzene ring, respectively; the single resonance corresponds to the *tert*-butyl groups at 1.37 ppm. The total number of protons of the above mentioned three resonances is 26 with intensity ratio of 1:1:4.5. Furthermore, the typical stretches for a nitrile group and aromatic rings can also be detected in IR spectrum of **3.1** at 2220 and 1597 cm⁻¹, respectively. Further oxidization of compound **3.1** with ^tBuOOH, and elemental S and Se¹⁰⁴⁻¹⁰⁸ was conducted to produce [(4-CN-PhO)(O)P(μ-N^tBu)]₂ (**3.2**), [(4-CN-PhO)(S)P(μ-N^tBu)]₂ (**3.3**) and [(4-CN-PhO)(Se)P(μ-N^tBu)]₂ (**3.4**), respectively (*Scheme 3.3*).

Scheme 3.3 Synthetic routes of [(4-CN-PhO)(O)P(μ-N^tBu)]₂ (**3.2**), [(4-CN-PhO)(S)P(μ-N^tBu)]₂ (**3.3**) and [(4-CN-PhO)(Se)P(μ-N^tBu)]₂ (**3.4**).

The dioxide derivative **3.2** is present as a single isomer in solution as shown by a single resonance at -7.84 ppm in its ³¹P-{¹H} NMR spectrum (*cf.*, **3.1**, δ 143.79),^{74,103} which is comparable with previously reported doubly-oxidised cyclophosph(V/V)azane derivatives (*cf.*, -6.00 in [(2,6-Me₂C₆H₃O)P(O)(μ-N^tBu)]₂).¹⁰⁹

In contrast, both bis(sulfide) (**3.3**) and bis(selenide) (**3.4**) derivatives show two resonances in their $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra, at 51.36 and 46.17 ppm, and at 47.04 and 39.56 ppm, respectively, indicating the existence of both *cis* and *trans* isomers in solution (Figure 3.2). Similar to that of compound **3.1**, the structure of compounds **3.2**, **3.3** and **3.4** has been further verified by various spectroscopies.

Figure 3.2 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **3.1-3.4**.

Alternative synthetic routes for the synthesis of compounds **3.1-3.4** were also studied. For example, the precursor $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]_2$ was firstly oxidised with $t\text{BuOOH}$, and elemental S and Se to generate derivatives of the type $[\text{Cl}(\text{E})\text{P}(\mu\text{-N}^t\text{Bu})_2]_2$, E = O (**3.5**), S (**3.6**) and Se (**3.7**), respectively. The corresponding cyclodiphosph(V/V)azane $[\text{Cl}(\text{E})\text{P}(\mu\text{-N}^t\text{Bu})_2]_2$ (E = O, S and Se) obtained were further reacted with 4-CN-PhOH/ Et_3N (route I) or 4-CN-PhOLi (route II) in a ratio of 1:2. Surprisingly, only compound **3.7** reacted with the nucleophile to produce the corresponding substituted product **3.4**, which was shown by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR studies. Unfortunately, there was no sign of formation of **3.2** and **3.3** during the reaction of 4-CN-PhOH/ Et_3N (route I) or 4-CN-PhOLi (route II) with **3.5** and **3.6** even after prolonged refluxing (Scheme 3.4).

Scheme 3.4 Attempted alternative synthetic routes for the synthesis of compounds **3.1-3.4**.

3.3 Crystal structures of compounds **3.1-3.4**

The low-temperature X-ray single crystal studies provided further evidence consistent with the proposed structures from our initial spectroscopic analyses. *Figures 3.3-3.6* show the solid-state structures of compounds **3.1- 3.4** including selected bonds lengths and angles. Compound **3.1** crystallized with four molecules per unit cell in the chiral space group $P2_12_12_1$. The P_2N_2 ring is puckered with a dihedral angle of 13.93° between N(1)/P(1)/N(2) and N(1)/P(2)/N(2) (sum of internal angles 358.1°) with the phosphorus and nitrogen atoms lying $0.08 \text{ \AA}$ above and below with respect to the mean plane of the P_2N_2 ring. In the solid state, the 4-CN-Ph-O groups in compound **3.1** adopt a *cis* (*exo, endo*) conformation,⁷³ and they are almost perpendicular to each other with a dihedral angle of 79.33° (*cf.*, [(2,6-Me₂C₆H₃O)P(μ -N^tBu)]₂, dihedral angle 88°).^{26,110} The mean P-N and P-O distances ($1.71 \text{ \AA}$ and $1.66 \text{ \AA}$) are within the range found for analogous compounds (*cf.*, [(2,6-Me₂C₆H₃O)P(μ -N^tBu)]₂ and [(C₆F₅O)P(μ -N^tBu)]₂; P-N 1.71 and $1.70 \text{ \AA}$, and P-O 1.66 and $1.69 \text{ \AA}$ respectively).^{26,109,110}

Figure 3.3 Molecular structure of *cis* (*exo*, *endo*) isomer of **3.1** showing all non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: N(1)-P(1) 1.705(1), N(1)-P(2) 1.720(1), N(2)-P(1) 1.696(1), N(2)-P(2) 1.702(1), P(1)-O(1) 1.678(1), P(2)-O(2) 1.658(1), P(1)-N(1)-P(2) 96.92(7), P(1)-N(2)-P(2) 97.97(7), N(2)-P(1)-N(1) 81.89(6), N(2)-P(2)-N(1) 81.27(6).

The cyclodiphosph(V/V)azane compounds **3.2-3.4** obtained displayed shorter P(V)-N and P(V)-O distances as compared to the unoxidised precursor **3.1**.¹⁰⁹ Less acute angles around the phosphorus atoms in the P₂N₂ rings, which can be seen for most of the analogous oxidised cyclodiphosph(III/III)azanes,¹⁰⁶ can be associated with both the absence of sterically demanding lone pair of electrons and the greater inductive effect of the P(V) atoms.⁴⁹ As shown in *Figure 3.4*, **3.2** crystallizes in the P2₁ space group, which consists of one molecule of cyclodiphosph(V/V)azane in the asymmetric unit and the 4-CN-Ph-O substituents adopt a *cis* (*endo*, *endo*) conformation. The dihedral angle between the planes of the aromatic rings is 41.8° (*cf.*, **3.1**, 79.3°) and the P₂N₂ ring is almost planar and slightly puckered only by 1.19° (sum of angles *ca.* 360°). The mean bond length of P=O, P-O and P-N is 1.459 Å, 1.591 Å and 1.663 Å, respectively, which is comparable with previously reported [R(O)P(μ-NR')]₂ analogues.^{50,109,111,112}

Figure 3.4 Molecular structure of the *cis (endo, endo)* isomer of **3.2** showing all non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: N(1)-P(2) 1.658(2), N(1)-P(1) 1.663(2), N(2)-P(2) 1.666(2), N(2)-P(1) 1.667(2), O(1)-P(1) 1.593(2), O(2)-P(1) 1.458(2), O(3)-P(2) 1.589(2), O(4)-P(2) 1.460(2), P(2)-N(1)-P(1) 94.85(1), P(2)-N(2)-P(1) 94.37(1), N(1)-P(1)-N(2) 85.28(1), N(1)-P(2)-N(2) 85.48(1).

Compounds **3.3** and **3.4** are shown in *Figures 3.5* and *3.6*. All their geometrical parameters, which can be found in *Chapter 2*, fall within the expected ranges for similar compounds of the type $[\text{RP}(\text{E})(\mu\text{-NR}')_2]$ ($\text{E} = \text{S}$ and Se) reported in the literatures.¹¹³⁻¹¹⁶ However, unlike compound **3.2**, *cis* (a) and *trans* (b) isomers of **3.3** and **3.4** can be separated by crystallization in acetone and THF at room-temperature. For structure of compounds **3.2**, **3.3a** and **3.3b**, the 4-CN-Ph-O substituents adopt an *endo-endo* configuration, whereas both *endo-endo* and *endo-exo* conformations are observed in **3.4a** and **3.4b**, which can probably be explained by the larger size of selenium compared to oxygen and sulphur. In **3.3a** and **3.4a**, the P_2N_2 rings are puckered by 4.84° and 8.62° (*cf.*, 13.9° in **3.1** and 1.2° in **3.2**), and the dihedral angles between the phenyl rings are 82.98° and 58.0° respectively; whereas the phenyl group substituents on the almost perfectly planar P_2N_2 rings in **3.3b** and **3.4b** are parallel to each other.

Figure 3.5 *Cis (endo, endo) isomer of 3.3a (left) and trans (endo, endo) isomer of 3.3b (left) showing all non-hydrogen atoms. Selected bond lengths [Å] and angles [°] for 3.3a: N(1)-P(2) 1.669(5), N(1)-P(1) 1.686(5), N(2)-P(2) 1.673(5), N(2)-P(1) 1.669(5), O(1)-P(1) 1.607(4), O(2)-P(2) 1.598(4), P(1)-S(1) 1.911(2), P(2)-S(2) 1.918(2), P(2)-N(1)-P(1) 95.1(3), P(2)-N(2)-P(1) 95.6(3), N(1)-P(1)-N(2) 84.3(2), N(1)-P(2)-N(2) 84.7(2). Selected bond lengths [Å] and angles [°] for 3.4b: N(2)-P(1) 1.680(1), N(3)-P(2) 1.696(1), O(1)-P(1) 1.622(9), O(2)-P(2) 1.622(0), P(1)-S(1) 1.904(5), P(2)-S(2) 1.896(5), P(1)-N(2)-P(1) 94.1(6), P(2)-N(3)-P(2) 95.8(5), N(2)-P(1)-N(2) 84.2(5), N(3)-P(2)-N(3) 85.9(6).*

An interesting feature of the lattice adopted by **3.4b** is the presence of triads of molecules forming a conical frustum supramolecular arrangement with diameters of 6.71 and 11.42 Å. Each diameter is defined by the circle circumscribing the equilateral triangle defined by the endo-meta (C15) and exo-ortho (C12) carbons and on each of the three phenyl groups (*Figure 3.7*, top). The planes of the aromatic rings are inclined 33.02° with respect to the mean plane defined by the three P(1) atoms on each of the molecules forming part of the triad. This arrangement resembles calixarene coordinated and uncoordinated structures.^{118,119} The presence of two water molecules with partial occupancy (0.05 and 0.11) within the cavities is a further similarity shown with calixarene arrangements. The vertical staggered stacking, rotated by 60°, of two of the ‘calixarene’ supramolecular arrangements through the open faces create ellipsoidal voids (axis of *ca.* 9.69 and 3.42 Å) in the lattice. The aggregation into infinite

columns of these ellipsoidal cavities parallel to the c-axis of the unit cell forms an ‘allihn condenser’ type channel.

Figure 3.6 Cis (*exo, endo*) isomer of **3.4a** (left) and trans (*endo, endo*) isomer of **3.4b** (right) showing all non-hydrogen atoms. Selected bond lengths [Å] and angles [°] for **3.4a**: N(1)-P(2) 1.676(2), N(1)-P(1) 1.684(2), N(2)-P(2) 1.685(2), N(2)-P(1) 1.683(2), O(1)-P(1) 1.611(2), O(2)-P(2) 1.605(2), P1-Se(1) 2.062(1), P(2)-Se(2) 2.062(1), P(2)-N(1)-P(1) 95.27(1), P(2)-N(2)-P(1) 94.99(1), N(1)-P(1)-N(2) 84.43(1), N(1)-P(2)-N(2) 84.61(1). Selected bond lengths [Å] and angles [°] for **3.4b**: P(1)-N(1) 1.675(6), P(1)-N(1#1) 1.665(6), N(1)-P(1#1) 1.665(6), P(1)-O(1) 1.594(5), Se(1)-P(1) 2.056(2); N(1#1)-P(1)-N(1) 84.7(3), N(1#1)-P(1)-Se(1) 122.3(2), N(1)-P(1)-Se(1) 121.9(2), O(1)-P(1)-N(1) 106.2(3), P(1#1)-N(1)-P(1) 95.3(3). Symmetry transformations used to generate equivalent atoms: #1 – $x+1, -y, -z$.

Figure 3.7 Unit cell of **3.4b** along *c*-axis (top), channel formed by 4-CN-Ph-O groups along the *a*-axis (bottom). *H* atoms have been omitted for clarity.

3.4 Air and hydrolytic stability

The different range of stabilities displayed by previously reported cyclodiphosphazane derivatives (*vide supra*) led us to further investigate the air and hydrolytic stability of compounds **3.2**, **3.3** and **3.4**. Surprisingly, the chalcogenide derivatives **3.2-3.4** were found to be remarkably air-stable, verified by $^{31}\text{P}\{-^1\text{H}\}$ NMR studies of samples stored “on the bench” over a period of more than three months (Figure 3.8).

Figure 3.8 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of compound **3.2**, **3.3** and **3.4** after exposed to air for 0, 60 and 120 days.

There are a few studies reporting air-stable cyclodiphosph(V/V)azane derivatives with different ranges of air-stabilities.^{14,46,99} However, as far as we know, no further studies were conducted on their hydrolytic stability. To explore this, 5 mg of each sample of **3.2**, **3.3** and **3.4** were dissolved in $\text{D}_8\text{-THF}/\text{D}_2\text{O}$ mixtures (1:0; 1:8; 1:4 and 1:1 ratios) in NMR tubes, and the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were recorded (*Figure 3.9*). Slow hydrolysis was observed at room-temperature for compound **3.2** over a period of two days, whereas compounds **3.3** and **3.4** were found to be extremely inert to hydrolysis even at higher-temperatures. For example, there is no sign of any hydrolysis while heating the samples of **3.3** and **3.4**, dissolved in $\text{D}_6\text{-Acetone}/\text{D}_2\text{O}$ (2:1) in sealed NMR tubes, from 40 to 100 °C in steps of 20 °C for two hours at the time.

Figure 3.9 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **3.2**, **3.3** and **3.4** in THF/ D_2O with ratio of 1:0, 8:1, 4:1 and 2:1.

3.5 Theoretical calculations

Computational results obtained at the B3LYP/6-311G++(2d,2p)// B3LYP/6-31G(d) level of theory and with IEFPCM implicit solvation indicate that the hydrolysis reaction pathway of compound **3.0**, $[\text{CIP}(\mu\text{-N}^t\text{Bu})]_2$, consists of 8 fast steps. As illustrated in *Scheme 3.5*, all the intermediate structures are listed along the main path, and the activation and reaction free energies for each step can be found in *Table 3.1*. The two chloride atoms on the P_2N_2 ring is replaced by hydroxyl groups, which originate from ambient water molecules, within the first two steps (INT1 and INT2), of which the energy barriers are 20.2 kcal/mol and 15.2 kcal/mol. These two reactions are fast but slightly endergonic at standard state (which implies molarity of 1 mol/dm³ for all molecules). The barriers and the reaction energies of the standard reactions are normally lower than the standard state ones because in typical experimental conditions, the concentration of HCl is much lower than 1 mol/dm³ though the concentration of water is about 55.6 mol/dm³. For example, the barrier and reaction free energies will be lower down by 5.1 kcal/mol, as compared to the standard state, with the concentration of

chloride as low as 0.01 mol/dm^3 and a water concentration of 55.6 mol/dm^3 . Moreover, the reaction can be further driven by the energy released from the dissociation of HCl. The first two steps are fast, followed by the formation of INT3, which a stable zwitterionic species is formed preceding a proton transfer step (activation energy of 17.4 kcal/mol and reaction energy of 0.8 kcal/mol). This zwitterionic species contain the negative and positive charges localized on the hydroxyl and the amine groups of the cyclodiphosphazane ring, respectively. Subsequently, the four-membered cyclodiphosphazane ring opens (INT4) with a small barrier of 6.4 kcal/mol . The next step involves reaction with one molecule of water (activation free energy of 27.2 kcal/mol), which leads to the release of POOH and the formation of $(^t\text{BuNH})_2\text{POH}$ (INT5). This step is favored by the non-standard state conditions, since the molarity of water is larger than one, and the concentration of POOH is much lower. Also, the formation of the species POOH (vide infra step 8) compels the reaction forward. Two *tert*-butylamine molecules were released by hydrolysis within the following two steps, 6 and 7, with the formation of the corresponding intermediates INT6 and INT7, respectively. These reactions are fast, with barriers of 8.1 kcal/mol and 22.1 kcal/mol , respectively. In the final step, POOH reacts with a molecule of water in rapid and exergonic fashion (barrier of 11.3 kcal/mol , reaction energy of -17.0 kcal/mol).

The hydrolysis reaction pathway of compound **3.0** has many side reactions. In this work, the alternative mechanisms to the one shown in *Scheme 3.5* has been explored (*Scheme 3.6*). Some of the alternative paths, like the ring opening through isomerization to monomer directly from the reactant structure (barrier of 55 kcal/mol and reaction energy of 24 kcal/mol), have unviable activation and/or reaction energies. However, other possible side reactions are found to be kinetically and thermodynamically viable. These include the formation and isomerization of P-OH to -PH=O, with

an activation energy of 21.5 kcal/mol and reaction energy of -6 kcal/mol. However, for this pathway, the hydrolysis pathway ceases as the formation of the zwitterion is prevented. This is supported by previously reported isolation and characterization of P(O)H isomer from cyclodiphosphazanes species.^{26,119} Conversely, no cyclodiphosphazane P(OH) isomers have been isolated. The addition of further water molecules to the ring is also unfavorable with barriers greater than 35 kcal/mol and reaction energies larger than 15 kcal/mol. Based on these calculations, it is not unreasonable to conclude that the -PH=O state is not part of the main reaction pathway even though it could exist in the solution.

Scheme 3.5 The proposed hydrolysis path for compound 3.0.

Scheme 3.6 Some of the alternative paths to the main hydrolysis reaction path of compound 3.0. A '~' symbol is used on energies that were only calculated on vacuum and small basis set.

The First Hydrolysis Step of Compounds 3.1 to 3.4:

The first step for the hydrolysis of compounds 3.1 to 3.4 (Scheme 3.7), which is similar for all four compounds, is the addition of a water molecule and the breaking of the P_2N_2 ring. This step is realized by the nucleophilic attack from a water molecule to a phosphorous atom within the P_2N_2 ring. During this step, the cleavage of the P-N bond followed by the formation of hydroxyl group on phosphorous center, and a hydrogen atom from the same water molecule goes to the neighboring nitrogen atom through a bridge water molecule. For compound 3.1-3.4, the free activation energy is 44.2, 42.2, 51.9 and 51.5 kcal/mol, respectively. The reactions of compounds 3.3 and 3.4 are both extremely slow and

Table 3.1 Standard State Free energies of the compound **3.0** reaction path.

Reaction step		Activation Energy (kcal/mol)	Reaction Energy (kcal/mol)
1.	R → INT1	20.2	4.0
2.	INT1 → INT2	15.2	6.6
3.	INT2 → INT3	17.4	0.8
4.	INT3 → INT4	6.4	2.7
5.	INT4 → INT5	27.2	0.0
6.	INT5 → INT6	8.1	-4.8
7.	INT6 → INT7	22.1	-0.3
8.	INT7 → P	11.3	-17.0

Activation and Reactions energies are presented independently for each reaction, and not in relation to the reactants, since the number of atoms in the models changes along the reaction.

3.2 is the fastest one among these four compounds. It also shows the reaction of compound **3.4** is particularly unfavorable, with a reaction energy of 8.8 kcal/mol. Other than that, the reaction energy for **3.1** and **3.3** is 4.1 and 3.3 kcal/mol, respectively. Only the compound **3.2** is exergonic reaction with a reaction energy of -0.3 kcal/mol.

Scheme 3.7 The first step of the hydrolysis reaction path for compounds **3.1** to **3.4**. E = O (**3.2**), S (**3.3**), Se (**3.4**).

Table 3.2 Standard state free energies relative to the first step of the hydrolysis reaction of compound **3.1** to **3.4**.

	Activation Energy (kcal/mol)	Reaction Energy (kcal/mol)
Compound 3.1	44.2	4.1
Compound 3.2	42.2	-0.3
Compound 3.3	51.9	3.3
Compound 3.4	51.5	8.8

We were able to optimize the transition state of compound **3.1** in vacuum but not in implicit solvent. The value presented corresponds to a structure optimized in implicit solvent were the main reaction coordinate was frozen with the respective vacuum value.

3.6 Comparison with experimental values

The hydrolytic tendency of all the five compounds calculated computationally agrees well with the experimental kinetic data we obtained. Based on the experimental observations, the compound **3.0** is found to be very reactive and reacts violently with water. Accordingly, compound **3.0** presents the barrier of 27.2 kcal/mol based on the calculations, which is the lowest barrier. It is 15.0 kcal/mol lower than that of compound **3.2**, the compound with the next smaller barrier. Moreover, the difference in reactivity between the compounds **3.1** and **3.2** is also in congruent with computational analysis. Compound **3.2** reacts with water about four times faster than compound **3.1**, which implies an activation energy difference of *ca.* 1 kcal/mol. The computed barrier of compound **3.2**, 42.2 kcal/mol is 2.0 kcal/mol lower than the barrier of compound **3.1**, 44.2 kcal/mol. At last, both the compounds **3.3** and **3.4** are extremely stable in aqueous environment. Through computational calculations, it was discovered that had these molecules followed a similar reaction mechanism to compound **3.2**, their activation energies would be 51.9 and 51.5 kcal/mol, respectively, about 7.3 kcal/mol higher than that of compound **3.1**. In terms of reaction rate, this energy difference means that the reaction would be more than 1 million times slower.

The trend of diminishing reactivity from compound **3.2** to **3.4** may be rationalized by the diminishing electronegativity of the atom bonded to phosphate: oxygen, sulphur, and selenium. This trend is stronger for the electronic component of the activation energy, for which the potential energy barriers are 37.4, 45.9, and 46.9 kcal/mol, respectively. Since the electronegativity of oxygen (3.44 in the Pauling scale) is much larger than the electronegativity of sulphur (2.58), the oxygen atom connected to the phosphorous atom of the cyclodiphosphazane ring in compound **3.2** withdraws more electronic density from the phosphorous atom than the sulphur atom of compound **3.3**, which makes compound **3.2** more susceptible to nucleophilic attack by water molecules. Accordingly, the potential energy barrier for compound **3.3** is 8.5 kcal/mol higher than that of compound **3.2**. This can be explained by the relative strength of the two electron withdrawing groups, by comparison and analysis of the NBO point charges. The NBO charge of the phosphorous atom is 2.50 in compound **3.2** and 1.94 in compound **3.3**. The electronic density of the phosphorous atom in compound **3.2** moved extensively to the oxygen substituent, with a charge of -1.08, but more modestly to the sulphur atom of compound **3.3** which has a charge of -0.53.

On the other hand, the potential energy barrier of compound **3.4** is only 1 kcal/mol higher than the barrier of compound **3.3**, which is compatible with the electronegativity of selenium (2.55) being practically the same as the electronegativity of sulphur (2.58). The NBO point charge of the phosphorous atom in compound **3.3** (1.94) is higher than the charge of phosphorous in compound **3.4** (1.86). Based on this line of reasoning, the higher overall charge in the phosphorous atom makes compound **3.3** more susceptible to nucleophilic attack than compound **3.4**. Additionally, we can also explain the excess electronic density in compound **3.4** to the less negative selenium atom, with a charge of -0.44, in comparison with the sulphur atom (-0.53). The differ-

ence in atomic size of selenium and sulphur to that of oxygen can also be responsible for some steric repulsion that hinders the attack of the water molecule to the phosphorous atom. Such a statement seems like a plausible explanation but is difficult to measure quantitatively with any degree of certainty. Furthermore, the calculated reaction barriers are also much higher than the observed experimental data. Compounds **3.1** and **3.2**, for example, have rate constants provided by the kinetic studies of their hydrolysis processes are $1.1 \times 10^{-6} \text{ s}^{-1}$ and $4.7 \times 10^{-6} \text{ s}^{-1}$, respectively. These values correspond to barriers of 25.6 and 24.7 kcal/mol at 298.15 K. The barriers from our calculations are *ca.* 18 kcal/mol higher. It is important to reiterate that our previous explanation does include some overestimation of the free energy barrier. Unlike calculations, the experiments are not performed in standard state conditions, with particular consideration of the high concentration of water in solution. However, that should only account for a difference of 2-3 kcal/mol. Another factor that could contribute to the overestimation of the barrier is the large stabilization of the reactants in the calculations. Especially in compounds **3.1** and **3.2**, the two water molecules involved in the reaction, adopt a very stable symmetric conformation with optimized hydrogen bonds in the reactants state. This is an artefact of the calculation. In reality, the compounds are completely surrounded by water molecules, and the nucleophilic water molecule comes directly from solution, without the cost of removing a previous interaction with the compound. A third factor for the differences in the barriers is also related with the description of the solvent water molecules. The transition states of these reactions should be stabilized by complex nets of hydrogen bonds from the water molecules in solution. Although we tried to incorporate some of this interaction through the use of an implicit solvent, it is clearly not sufficient. A more accurate, but much more costly computational approach, would include addition of explicit water molecules in the

models and possibly dynamic and sampling protocols. We reiterate, however, that for the purpose of this work, our approach answered the doubts raised by the experiments within a reasonable computational framework.

3.7 Conclusion

In conclusion, in this section, a set of chalcogenide cyclodiphosph(V/V)azane derivatives from a single cyclodiphosph(III/III)azane precursor were synthesized and characterized. Their air and moisture stability was also studied and proved to be the first example of a group of all the accessible chalcogenide derivatives obtained from a single cyclodiphosph(III/III)azane precursor that are air-stable over prolonged periods of time. Compounds **3.1** to **3.4** were improved tremendously in terms of air and moisture stability as compare to non-functionalized dimeric cyclodiphosph(III)azane compound **3.0**, and compounds **3.3** and **3.4** was inert to water even at a temperature as high as 100 °C. To gain better mechanistic insight into this unusual reaction, computational modelling and free energy was conducted, which suggests that the substituents on the phosphorus atom may potentially play a key role over the stability of the PN frameworks.

**Chapter 4: Metal-free steric C-N bond activation
during the oxidation of dimeric
macrocyclodiphosphazanes $[\{\text{P}(\mu\text{-NR})\}_2(\mu\text{-NR})]_2$
with chalcogen elements**

4.1 Introduction

The much greater kinetic lability of the bonds between main group elements, other than carbon, still represents a major challenge in the design of robust molecular inorganic frameworks in modern main group chemistry. Except for specific families of compounds based on strong covalent bonds (*e.g.*, silicate minerals, phosphates, phosphazene polymers, *etc.*), studies on the technological and industrial application of inorganic frameworks still lag far behind compared to their organic counterparts. In addition, the laborious and tedious synthetic routes involved throughout their production further handicap their applications. During the last few decades, significant efforts have been dedicated to the synthesis of inorganic macrocycles as prospective neutral or anionic ligands for coordination and host-guest chemistries (*Figure 4.1*).^{100,120-125} Among these, P-N based macrocyclodiphosphazanes are of particular interest due to their structural robustness stemming from the thermodynamic stability of P-N single bond ($290 \text{ kJ}\cdot\text{mol}^{-1}$, *cf.*, C-C single bond energy $346 \text{ kJ}\cdot\text{mol}^{-1}$).¹²⁶

Figure 4.1 Inorganic macrocycles as prospective neutral or anionic ligands for coordination and host-guest chemistries.

A significant number of synthetic methodologies have been developed for their rational design by fine-tuning macrocyclic steric and electronic properties.^{13,30,127-129} Macrocyclodiphosph(III/III)azane systems are commonly generated by reacting the dichlorocyclodiphosphazane $[\text{ClP}(\mu\text{-NR})]_2$ with a wide range of inorganic and organic

linkers to produce inorganic or hybrid macrocyclodiphosphazanes with a formula of $[\{P(\mu\text{-NR})\}_2(\mu\text{-X})]_n$ or $[\{P(\mu\text{-NR})\}_2(\mu\text{-LL}')_n]$, ($X = O, Se, NR$; $R = H, ^iPr$ and tBu), respectively.^{12,30,35,36,38,41,130} In the case of inorganic macrocyclodiphosphazanes, it is well-established that the ring size is dictated by the nature and steric bulk of the bridging atoms or groups present within the macrocycle backbone. For instance, tetrameric and hexameric macrocyclodiphosphazanes are formed when oxygen and selenium are acting as bridging atoms, (*Figure 4.2*, a and b, respectively); tetramers are favored over dimeric systems when the steric bulk of the bridging groups is reduced by truncating N^iPr to NH groups.^{31,32,34,36} Moreover, the use of halide anions as templates has also been a successful strategy to selectively produce pentamers over tetramer during the condensation reactions leading to formation of macrocyclic arrangements (*Figure 4.2*, c and d, respectively),^{32,33,131} Despite increasing in numbers, technological applications for macrocyclodiphosphazanes are still extremely limited due to their intrinsic bond lability that restricts their broader use. Recent reports have shown the enhancement on the stability of cyclodiphosph(III/III)azanes upon oxidation of the phosphorus centre.^{32,14,46,100,102,133,134} Inspired by these reports, we decided to investigate the stability of macrocyclodiphosphazanes of the type $[\{P(\mu\text{-NR})\}_2(\mu\text{-NR})_2]$ [$R = ^tBu$ (**4.1**) and iPr (**4.8**)] upon oxidation with chalcogen elements. Herein we report that unexpected C-N bond activation occurred during the oxidation process. Our experimental and theoretical studies demonstrate that steric factors, most probably steric strain release, play a crucial role in the metal-free activation of the C-N bonds herein described.

Figure 4.2 Inorganic macrocyclodiphosphazanes with a formula of $[{P(\mu\text{-NR})}_2(\mu\text{-X})]_n$ or $[{P(\mu\text{-NR})}_2(\mu\text{-LL'})]_n$ (a, $X = O$; b, $X = Se$; c and d, $X = NH$; $R = tBu$).

4.2 Syntheses of compounds 4.1-4.8

The starting point of our studies is the macrocyclodiphosphazane $[{P(\mu\text{-N}^tBu)}_2(\mu\text{-N}^tBu)]_2$ (**4.1**) previously synthesized *via* a condensation reaction between $[ClP(\mu\text{-N}^tBu)]_2$ and $[LiN^tBuP(\mu\text{-N}^tBu)]_2$ and was isolated as a co-crystal of **4.1**• $[LiN^tBuP(\mu\text{-N}^tBu)]_2$ (1:1 ratio), as reported by Chivers *at al.*³¹ Our work commenced with the isolation of **4.1**, which was achieved by recrystallization in THF. Treatment of **4.1** with an excess of $tBuOOH$ (1:8 ratio) in refluxing Tol for 8 hours resulted in the formation of the partially diagonally di-oxidised product $[(O)P(\mu\text{-N}^tBu)_2P]_2[\mu\text{-N}^tBu]_2$ (**4.2**) (*Scheme 4.1*) as determined by spectroscopic analyses. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4.2** revealed two sets of resonances at 79.87 ppm and 12.65 ppm, corresponding to P(III) and P(V) centers, respectively, while IR spectra revealed typical absorption stretches for the newly formed $P=O$ bonds at 1267 cm^{-1} . The three single resonances observed at 1.79 ppm, 1.77 ppm and 1.55 ppm (intensity ratio of 1:1:4) in the

room-temperature ^1H NMR spectrum of **4.2** are attributed to the P_2N_2 ring exogenous and endogenous *tert*-butyl groups, respectively. Attempts to achieve complete tetra-oxidation of **4.1** was unsuccessful even under much harsher reaction conditions (*i.e.*, much higher temperature) and extended reflux duration. Moreover, attempts to react **4.2** with an excess of elemental S and Se in order to produce the mixed tetra-oxidised frameworks $[(\text{O})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{S})]_2[\mu\text{-N}^t\text{Bu}]_2$ and $[(\text{O})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{Se})]_2[\mu\text{-N}^t\text{Bu}]_2$, respectively, was unsuccessful even after prolonged refluxing in Tol (36 hours), as determined by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy. Higher boiling point solvents, such as dimethylformamide (DMF), were also investigated which resulted in the decomposition of compound **4.2**. Following the partial oxidation obtained with $t\text{BuOOH}$, we proceeded to react **4.1** with elemental S and Se under analogous experimental conditions. A mixture of oxidizing agent (elemental S or Se) and compound **4.1** (molar ratio of 4.4:1) was refluxed in Tol and its progress of the reaction was observed by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy. Reflux was stopped when all of compound **4.1** was consumed and no new product resonance signals was observed. It was expected that the desired fully oxidised symmetrical products, $[\{\text{P}(\text{E})(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})]_2$ (E = S and Se), would display a single resonance within the range of $\sim 0 - 50$ ppm (*cf.*, 146.0 ppm in isolated **4.1**), which would be consistent with previously reported cyclophosph(V/V)azane derivatives.¹³⁵ To our surprise, the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **4.6** and **4.7** consist of two sets of signals at 34.85 and 30.93 ppm, and 24.86 and 22.26 ppm, respectively, indicating the formation of the fully oxidised asymmetric products. Compound $\text{P}_4(\mu\text{-N}^t\text{Bu})_3(\mu\text{-NH})_3\text{S}_4$ (**4.6**) and $\text{P}_4(\mu\text{-N}^t\text{Bu})_3(\mu\text{-NH})_3\text{Se}_4$ (**4.7**) were crystallized as a tetrasulfide/tetraselenide-oxidised product where three *tert*-butyl groups, two on the ring-bridging nitrogen atoms and one on the P_2N_2 ring, were cleaved off. The cleavage of $\text{N}-t\text{Bu}$ bonds resulted in the formation of three new $\text{N}-\text{H}$

bonds. Compound **4.6** and **4.7** are formed in quantitative spectroscopic yield as shown by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR studies and were isolated in good quantitative yields of 54% and 60%, respectively. The ^1H NMR spectra of **4.6** and **4.7** display single resonances at 1.59 ppm, 1.56 ppm and 1.23 ppm (ratios 1:1:1) and 1.62 ppm (broad) and 1.31 ppm (ratio 2:1), respectively, which can be assigned to *tert*-butyl groups on the ring nitrogen atoms. The presence of two broad singlets with intensity ratio 2:1 at 5.16 ppm and 4.13 ppm, and at 5.64 ppm and 4.28 ppm for **4.6** and **4.7**, respectively, correspond to the N-H protons; IR spectroscopy corroborate the ^1H NMR data, revealing typical N-H absorptions bands at 3345 cm^{-1} and 3398 cm^{-1} .

Scheme 4.1 Syntheses of compound **4.2** $[(O)P(\mu\text{-}^t\text{NBu})_2P]_2[\mu\text{-}^t\text{NBu}]_2$, **4.3** $[(S)P(\mu\text{-}^t\text{NBu})_2P]_2[\mu\text{-}^t\text{NBu}]_2$ and **4.4** $[(Se)P(\mu\text{-}^t\text{NBu})_2P]_2[\mu\text{-}^t\text{NBu}]_2$, **4.5** $P_4(\mu\text{-}^t\text{NBu})_4(\mu\text{-NH})_2\text{O}_4$, **4.6** $P_4(\mu\text{-}^t\text{NBu})_3(\mu\text{-NH})_3\text{S}_4$ and **4.7** $P_4(\mu\text{-}^t\text{NBu})_3(\mu\text{-NH})_3\text{Se}_4$.

Upon successful isolation of **4.6** and **4.7**, the problem of the oxygen-tetra-oxidised macrocycle syntheses became doubtful. Our initial conclusion is that the oxidant used is not potent enough to access the fully oxidised product. Therefore a more reactive oxidant *m*-Chloroperoxybenzoic acid was chosen instead. 10 hours of stirring in THF at room-temperature after *m*-Chloroperoxybenzoic acid was added dropwise to **4.1** gradually revealed a singlet at ~ 7 ppm in the *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum. This indicates the formation of the symmetrical macrocycle. Diffraction quality crystals of the product were obtained by slow evaporation of the crude mixture in THF, which revealed a fully oxidised product $\text{P}_4(\mu\text{-N}^t\text{Bu})_4(\mu\text{-NH})_2\text{O}_4$ (**4.5**), whereby two *tert*-butyl groups on the ring-bridging nitrogen atoms were cleaved off. ^1H NMR spectrum of compound **4.5** shows a singlet resonance signal at 1.63 ppm, which is attributed to the four remaining magnetically equivalent *tert*-butyl groups attached to the *endo*-cyclic nitrogen atoms. The formation of N-H bond was also corroborated by IR spectroscopy, as evidenced by the broad absorption band at 3348 cm^{-1} in the spectra.

To further evaluate the influence of stoichiometry and reaction conditions upon the formation of dioxidised, tetra-oxidised and/or any intermediate oxidised form, **4.1** was oxidised with S/Se in a ratio of 1:2.2 under identical experimental conditions. Moreover, alternative solvents, such as THF and CH_3CN , were explored under refluxing conditions and at room-temperature in both 1:4.4 and 1:2.2 molar ratios. In all cases a mixture of tetra-oxidised (**4.6** and **4.7**) and the di-oxidised (**4.3** and **4.4**) derivatives were observed *in situ* after prolonged reaction duration. Such an observation suggests that the fully oxidised cleaved product is the most thermodynamically stable product for both sulphur and selenium oxidised derivatives. To gain better understanding of the observed C-N bond cleavage upon oxidation of **4.1**, more efforts have been made to isolate the diagonally oxidised intermediates $[(\text{S})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{P}]_2[\mu\text{-N}^t\text{Bu}]_2$ (**4.3**) and

[(Se)P(μ -N^tBu)₂P]₂[μ -N^tBu]₂ (**4.4**). The reaction of compound **4.1** with 2.2 equivalents of sulphur or selenium in Tol afforded samples of **4.3** and **4.4** suitable for single crystal X-ray studies, which warrants further mechanistic studies. Similar to compound **4.2**, the ³¹P-{¹H} NMR spectrum show two sets of resonances at 101.63 ppm and 44.82 ppm, and 101.84 ppm and 54.04 ppm, for **4.3** and **4.4**, respectively, which correspond to the P(III) and P(V) centres. The signals for *tert*-butyl protons on the bridging and ring-nitrogen atoms can be found as three singlets at 1.92 ppm, 1.91 ppm and 1.66 ppm, for **4.3**, and 1.98 ppm, 1.96 ppm and 1.71 ppm, for **4.4**, with relative integrated intensity ratio of 1:1:4 in their room-temperature ¹H NMR spectra, consistent with the formation of diagonally oxidised structures.

4.3 Syntheses of compounds 4.1-4.8 via mechanochemical methods

Mechanochemistry has been proven to be an outstanding solvent-free and green alternative to conventional solution-based chemistry.¹³⁶⁻¹⁴⁰ However, the potential of mechanochemistry remains barely investigated in the synthesis of cyclodiphosphazanes. Due to lack of experimental investigation in this area, we were prompted to study the use of mechanochemistry for the observed C-N bond activation. Ball milling **4.1** with *m*-Chloroperoxybenzoic acid (1:2:2 molar ratio) for 3 hours in a Retsch MM400 mixer mill operating at 30 Hz loaded with a 10 mm stainless steel ball (4 g weight) successfully generated **4.2**, as evidenced by the ³¹P-{¹H} NMR spectrum of the crude sample. And the reaction of **4.1** with *m*-Chloroperoxybenzoic acid in a 1:4.4 ratio quantitatively afforded the tetra-oxidised compound **4.5**. Given our initial success using mechanochemistry for the synthesis of the di-oxidised product **4.2**, we ventured to explore its potential for the C-N bond activation and cleavage, which had been observed when S and Se were used in solution. Milling **4.1** with the respective

oxidizing agent (S or Se) for 3 hours in a Retsch MM400 mixer mill, successfully generated **4.6-4.7** in quantitative yields. The reduced reaction times are in stark contrast with those observed for our solution-based syntheses. Another significant difference is product selectivity: the reaction between **4.1** with 2.2 equivalence of Se forms exclusively compound **4.4** in the solid state, whereas when the same molar ratio was used in solution, compound **4.6** was always formed.

Figure 4.3 *In situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra for solution-based reaction and grinder reaction.

4.4 Crystal structures of compounds 4.2-4.9

Diffraction quality crystals were obtained by cooling saturated solutions of **4.2–4.9** in Tol at 7 °C (*Figure 4.4*). SC-XRD analysis revealed that the molecular structures of compounds **4.2-4.4** consist of a diagonally di-oxidised macrocyclodiphosphazanes with alternating P(III) and P(V) atoms. The P=E bond distances for the di-oxidised products are 1.456(5) Å, 1.9363(10) Å and 2.103(3) for **4.2** to **4.4** respectively, which are comparable with previously reported analogues (*cf.*, P=O: 1.459 in *cis*-[(4-CN-PhO)(O)P(μ -N^tBu)]₂, P=S: 1.927 Å in bis(sulfide) [Cy(H)N(S)P(μ -N^tBu)]₂ and P=Se: 2.056 in *cis*-[(4-CN-PhO)(Se)P(μ -N^tBu)]₂). The average P–N bond distances within the P₂N₂ ring and the P–N bridging bonds in **4.2-4.4** are slightly shorter than those observed in **4.1**.¹⁴¹ Upon oxidation, the P₂N₂ ring is almost planar with a smaller puckering angle of 3.7° in **4.2** (*cf.*, **4.1**, 14.5°), and is nearly perpendicular to the

macrocycle with dihedral angle of 89°. The same trends were also observed in **4.3** and **4.4** and this can be rationalized by the absence of sterically demanding lone pairs in one of the phosphorus atoms. In the case of the fully oxidised products **4.5**, **4.6** and **4.7**, the X-ray solid state structures of $P_4(\mu\text{-}N^t\text{Bu})_4(\mu\text{-NH})_2O_4$ (**4.5**) (Figure 4.5, a) shows a macrocyclodiphosphazane where all the phosphorus atoms have been oxidised and two NH groups on the ring-bridging nitrogen atoms by C-N bond cleavage. While the $P_4(\mu\text{-}N^t\text{Bu})_3(\mu\text{-NH})_3S_4$ (**4.6**) and $P_4(\mu\text{-}N^t\text{Bu})_3(\mu\text{-NH})_3Se_4$ (**4.7**) (Figure 4.5, b and c) crystal structures shows three N-^tBu bonds have been cleaved – two bridging and one within the P_2N_2

Figure 4.4 Solid-state structures of **4.2** (a), **4.3** (b), and **4.4** (c). The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **4.2**: N(1)–P(1) 1.691(5), N(2)–P(2) 1.788(5), N(2)–P(1) 1.676(5), N(3)–P(1) 1.682(5), N(3)–P(2) 1.785(5), N(4)–P(2) 1.741(5), N(4)–P(3) 1.689(5), N(5)–P(3) 1.681(5), N(6)–P(3) 1.681(5), N(5)–P(4) 1.779(5), N(6)–P(4) 1.789(5), N(1)–P(4) 1.732(5), O(1)–P(1) 1.456(4), O(2)–P(3) 1.457(5); N(1)–P(1)–O(1) 112.5(3), N(2)–P(1)–O(1) 118.1(3), N(6)–P(3)–O(2) 117.5(3), N(4)–P(3)–O(2) 112.7(3); **4.3**: N(1)–P(2) 1.742(2), N(1)–P(1) 1.684(2), N(2)–P(2) 1.745(2), N(2)–P(1) 1.684(2), N(3)–P(2) 1.749(2), S(1)–P(1) 1.9363(10); N(1)–P(1)–S(1) 116.86(9), N(2)–P(1)–S(1) 117.10(9), N(3)–P(2)–N(2) 108.99(11), N(3)–P(2)–N(1) 108.90(11), N(2)–P(1)–N(1) 86.45(11), N(2)–P(2)–N(1) 82.83(11), P(2)–N(2)–P(1) 95.23(12), P(2)–N(1)–P(1) 95.32(12); **4.4**: N(1)–P(2) 1.737(10), N(1)–P(1) 1.690(10), N(2)–P(2) 1.737(10), N(2)–P(1) 1.676(10), N(3)–P(1) 1.713(10), Se(1)–P(1) 2.102(3); N(1)–P(1)–Se(1) 116.9(4), N(2)–P(1)–Se(1) 116.5(4), N(3)–P(1)–Se(1) 116.3(4), N(1)–P(1)–N(2) 86.5(5), N(2)–P(1)–N(3) 107.6(5), N(1)–P(1)–N(3) 109.0(5).

Unit which might be due to the steric effect of sulphur and selenium. Where when E = O (**4.5**), S (**4.6**) and Se (**4.7**), P=E bond distances of 1.469 Å, 1.919 Å and 2.089 Å for **4.5**, **4.6** and **4.7**, respectively, are comparable with previously reported analogues (*cf.*, 1.47 Å in [^tBu(H)N(O)P($\mu\text{-}N^t\text{Bu}$)]₂, 1.927 Å in [Cy(H)N(S)P($\mu\text{-}N^t\text{Bu}$)]₂ and 2.0913 in

cis-[(μ -N^{*t*}Bu)₂(P(Se)N C₄H₈NMe)₂]]. The P–N average bond distances within the P₂N₂ ring and the P–N bridging groups for compound are 1.682 Å and 1.664 Å, in **4.5**, 1.686(5) Å and 1.687(12) Å, in **4.6**, and 1.700(5) Å and 1.651(5) Å, in **4.7**, which are much shorter than those observed in **4.1** (*cf.*, **4.1**, 1.791 and 1.763 Å, respectively).³¹ The P₂N₂ rings in **4.5**, **4.6** and **4.7** are almost planar with a puckered angle of 5.4, 2.8° and 6.7° (*cf.*, **4.1**, 14.5°), and it's nearly perpendicular to the macrocycle with dihedral angle of 89.8°, 88.9° and 86.2°. Moreover, upon oxidation, the P₂N₂ rings in both **4.5**, **4.6** and **4.7** exhibit less acute angles around the nitrogen atoms as compared to analogous oxidised cyclodiphospho(V/V)azanes. These observations can be rationalized by the presence of fewer *tert*-butyl groups along with the absence of sterically demanding lone pairs and greater inductive effect of the P(V) atoms.

Figure 4.5 Solid-state structures of **4.5** (a), **4.6** (b) and **4.7** (c). The *tert*-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **4.5**: N(1)–P(2) 1.680(4), N(1)–P(1) 1.679(4), N(2)–P(2) 1.670(4), N(2)–P(1) 1.687(4), N(3)–P(3) 1.698(4), N(3)–P(4) 1.673(4), N(5)–P(1) 1.669(4), N(5)–P(4) 1.659(4), N(6)–P(2) 1.664(4), N(6)–P(3) 1.664(4), O(1)–P(1) 1.465(3), O(2)–P(2) 1.469(3); O(3)–P(3) 1.471(3); O(4)–P(4) 1.472(3); N(1)–P(1)–O(1) 120.82(19), N(2)–P(1)–O(1) 120.80(19), N(5)–P(1)–S(1) 109.51(19), N(1)–P(2)–O(2) 119.89(19), N(2)–P(2)–O(2) 120.19(18), N(6)–P(3)–O(3) 108.97(18), N(5)–P(4)–O(4) 109.94(19); **4.6**: N(1)–P(2) 1.671(13), N(1)–P(1) 1.669(13), N(2)–P(2) 1.679(5), N(2)–P(1) 1.679(5), N(3)–P(3) 1.679(12), N(3)–P(2) 1.683(2), N(5)–P(3) 1.723(13), N(5)–P(4) 1.746(12), S(1)–P(1) 1.928(8), S(2)–P(2) 1.909(10); S(3)–P(3) 1.908(11); S(4)–P(4) 1.930(7); N(1)–P(1)–S(1) 121.6(9), N(2)–P(1)–S(1) 123.3(6), N(6)–P(1)–S(1) 109.0(6), N(1)–P(2)–S(2) 118.1(10), N(2)–P(2)–S(2) 122.6(8), N(5)–P(3)–S(3) 118.4(9), N(6)–P(4)–S(4) 110.2(5); **4.7**: N(1)–P(2) 1.717(5), N(1)–P(1) 1.682(5), N(2)–P(2) 1.723(5), N(2)–P(1) 1.700(5), N(3)–P(3) 1.716(4), N(3)–P(4) 1.675(5), N(5)–P(2) 1.604(5), N(5)–P(3) 1.613(5), Se(1)–P(1) 2.085(16), Se(2)–P(2) 2.102(16); N(1)–P(1)–Se(1) 121.8(18), N(2)–P(1)–Se(1) 118.6(17), N(6)–P(1)–Se(1) 109.3(17), N(1)–P(2)–Se(2) 115.1(17), N(2)–P(2)–Se(2) 116.3(18), N(5)–P(3)–Se(3) 109.3(18), N(6)–P(4)–Se(4) 107.5(17).

4.5 Mechanistic studies

In order to gain insights into the reaction mechanism, the reaction of **4.1** with an excess of elemental sulphur or selenium in Tol- d_8 was conducted in a sealed Young's tap NMR tube. The reaction was monitored by ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy for over 20 hours. The first two steps during the oxidation reaction of **4.1** with sulphur and selenium were similar as observed by the *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR data. As shown in *Figures 4.6* and *4.7*, the results suggest that the mono-oxidised species are formed initially (type **I**, in *Scheme 4.2*), as indicated by the appearance of signals at ~39, 108, 147 and 154 ppm – for sulphur - and ~54, 105, 143 and 152 ppm – for selenium – corresponding to one P(V) and three P(III) centers, respectively. As the reaction proceeds, the intensity of these signals decreases as two new resonances appear at ~45 and 101 ppm (~57 and 96 ppm for the sulphur derivative), which can be attributed to the P(V) and P(III) centres in compounds **4.3** and **4.4** (type **II**, in *Scheme 4.2*). These observations can be explained by the deactivating effect of a P(V) over the adjacent P(III) atoms within the same P_2N_2 ring due to the greater inductive effect of the former.

Figure 4.6 $^{31}\text{P}\{-^1\text{H}\}$ (a) and ^1H (b & c) NMR spectrum of monitoring the reaction of $[\{P(\mu\text{-}N^t\text{Bu})\}_2(\mu\text{-}N^t\text{Bu})]_2$ (**4.1**) with elemental S in a sealed NMR tube in Tol- d_8 , compound **a** (denoted in red) is isobutylene and the resonances of the two tert-butyl cleavage products were marked with *.

Figure 4.7 ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of monitoring the reaction of $[\{P(\mu\text{-}N^t\text{Bu})\}_2(\mu\text{-}N^t\text{Bu})]_2$ (**4.1**) with elemental Se in a sealed NMR tube in $\text{Tol-}d_8$.

Scheme 4.2 Plausible proposed mechanism for the *in situ* monitored reaction.

The reaction pathways divert slightly between sulphur and selenium derivatives throughout the subsequent oxidation steps as evidenced by NMR spectroscopy. During the reaction of **4.1** with sulphur, the formation of the tetra-oxidised compound (structure type **IV** in Scheme 4.2), with only two *tert*-butyl groups cleaved off, can be ob-

served prior to the formation of the final product **4.6**. This was indicated by the appearance, and subsequent disappearance, of the single resonances at 37 ppm and at 1.7 ppm in the $^{31}\text{P}\{-^1\text{H}\}$ and ^1H NMR spectra, respectively, as shown in *Figures 4.7* and *4.8*. Conversely, in the selenium analogue, spectroscopic evidence for the formation of the intermediate (structure type **IV**) was not observed throughout our studies. The generation of **4.4** was always observed prior to the formation of **4.7**, in which three *tert*-butyl groups were cleaved off. This is corroborated by ^1H NMR data, whereby the appearance of isobutylene (two new signals with intensity ratio 1:3 at 4.76 and 1.64 ppm) denote the formation of the byproduct (*Figure 4.9*, compound **a**).¹⁴²

Figure 4.8 $^{31}\text{P}\{-^1\text{H}\}$ (a) and ^1H NMR (b) spectrum of the in situ monitoring reaction of $[(\text{P}(\mu\text{-N}^t\text{Bu}))_2(\mu\text{-N}^t\text{Bu})]_2$ (**4.1**) with elemental S in a sealed NMR tube in $\text{Tol-}d_8$.

Figure 4.9 ^1H NMR spectrum of the in situ monitoring reaction of $[(\text{P}(\mu\text{-N}^t\text{Bu}))_2(\mu\text{-N}^t\text{Bu})]_2$ (**4.1**) with elemental Se in a sealed NMR tube in $\text{Tol-}d_8$.

Since a contraction of the P_4N_6 framework is observed upon oxidation (*vide supra*), the driving force for the observed C–N bond cleavage can be attributed to the release of steric strain. To further study the effect of steric on this particular P_4N_6 system, the less sterically hindered dimeric macrocyclodiphosphazane $[\{P(\mu-N^iPr)\}_2(\mu-N^iPr)]_2$ (**4.8**) was synthesized. It is important to note that frameworks of the type $[\{P(\mu-NR)\}_2(\mu-NR)]_2$ are not thermodynamically stable with respect to their isomeric adamantoid forms $[P_4(NR)_6]$.^{5,29} As compound **4.8** is less thermodynamically stable towards isomerization than **4.1**, milder reaction conditions were explored. Compound **4.8** was reacted with 4.4 equivalents of elemental selenium under refluxing ACN for 24 hours. The *in situ* ^{31}P - $\{^1H\}$ NMR spectrum showed a mixture of products corresponding to partially oxidised species, minor products, and a signal pattern consistent with a fully oxidised product, $P_4(\mu-N^iPr)_5(\mu-NH)Se_4$ (**4.9**) with only one iPr group having being cleaved. The ^{31}P - $\{^1H\}$ and 1H NMR spectra show signals at 55.25 and 30.65 ppm and at 6.06 and 5.34 ppm (ratio 1:2, respectively), which are consistent with the proposed structure for **4.9**. In contrast to **4.7**, compound **4.9** shows a 1:2 ratio for the NH groups in the 1H NMR spectrum (*cf.*, **4.7**, 2:1 ratio), indicating the presence of a mixture of both terminal and P_2N_2 mono-cleaved structures. This was further verified by single crystal X-ray diffraction data that revealed the cleavage of only one iPr group, disordered over the six nitrogen atoms present within the P_4N_6 backbone (*Figure 4.10*).

Figure 4.10 Molecular representation of two disordered species within the crystal structure of **4.9**, as determined by SC-XRD.

In addition, the mean P–N and P=Se bond distances in **4.9** found to be 1.700(10) and 2.075(4) Å, respectively, with the P₂N₂ rings being almost planar (puckered by 4.7°) and almost perpendicular to the macrocyclic plane (*ca.* 89°). Unfortunately, compound **4.9** readily decomposes upon isolation prohibiting any further characterization. Despite several attempts, it was not possible to achieve syntheses of analogues to **4.1** and **4.8** that contain less bulky substituents (*e.g.*, *n*Pr, Et or Me) or the isolation of analogous species from the oxidation reaction of **4.8** with other chalcogen oxidants.

4.6 Theoretical studies

Throughout our studies, when **4.1** is refluxed in Tol with an excess of *t*BuOOH only the diagonally di-oxidised product was obtained; whereas for the heavier chalcogen elements both di- and tetra-oxidised frameworks can be isolated. To rationalize the energetics of the reaction and to further elucidate the observed C–N bond cleavage, quantum chemical computations were carried out with the Gaussian 09 software package. Full geometry optimizations of stable species were performed in the gas phase by employing the hybrid density functional B3LYP with the Dunning's correlation consistent basis sets cc-pvdz. The B3LYP functional combines the Becke's three-parameter nonlocal hybrid exchange potential with the nonlocal correlation functional of Lee, Yang, and Parr.

In the first instance, thermodynamic effect was considered. Therefore, the enthalpies of reactants and products could be compared. The different isomers of the type **II** framework for *tert*-butyl and *iso*-propyl substituents (*i.e.*, **4.2A-C**, **4.3A-C** and **4.4A-C**, and **4.10A-C**, **4.11A-C** and **4.12A-C**, respectively) are shown in *Figure 4.11*, where the oxygen atoms (or sulphur and selenium) are placed in different positions of the cage. The values obtained indicate that the diagonally di-oxidised isomer **B** is the most

stable favourable isomer as indicated by the much lower calculated enthalpy, except in the case of **4.2**, where **A** is the most stable isomer by a small margin.

The calculated enthalpy of **4.10B** is 3.06 kcal/mol more stable than that of **4.10A**, and **4.10C** is 2.31 kcal/mol more stable than **4.10A** for the isopropyl derivate; while the energy difference found for the *tert*-butyl substituent is lower for the isomers **4.2A** and **4.2B** (just 0.32 kcal/mol) with **4.2C** being the least stable isomer with an energy of 3 kcal/mol greater than **4.2A**. The calculated thermodynamic data explains the formation of **4.10B** of the isopropyl derivative; whereas for the *tert*-butyl, the calculated enthalpy marginally favours **4.2A** over **4.2B**.

Figure 4.11 Theoretically possible isomers for di-oxidised products.

Furthermore, independent of the chalcogen element present, our experimental and theoretical studies (except marginally for **4.2**) are in agreement in which the expected dioxidised product would be the most thermodynamically stable one.

The enthalpies of the products were the only considered figure while explaining the only achievable diagonally oxidised product above, entropic contributions might also be significant, thus the Gibbs Energy would be more correct for the interpretation of the reaction outcome. When bulkier *tert*-butyl groups were placed on the nitrogen atoms, the energies difference between isomers is higher up to 8 kcal/mol (*Table 4.1*).

Besides, the greater size of both the selenium or sulphur atom and the substituent makes the preferred oxidation place being at the most distant diagonal positions. These computational results are corroborated by the X-ray crystal structures of compounds **4.3** and **4.4**, whereby the sulphur and selenium atoms of dioxidised cycles are in diagonal positions. This suggests that the thermodynamic factor controls the reaction outcome and these lower energies are governed by steric factors.

Table 4.1 Energies differences between isomers are in kcal/mol refer to isomer A.

	O		S		Se	
	4.2	4.10	4.3	4.11	4.4	4.12
Isomers	R = ^t Bu	R = ⁱ Pr	R = ^t Bu	R = ⁱ Pr	R = ^t Bu	R = ⁱ Pr
A	0.0	0.0	0.0	0.0	0.0	0.0
B	0.32	-3.06	-8.25	-2.78	-7.95	-2.58
C	2.98	-2.31	2.01	1.86	4.16	2.74

Further oxidation of compounds **4.3** and **4.4** with sulphur and selenium respectively, as we reported previously, would always lead to C-N cleavages which occur at the specific positions of the compound once the cage has been tetraoxidised.¹⁴¹ To understand this from a thermodynamic point of view, calculations have been made firstly for the hypothetical compound **4.10** where nitrogen atoms bearing a less bulky isopropyl groups. The computational results revealed that, for the hypothetical oxygen-tetraoxidised products with the **4.10B** (the most stable di-oxidised isomer) as the precursor or standard, it would always lead to thermodynamically more unstable structures with any number or position that cleavage would happen (*Table 4.2*). While for the atomically larger elements sulphur or selenium analogues, their tetra-oxidised derivatives would prefer only one C-N cleavage. According to the calculated energies, the energy difference between the cleavage on P₂N₂ and P₄N₆ is up to 8 kcal/mol, sug-

gesting the cleavage might preferentially occur on the major ring P₄N₆, despite experimental data revealing a mixture of both isomers present during the reaction. In contrast, their counterparts with *tert*-butyl groups on the nitrogen would allow for more C-N cleavages due to increased steric strain.

Table 4.2 Energies differences between hypothetical products with different number of cleavage and on different positions are in kcal/mol refer to hypothetical oxygen-tetra-oxidised products.

No. of Cleavage	O4		S4		Se4	
	R = ⁱ Pr	R = ^t Bu	R = ⁱ Pr	R = ^t Bu	R = ⁱ Pr	R = ^t Bu
0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.84	-7.64	-0.61	-33.90	-0.79	-40.22
1'	4.76	3.25	7.08	-19.84	7.34	-27.31
2	19.34	-16.71	3.56	-69.85	1.00	-81.36
1+1'	15.31	-1.76	9.11	-43.25	7.55	-53.78
3	29.29	-10.81	11.67	-69.64	8.50	-82.46
4	43.32	2.86	21.65	-64.45	17.60	-78.82
5	58.28	15.10	38.29	-50.31	34.69	-64.34
6	75.66	30.43	53.70	-38.15	49.83	-52.65

Cleavage at P₂N₂ positions are labelled ('), experimentally observed results are in bold.

Theoretically, the tetrakisoxide macrocycle was expected to release two *tert*-butyl groups, giving the most stable structure as low as -16.71 kcal/mol. This is in agreement in experimental formation of compound **4.5**. When sulphur was the chalcogen used, the energies of two most stable structures with losing two (-69.85 kcal/mol) and three (-69.64 kcal/mol) *tert*-butyl groups are almost the same (Table 4.2). The small energy difference between these two structures enables their coexistence. As observed experimentally, compound **4.6** with three *tert*-butyl groups losing was isolated and characterized by X-ray and multiple characterization methods, and the structure type **IV** in Scheme 4.2 with two *tert*-butyl groups losing is only observed *in situ* (Figure

4.6). In addition, compound **4.6** is always the final product successfully isolated with prolonged reaction time and excess oxidant. For the selenium analogue, the stability of the products increases with increasing loss of the bulky substituent, up to -82.5 kcal/mol (loss of three *tert*-butyl groups).

Scheme 4.4 Calculated coordinate reaction pathway for the **4.2**.

We have completed the coordinate reaction pathway for the rupture of the di-oxidised compounds substituted with *tert*-butyl in the gas phase. Although this process doesn't occur experimentally, we thought that the study could help us to a better understand of the process since we have already demonstrated the parallelism in this all oxidizations processes. From the scheme we envisage that the cleavage from the macrocyclic P_4N_6 ring is much easier than the one from the P_2N_2 , with an energy difference of *ca.* 30 Kcal/mol from one TSs to another, independently of taking enthalpies or Gibbs free energies (Scheme 4.4).

Scheme 4.5 Gibbs free energies differences are in kcal/mol refer to the initial non-cleavage product.

Scheme 4.6 Enthalpies energies differences are in kcal/mol refer to the initial non-cleavage product.

It was found that for both di- and tetra-oxidised cages, the cleavage of *tert*-butyl groups occur *via* a concerted step where the C-N and the C-H bonds are broken at the same time the new O-H bond is forming. Comparing the energies of the TSs of these two pathways, there is a big energy difference between the pathways for the P₂N₂ or macrocyclic P₄N₆ rings. For di-oxidised products this difference is about 34 kcal/mol while for the tetra-oxidised is even high (56 kcal/mol) (*Scheme 4.5* and *4.6*). This helps to explain the required high temperature (refluxing in Tol) condition for the cleavage proceeding and the formation of **4.5**, which both two *tert*-butyl groups cleavage occurred at the P₄N₆ ring.

Analyzing the TSs involved in these processes to compare the difference distances of C-N bonds on the P₄N₆ and P₂N₂ ring can indicate the cost of this reaction in certain extent. For example, the initial distances of C-N on the P₄N₆ ring was 1.55 Å and 1.50 Å for the P₂N₂ ring, suggesting that the cleavage might occur easier in the former case. Actually, the C-N distance on the P₄N₆ ring has grown until 2.47 Å while the hydrogen is migrating from the alkane to the electronegative oxygen in that TS. For the P₂N₂ ring the distance varies from the initial value 1.50 Å to 1.52 Å, that means the bond has not yet broken while the hydrogen is migrating. All the computational results revealed that the cleavage during the fully oxidation of compound **4.1** prefers occurring on the P₄N₆ ring regardless of the chalcogen used.

Figure 4.12 The TSs of *tert*-butyl cleavage on the P₄N₆ ring (left) and P₂N₂ ring (right).

4.7 Conclusion

In summary, we have shown that the oxidation reaction of $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})]_2$ (4.1) with group 16 elements would produce either diagonally oxidised product $[(O)P(\mu\text{-N}^t\text{Bu})_2P]_2[\mu\text{-N}^t\text{Bu}]_2$ (4.2), $[(S)P(\mu\text{-N}^t\text{Bu})_2P]_2[\mu\text{-N}^t\text{Bu}]_2$ (4.3), $[(Se)P(\mu\text{-N}^t\text{Bu})_2P]_2[\mu\text{-N}^t\text{Bu}]_2$ (4.4) without or fully oxidised product $P_4(\mu\text{-N}^t\text{Bu})_4(\mu\text{-NH})_2O_4$ (4.6), $P_4(\mu\text{-N}^t\text{Bu})_3(\mu\text{-NH})_3S_4$ (4.6), $P_4(\mu\text{-N}^t\text{Bu})_3(\mu\text{-NH})_3Se_4$ (4.7) with C-N cleavage by losing *tert*-butyl groups. In contrast, oxidation reaction of $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})]_2$ (4.8) with less steric substituents on nitrogen by elemental Se affording the fully oxidised product $P_4(\mu\text{-N}^i\text{Pr})_5(\mu\text{-NH})Se_4$ (4.9), showed only one substituent loss. Our experimental and theoretical studies demonstrate that steric factors, most probably steric strain release, play a crucial role in the activation of the C–N bonds. The work reported here highlights the potential of steric bond activation and its implications on a broader scope for application to main group frameworks in general. The rational design of synthetic approaches which fully exploit this approach in a wider range of main group frameworks is an exciting challenge in the area of metal-free bond activation.

Chapter 5: Mechanochemical syntheses of cyclodiphosphazanes; substitution and rearrangements

5.1 Introduction

Traditional synthetic methodologies, such as solution-based batch reactions, are considered to be tremendously wasteful despite their wide usage and well-established protocols. The use of bulk solvents to conduct chemical reactions and for product isolation is not environmentally-benign and can be deemed as energetically inefficient.¹⁴³ In recent years, the adoption of solid-state methodologies, as an alternate strategy to solution-based protocols, has garnered much attention from synthetic chemists. Mainly, there are two types of solid-state approaches: high-temperature solid-state and mechanochemical methods. Mechanochemistry refers to chemical reaction that is induced by the direct absorption of mechanical energy generated by typical methods such as shearing, stretching, and grinding.

Mechanochemistry, has recently gained much attention from synthetic chemists because it is an excellent solvent-free and atom-efficient alternative method, but also it enables access to novel organic transformation which cannot be obtained through traditional solution-based approaches. A great deal of previous research has been reported about applying mechanochemistry on organic syntheses, MOF syntheses, catalysis, and supramolecular chemistry.^{139,140,144-147} However, it is barely explored using mechanochemical methods in the synthesis of main group compounds. Only countable work, for example, Peters *et al.*¹⁴⁸ and Hanusa *et al.*^{149,150} reported strontium complexes and tris(allyl) complexes, respectively. Another example is the synthesis of indium(III) complexes through an orthogonal multi-step mechanochemical previously reported by our group.¹⁵¹ So far to our best knowledge, mechanochemistry remains poorly explored upon non-carbon backbones, and no studies have been reported before on syntheses of cyclodiphosphazanes using mechanochemical methods.

Cyclodiphosph(III/III)azanes, can be found in a multitude of topological arrangements affording enormous structure possibilities. Conventionally, syntheses of cyclodiphosphazanes has no tolerance of protic solvents stemming from their high air- and moisture-sensitivities. Therefore, the concept of Neat Grinding¹⁵², Liquid-Assisted Grinding(LAG)¹⁵³, Ion- and Liquid-Assisted Grinding (ILAG)¹⁵⁴, which is known as the solvent-free and nearly solvent-free processes, respectively, has brought the prospect of avoiding the tedious processes associated with the demand of strict anhydrous conditions while synthesizing cyclodiphosphazanes.

In this chapter, the first example of cyclodiphosphazanes synthesized by mechanochemical methodology is reported, and further studies on the application of grinding to synthesize a series of new cyclic and acyclic cyclodiphosphazane frameworks is investigated. All the structures obtained were fully characterized with various spectroscopic method and X-ray diffraction studies.

5.2 Syntheses of compounds 5.1-5.4: acyclic substitution of cyclodiphosphazanes via mechanochemistry method

The most commonly used method for the synthesis of functionalized cyclodiphosphazanes is the solution based nucleophilic substitution reactions, generally on dichlorocyclodiphosph(III/III)azane $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$. In these reactions, the outcomes can be affected by several factors in which the design or controlled syntheses of a desired structure becomes formidable. Specifically, in the reaction between $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ and 1,2-phenylenediamine, the dimeric macrocyclophosphazane $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\{1,2\text{-(NH)}_2\text{C}_6\text{H}_4\}]_2$ can be obtained with 16 hours of stirring in Tol in the presence of Et_3N at room-temperature; whereas the overnight reflux in THF/ Et_3N produces the monomer $[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\{1,2\text{-(NH)}_2\text{C}_6\text{H}_4\}]$ only. The choice of solvent is also important

given the fact that compound $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ is soluble in most solvents. Generally, protic solvents are required to dissolve the nucleophiles containing polar functionalities. Hence, mechanochemistry opens a prospective alternate access to those cases. Our initial foray into mechanochemistry involved the neat grinding of compound $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ with a series of mono-functionalized organic nucleophiles. The test reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ with 4-aminopyridine was conducted using a Retsch MM400 mixer mill loaded with a 10 mm stainless steel ball (4 g weight) at the frequency of 30 Hz, in the presence of 2.2 equivalent of Et_3N added to stabilize the HCl that was generated. 90 minutes of milling successfully generated compound **5.1**, which is confirmed by $^{31}\text{P}\{-^1\text{H}\}$ (NMR) spectroscopy. Subsequently, using the same experimental conditions, reactions of ethyl-4-aminobenzoate, 4-cyanobenzoic acid and 2-pyrimidinamine afforded their corresponding products **5.2-5.4** in quantitative yields (Scheme 5.1).

Scheme 5.1 Synthetic routes of the compounds **5.1-5.4**.

According to *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR data, only the *cis* acyclic cyclodiphosphazane isomers were formed (**5.1-5.4**), as observed by the presence of only one singlets at ~ 108, 103, 172 and 113 ppm, respectively. Both *cis* and *trans* isomers are obtained for

5.1, evidenced by two single resonances at δ 117.3 ppm (*trans*) and 105.2 ppm (*cis*). However, only the *cis* isomer was isolated by crystallization from Tol. The proposed structures are further confirmed by room-temperature ^1H NMR and FT-IR spectra of compounds **5.1** -**5.4**. The IR absorption bands at 1699, 1688, and 2228 cm^{-1} connote the presence of carbonyl and nitrile groups in **5.2** and **5.3**, which meant these functional groups remain intact during the reaction. The successful syntheses of above cyclodiphosphazanes gives confidence and provides the opportunity for further studies to be conducted towards the synthesis of more complex cyclodiphosphazane structures.

5.3 Crystal structures of compounds 5.1-5.4

Low-temperature X-ray single crystal analysis revealed that the structures of compounds **5.1** -**5.4** are acyclic substituted cyclodiphosphazanes, holding a *cis* conformation, which is consistent with the proposed structures from our initial spectroscopic analyses. Based on SC-XRD, the P-N bond distances and angles for all the four compounds are within the ranges found for the previously reported analogues (*Figure 5.1-5.4*). The exocyclic P-N bond mean distances for **5.1** and **5.2** is 1.708 Å and 1.705 Å, respectively, which is comparable to that of analogous compound $[\text{P}(\mu\text{-N}^t\text{Bu})\text{N}(\text{H})\text{C}_6\text{H}_5]_2$ (1.689 Å). The only exception is that the P-O(CO) bond distance in **5.3** (1.730(1)-1.745(1) Å) is remarkably longer than that found for $[\text{p-CN-Ph-O-P}(\mu\text{-N}^t\text{Bu})]_2$ (1.658(1)-1.678(1) Å) which can be due to the presence of the carbonyl group (*cf.*, 1.7308(8) - 1.7394(9) in $[\text{CF}_3\text{C}(\text{O})\text{OP}(\mu\text{-TerN})]_2$).

All the endocyclic N-P-N bond angles of the acyclic disubstituted reported in this study (**5.1**: 80.42(11)-80.91(11)°; **5.2**: 80.7(2)-81.0(2)°; **5.3**: 81.64(7)-81.93(7)°) are also found to be comparable to that of structural analogue $[\text{P}(\mu\text{-N}^t\text{Bu})\text{N}(\text{H})\text{C}_6\text{H}_5]_2$ (80.96(11)°). While the O-P-N bond angles of **5.3** are measured to be in the range of

96.44(7)-102.69(7)° which are akin to that found in the macrocyclic arrangements. The P-N-P bond angles for all the disubstituted acyclic compounds **5.1-5.3** are also similar to that of $[\text{P}(\mu\text{-N}^t\text{Bu})\text{N}(\text{H})\text{C}_6\text{H}_5]_2$ (96.86(11)°). Exocyclic N-P-N of the acyclic compounds are measured to be in the range of 102.83(13)-105.90(12)° for **5.1** and 101.5(2)-103.3(2)° for **5.2**.

Figure 5.1 Solid-state structure of **5.1**. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.1**: N(1)–P(2) 1.709(2), N(1)–P(1) 1.719(2), N(2)–P(2) 1.702(2), N(2)–P(1) 1.709(2), N(3)–P(1) 1.697(3), N(5)–P(2) 1.719(3); N(3)–P(1)–N(2) 105.90(12), N(3)–P(1)–N(1) 102.98(13), N(2)–P(1)–N(1) 80.42(11), N(2)–P(2)–N(1) 80.91(11), P(2)–N(1)–P(1) 98.56(12), P(2)–N(2)–P(1) 99.25(12).

Figure 5.2 Solid-state structure of **5.2**. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.2**: N(1)–P(2) 1.717(5), N(1)–P(1) 1.726(5), N(2)–P(2) 1.714(5), N(2)–P(1) 1.694(5), N(3)–P(1) 1.708(5), N(4)–P(2) 1.702(5); N(2)–P(1)–N(1) 81.0(2), N(2)–P(1)–N(3) 101.5(2), N(3)–P(1)–N(1) 102.9(2), N(4)–P(2)–N(2) 102.9(2), N(4)–P(2)–N(1) 103.3(2), N(2)–P(2)–N(1) 80.7(2).

Interestingly, compound **5.3** is, as far as we know, the first crystallographically characterized acyclic carboxyl substituted cyclodiphosphazane derived from $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ via direct nucleophilic substitution on the phosphorus centres. The previously reported cyclodiphosphazane $[\text{CF}_3\text{PC}(\text{O})\text{O}(\mu\text{-N}^t\text{Bu})]_2$ by Shreeve *et al.*,¹¹⁰ which was generated by the reaction of $[\text{ClP}(\mu\text{-N}^t\text{Bu})_2]$ with silver trifluoroacetate, would rearrange to give a more stable form $[\text{CF}_3\text{PCOP}(\text{O})(\mu\text{-N}^t\text{Bu})]_2$ via a Michaelis-Arbuzov-type mechanism. $[\text{CF}_3\text{C}(\text{O})\text{OP}(\mu\text{-TerN})]_2$ (Ter = 2,6-dimethylphenyl) is the

Figure 5.3 Solid-state structure of **5.3**. The *tert*-butyl units are drawn as wireframes in all the graphical representations. *H* atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.3**: N(1)–P(2) 1.724(3), N(1)–P(1) 1.733(3), N(2)–P(2) 1.730(3), N(2)–P(1) 1.716(3), N(3)–P(1) 1.716(3), N(5)–P(2) 1.715(3); N(2)–P(1)–N(1) 81.49(13), N(1)–P(2)–N(2) 81.38(13), N(3)–P(1)–N(1) 105.66(13), N(3)–P(1)–N(2) 100.20(13), N(5)–P(2)–N(1) 99.65(13), N(5)–P(2)–N(2) 106.68(14).

Figure 5.4 Solid-state structure of **5.4**. The *tert*-butyl units are drawn as wireframes in all the graphical representations. *H* atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.4**: N(1)–P(2) 1.6946(15), N(1)–P(1) 1.7028(14), N(2)–P(2) 1.6948(5), O(1)–P(1) 1.7297(13), O(3)–P(2) 1.7446 (12); N(1)–P(1)–N(2) 81.64(7), N(1)–P(2)–N(2) 81.93(7), P(2)–N(1)–P(1) 98.03(8), P(2)–N(2)–P(1) 98.26(7), N(1)–P(1)–O(1) 101.65(7), N(2)–P(1)–O(1) 96.44(7), N(1)–P(2)–O(3) 102.69(7), N(2)–P(2)–O(3) 96.92(7).

only example of crystallographically characterized carboxyl containing cyclodiphosph(III)azane, which was previously described by Brückner and coworkers through the biradicaloid precursor $[P(\mu\text{-TerN})]_2$ upon the reaction with silver trifluoroacetate.¹⁵⁵ However, there was no observed rearrangement taking place for this compound which might be attributed to the high steric nature of Ter substitutes on the endocyclic nitrogen atoms. Compound **5.3** is found to be stable in different solvents and at a wide range of temperatures, suggesting the importance of the aromatic substituent for affecting its stability.

5.4 Syntheses of compounds 5.5 and 5.6

The successful preparation of the above acyclic disubstituted cyclodiphosphazanes led us to further investigate the application of mechanochemistry in the synthesis of more complex cyclophosphazane-based topologies.

Topological properties of a P–N covalent framework in cyclophosph(III)azanes are considered to be affected by steric and stoichiometric factors. A classic illustration of such strict steric control in cyclophosphazanes can be observed in dimeric $[\text{XP}(\mu\text{-NR})]_2$ units are that generally contain sterically demanding groups (*e.g.*, $\text{R} = \text{'Bu}$), while trimers $[\text{XP}(\mu\text{-NR})]_3$ and larger structures can be only observed with smaller substituents (*e.g.*, $\text{R} = \text{Me, Et}$) (*Figure 5.5, I and II*). Whereas the four-membered P–N ring in a dimeric cyclophosph(III)azane maximizes space available for sterically demanding groups, this occurs at the expense of increased ring strain. Steric factors also play a crucial role in the oligomerization of cyclic arrangements (**V**), as less sterically demanding bridging substituents permit the formation of larger macrocyclic arrangements, $[\text{P}(\mu\text{-NR})]_2(\mu\text{-NR})_n$ ($n = 4, 5$).

Figure 5.5 Selected types of phosph(III)azane molecular structures.

For different cyclophosph(III)azane isomers, the steric volume of the substituent on the nitrogen atom is believed to control the stability and accessibility of the different

available topologies. Topologically different isomers can also interconvert under suitable experimental conditions. The conversion between two topological isomers can be rationalized using a concerted twist mechanism. For example, the isomerization of the macrocyclic arrangement **V** was proposed to occur *via* a P-NR-P unit rotation to generate the more thermodynamically stable adamantoid structure **VI**.

Scheme 5.2 Isomerization via twist mechanism between **V** and **VI**.

The *iso*-propyl (*i*Pr) substituted macrocyclic structure, $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})]_2$ (**4.8**), interconverts into its thermodynamically preferred adamantoid form $P_4(\text{N}^i\text{Pr})_6$ (**5.5**) upon heating in a sealed tube. However, subsequent studies on the more sterically hindered *tert*-butyl (*t*Bu) analogue, $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})]_2$ (**4.1**), revealed no trace of its adamantoid isomer even after prolonged heating. Moreover, it was established that the direct syntheses of adamantoid $P_4(\text{NR})_6$ structures, by reacting PCl_3 with RNH_2 , is only successful for less sterically hindered amines (*i.e.*, $\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$). With bulkier substituents, such as *tert*-butyl groups, this methodology is not able to produce the desired $P_4(\text{NR})_6$ adamantoid topology. Hence, experimental evidence collected over the last two decades led to the general conclusion that the formation of the adamantoid $P_4(\text{N}^t\text{Bu})_6$ (**5.6**) framework is impossible due to its highly sterically encumbered nature. We now demonstrate that this so far elusive molecular structure is readily accessible by avoiding bulk solvents and adopting an alternate approach, based on ball milling in the presence of catalytic additives.

Scheme 5.3 The isodesmic isomerization of $[\{P(\mu\text{-NR})\}_2(\mu\text{-NR})_2]$ (**V**) into $P_4(\text{NR})_6$ (**VI**) by ball milling (left) has thus far been difficult (for **5.5**) or impossible (for **5.6**) to achieve by solution methods (right). The symbol for mechanical milling was proposed by Hanusa et al.

The first target of our study was the interconversion of $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})_2]$ (**4.8**), type **V**, into its adamantoid isomer $P_4(\text{N}^i\text{Pr})_6$ (**5.5**). Previously, this rearrangement was reported to be only possible at elevated temperatures (160 °C), upon prolonged heating for 12 days. An attempt to conduct the isomerization of **4.8** by milling for 90 minutes in a Retsch MM400 mixer mill at the frequency of 30 Hz loaded with a 10 mm stainless steel ball was unsuccessful, as observed by $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectroscopy. However, the revised techniques of liquid-assisted grinding (LAG) and ion- and liquid-assisted grinding (ILAG), where either a small amount of a liquid or a combination of a catalytic amount of a liquid and a salt additive is added to induce and direct mechanochemical transformations, was investigated. As expected and excitingly, milling **4.8** in the presence of a small amount of Tol or THF (10 μL per 10 mg of solid reactant, translate to the η parameter¹⁵⁶ of 1 $\mu\text{L}/\text{mg}$) enabled the unprecedented room-temperature isomerization to afford the adamantoid isomer **5.5** in *ca.* 20% yield. Screening of different liquid and solid additives revealed that the presence of 20% by weight of LiCl led to the almost quantitative production of **5.5** after 90 minutes milling, in stark contrast to extended time and harsh reaction conditions previously reported (*vide supra*). The formation of **5.5** was also confirmed by ^1H , ^{13}C and $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR solution and solid-state spectroscopic techniques. The ^1H NMR spectrum of **5.5** in ace-

tone-d₆ shows two sets of resonances at 3.58 and 1.32 ppm, corresponding to all the six *iso*-propyl groups under the identical chemical environment, and a singlet at ~84 ppm can be found in the ³¹P-{¹H} spectrum of **5.5**, which is consistent with that reported in the literature.²⁹

Figure 5.6 ³¹P-{¹H} NMR spectra of [$\{P(\mu\text{-}^i\text{NBu})_2(\mu\text{-}^i\text{NBu})_2\}$] (**4.1**) (top) and $P_4(^i\text{NBu})_6$ (**5.6**) (bottom) in C_6D_6 .

Investigation of milling **4.1** in the presence of different additives was also performed (Table 5.1). Similar to the mechanochemical reaction of **4.8**, milling of **4.1** in the presence of 20% LiCl produced the previously elusive compound **5.6** quantitatively after 90 minutes. Such a result is astonishing given that **4.1** was reported to be inert even at 150 °C after 24 days of heating. Compound **5.6** was also characterized by ¹H, ¹³C and ³¹P-{¹H} NMR spectroscopy. The ³¹P-{¹H} NMR spectra for **5.6** revealed a singlet at δ 54.47 ppm, which is comparable to that found for the ⁱPr analogue, at δ 84.0 ppm (*cf.*, 146 ppm in **4.1**). The ¹³C NMR spectrum shows two single resonances at δ 59.29 and δ 31.38 ppm (*cf.*, δ 58 and δ 29 ppm in **4.1**). In contrast to the precursor **4.1**, the ¹H NMR spectrum of **5.5** shows only one single resonance at δ 1.51 ppm (*cf.*, 1.57 and 1.53 ppm in **4.8**), which confirmed the isomerization to an adamantoid structure.

Table 5.1 Conversion of **4.1** to **5.6** with grinding in the presence of different additives

additive	Ratio /Amount	Frequency /Hz	Ball Size /mm	Time/hour	Conversion /%
None	-	30	10	1.5	0
Tol	0.1 ml	30	10	1.5	5
THF	0.1 ml	30	10	1.5	4
DMF	0.1 ml	30	10	1.5	3
LiCl	1/10	30	10	1.5	0
LiCl	1/5	30	10	1.5	100
LiCl	1/3	30	10	1.5	30
LiBr	1/10	30	10	1.5	0
LiBr	1/5	30	10	1.5	6
NaCl	1/5	30	10	1.5	6

5.5 Crystal structures of compound 5.5 and 5.6

Figure 5.7 Solid-state structure of **5.5**. The iso-propyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.5**: N(1)-P(1) 1.719(15), N(1)-P(2) 1.715(15), N(2)-P(2) 1.723(14), N(2)-P(3) 1.730(14), N(3)-P(3) 1.698(14), N(3)-P(1) 1.708(14), N(4)-P(4) 1.700(14), N(4)-P(2) 1.724(14), N(5)-P(1) 1.707(14), N(5)-P(4) 1.732(14), N(6)-P(3) 1.685(14), N(6)-P(4) 1.695(13); P(2)-N(1)-P(1) 123.4(8), P(2)-N(2)-P(3) 125.5(9), P(3)-N(3)-P(1) 122.0(9), P(4)-N(4)-P(2) 123.6(9), P(1)-N(5)-P(4) 125.0(9), P(3)-N(6)-P(4) 125.5(10), N(5)-P(1)-N(3) 101.0(9), N(1)-P(2)-N(2) 98.4(8), N(3)-P(3)-N(2) 100.6(10), N(6)-P(4)-N(4) 104.0(10).

The low-temperature single crystal X-ray diffraction structures of **5.5** and **5.6** are in agreement with the initial spectroscopic analyses for these compounds (Figure 5.7 and 5.8). Compound **5.6** crystallizes in a $P\bar{3}m1$ space group, there are two molecules in the asymmetric unit for **5.6**. The structural parameters are consistent with the previously

less sterically hindered analogues. It is noteworthy that the average P-N distance in **5.6** (1.719 Å) is longer than that in analogues with less sterically demanding N-substituents (*cf.*, 1.69 and 1.708 Å in P₄(NMe)₆ and P₄(NEt)₆, respectively), which can be rationalized by the presence of the bulky substituent *tert*-butyl groups.

Figure 5.8 Solid-state structure of **5.6**. The *tert*-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **5.6**: N(1)-P(1A) 1.715(5), N(1)-P(2) 1.7175(15), N(1)-P(2A) 1.785(6), N(2)-P(2A) 1.714(3), N(2)-P(1) 1.722(3), N(2)-P(2) 1.725(3), N(3)-P(4) 1.704(4), N(3)-P(3) 1.7085(19); P(1A)-N(1)-P(2A) 122.0(4), P(1)-N(2)-P(2) 122.66(18), N(1)-P(2)-N(2) 100.97(12), N(2)-P(2A)-N(1) 98.7(2).

The facile formation of **5.6** by milling in the presence of catalytic amount of LiCl is surprising and in contrast to the established understanding of cyclodiphosphazane chemistry. Therefore, we decided to verify the viability of the isodesmic **4.1**→**5.6** isomerization through single molecule *ab initio* calculations. Geometry optimization and frequency calculations were performed at the B3LYP/B1 level. Single-point calculations were also performed with the 6-311+G(d,p) basis set (henceforth B2). *Figure 5.9* shows the energy diagram of the isomerization, obtained at the B3LYP/B2//B3LYP(B1) +ZPE level, where ZPE stands for zero-point vibrational energy.

Figure 5.9 Energy diagram (in kcal/mol) for the isodesmic isomerization of **4.1**→**5.6**, obtained at the B3LYP/B2//B3LYP(B1) +ZPE level.

In contrast to that previously reported in the literature, where the twist mechanism was suggested for this type of isomerization, our computational study suggests a stepwise mechanism instead. The first step involves the formation of one P–N bond, while two more are cleaved in the second step (**TS1**). The postulated intermediate **Int1** adopts a bicyclic [3,1,1] structure, (type **III** in Figure 5.5). Such cyclophosph(III)azane topological structure has been previously reported (*e.g.*, for R = Cl, N₃, N(SiMe₃)₂), confirming the plausibility of the proposed mechanism. However, we have so far not been able to experimentally isolate **Int1** intermediate. Subsequently, Int1 transform into the adamantoid product *via* **TS2**. The overall reaction is exothermic (~35 kJ·mol⁻¹), but involves very high energy barriers. This might help explain the previous unsuccessful tryouts made to access the arrangement **5.6** with traditional methods.

It is tempting to rationalize the unprecedented formation of **5.6** by milling as a result of changes in the electronic structure of reactants caused by mechanical shear, as proposed by Gilman¹⁵⁷ for chemical reactions triggered by mechanical forces. However,

such effects of shear on chemical reactivity have been reported for polymers, in which pulling onto a molecular chain causes a mechanical effect on a reactive (mechanophore) site. For small molecules like **4.1**, milling is more likely to cause the formation of a high-energy amorphous phase that serves as a non-conventional and continuously agitated reaction environment. Therefore, we believe that the herein presented formation of a previously inaccessible molecule illustrates the transformative potential that switching to a solvent-free or solvent-reduced environments can have on established chemical syntheses.

5.6 Conclusion

In summary, we have successfully synthesized cyclodiphosphazanes **5.1-5.4** *via* a mechanochemical nucleophilic substitution reaction of dichlorocyclodiphosph(III/III)azane [ClP(μ -N^tBu)]. To the best of our knowledge, the herein described results are the first mechanochemical transformation of inorganic frameworks composed of non-carbon backbones. In addition, this work also demonstrates the importance of the reaction environment in promoting chemical transformations inaccessible by conventional means. Such utilization of solvent-free mechano-synthesis is not restricted to cyclodiphosphazanes, but could also be implemented other main group elements and reactions. Our studies presently realize the previously inaccessible but desired isodesmic isomerization of **4.1** into the extremely sterically encumbered system **5.6**. The principles demonstrated by our study potentially open up a broad area of previously unexplored inorganic transformations, enabled by mechanochemistry, which may be extendable to wider range of main group inorganic molecules and framework systems.

Chapter 6: Novel acyclic trimeric cyclodiphosphazanes $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-E})[\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2\text{N}(\text{H})\text{R}]_2$

6.1 Introduction

Ligands containing heteroatoms (*e.g.*, phosphorus, nitrogen) are good candidates for augmenting catalysts, due to their strong binding ability to the early transition metals, and their mode of coordination and ligand hapticity can be varied. Cyclodiphosph(III/III)azanes, containing both phosphorus and nitrogen atoms, which can act as coordinating sites, have been explored extensively as an excellent multi-site or multidentate coordinative type of ligands, mainly as neutral or dianionic ligands for s and p-block as well as transition metals.^{23,99,158-162} The dianionic bis(amido)P ligands have also been studied for possible applications in catalysis and as a ligand for main group metals.^{97,99,163-165} These complexes typically involve chelation of the metal atoms through the exocyclic nitrogen atoms or additional coordination by an endocyclic nitrogen atom may also occur to give a seco-hetero cube arrangement (*Figure 6.1*, a & b).

In addition, the sterically demanding bis(phosphite) ligands have been proved to be able to stabilize the transition metals with low coordination numbers and/or unusual oxidation states, therefore leading to high reactivity which result in good regioselectivity during the catalytic processes.¹⁶⁶⁻¹⁶⁹ This is still an unexplored field for ligands based on cyclodiphosph(III/III)azane backbones.

Figure 6.1 Dianionic bis(amido)P ligands (a & b) and large bit bis(phosphite) ligands (c & d).

Herein, we report the first example of an acyclic trimeric cyclodiphosphazane as a potential large bite angle ligand with possible application of stabilizing transition metals with low coordination numbers and/or unusual oxidation states, based on steric bulk.

6.2 Syntheses of compounds 6.2-6.5

Our initial attempts to synthesize a mixed bis-dimer $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^i\text{Pr})]_2$ with *tert*-butyl groups on the ring nitrogen and the isopropyl groups on the bridging nitrogen atoms, was by a condensation reaction of $[\text{Cl}\{P(\mu\text{-N}^t\text{Bu})\}]_2$ with lithiated cyclodiphosphazane **6.1** $[\text{}^i\text{Pr}(\text{Li})\text{N}\{P(\mu\text{-N}^t\text{Bu})\}]_2$. While, with 12 hours refluxing in Tol, the reaction monitoring *in situ* ^{31}P - $\{^1\text{H}\}$ NMR spectra did not show any resonances around 140~150 ppm, which was expected for the desired product $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^i\text{Pr})]_2$ (*cf.*, 147 ppm in $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})]_2$ and 145 ppm in $[\{P(\mu\text{-N}^t\text{Bu})\}_2(\mu\text{-N}^t\text{Bu})]_2$). The formed product isolated through crystallization was proved to be the acyclic trimeric cyclodiphosphazane **6.2** $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^i\text{Pr})P(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^i\text{Pr}]_2$ by single-crystal X-ray diffraction studies (*Scheme 6.1*).

Scheme 6.1 Synthetic route of compound **6.2** $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^i\text{Pr})P(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^i\text{Pr}]_2$.

An alternative route was designed and utilized to synthesize compound **6.2**, as shown in *Scheme 6.2*, in which an asymmetrically substituted cyclodiphosphazane $\text{Cl}[P(\mu\text{-N}^t\text{Bu})]_2\text{N}(\text{H})^i\text{Pr}$ was synthesized prior to reacting with compound **6.1** $[\text{}^i\text{Pr}(\text{Li})\text{N}\{P(\mu\text{-N}^t\text{Bu})\}]_2$ in a ratio of 2 to 1 in refluxing Tol. This strategy successfully afforded the

acyclic trimeric cyclodiphosphazane **6.2** $\{ \{ \text{P}(\mu\text{-N}^i\text{Bu}) \}_2[(\mu\text{-N}^i\text{Pr})\text{P}(\mu\text{-N}^i\text{Bu})_2\text{PN}(\text{H})^i\text{Pr}]_2$, as evidenced by *in situ* ^{31}P - $\{^1\text{H}\}$ NMR spectra.

Scheme 6.2 Synthetic routes of compound **6.2-6.5**.

The structure of compound **6.2**, as crystallographically determined as an “M” shape, makes it a potential $2e^-$ large bite ligand, upon deprotonation of the NH atoms. Moreover, the vast majority of studies on cyclodiphosphazanes have shown that the steric nature of the substitutes on the P_2N_2 ring could largely affect the configuration and conformation of their topologies. Therefore, using a similar synthetic method to produce compound **6.2**, attempts have been made to synthesize the acyclic trimeric

cyclodiphosphazane frameworks bridged by different sterically bulky R groups (*Scheme 6.2*). The condensation reaction between $\text{Cl}[\text{P}(\mu\text{-N}^t\text{Bu})]_2\text{NH}^t\text{Bu}$ and $[\text{Pr}(\text{Li})\text{N}\{\text{P}(\mu\text{-N}^t\text{Bu})\}]_2$, $[\text{H}_2\text{N}\{\text{P}(\mu\text{-N}^t\text{Bu})\}]_2$ and $[\text{LiO}\{\text{P}(\mu\text{-N}^t\text{Bu})\}]_2$, using a stoichiometric ratio of 2 :1, in the presence of excess amounts of Et_3N as the Brønsted base whenever it is necessary, produced the compounds $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-E})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}]_2$ ($\text{E} = \text{N}^t\text{Pr}$, **6.3**; NH , **6.4**; O , **6.5**) in the isolated yields of 37%, 83% and 56% respectively. Successful isolation by crystallization allowed for complete characterization of compounds **6.3-6.5**. The $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectrum of compound **6.3-6.5** shows three sets of resonances at ~110, 108, and 99 ppm; 113, 104, and 101 ppm; and 140, 139, and 119 ppm respectively, corresponding to three different magnetically-inequivalent phosphorus atoms in each structure. For ^1H NMR of compounds **6.3** and **6.4**, all the protons of the six *tert*-butyl groups on the *endo*-cyclic nitrogen atoms present as singlets at 1.48 and 1.49 ppm for each, with the intensity ratio of 3:1 to the two *tert*-butyl groups on the terminal nitrogen atoms with the chemical shift at 1.63 and 1.28 ppm. The observed difference, three singlets at 1.56, 1.50 and 1.28 ppm with intensity ratio of 1:2:1 shown in the ^1H NMR of compounds **6.5**, can be attributed to the two *tert*-butyl on the bridging P_2N_2 ring, four on the terminal P_2N_2 ring, and two on the terminal nitrogen atoms.

6.3 Crystal structures of compounds 6.2-6.5

The solid-state structure of **6.2** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^t\text{Pr})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Pr}]_2$ as determined by SC-XRD, shows an acyclic poly-cyclodiphosphazane backbone containing three P_2N_2 rings bridged by N^tPr groups, as shown in *Figure 6.2*. The two ending P_2N_2 rings facing to each other and both adopt a *cis*-endo confirmation to the centre P_2N_2 ring, which makes the whole molecule resemble the shape of the letter “M”. The two

*i*Pr groups on the terminal nitrogen atoms contain a *cis*-endo confirmation, resulting in the two hydrogen atoms on them pointing to each other. The long distance of 7.805 Å between N1---N10 is comparable with the reported Si---Si distance 7.755 Å in SiNSi as described by Driess *et al.*¹⁷⁰ Meanwhile, the sterically demanding bulky substituents on the P₂N₂ four member rings enable the molecule to act as a large bite-angle ligand, which can be used to potentially stabilize the low coordination numbers and/or unusual oxidation states transition metals..

Figure 6.2 Solid-state structure of **6.2**. The iso-propyl and tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **6.2**: N(1)–P(1) 1.649(3), N(2)–P(1) 1.748(2), N(2)–P(2) 1.726(2), N(3)–P(1) 1.751(2), N(3)–P(2) 1.728(2), N(4)–P(3) 1.717(2), N(5)–P(3) 1.734(2), N(6)–P(3) 1.747(2), N(5)–P(4) 1.742(2), N(6)–P(4) 1.744(2), N(7)–P(4) 1.716(2), N(7)–P(5) 1.730(2), N(8)–P(5) 1.734(2), N(8)–P(6) 1.749(2), N(9)–P(5) 1.730(2), N(9)–P(6) 1.739(2), N(10)–P(6) 1.651(2); N(1)–P(1)–N(2) 104.66(13), N(2)–P(1)–N(3) 82.12(11), P(2)–N(2)–P(1) 96.96(11), P(3)–N(4)–P(2) 122.06(13), N(4)–P(3)–N(5) 106.37(11), P(4)–N(6)–P(3) 96.53(12), P(4)–N(7)–P(5) 121.79(13), P(5)–N(8)–P(6) 96.85(12), N(9)–P(6)–N(8) 82.17(11), N(10)–P(6)–N(8) 106.45(13).

The P–N average bond distances within the P₂N₂ ring, the bridging P–N and the terminal P–N are 1.739(5), 1.723(2) and 1.650 Å respectively (*cf.*, 1.726 and 1.664 Å in [tBu(H)NP(μ-N^tBu)]₂). The acyclic bridging P–N bond in compound **6.2** is much longer than the acyclic terminal P–N bond due to the steric effect. A typical geometry of cyclodiphosphazanes, consisting of all lone pairs of electrons on the acyclic nitrogen atoms to be almost parallel to the P₂N₂ ring, remains in compound **6.3**. The torsion angle around all the phosphorus centres are similar and with the average value ∼104.5°,

which is comparable with the reported analogous compounds (103.2° in $[\text{tBu(H)NP}(\mu\text{-N}^t\text{Bu})]_2$).

As shown in *Figure 6.3*, the structure of compound **6.3** is very similar to that of compound **6.2** with the only difference being that the substituent on the pendant nitrogen atoms for compound **6.3** are *tert*-butyl groups instead of *iso*-propyl groups (compound **6.2**). Therefore, the interatomic bond lengths and angles obtained for **6.3** are almost similar to that for **6.2**. For instance, the mean distance for P-N bonds within the P_2N_2 ring in **6.3** is $1.738 \text{ \AA}$ (*cf.*, $1.739 \text{ \AA}$ for **6.2**). The bridging P-N and the terminal P-N average bond distances are 1.720 and $1.628 \text{ \AA}$ respectively. Moreover, the distance between N1 and N10 is $7.684 \text{ \AA}$, which is comparable with that found for **6.2**.

Figure 6.3 Solid-state structure of **6.3**. The *iso*-propyl and *tert*-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [$\text{\AA}$] and Angles [$^\circ$] for **6.3**: $\text{N}(1)\text{--P}(1)$ $1.621(8)$, $\text{N}(2)\text{--P}(1)$ $1.750(2)$, $\text{N}(2)\text{--P}(2)$ $1.730(2)$, $\text{N}(3)\text{--P}(1)$ $1.745(2)$, $\text{N}(3)\text{--P}(2)$ $1.724(2)$, $\text{N}(4)\text{--P}(3)$ $1.709(2)$, $\text{N}(5)\text{--P}(3)$ $1.745(2)$, $\text{N}(6)\text{--P}(3)$ $1.742(2)$, $\text{N}(5)\text{--P}(4)$ $1.739(2)$, $\text{N}(6)\text{--P}(4)$ $1.741(2)$, $\text{N}(7)\text{--P}(4)$ $1.706(2)$, $\text{N}(7)\text{--P}(5)$ $1.733(2)$, $\text{N}(8)\text{--P}(5)$ $1.726(2)$, $\text{N}(8)\text{--P}(6)$ $1.749(2)$, $\text{N}(9)\text{--P}(5)$ $1.724(2)$, $\text{N}(9)\text{--P}(6)$ $1.749(2)$, $\text{N}(10)\text{--P}(6)$ $1.634(7)$; $\text{N}(1)\text{--P}(1)\text{--N}(2)$ $102.7(4)$, $\text{N}(2)\text{--P}(1)\text{--N}(3)$ $81.53(10)$, $\text{P}(2)\text{--N}(2)\text{--P}(1)$ $97.13(11)$, $\text{P}(3)\text{--N}(4)\text{--P}(2)$ $121.79(12)$, $\text{N}(4)\text{--P}(3)\text{--N}(5)$ $109.38(10)$, $\text{P}(4)\text{--N}(6)\text{--P}(3)$ $96.30(10)$, $\text{P}(4)\text{--N}(7)\text{--P}(5)$ $121.47(12)$, $\text{P}(5)\text{--N}(8)\text{--P}(6)$ $97.16(12)$, $\text{N}(9)\text{--P}(6)\text{--N}(8)$ $81.65(10)$, $\text{N}(10)\text{--P}(6)\text{--N}(8)$ $99.2(3)$.

Due to the smaller substituents (protons) on the acyclic bridging nitrogen atoms, as shown in *Figure 6.4*, compound **6.4** contains a much longer N1---N10 distance, as compared to compound **6.2** and **6.3**, which is possibly caused by the huge deduct of steric demands on N4 and N7. The average angle between P2-N4-P3 and P4-N7-P5 is $\sim 126^\circ$, which is much larger than that of **6.3** (121°). These results inspire us to design

other cyclodiphosphazane compounds that allow for the tuning of the bite angle of the acyclic trimers.

Figure 6.4 Solid-state structure of **6.4**. The *tert*-butyl units are drawn as wireframes in all the graphical representations. *H* atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **6.4**: N(1)–P(1) 1.641(4), N(2)–P(1) 1.765(4), N(2)–P(2) 1.717(2), N(3)–P(2) 1.740(2), N(4)–P(2) 1.694(3), N(4)–P(3) 1.788(3), N(5)–P(3) 1.783(4), N(6)–P(3) 1.727(4); N(1)–P(1)–N(2) 102.6(19), N(3)–P(2)–N(2) 84.9(17), P(2)–N(2)–P(1) 96.4(17), P(2)–N(2)–P(3) 124.0(2), N(6)–P(3)–N(5) 82.0(16), N(5)–P(3)–N(4) 102.4(17).

This led to the design and syntheses of acyclic trimeric cyclodiphosphazane $\{P(\mu\text{-}N^t\text{Bu})\}_2[(\mu\text{-}O)P(\mu\text{-}N^t\text{Bu})_2PN(H)^t\text{Bu}]_2$ **6.5**. Crystallization in the minimum amount of hot THF afforded diffraction quantity crystals of **6.5** (Figure 6.5). Analysis of the solid-state structure of **6.5** revealed that three P_2N_2 ring units were joint together by two oxygen atoms, forming a framework in an arch bridge shape. This significantly reduces the distance between N1 and N10 to 6.602 Å, due to the nature of the bridging atoms and the P–O bonds locked in a *cis-endo* confirmation. The P–N average bond distances within the P_2N_2 ring, the bridging P–O and the terminal P–N found for **6.5** are 1.716, 1.661 and 1.681 Å respectively, which falls into the ranges found for previously reported analogues.

Figure 6.5 Solid-state structure of **6.5**. The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **6.5**: N(1)–P(1) 1.676(4), N(2)–P(1) 1.808(4), N(2)–P(2) 1.692(2), N(1)–P(2) 1.705(2), O(1)–P(2) 1.6771(18), O(1)–P(3) 1.6447(17), N(3)–P(3) 1.7158(19), N(4)–P(3) 1.7018(19); N(1)–P(1)–N(2) 80.33(17), N(1)–P(2)–N(2) 82.94(10), P(2)–N(1)–P(1) 99.58(16), P(2)–N(2)–P(1) 95.03(15), P(3)–O(1)–P(2) 124.74(10), N(1)–P(1)–N(5) 101.8(3), N(3)–P(3)–N(4) 81.32(10).

Herein, we have synthesized and reported the first examples of acyclic trimeric cyclodiphosphazanes **6.2** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^i\text{Pr})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^i\text{Pr}]_2$, **6.3** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-N}^i\text{Pr})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}]_2$, **6.4** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-NH})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}]_2$, and **6.5** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}]_2$, which can potentially be used as large bite angle ligands, to stabilize transition metals with unusual oxidation states. Further studies into this system is currently ongoing in our group.

6.4 Syntheses and crystal structure of O-bridged hexameric macrocyclodiphosphazane $\{(\mu\text{-O})[\text{P}(\mu\text{-N}^t\text{Bu})]\}_6$ (compound **6.6**)

Macrocyclodiphosph(III/III)azane systems are commonly generated by reacting the cyclodiphosphazane $[\text{CIP}(\mu\text{-NR})]_2$ with a wide range of inorganic and organic linkers to produce inorganic or hybrid macrocyclodiphosphazanes with a formula of $[\{\text{P}(\mu\text{-NR})\}_2(\mu\text{-X})]_n$ or $[\{\text{P}(\mu\text{-NR})\}_2(\mu\text{-LL}')]_n$, (X = O, Se, NR; R = H, ^iPr and ^tBu), respectively. As mentioned earlier, the size of macrocyclodiphosphazanes is mainly controlled by the nature of linkers, as well as its relative stoichiometric ratio. In most

cases, using the same cyclodiphosphazane precursor $[\text{ClP}(\mu\text{-NR})]_2$, the ring size of the macrocycle products are determined by the chosen linker. In particular, for inorganic linkers, it has been well-established that their size is dictated by the nature and steric bulk of the bridging atoms. For instance, tetrameric and hexameric macrocycles are formed when oxygen and selenium are used as bridging atoms; whereas tetramers are favored over dimeric systems when the steric bulk of the bridging groups is reduced by truncating N^iPr to NH groups.

In all the above-mentioned case, we believed that this could be traced back to the use of single unit cyclodiphosphazanes as precursors. Therefore, our new synthetic approach, henceforth, is to control the size of the macrocycles *via* a condensation reaction using acyclic poly-cyclodiphosphazanes as precursors. Specifically, the herein described reaction between acyclic trimeric cyclodiphosphazanes would form hexameric macrocyclodiphosphazane.

The slow dropwise addition of $[\text{LiOP}(\mu\text{-N}^t\text{Bu})]_2$ (generated *in situ* in THF) to a solution of $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ in a stoichiometric ratio of 1:2 at low-temperature afforded the *O*-bridged acyclic trimeric cyclodiphosphazane $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-NH})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$ (**6.7**) (Scheme 6.3). *In situ* ^{31}P - $\{^1\text{H}\}$ NMR spectrum revealed that the reaction quantitatively formed **6.7**, with three sets of product resonances at ~ 140 , ~ 162 and ~ 198 ppm, corresponding to the center, bridging and terminal phosphorus atoms, respectively (Figure 6.6).

Scheme 6.3 Synthetic route of compound **6.7** $\{\text{P}(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-O})\text{P}(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$

Figure 6.6 *In situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of compound **6.7** $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-NH})P(\mu\text{-N}^t\text{Bu})_2\text{PCl}]_2$.

Despite the meticulous care taken when handling the product, all the attempts made to obtain the diffraction quality crystals of **6.7** were not successful, possibly due to the extreme air- and moisture- sensitivity of the compound. The isolation of compound **6.7** was also unsuccessful due to the same reason, as well as its high solubility in most organic solvents, which makes the washing work-up method not feasible. The subsequent controlled hydrolysis of compound **6.7** with $\text{H}_2\text{O}/\text{Et}_3\text{N}$ followed by the lithiation produced acyclic trimeric cyclodiphosphazane $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-NH})P(\mu\text{-N}^t\text{Bu})_2\text{POLi}]_2$ (**6.8**), when combined with **6.7** in a 1:1 stoichiometric ratio would form the *O*-bridged hexameric macrocyclodiphosphazane $\{(\mu\text{-O})[P(\mu\text{-N}^t\text{Bu})]_2\}_6$ (Scheme 6.4). Formation of the hexameric macrocycle was evidenced by *in situ* $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum which showed a main singlet at ~ 138 ppm.

Figure 6.7 Solid-state structure of **6.6** (left, top view; right, side view). The tert-butyl units are drawn as wireframes in all the graphical representations. H atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected Bond Lengths [Å] and Angles [deg] for **6.6**: N(1)–P(1) 1.710(6), N(2)–P(1) 1.712(6), N(2)–P(2) 1.718(6), N(1)–P(2) 1.688(6), O(1)–P(1) 1.655(5); N(1)–P(1)–N(2) 81.4(3), N(1)–P(2)–N(2) 81.8(3), P(2)–N(1)–P(1) 98.1(3), P(2)–N(2)–P(1) 96.9(3), P(1)–O(1)–P(6) 121.7(3).

6.5 Conclusion

In this chapter, we have successfully synthesized the first family of acyclic trimers with formula of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-E})P(\mu\text{-N}^t\text{Bu})_2PN(\text{H})\text{R}]_2$ (**6.2**: E = N^{*i*}Pr, R = ^{*i*}Pr; **6.3**: E = N^{*i*}Pr, R = ^{*t*}Bu; **6.4**: E = NH, R = ^{*t*}Bu; **6.5**: E = O, R = ^{*t*}Bu). The SC-XRD data of the compound **6.2-6.5** represents a long distance between the two terminal nitrogen atoms N1 and N10. This provides the possibility of the application of these trimers as large-bite ligands or pincer ligands to stabilize the transition-metals with low coordination numbers and/or unusual oxidation states. In addition, inspired by the *O*-bridged trimer **6.5**, the first *O*-bridged hexameric macrocyclodiphosphazane $\{(\mu\text{-O})[P(\mu\text{-N}^t\text{Bu})]_2\}_6$ containing only P(III) centres in the backbone was synthesized and fully characterized using various spectroscopic techniques.

Conclusions and outlook

Firstly, a set of chalcogenide cyclodiphosph(V/V)azane derivatives from a single cyclodiphosph(III/III)azane precursor was synthesized and characterized. Their air- and moisture- stability was also studied and proved to be the first example of a group of all the accessible chalcogenide oxidised derivatives obtained from a single cyclodiphosph(III/III)azane precursor that are air-stable over prolonged periods of time. Compounds **3.1** to **3.4** were improved tremendously regarding air- and moisture- stability as compared to non-functionalized dimeric cyclodiphosph(III)azane compound **3.0**, and compound **3.3** and **3.4** was inert to water even at temperatures as high as 100 °C. Besides, the oxidation reaction of **4.1** with group 16 elements would produce either diagonally oxidised product **4.2**, **4.3**, **4.4** without or fully oxidised product **4.6**, **4.6**, **4.7** with C-N cleavage by losing *tert*-butyl groups. In contrast, oxidation reaction of **4.8** with less steric substituents on nitrogen by elemental Se affording the fully oxidised product **4.9**, showed only one substituent loss. Our experimental and theoretical studies demonstrate that steric factors, most probably steric strain release, play a crucial role in the activation of the C–N bonds. The work reported here highlights the potential of steric bond activation and its implications on a broader scope for application to main group frameworks in general. The rational design of synthetic approaches which fully exploit this approach in a wider range of main group frameworks is an exciting challenge in the area of metal-free bond activation. Both of these two projects results have shown that it is feasible to stabilizing the cyclodiphosphazane frameworks by oxidizing their phosphorus centres.

Moreover, we have successfully synthesized cyclodiphosphazanes **5.1-5.4** via a mechanochemical nucleophilic substitution reaction of dichlorocyclodiphosph(III/III)azane [ClP(μ -N^{*t*}Bu)]. To the best of our knowledge, the herein described results are the first

mechanochemical transformation of inorganic frameworks composed of non-carbon backbones. More importantly, our studies presently realize the previously inaccessible but desired isodesmic isomerization of **4.1** into the extremely sterically encumbered system **5.6**. The principles demonstrated by our study potentially open up a broad area of previously unexplored inorganic transformations, enabled by mechanochemistry, which may be extendable to wider range of main group inorganic molecules and framework systems.

Last but not the least, we have synthesized the first family of acyclic trimers with formula of $\{P(\mu\text{-N}^t\text{Bu})\}_2[(\mu\text{-E})P(\mu\text{-N}^t\text{Bu})_2PN(\text{H})\text{R}]_2$ (**6.2**: E = N^{*i*}Pr, R = ^{*i*}Pr; **6.3**: E = N^{*i*}Pr, R = ^{*t*}Bu; **6.4**: E = NH, R = ^{*t*}Bu; **6.5**: E = O, R = ^{*t*}Bu). The SC-XRD data of the compound **6.2-6.5** represents a long distance between the two terminal nitrogen atoms N1 and N10. This provides the possibility of the application of these trimers as large-bite ligands or pincer ligands to stabilize the transition metals with low coordination numbers and/or unusual oxidation states. In addition, inspired by the *O*-bridged trimer **6.5**, the first *O*-bridged hexameric macrocyclodiphosphazane $\{(\mu\text{-O})[P(\mu\text{-N}^t\text{Bu})]_2\}_6$ (**6.6**) with only P(III) centres in the backbone was synthesized and fully characterized with various spectroscopies. The structure of compound **6.6** also resembles that of crown ethers (18-crown-6), which might allow one to envisage its use as an encapsulating macrocyclic ligand for large cations.

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