Templating and Selection in the Formation of Macrocycles Containing $[\{P(\mu\text{-}NtBu)_2\}(\mu\text{-}NH)]_n$ Frameworks: Observation of Halide Ion Coordination

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Abstract: Amination of $[ClP(\mu\text{-}NtBu)]_2$ (**1**) using NH_3 in THF gives the cyclophospha(III)zane dimer $[H_2NP(\mu\text{-}NtBu)]_2$ (**2**), in good yield. ^{31}P NMR spectroscopic studies of the reaction of **1** with **2** in THF/Et_3N show that almost quantitative formation of the cyclic tetramer $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_4$ (**3**) occurs. The remarkable selectivity of this reaction can (in part) be attributed to pre-organisation of **1** and **2**, which prefer *cis* arrangements in the solid state and solution. The macrocycle **3** can be isolated in yields of 58–67% using various reaction scales. The isolation of the major by-product of the reaction (ca. 0.5–1% of samples of **3**), the pentameric, host–guest complex $[\{P(\mu\text{-}NtBu)_2\}_2(\mu\text{-}NH)]_5(HCl)\cdot 2THF]$ (**4**$\cdot$2THF), gives a strong indication of the mechanism involved. In situ ^{31}P NMR spectroscopic studies support a stepwise condensation mechanism in which Cl^- ions play an important role in templating and selection of **3** and **4**. Amplification of the pentameric arrangement occurs in the presence of excess LiX (X = Cl, Br, I). In addition, the cyclisation reaction is solvent- and anion-dependent. The X-ray structures of **2** and **4**$\cdot$2THF are reported.

Keywords: host–guest systems · macrocycles · phosphorus

Introduction

'Inorganic' macrocycles (whose backbones are not based on carbon) are rare in comparison to their well-established carbon counterparts, such as crown ethers, calixarenes and cyclophanes,[1] and there have been few systematic studies of their synthesis and coordination behaviour. Two recently explored classes of inorganic ligands of this type are mercuracarborands[2] and cyclic s-block amides[3] that, by virtue of the presence of electropositive metals within their backbones, behave as Lewis acids in the coordination of various anions. More conventional Lewis base behaviour has been observed for certain cyclophospha(v)zenes, such as $[P(NMe_2)_2N]_6$,[4] and small Si/N macrocyles of the type $[(R_2Si)NH]_4$;[5] however, macrocyclic Lewis bases are particularly rare. In earlier work we characterised the neutral Group 15 macrocycle $[\{[Sb(\mu\text{-}NR)]_2(\mu\text{-}NR)\}_6]$ (R = 2-MeO-C_6H_4), composed of six $[\{Sb(\mu\text{-}NR)\}_2]$ rings linked into a cyclic structure by μ-NR groups.[6a] A similar hexameric macrocycle has also been obtained from the reaction of $SbCl_3$ with PhNHLi.[6b] More recently we showed that the 1:1 reaction of $[ClP(\mu\text{-}NtBu)]_2$ (**1**) with $[H_2NP(\mu\text{-}NtBu)]_2$ (**2**) in THF/Et_3N gives the new cyclophospha(III)zane $[\{P(\mu\text{-}NtBu)\}_2NH]_4$ (**3**) in good yield.[7] The compound is composed of four, four-membered $[P(\mu\text{-}NtBu)]_2$ rings joined together by bridging NH groups into a macrocyclic structure (Figure 1). The arrangement of the $[P(\mu\text{-}NtBu)]_2$ ring units of **3**, almost perpendicular to the mean plane of the macrocyclic core, can be compared to that found in calixarenes, while the alignment of the N–H protons towards the centre of the ring, is comparable with the arrangement in porphyrins.[1] Some indication of the coordination characteristics of deprotonated frameworks of this type is provided by the structure of $[\{[Sb(\mu\text{-}NCy)\}_2N]_3](Li\cdot 3THF)_3\cdot LiN{=}NH$, in which conical distortion of the cyclic $[\{Sb(\mu\text{-}NCy)\}_2N]_3^{3-}$ trianion allows the binding of four Li^+ ions within the cavity, despite the presence of an apparently sterically congested ligand periphery.[8] Significantly, both the neutral NCy and anionic μ-N centres are involved in metal coordination.

We present here a full account of the synthesis of **3**, including a new multigram procedure that allows the synthesis of large batches of the compound. We also report the X-ray structure of the precursor **2**, which shows that this species

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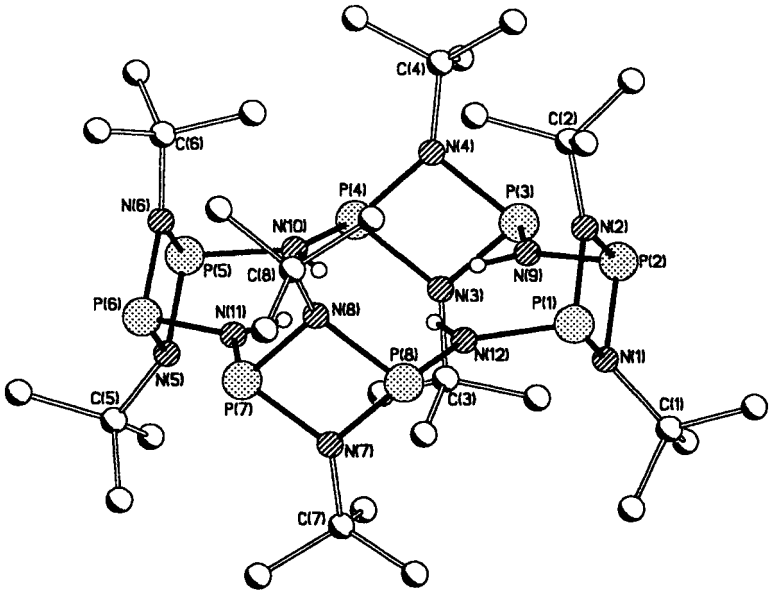
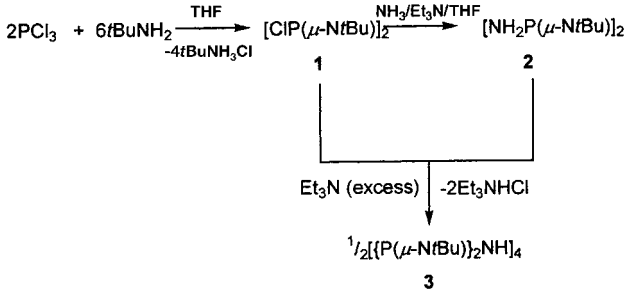


Figure 1. Structure of the tetramer **3**.

adopts a *cis* conformation in the solid state (like the dichloride **1**). The latter provides strong support for our initial proposition that the selective formation of **3** (rather than of a polymeric alternative) relies on pre-organisation of the substrates. The host–guest adduct $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_5 \cdot HCl$ (**4**), which was observed initially in a ^{31}P NMR study of crude **3**, has also been fully characterised.

Results and Discussion

Synthetic studies: The slow addition of $tBuNH_2$ (3 equiv) to a solution of PCl_3 (1 equiv) in THF at $-78\,^{\circ}C$ gives the dimer $[ClP(\mu\text{-}NtBu)]_2$ (**1**) in good yield (ca. 70 %)(Scheme 1). This



Scheme 1.

method is different from that reported earlier for the synthesis of **1**, in which PCl_3 was treated with $tBuNH_2$ (2:3 equiv) in the presence of Et_3N (3 equiv).[10] Despite the use of excess $tBuNH_2$ for this purpose in our route, little of the non-symmetric dimer $[tBuNHP(\mu\text{-}NtBu)_2PCl]$ is generated provided the temperature of the reaction mixture is kept at $-78\,^{\circ}C$ for at least 3 h after complete addition of the $tBuNH_2$. Efficient stirring of the reaction is also essential. $[tBuNHP(\mu\text{-}NtBu)_2PCl]$ can easily be separated from **1** by distillation through a Vigreux column (**1** distilling at 86 °C and $[tBuNHP(\mu\text{-}NtBu)_2PCl]$ at 96 °C, both at 0.2 mmHg). Furthermore the reaction can be scaled up without significant reduction in the yield of **1** (see Experimental Section).

The slow addition of a solution of **1** in THF to a concentrated solution of NH_3 in THF/Et_3N at $-78\,^{\circ}C$ produces good yields of the diamino dimer $[H_2NP(\mu\text{-}NtBu)]_2$ (**2**) (48–58 %), the compound being extracted by washing with *n*-pentane in which it is reasonably soluble (Scheme 1). Highest yields are obtained if the NH_3 solution is prepared by bubbling NH_3 gas through THF at $-78\,^{\circ}C$. Although a large volume of *n*-pentane is required for the extraction of this compound, the use of a Soxhlet extractor was avoided since **2** is apparently slightly thermally unstable, an insoluble decomposition product being formed on prolonged storage of the compound even at room temperature. However, compound **2** is tolerant to hydrolysis and pre-dried *n*-pentane was found not to be required for its extraction. Again the reaction can be scaled up to allow the preparation of large amounts of **2** (ca. 10—20 g) (see Experimental Section). Compound **2** was stored as a solid at $-5\,^{\circ}C$ to prevent decomposition. The formation of **2** is seen in particular in the ^{31}P NMR spectrum by the observation of an up-field shift from $\delta = 207.6$ ppm in **1** to $\delta = 100.2$ ppm in **2** (relative to 85 % H_3PO_4). The chemical shift observed for **2** is indicative of a *cis* conformation for the NH_2 groups relative to the P_2N_2 ring, based on the correlation reported earlier by Norman et al.[9] The chemical shifts for *trans* amidophospha(v)zane isomers are normally found in the range $\delta = 166$—185 ppm, while *cis* isomers occur in the range $\delta = 96$—108 ppm (relative to 85 % H_3PO_4/D_2O). The observation of splitting of the symmetrical and asymmetrical N–H stretching bands in the IR spectrum of solid **2** (symm. 3402 (doublet), asymm. 3291 (doublet)) was an intriguing spectroscopic feature which provided an initial indication of extensive hydrogen bonding in the solid-state structure of the compound (shown later by X-ray structural determination).

The ^{31}P NMR spectrum of the final reaction mixture of **1** and **2** in THF/Et_3N shows that the formation of the tetramer **3** is almost quantitative. The selectivity of the reaction producing **3** can be attributed to the *cis* conformations of both **1** and **2**, that is, cyclisation rather than polymerisation is pre-organised. It has previously been shown that the *cis* isomer of **1**[12] is the most stable form in the solid state and solution, and ^{31}P NMR spectroscopic evidence (noted previously) and the later structural characterisation of **2** confirms that this is also the case for this compound. Subsequently, we were able to scale up the reaction between **1** and **2**. The macrocycle **3** can be isolated in good yields of 67 % (2.12 mmol scale)[7] by

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extraction of the residue with *n*-pentane. In contrast to the purification of **2**, the use of dry *n*-pentane is essential at this stage. However, since **3** is significantly more thermally stable than **2**, Soxhlet extraction can be employed for larger scale synthesis. This procedure allows the convenient synthesis of large amounts of **3** (ca. 40—50 mmol scale, that is, ca. 10—11 g of **3**) without the need for costly quantities of pre-dried solvent (see Experimental Section). ^{31}P and ^{1}H NMR spectroscopy reveal that **3** is obtained in high purity (95–100%) in both the small-scale and large-scale syntheses, without the need for any further purification. However, there is a slight reduction in the overall yield in the larger scale reactions (to ca. 58%). Single crystals of **3** are obtained readily by dissolving a suspension of the crude compound (obtained after removal of the solvent from the extraction) in *n*-pentane with a minimum amount of THF, and storing at room temperature. Solid **3** is air-stable for at least six hours at 25 °C (monitored by ^{31}P NMR spectroscopy).

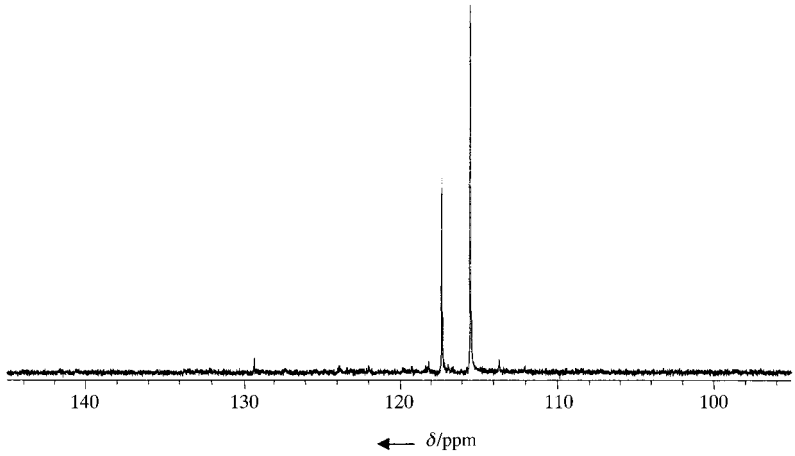


Figure 3. ^{31}P NMR spectrum of isolated **4** in toluene.

Minor impurities are observed in crude samples of **3**. In particular, a by-product forms about 0.5–1% of the crude material (estimated by ^{31}P NMR spectroscopy). This species is only fully apparent in the low-temperature ^{31}P NMR spectra of crude **3** in THF (Figure 2), being characterised by a minor resonance at $\delta = 117.3$ ppm and by a major resonance at $\delta = 115.5$ ppm. Luckily from one large-scale preparation of **3** we were able to isolate a small quantity (ca. 50 mg) of this by-product, sufficent for spectroscopic analysis and X-ray structural determination (see Experimental Section). This species is the unusual host–guest complex $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_5(HCl)$ (**4**), composed of a pentameric macrocyclic ring which coordinates a central HCl molecule (see later discussion of the structure of the complex). The ^{31}P NMR spectrum of isolated **4** in toluene (Figure 3) shows two resonances at $\delta = 115.5$ and 117.3 ppm (ratio ca. 4:1). However, the ratio of these two resonances is markedly different in the ^{31}P NMR spectrum of **4** in THF, in which the resonance at about $\delta = 117$ ppm is only just observable (Figure 2). We attribute this solvent-dependence to a dissociative equilibrium between intact **4** ($\delta = 115.5$ ppm) and the free pentamer $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_5$ ($\delta = 117.3$ ppm) and HCl.

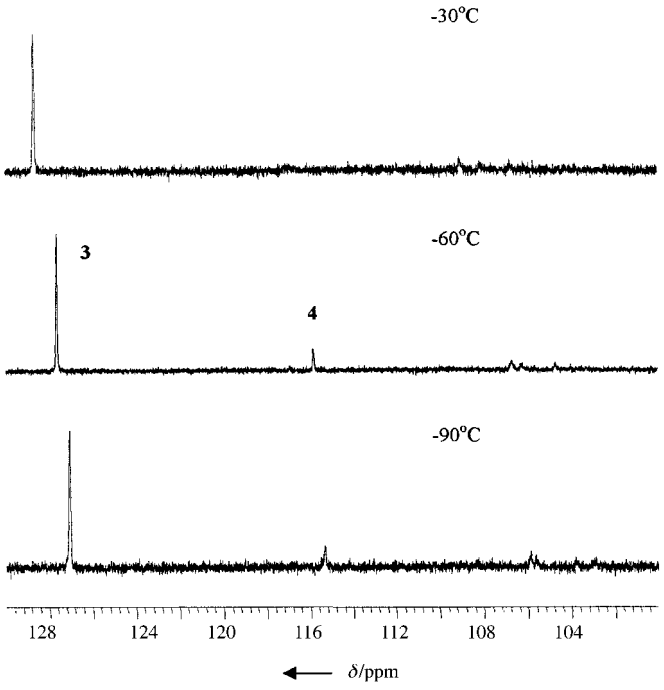
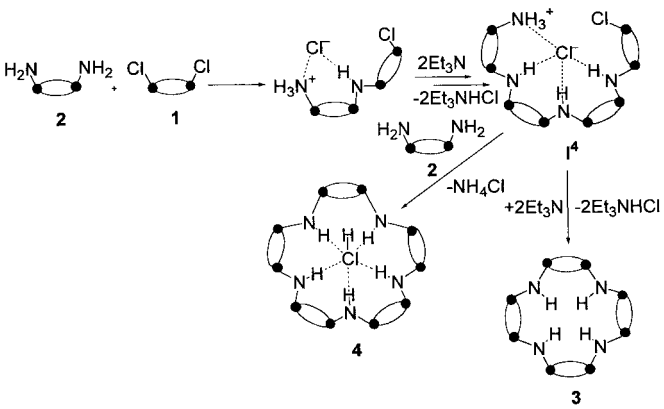


Figure 2. ^{31}P NMR spectroscopic study in THF, showing the effect of cooling crude **3** and the appearance of by-product **4**.

Mechanism of formation of 3 and 4: The mechanism of formation of **3** was assumed initially to follow a simple course, involving stepwise condensation of units of **1** and **2**. However, the formation and isolation of the pentameric backbone of **4** cannot be explained easily by a simple condensation process, which could only generate macrocycles containing an even number of P_2N_2 dimer units. Instead, we suggest a divergent mechanism by which the production of **3** and **4** are linked by a common intermediate. The key assumption of the mechanism shown in Scheme 2 is that the growing backbone of the



Scheme 2.

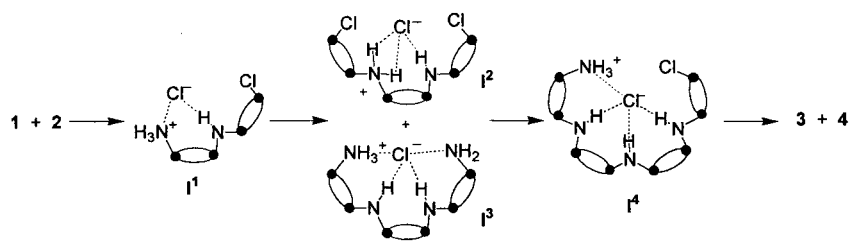
macrocycle is likely to be a highly effective trap for HCl generated by condensation of the NH_2 and Cl groups of **1** and **2** (thus competing with Et_3N as the Brønsted base). This mechanism introduces the possibility that templating by Cl^- may (in addition to pre-organisation of **1** and **2**) also play a role in the selectivity of the cyclisation reaction. The hydrogen bonding of the developing oligomer to Cl^- ultimately leads to the intermediate **I⁴** which terminates in an NH_3^+ and Cl group. Formation of **3** can readily be envisaged by the loss of HCl from intermediate **I⁴**, followed by ring closure in the presence of Et_3N. However, the formation of **4** can only occur by nucleophilic substitution of the NH_3^+ terminus by a further molecule of **2** (with the elimination of NH_4Cl).

^{31}P NMR spectroscopic studies of the cyclisation reaction under various conditions (see Experimental Section) provide good support for this mechanism. Significantly, ^{31}P NMR studies reveal that **4** is not obtained by an equilibration reaction of **3** with HCl or Et_3NHCl, nor is the incorporation of HCl into **3** observed. Thus, **3** and **4** are not in dynamic equilibrium under the reaction conditions involved. This is perhaps unsurprising, since equilibrium of this type would have to involve cleavage then reformation of thermodynamically stable P–N bonds. It therefore can be concluded that **3** and **4** arise from different or, more probably, divergent reaction pathways (like that shown in Scheme 2). One consequence of the mechanism shown in Scheme 2 should be that the formation of **4** is encouraged by a deficiency of Et_3N. The reaction of **1** and **2** (1:1 equivalents) in THF in the absence of Et_3N gives a complicated mixture of products containing little of the tetramer **3**. Instead, the pentamer **4** forms approximately 50% of the product mixture, together with other products whose resonances occur at about $\delta = 200$ and 140 ppm in the ^{31}P NMR spectrum. The latter resonances are absent in the ^{31}P NMR spectrum of the same reaction in the presence of Et_3N. The observation of extensive P–P coupling *between* these resonances shows that they are related. The major species appears as a pair of doublets; the J(P,P) coupling constant of 84.0 Hz is consistent with a two-bond interaction (i.e., P-N-P). The observed chemical shifts for these species (which can be compared to those of **1** ($\delta =$ 207.6 ppm) and **2** ($\delta = 100.2$ ppm)) lead us to speculate that the resonances at about $\delta = 200$ and 140 ppm arise from chain oligomers, containing NH_3^+ and Cl termini (e.g., **I¹** and **I⁴** in Scheme 3) or exclusively Cl termini (e.g., **I²** in Scheme 3). As the stoichiometric ratio of **2** to **1** is increased, the relative amount of tetramer **3** decreases with respect to the pentamer **4**. Now, however, the only by-products formed are found at about $\delta = 100$ ppm in the ^{31}P NMR spectra. Based on the observed chemical shifts of these species and the fact that they are generated in the presence of excess **2**, these species are probably chain oligomers possessing NH_2 and/or NH_3^+ termini (e.g., **I³** in Scheme 3).

Investigation of the reaction of **1** and **2** (1:1 equiv) in THF/Et_3N in the presence of an excess of LiCl (3 equiv) reveals that tetramer formation is suppressed and formation of the pentamer **4** is amplified under these conditions. This reaction leads to a final product mixture containing about 40% of the pentamer **4** and about 40% of the tetramer **3** (together with other unidentified products) (cf. 0.5–1% of **4** formed in the absence of LiCl). This amplification of the pentamer in the presence of excess chloride ions presumably results from the suppression of the dissociation of Cl^- anions from hydrogen-bonded chain intermediates (in particular, **I⁴** in Scheme 3). Further amplification of the pentameric host–guest complex occurs in the presence of excess LiBr or LiI. However, an additional resonance appears in the ^{31}P NMR spectra of the product mixtures at $\delta = 114.0$ ppm (LiBr) and $\delta = 113.9$ ppm (LiI), suggesting the incorporation of the Br^- and I^- ions into the pentameric macrocycle in these cases (presumably as LiX or HX; X = Br, I). Support of this comes from positive-ion electrospray mass spectrometry, which clearly shows the presence of $[\{P(\mu\text{-N}t\text{Bu})\}_2(\mu\text{-NH})]_5(Br)H_2]^+$ in the reaction involving LiBr. Most notably, the reaction of **1** and **2** (1:1 equiv) in the presence of Et_3N (ca. 10 equivalents) and LiI (10 equiv) in THF leads to a product solution containing about 70% of the presumed I-pentamer, together with the tetramer **3** and HCl-pentamer **4**. Performing the same reaction now in toluene as the solvent leads to the formation of the I-pentamer as the major product, together with a minor amount of **4** and several other minor unidentified species (at about $\delta = 250$, 155 and 78 ppm). No resonances due to **3** are observed. A section of the ^{31}P NMR spectrum, in the pentamer/tetramer region, is shown in Figure 4. The broad resonance underneath the resonances for **4** and the I-pentamer is believed to be due to exchange equilibrium between these two species.

In summary, the results of ^{31}P NMR spectroscopic studies show that 1) the presence of Et_3N is essential for the high yield formation of the tetramer **3**, 2) the ratio of tetramer to pentamer is dependent on the presence and concentration of halide ions (excess halide ions favouring the pentameric macrocyle), and 3) the solvent can be important to the distribution of the products.

X-ray structural studies: The low-temperature X-ray structures of **2**, **3** and **4** have been obtained. Since we have communicated the structure of **3** previously, only selected details of this compound will be provided here to aid comparison between these compounds. Details of the structural refinements and data collections on the new compounds **2** and **4** are given in Table 1. Table 2 and Table 3 list key bond lengths and angles for **2** and **4**, respectively.



Scheme 3.

The low-temperature X-ray structure of **2** (Figure 5) pro-

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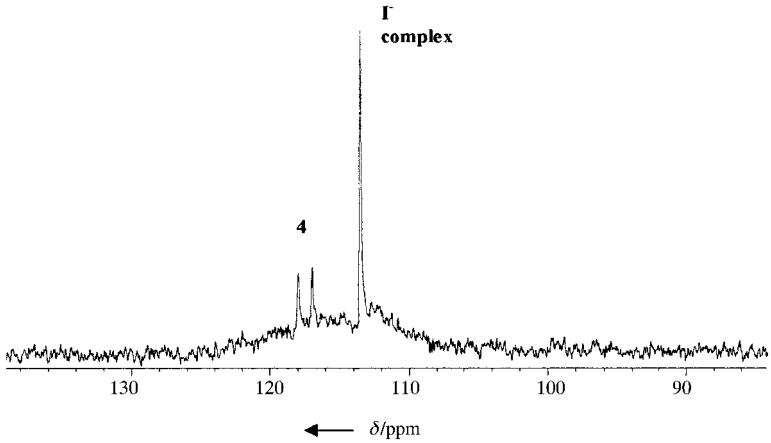

Figure 4. Product solution obtained from 1:1 reaction of **1** and **2** (in toluene/about 10 Et_3N) together with three equivalents of LiI.

Table 1. Details of the structural refinements and data collections of $[H_2NP(\mu\text{-}NtBu)]_2$ (**2**) and $[\{P(\mu\text{-}NtBu)\}_2(\mu\text{-}NH)]_5\cdot(HCl)\cdot 2THF$ (**4**·2THF).

Compound[a]	**2**	**4**
empirical formula	$C_8H_{22}N_4P_2$	$C_{48}H_{112}ClN_{15}O_2P_{10}$
M_r	236.24	1276.68
crystal system	triclinic	tetragonal
space group	$P\bar{1}$	$I4_1/amd$
a [Å]	7.9139(3)	21.5511(5)
b [Å]	9.3786(4)	21.5511(5)
c [Å]	9.9605(5)	29.9144(9)
α [°]	79.294(3)	90
β [°]	86.735(3)	90
γ [°]	73.754(3)	90
V [Å^3]	697.40(5)	13893.7(6)
Z	2	8
ρ_{calcd} [Mg m^{-3}]	1.125	1.221
total data	8023	21800
unique data (R_{int})	3164 (0.036)	3232 (0.064)
R indices ($F^2 > 2\sigma(F^2)$]	0.050, 0.140	0.061, 0.163
R indices (all data)	0.060, 0.148	0.082, 0.181
goodness of fit on F^2	1.07	1.05

[a] Data in common, $T = 180(2)$ K, $\lambda = 0.7107$ Å.

Table 2. Key bond lengths and angles for $[H_2NP(\mu\text{-}NtBu)]_2$ (**2**).[a]

Bond lengths [Å]			
P(1)–N(1)	1.656(2)	P(2)–N(4)	1.722(2)
P(1)–N(3)	1.747(2)	P(1)···P(2)	2.5936(8)
P(1)–N(4)	1.719(2)		
P(2)–N(2)	1.662(2)		
P(2)–N(3)	1.730(2)		
bond angles [°]			
N(1)-P(1)-N(3)	107.1(1)	N(3)-P(2)-N(4)	121.11(9)
N(1)-P(1)-N(4)	105.4(1)	P(1)-N(3)-P(2)	96.49(9)
N(3)-P(1)-N(4)	80.64(9)	P(1)-N(4)-P(2)	97.8(1)
N(1)-P(1)···P(2)	121.39(9)		
N(2)-P(2)-N(3)	103.5(1)		
N(2)-P(2)-N(4)	108.4(1)		
hydrogen bonds[a]			
D–H···A	H···A	D···A	D–H···A
N(1)-H(1N)···P(1)^{i}	2.82(4)	3.636(2)	149(3)
N(2)-H(4N)···P(2)^{iii}	3.11(3)	3.776(2)	145(3)
N(1)-H(2N)···N(2)^{iii}	2.55(4)	3.213(3)	135(3)
N(2)-H(3N)···N(3)^{iii}	2.66(4)	3.442(3)	152(3)

[a] Symmetry transformations used to generate equivalent atoms; I: $-x$, $-y$, $-z$; ii: $1-x$, $-y$, $1-z$; iii: $-x$, $-y$, $1-z$.

vides important further support for our hypothesis that almost quantitative formation of **3** is pre-organised by the preferred *cis* geometries of the precursors. Molecules of **2** contain puckered P_2N_2 ring units (the puckering angle being 157.2°); a common feature in the solid-state structures of *cis* dimers of the type $[XP(\mu\text{-}NR)]_2$[14] (the *trans* isomers having almost planar ring units[15]). Also akin to the majority of other previously characterised *cis* dimers is the displacement of the bridging *t*Bu substituents within the ring of **2** away from the more sterically hindered side of the molecule. The P–N bonds within this ring (range 1.719(2) – 1.747(2) Å) are typical of those found in related, symmetrical amido-phospha(III)zanes of the type $[R_2NP(\mu\text{-}NR')]_2$ (range 1.70 – 1.76 Å), as are the endocyclic P-N-P (mean 97.1°) and N-P-N (mean 80.8°) angles. The terminal P–N bonds to the *cis* NH_2 groups (mean 1.659 Å) are, not surprisingly, significantly shorter than the mean of 1.730 Å found within the P_2N_2 ring unit. Although a number of dimers of the type $[XP(\mu\text{-}NR)]_2$ have been structurally characterised,[14, 15] **2** is the first diamino dimer of this type. The most closely related species is the non-symmetrical amido compound $[tBuNHP(\mu\text{-}NR)_2PNH_2]$,[16] prepared in a similar way to **2**, by the reaction of NH_3 with the monochloride $[tBuNHP(\mu\text{-}NR)_2PCl]$. The cyclophosph(v)azene $[P(NH_2)_2N]_3$ is also worthy of mention.[17]

Table 3. Key bond lengths and angles for $[\{P(\mu\text{-}NtBu)\}_2(-NH)]_5(HCl)\cdot 2THF$ (**4**·2THF).[a]

Bond lengths [Å]			
P(1)–N(1)	1.744(3)	P(5)–N(6)	1.694(3)
P(1)–N(2)	1.687(4)	P(5)–N(5)	1.746(4)
P(2)–N(2)	1.689(4)	P···P in P_2N_2 rings	mean 2.618
P(2)–N(3)	1.753(3)		
P(3)–N(4)	1.684(4)		
P(3)–N(3)	1.748(3)		
P(4)–N(4)	1.685(4)		
P(4)–N(5)	1.747(3)		
bond angles [°]			
N(1)-P(1)-N(2)	104.2(2)	P(1)-N(2)-P(2)	120.9(3)
N(1)-P(1)-N(1A)	82.3(2)	P(3)-N(4)-P(4)	121.2(3)
N(3)-P(2)-N(2)	104.0(2)	P(5)-N(6)-P(5A)	121.4(4)
N(3)-P(2)-N(3A)	82.1(2)	P(1)-N(1)-P(1A)	97.2(2)
N(4)-P(3)-N(3)	104.9(2)	P(2)-N(3)-P(3)	97.0(2)
N(3)-P(3)-N(3A)	82.6(2)	P(4)-N(5)-P(5)	97.0(2)
N(4)-P(4)-N(5)	104.9(2)	puckering of P_2N_2 rings	mean 169.8
N(5)-P(4)-N(5A)	82.6(2)		
N(5)-P(5)-N(6)	104.6(2)		
N(5)-P(5)-N(5A)	82.7(2)		
hydrogen bonds			
D–H···A	H···A	D···A	D–H···A
N(2)-H(2N)···Cl(1)	2.56(1)	3.434(4)	175(5)
N(4)-H(4N)···Cl(1)	2.52(1)	3.398(4)	179(5)
N(6)-H(6N)···Cl(1)	2.55(1)	3.434(6)	180

[a] Symmetry transformations used to generate equivalent atoms: A: $-x+1$, y, z; B: x, $-y+1/2$, z.

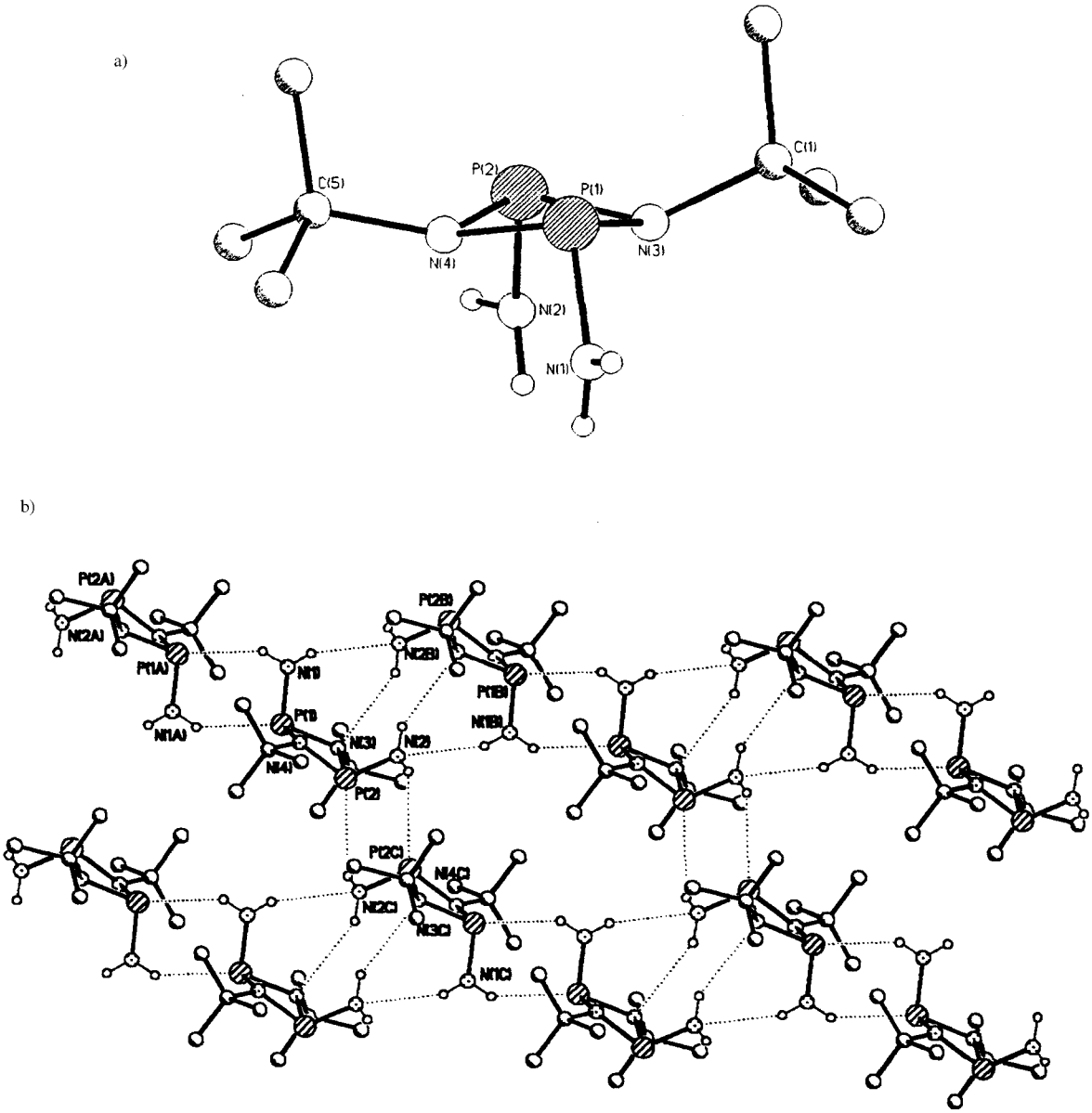

Figure 5. a) Structure of dimer molecules of **2**, b) formation of polymeric sheets through bifunctional hydrogen bonding.

Perhaps the most interesting feature of the solid-state structure of **2** is the association of the dimer units through hydrogen bonding. Molecules are linked by a combination of N–H···N and N–H···P hydrogen bonds into sheets (Figure 5b). These sheets are composed of dimer pairs associated into centrosymmetric cyclic units exclusively by N–H···N hydrogen bonds, between pairs of NH_2 groups (N(1)···N(2B) 3.213(3) Å {N(1)–H···N(2B) 2.55(4) Å}, N(1)–H···N(2B) 135(3)°) and NH_2 and bridging N*t*Bu groups (N(2B)···N(3) 3.442(3) {N(2B)–H···N(3) 2.66(4) Å}, N(2B)–H···N(3) 152(3)°). Adjacent units are then linked together, around inversion centres, by N–H···P hydrogen bonds (N(1A)···P(1) 3.636(2) Å {N(1A)–H···P(1) 2.82(4) Å}, N(1A)–H···P(1) 149(3)°, and N(2C)···P(2) 3.776(2) Å {N(2C)–H···P(2) 3.11(3)}, N(2C)–H···P(2) 145(3)°). The different use of the two NH_2 groups in hydrogen bonding in **2** (N(1) being an H-bond donor and N(2) being an H-bond donor *and* acceptor) explains the splitting of the N–H stretching vibrations in the IR spectrum in the solid state into two doublets centred at 3402 (symmetric) and 3291 cm^{-1} (asymmetric). In the related species [*t*BuNHP(μ-NR)$_2$PNH$_2$], the presence of a sterically demanding *t*BuNH group on one of the P centres prevents such (presumably weak) hydrogen bonding from occurring.[16] Only a few N–H···P^{III} intermolecular hydrogen-bonded compounds have previously been characterised in the solid state, the shortest H···P contacts in these species (range 2.81 – -2.87 Å)[18] are similar to the shortest contacts in **2**.

The structure of the tetrameric macrocycle [{P(μ-N*t*Bu)}$_2$(μ-NH)]$_4$ (**3**) (Figure 1) can be compared directly with the pentameric unit of **4** (Figure 6). Complex **4** is a host – guest adduct of the macrocycle [{P(μ-N*t*Bu)}$_2$(μ-NH)]$_5$ with HCl. The fifteen atoms forming the [(P···P)N]$_5$ macrocylic backbone of the pentameric [{P(μ-N*t*Bu)}$_2$(μ-NH)]$_5$ unit lie exactly in a plane. The arrangement of the five N–H groups towards the centre of the macrocycle creates a cavity of about 6.8 Å in diameter (with respect to the N atoms of the ring). This

  0947-6539/02/0815-3382 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 15

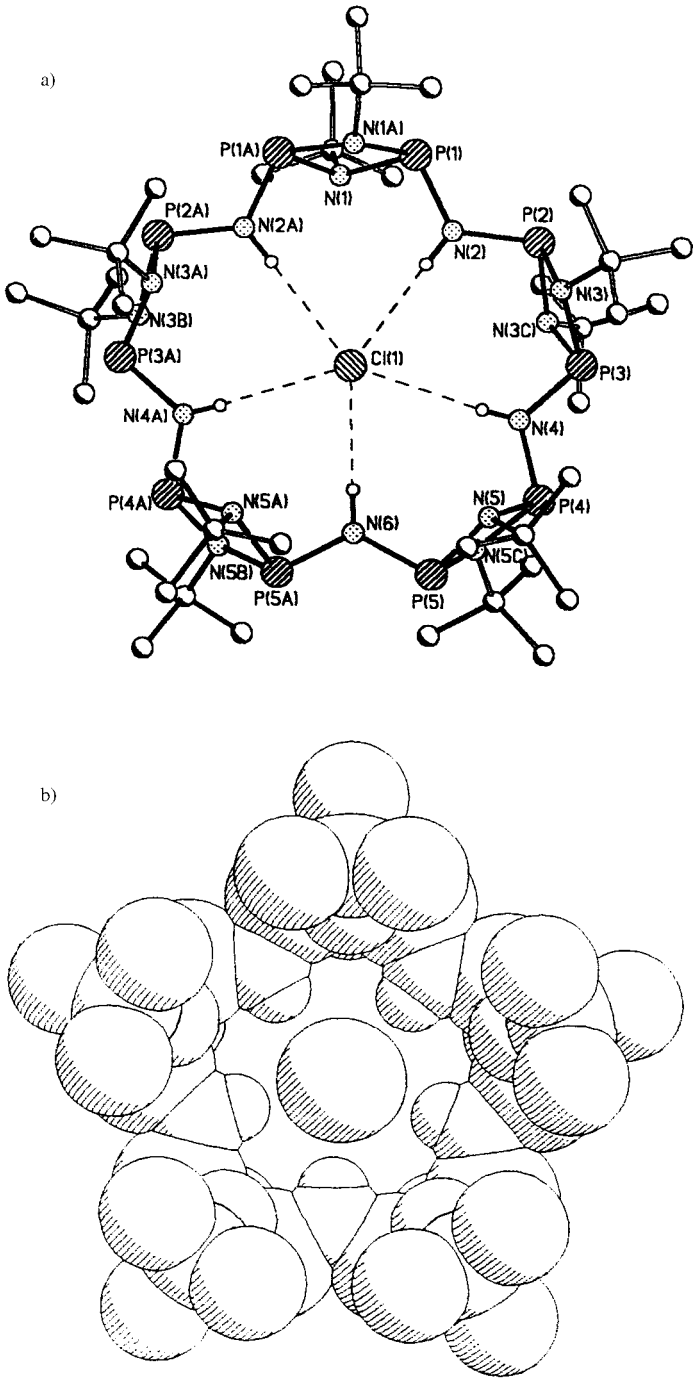

Figure 6. a) Structure of the pentameric, host–guest complex **4** (the disordered THF sites have been omitted for clarity), b) Space-filling diagram of the complex.

compares to a mean diameter of 5.22 Å for the cavity of the tetramer **3** (with respect to the N centres).[7, 19] The Cl^- ion of **4** is hydrogen-bonded to all five of the *endo* N–H protons within the macrocyclic cavity (H(2N) $\cdots$ Cl(1) 2.56(1) Å, H(4N) $\cdots$ Cl(1) 2.52(1), H(6N) $\cdots$ Cl(1) 2.55(1) Å).[20] Despite the location of the N–H protons in the Fourier difference map, the position of the H atom of the HCl monomer is uncertain. However, the sp^2-like geometry of the bridging N(-H) groups (P-N(2,4,6)-P mean of 121.2°) argues against the bonding of this proton to one of the bridging N–H groups (unless disordered over all five N–H positions). More likely is the bonding of this proton to the Cl^- ion (disordered above and below the crystallographic mirror plane of the macrocyle). The presence of two disordered THF ligands within the cavities created by the five *t*Bu groups above and below the Cl atom of **4** appears to add some support for the view that the HCl monomer is located at the centre of the macrocyclic ring, that is, with the proton available for potential (THF)O $\cdots$ H bonding. However, both O sites of the two disordered components of these THF ligands do not appear to be orientated appropriately for potential hydrogen bonding to the HCl proton. The structure of **4** is related to host–guest adducts of sapphyrins (expanded porphyrins),[21a] in particular the pentapyrrole HF complex $[\{3\text{-Me-4-Et-pyrNH}\}_5(CH_2)_4F][PF_6]$ (pyrN = pyrrole) which contains a similar arrangement of five N–H groups surrounding a central F^- ion.[21b] However, the core sizes in these complexes are significantly smaller than that in **4** (at about 5.5 Å in the pentaporphyrins, with respect to the five N centres).[21c]

The bond lengths and angles within the P_2N_2 ring units of **4** are similar to those found in **2** and **3** (P–N mean 1.748 Å, P-N-P mean 97.1°, N-P-N mean 82.5°; cf. 1.73 Å, 97.2° and 80.8°, and 1.72 Å, 98.0° and 81.4° for the corresponding mean values in **2** and **3**, respectively). In addition, the P–N bonds to the dimer-bridging N–H groups of **4** (mean 1.688 Å) are only slightly shorter than those found in the cyclic tetramer **3** (mean 1.703 Å). However, one significant difference between the pentameric unit of **4** and the tetramer **3** are the larger P-N-P *exo* angles at the N–H groups of **3** (mean 127.8°; cf. 121.2° in **4**). This may suggest that there is more ring strain in the tetramer **3** than in the pentamer **4**. There are also noticeable differences in the orientation of the *t*Bu groups with respect to the P_2N_2 ring units in both compounds, and in the geometries of their P_2N_2 ring constituents. In **4** (Figure 6), all of the *t*Bu groups are orientated away from the centre of the macrocyclic cavity and the P_2N_2 ring units are slightly folded about their N $\cdots$ N vectors (mean dihedral angle 169.8°). However, in **3** (Figure 1) the P_2N_2 ring units are planar and two opposite *t*Bu groups on each side of the macrocycle are in the planes of their P_2N_2 rings, while the other two are distorted out of the planes of their respective P_2N_2 rings. Presumably, this difference results from the inclusion of the THF ligands on either side of the cavity of **4** (forcing the *t*Bu groups outwards, with associated puckering of the P_2N_2 rings), and the greater steric congestion in the core of **3** (resulting in adjustment in the orientation of the *t*Bu groups).

The formation of pentameric **4** together with the tetrameric **3** is worthy of particular note. Zheng et al. have shown that ligand-controlled self-assembly of macrocyclic lanthanide (Ln) hydroxotyrosinato complexes containing $[Ln_3(\mu\text{-}OH)_4]_n$ cores can be achieved using different halide ions.[22] For example, the hydrolytic reactions of $Eu(ClO_4)_3$ with tyrosine and in the presence of added Cl^- ions gives a pentameric molecular framework (n = 5) containing a metal-bonded Cl^- ion within the macrocyclic cavity,[22a] whereas a similar reaction of $Dy(ClO_4)_3$ in the presence of I^- ions gives a tetrameric arrangement ($n = 4$) in which two I^- ions are accommodated above and below the cavity by O–H $\cdots$ I hydrogen bonding.[22b] Similar anion-templating effects have

also been reported by Müller et al. in regard to poly(oxovanadate) cages.[23] The 'kinetic-templating' effect observed by Hawthorne and co-workers in the formation of 'mercuracarborands' is perhaps more closely related to our current study, than those of lanthanide and vanadium oxo compounds.[2] The reaction of $[1,2\text{-}C_2B_{10}H_{10}]^{2-}$ with HgX_2 gives cyclic trimers $[\{1,2\text{-}C_2B_{10}H_{10}\}Hg]_3$ in the absence of a coordinating anion (e.g., X = AcO^-), whereas tetrameric, host–guest complexes $[(\{1,2\text{-}C_2B_{10}H_{10}\}Hg)X_n]_4^{n-}$ are obtained in the presence of coordinating anions (e.g., X = Cl, Br ($n=1$); X = I ($n=1$ or 2)).[2] The formation of the tetramer **3** and host–guest complex **4** is directly relevant to a number of macrocyclic organic receptor systems, in which the selection of a specific macrocyclic host can occur by the addition of anions, cations and neutral guest molecules.[24, 25] However, clearly in our case the formation of the tetrameric macrocycle is far more favourable than that of the pentamer, and (as revealed by ^{31}P NMR spectroscopic studies) there is in no sense a dynamic equilibrium between them.

Conclusion

The current study provides further support for the idea that selective formation of the tetrameric macrocycle **3** is preorganised by the favoured *cis* conformations of the precursors **1** and **2**. Compound **2** has an intricate sheet structure in the solid state, with a hydrogen-bonded architecture that is also a direct consequence of the *cis* conformation of the molecular building blocks. The formation of the pentameric HCl adduct **4** (along with **3**) suggests that a divergent mechanism is involved in the cyclisation reaction of **1** and **2**. The results of ^{31}P NMR spectroscopic studies on this reaction under various conditions show that the presence of Et_3N, halide ions and different reaction solvents has significant effects on the distribution of the products. Most significantly, the formation of pentameric host–guest adducts is encouraged in the presence excess halide ions, which presumably template the pentameric arrangement. In the light of these studies, further work on the applications of $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}NH)]_n$ macrocycles in the coordination of anionic and neutral hosts may be of interest.

Experimental Section

General: Compounds **1**, **2** and **4** are air- and moisture-sensitive. All the compounds **1**–**4** were handled on a vacuum and toluene were dried by distillation over sodium/potassium alloy prior to the reactions. PCl_3 was distilled immediately prior to use. Anhydrous $tBuNH_2$ was used as supplied (Aldrich). The products were isolated and characterised with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440 Elemental Analyser. Phosphorus analysis was carried out using spectrophotometric means. ^1H and ^{31}P NMR spectra were recorded on a Bruker WM 400 MHz spectrometer in dry deuterated THF or toluene (using the solvent resonances as the internal reference standard for ^1H and 85% H_3PO_4/D_2O for ^{31}P). The small-scale syntheses of **1**, **2** and **3** were reported in reference [7].

Large-scale synthesis of 1: Using the same conditions and method as previously reported in reference [7], the reaction of PCl_3 with $tBuNH_2$ can easily be scaled up using four times the amount of reagents and solvent, that is, dropwise (1 h) addition of $tBuNH_2$ (240 mL, 2.284 mol) to a solution of PCl_3 (66.4 mL, 0.76 mol) in THF (1.2 L) at −78 °C for 4 h. The yield is generally only slightly reduced compared to the lower scale reaction (ca. 60%, rather than 67%). It is extremely important, however, that the reaction is held at −78 °C for at least three hours after addition of the $tBuNH_2$ (otherwise significant amounts of [$tBuNHP(\mu\text{-}N)PCl$] are obtained). Efficient mixing of the reaction is essential.

Large-scale synthesis of 2: A saturated solution of NH_3 in THF and Et_3N (140 mL) was prepared by bubbling NH_3 gas through THF (1.5 L) at −78 °C (1.5 h). A solution of **1** (35.0 g, 127.4 mmol) in THF (450 mL) was added dropwise to this solution at −78 °C over the course of 2 h. The reaction mixture was stirred for a further 12 h at room temperature, before the solvent was removed under vacuum. The white powdery residue was extracted with *dry* *n*-pentane (4 × 500 mL) by filtration. The combined extracts were reduced in volume to about 250 mL (i.e., well past the point of initial precipitation of **2**) and the solid was then dissolved by addition of THF (12 mL) and persistent, careful heating. Storage at −5 °C (12 h) gave a first (major) batch of **2** as large crystalline needles. A further batch was obtained by further storage of the filtrate at −5 °C, after removal of about 100 mL of the solvent under vacuum. Yield over two batches 17.7g (58.5%). The slight modification of the original procedure of preparing the NH_3 solution in THF at −78 °C rather than at room temperature results in a significant (ca. 10%) increase in the yield.

Large-scale synthesis of 3: A solution of **1** (11.65 g, 43.37 mmol) in THF (200 mL) was added dropwise to a solution of **2** (10.00 g, 42.37 mmol) in THF (2 L) and Et_3N (70 mL) at −78 °C over the course of 2 h with stirring. The mixture was allowed to warm to room temperature after 3 h, and stirred for a further 12 h. The solvent was removed under vacuum and the dry, white residue was extracted with *n*-pentane (600 mL) using a Soxhlet extractor (20 h). The solvent was removed under vacuum. Yield 10.7 g (58%). The spectroscopic data were identical to that reported in reference [7].

Characterisation of 4: Compound **4** was obtained fortuitously as a principal byproduct in a large-scale synthesis of **3** (as described above). Since the complex is significantly less soluble than **3**, it can be separated by fractional crystallisation from pentane/THF (ca. 50 mg). Analytical and spectroscopic data for the complex were obtained: IR (Nujol, NaCl): $\tilde{\nu}=3583.5\ cm^{-1}$ (N–H str.); ^1H NMR (400.132 MHz, [D_8]toluene, 25 °C): $\delta=4.92$ (br. s, 5H), 3.58 (4H; CH_2O, THF), 1.51 (4H; CH_2CH_2, THF), 1.49 (s, 90H; *t*Bu); ^{31}P NMR ([D_8]toluene, +25 °C, 161.976 MHz, relative to 85% H_3PO_4/D_2O): $\delta=115.5$ (s, *intact* **4**), 117.3 (s, **4**-HCl) (relative intensity 4:1, respectively). Elemental analysis: calcd (%) for **4**: C 45.1, H 8.8, N 16.5, P 24.3, Cl 2.8; found: 45.0, H 8.6, N 15.0, P 21.8, Cl 2.5.

In situ ^{31}P NMR spectroscopic studies: To ensure full mixing and equilibration of reactions of **1** and **2** under various conditions, NMR samples were prepared from individual reactions using 0.42 mmol of **1** and **2** in THF or toluene (30 mL). Spectra were recorded on the product solutions using [D_6]acectone-filled capillaries inside the NMR tubes to obtain a lock. Ultra-dry LiCl, LiBr and LiI were acquired from Aldrich (99.99%).

X-ray crystallography: Crystals of **2** and **4** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture.[27] X-ray intensity data for all were collected by using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares on F^2.[28] One disordered solvate THF molecule per half molecule of **4** was located, in two orientations of equal occupancy. The amino hydrogen atoms were directly located in Fourier difference syntheses based on data with $\theta < 20°$. No suitable maximum could be located for the hydrogen atom of the HCl, which would be expected to be disordered above and below the mirror plane through the macrocycle ring. All other hydrogen atoms were included in idealised positions. CCDC-179900 (**2**) and CCDC-179901 (**4**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road CB2 1EZ, UK; fax (+44) 1223-336-033; or e-mail deposit@ccdc. cm.ac.uk).

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