Recent advances in organophosphorus–chalcogen and organophosphorus–pincer based macrocyclic compounds and their metal complexes†

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The design and development of phosphorus based macrocycles containing one or more other heteroatoms is of crucial importance for the enhancement of modern synthetic chemistry. In recent years focus on phosphorus based macromolecules has led to intriguing and innovative structures with a variety of applications, including photophysical and host–guest properties, and in organic synthesis. This article summarizes the recent advancements in the synthesis of macromolecules that consist of organophosphorus–chalcogen (P−E, P=E; E = O, S, Se) and organophosphorus–pincer based macrocyclic ligands and their transition metal complexes with emphasis given to synthetic methodologies. The reactions involve the modification of simple macrocycles with phosphorus sources or phosphorus-based chalcogen-generating reagents. Transition metal complexes of phosphine-based macrocyclic pincer ligands and their reactivity are also included.

Introduction

The last few decades have witnessed immense growth in the development of new methods for the synthesis of sophisticated organic compounds, with special emphasis on macrocyclic compounds.1–14 Macrocycles embedded with different heteroatoms and donor functionalities can undergo self-assembly with or without metal atoms/ions to form a 1D, 2D or 3D-network with different ring sizes and molecular cavities.15–17 Such molecules with defined cavities can identify and selectively bind cations, anions or neutral molecules of different sizes and shapes including chiral molecules and find a wide range of applications in supramolecular chemistry,18 materials science19,20 and drug delivery.21,22 Molecules such as crown ethers,23 cyclodextrins,24 cryptands,25 calixarenes26 and resorcinalenes27,28 have offered impressive model structures for molecular recognition, noncovalent-bond interactions and self-assembly.

Functionalised macrocycles are even better as they can serve as hubs for the manufacture of sophisticated molecular architectures, optoelectronic devices, sensing devices and specialized materials.20,29,30 In addition, macrocycles with 12 or more atoms in the ring possess efficient biological activity, especially in chemotherapy for a wide variety of cancers and tumours.31 Phosphorus possesses a maximum covalency of six and oxidation states ranging from −3 to +5. Both nature and industry illustrate the structural diversity of phosphorus compounds.32 In order to achieve innovative phosphorus-based functional materials, the advancement of the interface between phosphorus chemistry and phosphorus macrocycles is captivating but highly challenging. In the last few decades, several methodologies have been developed for the synthesis of phosphorus macrocycles33,34 and attention has been paid to macrocycles containing both P(v) and P(III) atoms because of their distinct geometries, reactivity and complexation behaviour.35,36 Examples include phosphines, phosphine oxides, phosphates, phosphonium salts, phosphonates, and phosphoranes.37 Phosphorus–nitrogen compounds have been extensively studied, but reports on phosphorus-macrocycles containing chalcogens and carbon are scarce.

In this context, attempts are made in this perspective article to give a brief account of phosphorus-based macrocycles containing P−E (E = O, S or Se) and P–C bonds in the ring system with emphasis on synthetic methodologies. Metal complexes of representative macrocycles are also included in the discussion. The discussion revolves around the following sections: 1. phosphorus–chalcogen based macrocycles having P−E and P=E (E = O, S and Se) linkages, 2. phosphorus–chalcogen based macrocycles bearing a P2N2 scaffold, 3. phosphorus macrocycles with a pincer scaffold, and 4. transition metal complexes of phosphorus–chalcogen and phosphine–pincer based macrocyclic compounds.

†This perspective article is dedicated to Prof. Joel T. Mague on the occasion of his 80th birthday.
History and development of phosphorus-containing macrocycles

The historical background of phosphorus-containing macrocycles dates back more than 100 years, when Stokes (in 1897) formulated and isolated tri- and tetraphosphonitrilic chlorides and their higher analogues \([\text{PNCI}_2]_n\) \((n = 5, 6 \text{ or } 7)\). During the same period Michaelis and Schroeter\(^{39}\) (in 1894) reported the reaction of PCl\(_3\) with aniline hydrochloride which resulted in the formation of chlorophosphazane \([\text{ClPNPh}]_3\), the X-ray structure of which was confirmed only in 1971.\(^{40}\) However, phosphorus containing macrocycles made their appearance only in the 1970s, a few years after Pedersen discovered crown ethers and their distinctive coordinating properties in 1967.\(^{41}\) The long silence related to phosphorus chemistry might be due to the absence of enthusiasm, tedious synthetic methods, non-availability of appropriate reagents, low yields, and/or instability (especially in the case of phosphines) issues. Nevertheless, apart from the prospective complex-forming abilities often witnessed with heteroatom-containing macrocycles, phosphorus macrocycles may acquire the benefit of the exceptional features of phosphorus species such as versatile coordination behaviour (potentially from 2 to 6) and a variety of chemical reactions comparable to carbon analogues.\(^{42}\)

In 1994, Caminade and Majoral published a comprehensive review devoted to the synthesis of phosphorus-containing macrocycles and cryptands.\(^{43}\) The synthetic strategy involved the cleavage of smaller phosphorus-containing rings to form tri- and tetraphosphonitrilic chlorides and their higher analogues \([\text{PNCl}_2]_n\). During the same period, Maravanji S. Balakrishna and co-workers prepared macrocycles 1–3 containing P–O, P–S, P–N, P–N–N and P–Si bonds with phosphorus atoms in diverse valence states. Later a number of novel articles and reviews appeared on phosphorus macrocycles containing one or more other heteroatoms such as selenium, oxygen,\(^{44}\) and nitrogen,\(^{44}\) or heterocycles such as pyrrole,\(^{45,46}\) thiophene,\(^{47}\) phosphole,\(^{48}\) and even chiral phosphorus-containing catenanes.\(^{49}\)

**Phosphorus–chalcogen based macrocycles**

Macrocycles embedded with heavier \(p\)-block elements are very unusual and often exhibit rare structural features.\(^{50,51}\) In general, the known approaches for the preparation of these heterocyclic compounds are multistep low yield reactions involving very toxic reagents and harsh reaction conditions. Organic macrocycles containing multiple sulfur linkages are essential for understanding the functions and structures of proteins in chemical biology.\(^{52,53}\) In certain ways, organic sulfides, unlike their oxygen analogues, exhibit a variety of properties and are potential pro-drug molecules.\(^{54,55}\) These molecules with structural diversity are less basic, less polar, and more nucleophilic, and can be easily oxidized to form sulfoxides and sulfones.\(^{56,57}\)

Macromolecules containing azomethine fragments are often used as ligands in transition metal chemistry.\(^{58}\) These macrocycles are synthesized by reacting the hydrazides of thiophosphonic and phosphonic acids with dialdehydes. Burilov and co-workers prepared macrocycles 1–3 containing P–O, nine-membered and larger macrocycles comprising P–C, P–O, P–S, P–N, P–N–N and P–Si bonds with phosphorus atoms in diverse valence states. Later a number of novel articles and reviews appeared on phosphorus macrocycles containing one or more other heteroatoms such as selenium, oxygen,\(^{44}\) and nitrogen,\(^{44}\) or heterocycles such as pyrrole,\(^{45,46}\) thiophene,\(^{47}\) phosphole,\(^{48}\) and even chiral phosphorus-containing catenanes.\(^{49}\)

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bonds and azomethine moieties by reacting bis-\((o\text{-formylphenyl})\text{phenylthioxophosphonate}\) (I) with aromatic diamines (II) in benzene, as outlined in Scheme 1.\textsuperscript{59}

The synthesis of unsymmetrical phosphorus(III)–arene macrocycles (4 and 5) \textit{via} the phosphorylation reaction was reported by Abramov and co-workers.\textsuperscript{60} Under solvent-free conditions, bisphenols III and IV were reacted with two equivalents of phosphonous diamide to afford bisphosphonamidites V and VI, which were again reacted with IV and III, respectively, to form unsymmetrical phosphorus(III)–arene macrocycle 4 as shown in Scheme 2. The oxidation of 4 with sulfur afforded bissulfide 5.

Macrocyclic compounds 6a–i were obtained by reacting equimolar quantities of 2,2′-methylene(methyl)bis(4,6-di-tert-butyl-phenol) with tertiary phosphines in the presence of sodium hydride in dry THF at 45–50 °C, followed by oxidation with \(\text{H}_2\text{O}_2\), S or Se, as shown in Scheme 3.\textsuperscript{61} Macrocycles 7a/b were also prepared by reacting 2,2′-methylene(methyl)bis(4,6-di-tert-butyl-phenol) with phosphine oxides. These macrocycles 6a–i and 7a/b showed moderate \textit{in vitro} antibacterial and antifungal activities.

In order to prepare cyclic polysulfides, numerous synthetic approaches have been developed involving either elemental sulfur or sulfur-transfer reagents. In addition, arylphosphine-based polychalcogenides such as Lawesson’s (LR) and Woollins’ (WR) reagents (four-membered phosphorus–chalcogen rings) have been prepared and used as effective thionation and selenation reagents in the generation of a variety of macrocycles.\textsuperscript{62–69} Woollins and co-workers reported a “one pot” three-component condensation through a small ring expansion of thionation reagents (Lawesson’s reagents: 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR) or its ferrocene analogue, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (FcLR)) and selenation reagents (Woollins’ reagent: 2,4-diphenyl-1,3,2,4-diselenadiphosphetan-2,4-diseleneide (WR)) to prepare phosphorus and chalcogen containing heterocycles as shown in Schemes 4–9. Phosphorus and sulfur

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**Scheme 1** Synthesis of phosphacyclanes 1–3.

**Scheme 2** Synthesis of an unsymmetrical phosphorus(III)–arene macrocycle with the P–O linkage.
containing 12- and 16-membered macrocycles 8a–j were synthesized using a one-pot three-component reaction, involving [PhP(S)(μ-S)]$_2$, dithiol and alkyl or aryl dibromides in the presence of two equivalents of sodium hydride, as shown in Scheme 4. A similar reaction of [FcP(S)(μ-S)]$_2$ also produced 12- and 18-membered phosphorus–sulfur macrocycles 9a–n in moderate to excellent yields (Scheme 5). A seven-membered heterocycle 10 was also obtained as a minor product (18% to 24%) when o-xylene dibromide was used. The seven-membered heterocyclic product of type 10 was found to be a decomposed fragment of macrocycles, where 1,2-bis(bromomethyl)benzene was used (Scheme 5).

Using similar methods, a library of organophosphorus–chalcogen macrocycles bearing double OP(S)$_n$ or OP(Se)$_n$ scaffolds have been generated using primarily chalcogen transfer reagents as shown in Schemes 6–9. 9- to 15-membered phosphorus–sulfur heterocycles 11a–o were prepared by treating [FcP(S)(μ-S)]$_2$ with disodium alkane-bis(olate)s (generated in situ from dialcohols and NaH) followed by the addition of various nucleophilic reagents such as dibromides, as shown in Scheme 6. Using a similar procedure, macrocycles 12a–j were also prepared in excellent yield as shown in Scheme 7.

The reactions of [FcP(S)(μ-S)]$_2$ and [PhP(Se)(μ-Se)]$_2$ with highly branched disodium 2,2-dibutylpropane-1,3-bis(olate) and α,α′-dibromo-o-xylene resulted in the formation of unexpected nine-membered macrocycles 15 and 16, embedded with P–E–E–P (E = S, Se) linkages, as major products, instead of expected 11-membered macrocycles 13 and 14 as shown in Scheme 8. However, macrocycle 17 obtained in a similar reaction was found to be air- and moisture sensitive; silica gel column purification and crystallization resulted in the formation of seven-membered trithiophosphorus heterocycle 10 as a major stable product (Scheme 9), which is the decomposition product of 17, as mentioned earlier in Scheme 5. 12- to 15-membered phosphorus–selenium macrocycles 18a–d were also synthesized in a similar manner as shown in Scheme 9.

The reaction between Schiff base derivatives (2-en-1-imines) and [PhP(Se)(μ-Se)]$_2$ led to the isolation of a series of four-,
Scheme 5  Synthesis of phosphorus–sulfur macrocycles 9a–n and 10.

Scheme 6  Synthesis of phosphorus–chalcogen macrocycles 11a–o.

Scheme 7  Synthesis of phosphorus–chalcogen macrocycles 12a–j.
five- and six-membered 1,2-azaphospholidines containing one or two N-P-Se linkages, as shown in Schemes 10 and 11. Heterocycles 22a and 22b were obtained from the reactions of the corresponding Schiff bases with [PhP(Se[(μ-Se)]$_2$]$_2$ via [3 + 2] and [1 + 4] cycloaddition reactions, respectively (Scheme 10). A series of saturated five-membered heterocyclic rings 22c–i were also prepared in moderate to good yields (34–67%) by the reactions of substituted Schiff bases (having a conjugated C=C link) with [PhP(Se[μ-Se])]$_2$, involving both cycloaddition and reduction reactions, as shown in Scheme 10. However, the source of hydrogen responsible for the reduction process (for 22c–i) is not mentioned in the paper. Surprisingly, under similar reaction conditions, the treatment of a Schiff base having a –SCH$_3$ group, attached to an aminophenyl ring, with [PhP(Se[μ-Se])]$_2$ afforded an unexpected five-membered heterocycle 22j via a [2 + 3] cycloaddition reaction. The reaction pathways for the formation of compounds 22a–j can be described as follows: substitution of one of the bridging selenium atoms in [PhP(Se[(μ-Se)]$_2$], by the C=N group of the Schiff base resulted in five-membered heterocycle 22a, whereas the formation of 22b was due to the cycloaddition of a P=Se bond across the C=C–C=N bond involving a six-membered intermediate which eventually lost a Se atom. The heterocycles 22c–i were also accomplished by the same mechanism as 22b but with further reduction of the C=N double bond in the five-membered ring. The five-membered heterocycle 22j is a product of the reaction between the PhP(Se)Se moiety and Schiff base through a cycloaddition reaction and further reduction. The formation of 22l involved a similar reaction sequence, but unexpected product 22k was also obtained in the same reaction in 18% yield due to the C=N cleavage of the Schiff base and the –NCH$_2$Ph fragment replacing one of the selenium atoms in [PhP(Se)[μ-Se]]$_2$, as shown in Scheme 10. The ortho-fused heterocycles 22m and 22n were obtained in similar reactions as shown in Scheme 11. The six-membered intermediate VII obtained from the [4 + 2] cycloaddition reaction of Schiff bases with [PhP(Se)[μ-Se]]$_2$ undergoes further [4 + 2] cycloaddition reaction with [PhP(Se)[μ-Se]]$_2$, to form an unstable intermediate VIII, which transforms into ortho-fused heterocycles 22m and 22n through a ring contraction with the elimination of two Se atoms, as shown in Scheme 11.

The reaction of [PhP(Se)[μ-Se]]$_2$ with alkyd diols in the presence of NaH resulted in acids which on further treatment with butylamine followed by oxidation with I$_2$/KI yielded eight-, nine- and ten-membered rings (23a–c) as shown in Scheme 12. A similar reaction of [PhP(Se)[μ-Se]]$_2$ with aromatic diols resulted in macrocycles 24 and 25 (Scheme 12). Using a similar procedure, the authors also prepared a series of macrocycles 26a–f as shown in Scheme 13. These macrocycles were synthesized by treating various dibromides (Br–Br, R = –(CH$_2$)$_n$– or –CH$_2$C$_6$H$_4$CH$_2$– or –CH$_2$C$_6$H$_4$C$_6$H$_4$CH$_2$–) with the sodium salt of the monomers of [PhP(Se)[μ-Se]]$_2$ at ambient temperature. An unexpected 14-membered macrocycle 28 along with 27 was obtained in a similar reaction involving disodium butane-1,4-bis-olate and 1,4-dibromobutanol, as described in Scheme 13. Due to the presence of stereoegenic phosphorus centers in 28 (swapping of Se and Ph positions on phosphorus atoms), two isomers were observed: (S,R)-28a and (S,S)-28b. The two isomers, R,R,S,S and R,S,S,S of 28 were crystallised independently. DFT calculations depicted the relative energies of (S,S)-28a, (S,R)-28b, (S,S)-28b, and (S,R)-28a as 4.5, 0.0, 7.4 and 13.5 kJ mol$^{-1}$, respectively. Thus, more stable
conformers, each of the rac and meso isomers, were crystallized.

Monocoordinated phosphinidenes [A, Chart 1] are often regarded as phosphorus analogues of carbenes having a neutral P\(^{\text{IV}}\) center, whereas phosphinidene chalcogenides (R–P=\(\text{E}\)) are the oxidized form of phosphinidenes (P\(^{\text{IV}}\) → P\(^{\text{VIII}}\)). In the recent past, phosphinidene chalcogenides have been employed in transition metal chemistry, cycloaddition reactions, designing many unique phosphine ligands, and also in the construction of larger \([\text{RPE}]_n\) rings (D and E, Chart 1). Although numerous examples of the type \([\text{RPE}]_2\) (C, Chart 1) with pentavalent phosphorus atoms are known, 64,92 the series of the type \([\text{RPE}]_2\) with trivalent phosphorus atoms is unstable and less extensive. Mechanistic investigations using density functional theory (DFT) calculations suggested that the P\(^{\text{VIII}}\) centers in C (Chart 1) can exhibit a Lewis acidic character and often readily react with strong nucleophiles like NHCs and cleave the four-membered ring by trapping the monomers Ar\(^*\)-P=\(\text{E}\) and Ar\(^*\)-P=\(\text{E}\). Therefore, to stabilize the four-membered phosphorus–chalcogen rings of the type \([\text{RPE}]_2\), pentavalent phosphorus centers were considered. 64,92 Ragogna and co-workers reported the synthesis of \([\text{RPE}]_2\) heterocycles of the type C (Chart 1) by stabilizing the P\(^{\text{VIII}}\) center with bulky aromatic groups as shown in Scheme 14. 93,94

Heterocycles of the type \([\text{RPE}]_2\) (29a, E = S; 29b, E = Se) were obtained by treating (Me\(_3\)Si)_2\(\text{E}\) (E = S, Se) with Ar\(^*\)PCl\(_2\) (Ar\(^*\) = 2,6-Mes\(_2\)C\(_6\)H\(_3\), Mes = 2,4,6-(CH\(_3\))\(_3\)C\(_6\)H\(_2\)) in a 1:1 ratio (Scheme 14) which symbolize the first examples of four-membered \([\text{RPE}]_2\) rings. These compounds react through ring expansion to form heterocycles of the type \([\text{RPE}]_3\) (30a, E = S; 30b, E = Se), with the addition of a Lewis base, as shown in Scheme 14. In 2016, Weigand and co-workers reported the synthesis of tetracationic eight-membered phosphorus sulfur heterocycles 31a/b [\(\text{RPS}\)]\(_4\)\(^{4+}\) (31a, \(\text{R} = \text{Me}\); 31b, \(\text{R} = \text{iPr}\)), by reacting...
the imidazoliumyl-substituted P(III) cations of the type \([\text{RPCl}_2]^+\) (R = imidazolium-2-yl; R’ = Me, iPr) with (Me₃Si)₂S as shown in Scheme 15. The P₄S₄ rings possess a crown conformation similar to S₈.

The cyclocondensation of \([\text{MeN(PhPCl)}_2]\) with Na₂E (E = S, Se) resulted in eight-membered macrocycles of the type \([(\text{RP})_4(\text{RN})_2E_2]\) (32a, E = S; 32b, E = Se) in good yield as shown in Scheme 16. The reaction of \([\text{MeN(PhPCl)}_2]\) with Na₂Te or (Me₃Si)₂Te did not produce the corresponding tellurium derivatives; instead, deposition of elemental tellurium as a metallic mirror and/or as a black precipitate was observed. The oxidative ring contraction of 32a/b was observed on treatment with elemental sulfur (S₈) or gray selenium (Se_{gray}) in toluene at 111 °C resulting in four-membered rings of the type 33a/b.

Although organophosphorus–sulfur and –selenium compounds have been well studied, the reports on analogous tellurium derivatives \([\text{Te}_{m}(\text{RP})_n]\) are scarce. Attempts to synthesize organophosphorus–tellurium heterocycles resulted in a mixture of products which are identified using \(^{31}\text{P}\) and \(^{125}\text{Te}\) NMR data, and mass spectrometry. The synthetic approaches initially developed by du Mont, Karaghiosoff and Tokitoh yielded various organophosphorus(III)–tellurium heterocycles with different structural arrangements as depicted in Chart 2.
However, organophosphorus(III)—tellurium heterocycles (34–39) were prepared by Woollins and coworkers by reacting sterically demanding dichlorophosphines, RPCl$_2$ (R = Fc, Ad, Mes*O, Mes*, Trt) with Na$_2$Te$_2$ in THF, as described in Scheme 17.$^{105}$ In the case of Mes*OPCl$_2$ and FeCl$_2$, only heterocycles 34 and 35 were isolated, whereas in the case of AdPCl$_2$, under similar reaction conditions, a minor product 36a was also obtained along with the major product 36b.

Scheme 11 Phosphorus—selenium—nitrogen heterocycles: cycloaddition ortho-fused derivatives 22m/n of the corresponding Schiff bases analogues.

Scheme 12 Synthesis of eight-, nine-, and ten-membered rings with P—Se—Se—P linkages.

However, organophosphorus(III)—tellurium heterocycles (34–39) were prepared by Woollins and coworkers by reacting sterically demanding dichlorophosphines, RPCl$_2$ (R = Fc, Ad, Mes*O, Mes*, Trt) with Na$_2$Te$_2$ in THF, as described in Scheme 17.$^{105}$ In the case of Mes*OPCl$_2$ and FeCl$_2$, only heterocycles 34 and 35 were isolated, whereas in the case of AdPCl$_2$, under similar reaction conditions, a minor product 36a was also obtained along with the major product 36b.
The reactions of Mes*PCl₂ and TrtPCl₂ with an equimolar quantity of Na₂Te₂ yielded tritelluratriphosphorinanes (Mes*PTe)₃ and (TrtPTe)₃ as the major products, respectively. In the reaction of Mes*PCl₂, bisphosphene (Mes*P=PMes*) was detected as a major by-product along with elemental Te. The macrocycles 39a/b (39a, R = Ad; 39b,
**Perspective**

The utility of cyclodiphosphazanes of the type \([R'P(\mu-NR)]_2\) as both anionic and neutral ligands with both main group and transition elements is well documented.\(^{3,107}\) Dichlorodiphosphazanes \([\text{ClP}(\mu-NR)]_2\) have been extensively used in the synthesis of various macrocyclic derivatives\(^{15,16,108}\) and polydentate ligands showing catalytic and biological applications.\(^{109,110}\) Cyclodiphosphazanes usually exist in either the cis- or trans-isomeric form. Since the energy difference is very small (4–40 kJ mol\(^{-1}\)), most of the derivatives prefer a thermodynamically stable cis conformation in the solid state (Scheme 18).\(^{111,112}\) In the last two decades, \(P_2N_2\) entities or cyclophosph(III)azanes have emerged as powerful scaffolds for generating a variety of inorganic–organic macrocycles \([P(\mu-NR)]_2(\mu-LL')_n\) (LL' = organic linker).\(^{3,112,113}\) The synthesis

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**Scheme 15** Synthesis of tetrameric imidazoliumyl-substituted phosphorus–sulfur heterocycle 31.

**Scheme 16** Synthesis of macrocycles 32a/b and their oxidative ring contraction to yield four membered rings of type 33a/b.

**Chart 2** Structural arrangements of organophosphorus(III)–tellurium heterocycles Te\(_{\text{m}}\)(RP)\(_n\).

R = \(\text{t-Bu})\) were obtained from the reactions of RPCl\(_2\) (R = Ad, \(\text{t-Bu})\) with \([\text{Li(TMEDA)}]_2[\text{BuN(Te)P(\mu-N\text{t-Bu})_2P(\text{Te})N\text{t-Bu}}]\) (IX) (IX was previously reported by Chivers and co-workers\(^{106}\)) in toluene at \(-78^\circ\)C and the molecular structures were confirmed by single-crystal X-ray analysis.

Phosphorus–chalcogen based macrocycles bearing a \(P_2N_2\) scaffold

The utility of cyclodiphosphazanes of the type \([R'P(\mu-NR)]_2\) as both anionic and neutral ligands with both main group and transition elements is well documented.\(^{3,107}\) Dichlorodiphosphazanes \([\text{ClP}(\mu-NR)]_2\) have been extensively used in the synthesis of various macrocyclic derivatives\(^{15,16,108}\) and polydentate ligands showing catalytic and biological applications.\(^{109,110}\) Cyclodiphosphazanes usually exist in either the cis- or trans-isomeric form. Since the energy difference is very small (4–40 kJ mol\(^{-1}\)), most of the derivatives prefer a thermodynamically stable cis conformation in the solid state (Scheme 18).\(^{111,112}\) In the last two decades, \(P_2N_2\) entities or cyclophosph(III)azanes have emerged as powerful scaffolds for generating a variety of inorganic–organic macrocycles \([P(\mu-NR)]_2(\mu-LL')_n\) (LL' = organic linker).\(^{3,112,113}\) The synthesis
and coordination chemistry of cyclodiphosphazanes including some catalytic and biological applications were surveyed recently in a perspective article titled: “Cyclodiphosphazanes: options are endless”.114 One of their principal features is their numerous topological structures varying from simple monomeric to polymeric and cage like arrangements.15,16,115–117

The synthesis of dimeric and tetrameric macrocycles of cyclodiphosphazanes derived from resorcinol was reported by Balakrishna and co-workers, as depicted in Scheme 18.118 The treatment of cis-[ClP(μ-N\text{tBu})]2 with resorcinol in diethyl ether at 0 °C in the presence of Et\text{3}Na afforded a mixture of dimeric and tetrameric compounds ([P(μ-N\text{tBu})2{1,3-(O)2-C6H4}]2 (40) and ([P(μ-NBu)]2{1,3-(O)2-C6H4}]4 (41), which were separated by fractional crystallization. The reactions of dimer with H2O2 and elemental selenium resulted in corresponding chalcogenides 42a and 42b, respectively. The molecular structures of both di- and tetramers were confirmed by single crystal X-ray analysis.

Cyclophosph(III)azane based macrocycles of the type [P(μ-NR)]2(μ-X)]n (X = NH, O) are uncommon cases where substantial methodological advances have been achieved.112 Wright and co-workers mainly utilised precursors L and M (Chart 3) in the synthesis of macrocycles of the type [(P[μ-NR])]3 (X = NH, O).119–122 The reaction of [ClP(μ-NR)]2 with LiSH resulted in [S\text{v}(H)-P(μ-NR)]2 (N), Chart 3, which is a potential new building block for generating macrocycles of the type [(P[μ-NR])]2(μ-S)]n.123

The dropwise addition of a THF solution of [ClP(μ-N\text{tBu})]2 to a solution of H2S at −78 °C resulted in the formation of compound 43 in 10–38% yield. Nevertheless, the reaction of [ClP(μ-N\text{tBu})]2 with the in situ generated solution of LiSH in THF at −78 °C afforded significantly higher yields of 43 (83%). Although the X-ray analysis confirmed the cis-conformation for 43 (Chart 4),123 the 31P NMR spectrum revealed the isomerization of cis-43 in toluene solution to the trans isomer with a cis: trans ratio of 7:1. Although attempts to isolate compounds such as [S\text{v}(H)-P[μ-NR]]2 (44, R = 2,6-iPr2C6H3; 45, R = 2,4,6-Me3C6H2; 46, R = Ph2CH–) (Chart 4)123 were hampered, either due to the decomposition or instability of the desired product in solution at room temperature, immediate workup resulted in the isolation of 44–46 in moderate yields.

Chivers and co-workers developed a novel strategy for the synthesis of p-block macrocycles using diianionic P2N2
Scheme 18  Synthesis of di- and tetrameric cyclodiphosphazanes derived from resorcinol and chalcogenide (O, Se) dimers.

Chart 3  Structures of the key precursors used in the synthesis of various macrocycles having the P$_2$N$_2$ scaffold.

Chart 4  Structure of potential building blocks: inorganic phosphorus–sulfur macrocycles 43–46.
scaffolds, as described in Scheme 19. For example, 15-membered macrocycles of the type $48a/b \cdot \text{BuN}=\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{E-E} \right)_{2}$ ($48a, \ E=\text{S}$; $48b, \ E=\text{Se}$) were prepared by oxidizing dianions of the type $[\text{Ef} \left( \text{BuN} \right) \text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \text{NBu} \right) \text{E}]^{2-}$ ($47a, \ E=\text{S}$; $47b, \ E=\text{Se}$) with I$_{2}$. These macrocycles consist of P$_{2}$N$_{2}$ scaffolds bridged by $\mu$-$\text{E}$-$\mu$-$\text{E}$ linkers ($\text{E}=\text{S}$ or Se). The X-ray analysis showed the planar arrangement of the P$_{2}$N$_{6}$ motifs in $48a$ and $48b$ in the solid state. An interesting ring transformation was achieved when the trimeric diselenide $48b$ was oxidized with I$_{2}$ to produce $[\text{BuN}=\text{P} \left( \mu-\text{N} \text{Bu} \right)_{2} \text{P} \left( \mu-\text{N} \text{Bu} \right) \left( \mu-\text{Se-Se-Se-Se} \right)]$ (49) having a puckered seven-membered ring in which the P$_{2}$N$_{2}$ scaffold is bridged by a tetratellurido ($\text{Se-Se-Se-Se}$) unit, resembling a basket handle as shown in Scheme 19.

The preceding structural and theoretical investigations have revealed that the negative charge of the species containing $[\text{R}_{4} \text{P} \left( \mu-\text{E} \right)_{n}]^{n-}$ anions ($\text{E}=\text{O, S, Se, NR, etc.}$) routinely lies predominantly on E.$^{126-130}$ In this regard, Wright and co-workers showed that the oligomerisation of P$_{2}$N$_{2}$ units can be achieved by the reaction of the deprotonated P(=O) group with a P–Cl bond which probably proceeds through a change of the nucleophile center from phosphorus to oxygen, as shown in Scheme 20. The first example of the crown-like phosphazene based macrocycle $[\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{O} \right)_{2}]$ (50), containing oxo-bridges was synthesized by condensing P$_{2}$N$_{2}$ rings possessing P(=O) and P–Cl moieties. The authors also reported a sulfur bridged hexamer $[[\text{Se}=\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{Se} \right)]_{2}$ (51a) by reacting $[[\text{Cl}]\text{Se}=\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{Se} \right)]_{2}$ with an excess of sodium as shown in Scheme 21. The sulfur analogue 52b was also prepared by the reduction of cyclodiphosphazane $[[\text{Se}=\text{Cl}]\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{Se} \right)]_{2}$ (51b) with sodium in toluene under refluxing conditions (Scheme 21). The above reaction was even found to proceed via two different pathways, as outlined in Scheme 22. In one of the pathways, the Wurtz-type reaction was observed involving the initial elimination of NaCl from 51b followed by head-to-tail cyclization to produce the hexameric macrocycle $[\text{S}=\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{S} \right)]_{6}$ (52b) in 13.6% yield (with respect to 51b) as described in Scheme 22. In the second pathway, the reduction of the P–S bonds of 51b resulted in colorless singlet biradicaloid diides $[\text{S} \cdot \text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{S} \right)]_{2}$ (53). The mixture of cis- and trans-51b on treatment with an excess of sodium metal in toluene under refluxing conditions gave a mixture of products: 52b, a 3D polymer 54 and a 2D polymer 55, as shown in Scheme 22. Interestingly, after the isolation of soluble $[[\text{S} \cdot \text{Cl}]\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{S} \right)]_{6}$ (52b) through filtration, the residue was washed with cold and hot THF to isolate the pure products $[[\text{S} \cdot \text{Cl}]\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{S} \right)]_{6}$ (52b) instead of $[[\text{S} \cdot \text{Cl}]\text{P} \left( \mu-\text{NC}_{\text{Bu}} \right)_{2} \text{P} \left( \mu-\text{S} \right)]_{6}$ (53). The solid-state structure of 54 shows a tetraselenium macrocycle comprising three tert-butyl groups, two on the ring-bridging nitrogen atoms and one on the P$_{2}$N$_{2}$ ring, which indicates unexpected C–N bond cleavage and N–H bond formation. In contrast, the oxidation of the less sterically hindered 57 yielded P$_{4} \left( \mu-\text{NPr} \right)_{6} \left( \mu-\text{NH} \right) \text{Se}_{4}$ (60) with the loss of only one sub-
The single crystal X-ray analysis indicated the cleavage of one of the iPr groups which is diffused over six nitrogen atoms of 60, and co-crystallization of two species as shown in Scheme 23. The mechanism concerning the C–N bond activation is described in Scheme 24.132

**Phosphorus macrocycles with a pincer scaffold**

The new avenues in synthetic strategies for constructing supramolecular architectures enable chemists to design novel species with wider applications. Phosphine-based pincer com-
Scheme 22 Synthesis of S-bridged macrocycles 52b, 54 and 55.

Scheme 23 Synthesis of macrocycles 59 and 60.
plexes are an important class of organometallic compounds with numerous catalytic applications\textsuperscript{134–136} such as the formation of rare $\sigma$-methane complexes,\textsuperscript{137} alkane dehydrogenation,\textsuperscript{138} activation of C(sp$^3$)–F bonds\textsuperscript{139} etc.

The synthesis of the first example of diphosphametacyclophane, $m$-{C(O)-C$_6$H$_4$[C(O)PMe]}$_2$ \textcircled{61}, was achieved by the reaction of isophthaloyl chloride (1,3-benzenedicarbonyl dichloride) and methyl-bis(trimethylsilyl)phosphane under mild conditions in high yields by Crossley and co-workers, as depicted in Scheme 25.\textsuperscript{140} In a similar manner, the authors also reported diphosphametacyclophanes $m$-{C(O)-C$_6$H$_3$-5-$R'$-(C-(O)PMe)}$_2$ \textcircled{62a–e} ($R'$ = I, Me, $t$Bu, Ph, and $p$-NCC$_6$H$_4$) and the analogues $m$-{C(O)-C$_5$H$_3$N-(C(O)PMe)}$_2$ \textcircled{63} and $m$-{C(O)-C$_6$H$_4$-(C(O)-PPh)}$_2$ \textcircled{64} through the condensation of MeP(SiMe$_3$)$_2$ with a series of 5-substituted isophthaloyl chlorides (5-$R'$C$_6$H$_3$-2,6-{C(O)Cl}$_2$; $R'$ = I, Me, $t$Bu, Ph, and $p$-NCC$_6$H$_4$), as described in Scheme 25.\textsuperscript{141} The solid state structures of these cyclophanes \textcircled{62a–e}, \textcircled{63} and \textcircled{64} showed butterfly-like conformations with $P$-organyl substituents adopting mutually exo arrangements.

In 2017, Balakrishna and co-workers isolated the first examples of tri- and tetraphosphametacyclophanes, $m$-{C(O)-C$_5$H$_3$N(C(O)PPh)}$_3$ \textcircled{65} and $m$-{C(O)-C$_6$H$_4$N(C(O)-PPh)}$_4$ \textcircled{66} by treating 2,6-pyridinedicarbonyl chloride with phenylphosphine in the presence of triethylamine as shown in Scheme 26.\textsuperscript{142} The mass spectrum of the reaction mixture revealed the presence of both tri- and tetramers which were separated by fractional crystallization and structurally characterized. The trimer \textcircled{65} was obtained as a major product. However, the DFT studies have shown that the phosphametacyclophanes prefer the tetrameric structure \textcircled{66} (−12.8 kcal mol$^{-1}$) over the trimeric structure \textcircled{65} (−6.7 kcal mol$^{-1}$), thus indicating that the trimer is a kinetic product.

Recently Chaplin and co-workers reported the synthesis of phosphine-based macrocyclic pincer ligands \textcircled{67a/b} \textcircled{67a} or PNP–pincer, $X$ = CH$_2$; \textcircled{67b} or PONOP–pincer, $X$ = O) by a sequential eight-step method involving borane protection, ring-closing olefin metathesis, chromatographic separation of the trans-isomer from the cis-substituted diastereomers, and borane deprotection, as shown in Scheme 27.\textsuperscript{143} The configurations were established by single crystal X-ray diffraction. Using a similar synthetic procedure, macrocyclic pincer ligands \textcircled{68a/b} \textcircled{68a} or PCP–pincer, $X$ = CH$_2$; \textcircled{68b} or POCOP–pincer, $X$ = O) were prepared starting from meta-xylene and resorcinol, where the P-donors are trans-substituted with a tetradecamethylene linker, as shown in Scheme 28.\textsuperscript{144} The trimer \textcircled{66} (PCP–pincer, $X$ = CH$_2$) was prepared using a seven-step asymmetric synthetic protocol involving (−)-cis-1-amino-2-indanol as a chiral auxiliary and ring-closing olefin metathesis (Scheme 28a). Resorcinol based macrocycle \textcircled{68b} was obtained in analytically pure form in 30% yield involving a non-diastereoselective path (Scheme 28b), where the separation of the unwanted cis-substituted by-product was accomplished by chromatography.

**Transition metal chemistry of phosphorus–chalcogen and phosphine–pincer based macrocyclic compounds**

Although a plethora of phosphorus based macrocycles have been synthesized and well characterized, their utility in tran-
Scheme 25  Synthesis of diphosphametacyclophanes.

Scheme 26  Synthesis of tri- and tetra-phosphametacyclophanes.

Scheme 27  Synthesis of macrocyclic phosphine-based pincer ligands 67a/b.
sition metal chemistry and catalytic applications is scarce. Phosphorus(III) based macrocycles with or without other donor atoms can show interesting coordination modes and find applications in organic transformations. Furthermore, multi-metalllic complexes can promote simultaneously more than one type of organic transformation with atom economy which is very important in the pharmaceutical industry. In this context, this section is devoted to the elaboration of the transition metal chemistry of various phosphorus based macrocycles.

Four- and six-membered macrocyclic rings of the type \([\text{Ar}^*\text{PE}]_2\) (29a, E = S; 29b, E = Se) and \([\text{Ar}^*\text{PE}]_3\) (30a, E = S; 30b, E = Se) (Ar* = 2,6-Mes_2C_6H_3) on treatment with CuCl and AgOTf produced complexes 69–72, as shown in Scheme 29. The addition of an excess of CuCl to either 29a/b or 30a/b in dichloromethane resulted in the formation of tetracopper cage complexes 73a/b (73a, E = S; 73b, E = Se, Scheme 29).

Macrocycles of the type \([\text{PPh}_2(\text{NMe})E]_2\) (32a, E = S, 32b, E = Se) demonstrated interesting coordination behaviour due to the presence of several donor atoms. The reaction of 32a and 32b with AgOTf resulted in polynuclear complexes 74–79 (Chart 5). The selective formation of mononuclear sandwich complexes 74 [Ag(32a)_2][OTf] and 77 [Ag(32b)_2][OTf] was observed when a CH_2Cl_2 solution of 32a/b was reacted with AgOTf in a 2 : 1 ratio. A similar reaction of 32a/b with AgOTf in a 1 : 1 ratio produced dinuclear sandwich complexes 75 [Ag_2(32a)_2][OTf] and 78 [Ag_2(32b)_2][OTf]. Interestingly, the 2 : 3 reaction of selenide 32b with AgOTf yielded a highly reac-
The reactions of [Rh(biph)(dtbpm)Cl] (biph = biphenyl; dtbpm = bis(di-tert-butylphosphino)methane) (precursor first described by Jones\textsuperscript{145}) with isolated 67a (PNP–pincer, X = CH\textsubscript{2}) or an \textit{in situ} generated sample of 67b (PONOP–pincer, X = O) in weakly coordinating solvents such as fluorobenzene, followed by the addition of Na[Bar\textsubscript{4}]\textsuperscript{144} yielded complexes 84a/b (Scheme 31a\textsuperscript{144}). The solid-state structures of 84a/b demonstrate rhodium atoms adopting a distorted square pyramidal geometry. The prolonged reactions (2–5 days at 85 °C) of 84a/b result in the formation of 84a/b' (Scheme 31b\textsuperscript{144}).
with dihydrogen (1 atm) in 1,2-difluorobenzene (DFB) resulted in the hydrogenolysis of the biphenyl ligand and the formation of \(85a/b\) (Scheme 31a). In situ generated \(85a/b\) on treatment with ethylene (1 atm) afforded the corresponding C2 symmetric \(\pi\)-complexes \(86a/b\) accompanied by the formation of ethane in quantitative yield within 5 min at RT (Scheme 31a). In both the instances, no organometallic intermediates were detected and biphenyl was found to be the exclusive by-product. The C2 symmetric carbonyl compounds \(87a/b\) were obtained through the replacement of ethylene in \(86a/b\) with carbon monoxide (1 atm).

Similarly, rhodium dihydrogen complexes \(88a/b\) were obtained in quantitative yield by reacting pro-ligands \(68a\) (PCP–pincer, \(X = \text{CH}_2\)) and \(68b\) (POCOP–pincer, \(X = \text{O}\)) with \([\text{Rh}](\text{COE})_2\text{Cl}\) \((\text{COE} = \text{cyclooctene})\) followed by treatment with KO\(\text{Bu}\) at 120 °C under H\(_2\) (1 atm) as shown in Scheme 31b. 144 Dihydrogen complexes \(88a/b\) reacted with CO (1 atm) to yield C2 symmetric complexes \(89a/b\) (Scheme 31b). Complexes \(89a/b\) on treatment with PhIC\(_2\) undergo oxidative addition to form Rh\(^{\text{III}}\) complexes \(90a/b\) in 80/48% overall yield, which can be completely reversed by treating with three equivalents of \(\text{PrMgCl-Cl}\) in THF followed by recrystallisation from SiMe\(_4\), as shown in Scheme 31b.

In a similar way, the reactions between macrocycles \(68a\) (PCP–pincer, \(X = \text{CH}_2\)) or \(68b\) (POCOP–pincer, \(X = \text{O}\)) and \([\text{Ir}](\text{COE})_2\text{Cl}\) \((\text{COE} = \text{cyclooctene})\) afforded tetrahydride complexes \(91a/b\), which on further treatment with CO (1 atm) resulted in carbonyl complexes \(93a/b\) as shown in Scheme 31c. 144 Thermolysis of \(91a/b\) under CO (1 atm) at 120 °C in the presence of tert-butylethylene (TBE) resulted in the formation of C2 symmetric Ir\(^{\text{II}}\) carbonyl complexes \(93a/b\). The temporary development of \(92a/b\) was also noticed during the formation of the Ir-carbonyl complex \(93a/b\). The oxidative addition of PhIC\(_2\) to \(93a/b\) yields Ir\(^{\text{III}}\) complexes \(94a/b\), which on reduction with KC\(_8\) revert back to Ir\(^{\text{II}}\) complexes \(93a/b\), as shown in Scheme 31c.

The selective cleavage of the carbon–carbon single bond is a much-needed dislocation for many potential applications in organic chemistry. The incorporation of a transition metal in these linkages is an appealing and conceptually straightforward approach, but is usually correlated with adverse thermodynamics and orbital directionality, which confers high activation barriers to alternate metal-based reactivity. 146–148 Chaplin and co-workers illustrated the oxidative addition of an interlocked 1,3-diyne to a rhodium(i) center by utilizing a
macroyclic phosphinite pincer ligand with bulky phosphorus substituents, as outlined in Scheme 32.149 The rhodium(III)bis(alkynyl) product was trapped by reacting with CO or consumed through an irreversible reaction with dihydrogen throughout the selective hydrogenolysis of the C–C σ-bond (Scheme 32). The reaction of the Rh complex, trans-90b with \( \text{Ar}^\prime \text{C}_2\text{MgCl·LiCl} \) afforded bis-(alkynyl)carbonyl complex 95 which on decarbonylation with \( \text{Me}_3\text{NO} \) yielded complex 96 (Scheme 32). To analyze the impact of diyne interference within the macrocyclic ligand, CO was bubbled through a solution of 96 in [D₈]toluene at RT which resulted in carbonyl complex 97 in quantitative yield. In the associative substitution of \( \text{Ar}^\prime \text{C}_4\text{Ar}^\prime \) with CO, this complex can be considered as an intermediate, but in this case, the diyne dissociation appeared to be controlled by steric restrictions enforced by tight binding within the ring. For comparison, an acyclic complex similar to that of 96 was also prepared and found to produce a Rh carbonyl derivative through the rapid displacement of diyne under CO (1atm) at 25 °C. On heating the complex 96 in [D₈]toluene under H₂ (1 atm) at 358 K, dihydrogen complex 98 was formed.
by the elimination of two equivalents of Ar′CH2CH3 (24 h, Scheme 32). These experiments suggest the rate-determining insertion of the metal into the C(sp)–C(sp) bond accompanied by hydrogenolysis. To disprove substitution reaction pathways, the E-ene derivative 99 was also synthesized by stepwise proton and hydride transfer and found to be thermally stable under H2 (1 atm) (Scheme 32). The molecular structures of the complexes 95–97 have been confirmed by single crystal X-ray analysis.

The conversion of terminal alkynes into conjugated enynes by a metal-mediated coupling reaction is an appealing and atom-economical approach for the preparation of a wide range of conjugated enynes. Chaplin and co-workers illustrated a unique strategy for tuning the reactivity of the Rh-PNP pincer complexes of a macrocyclic ancillary ligand that facilitates the formation of conjugated enynes from terminal alkynes rather than vinylidene derivatives, as depicted in Scheme 33.150 The treatment of macrocycle 67a (PCNCP-pincer, X = CH2) with [Rh(COD)2][BARF4] (COD = 1,5-cyclooctadiene, ArF = 3,5-(CF3)2C6H3) afforded pincer complexes, trans- and cis-100, which on further treatment with an excess of HC≡CtBu (2.5 equiv.) at RT yielded the corresponding vinylidene derivatives 101 and 103, respectively, in quantitative spectroscopic yield, but under different timeframes. For the completion of the above reaction, the complex 101 took 5 min, whereas the complex 103 required 42 h probably due to the presence of the strongly bound COD in the latter. In the presence of an excess of terminal alkyne (HC≡CtBu), the unstable complex 101 slowly converted into an E-ene complex 102 because of the destabilizing interaction with the methylene linker and vinylidene. Even the treatment of the Rh complex cis-100 with independently synthesised E-BuC≡C(H)≡C(H)3Bu in DFB did

Scheme 32 Oxidative addition reactions of the C(sp)–C(sp) bond to rhodium(i) pincer complexes.
not produce the E-enyne complex 102 indicating that it can only result from homocoupling directly through the ring. An opposite trend was observed in the case of the vinylidene complex 103 and no further conversion to 102 was observed because of the absence of the destabilizing interaction with the methylene linker due to the cis orientation of the tetradecamethylene linker. The molecular structures of both the complexes 102 and 103 were confirmed by single crystal X-ray analysis.

**Conclusions**

This study illustrates a generalized and systematic approach that demonstrates the versatility in the synthesis of a wide variety of phosphorus–chalcogen macrocycles with different shapes and sizes. It is anticipated that these routes would be very useful for the synthesis of such versatile molecules which will be readily accessible for further investigations into their chemistry and biological applications. The larger size of the molecular cavity and its rigidity, especially in the case of phosphorus–chalcogen macrocycles with the P$_2$N$_2$ scaffold should make its host–guest chemistry interesting, specifically when it comes to softer metals or even metal–metal bonded fragments. Also, there is enormous potential for the formation of distinct networks through complexation with transition metals and/or trapping metal ions by utilising a combination of cavities and peripheral metal coordination. The crown like conformation witnessed in [RPE]$_4$ (E = S, Se) can be exploited to prepare transition metal sandwich complexes including mono-, di-, tri-, and tetrnuclear species or high nuclearity clusters. These complexes can also assist in transmetalation reactions to permit the synthesis of a wide range of homo- and heterometallic complexes. Sterically fine tuned macrocyclic pincer ligands can be used selectively to form mono, bi-, tri or tetrnuclear complexes for desired organic transformations. Macrocycles comprising P–C bonds are the most encouraging compounds due to their resistance to hydrolysis, which considerably extends the opportunity for their practical applications. Considering all these aspects, the design of a new class of phosphorus macrocycles to be employed as “smart” resources with new features and potential applications will be a worthwhile area of interest for future studies.

![Scheme 33](image-url) Terminal alkyne coupling reactions promoted by rhodium pincer complexes.
Conflicts of interest

There are no conflicts to declare.

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