Toroidal Main Group Macrocycles: New Opportunities for Cation and Anion Coordination

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Dedicated to the memory of Dr. Ron Snaith

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Inorganic macrocycles, possessing molecular frameworks composed entirely of elements other than carbon, are rare. Even rarer are species analogous to classical organic macrocycles (like crown ethers) that possess the potential ability to coordinate metal ions within their cavities. Recent studies reveal an emerging structural class of valence-isoelectronic main-group ligands of general formula $[\{E(\mu\text{-}E'R)\}_2Y]_n^{x-}$, which possess fascinating coordination characteristics. Such species can coordinate metal ions within their cavities (using the donor centres Y and E′), their peripheral donor centres (E′) (in an *exo* fashion) and are also capable of coordinating anions (where Y = N–H). This short review highlights the recent synthetic and structural studies of these unusual ligand systems and pinpoints potential future areas of development.

Introduction

Classical macrocyclic ligands based essentially on carbon backbones (such as crown ethers, calixarenes and cyclophanes) have a central role in modern coordination chemistry.[1] Modification of the donor or acceptor atoms (or groups) within these arrangements has provided an ever-growing class of ligand arrangements which are capable of coordinating cations,[2] anions or neutral guest molecules.[3] In contrast, "inorganic" counterparts whose frameworks are constructed from elements other than carbon are still relatively rare, and their coordination behaviour has been little studied. There are a number of obvious reasons for this situation. Firstly and perhaps most importantly, owing to the greater range of available orbitals and hybridisation states, a far more diverse range of bonding connectivities

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

and geometries are characteristic of elements after the first period of the periodic table. An associated feature is the availability of various oxidation states. These factors make rational design of cyclic systems complicated and often limit the applications of synthetic stategies. A second factor is the commonly lower thermodynamic stability and polar nature of bonds to these elements, leading to thermodynamically less robust and/or kinetically more labile ligand arrangements.

Of the few inorganic macrocycles so far investigated the most common type are acceptors (or Lewis acids), particularly those based on electropositive metals.[4−6] An example of this class recently reported are the so-called "inverse-crowns" investigated by Mulvey and co-workers.[4] These macrocyclic, (mainly) alkali or alkaline earth metal amides have been shown to be capable of coordinating various inorganic and organic anions within their cavities. The complex $[(tmp)_6Na_4Mg_2(C_6H_3CH_3)]$ (**1**) (Figure 1) is a particularly interesting example that illustrates a fascinating feature of inverse crowns, the ability to stabilise and direct the formation of highly unusual organic anions (in this case a 2,5-deprotonated $[C_5H_4CH_3]^{2-}$ dianion). Conceptually related mercury(II) metallacarborands investigated earlier by Hawthorne and co-workers are examples of rigid ligand frameworks of this type, which are capable of anion-selective behaviour (an example of which is shown in Figure 2).[5]

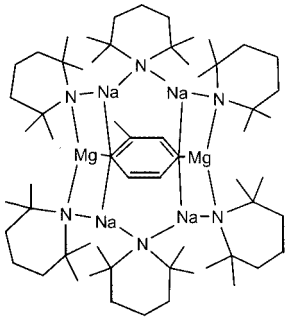


Figure 1. Structure of the inverse crown $[(tmp)_6Na_4Mg_2(C_6H_3CH_3)]$ (**1**), with coordination of a 2,5-deprotonated toluene at the center of the cavity

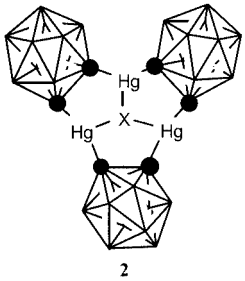


Figure 2. Structure of a trimeric mercury(II) metallacarborand coordinating a halide ion (X) within the cavity

Far rarer than Lewis acidic inorganic arrangements are macrocycles which (like crown ethers) are potentially capable of cation coordination. Examples of this type include organophosphorus macrocycles, such as the octamer $[1,2\text{-}C_6H_4P_2]_8$, composed of a 16-membered ring of P atoms, and the tetrameric anion $[1,2\text{-}C_6H_4P_2]_4^{4-}$.[7] In addition, a few macrocyclic cyclophosph(v)azanes, such as $[(Me_2N)_2PN]_6$, are also known.[8] Our interest in the area of inorganic macrocycles has derived from a general interest in inorganic donor ligands based on p-block element/nitrogen and phosphorus frameworks.[9,10] This short review aims to highlight an emerging class of structurally related, valence-isoelectronic p-block macrocycles of general formulae $[\{E(\mu\text{-}E'R)\}_2Y]^{x-}$ (Figure 3), in which dimeric $\{E(\mu\text{-}E'R)\}_2$ ring units are bridged into neutral or anionic cyclic arrangements via heteroatomic groups or atoms (Y).

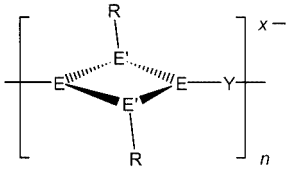


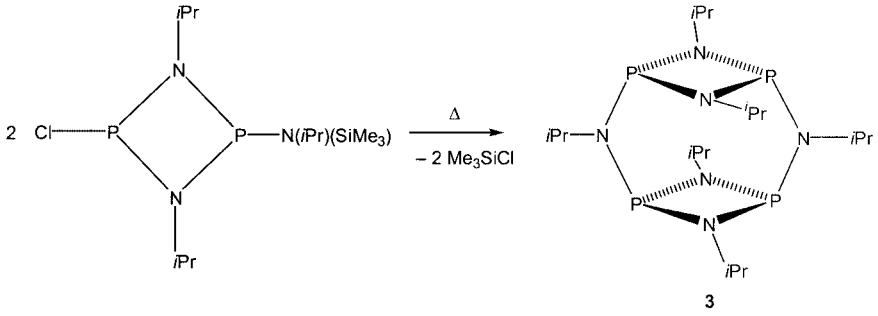
Figure 3. Structural arrangement of the macrocycles

An early indication of the existence of this structural class of macrocycles was provided by the seminal work of Scherer et al., who showed that the phosph(III)azane $[\{P(\mu\text{-}N\mathit{i}Pr)\}_2N\mathit{i}Pr]_2$ (**3**) is obtained by the thermolysis reaction of $[ClP(\mu\text{-}N\mathit{i}Pr)_2PN(\mathit{i}Pr)(SiMe_3)]$ (Scheme 1).[11] More recently, it has been shown that the similar dimeric macrocycle $[\{P(\mu\text{-}N\mathit{t}Bu)\}_2N\mathit{t}Bu]_2$ (**4**) can be obtained by the reaction of the symmetric dimer $[ClP(\mu\text{-}N\mathit{t}Bu)]_2$ with $[\mathit{t}BuNP(\mu\text{-}N\mathit{t}Bu)]_2^{2-}$ (Scheme 2).[12] A. D. Norman and co-workers were the first to suggest that smaller chain and cyclic arrangements of this kind may represent homologues of a broader family of compounds.[13] However, prior to our studies cyclic arrangements had been restricted to dimeric macrocycles of group-15 elements only.

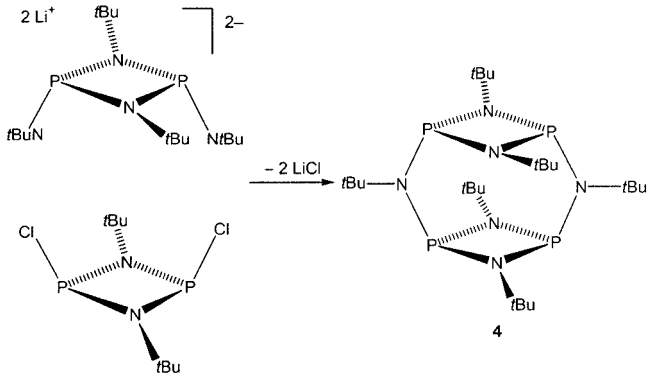
Higher Homologues of Group 15

Our interest in macrocyclic species of this type came about by the chance discovery that the deprotonation reaction of the lithium tris(amidostannate) $[Sn(HNma)_3Li{\cdot}2thf]$ (H_2Nma = 2-methoxyaniline) (**5**) with $Sb(NMe_2)_3$ gives the hexameric macrocycle $[\{Sb(\mu\text{-}Nma)\}_2(\mu\text{-}Nma)]_6$ (**6**), rather than the anticipated heterometallic cage $[Sb(\mu\text{-}Nma)_3Sn]Li$ (**7**).[14] This reaction presumably occurs by elimination of $[Sn(NMe_2)_3Li]$ as a "leaving group" (Scheme 3).[15] Interestingly, **6** can also be obtained by the transmetallation reaction of the $[Sb(Nma)_3]^{3-}$ trianion with $SbCl_3$, a process which can be seen as an inorganic example of masked functionality (Scheme 4).[16]

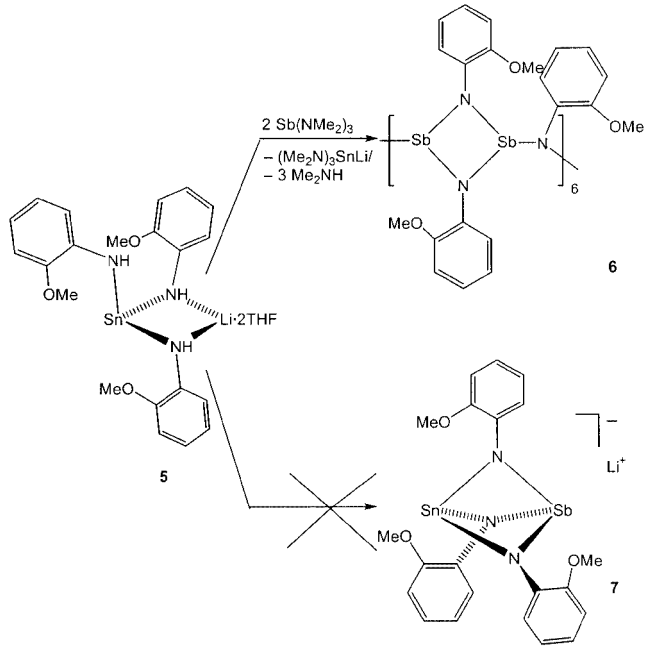
The solid-state structure of **6** (Figure 4) has an all-*trans* arrangement of the dimer units and a macrocyclic cavity of ca. 13.8 Å (measured between opposite Sb^{III} centers). This was the first example of a higher oligomer of this type for



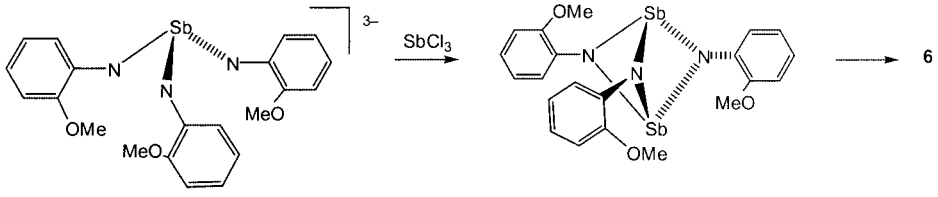
Scheme 1



Scheme 2



Scheme 3



Scheme 4

group 15. More recently, N. C. Norman and co-workers showed that the similar hexameric macrocycle $[\{Sb(\mu\text{-}NPh)\}_2(\mu\text{-}NPh)]_6$ (**8**) can be readily prepared by the reaction of $SbCl_3$ with PhHLi.[17] The observation of hexameric ring units for both **6** and **8**, rather than dimeric macrocycles like **3** and **4**, gives a fundamental clue to the factors directing ring sizes of the homologues $[\{E(\mu\text{-}NR)\}_2NR]_n$.

In considering the formation of higher homologues of the type $[\{E(\mu\text{-}NR)\}_2NR]_n$ (with $n > 2$, like **7** and **8**), a number of factors need to be considered. Perhaps the most important factor influencing the size of macrocycle obtained is the steric demands of the organic substituents (R). The steric influence of the dimer-bridging NR groups is likely to be most critical in this respect. As depicted in Figure 5, for dimeric ($n = 2$) macrocycles the disposition of dimer-bridging NR groups *exo* to the cavity will minimise steric congestion. This dimeric structure is likely to be observed for R groups with moderately large steric demands (as is the case with **3** and **4**). However, in order to sustain the *exo* orientation of these groups for higher homologues ($n > 2$) some or all of the $[P(\mu\text{-}NR)]_2$ units will have to adopt *trans* orientations. This situation is likely to lead to increased ring strain for intermediately sized macrocycles. As the size of the macrocycle increases increased preference for *trans* conformations of the ring units is expected in order to minimise ring strain and at the same time prevent unfavourable *endo* orientation of the dimer-bridging NR groups. These simple considerations therefore suggest that macrocycles of the type $[\{E(\mu\text{-}NR)\}_2NR]_n$ are most likely to occur for $n = 2$ and for larger ring units, where an all-*trans* conformation of the dimeric ring units matches the geometric constraints (as presumably occurs for the hexameric macrocycles **6** and **8**).

A significantly different set of circumstances occurs where the dimer-bridging NR groups have very low steric demands. Now a *cis* configuration of the dimeric ring units can be sustained even for rings beyond $n = 2$. Such occurs

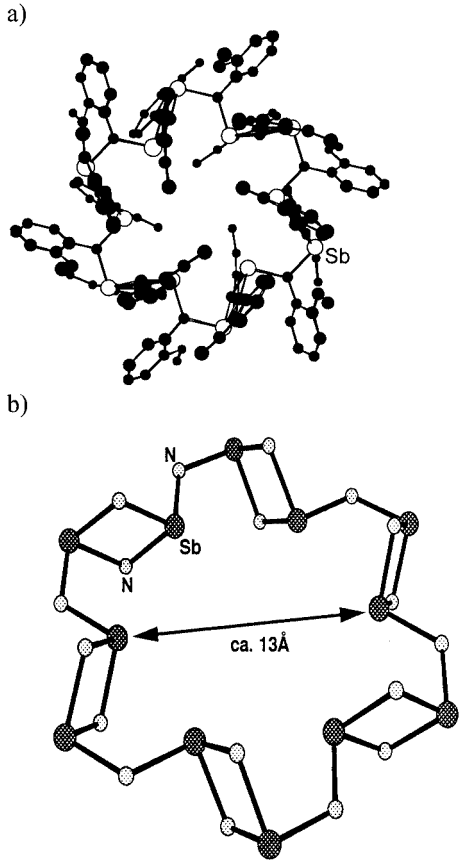


Figure 4. a) Structure of the hexamer **6**; b) core arrangement with ma groups removed

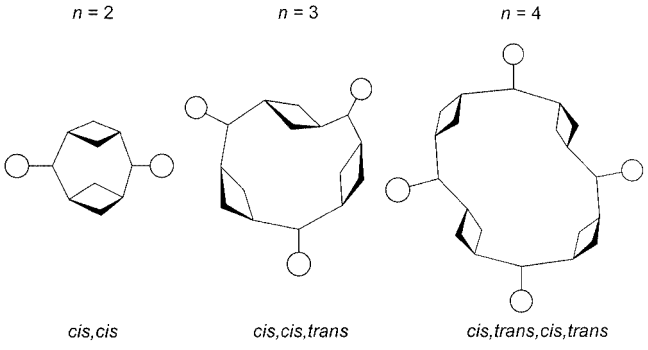


Figure 5. The transition from *cis* to *trans* conformations in macrocycles with increasing *n*

in the case of the tetrameric macrocycle $[\{P(\mu\text{-}NtBu)\}_2NH]_4$ (**9**) (Figure 6), obtained in almost quantitative yield (95−100%) from the condensation reaction of the symmetric dimers $[ClP(\mu\text{-}NtBu)]_2$ (**10**) and $[H_2NP(\mu\text{-}NtBu)]_2$ (**11**) in the presence of Et_3N (Scheme 5).[18] The *cis* conformations of the dimer ring constituents of **9** mean that the four N−H protons are now directed *endo* to the cavity, with the twelve P···P−N units defining the macrocyclic ring being almost in one plane. The transannular N···N separation between opposite pairs of N centers within the cavity of **9** differ by only ca. 0.05 Å, with the size of the cavity being ca. 5.22 Å. Presumably, the formation of a tetrameric macrocycle is a further consequence of the low steric demands of the dimer-bridging N−H groups of **9**, allowing aggegation to occur beyond simple dimers like **3** and **4.** The arrangement of **9** is reminiscent of organic ligands such as tetraazacyclotetradecanes (i.e., based on $[CH_2CH_2NH]_4$). However, the latter have significantly smaller cavities (range 4.07−4.29 Å).[19]

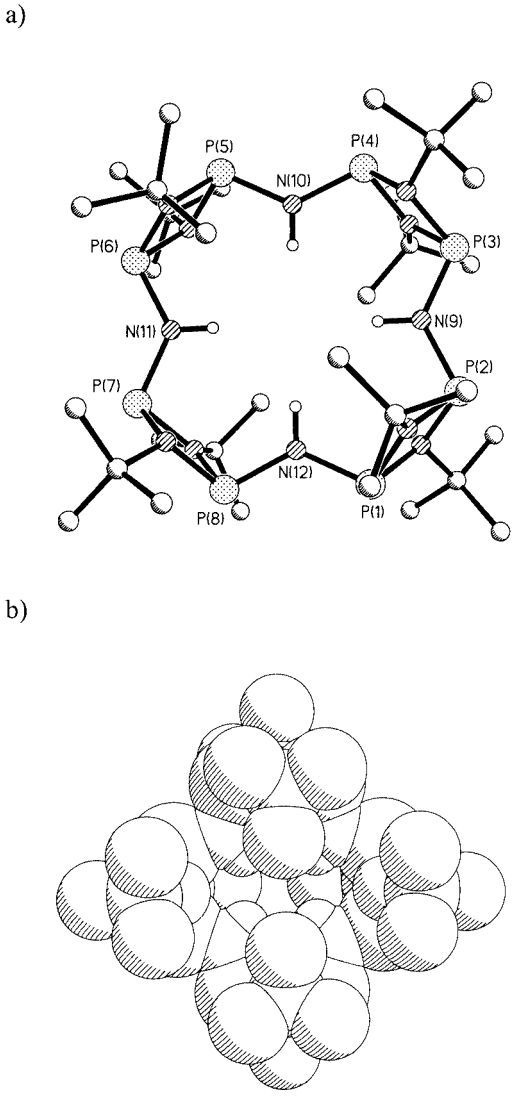
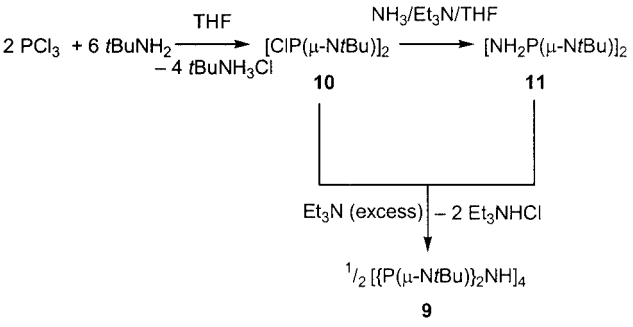


Figure 6. a) Structure of the tetramer **9**; b) space-filling diagram of **9** showing the crowding of the core



Scheme 5

An important kinetic feature involved in the formation of **9** is "pre-organisation" of the dimer precursors **10** and **11**. The latter have both been shown to adopt *cis* conformations of the Cl and NH_2 substituents in the solid state and solution.[20,21] Indeed, in the case of **11** this *cis* conformation results in cyclisation of the dimers in the solid state via N−H···N hydrogen bonding.[20] Pre-organisation is primarily responsible for the near quantitative formation of the macrocyclic arrangement of **9**, rather than of polymeric alternatives. This is a rare (if not unprecedented) example of pre-organisation for an inorganic system. A further aspect of the mechanism by which **9** is formed is indicated by the formation of minor amounts of the host−guest complex $[\{P(\mu\text{-}NtBu)\}_2NH]_5$·HCl (**12·HCl**) along with **9** in the condensation reaction of **10** and **11** (Figure 7).[20] Like **9**, the dimer units of **12·HCl** adopt *cis* conformations, with the complex being composed of the pentameric macrocyclic ring $[\{P(\mu\text{-}NtBu)\}_2NH]_5$ (**12**) coordinating an HCl unit at the centre of the cavity via five N−H···Cl hydrogen bonds to all of the dimer-bridging N−H groups (N···Cl mean 3.6 Å, H···Cl 2.57−2.66 Å). The arrangement of the five N−H groups towards the centre of the macrocyclic unit creates a cavity of ca. 6.8 Å in diameter (measured with respect to the N atoms of the ring). The structure of **12·HCl** is similar to host−guest adducts of sapphyrins (expanded porphyrins),[22] in particular the pentapyrrole−HF complex $[\{3\text{-Me-4-Et-pyrNH}\}_5(CH_2)_4\cdot F][PF_6]$ (pyrN = pyrrole) which contains a similar arrangement of five N−H groups surrounding a central F^- anion.[22c] However, the core sizes in these complexes are significantly smaller than that in **12** (at ca. 5.5 Å in the pentaporphyrins, with respect to the five N centres[22]).

The isolation of **12·HCl** indicates that, in addition to pre-organisation, the formation of **9** may also rely on templating by Cl^- ions in the reaction. Extensive in situ ^{31}P NMR spectroscopic studies of the reactions of the dimers **10** and **11** under various conditions show that **9** and **12·HCl** are not in dynamic equilibrium with each other.[20] The most likely mechanism by which **9** and **12·HCl** are formed is by a divergent pathway like that shown in Scheme 6. The growing chain effectively competes with Et_3N as the Brønsted base in this reaction, so that N−H···Cl hydrogen bonding templates cyclisation. The pivitol intermediate **I[4]** can either eliminate HCl in the presence of Et_3N to form **9** or react with another molecule of **11** to give **12·HCl**. It is noteworthy in this regard that the formation of a pentameric macrocycle would be impossible by a simple, stepwise condensation pathway involving **9** and **10**, for which only macrocycles containing an even number of ring units (*n*) could be obtained.

A further discovery made during these ^{31}P NMR spectroscopic investigations is that the formation of the pentamer **12** can be biased by addition of excess lithium halide salts.[20] The high concentration of halide ions present presumably supresses the elimination of HX involved in the formation of **9**. The ability for the halide ions to template the formation of **12** is in the order $I^- > Br^- > Cl^-$. In the case of LiI, only the host−guest complex **12·HI** is generated

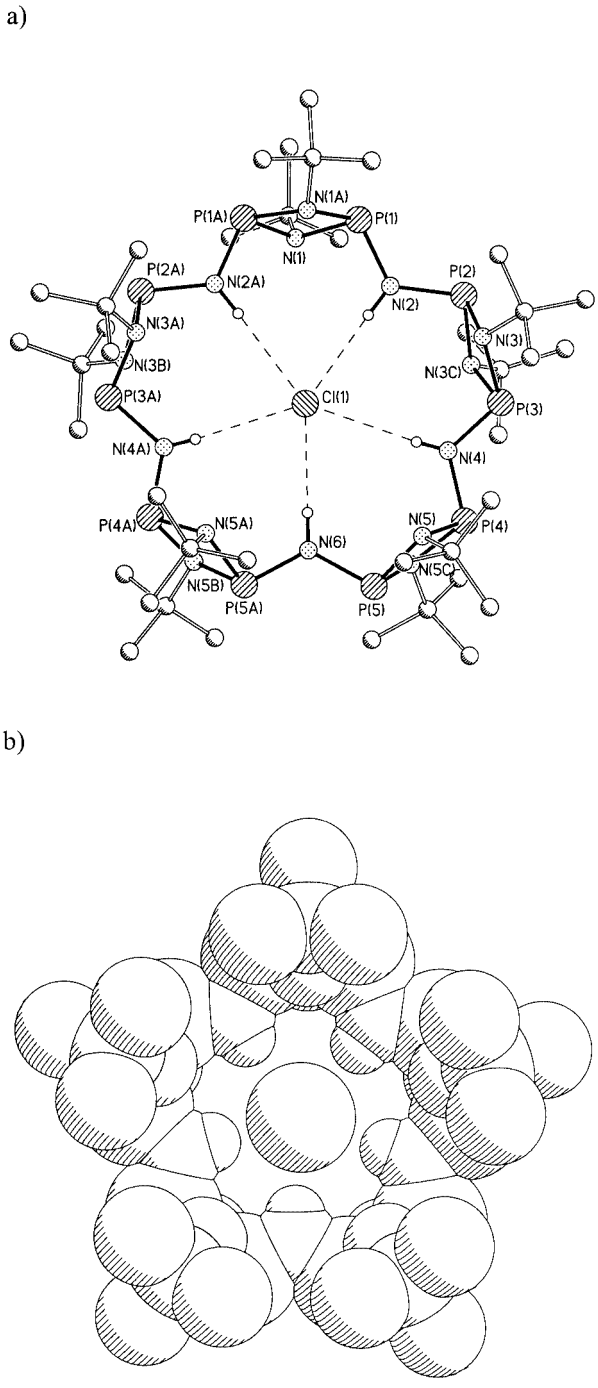
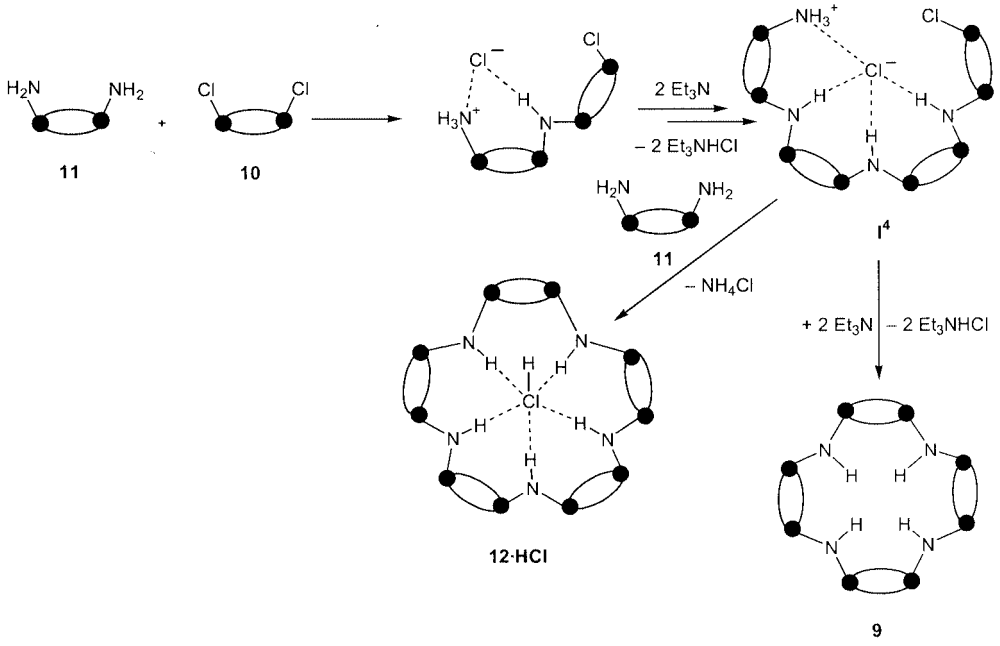


Figure 7. a) Structure of host−guest complex **12·HCl**; b) space-filling diagram of the molecule

(without **9**). This observation is broadly consistent with the size of the macrocyclic cavity of **12** (ca. 6.8 Å), which appears to be better suited to coordination of I^- (typical N···I 3.46 Å) than Cl^- (typical N···Cl 3.00−3.20 Å).[23]

At first sight, it might be expected that the presence of *cis* subunits within macrocycles of the type $[\{P(\mu\text{-}NR)\}_2NH]_n$ would limit the ring size obtainable, since beyond a particular point addition of further units would result in unfavourable ring strain. However, the formation of the tetrameric

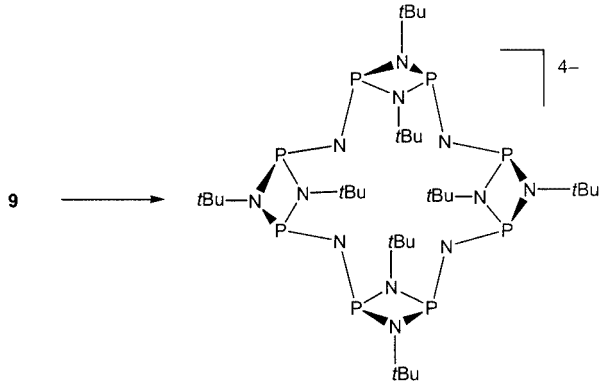


Scheme 6

and pentameric arrangements of **9** and **12** provides direct evidence that the dimeric [{P(μ-N*t*Bu)}$_2$NH] constituents of these macrocycles are in fact highly flexible. Relatively small changes in the endocyclic P−N−P and N−P−N angles within the [{P(μ-N*t*Bu)}$_2$NH] units, in the exocyclic N(*t*Bu)−P−NH angles, and in the puckering of the P_2N_2 ring units result in a significantly different bite distance (α) between adjacent N(−H) atoms within the tetramer **9** (mean 3.7 Å) compared to the pentamer **12** (mean 4.0 Å). For macrocycles like **9** and **12**, it can be shown that Equation (1) gives the relationship between the radius of the cavity (*r*) (expressed with respect to the N atoms), the number of [{P(μ-NR)}$_2$(NH)] units (*n*) and the bite distance (α). The effect of the increase in the bite distance in going from **9** to **12** (of 0.3 Å) therefore accounts for a ca. 0.2 Å increase in the size of the cavity (compared to the cavity size which would be present if the bite distance remained the same as in **9**).

$$r^2 = \frac{\alpha^2}{2(1 - \cos 2\pi/n)} \quad (1)$$

The ability of these macrocycles to coordinate anions within their cavities is witnessed in the structure of **12·HCl**. However, a more obvious potential property of macrocycles of this type is the coordination of metal cations. The attempted deprotonation of the tetramer **9** with various main-group reagents has so far failed to generate the desired tetraanion [{P(μ-N*t*Bu)}$_2$N]$_4^{4-}$ (Scheme 7).[24] In the case of s-block organometallic reagents (including MeLi, *t*BuLi and *n*BuLi), no reactions are observed. It can be noted that the dimer [*t*BuNHP(μ-N*t*Bu)]$_2$ (**13**) is fully deprotonated by *n*BuLi in toluene or THF.[12,25] Thus, the apparently low acidity of the N−H protons of **9** appears to stem from the extreme steric hindrance due to the *t*Bu groups, which fully shield the cavity to the approach of the base (Figure 6, b). With more forcing conditions, decomposition of the macrocyclic structure can arise. For example, the reaction of **9** with $PhCH_2K$ gives [*t*BuNHP(μ-N*t*Bu)]$_2$ (**13**) and/or [(*t*BuN)$_2$PK]$_\infty$ (**14**) as the only P-containing products (depending on the stoichiometry used).[24]



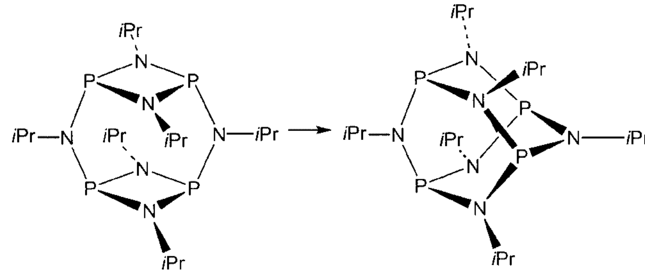
Scheme 7

Nonetheless, macrocyclic anions can be generated by alternative synthetic approaches. For example, the reaction of the dimer [Me$_2$NSb(μ-NCy)]$_2$ (**15**) with "active" $LiNH_2$ (generated in situ from NH_3 and *n*BuLi) gives [{Sb(μ-NCy)}$_3$(Li·THF)$_3$(LiN=NH)] (**16**).[26] Remarkably, the trimeric [({Sb(μ-NCy)}$_2$N)$_3$]$^{3-}$ trianion of **16** is produced by double-deprotonation of the NH_2^- anion (according to Scheme 8). The unexpected presence of an N=NH$^-$ anion in this arrangement has been confirmed by IR and ^{15}N NMR spectroscopic studies. The X-ray crystallographic study of **16** shows that it contains a cone-shaped [({Sb(μ-

NCy)}$_2$N)$_3$]$^{3-}$ trianion, which is reminiscent of the arrangement of coordinated or uncoordinated calixarenes (Figure 8).[1] This trianion coordinates one Li^+ cation within the macrocyclic cavity, using the anionic μ-N centres. The remaining four, symmetry-related Li^+ cations reside above the macrocyclic cavity and are coordinated by the anionic μ-N and neutral NCy centres. The $N{=}NH^-$ anion then caps the structure, along the virtual C_3 axis of the cage.

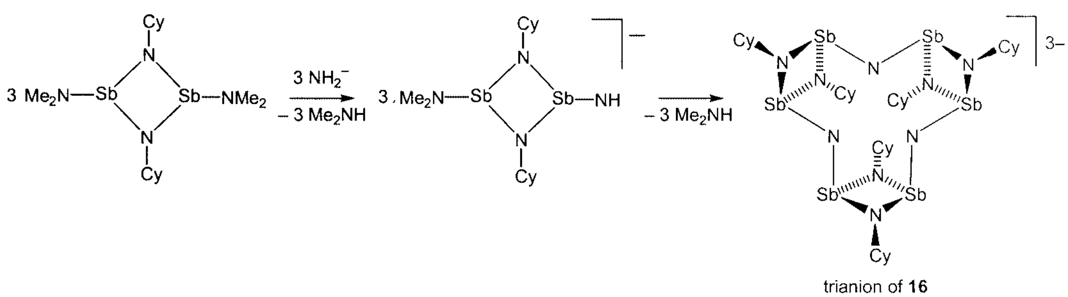
Macrocyclic and Adamantane Alternatives

In a previous study Scherer et al. had shown that the dimeric macrocycle [{P(μ-N*i*Pr)}$_2$N*i*Pr]$_2$ (**3**) reverts to adamantane alternative [P_4(μ$_3$-N*i*Pr)$_6$] (**17**) on prolonged heating in the solid state (Scheme 9).[11] In contrast, a more recent study of the related macrocycle [{P(μ-N*t*Bu)}$_2$N*t*Bu]$_2$ (**4**) showed that this species does not rearrange into the adamantane under similar conditions.[22b] These limited studies suggest that the stability of the macrocyclic arrangements described in the previous section are dependent on the steric demands of the organic substituents. Clearly, the macrocyclic structure will be favoured where sterically more demanding substituents are present since the dimeric P_2N_2



3 **17**

Scheme 9



Scheme 8

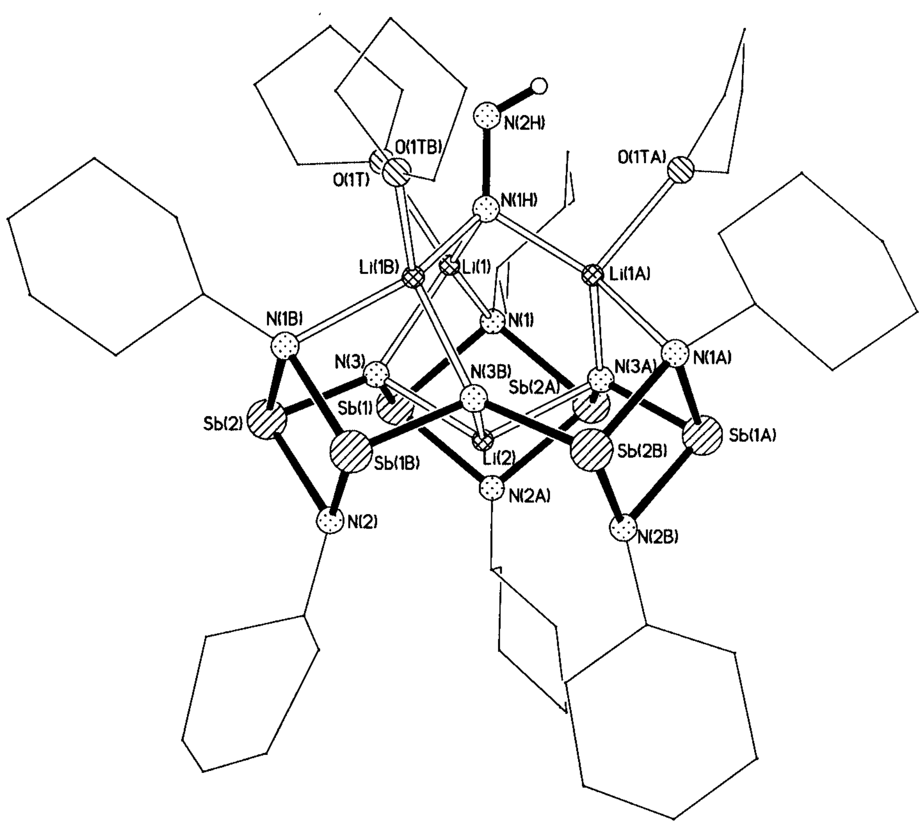
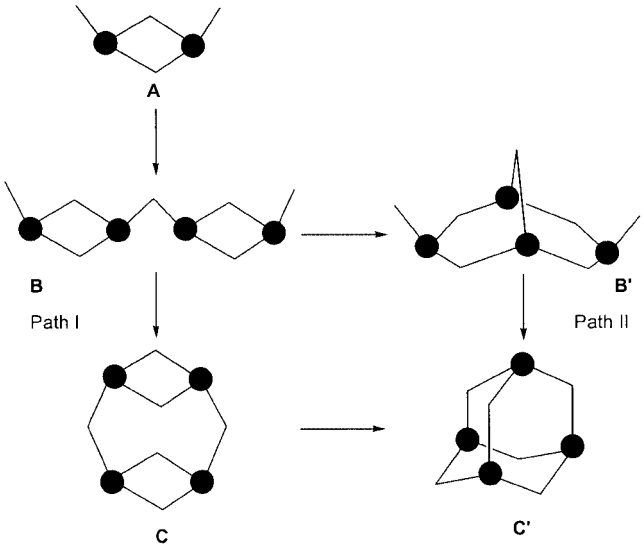


Figure 8. Structure of **16**

ring constituents maximise the space available. On the other hand, the six-membered ring constituents of the adamantane arrangement will result in an inherent increase in steric congestion, and such an arrangement is likely only to be formed where sterically less demanding sustituents are present. Although the mechanism by which **3** is converted into **17** is not known, as noted in Scheme 8 the rearrangement can be described by a facile "twist" of one of the (iPrN)P_2 units.

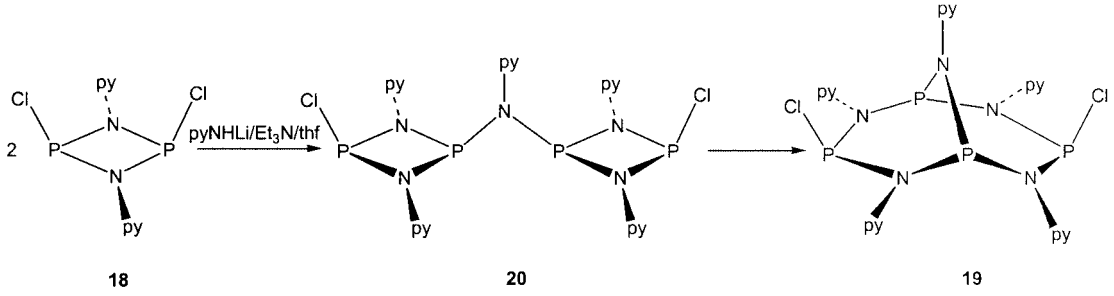
A recent study of the synthesis of the dimer [ClP(μ-Npy)]$_2$ (py = 2-pyridyl) (**18**) indicates the potential generality of this twist process in this area.[27] Attempts to prepare **18** from pyNHLi and PCl_3 in the presence of Et_3N give **18** together with the nonaphosphazane [$ClP_4(Npy)_5$] (**19**). Low-temperature ^{31}P NMR spectroscopic studies reveal that the reaction of **18** with pyNHLi/Et_3N gives **19**. The likely intermediate in this reaction is [{ClP(μ-Npy)P}$_2$(μ-Npy)] (**20**), the chain isomer of **19** which can also be detected prior to rearrangement (Scheme 10). DFT calculations on the rearrangement of the model chain species [{ClP(μ-NR)P}$_2$(μ-NR)] into the nonaphosphazanes [$ClP_4(NR)_5$] (R = H, Me) show that the thermodynamics of this reaction are dependent on the steric demands of the R group. The rearrangement being most favourable for least sterically demanding substituents.

This result gives a key insight into the relationship between various imidophosphazane frameworks that have been characterised previously. The relationship between these frameworks can be represented mechanistically in Scheme 11. It appears that there are two possible modes of reaction of imidophosphazane dimers **A**: Path I (leading to macrocyclic arrangements) or Path II (leading to adamantane arrangements). The twist process observed in the conversion of **20** into **19** is pivotal in the selection of the two alternative arrangements. As is the case in the rearrangement of the dimeric macrocycle [{P(μ-NiPr)}$_2$NiPr]$_2$ (**3**) into the adamantane [$P_4(\mu_3$-NiPr$)_6$] (**17**),[11] the steric demands of the R group is the decisive factor governing which Path (I or II) will be followed. The rearrangement of the chain isomer **B** into the nonaphosphazane **B′** is only favoured where sterically less demanding substituents are present, since otherwise the steric congestion would be too great within the six-membered ring units of the latter. Closure of **B′** with a further P center results in the adamantane structure **C**. In the case of sterically more demanding R groups, the dimeric ring units of **B** will be sustained on steric grounds. Closure with a further P center will lead to the macrocyclic isomer **C**.



Scheme 11

Whether the importance of steric factors in the formation of macrocyclic and adamantane alternatives will limit the range of organic substituents that can be introduced into larger macrocycles of the type [{P(μ-NR)}$_2$(NH)]$_n$ is not yet known. However, a recent study indicates one potential way by which the undesired adamantane pathway may be avoided. Coordination of CuCl to the P centers of the dimer [ClP(μ-Npy)]$_2$ (**18**) before cyclisation with H_2O in the presence of pyridine gives [{P(μ-Npy)}$_2$(μ-O)]$_2${CuCl(pyridine)$_2$}$_4$ (**21**) (Figure 9), containing a dimeric macrocyclic core arrangement.[24] The potential to revert to the apparently thermodynamically more stable adamantane arrangement in this case is avoided by the increased steric demands of the *P*-coordinated metal fragments. This also has the effect of limiting the ring size of the macrocycle generated to a dimer. The structure of **21** reveals an additional property of this type of ligand arrangement not previously observed, their ability to employ the soft P centers in the coordination of metals at the periphery of the macrocycles.



Scheme 10

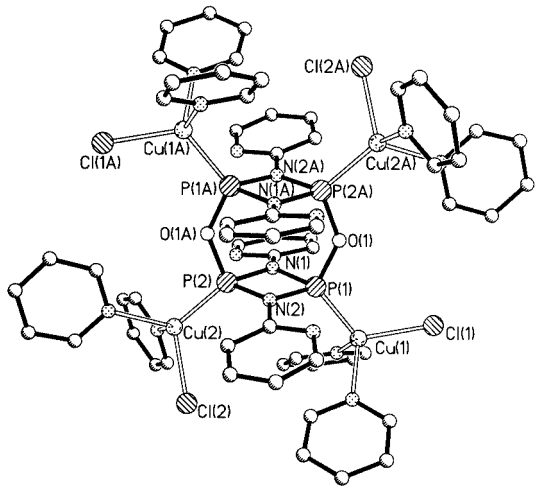


Figure 9. Structure of **21**

Valence-Isoelectronic Macrocycles Containing Other p-Block Elements

The applications of isoelectronic principles in the rationalisation and prediction of structure and bonding are long established in the area of main-group chemistry. Recently, these ideas have formed the basis of reviews concerning p-block element−N ligand systems.[28] In the context of the class of the macrocycles which the current review concerns, it can be seen that replacement of the P centers of a dimeric macrocycle of the type $[\{P(\mu\text{-}E'R)\}_2(\mu\text{-}E'R)]_2$ (E′= N or P, like **3** and **4** discussed in the previous section) with a +2 oxidation-state group-14 metal center (E) or with an organo group-13 metal fragment (R−E; E = group-13 element) would give valence-isoelectronic tetraanions of the type $[\{E(\mu\text{-}E'R)\}_2(\mu\text{-}E'R)]_2^{4-}$ and $[\{R'E(\mu\text{-}E'R)\}_2(\mu\text{-}E'R)]_2^{4-}$, respectively (Figure 10).

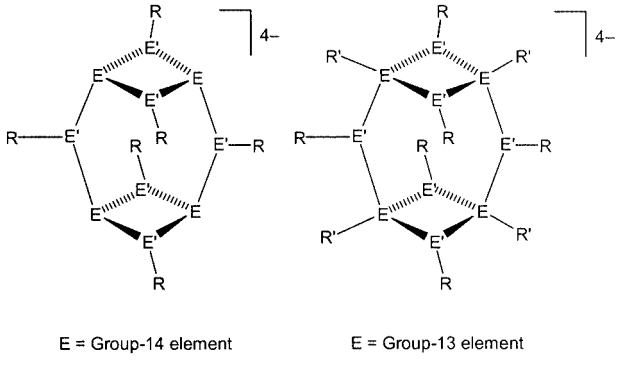
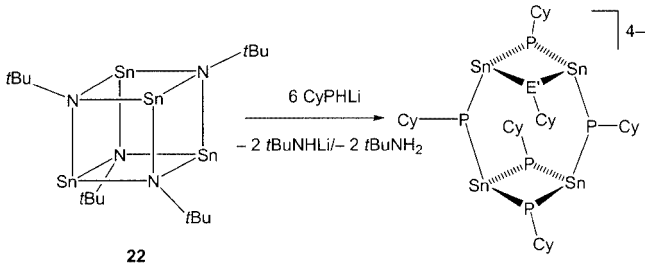
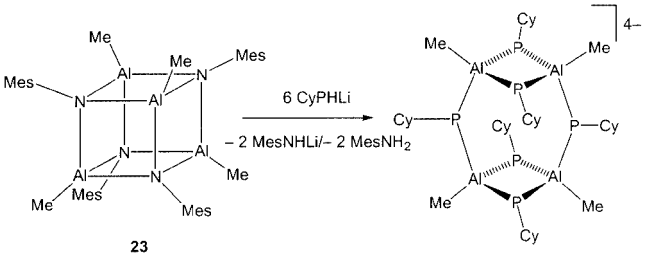


Figure 10. Valence-isoelectronic group-13 and -14 dimers

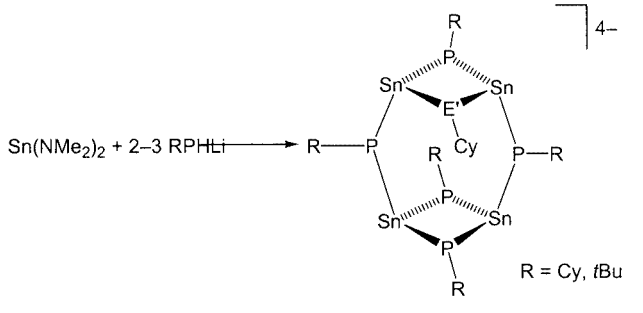
In practice the formation of isoelectronic anions of this type is not simple and different synthetic strategies have to be employed to those used in the related P−N systems. One earlier synthetic approach which we employed is the "templating" reaction of cubanes such as $[Sn(NtBu)]_4$ (**22**)[29] and $[MeAl(NMes)]_4$ (**23**)[30] with CyPHLi (Schemes 12 and 13, respectively). These reactions involve replacement of all four of the imido (RN^{2-}) ligands of the **22** and **23** with organophosphide groups (RP^{2-}). It can be noted that the related reactions with metallated primary amines (RNHLi) do not produce related macrocyclic frameworks.[29] More recently, however, we have found that group-14 frameworks of this type can be obtained in a more straightforward manner by the direct reactions of $Sn(NMe_2)_2$ with RPHLi (R= *t*Bu, Cy) (Scheme 14).[31] This strategy is restricted to aliphatic phosphides and to Li as the metal, as extensive coupling of the RP groups occurs in reactions involving aromatic phosphides or with aliphatic phosphides of the heavier alkali metals.[32] For example, the analogous reaction of MesPHLi with $Sn(NMe_2)_2$ in the presence of the Lewis base ligand TMEDA (= $Me_2NCH_2CH_2NMe_2$) gives $[\{Sn(\mu\text{-}PMes)\}_2(PMesPMes)](Li{\cdot}TMEDA)_2$ (**24**) (Mes= 2,4,6-$Me_3C_6H_3$), containing an $[Sn(\mu\text{-}PMes)\}_2(PMesPMes)]^{2-}$ dianion in which two of the MesP groups have coupled to form a $[MesPPMes]^{2-}$ unit (Scheme 15).[31]



Scheme 12

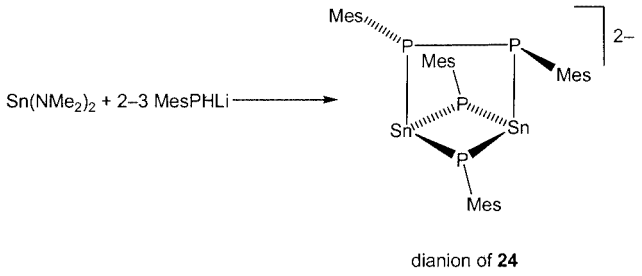


Scheme 13



Scheme 14

The structure of $[\{Sn(\mu\text{-}PtBu)\}_2(\mu\text{-}PtBu)]_2{\cdot}(Li{\cdot}THF)_4$ (**25**) (shown in Figure 11) illustrates the mode of Li^+ coordination found in all of the lithium complexes containing macrocyclic, valence-isoelectronic group-13 and -14 anions



Scheme 15

of this type. The $[\{Sn(\mu\text{-}PtBu)\}_2(\mu\text{-}PtBu)]_2^{4-}$ of **25** coordinates the four Li^+ cations using both the μ-P*t*Bu groups within the dimeric ring units and those bridging the dimer units together. This coordination mode is the same as that seen for the three of the Li^+ cations by the $[(\{Sb(\mu\text{-}NCy)\}_2N)_3]^{3-}$ trianion of **16** (discussed above).[26]

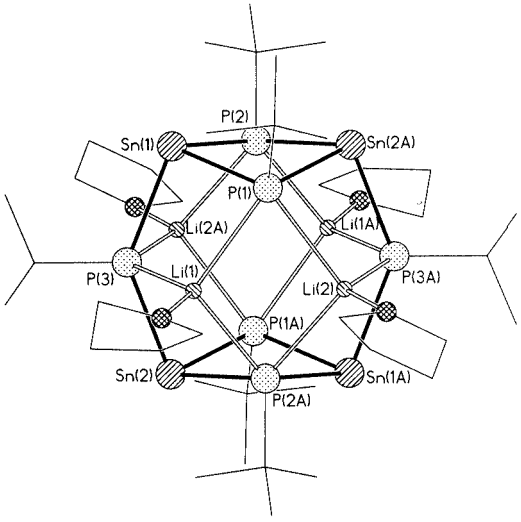


Figure 11. Structure of **25**

Future Prospects

This review has highlighted recent developments in this area. However, there is clearly much more to be done in extending the range of macrocycles available, both for group-15 systems and their valence-isoelectronic analogues, and in understanding and utilising the factors affecting the ring size of these species in general. Studies to date have pinpointed three distinctive coordination characteristics of this new class of macrocyclic ligands: the ability to coordinate metal ions within the cavity (in the case of deprotonated species), coordination of anions within the cavity (in the case of macrocycles having *endo* N−H functionality) and metal ions outside the cavity (using, for example, P centres within the macrocyclic backbone). Future studies will investigate these coordination patterns particularly with a view to (i) the synthesis of mixed-metal complexes, by utilising a combination of cavity and peripheral metal coordination, and (ii) the templating of macrocycles using anion coordination.

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