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Insights into the formation of inorganic heterocycles *via* cyclocondensation of primary amines with group 15 and 16 halides

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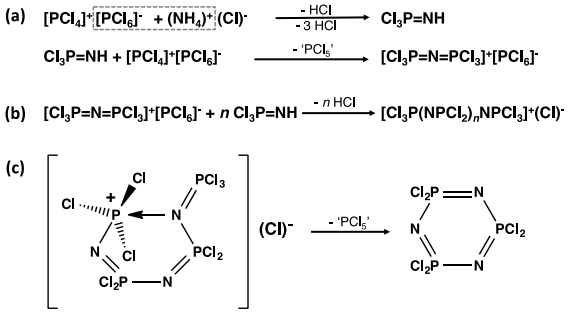
Cyclocondensation is a major preparative route for the generation of inorganic heterocycles especially in the case of ring systems involving a Group 15 or 16 element linked to nitrogen. This Perspective will consider recent experimental and computational studies involving the reactions of primary amines (or their synthetic equivalents) with pnictogen and chalcogen halides. The major focus will be a discussion of the identity and role of acyclic intermediates in the reaction pathways to ring formation, as well as the nature of the heterocycles so formed. The similarites and differences between the chemistry of group 15 and 16 systems are emphasised with a view to providing signposts for further investigations.

1. Introduction

Cyclocondensation is a common route for the generation of inorganic heterocycles involving p-block element-nitrogen rings.[1] In the case of the *unsaturated* inorganic heterocycles known as cyclophosphazenes $(NPCl_2)_n$ it has been well-established with the aid of ^{31}P NMR spectroscopy and conductivity measurements that the formation of a variety of ring sizes (n = 3-8) by reaction of phosphorus pentachloride and ammonium chloride in a high-boiling solvent, *e.g.* 1,1,2,2-tetrachloroethane, involves the following three steps: (a) generation of an acyclic building block, the "*key intermediate*" (b) chain growth involving this building block, and (c) intramolecular cyclisation (Scheme 1).[2] The construction of the classic *unsaturated* chalcogen-nitrogen cage molecule S_4N_4, which is conveniently prepared via cyclocondensation of $S[N(SiMe_3)_2]_2$ with equimolar amounts of SCl_2 and SO_2Cl_2,[3] may be even more complex. Indeed, in a recent book Ghosh and Berg speculated that the production of this eight-membered ring from these reagents involves more than ten steps.[4]

Cyclocondensation is an especially rich source of *saturated* ring systems of the type $(XENR)_n$ (X = halogen; E = P, As, Sb, Bi; R = alkyl, aryl), $(ENR)_n$ (E = S, Se, Te; R = alkyl) or the selenium-rich heterocycles $(E_n(NR)_{n-1})$ (E = Se, R = alkyl). When primary amines RNH_2 or their synthetic equivalents, *e.g.* RNR'_2 (R' = $SiMe_3$), RNR'Li (R' = $SiMe_3$) or $[Sn(\mu\text{-}NR)]_2$, are used as the wellspring of nitrogen, the nature of the products formed is dependent on a variety of factors, including (i) the size or electronegativity of the R group, (ii) the identity of the Group 15 or 16 element, (iii) reaction conditions such as temperature, solvent polarity or the concentration of the reagents, and (iv) the identity of the base used as an HX scavenger in the cyclocondensation reactions. Investigations of the reactions of pnictogen halides with primary amines or their synthetic equivalents were included in a critical review of the chemistry of pnictogen(III)-nitrogen rings published ten years ago (literature coverage up to mid-2006).[5] The corresponding reactions involving chalcogen halides have not been reviewed previously.



Scheme 1 Formation of cyclophosphazenes by cyclocondensation of phosphorus pentachloride with ammonium chloride; the cyclisation step (c) is shown only for n = 1 to give a six-membered ring. Larger rings will be formed from the acyclic intermediate in (b) when n = 2, 3 etc.

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The purpose of this Perspective is to evaluate the more recent (post-2006) studies of the formation of inorganic heterocycles incorporating a Group 15 or 16 element and NR groups via cyclocondensation with an emphasis on (a) the identification of the initially formed acyclic intermediates and (b) the influence of the factors (i-iv) mentioned in the previous paragraph on the nature of the final cyclic products. In this context, we will draw attention to the similarities and differences between the Group 15 and 16 systems with a view to providing a springboard for future investigation in this area of main group chemistry. Earlier work covered in the previous review[5] will only be included when it provides an essential background to these objectives.

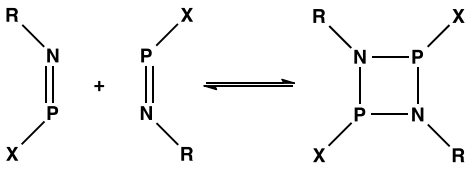
2. Formation of pnictogen(III)-nitrogen rings via cyclocondensation

2.1. General comments

The most common class of heterocycles of the type $[XPNR]_n$ are the four-membered rings $[ClP(\mu\text{-}NR)]_2$ known as cyclophospha(III)diazanes, which provide the source of the P_2N_2 scaffold for the construction of a wide variety of inorganic macrocycles with possible applications in host-guest chemistry as championed by Wright and co-workers.[6,7] As asserted in a recent review by Balakrishna, the coordination chemistry of cyclodiphosphazanes also offers "endless options" including potential applications in catalysis and as anticancer agents.[8] Finally, these small rings are potential sources of high molecular weight polyphosphazane polymers such as $(\text{-ClPNR-})_n$, via ring-opening, although that objective has yet to be realized.

2.2 Cyclocondensation reactions of pnictogen trihalides and primary amines

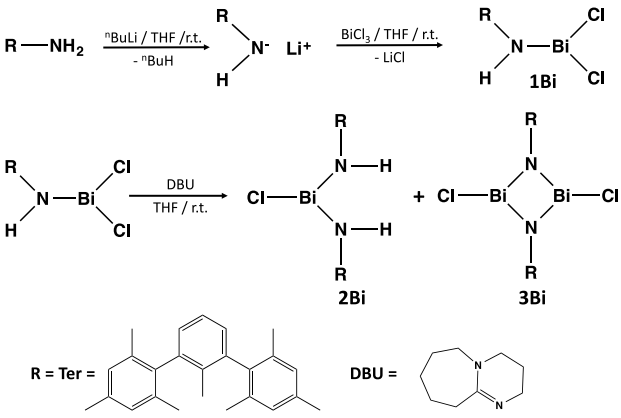
2.2.1 Monomers (iminopnictanes) and dimers (cyclodipnictadiazanes). Although four-membered rings $[XE(\mu\text{-}NR)_n$ (X = halogen; E = P, As, Sb, Bi; R = alkyl, aryl) are the most common result of reactions of pnictogen trihalides and primary amines,[5] in 1988 Niecke and co-workers isolated the stable monomeric iminophosphane (ClP=NMes*) (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) from treatment of PCl_3 with Mes*NH_2 in the presence of NEt_3.[9] Although the steric bulk of the Mes* substituent undoubtedly contributes to the stability of the monomer, electronic stabilization may also be involved since the installation of *m*-terphenyl (Ter = 2,6-$Ph_2C_6H_2$) group, which is well-known to provide kinetic stabilization for reactive main-group functionalities,[10] gives rise to the stable dimer $[ClP(\mu\text{-}NTer)]_2$ isolated in the solid state by Schulz, Villinger and co-workers.[11] The same group demonstrated by variable temperature ^{1}H NMR spectroscopy in CH_2Cl_2 that the cyclic diarsadiazane $[ClAs(\mu\text{-}NMes^*)]_2$ is involved in a dimer-monomer equilibrium over the range 233-298 K with a very small (2.2 kJ mol-1) enthalpy of monomerisation.[12] These results reinforce the earlier assertion of Burford and co-workers that the presence of steric strain may destabilize the



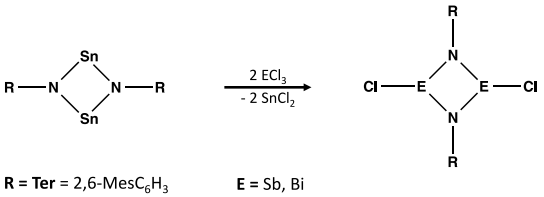
Scheme 2 Monomer-dimer equilibrium for $(XENR)_n$ (n = 1,2).[1]

dimers $(XENR)_2$ (X = halogen; E = P, As) with respect to the corresponding monomers (Scheme 2).[13]

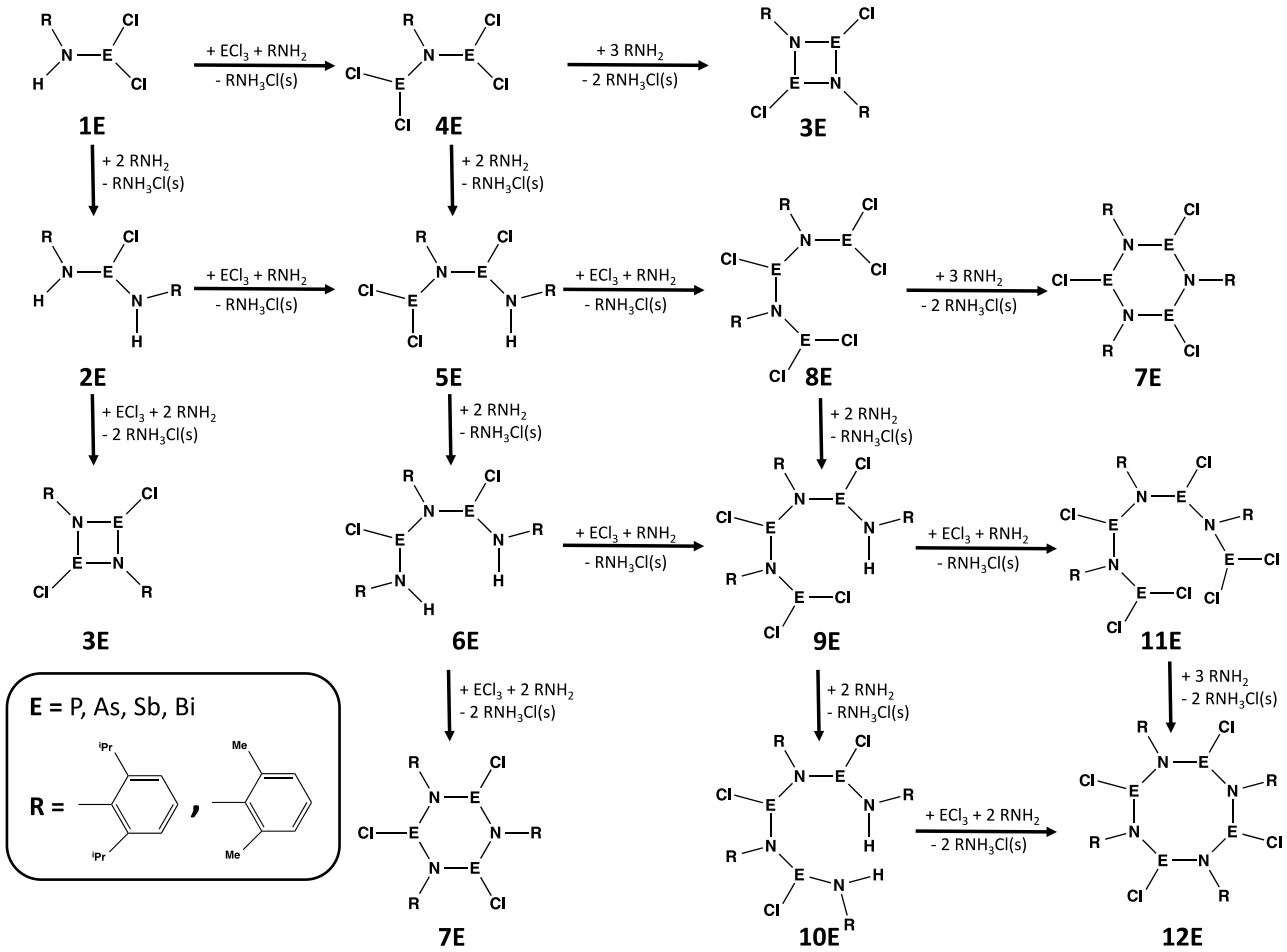
Monomers incorporating the heavier pnictogens (XENR) (X = halogen; E = Sb, Bi) have not been isolated. Moreover, the dimers of the type $[XE(\mu\text{-}NR)]_2$ (X = halogen; E = Sb, Bi) are commonly formed in low yields from cyclocondensation reactions of primary amines with EX_3 (E = Sb, Bi; X = halogen) owing to side reactions involving E–N bond cleavage. Nevertheless, Stahl reported the preparation of $[ClSb(\mu\text{-}N^tBu)]_2$ from the one-pot reaction of $SbCl_3$ and *tert*-butylamine in the presence of trimethylamine;[14] subsequently, the four-membered ring structure was confirmed by an X-ray study.[15] More recently, Schulz and co-workers described the characterisation of the first example of a dichlorocyclodibismadiazane $[ClBi(\mu\text{-}NR)]_2$ **(3Bi)** as red crystals.[16] The synthesis involved the isolation of the acyclic intermediate $Cl_2Bi(NHR)$ (**1Bi**), [R = Ter = 2,6-$MesC_6H_3$)] followed by cyclization in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) as illustrated in Scheme 3; yellow crystals of the acyclic by-product $ClBi(NHR)_2$ (**2Bi**, R = Ter) were also formed in significant amounts. Although these bismuth-nitrogen compounds are moisture-sensitive, they exhibit remarkable thermal stability (T_{decomp} **1Bi**, 189; **2Bi**, 220;



Scheme 3 Two-step synthesis of a dichlorocyclodibismuthane.[16]



Scheme 4 Synthesis of cyclodipnictadiazanes via transmetallation.[18]



Scheme 5 Acyclic intermediates in the cyclocondensation reactions of pnictogen trihalides with primary amines.

3Bi, 205 °C).[16]

In order to circumvent the complications engendered by HCl elimination in the cyclocondensation reactions of ECl_3 (E = Sb, Bi), Schulz, Villinger and co-workers utilised a three–step process involving the formation of the triflates [TfOSb(μ-NMes*)]$_2$ (Tf = $CF_3SO_3^-$) from an acyclic precursor, followed by reaction with Me_3SiX to produce the series of halides [XSb(μ-NMes*)]$_2$ (X = F, Cl, Br, I).[17] A more elegant synthesis by the same group invoked the use of the distannadiazane [Sn(μ-NTer)]$_2$ as a primary amine equivalent in a transmetallation process to give the cyclodipnictadiazanes [ClE(μ-NTer)]$_2$ (E = Sb, Bi) in good yields (Scheme 4).[18]

2.2.2 Acyclic intermediates in the formation of cyclodipnictadiazanes. Pioneering early work by Burford and co-workers on the reactions of pnictogen trihalides and primary amines or their synthetic equivalents [RNHLi or RN(SiMe$_3$)Li] have provided important insights into the identity of the intermediates formed prior to cyclocondensation.[5,19,20] The use of sterically encumbered amines, *e.g*. DippNH_2 (Dipp = 2,6-diisopropylphenyl), DmpNH_2 (Dmp = 2,6-dimethylphenyl) combined with ^{31}P NMR monitoring of reactions was especially informative for reactions involving PCl_3, but the heavier pnictogens (As, Sb Bi) were also included in their studies the results of which are summarised in Scheme 5.

The 1:1 and 2:1 adducts of a primary amine with the pnictogen trichloride (RNH_2•ECl_3 and $2RNH_2$•ECl_3, respectively) can undergo dehydrochlorination to give either **1E** or **2E**,[20] which may be regarded as "key intermediates" (*cf*. step (a) in Scheme 1). The eliminated HCl will be consumed by the excess of primary amine resulting in the precipitation of organoammonium chloride RNH_3Cl. **1E** and **2E** react with ECl_3 to give the chain molecules **4E** and **5E**, respectively (*cf*. step (b) in Scheme 1). In the case of PCl_3**,** pure crystalline samples of DippN(H)PCl_2 (**1P,** R = Dipp) and DippN(PCl_2)$_2$ (**4P**, R = Dipp) have been isolated and spectroscopically characterized.[19] In the case of the antimony systems, the primary adducts RNH_2•ECl_3 and $2RNH_2$•ECl_3 (R = Dmp) have been structurally characterised in a co-crystal.[20] More significantly, the acyclic distibadiazane **5Sb** (R = Dmp) was isolated, albeit in very low yield.[20] By contrast, the reaction of Mes*NH_2 with $SbCl_3$ yielded a mixture of mono- and di-substituted products **1Sb** (R = Mes*) and **4Sb** (R = Mes*) depending on the stoichiometry and nature of the base.[18] The X-ray structure of **5Sb** depicted in Fig. 1 is especially interesting in the context of the subsequent intramolecular cyclisation step (*cf*. step (c) in Scheme 1). The

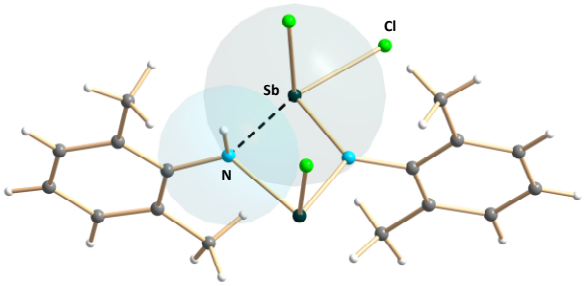


Fig. 1 Molecular structure of (Dmp)N(H)SbCl[μ-(Dmp)N]SbCl$_2$ (**5Sb**).[20] The van der Waals radii of antimony and nitrogen are indicated as transparent spheres.

structure incorporates a close intramolecular Sb–N contact of 2.521(2) Å, *cf*. mean value of 2.057(2) Å in the Sb–N–Sb–N unit, foreshadowing ring formation via HCl elimination to give the cyclodistibadiazane [ClSb(μ-NDmp)]$_2$.[20]

More recently, Schulz, Villinger and co-workers have shown that the intermediates formed in the reactions of ECl_3 (E = P, As) with the sterically encumbered amine $TerNH_2$ (Ter = 2,6-$MesC_6H_3$, see Scheme 3) are dependent on the nature of the base used as an HCl scavenger as well as the identity of the Group 15 element.[21] The use of an excess of triethylamine produced either $TerN(PCl_2)_2$ (**4P**) or $TerN(H)AsCl_2$ (**1As**), whereas $TerN(H)PCl_2$ (**1P**) was formed in the reaction with ^{n}BuLi. A further contrast between the behaviour of the group 15 elements involves the formation of the cyclodipnictadiazanes [ClE(μ-NTer)]$_2$ from **1P** or **1As**, which is achieved with Et_3N for E = P, but requires the use of the strong base DBU for E = As.[21]

2.2.3 Larger ring systems and ring transformations. Although four-membered rings [XE(μ-NR)]$_n$ (*n* = 2) are by far the predominant inorganic heterocycles formed from the cyclocondensation of pnictogen trihalides and primary amines (or their synthetic equivalents), six-membered rings (*n* = 3) are formed when R is a small alkyl group. Thus, the reactions of an excess of PX_3 (X = Cl, Br) with $(MeNSiMe_2)_3$ or $(Me_3Si)_2NMe$, which can be regarded as synthetic equivalents of $MeNH_2$, yield the cyclic trimers [XP(μ-NMe)]$_3$ whose identities were established by ^{31}P NMR spectroscopy and mass

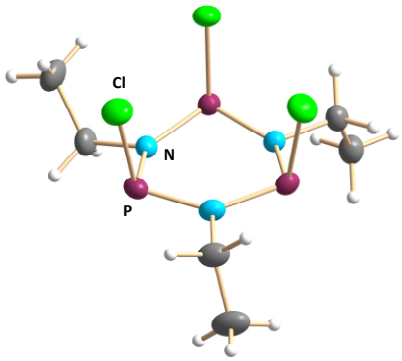
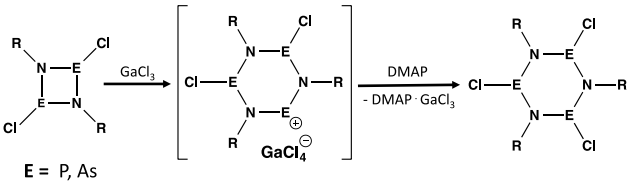


Fig. 2 Molecular structure of *cis*-[ClP(μ-NEt)]$_3$.[24]



Scheme 6. Ring expansion promoted by Lewis acids (DMAP = 4-(dimethylamino)pyridine).[13b-d]

spectrometry.[22] The related ring system [ClP(μ-NEt)]$_3$ is obtained in good yield from the reaction of PCl_3 with ethylamine hydrochloride $[EtNH_3]Cl$ in boiling 1,1,2,2-tetrachloroethane,[23] and it has been structurally characterised as the cis isomer (Fig. 2).[24]

The formation of six-membered and larger rings in the cyclocondensation process can readily be envisaged to follow stepwise condensation processes involving both ECl_3 and RNH_2, as shown in Scheme 5. The chain extension is followed by intramolecular cyclisation with HCl elimination [*cf.* steps (b) and (c) in Scheme 1].

Burford and co-workers have demonstrated that trimeric cyclophosphazanes may also be formed from the corresponding dimers under the influence of Lewis acids when the substituents on nitrogen are moderately bulky.[13a, b] Thus, treatment of [XP(μ-NR)]$_2$ (X = Cl, Br; R = Dmp, Dipp) with gallium trihalides followed by DMAP [4-(dimethylamino)pyridine] produces the corresponding trimers [XP(μ-NR)]$_3$; the ring expansion occurs via a cationic intermediate formed by halide abstraction (Scheme 6). A similar ring transformation has also been observed for the corresponding arsenic heterocycles [XAs(μ-NR)]$_2$.[13c] Significantly, Wright and co-workers have observed that dimer-trimer ring transformation is reversible in the case of

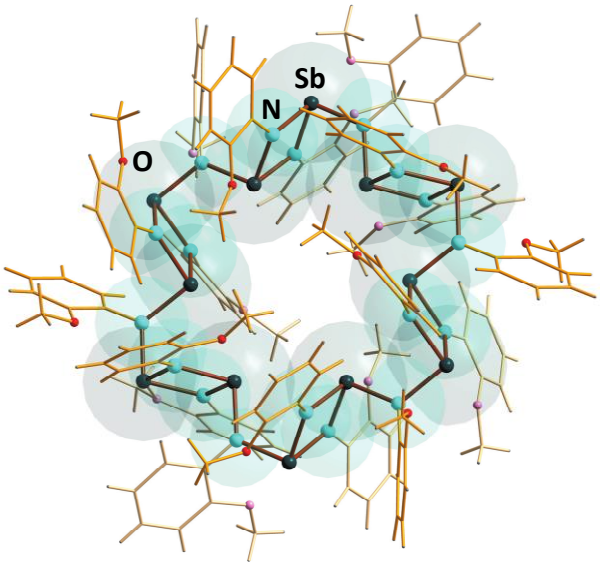


Fig. 3 Molecular structure of [Sb_{12}{N(2-MeO)C_6H_4}$_{18}$].[25b] The van der Waals radii of antimony and nitrogen are indicated as transparent spheres.

$[ClP(\mu\text{-}NEt)]_n$ (n = 2,3), *i.e.* when the substituent on the nitrogen atoms is small.[26] Distillation of the trimer under reduced pressure results in quantitative formation of the dimer, which reverts to the six-membered ring upon heating at 130 °C for 12 h.

Undoubtedly, the most remarkable outcome of the cyclocondensation processes under consideration involves the reaction of $SbCl_3$ and three equivalents of Li[N(H)Ph] to give the macrocycle $[Sb_{12}(NPh)_{18}]$ (85% yield), which is comprised of six Sb_2N_2 rings bridged by anilido groups {$[Sb_{12}\{N(m\text{-}MeO)C_6H_4\}_{18}$ shows the same Sb-N-framework; see Fig. 3}.[25] The scope of this isolated example of macrocycle formation from the cyclocondensation reactions of primary amines with pnictogen trihalides merits further investigation.

3 Formation of chalcogen-nitrogen rings via cyclocondensation

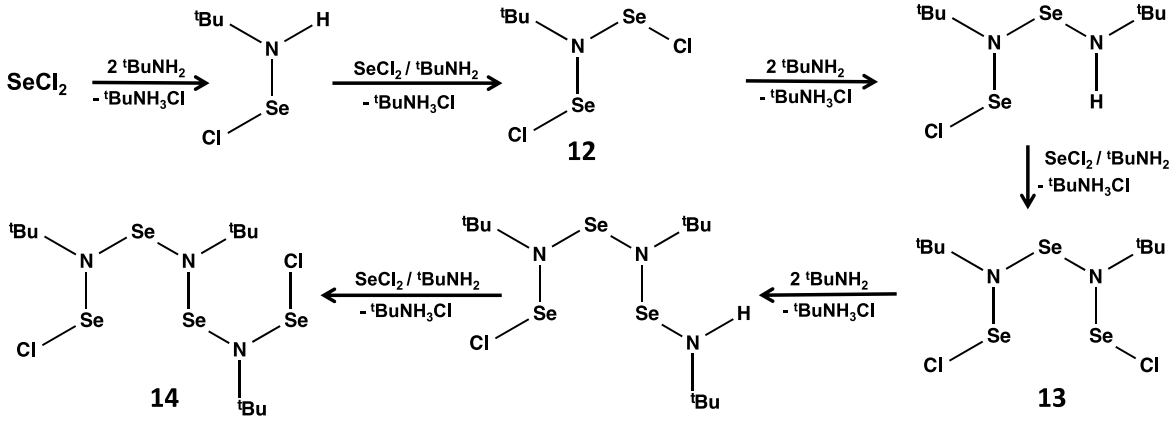
3.1 General comments

The classic inorganic heterocycles known as cyclic sulfur imides are formally related to *cyclo*-S_8 by the replacement of one or more of the S atoms with an NH group and can be represented by the general formula $S_{8-n}(NH)_n$ (n = 1-4);[26] selenium or tellurium analogues of the type $E_{8-n}(NH)_n$ (E = Se, Te) are unknown. These prototypical sulfur imides do not fall under the purview of this perspective, which is limited to organic derivatives derived from primary amines, *e.g.* $[E(\mu\text{-}NR)]_n$ (n = 3, E = Se, Te; n = 4, E = S, Se) and related chalcogen-nitrogen heterocycles that embody chalcogen-chalcogen bonds. Studies of the cyclocondensation reactions of sulfur halides and primary amines (or their synthetic equivalents) have been sporadic (Section 3.3); however, compared to the reactions with pnictogen trihalides, the availability of catenated dichlorochalcogenanes such as S_xCl_2 (x = 2-7) and Se_2Cl_2 offers additional scope to this aspect of chalcogen-nitrogen chemistry through the possible formation of chalcogen-rich rings. By contrast to the information available for dichorosulfanes, the reactions of dichloroselanes, especially those of selenium(II) dichloride with *tert*-butylamine have been investigated comprehensively and a combination of experimental and computational approaches have provided important insights into the reaction pathways for the formation of cyclic products through the identification of acyclic intermediates as discussed in Section 3.4.

3.2 Monomers RNE (E = S, Se) (chalcogenonitrosyls) and ArNSS (*N*-thiosulfinylanilines)

The chalcogenonitrosyls RN=E (E = S, Se) are formally isovalent with iminopnictanes RN=ECl (E = P, As) (Section 2.2.1), if one of the non-bonding pairs of electrons on the chalcogen atom in the former is considered equivalent to the bonding pair in the E–Cl bond of the latter. This class of chalcogen-nitrogen compounds is only formed as a transient species, usually with R =aryl, which can be trapped as a Diels-Alder adduct, *e.g*. with dimethylbutadiene.[27] In the case of selenonitrosoarenes ArN=Se, the selenium(II) synthon $PhSO_2SeCl$ has been used as the selenium source in reactions with $ArNH_2$ (Ar = 4-XC_6H_4, X = Br, Me) in the presence of triethylamine at 0 °C in CH_2Cl_2.[28] Dimerisation of chalcogenonitrosyls ArN=E (E = S, Se) has not been observed, however larger cyclic oligomers $(RNE)_n$ (R = ^{t}Bu, n = 3; R = Me, ^{t}Bu, n = 3,4) are formed in the cyclocondensation reactions of $SeCl_2$ with primary amines (or their synthetic equivalents) (Section 3.5).

The use of bulky arylamines effects a particularly interesting result in the reaction with S_2Cl_2 to produce the red-purple N-thiosulfinylaniline ArNSS (Ar = 2,6-dimesityl-4-methylphenyl)[29] as an oil, which is transformed into the cyclic sulfur imide $ArNS_5$ up on passage through a silica gel column.[30] In the context of the information available for iminopnictanes, the reactions of $SeCl_2$ generated *in situ* in THF [31] with very bulky arylamines merit investigation with a view to the stabilization of monomeric or dimeric ArNSe species. Support for this suggestion comes from the observation that the presence of a bulky Mes* substituent on the two nitrogen atoms greatly enhances the thermal stability of selenium(IV) diimides RN=Se=NR compared to their alkyl counterparts (R = ^{t}Bu, Ad) (see Section 3.6). Thus, thermally stable Mes*N=Se=NMes* is isolated as black crystals in 90% yield from the reaction of



Scheme 7 Reaction pathway for formation of imidoselenium(II) dichlorides $ClSe[N(^tBu)Se]_nCl$ (**12**, n = 1, **13**, n = 2, **14**, n = 3).[37]

Mes*N(H)Li with $SeCl_4$ in THF, which was isolated as the energetically least favourable *anti,anti*-conformer, presumably due to the influence of the bulky organic groups.[32]

3.3 Cyclocondensation reactions of sulfur halides with primary amines

The first investigation of the preparation of organic derivatives of cyclic sulfur imides via cyclocondensation involved the reaction of gaseous $MeNH_2$ with SCl_2 in hexane, but a laborious procedure was necessary to separate of the major product $S_4(NMe)_4$ from by-products, which included two isomers of $S_5(NMe)_3$ as well copious amounts of $[MeNH_3]Cl$.[33] The structures of $S_4(NMe)_4$ and the $S_5(NMe)_3$ isomers were inferred on the basis of elemental analyses and spectroscopic (IR and NMR) data.[33a] Subsequently, $S_4(NMe)_4$ was shown by a single crystal X-ray analysis to form a crown-shaped eight-membered ring similar to that of the parent heterocycle $S_4(NH)_4$ with a nearly planar configuration at the nitrogen atoms (Fig. 4a).[33b] In a subsequent comprehensive examination of this cyclocondensation process Gordon and Heal determined that reactions of *aqueous* methylamine (surprisingly) with dichorosulfanes S_xCl_2 (x = 1,2,3,5,7) offer a versatile source of a wide range of *N*-methyl sulfur imides. The yields of S_7NMe, the di-substituted isomers 1,3-, 1,4- and 1,5-$S_6(NMe)_2$, as well as the tri-substituted derivatives 1,3,5- and 1,3,6-$S_5(NMe)_3$ could be optimised by varying the chain length in the reagents S_xCl_2.[34] In a more recent application of S_2Cl_2 Woollins and co-workers showed that the six-membered rings 1,4-$S_4(RN)_2$ (R = Et, Bz) are obtained in moderate yields (25-35 %) from the cyclocondensation of S_2Cl_2 with the appropriate primary amine in diethyl ether when high-dilution conditions are employed.[35] The crystal structures of 1,4-$S_4(NR)_2$ revealed a cyclohexane-like ring however, in contrast to eight-membered cyclic sulfur imides, a substantial degree of pyramidalisation at the nitrogen atoms is observed (Fig 4b).[34]

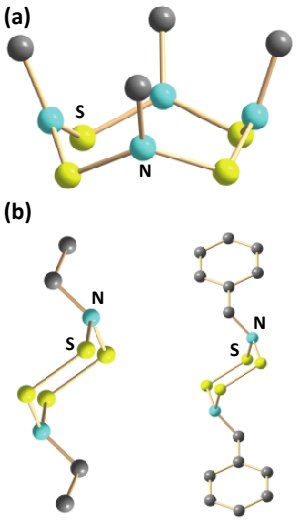


Fig. 4 Molecular structures of (a) 1,3,5,7-$S_4(NMe)_4$ [33a] and 1,4-$S_4(NR)_2$ (R = Et, Bz).[33b]

3.4 Acyclic intermediates in the formation of cyclic selenium imides

None of the acyclic intermediates involved in the formation of cyclic sulfur imides via cyclocondensation have been identified. However, Laitinen, Chivers and co-workers have carried out comprehensive studies of the reactions of *tert*-butylamine with $SeCl_2$ using different stoichiometries and various concentrations of reagents in order to identify the intermediates that are created *en route* to the formation of cyclic selenium imides. These investigations have revealed a homologous series of highly moisture-sensitive imidoselenium(II) dichlorides $Cl[N(^tBu)Se]_nCl$ (**12**, n = 1; **13**, n = 2; **14**, n =3), which have been isolated and structurally characterised (Fig. 5) and shown to act as building blocks in the creation of cyclic selenium imides,.[36,37] In contrast to the analogous sulfur chemistry, the availability of a moderately abundant isotope (^{77}Se, I = ½, 7.7 %) for NMR studies has been a crucial advantage for monitoring reactions and identifying both the intermediates and the final products in the $SeCl_2$ reactions, *cf*. the use of ^{31}P NMR spectroscopy in cyclocondensation reactions of PCl_3 with amines (Section 2.2.2).

A reaction pathway that accounts for the sequential formation of the acyclic building blocks **12**-**14** is depicted in Scheme 7. The initial step involves the formation of $^tBuN(H)SeCl$, *cf*. $RN(H)ECl_2$ (**1E**) in the pnictogen systems (Scheme 5 and Section 2.2.2). Although this intermediate has not been isolated, it seems reasonable to invoke its role as a source of "^tBuNSe" units in the formation of the longer chains. Thus, the first two steps in pathway for the formation of cyclic selenium imides resemble those involved for the pnictogen trichloride reactions with primary amines, *i.e.* (a) formation of an acyclic building block followed by (b) chain growth involving

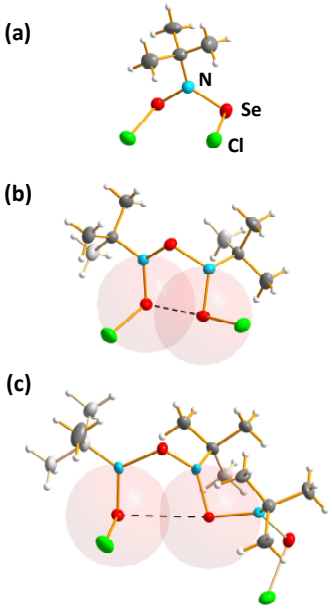


Fig. 5 Molecular structures of $Cl[N(^tBu)Se]_nCl$ (a) **12**, n = 1,[36] (b) **13**, n = 2,[36] (c) **14**, n = 3.[37] The van der Waals radius of selenium is indicated as transparent spheres.

this intermediate.

The calculated PBE0/def2-TZVPP Gibbs energies at 298K for the successive formation of ClSe[N(ᵗBu)Se]$_n$Cl in the reaction of $SeCl_2$ and $^tBuNH_2$ in THF are -169, -153 and -134 kJ mol^{-1} for n = 1, 2 and 3, respectively, indicating that these reactions are very favourable.[37] Similar calculations of the reactions involving SCl_2 and $^tBuNH_2$ in THF indicate that the formation of the analogous imidosulfur chlorides ClS[N(ᵗBu)S]$_n$Cl should be even more favourable (see Fig. 6).[38] These species, however, are still unknown.

3.5 Cyclic selenium imides: mechanism of ring formation

The final products of the cyclocondensation reactions of *tert*-butylamine with $SeCl_2$ are the cyclic selenium imides $Se_3(N^tBu)_2$ (**12**, R = ᵗBu), $Se_3(NR)_3$ (**13**, R = ᵗBu), $Se_4(N^tBu)_4$ (**15**, R = ᵗBu), $Se_6(N^tBu)_2$ (**16**), $Se_9(N^tBu)_6$ (**17**); their atomic arrangements are illustrated in Fig. 7. The eight- and fifteen-membered rings, **16** and **17,** were first reported by Roesky *et al*. who used the cyclocondensation reactions of the primary amine equivalent ᵗBu(Me$_3$Si)NLi with either Se_2Cl_2 or $SeOCl_2$ in THF at -78 °C.[39] The eight-membered ring $Se_4(NMe)_4$ (**15**, R = Me) was isolated in excellent yield (91 %) from the reaction of $SeCl_2$ with the primary amine equivalent $(Me_3Si)_2NMe$,[40] *cf*. the preparation of the six-membered rings $(XPNMe)_3$ (X = Cl, Br) from PX_3 and the same reagent (Section 2.2.3).[22] Importantly, the ^{77}Se NMR chemical shift of $Se_4(NMe)_4$ facilitated the identification of the elusive *tert*-butyl derivative $Se_4(N^tBu)_4$ (**15**, R = ᵗBu), which is observed as a major product of the cyclocondensation reactions.

A cursory inspection of the composition of the cyclic selenium imides illustrated in Fig. 5 reveals that the major difference between the cyclocondensation reactions of primary amines with pnictogen trihalides described in Section 2 and those with selenium dichloride is the formation of catenated structures in the latter case, *i.e*. cyclic selenium imides that incorporate –Se–Se– or –Se–Se–Se- linkages. This observation must be considered in any proposal for the

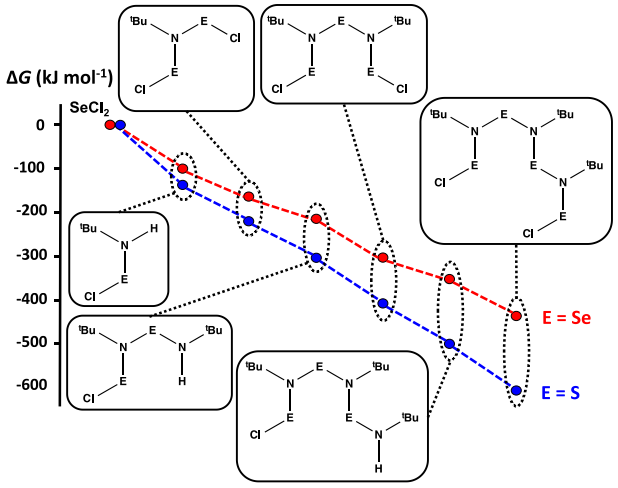


Fig. 6 Energetics for reactions of chalcogen dihalides ECl_2 (E = S, Se) with $^tBuNH_2$ (see Scheme 7).[37,38]

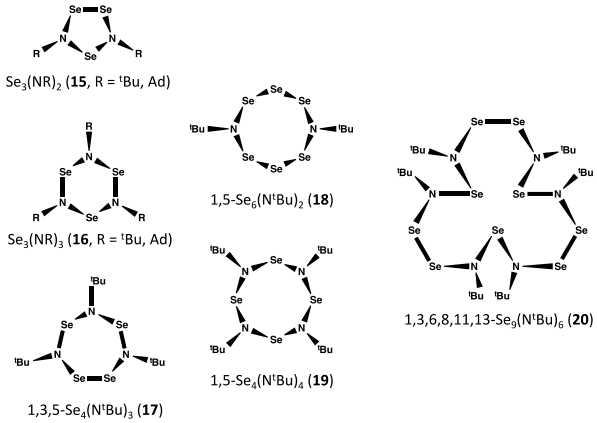


Fig. 7 Cyclic selenium imides; $Se_4(N^tBu)_3$ (**17**) is only known as a ligand in a metal complex (Section 3.6).[41]

cyclisation step in the cyclocondensation reaction of $SeCl_2$ and $^tBuNH_2$. By means of experiments involving reactions of isolated imidoselenium(II) chlorides, Laitinen, Chivers and co-workers have shown that treatment of these bifunctional building blocks with $^tBuNH_2$ occurs by concurrent pathways involving either (a) nucleophilic substitution to give $Se_n(N^tBu)_n$ (n = 3, 4) or (b) reduction to generate rings with Se–Se bonds, $Se_n(N^tBu)_{n-1}$ (n = 3, 4), as exemplified in Scheme 8. The calculated Gibbs energies for these process are strongly favourable, especially for the reduction pathway to give catenated ring systems, which involves the thermodynamically favourable formation of the diazene $^tBuN{=}N^tBu$ as a by-product.

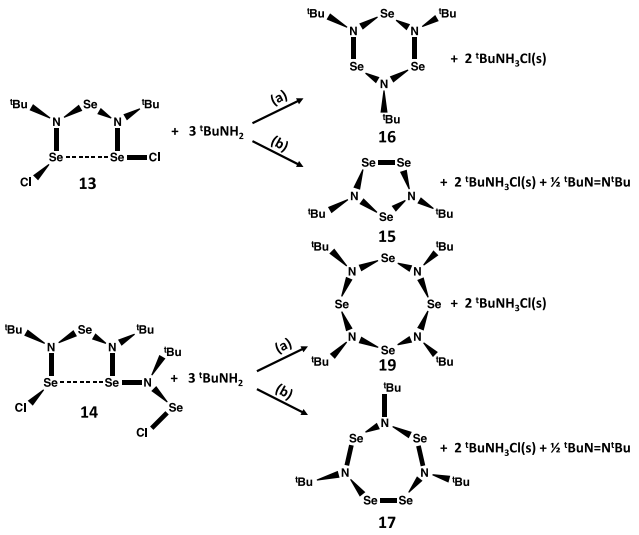
3.6 Cyclic selenium imides and acyclic selenium(IV) dimides: ring transformations

A significant feature of the chemistry of cyclophosphazanes is the occurrence of ring transformations under the influence of Lewis acids or heat (Section 2.2.3). Although the fifteen-membered selenium-nitrogen ring **20** is formally a trimer of the five-membered ring **15** (R = ᵗBu), no evidence for the interconversion of these cyclic oligomers has been presented. There are, however, some indications that ring transformations of cyclic selenium imides can be promoted by certain metal dihalides based on investigations of selenium(IV) diimides.

The *acyclic* selenium(IV) diimides RN=Se=NR [R = ^{t}Bu,, Ad (Ad = adamantyl)] are prepared by the reactions of primary amines with selenium(IV) tetrachloride $SeCl_4$.[42] An X-ray structural determination of the adamantyl derivative AdN=Se=NAd disclosed a monomeric structure.[43] While the [2 + 2] cyclodimerisation has been deduced to be slightly endergonic in solution, a combination of experimental and computational studies have demonstrated that the cyclodimerisation of the *tert*-butyl derivative ^{t}BuN=Se=N^{t}Bu is facilitated by group 12 metal dihalides MCl_2 (M = Cd, Hg).[44] The cyclic, dimeric ligand in the MCl_2 complexes formed in this way is structurally analogous to the known structure of the corresponding tellurium(IV) imide, ^{t}BuNTe(μ-N^{t}Bu)TeN^{t}Bu, which is dimeric in the solid state, as the free ligand.[45] ^{t}BuNSe(μ-N^{t}Bu)SeN^{t}Bu once formed is kinetically inert in solution, as can be deduced from the reaction energetics shown in Fig. 8.

In the absence of a metal dihalide, the decomposition of thermally unstable selenium(IV) diimides RN=Se=NR (R = ^{t}Bu,, Ad) in THF solution at ambient temperatures is a rich source of cyclic selenium imides.[46,47] The predominant products are the five-membered ring $Se_3(NR)_2$ (**15**, R = ^{t}Bu, Ad) and the six-membered ring $Se_3(NR)_3$ (**16**, R = ^{t}Bu, Ad); the larger rings $Se_6(N^tBu)_2$ (**18**) and $Se_9(N^tBu)_6$ (**20**) are also observed by ^{77}Se NMR spectroscopy for the *tert*-butyl derivatives.[46]

The seven-membered ring $Se_4(N^tBu)_3$ (**17**) depicted in Fig. 5 has not been isolated in the reaction of $SeCl_2$ with ^{t}BuNH$_2$, however it has been identified in the palladium complex **[**$PdCl_2$**17]**, which is formed in small amounts, together with [$PdCl_2$**19**] from the reaction of ^{t}BuN=Se=N^{t}Bu with $PdCl_2(NCPh)_2$ in THF for 16 h.[41] In a separate experiment it was shown by ^{77}Se NMR spectroscopy that the six-membered ring $Se_3(N^tBu)_3$ (**13**) is transformed into the corresponding cyclic tetramer $Se_4(N^tBu)_4$ (**19**) in the presence of [$PdCl_2(NCPh)_2$],



Scheme 8. Formation of cyclic selenium imides from reactions of ClSe[N(^{t}Bu)Se]$_n$Cl (**13**, *n* = 2; **14**, *n* = 3) and ^{t}BuNH$_2$ via (a) nucleophilic substitution or (b) reduction.[37]

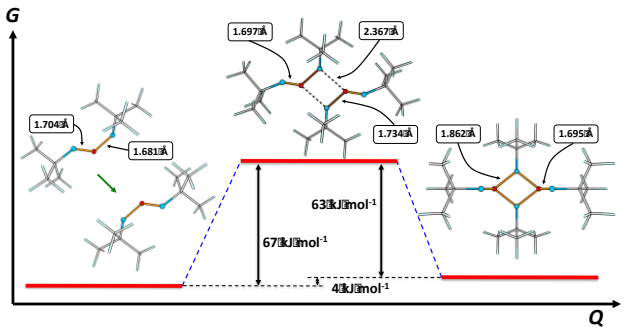


Fig. 8. Reaction profile of the cyclodimerisation of ^{t}BuN=Se=N^{t}Bu indicating energies and the changes in inter- and intra-molecular selenium-nitrogen bond lengths that occur during the monomer-dimer transformation.[37]

suggesting that ring transformations of the cyclic selenium imides may be promoted in the presence of a metal centre.[41] The seven-membered $Se_4(N^tBu)_3$ ring in [$PdCl_2$**17**] is *Se*,*Se*-chelated to palladium *via* the selenium atoms that have two nitrogen neighbours, while the bidentate coordination mode for the eight-membered $Se_4(N^tBu)_4$ ring in [$PdCl_2$**19**] involves two antipodal selenium atoms (Fig. 9).

3. 7 Cyclic tellurium imides

The only cyclic tellurium(II) imide that has been isolated and structurally characterised is the highly moisture–sensitive, six-membered ring $Te_3(N^tBu)_3$, *cf*. **16** (R = ^{t}Bu) in Fig. 5, which is formed as a minor product from the reaction of $TeCl_4$ with LiN(H)^{t}Bu; the major product of this reaction is the dimeric tellurium(IV) diimide ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu.[45] The reduction of Te(IV) to Te(II) has also been observed in reactions of $TeCl_4$ with lithium amides $LiNR_2$, which generate $Te^{II}(NR_2)_2$ (R = Me, $SiMe_3$) derivatives.[48,49] The tellurium(II) reagent $TeCl_2$ is

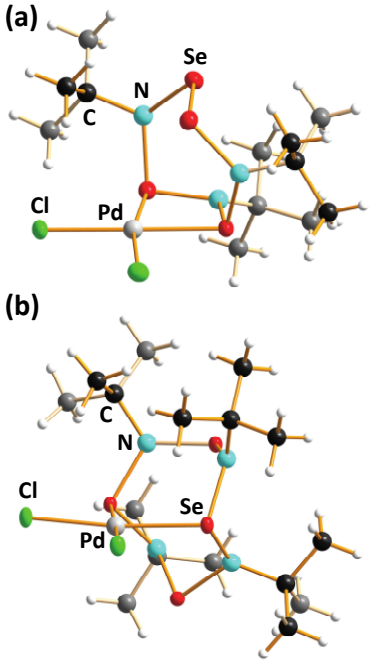


Fig. 9 Molecular structures of (a) [$PdCl_2${*Se*,*Se'*-$Se_4(N^tBu)_3$] and (b) [$PdCl_2${*Se*,*Se'*-$Se_4(N^tBu)_4$].[41]

unstable with respect to disproportionation, however the reactions of primary amines or their synthetic equivalents with adducts of the type $TeCl_2.L_2$ (L = tetramethylthiourea,[50] PEt_3;[51] L_2 = bipyridyl[52]) are a potentially rich source of tellurium imide chemistry.

4. Conclusions

This comparison of the cyclocondensation reactions of primary amines with pnictogen or chalcogen halides has pinpointed a number of similarities in the reactions pathways, as well as some significant differences. In common with the formation of cyclophosphazenes (Scheme 1), the synthesis of cyclopnictazanes and cyclic selenium imides both involve three steps: (a) generation of an acyclic building block, (b) chain growth incorporating this building block, and (c) intramolecular cyclisation, as illustrated in Schemes 5 and 8, respectively. In the Group 15 systems examples of the monomeric building blocks, *e.g.* $DippN(H)PCl_2$ (**1P**, R = Dipp), have been structurally characterised. By contrast, a representative of the initial acyclic intermediate RN(H)SeCl (Scheme 7), assumed to be formed in the chalcogen systems, has not been isolated. However, a series of acyclic imidoselenium(II) dichlorides $ClSe[N(^tBu)Se]_nCl$ (*n* = 1-3, **12-14**) resulting from chain growth have been structurally identified. A combination of experimental and theoretical studies has shown that the members of this oligomeric series are essential precursors for the formation of cyclic selenium imides. A second important difference between the Group 15 and 16 chemistry is the generation of catenated ring systems for the chalcogens even when the source of chalcogen is not catenated, *e.g*. $SeCl_2$. This disparity can be attributed to two concurrent cyclisation processes, *viz*. nucleophilic substitution and reduction, in the reactions of $ClSe[N(^tBu)Se]_nCl$ (**12-14**) with *tert*-butylamine.

This Perspective also highlights a number of potential areas for future investigations, primarily in the area of chalcogen-nitrogen chemistry. In the light of the extensive information available for Group 15 systems, the reactions of $SeCl_2$ with bulky aryl amines $ArNH_2$ (*e.g.* Ar = Mes*, Dipp, Dmp, Ter) merit attention with a view to the isolation and characterization of (a) monomeric ArN=Se derivatives, (b) intermediates of the type ArN(H)SeCl or (c) four-membered rings $Se_2(NAr)_2$, which could act as an *in situ* source of the corresponding monomers ArN=Se. Similar investigations may be envisaged for the sulfur systems, although the instability of SCl_2 is an impediment to such studies. Moreover, the availability of a convenient NMR nucleus for monitoring reactions is a decided advantage for selenium. Transmetallation reactions involving cyclic tin reagents $[Sn(\mu\text{-}NR)]_2$ and $SeCl_2$ or $TeCl_2.L_2$ adducts (*vide supra*) are a potentially versatile source of cyclic selenium or tellurium imides (*cf*. Scheme 4). Indeed, the entire area of tellurium imide chemistry is open for creative approaches to novel Te–N heterocycles that may exhibit different structural arrangements compared to the Se-N rings depicted in Fig. 5.[53] Furthermore, cyclic tellurium imides of the type $(TeNR)_n$ could act a source of tellurium(0), *cf*. R_3PTe,[54] for the generation of metal telluride semiconductors through the thermodynamically favourable oxidative elimination of diazenes RN=NR.

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