Chemistry of pnictogen(III)–nitrogen ring systems

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This *critical review* covers significant recent advances in the chemistry of pnictogen(III)–nitrogen ring systems, also known as cyclopnict(III)azanes. The synthetic methodologies and reactions of the heavier pnictogen systems are compared with the well-developed chemistry of cyclophosph(III)azanes. Particular attention is focused on ring-oligomerization processes and the use of four-membered E_2N_2 rings as building blocks for the synthesis of macrocyclic molecules. Main-group element and transition-metal complexes are also discussed (95 references).

1 Introduction

Four-membered rings of the type $[XP(\mu\text{-}NR)]_2$, containing alternating phosphorus(III) and nitrogen centres are known as cyclodiphosph(III)azanes (or diazadiphosphetidines). Current interest in this well-known inorganic heterocycle includes the use of the P_2N_2 scaffold in the construction of macrocycles and in ligands for metal complexes for applications in homogeneous catalysis. In addition, the prospect of generating high molecular weight polymers of the type $(–XPNR–)_n$ provides an incentive for studies of ring-transformation processes. Early work in this area is discussed in several reviews,[1,2] the latest of which covers the literature up to the end of 1999 and focuses on main-group complexes.[3] The coordination chemistry of related P(V)/P(V) systems has also been surveyed recently.[4]

The chemistry of heavier pnictogen (As, Sb, Bi) analogues of this classic inorganic ring system (cyclodipnict(III)azanes)† has been slower to develop. In this review the challenges involved in the development of this chemistry will be discussed and comparisons with P_2N_2 systems will be made in the context of the most recent advances in cyclophosph(III)azane chemistry. Wright and Beswick have briefly discussed the formation of the Sb_2N_2 ring[5] and the same group has also described early work on E_2N_2-derived macrocycles (E = P, Sb) as part of a microreview.[6]

2 Synthetic methods

Three types of derivatives are pivotal in the systematic development of cyclopnictazane chemistry. The simplest cyclodiphosph(III)azanes are the dihalo derivatives, $[ClP(\mu\text{-}NR)]_2$ (type **I**, Chart 1), which can be readily synthesized by the reaction of a primary amine with PCl_3. Bis(organylamino) derivatives of the type **II** (R = R′) are obtained by treatment of PCl_3 with an excess of a primary amine. The hetero-substituted derivatives (**II**, R ≠ R′) are prepared by reaction of **I** with a lithium amide or an excess of a

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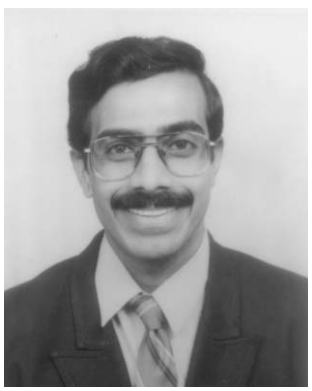
† In this article the terms cyclodipnictazane, cyclotripnictazane *etc.* will be used to refer to saturated E_2N_2, E_3N_3 (E = P, As, Sb, Bi) rings, respectively.



Maravanji Balakrishna

Maravanji Balakrishna was born in Karnataka, India. He received his BSc and MSc degrees from Mysore University and a PhD degree from the Indian Institute of Science, Bangalore under the direction of Professor S. S. Krishnamurthy. He carried out post-doctoral work with Professor Ron Cavell at the University of Alberta (Canada) and with Professor Joel Mague at Tulane University (USA). He is currently a Full Professor at the Indian Institute of Technology, Bombay. He spent a sabbatical year (2005–2006) in the laboratory of Professor Tris Chivers (University of Calgary, Canada). His research interests span the areas of main-group chemistry, organometallic chemistry and homogeneous catalysis.

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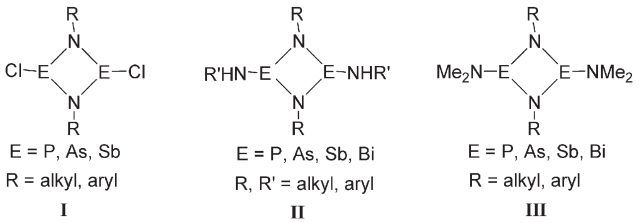


Chart 1

primary amine. Although these methods may be employed in the case of heavier pnictogens, alternative reaction pathways that involve cleavage of the weaker, more labile E–N bonds (as compared to P–N bonds) may also occur, particularly in the reactions with primary amines. Other methods for the synthesis of cyclodipnict(III)azanes (As, Sb, Bi) involve the treatment of ECl_3 with lithium amides or silylated lithium amides, although the latter case is restricted to three examples. Prior to our recent work, the only isolated examples of type **II** cyclodipnict(III)azanes of antimony and bismuth had been prepared by the reaction of the metal halide with a lithium amide. However, this approach is not generally applicable, as illustrated by the reaction of $SbCl_3$ with LiNHPh, which produces the macrocycle $Sb_{12}(NPh)_{18}$ (Section 6). The bis(dimethylamino) derivatives **III** (E = As, Sb, Bi) are prepared by transamination reactions of the strong bases $E(NMe_2)_3$ with primary amines. We have recently prepared a series of cyclodistib(III)azanes of the type **II** from the metathetical reaction of $[ClSb(\mu\text{-}N^tBu)]_2$ with lithium amides (Section 5.1).

In summary, as a result of the limitations of the various synthetic approaches, the range of known E_2N_2 systems (E = As, Sb, Bi) is more restricted than for P_2N_2 derivatives, especially for bismuth. For example, **I** (E = Bi), **II** (E = Bi; R = alkyl) and **III** (E = Bi; R = aryl) are unknown.

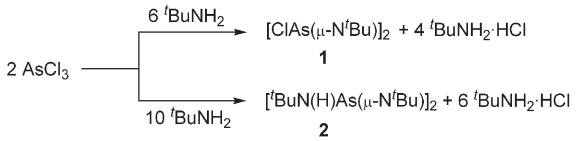
Tristram Chivers

Tristram Chivers, a native of Bath, England, received his BSc, PhD and DSc degrees all from the University of Durham (UK). After post-doctoral work at the University of Cincinnati and a two-year appointment as a Tutorial Fellow at the University of Sussex, he came to Canada in 1967 as a Teaching Post-doctoral Fellow at the University of British Columbia. He joined the University of Calgary in 1969 and served as Head of the Chemistry Department from 1977 to 1982. He currently holds the title of University Professor and Professor of Chemistry. His primary research interests are in the general area of main-group element chemistry with emphasis on inorganic ring systems. He received the Alcan Lecture Award of the Canadian Society for Chemistry (CSC) in 1987, the E.W.R. Steacie Award from the CSC in 2001, and the Royal Society of Chemistry Award (UK) for Main-Group Element Chemistry in 1993. He was elected a Fellow of the Royal Society of Canada in 1991.

2.1 Cyclocondensation reactions of pnictogen halides

2.1.1 Primary amines. The cyclocondensation of primary amines with PCl_3 is a very efficient method for the synthesis of cyclodiphosph(III)azanes. However, this synthetic route produces more varied results when applied to the heavier pnictogens and the greatest success has been observed in the analogous arsenic chemistry. In 1960 Olah and Oswald prepared cyclodiars(III)azanes of the type $[ClAsNR]_2$ by reaction of a primary amine with $AsCl_3$ in a 2 : 1 molar ratio and a dimeric structure was proposed for the *tert*-butyl derivative (**1**).[7] Interestingly, the yield of **1** was 66.5%, presumably due to the use of only two equivalents of primary amine.[7] Later work demonstrated that the use of an excess of $^tBuNH_2$ produces $[^tBuN(H)As(\mu\text{-}N^tBu)]_2$ (**2**) (Scheme 1).[8] The trimer $[ClAs(\mu\text{-}NMe)]_3$ has been isolated from the reaction of $AsCl_3$ with $MeNH_2$.[9] Burford *et al*. have recently reported that the arsenic compounds $[ClAs(\mu\text{-}NDipp)]_2$ and $[ClAs(\mu\text{-}NDmp)]_2$ (Dipp = 2,6-$^iPr_2C_6H_3$, Dmp = 2,6-$Me_2C_6H_3$) can be prepared by the cyclocondensation route, albeit in low yields (Section 3).[10]

The dimethylamino derivative $[Me_2NAs(\mu\text{-}N^tBu)]_2$ (**3**, Chart 2) and aryl derivatives of the type $[ArAs(\mu\text{-}NC_6H_5)]_2$ (**4**) can be prepared from the cyclocondensation of the appropriate primary amine and Me_2NAsCl_2[8] or $ArAsCl_2$.[11,12] Interestingly, the tetramer $[Cp^*As(\mu\text{-}NH)]_4$, a rare example of a cyclotetrapnict(III)azane, is generated from the reaction of Cp^*AsCl_2 and ammonia in diethyl ether.[13] The reaction of methylamine with $Cp'AsX_2$ (X = Cl, I) produces the cyclopentadienyl derivatives $[Cp'As(\mu\text{-}NR)]_2$ (**5a** and **5b**) respectively.[13] However, when *tert*-butylamine is reacted with Cp^*AsCl_2, only the monomeric compound $Cp^*AsCl(NH^tBu)$ is obtained. Presumably the increased steric bulk of the primary amine hinders the cyclocondensation in this case. Treatment of $Cp^*AsCl(NH^tBu)$ with either Me_3SnNEt_2 or $NaN(SiMe_3)_2$ provides a driving force strong enough to generate the cyclodiars(III)azane $[Cp^*As(\mu\text{-}N^tBu)]_2$ (**5c**).[13]



Scheme 1

The cyclodistib(III)azane $[ClSb(\mu\text{-}N^tBu)]_2$ (**6**) was first prepared by the reaction of $SbCl_3$ with $LiN(SiMe_3)^tBu$ (Section 2.1.2).[14] However, Stahl has recently shown that the

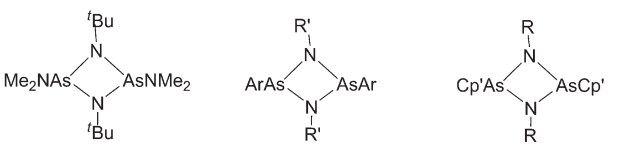


Chart 2

compound **6** can be prepared in a simple one-pot synthesis, albeit with slightly lower yields, as shown in eqn (1).[15] No other antimony compounds of the type **I** have been isolated to date and the analogous bismuth compounds are unknown.

$$2\,SbCl_3 + 3\,{}^tBuNH_2 \xrightarrow{3\,NEt_3} \underset{\mathbf{6}}{[ClSb(\mu\text{-}N{}^tBu)]_2} \quad (1)$$

Monomeric iminoarsanes have often been invoked as intermediates in the formation of the dimeric structures.[7,8,13] However, substituents that provide kinetic or electronic stabilization of the As=N double bond are necessary for the isolation of such species, *e.g.* Mes*N=As-NHMes*,[16] TfmpAs=NTfmp (Mes* = 2,4,6-[$^tBu_3C_6H_2$], Tfmp = 2,4,6-$(CF_3)_3C_6H_2$).[17] Burford *et al.* have provided some insights into the mechanism of the cyclocondensation process through examination of the reactions of sterically moderate primary amines, *e.g.*, $DippNH_2$, $DmpNH_2$, with pnictogen trihalides in a variety of stoichiometric ratios. Several key intermediates were isolated and structurally characterized for both the phosphorus and antimony systems.[18,19] Furthermore, reactions with PCl_3 were monitored by ^{31}P NMR spectroscopy allowing for the identification of other species present in solution. On the basis of these studies, the overall reaction sequence illustrated in Scheme 2 was proposed. In contrast to earlier proposals, this reaction scheme does not require the formation of monomeric iminopnictazanes as precursors to the cyclic systems. Instead, the E_2N_2 framework is built up by a sequence of intramolecular dehydrochloride couplings, *e.g.* **IV** → **V** or **VII** → **VIII**, **IX** → **X**, accompanied by reactions of the intermediates with either ECl_3 or RNH_2. Species of the type **V** and **VI** (E = P) and **IX** (E = Sb), together with a cyclotristib(III)azane (**XI**) (R = Dmp) have been isolated and characterized by X-ray crystallography.[18,19] Dimer → trimer ring transformations (**X** → **XI**) are discussed in Section 3.

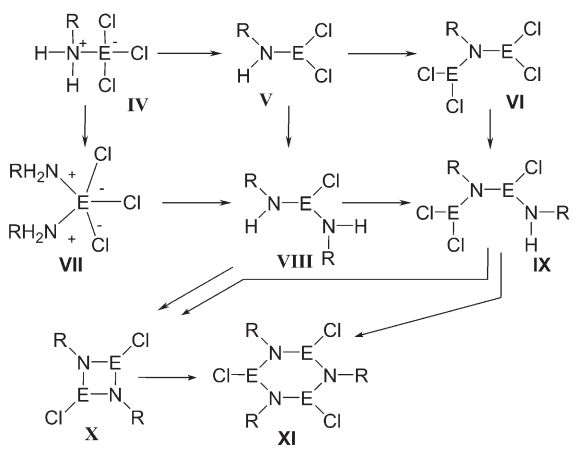
2.1.2 Amidolithium or silylated amidolithium reagents. Lithium amides have been employed in the synthesis of heavy cyclodipnict(III)azanes and have produced the only isolated examples of type **II** compounds of antimony and bismuth. As is typical in this chemistry, the product of the reaction is often dependent on the identity of the pnictogen. For example, the reaction of $PhAsCl_2$ with two equivalents of $LiHN{}^tBu$ affords the acyclic bis(amino) derivative $PhAs(NH{}^tBu)_2$, whereas similar reactions of $PhECl_2$ (E = Sb, Bi) produce cyclodipnict(III)azanes $[PhE(\mu\text{-}N{}^tBu)]_2$ (**7**, Chart 3) in good yields, presumably by condensation of $^tBuNH_2$.[20] An analogous condensation process was also invoked to explain the formation of the imidoantimony macrocycle $Sb_{12}(NPh)_{18}$ from $SbCl_3$ and LiNHPh *via* the intermediacy of $Sb(NHPh)_3$ (Section 6).[21]

Roesky *et al.* prepared the cyclodiars(III)azane $[DippN(H)As(\mu\text{-}NDipp)]_2$ (**8**, E = As) by treatment of DippNHLi with $AsCl_3$ in a 3 : 1 molar ratio (eqn (2)).[22] This method was later used to produce the first structurally characterized cyclodibism(III)azane (**8** E = Bi).[23] Burford and coworkers have extended this synthesis to the entire congeneric series of cyclic bis(amido)dipnict(III)azanes (**8**, E = P, As, Sb, Bi) (type **II**) and showed that the combination of one equivalent of $LiNH{}^tBu$ and two equivalents of DippNHLi facilitates the isolation of **8**.[24] The antimony compound $[DmpN(H)Sb(\mu\text{-}NDmp)]_2$ (**9**, Dmp = 2,6-$Me_2C_6H_3$) has also been prepared by the route shown in eqn (2).[21]

$$2ECl_3 + 6LiNHDipp \rightarrow [Dipp(H)NE(\mu\text{-}NDipp)]_2 \quad (2)$$

Metal amides have also been used to synthesize cyclodipnict(III)azanes of the type **I**. The reaction of two equivalents of KN(H)(Tfmp) with $AsCl_3$ affords the compound **10a** in 58% yield.[25] It is highly probable that the analogous reaction of LiN(H)(Mes*) with $SbCl_3$ generates the (unisolated) compound $[ClSb(\mu\text{-}NMes^*)]_2$. This is evinced by the *in situ* reaction with AgOTf (OTf = $CF_3SO_3^-$) which results in the isolable compound $[OTfSb(\mu\text{-}NMes^*)]_2$ (Section 3).

There are a few reported examples where silylated lithium amides have been successfully used to prepare derivatives of the type **I**. The chloro- and bromo-cyclodistib(III)azanes $[XSb(\mu\text{-}N{}^tBu)]_2$ (X = Cl, Br) have been synthesized by the 1 : 1 reaction of SbX_3 with $LiN(SiMe_3)({}^tBu)$.[14] This synthetic route was later used to make the arsenic analogue $[ClAs(\mu\text{-}N{}^tBu)]_2$ (**1**), which was isolated in 90% yield and the proposed dimeric structure was confirmed.[26] Similarly, the compound $[2\text{-}(6\text{-}Me)C_5H_3NAsCl]_2$ (**10b**) was obtained from reaction of equimolar amounts of $AsCl_3$ and [2-(6-Me)pyridyl]$(SiMe_3)NLi{\cdot}OEt_2$.[27,28] The analogous 1 : 1



Scheme 2

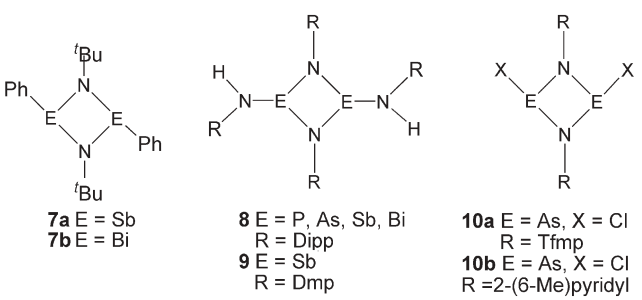
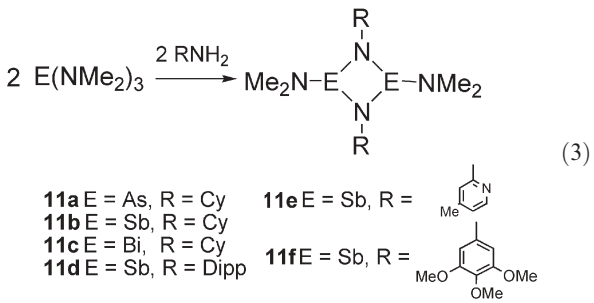


Chart 3

reaction of the silylated lithium amide with $SbCl_3$ results in the formation of the compound $\{[2\text{-}(6\text{-Me})\text{pyridyl}](SiMe_3)\}_2SbCl$, the product of the 2 : 1 reaction.[29]

2.2 Transamination reactions

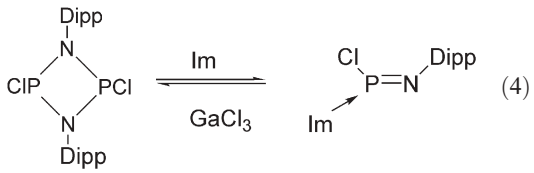
In 1963 Nöth *et al.* reported the first example of the synthesis of a heavy cyclodipnict(III)azane by transamination.[8] The dimer $[Me_2NAs(\mu\text{-}N^tBu)]_2$ was obtained by reaction of equimolar amounts of $As(NMe_2)_3$ and *tert*-butylamine. More recently, Wright has championed the use of the powerful bases $E(NMe_2)_3$ (E = As, Sb, Bi) for the synthesis of dimethylamido derivatives $[Me_2NE(\mu\text{-}NR)]_2$ (**11a–f**, type **III**, eqn (3)).[5,30] Wright and others have observed that, in general, the compounds **11** do not react further with primary amines to give compounds of the type **II**.[5,8] However, Wright has recently reported the bis(amido)cyclodiarsazanes $[CyN(H)As(\mu\text{-}NCy)]_2$ and $[mtaN(H)As(\mu\text{-}Nmta)]_2$ (mta = 5-methylthiazolyl) prepared by this method.[31,32] While not structurally characterized, the identity of the former compound was assigned by mass spectrometry and the latter compound was identified by IR and ^1H NMR spectroscopic data; surprisingly, the ^1H NMR data obtained did not integrate correctly for the assigned cyclodiars(III)azane structure.[32] Regardless of the limitations observed in using the compounds **11** to prepare cyclodipnict(III)azanes of the type **II**, Wright has demonstrated that the dianions $[R'NE(\mu\text{-}NR)]_2^{2-}$ are readily prepared by reactions of **11** with lithium amides (Section 5.4).



(3)

3 Oligomerization reactions and ring transformations

Burford *et al.* have investigated oligomerization reactions and ring transformations between dimeric and trimeric pnict(III)azanes in the context of an alkene/cyclobutane analogy.[33,34] Such studies are expected to provide insight into the generation of phosphazane polymers $(–RE{=}NR')_n$, *e.g.*, by a ring-opening polymerization process. The delicate balance between monomers and dimers is illustrated by the observation that Mes*NPCl is a monomer in the solid state,[35] whereas the slightly smaller Dipp substituent allows dimerization to the more common four-membered P_2N_2 ring (**8**).[18,24] Interestingly, treatment of the dimer $(DippNPCl)_2$ with the N-heterocyclic carbene ligand 1,3-di*iso*-propyl-4,5-dimethylimidazolyl-2-ylidene (Im) causes dissociation of the P_2N_2 framework to give the adduct DippNP(Im)Cl; this process can be reversed by the addition of a strong Lewis acid to the adduct (eqn (4)).[36]



(4)

Burford and coworkers have also carried out a comparative study of the stabilities of the alkene analogues RN=ER′ (E = P, As, Sb) with respect to the corresponding dimers (cyclobutane analogues) by using Mes* groups on N and a chloro or triflate ($CF_3SO_3^-$) substituent on the pnictogen.[34] For the triflate derivative of the phosphorus system both the monomer **12**[37] and the dimer **13** (Chart 4) were isolated and it was shown that the dimer dissociates into the monomer in the melt. The arsenic derivative was obtained as the dimer **14a** in the solid state, but a colour change from yellow to red was observed upon heating, both in the solid state and in solution, suggesting dissociation into a monomer under those conditions.[16,34] The dimeric antimony derivative **14b** exhibited no evidence of dissociation indicating that the larger Sb_2N_2 platform is able to accommodate the steric strain imposed by bulky Mes* groups.

The lability of the E–N bond in cyclodipnict(III)azanes under the influence of the strong Lewis acid $GaCl_3$, followed by the addition of 4-dimethylaminopyridine (DMAP), has also been demonstrated for both the P_2N_2 and As_2N_2 ring systems.[10,38] The moderate steric influence of Dipp or Dmp substituents on nitrogen thermally destabilizes the four-membered E_2N_2 rings (**15**) with respect to the corresponding six-membered E_3N_3 rings (**16**) (Scheme 3). For the phosphorus system, an unusual cyclophosphazanium tetrachlorogallate (**17**, E = P, R = Dipp) was identified as an intermediate in the ring transformation process (Scheme 3).

In contrast to the Lewis acid-assisted dissociation of cyclic dimers, Wright and coworkers have observed reversible interconversion between the dimer $[ClPNEt]_2$ (**19**) and the trimer $[ClPNEt]_3$ (**20**) under thermal conditions.[39] The 1 : 1 reaction of PCl_3 with $[EtNH_3]Cl$ in the presence of Et_3N (as a solvent) produces the trimer (**20**) exclusively. On distillation

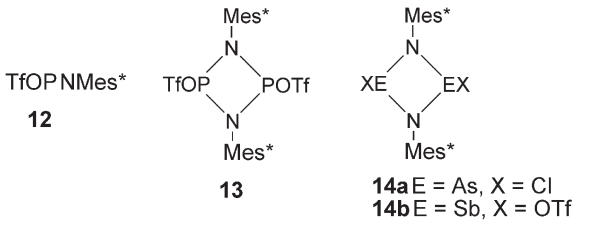
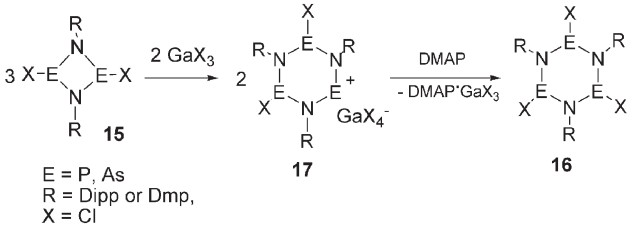
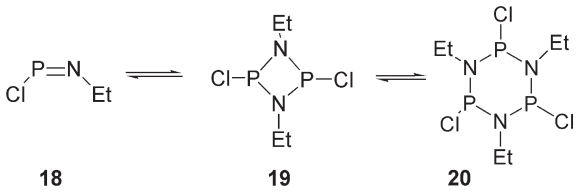


Chart 4



Scheme 3



18 **19** **20**

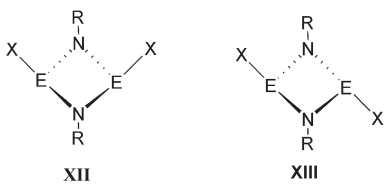
Scheme 4

under reduced pressure, the trimer transforms into the dimer (**19**) quantitatively. Quantitative reversion to the trimer occurs on heating the dimer at 130 °C for 12 h (Scheme 4). This thermally induced process has been compared to the cracking of dicyclopentadiene into cyclopentadiene in a retro-Diels–Alder reaction.[39] The ring expansion involves the formal insertion of the monomer [ClP=NEt] (**18**) into the dimer **19**. Semi-empirical calculations show that this is the most thermodynamically favourable pathway.[39] Both the Lewis acid-mediated and the thermal cracking routes open new avenues for oligomerization and, possibly, polymerization processes of cyclopnict(III)azanes.

4 Geometrical isomers

Cyclodipnict(III)azanes can exist as *cis* or *trans* isomers (**XII** and **XIII**, Chart 5). As pointed out by Stahl, most cyclodiphosph(III)azanes are thermodynamically more stable as the *cis* isomer while the *trans* isomer is the kinetic product.[3] In general, the *cis* isomers have puckered P_2N_2 rings, whereas the rings in the *trans* isomers are planar.

A summary of the geometrical preferences for structurally characterized As, Sb and Bi systems is given Table 1. The dichlorocyclodiars(III)azanes $[ClAs(\mu\text{-}N^tBu)]_2$ (**1**) and $[ClAs(\mu\text{-}N\{(2\text{-pyridyl(Me-6)}\})]_2$ (**8**) show *cis* geometry with



XII **XIII**

Chart 5

As_2N_2 ring puckering, whereas the sterically demanding Tfmp and Mes* derivatives $[ClAs(\mu\text{-NTfmp})]_2$ and $[ClAs(\mu\text{-NMes*})]_2$ exist as the *trans* isomers with a planar As_2N_2 ring. The cyclopentadienyl-arsenic derivatives $[Cp'As(\mu\text{-NMe})]_2$ provide a cogent illustration of the subtle influences on geometrical preference. The derivative **5b** ($Cp' = C_5{}^iPr_4H$) exists as the *trans* isomer, whereas the less bulky C_5Me_5 groups in **5a** prefer a *cis* geometry. Steric arguments alone cannot account for the structure observed in the solid state, as demonstrated by the bis(amido) derivative $[DippN(H)As(\mu\text{-NDipp})]_2$ (**8**), which adopts a *cis* geometry even though there are four reasonably bulky Dipp substituents.

As indicated in Table 1, the majority of cyclodistib(III) azanes exhibit *trans* geometry in the solid state. Until our recent work, the compound $[Me_2NSb(\mu\text{-NDipp})]_2$, prepared by Wright and co-workers, was the only structurally characterized *cis* cyclodistibazane.[40] It was suggested that $[Me_2NSb(\mu\text{-NDipp})]_2$ adopts a *cis* geometry in order to prevent the steric congestion at the periphery of the ring that would occur in a *trans* arrangement.[40] The mixed cyclodistibazane $[DmpN(H)Sb(\mu\text{-}N^tBu)]_2$ (**25c**, Section 5.1) has now been obtained in the solid state as the *cis* isomer.[41] Interestingly, both the *cis* and *trans* isomers have been isolated and structurally characterized for $[DippN(H)Sb(\mu\text{-}N^tBu)]_2$ (**25b**, Section 5.1).[41] The amido protons of the (H)NR substituents adopt an *endo*, *endo* configuration for both of the *cis* isomers.

Although the solid-state structure of $[ClSb(\mu\text{-}N^tBu)]_2$ (**6**) has been revealed to be the *cis* isomer,[41] the derivatives $[XSb(\mu\text{-}N^tBu)]_2$ ($X = N_3$, O^tBu), prepared by nucleophilic substitution reactions (Section 5.1), are isolated as *trans* isomers.[15] The azido derivative adopts an *endo*,*endo* conformation whereas the *tert*-butoxy analogue exists as the *exo*,*exo* isomer presumably as a result of steric effects. The *tert*-butyl derivative $[^tBuSb(\mu\text{-}N^tBu)]_2$ is also obtained as the *trans* isomer in the solid state.[42]

To date, only two structural studies have been reported for bismuth derivatives. Both $[DippN(H)Bi(\mu\text{-NDipp})]_2$[26] and $[PhBi(\mu\text{-}N^tBu)]_2$[20] exist as *trans* isomers with planar Bi_2N_2 rings.

Solution NMR studies of cyclodiphosph(III)azanes have clearly demonstrated the presence of *cis* and *trans* isomers for many derivatives. In particular, it is possible to distinguish

Table 1 Geometrical isomers of cyclodipnict(III)azanes (E = As, Sb, Bi)

Cyclodipnictazane	Isomer	Cyclodipnictazane	Isomer
$[ClAs(\mu\text{-}N^tBu)]_2$[26]	*cis*	$[ClAs(\mu\text{-NDmp})]_2$[10]	*cis*
$[ClAs(\mu\text{-}N\{(2\text{-pyridyl(Me-6)}\})]_2$[27]	*cis*	$[ClAs(\mu\text{-NDipp})]_2$[10]	*cis*
$[ClAs(\mu\text{-NTfmp})]_2$[25]	*trans*	$[ClAs(\mu\text{-NMes*})]_2$[34]	*trans*
$[(C_5Me_5)As(\mu\text{-NMe})]_2$[13]	*cis*	$[(C_5{}^iPr_4H)As(\mu\text{-NMe})]_2$[13]	*trans*
$[DippN(H)As(\mu\text{-NDipp})]_2$[24]	*cis*	$[(4\text{-Br-}C_6H_4)As(\mu\text{-NPh})]_2$[11]	*trans*
$[ClSb(\mu\text{-}N^tBu)]_2$[41]	*cis*	$[^tBuSb(\mu\text{-}N^tBu)]_2$[42]	*trans*
$[N_3Sb(\mu\text{-}N^tBu)]_2$[15]	*trans*	$[^tBuOSb(\mu\text{-}N^tBu)]_2$[15]	*trans*
$[PhSb(\mu\text{-}N^tBu)]_2$[20]	*trans*	$[Me_2NSb(\mu\text{-NDipp})]_2$[40]	*cis*
$[Me_2NSb(\mu\text{-}N\{C_6H_2(OMe)_3\text{-}3,4,5\}\})]_2$[30]	*trans*	$[Me_2NSb(\mu\text{-}N\{2\text{-pyridyl(Me-4)}\})]_2$[30]	*trans*
$[DmpN(H)Sb(\mu\text{-NDmp})]_2$[21]	*trans*	$[DippN(H)Sb(\mu\text{-NDipp})]_2$[24]	*trans*
$[DmpN(H)Sb(\mu\text{-}N^tBu)]_2$[41]	*cis*	$[(TfO)Sb(\mu\text{-NMes*})]_2$[34]	*trans*
$[DippN(H)Sb(\mu\text{-}N^tBu)]_2$[41]	*cis*	$[DippN(H)Sb(\mu\text{-}N^tBu)]_2$[41]	*trans*
$[DippN(H)Bi(\mu\text{-NDipp})]_2$[23]	*trans*	$[PhBi(\mu\text{-}N^tBu)]_2$[20]	*trans*

between the isomers from their markedly different ^{31}P NMR chemical shifts.[43] Unfortunately, there is no analogous simple NMR handle for the heavier pnictogens. Consequently, there are few reports of comprehensive NMR studies on heavier cyclodipnict(III)azanes, and in most cases only a single isomer is observed in solution. The first such study examined the derivatives $[RSb(\mu\text{-}N^tBu)]_2$ (R = alkyl, alkoxy, aryloxy and silyl), which indicated that an equilibrium exists between *cis* and *trans* isomers in solution.[42] With the exception of $[Me_2NSb(\mu\text{-}NDipp)]_2$, for which only a single isomer is observed in solution, Wright has indicated that the dimethylamido derivatives of the type $[Me_2NSb(\mu\text{-}NR)]_2$ also exist as a mixture of *cis* and *trans* isomers in solution,[5,40] although definitive NMR data are lacking.[30,44] Norman and co-workers observed four equal intensity resonances for the methyl substituents in the ^1H NMR spectrum of [DmpN(H)Sb(μ-NDmp)]$_2$ (**9**), which were attributed to the presence of an equal mixture of *cis* and *trans* isomers.[21] More detailed NMR studies have been performed on the mixed cyclodistib(III)azanes $[RN(H)Sb(\mu\text{-}N^tBu)]_2$ (Section 5.1).[41] These compounds are initially formed as a mixture of *cis* and *trans* isomers, which are easily separated in the case of $[DippN(H)Sb(\mu\text{-}N^tBu)]_2$ owing to solubility differences. The isomers can be readily distinguished in the ^1H NMR by the chemical shift of the amido NH protons, which are more shielded in the *cis* isomer, due to the *endo*,*endo* configuration of the N(H)R substituents. Interestingly, *trans*-$[DippN(H)Sb(\mu\text{-}N^tBu)]_2$ slowly (days) isomerizes in solution to *cis*-$[DippN(H)Sb(\mu\text{-}N^tBu)]_2$, clearly indicating that the *trans* isomer is the kinetic product, whereas the *cis* isomer is the thermodynamic product.

In summary, on the basis of the limited structural data available, two trends are clear. Firstly, the dichloro arsenic compounds (type **I**) tend to adopt a *cis* configuration in the solid state, although the *trans* isomer is observed when the imido groups are very bulky. Secondly, there is a trend towards the preferential formation of *trans* isomers in the solid state for the heavier pnictogens Sb and Bi. In solution, however, NMR data indicate the co-existence of *cis* and *trans* isomers for certain derivatives. As described by Stahl,[3] the mechanism of the *cis*–*trans* interconversion for cyclodiphosph(III)azanes may involve (a) pyramidal inversion at the pnictogen centre (b) edge inversion at the imino nitrogen or (c) cycloreversion (ring-opening). In view of the recent work on ring-transformation processes and the lability of E–N (E = As, Sb, Bi) bonds (Section 3), the latter mechanism is a likely alternative to the closed-ring processes (a) and (b) for cyclodipnict(III)azanes containing the heavier pnictogens. High level computational studies are needed to shed light on the trends in configurational preferences as a function of the pnictogen for these inorganic ring systems.

5 Reactions of cyclodipnict(III)azanes

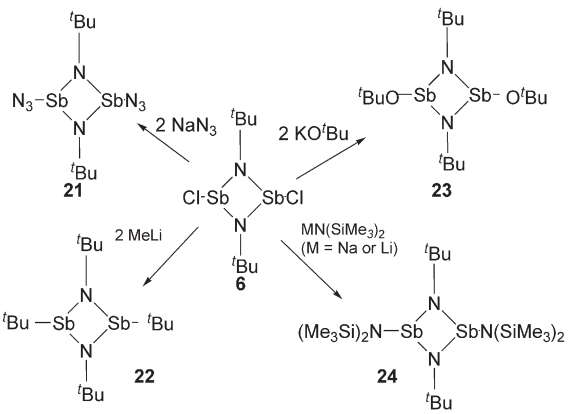
The most common reactions of cyclodipnict(III)azanes involve the three types **I**, **II** and **III** introduced in Section 1 (Chart 1). The dichloro compounds (type **I**) are readily susceptible to nucleophilic substitution reactions; the use of difunctional nucleophilic reagents leads to the formation of macrocyclic systems based on E_2N_2 building blocks (Section 6). The bis(alkylamino) compounds (type **II**) serve as precursors to the corresponding dianionic ligands *via* metallation and, hence, to metal complexes that are of interest in catalytic applications (Section 7.2). The bis(dimethylamino) compounds (type **III**) are also important intermediates in the generation of these dianionic ligands, especially for the heavier pnictogens, as well as for the construction of tetrameric cubanes.

5.1 Nucleophilic substitution reactions

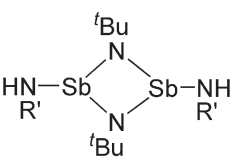
Some examples of the nucleophilic substitution reactions of $[ClSb(\mu\text{-}N^tBu)]_2$ (**6**) are shown in Scheme 5. The azido, *tert*-butyl and *tert*-butoxy derivatives $[XSb(\mu\text{-}N^tBu)]_2$ **21**,[15] **22**[42] and **23**,[15] respectively, have all been isolated as the *trans* isomers in the solid state (Section 4).

It has recently been shown that the compound $[ClSb(\mu\text{-}N^tBu)]_2$ can be used to prepare both homo- and hetero-substituted cyclodistib(III)azanes of the type **II** by reaction with lithium amides.[41] The compounds **25** are obtained in high yields (80–90%) and the structures of **25b** and **25c** have been determined (Chart 6). Interestingly, both the *cis* and *trans* isomers of compound **25b** have been isolated and completely characterized in solution and in the solid state (Section 4).[41] These bis(amido) derivatives are especially important for the generation of dianionic ligands of the type $[R'NE(\mu\text{-}NR)]_2^{2-}$ by metallation with, for example, ^{n}BuLi (Section 5.4).

The reactions of the bis(dimethylamido) derivatives $[Me_2NE(\mu\text{-}NCy)]_2$ (E = Sb, Bi) with PhOH or 2-pyOH give the unusual tetrameric cubanes $[PhOSb(\mu\text{-}NCy)]_4$ (**26a**) and $[2\text{-pyOBi}(\mu\text{-}NCy)]_4$ (**26b**), respectively (eqn (5)).[45]

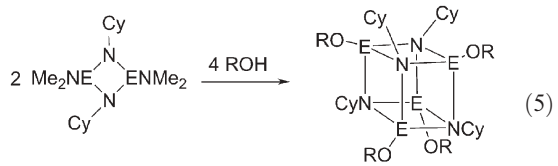


Scheme 5



25a R' = ^{t}Bu
25b R' = Dipp
25c R' = Dmp

Chart 6



26a E = Sb, R = Ph
26b E = Bi, R = 2-pyridyl

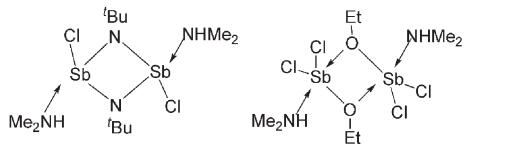
When the substituent on the pnictogen centre is an alkyl or aryl group, treatment with nucleophilic reagents results in the cleavage of pnictogen–nitrogen bonds. For example, the cyclodiars(III)azanes $[ArAs(\mu\text{-}N^tBu)]_2$ (Ar = aryl) produce monomeric esters $ArAs(OR)_2$ upon reaction with alcohols.[11] The lability of As–N bonds in cyclodiars(III)azanes is also illustrated by the formation of the tricyclic compounds $As(\mu\text{-}NR)(\mu\text{-}NSN)_2As$ (R = ^{t}Bu, Ph) upon reaction of **1** with the potassium salt of the dianion SN_2^{2-}.[46]

Further examples of nucleophilic substitution reactions of dichlorocyclodipnict(III)azanes of type **I** are included in the discussion of the formation of macrocyclic systems in Section 6.

5.2 Lewis acid behaviour

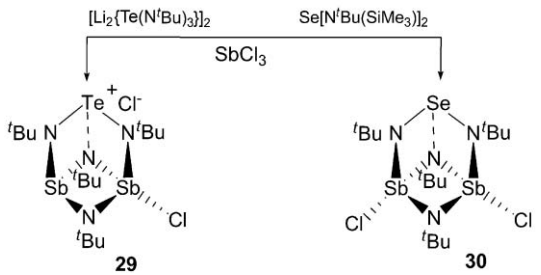
The Lewis acidity of the antimony centres in $[ClSb(\mu\text{-}N^tBu)]_2$ (**6**) is indicated by the isolation of the bis-dimethylamine adduct $[SbCl(NHMe_2)(\mu\text{-}N^tBu)]_2$ (**27**, Chart 7), albeit in low yield, upon treatment of $SbCl(NMe_2)_2$ with three equivalents of $^tBuNH_2$.[44] A related bis-dimethylamine adduct (**28**) is obtained from $SbCl_2(NMe_2)$ and ethanol.[44]

The interesting tricyclic compounds **29** and **30** are obtained by disparate transformations, as depicted in Scheme 6.[47,48] The structures of **29** and **30** differ only in the ionization of one of the Sb–Cl bonds in the tellurium derivative. They can be viewed as adducts of the cyclodistib(III)azane $[ClSb(\mu\text{-}N^tBu)]_2$ (**6**) with *N*,*N*′-*tert*-butyl tellurium or selenium diimide, respectively. The two nitrogens of the chalcogen diimide act as Lewis base donors towards the two antimony centres; in addition, there is a weak interaction between one nitrogen of the Sb_2N_2 ring and the chalcogen centre.



27 **28**

Chart 7



29 **30**

Scheme 6

5.3 Oxidation

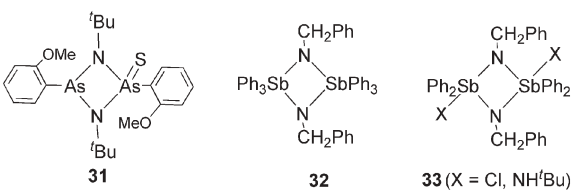
The two phosphorus(III) centres in cyclodiphosph(III)azanes are readily oxidized by sulfur or selenium to the corresponding P(V)/P(V) systems.[4] Oxidation of heavier pnictogen centres in cyclodipnict(III)azanes by chalcogens is considerably more difficult. The only example of oxidation of heavier pnictogen centres by chalcogens involves the synthesis of the monosulfide **31** (Chart 8) by treatment of the corresponding cyclodiars(III)azane with elemental sulfur.[12]

The reaction of the bis(*tert*-butylamido) derivative $[^tBuN(H)P(\mu\text{-}N^tBu)]_2$ with tellurium produces only a 5% yield of the corresponding monotelluride, even under forcing conditions.[49] However, the nucleophilicity of the phosphorus(III) centres is greatly enhanced in the dianion $[^tBuNP(\mu\text{-}N^tBu)]_2^{2-}$ which, as the dilithium derivative, produces the corresponding ditelluro ligand upon heating in toluene in the presence of TMEDA.[50] By analogy, it can be predicted that the heavy pnictogen(III) centres in the dianions $[RNE(\mu\text{-}NR)]_2^{2-}$ (E = As, Sb, Bi; Section 5.4) will be more susceptible than neutral bis(alkylamido) derivatives to oxidation by chalcogens.

The cyclodistib(V)azanes **32** and **33** can be prepared by reactions of Ph_3SbCl_2 or Ph_2SbCl_3 with the appropriate primary amine or lithiated amine in the correct stoichiometry.[51]

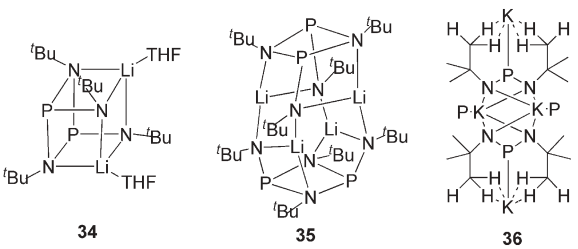
5.4 Formation of $[RNE(\mu\text{-}NR)]_2^{2-}$ dianions

Bis(alkylamido)cyclodipnict(III)azanes of the type **II** are important reagents for the synthesis of the corresponding $[RNE(\mu\text{-}NR)]_2^{2-}$ dianions. However, with the exception of a single arsenic compound,[52] and two antimony derivatives,[41,53] this has only been realized for cyclodiphosph(III)azanes. The phosphorus derivative $[^tBuN(H)P(\mu\text{-}N^tBu)]_2$ is readily metallated with ^{n}BuLi in THF or toluene to give the dimeric complex $[^tBuN(Li{\cdot}THF)P(\mu\text{-}N^tBu)]_2$ (**34**, Chart 9)[54] or, in the absence of THF solvation, the tetramer **35**,[55] respectively. Main-group element complexes of this chelating ligand have been discussed by Stahl.[3] By contrast to the formation of **34**



31 **32** **33** (X = Cl, NH^{t}Bu)

Chart 8

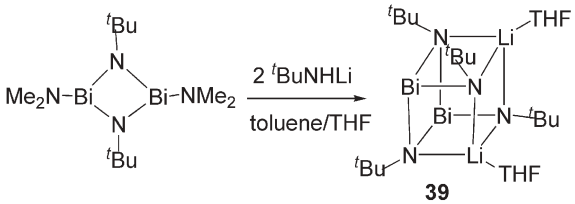


34 **35** **36**

Chart 9

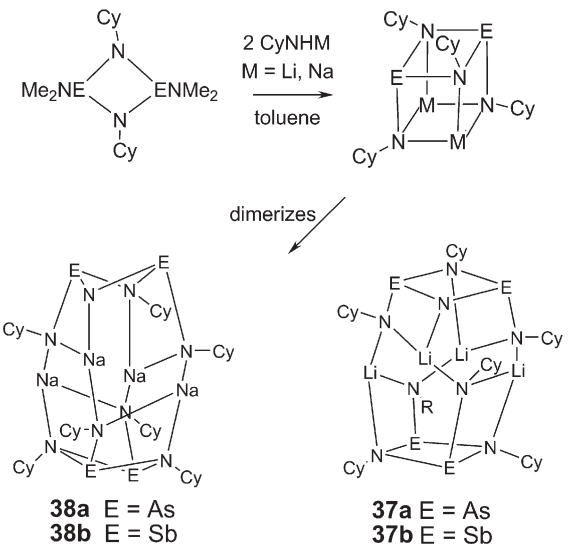
and **35**, the reaction of $[^tBuN(H)P(\mu\text{-}N^tBu)]_2$ with an excess of benzylpotassium in boiling toluene produces $[(^tBuN)_2PK]_\infty$ (**36**), with a three-dimensional network structure.[56] A combination of NMR studies and DFT calculations indicate that the formation of $[(^tBuN)_2P]^-$ monoanions in **36** is thermodynamically controlled, whereas the generation of dimeric $[RNP(\mu\text{-}NR)]_2^{2-}$ dianions in **34** and **35** is kinetically controlled.[56]

There are only a few reports of As, Sb and Bi analogues of **34** and **35**. The majority of these complexes have been prepared by Wright and co-workers *via* the reaction of a lithium amide with the bis(dimethylamido)cyclodipnict-(III)azanes **III**. For example, the reaction of $[(Me_2N)As(\mu\text{-}N^tBu)]_2$ with CyNHLi gives $[\{As_2(NCy)_4\}_2Li_4]$ (**37a**), the result of face-to-face dimerization of two $[As_2(NCy)_4]$ cubanes (Scheme 7).[57] The analogous sodium derivative (**38a**) is obtained from the reaction between $[(Me_2N)As(\mu\text{-}N^tBu)]_2$ and CyNHNa.[58] The corresponding imido-antimony clusters (**37b** and **38b**) are made in a similar manner.[59,60] In contrast to the tetrameric complexes **37** and **38**, the imido-bismuth cluster **39** is obtained as a dimer with a distorted cubane structure (eqn (6)). The observed structural differences between these complexes has been attributed to the solvation of the lithium centres, which prevents the association of the discrete cubane fragments.[61]



(6)

The bis(amido)cyclodistib(III)azanes **25** are suitable precursors for the generation of $[RNSb(\mu\text{-}NR)]_2^{2-}$ dianions by metallation reactions with ^{n}BuM (M = Li, Na). The complexes **40** and **41** (Chart 10) have recently been prepared *via* this synthetic strategy.[41,53] During the course of this work, unexpected reactivity differences between the *cis* and *trans*



Scheme 7

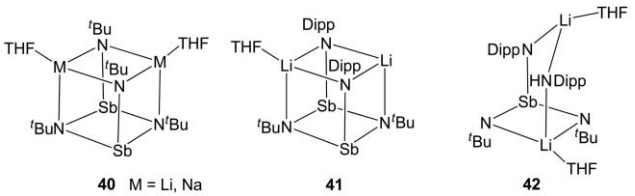


Chart 10

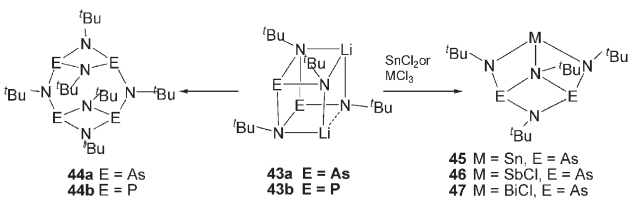
isomers of $[Dipp(H)NSb(\mu\text{-}N^tBu)]_2$ were observed.[41] Whereas the reaction of *trans*-$[Dipp(H)NSb(\mu\text{-}N^tBu)]_2$ with two equivalents of ^{n}BuLi readily produces the *cis* dilithiated cubane complex **41**, the corresponding reaction of *cis*-$[Dipp(H)NSb(\mu\text{-}N^tBu)]_2$ furnishes **42** in significant yields rather than **41**. This remarkable difference in reactivity is attributed to the *endo*,*endo* configuration of the NH-Dipp protons, which are heavily sterically shielded in *cis*-$[Dipp(H)NSb(\mu\text{-}N^tBu)]_2$.[41]

The reaction of the dilithiated reagent $[(Li)^tBuNAs(\mu\text{-}N^tBu)]_2$ (**43a**) with $[ClAs(\mu\text{-}N^tBu)]_2$ (**1**) produces the tricyclic compound $[As_4(N^tBu)_6]$ (**44a**), in which two As_2N_2 rings are bridged by two imido (N^tBu) groups (Scheme 8).[52] The structurally analogous phosphorus compound $[P_4(N^tBu)_6]$ (**44b**) is prepared in a similar manner.[55] Interestingly, the isopropyl derivative of **44b** is converted to the adamantyl-like isomer upon heating.[62] The heterometallic tricyclic compounds **45–47** are obtained from reactions of $[(Li)^tBuNAs(\mu\text{-}N^tBu)]_2$ with $SnCl_2$ or MCl_3 (M = Sb or Bi) (Scheme 8). The all-antimony analogue of **46** (E = Sb) has been reported as a minor product of the cyclocondensation of $SbCl_3$ with *tert*-butylamine.[52,63] To date, no experimental details or spectroscopic characterization for the compounds **43a**, **44a** and **45–47** have been reported.[52] However, we have recently developed an efficient one-pot synthesis of the complex **43a** and have fully characterized the complex both in solution and the solid state.[53]

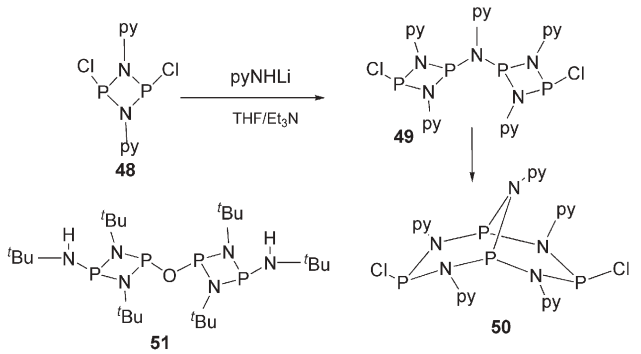
6 Macrocyclic systems

The discovery of the isopropyl analogue of **44b** provided the forerunner for studies of macrocyclic systems in which E_2N_2 rings are connected by difunctional bridging groups such as NH, NR or 1,2-XYC_6H_4 (X = Y = NH, X = Y = O). The presence of *endo*-protons enables this class of inorganic macrocycle to encapsulate anions within the cavity.[6] In this section the discussion of this interesting class of anion-acceptor is organized according to increasing ring size.

The formation of **50** from the reaction of $[ClP(\mu\text{-}Npy)]_2$ (**48**) with pyNHLi in a 2 : 1 molar ratio is thought to occur *via* the



Scheme 8



Scheme 9

imido-bridged bicyclic intermediate **49** (Scheme 9).[64] This transformation is driven by the relief of steric strain in going from the four-membered rings in **49** to six-membered rings in **50**. A similar ring expansion occurs in the conversion of the isopropyl derivative of **44b** to the adamantyl-like isomer (Section 5.4).[62] Compound **50** is also formed as a minor product (*ca.* 10%) in the synthesis of the cyclodiphosph(III)azane **48**, from the direct reaction of PCl_3 with pyNHLi in a 1 : 1 molar ratio. In contrast, only trace amounts of the analogous cyclic compound are observed in the reaction of PCl_3 with 6-methyl-pyridylaminolithium to produce the cyclodiphosph(III)azane $[ClP(\mu\text{-N-6-Me-py})]_2$, implying that the rearrangement is sterically inhibited in this case.[64] Attempts to prepare the μ-oxo bridged compound **51** (*cf*. **49**) by hydrolysis of ^{t}BuN(H)P(μ-N^{t}Bu)$_2$PCl resulted only in the formation of ^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(O)H. However, this compound can be lithiated with ^{n}BuLi and then treated with ^{t}BuN(H)P(μ-N^{t}Bu)$_2$PCl to give **51**.[65]

Several potential building blocks for the formation of macrocyclic systems have recently been reported by Wright and co-workers.[66] The hetero-substituted cyclodiphosph(III) azane **52** was used to prepare the remarkable tricyclic system **53** (Chart 11),[66] which contains two cyclodiphosph(III)azanes linked by a cyclodistib(III)azane. The presence of the two terminal amido substituents offers interesting possibilities for the construction of novel macrocycles. For example, treatment of **53** with two equivalents of *n*-butyl-lithium followed by reaction with a type **I** cyclodipnict(III)azane $[ClE(\mu\text{-N}^t\text{Bu})]_2$ (E = P, As, Sb) should generate novel tetrameric macrocycles with different cavity sizes. In a similar manner, the trianion **54**[66] or the dianion derived from **55**,[67] could be cyclized to produce trimeric macrocycles. In the former case, the resulting monoanionic macrocycle would be an interesting candidate for cation host–guest chemistry (*cf*. the trianionic macrocycle **66**).

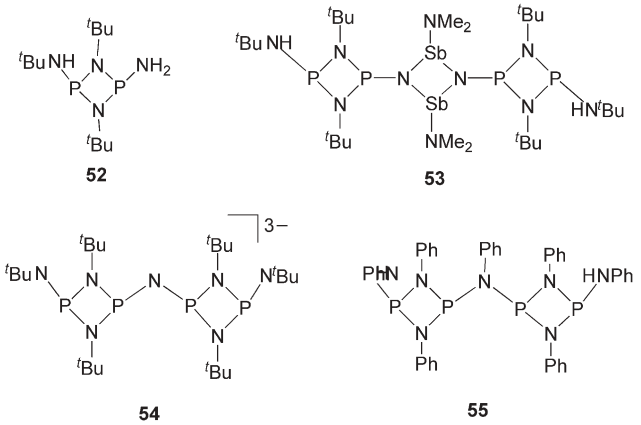


Chart 11

Early studies on the reactions of dichlorocyclodiphosph(III) azanes with difunctional alcohols or amines invariably resulted in the isolation of monomeric compounds.[43] However, the outcome of such reactions is markedly dependent on the nature of the difunctional reagent, as well as reaction conditions, and several dimeric systems, *e.g*., **56**[68] and **57**,[69] have been characterized recently (Chart 12).

In the case of heterodifunctional aromatic amines a regioselective synthetic route to dimeric systems has been developed.[70] Initial studies revealed that the reaction of $[ClP(\mu\text{-NR})]_2$ with 1,2-1-YH-2-NH_2-C_6H_4 in the presence of Et_3N affords the dimers $[\{P(\mu\text{-N}^t\text{Bu})\}_2\{1,2\text{-1-YH-2-NH}_2\text{-C}_6\text{H}_4\}]_2$ as a mixture of *cis* and *trans* isomers. In the case of Y = O (**60**, Chart 13)) there is a distinct preference for the *cis* isomer (*cis* : *trans* 85 : 15), whereas the *trans* isomer is the dominant form (*cis* : *trans* 10 : 90) for Y = S (**61**). Interestingly, the reaction of **58** with ^{n}BuLi followed by cyclization with $[ClP(\mu\text{-N}^t\text{Bu})]_2$ produces **60** exclusively as the *trans* isomer. The analogous reaction of **59** results in the formation of **61** as the pure *cis* isomer. A combination of NMR studies and theoretical calculations indicated that the preference for *cis* or *trans* isomers is controlled by kinetic rather than thermodynamic considerations.[70]

Treatment of $[ClP(\mu\text{-N}^t\text{Bu})]_2$ with 1,5-diamino-naphthalene in THF yielded the trimeric macrocycle $[\{P(\mu\text{-N}^t\text{Bu})\}_2\{1,5\text{-(NH)}_2\text{C}_{10}\text{H}_6\}]_3$ (**62**, Chart 14). This compound has been likened to a calixarene, in part by analogy with the cone-like shape adopted in the solid state.[71] Significantly, **62** crystallizes with two molecules of toluene within the cavity of the molecule, mimicking the behaviour of calixarenes and

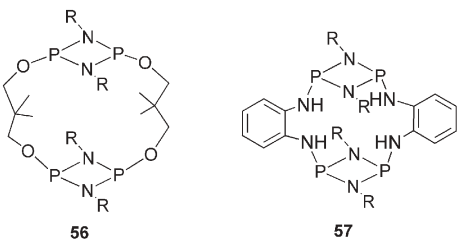


Chart 12

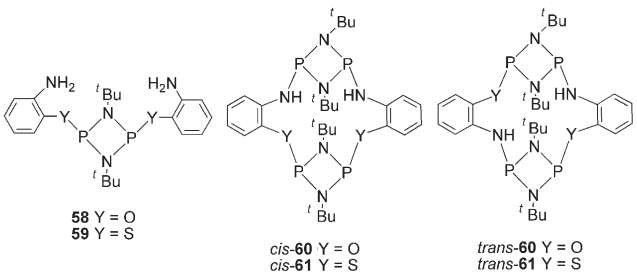


Chart 13

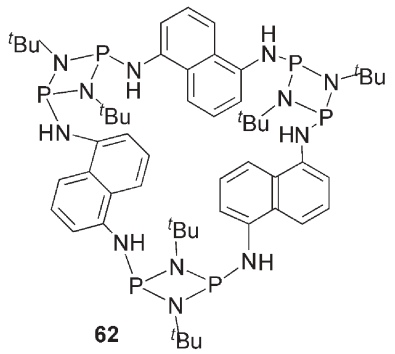


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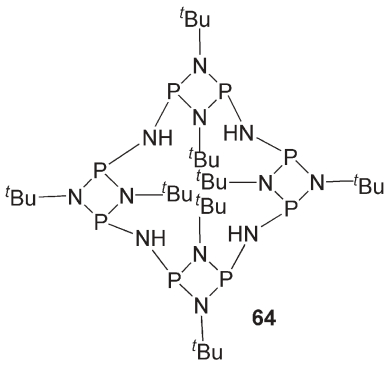
Chart 14



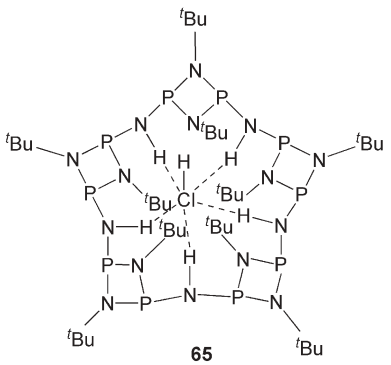
64

Chart 16

suggesting the potential for interesting host–guest chemistry. In contrast, the reaction of $[ClP(\mu\text{-}N^tBu)]_2$ with *p*-phenylenediamine produces the tetrameric compound $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2C_6H_4\}]_4$ (**63**, Chart 15).[72] The solid-state structure of **63** revealed a substantially more flexible macrocyclic skeleton than that observed in **62**, and the molecule adopts a folded conformation in which four of the NH protons are *endo* with respect to the interior of the macrocycle.[72] ^1H and ^{31}P NMR studies indicated that below 60 °C the solution structure was consistent with the solid-state structure, but at higher temperatures it was possible to scramble the *exo* and *endo* NH groups, further demonstrating the flexibility of the macrocycle. The presence of the *endo* NH protons within the macrocyclic cavity could potentially be exploited for anion encapsulation.[72]

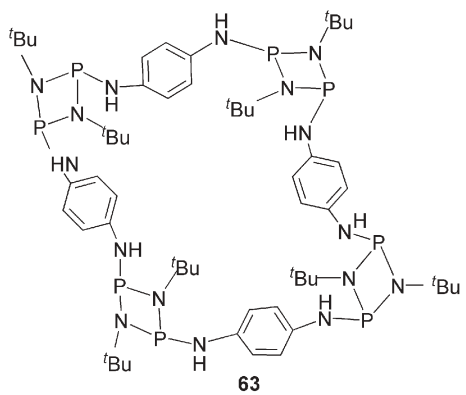
The cyclocondensation of $[ClP(\mu\text{-}N^tBu)]_2$ and $[H_2NP(\mu\text{-}N^tBu)]_2$ also produces a tetrameric macrocycle, $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$ (**64**, Chart 16).[73] In addition, the same reaction furnished a 1% yield of the host–guest complex (**65**, Chart 17) in which a pentameric macrocycle encapsulates a chloride ion.[74] Detailed studies demonstrated that the formation of tetrameric and pentameric macrocycles occurs *via* a divergent pathway. It was found that the macrocycles do not interconvert, suggesting that the formation of a tetramer or pentamer is kinetically driven, with little or no thermodynamic influence.[74,75] Furthermore, it was observed that if the cyclocondensation was performed in the presence of lithium halides, the formation of the tetramer could be suppressed. Significantly, it was possible to produce exclusively the pentameric macrocycle in the presence of lithium iodide.[75] Further studies exploring the potential host–guest chemistry of these macrocycles would be of interest.

There are no well-characterized As_2N_2 macrocycles although the compound **44a** has been reported without structural or spectroscopic details.[52] By contrast, both trimeric and hexameric systems involving Sb_2N_2 building blocks are known. The trianionic macrocycle $[\{Sb(\mu\text{-}NCy)\}_2N]_3^{3-}$ (**66**, Chart 18) was obtained as the trilithium derivative from the reaction of $[Me_2NSb(\mu\text{-}NCy)_2]_2$ and $LiNH_2$.[76] The compound was found to incorporate a molecule of LiN=NH in the solid-state structure. Interestingly, this complex also adopts a calixarene-like cone conformation, with one of the four lithium atoms encapsulated deep within the cavity of the



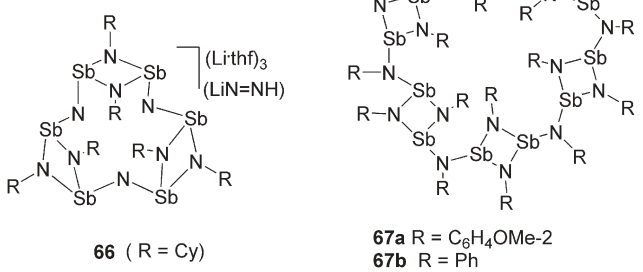
65

Chart 17



63

Chart 15



66 (R = Cy)

67a R = C_6H_4OMe-2
67b R = Ph

Chart 18

macrocycle. The remaining three lithium ions are located around the upper rim of the macrocycle and likely contribute to the rigid cone conformation.

Twenty-four membered (hexameric) Sb_2N_2 macrocycles (**67a** and **67b**) have been obtained in two ways. Wright and co-workers unexpectedly isolated **67a** in 26% yield from the reaction of $Sb(NMe_2)_3$ with the trisamidostannate complex $[RN(H)Sn(\mu\text{-}N(H)R)_2Li]$ (R = 2-$MeOC_6H_4$).[77] The solid-state structure of **67a** consists of six Sb_2N_2 rings linked by bridging imido groups. The Sb centres exhibit Sb–O contacts involving *ortho*-methoxy groups that give rise to alternating four- and five-coordinate Sb(III) centres.[77] It was suggested that formation of the macrocycle could be due to the presence of these Sb–O interactions.[77] However, the structurally similar Sb_2N_2 macrocycle $[Sb_{12}(NPh)_{18}]$ (**67b**) was obtained in 85% yield by Norman *et al.* from the cyclocondensation reaction between $SbCl_3$ and three equivalents of Li[N(H)Ph].[21] The hexamer **67b** is presumably generated *via* the intermediate formation of $Sb(NHPh)_3$ followed by loss of $PhNH_2$ in a condensation process. The isolation of **67b** demonstrated that the formation of these macrocycles is not dependent on intramolecular secondary-bonding interactions.

7 Transition-metal complexes

There has been increasing interest in the coordination chemistry of cyclodiphosph(III)azanes over the last 20 years, and the early work has been reviewed previously.[2] By contrast, there are only a handful of reports exploring the analogous chemistry of the heavier cyclodipnict(III)azanes. There are two common coordination modes observed in complexes of cyclodiphosph(III)azanes with transition metals. The first involves adducts of neutral ligands in which the phosphorus(III) centres act as two-electron donors towards transition-metal fragments. The second is represented by *N*,*N*′-chelated complexes between the dianions $[RNP(\mu\text{-}NR)]_2^{2-}$ (Section 5.4) and transition metals. For the heavier cyclodipnict(III)azanes (As, Sb, Bi) only the latter coordination mode has been observed. In this final section these two types of complexes will be discussed separately commencing with recent work on the ligand behaviour of cyclodiphosph(III)azanes followed by related studies with the heavier pnictogen systems.

7.1 Complexes with neutral cyclodipnict(III)azanes

The presence of two phosphorus centres in cyclodiphosph(III)azanes offers the possibility for the coordination of one or two metal centres and, in the latter case, the potential to generate mixed-metal complexes. Some representative examples include the 1 : 1 and 1 : 2 complexes **68** and **69**, respectively,[78,79] and the 2 : 1 complex **70** (Chart 19).[80]

The *cis* conformation of cyclodiphosph(III)azanes containing donor functionalities in the substituents on the P(III) centres has been exploited to generate a variety of transition-metal complexes including metallated macrocycles and coordination polymers.[78,81] The products of the reaction of the cyclodiphosph(III)azanes $[ROP(\mu\text{-}^tNBu)]_2$ [R = C_6H_4OMe-2, CH_2OCH_2X (X = NMe_2, SMe, OMe)] with $[Rh(CO)_2Cl]_2$ depend on the identity of the hemilabile pendant arms, as well

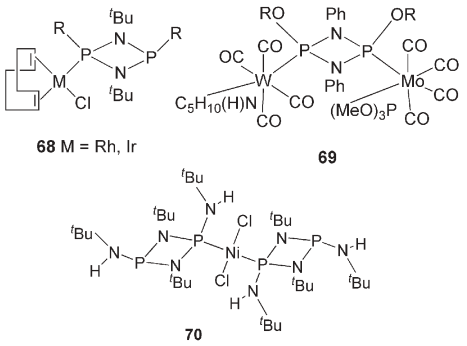
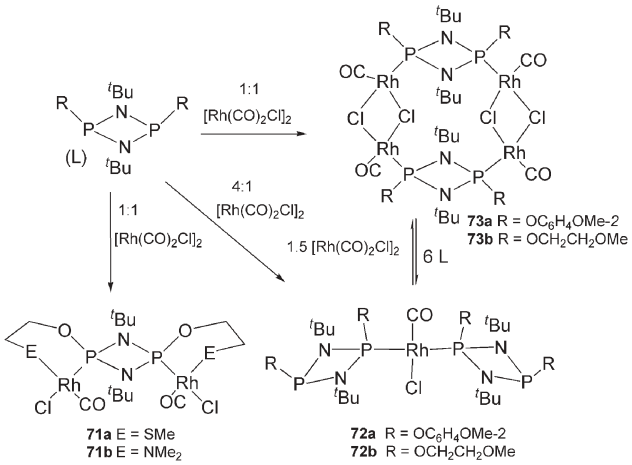


Chart 19

as reaction conditions. The formation of mono-, bi- or tetra-nuclear complexes (**71**–**73**) has been established (Scheme 10).[78,81] The tetra-nuclear complexes (**73a,b**) undergo quantitative conversion into the mono-nuclear analogues (**72a,b**) on treatment with an excess of ligand. This transformation is reversed by treatment of the mono-nuclear complexes with $[Rh(CO)_2Cl]_2$. Coordination polymers, composed of alternating P_2N_2 and Cu_2X_2 rings arranged in a zigzag fashion, are obtained from the reaction of $[2\text{-}MeOC_6H_4OP(\mu\text{-}^tNBu)]_2$ with CuX (X = Cl, Br, I) in 1 : 1 molar ratio.[82]

The remarkable tetra-nuclear Cu(I) complex (**74**, Chart 20) is produced from the reaction of $[ClP(\mu\text{-N-2-py})]_2$ with CuCl in the presence of H_2O and pyridine.[83] The complex contains a bis-μ-oxo bridged tricyclic ligand which is an isoelectronic analogue of the $P_4(N^tBu)_6$ isomer **44b**. Interestingly, it was



Scheme 10

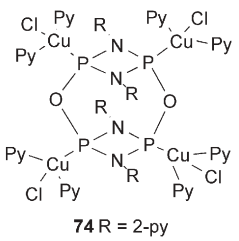
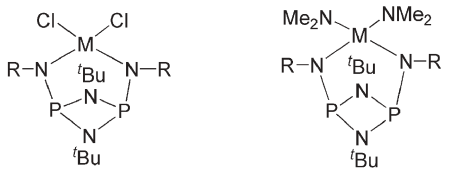


Chart 20



75 M =Ti,**76** Zr,**77** Hf **78** M =Ti, **79** Zr, **80** Hf

R = ^{t}Bu, Ph, CHPh$_2$, 2,6-Et$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,5-^{t}Bu$_2$C$_6$H$_3$

Chart 21

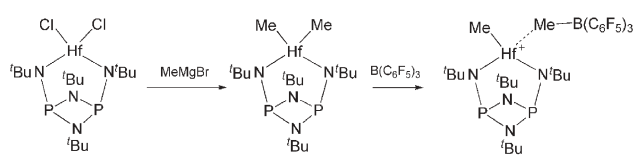
found that the generation of the tricyclic ligand requires the coordination of copper to the phosphorus centres. This was clearly demonstrated when [ClP(μ-N-2-py)]$_2$ was treated with water and pyridine in the absence of CuCl, resulting in the formation of a mixture of products; the observed reactivity was attributed to steric effects upon metal coordination.[83]

7.2 Complexes of [RNE(μ-NR)]$_2^{2-}$ dianions

Stahl and co-workers have prepared the monomeric group 4 complexes [(^{t}BuNP)$_2$(^{t}BuN)$_2$}MCl$_2$ (**76**, **77**, R = ^{t}Bu, Chart 21) by the metathetical reaction of [^{t}BuN(Li)P(μ-^{t}NBu)]$_2$ and MCl$_4$.[84] Initially it was reported that the titanium analogue (**75**, R = ^{t}Bu) cannot be made in the same manner because the [^{t}BuNP(μ-N^{t}Bu)]$_2^{2-}$ dianion reduces the metal to the trivalent state.[85] However, **75** (R = ^{t}Bu) has recently been prepared using this synthetic procedure.[86] Alternatively, this complex can be synthesized from the neutral ligand [^{t}BuN(H)P(μ-N^{t}Bu)]$_2$ and TiCl$_4$.[85] A characteristic structural feature of these and related group 4 metal complexes is the involvement of one nitrogen of the P$_2$N$_2$ ring in a weak, intramolecular interaction with the metal centre (*cf.* **29** and **30**).

An alternative route to group 4 complexes involves the transamination reactions of bis(amido)cyclodiphosph(III) azanes [RN(H)P(μ-^{t}NBu)]$_2$ and M(NMe$_2$)$_4$ (M = Ti, Zr, Hf). This method generates the *N*,*N*′-chelated complexes [{RN(H)P(μ-^{t}NBu)}$_2$]M(NMe$_2$)$_2$ (**78–80**) which, on further treatment with Me$_3$SiCl, produce the corresponding dichloro derivatives [{RN(H)P(μ-^{t}NBu)}$_2$]MCl$_2$ (**75–77**).[86–88] The hafnium complex **77** (R = ^{t}Bu) reacts with CH$_3$MgBr to give the dimethyl derivative **81**, which readily forms the zwitterionic species [{^{t}BuNP(μ-N^{t}Bu)}$_2$Hf(CH$_3$)(μ-CH$_3$)]B(C$_6$F$_5$)$_3$ (**82**) upon addition of B(C$_6$F$_5$)$_3$ (Scheme 11). The reactions of the dichloro derivatives (**76** and **77**) with PhCH$_2$MgBr in diethyl ether or THF afforded the corresponding mono- or di-benzyl substituted complexes.[89]

Many of the group 4 metal complexes **75–82** have been shown to be catalytically active in the polymerization of ethene.[86–89] The activity and the stability of the catalyst were found to be dependent on the nature of the imido substituents.



Scheme 11

In general, the complexes with the least bulky substituents showed the highest activity, but also the lowest stability. For the titanium and zirconium complexes, the moderately bulky Dipp substituents were found to provide a reasonable balance of activity and stability.[86,87] As discussed by Stahl, the most likely pathway to catalyst deactivation in these systems involves the destructive ring-opening of the cyclodiphosph(III)azane, initiated by Lewis acid coordination to the phosphorus lone pair.[85] Indeed, of the complexes **75–82** used in ethene polymerization studies, those with the least sterically protected phosphorus centres were shown to be the most readily deactivated.

In contrast to the other metal complexes of the [^{t}BuNP(μ-N^{t}Bu)]$_2^{2-}$ dianions discussed so far, those involving nickel(II) form strained three-membered rings through coordination to P(III) and N atoms rather than a strain-free *N*,*N*′-chelated metallacycle.[80,90] The isolation of three-membered metallacycles is relatively common in nickel(II) chemistry.[80] Thus, reaction of [^{t}BuN(Li)P(μ-^{t}NBu)]$_2$ with *trans*-[NiCl$_2$}P(^{n}Bu)$_3$}$_2$] produces the di-nickelazaphosphirane (**83**, Chart 22) while the asymmetric cyclodiphosph(III)azane [^{t}BuN(Li)P(μ-^{t}NBu)$_2$PO^{t}Bu] reacts with *trans*-[NiCl$_2$-{P(^{n}Bu)$_3$}$_2$] to give the nickelaazaphosphirane (**84**).[90]

The reaction of ZrCl$_4$ with [^{t}BuN(H)P(μ-^{t}NBu)]$_2$ in the presence of ^{n}BuLi produces the imidozirconium complex (**85**, Chart 23) in which the zirconium centre is *N*,*N*′-chelated by a dianionic [^{t}BuNP(μ-N^{t}Bu)]$_2^{2-}$ ligand and coordinated in an *N*-monodentate fashion to a monoanionic [^{t}BuNP(μ-N^{t}Bu)$_2$-PN(H)^{t}Bu]$^-$ ligand.[91]

Transition-metal complexes in which the dianions [RNE(μ-NR)]$_2^{2-}$ serve as ligands are rare for E = As, Sb and are unknown for E = Bi. Attempts to prepare such complexes *via* metallation reactions of neutral bis(amido) cyclodiars(III)azanes resulted in the cleavage of the As$_2$N$_2$ ring. For example, the reaction of [DippN(H)As(μ-NDipp)]$_2$ with bis(trimethylsilyl)amido group 12 reagents generates monomeric [As(NDipp)$_2$]$^-$ ligands that form four-membered rings with the metal centres (**86**) (Scheme 12).[22] The reaction of the

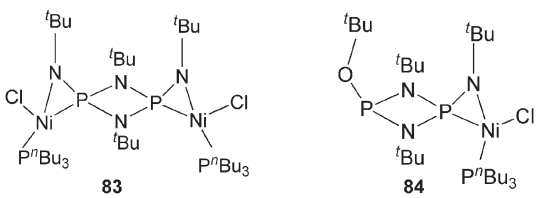


Chart 22

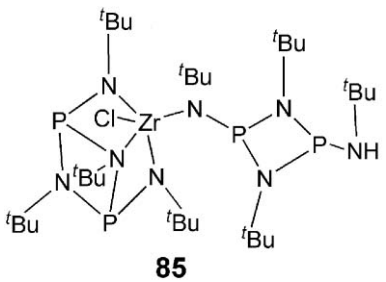
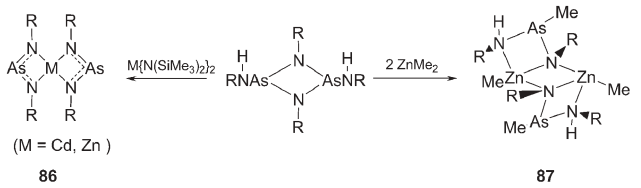


Chart 23



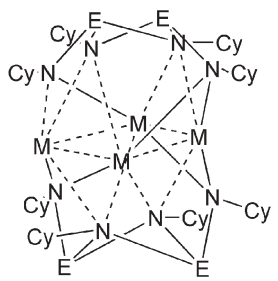
Scheme 12

cyclodiars(III)azane $[CyN(H)As(\mu\text{-}NCy)]_2$ with dimethylzinc produced the tricyclic complex $[\mu\text{-}MeAs(\mu\text{-}N(H)Cy)(\mu\text{-}NCy)\mu_3\text{-}ZnMe]_2$ (**87**) formed by transfer of a methyl group from zinc to arsenic (Scheme 12).[92]

Transmetallation reactions between $[\{Sb_2(NCy)_4\}_2Li_4]$ (**37b**) and CuCl or $Ag(CH_3COO)$ give the cage complexes $[\{Sb_2(NCy)_4\}_2M_4]$ (**88**a M = Cu;[93] **88b** M = Ag,[94] Chart 24). The arsenic analogue **88c** was also prepared by treatment of $[\{As_2(NCy)_4\}_2Na_4]$ (**38a**) with CuCl, albeit in low yield (5%).[58] The M_4 core in these tetrameric complexes is essentially square planar and the Sb_2N_2 rings are more puckered than in the corresponding alkali-metal derivatives.

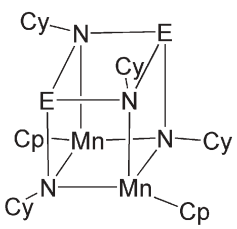
The only other reported transition-metal complexes of $[RNE(\mu\text{-}NR)]_2^{2-}$ dianions are also prepared *via* transmetallation. The heterometallic cubanes **89a** and **89b** (Chart 25) are obtained by the reaction of $[\{E_2(NCy)_4\}_2M_4]$ (E = As, Sb; M = Na, Li) with $MnCp_2$ (eqn (7)).[95] These are the only examples of paramagnetic metal complexes of $[RNE(\mu\text{-}NR)]_2^{2-}$ (E = As, Sb) dianions.

$$[\{E_2(NCy)_4\}_2M_4] + 4\,MnCp_2 \longrightarrow 2\,[\{E_2(NCy)_4\}(MnCp_2] + 4\,CpM \quad (M = Li, Na) \qquad (7)$$



88a M = Cu, E = Sb
88b M = Ag, E = Sb
88c M = Cu, E = As

Chart 24



89a E = As
89b E = Sb

Chart 25

Summary and outlook

The slow progress in the chemistry of E_2N_2 ring systems involving the heavier pnictogens compared to that of P_2N_2 rings can be attributed to several factors. The lability of E–N bonds poses special challenges, especially for the development of the chemistry of bismuth(III)–nitrogen ring systems. The discovery of a suitable synthesis of dichloro derivatives of type **I** for bismuth would be a significant step forward.

The lack of a suitable NMR-active nucleus for monitoring reactions involving the heavier pnictogens is also an impediment to the advancement of the chemistry of pnictogen(III)-nitrogen rings. By comparison, ^{31}P NMR spectroscopy has provided important insights into the formation and reactions of phosphorus-containing systems, *e.g.* ring-oligomerization processes. Information gained from these studies is likely to be useful in the design and synthesis of polymers of the type $[-(R)EN(R')-]_\infty$. ^{31}P NMR studies have also been important in the impressive development of macrocyclic anion-acceptor systems constructed from P_2N_2 building blocks. The existence of the unique hexameric Sb_2N_2-based macrocycles suggests that a rich macrocyclic chemistry may also be accessible for the heavier pnictogens. The appropriate building blocks are available for the construction of macrocyclic systems with the potential for a variety of host–guest interactions.

Although several dianions $[RNE(\mu\text{-}NR)]_2^{2-}$ (E = As, Sb, Bi) are known, investigations of main-group or transition-metal complexes of these chelating ligands are sparse. This is another area that is ripe for development from the viewpoint of catalytic systems or as single-source precursors to metal pnictides.

Acknowledgements

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References

1 R. Keat, *Top. Curr. Chem.*, 1982, **102**, 89.
2 M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. F. Nixon and J. C. T. R. B. S. Laurent, *Coord. Chem. Rev.*, 1994, **129**, 1.
3 L. Stahl, *Coord. Chem. Rev.*, 2000, **210**, 203.
4 G. G. Briand, T. Chivers and M. Krahn, *Coord. Chem. Rev.*, 2002, **233–234**, 237.
5 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373.
6 E. L. Doyle, L. Riera and D. S. Wright, *Eur. J. Inorg. Chem.*, 2003, 3279.
7 G. A. Olah and A. A. Oswald, *Can. J. Chem.*, 1960, **38**, 1428.
8 H. J. Vetter, H. Strametz and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 218.
9 J. Weiss and W. Eisenhuth, *Z. Naturforsch.*, 1967, **22b**, 454.
10 N. Burford, J. C. Landry, M. J. Ferguson and R. McDonald, *Inorg. Chem.*, 2005, **44**, 5897.
11 G. I. Kokorev, I. A. Litvinov, V. A. Naumov, S. K. Batrutdinov and F. D. Yambushev, *Zh. Obshch. Khim.*, 1989, **59**, 1556.
12 G. I. Kokorev, I. A. Litvinov, V. A. Naumov and S. K. Batrutdinov, *Zh. Obshch. Khim.*, 1990, **60**, 1852.
13 E. V. Avtomonov, K. Megges, X. Li, J. Lorberth, S. Wocadlo, W. Massa, K. Harms, A. V. Churakov and J. A. K. Howard, *J. Organomet. Chem.*, 1997, **544**, 79.
14 N. Kuhn and O. J. Scherer, *Z. Naturforsch.*, 1979, **34b**, 888.
15 D. C. Haagenson and L. Stahl, *Inorg. Chem.*, 2001, **40**, 4491.

16 P. B. Hitchcock, M. F. Lappert, A. K. Rai and H. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1986, 1633.
17 J-T. Ahlemann, A. Künzel, H. W. Roesky, M. Noltemeyer, L. Markovskii and H-G. Schmidt, *Inorg. Chem.*, 1996, **35**, 6644.
18 N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, C. L. B. MacDonald, R. Ovans, A. D. Phillips, P. J. Ragogna and D. Walsh, *Can. J. Chem.*, 2002, **80**, 1404.
19 N. Burford, E. Edelstein, J. C. Landry, M. J. Ferguson and R. McDonald, *Chem. Commun.*, 2005, 5074.
20 G. G. Briand, T. Chivers and M. Parvez, *Can. J. Chem.*, 2003, **81**, 169.
21 R. Bryant, S. C. James, J. C. Jeffery, N. C. Norman, A. G. Orpen and U. Weckenmann, *J. Chem. Soc., Dalton Trans.*, 2000, 4007.
22 U. Wirringa and H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1628.
23 U. Wirringa, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1994, **33**, 4607.
24 N. Burford, T. S. Cameron, K.-C. Lam, D. J. LeBlanc, C. L. B. McDonald, A. D. Philips, A. L. Rheingold, L. Stark and D. Walsh, *Can. J. Chem.*, 2001, **79**, 342.
25 J-T. Ahlemann, H. W. Roesky, R. Murugavel, E. Parisini, M. Noltemeyer, H-G. Schmidt, O. Müller, R. Herbst-Irmer, L. N. Markovskii and Y. G. Shermolovich, *Chem. Ber.*, 1997, **130**, 1113.
26 R. Bohra, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **C40**, 1150.
27 P. C. Andrews, C. L. Raston, B. W. Skelton, V-A. Tolhurst and A. H. White, *Chem. Commun.*, 1998, 575.
28 C. L. Raston, B. W. Skelton, V.-A. Tolhurst and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 1279.
29 C. L. Raston, B. W. Skelton, V-A. Tolhurst and A. H. White, *Polyhedron*, 1998, **17**, 935.
30 A. J. Edwards, M. A. Paver, M.-A. Rennie, P. R. Raithby, C. A. Russell and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1994, 2963.
31 A. Bashall, A. D. Bond, A. D. Hopkins, S. J. Kidd, M. Mcpartlin, A. Steiner, R. Wolf, A. D. Woods and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2002, 343.
32 A. D. Bond, F. Garcia, K. Jantos, G. T. Lawson, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2002, 1276.
33 N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, M. Lumsden, C. L. B. Macdonald, R. McDonald, A. D. Phillips, P. J. Ragogna, R. W. Schurko, D. Walsh and R. E. Wasylishen, *J. Am. Chem. Soc.*, 2002, **124**, 14012.
34 N. Burford, T. S. Cameron, C. L. B. Macdonald, K. N. Robertson, R. Schurko and D. Walsh, *Inorg. Chem.*, 2005, **44**, 8058.
35 E. Niecke, M. Nieger and F. Reichert, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1715.
36 N. Burford, C. A. Dyker, A. D. Phillips, H. A. Spinney, A. Deckon, R. McDonald, P. J. Ragogna and A. L. Rheingold, *Inorg. Chem.*, 2004, **43**, 7502.
37 E. Niecke, R. Detsch, M. Nieger, F. Reichert and W. W. Schoeller, *Bull. Soc. Chim. Fr.*, 1993, **130**, 25.
38 N. Burford, K. D. Conroy, J. C. Landry, P. J. Ragogna, M. J. Ferguson and R. McDonald, *Inorg. Chem.*, 2004, **43**, 8245.
39 F. Garcia, R. A. Kowenicki and D. S. Wright, *Dalton Trans.*, 2005, 2495.
40 M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. A. Paver, P. R. Raithby and D. S. Wright, *Polyhedron*, 1998, **17**, 745.
41 D. J. Eisler and T. Chivers, *Inorg. Chem.*, 2006, **45**, in press.
42 B. Ross, J. Belz and M. Nieger, *Chem. Ber.*, 1990, **123**, 975.
43 S. S. Kumaravel, S. S. Krishnamurthy, T. S. Cameron and A. Linden, *Inorg. Chem.*, 1988, **27**, 4546.
44 A. J. Edwards, N. E. Leadbeater, M. A. Paver, P. R. Raithby, C. A. Russell and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1994, 1479.
45 J. F. Bickley, A. D. Bond, F. Garcia, K. Jantos, G. T. Lawson, M. McPartlin, A. Steiner and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2002, 4629.
46 M. Herberhold, D. Berthold and K. Schamel, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **73**, 249.
47 T. Chivers and G. Schatte, *Inorg. Chem.*, 2002, **41**, 1002.
48 M. Björgvinsson, H. W. Roesky, F. Pauer and G. M. Sheldrick, *Chem. Ber.*, 1992, **125**, 767.
49 G. Briand, T. Chivers, M. Parvez and G. Schatte, *Inorg. Chem.*, 2003, **42**, 525.
50 G. Briand, T. Chivers and M. Parvez, *Angew. Chem., Int. Ed.*, 2002, **41**, 3468.
51 M. C. Copsey, S. B. Gallon, S. K. Grocott, J. C. Jeffery, C. A. Russell and J. M. Slattery, *Inorg. Chem.*, 2005, **44**, 5495.
52 M. Veith, A. Rammo and M. Hans, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **93-94**, 197.
53 D. J. Eisler and T. Chivers, unpublished results.
54 I. Schranz, L. Stahl and R. Staples, *Inorg. Chem.*, 1998, **37**, 1493.
55 J. K. Brask, T. Chivers, M. L. Krahn and M. Parvez, *Inorg. Chem.*, 1999, **38**, 290.
56 A. D. Bond, E. L. Doyle, F. Garcia, R. A. Kowenicki, D. Moncrieff, M. McPartlin, L. Riera, A. D. Woods and D. S. Wright, *Chem.–Eur. J.*, 2004, **10**, 2271.
57 M. A. Beswick, E. A. Harron, A. D. Hopkins, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1999, 107.
58 A. Bashall, M. A. Beswick, E. A. Harron, A. D. Hopkins, S. J. Kidd, M. McPartlin, P. R. Raithby, A. Steiner and D. S. Wright, *Chem. Commun.*, 1999, 1145.
59 R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1994, 1481.
60 A. Bashall, M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 1389.
61 A. J. Edwards, M. A. Beswick, J. R. Galsworthy, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell, K. L. Verhorevoort and D. S. Wright, *Inorg. Chim. Acta*, 1996, **248**, 9.
62 O. J. Scherer, K. Andres, C. Krüger, Y.-H. Tsai and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 571.
63 The structural details for **46** are available in the CCDC, #233882, M. Nieger, private communication.
64 A. Bashall, E. L. Doyle, F. Garcia, D. J. Linton, D. Moncrieff, M. McPartlin, A. D. Woods and D. S. Wright, *Chem.–Eur. J.*, 2002, **8**, 5723.
65 L. Doyle, F. Garcia, S. M. Humprey, R. A. Kowenicki, L. Riera, A. D. Woods and D. S. Wright, *Dalton Trans.*, 2004, 807.
66 M. A. Beswick, B. R. Elvidge, N. Feeder, S.J. Kidd and D.S. Wright, *Chem. Commun.*, 2001, 379.
67 M. L. Thompson, R. C. Haltiwanger and A. D. Norman, *J. Chem. Soc., Chem. Commun.*, 1979, 647.
68 P. Kommana and K. C. Kumara Swamy, *Inorg. Chem.*, 2000, **39**, 4384.
69 F. Garcia, R. A. Kowenicki, I. Kuzu, L. Riera, M. McPartlin and D. S. Wright, *Dalton Trans.*, 2004, 2904.
70 F. Garcia, J. M. Goodman, R. A. Kowenicki, M. McPartlin, L. Riera, M. A. Silva, A. Wirsing and D. S. Wright, *Dalton Trans.*, 2005, 1764.
71 F. Dodds, F. Garcia, R. A. Kowenicki, M. McPartlin, A. Steiner and D. S. Wright, *Chem. Commun.*, 2005, 3733.
72 F. Dodds, F. Garcia, R. A. Kowenicki, S. P. Parsons, M. McPartlin and D. S. Wright, *Dalton Trans.*, 2006, 4235.
73 A. Bashall, E. L. Doyle, C. Tubb, S. J. Kidd, M. McPartlin, A. D. Woods and D. S. Wright, *Chem. Commun.*, 2001, 2542.
74 A. Bashall, A. D. Bond, E. L. Doyle, F. Garcia, S. Kidd, G. T. Lawson, M. C. Parry, M. McPartlin, A. D. Woods and D. S. Wright, *Chem.–Eur. J.*, 2002, **8**, 3377.
75 F. Garcia, J. M. Goodman, R. A. Kowenicki, I. Kuzu, M. McPartlin, M. A. Silva, L. Riera, A. D. Woods and D. S. Wright, *Chem.–Eur. J.*, 2004, **10**, 6066.
76 F. Garcia, D. J. Linton, M. McPartlin, A. Rothenberger, A. E. H. Wheatley and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2002, 481.
77 M. A. Beswick, M. K. Davies, M. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1508.
78 P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Inorg. Chem.*, 2005, **44**, 7925.
79 V. S. Reddy, S. S. Krishnamurthy and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1994, 2661.
80 I. Schranz, G. R. Lief, C. J. Carrow, D. C. Haagenson, L. Grocholl, L. Stahl, R. J. Staples, R. Boomishankar and A. Steiner, *Dalton Trans.*, 2005, 3307.

81 P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Organometallics*, 2005, **24**, 3780.
82 P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Inorg. Chem.*, 2006, **45**, 6678.
83 A. D. Bond, E. L. Doyle, F. Garcia, R. A. Kowenicki, M. McPartlin, L. Riera and D. S. Wright, *Chem. Commun.*, 2003, 2990.
84 L. Grocholl, L. Stahl and R. J. Staples, *Chem. Commun.*, 1997, 1465.
85 D. F. Moser, C. J. Carrow, L. Stahl and R. J. Staples, *J. Chem. Soc., Dalton Trans.*, 2001, 1246.
86 K. V. Axenov, V. Kotoy, M. Klinga, M. Leskelä and T. Repo, *Eur. J. Inorg. Chem.*, 2004, 695.
87 K. V. Axenov, M. Klinga, M. Leskelä, V. Kotoy and T. Repo, *Eur. J. Inorg. Chem.*, 2004, 4702.
88 K. V. Axenov, M. Klinga, M. Leskelä and T. Repo, *Organometallics*, 2005, **24**, 1336.
89 K. V. Axenov, I. Kilpelainen, M. Klinga, M. Leskelä and T. Repo, *Organometallics*, 2006, **25**, 463.
90 G. R. Lief, C. J. Carrow, L. Stahl and R. J. Staples, *Chem. Commun.*, 2001, 1562.
91 G. Bai, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *J. Chem. Soc., Dalton Trans.*, 2002, 2437.
92 A. D. Bond, A. D. Hopkins, A. Rothenberger, R. Wolf, A. D. Woods and D. S. Wright, *Organometallics*, 2001, **20**, 4454.
93 D. Barr, A. J. Edwards, S. Pullen, M. A. Paver, P. R. Raithby, M. A. Rennie, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1875.
94 M. A. Beswick, N. L. Cromhout, C. N. Harmer, M. A. Paver, P. R. Raithby, M. -A. Rennie, A. Steiner and D. S. Wright, *Inorg. Chem.*, 1997, **36**, 1740.
95 A. Bashall, M. A. Beswick, H. Ehlenberg, S. J. Kidd, M. McPartlin, J. S. Palmer, P. R. Raithby, J. M. Rawson and D. S. Wright, *Chem. Commun.*, 2000, 749.

