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Cyclization of *C*-phosphorylated (P^{III}) arylformamidines to 3*H*-1,3-benzazaphospholes

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ABSTRACT

A synthesis of 3*H*-1,3-benzazaphospholes starting from *C*-phosphorylated P(III) arylformamidines has been developed. Electron-donating substituents were found to enhance markedly the rate of the cyclization, with substituents at the *meta* position having the greatest effect. A plausible mechanism of the cyclization was proposed based on DFT calculations.

1. Introduction

3*H*-1,3-Benzazaphospholes have been little studied, but represent a class of potential organophosphorus ligands. The main approach to 3*H*-1,3-benzazaphospholes is based on alkylation of 1*H*-1,3-benzazaphospholes, whose syntheses have been much better developed.[1] Thus, 1*H*-1,3-benzazaphospholes bearing hydrogen at the nitrogen atom are easily lithiated with *tert*-butyl lithium to give stable lithium phospholides. They can be alkylated at the phosphorus atom by soft electrophiles, such as alkyl halides providing 3*H*-1,3-benzazaphospholes. Bulkier substituents at position 2 facilitate the alkylation at the phosphorus atom.[2] It should be mentioned that 1*H*-1,3-benzazaphospholes are aromatic compounds, in contrast to 3*H*-1,3-benzazaphospholes.[3]

Some 3*H*-1,3-benzazaphospholes have been synthesized by the reaction of alkyl(aryl)dichlorophosphines with dilithiated aldimine prepared by treatment of phenyl isocyanide with *tert*-butyl lithium, but the method is limited exclusively to 2-*tert*-butyl derivatives.[4] Previously we showed that *C*-phosphorylated arylformamidine **4b**, prepared by the reaction of dimethylamine with *N*,*N*-dimethyl-*N*′-*p*-tolylcarbamimidoyldibromophosphine, transformed into the corresponding 3*H*-benzazaphosphole in vacuum distillation 123–125 °C/0.03 Torr.[5] The scope of the method was limited by the poor accessibility of *C*-phosphorylated arylformamidines of type **4** and for a long time remained unexplored. Further investigations became possible when a new and original method was found for the synthesis of P^{III}-phosphorylated *N*-arylformamidines bearing substituents both at the aromatic nucleus and at the phosphorus atom.[6]

The objective of the current work is an experimental and theoretical study of factors influencing the cyclization of *C*-phosphorylated *N*-arylformamidines to 3*H*-1,3-benzazaphospholes.

2. Results and discussion

To study the reaction in detail, a series of phosphorylated amidines **4** were prepared (Scheme 1), both with electron-donating and electron-withdrawing substituents at the benzene ring (compounds **4a**–**m**) and bulky substituents at the phosphorus atom (compounds **4n**–**p**). Detailed synthetic procedures are described in our previous work.[6] New compounds **2d**, **2f**–**2h**, **3d**, **3f**–**3h**, and **4d**, **4f**–**4h** were synthesized analogously. Their physical constants and

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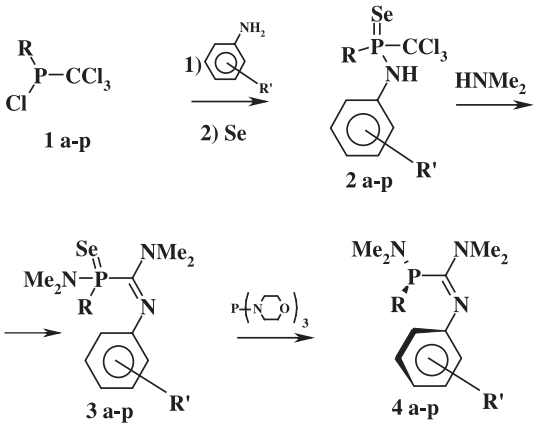
spectroscopic properties are given in the Experimental part. The list of synthesized compounds is given in Table 1.



Scheme 1. Synthesis of the starting materials **4a**–**p**.

Table 1
Substitution patterns in compounds **1**–**5**

Entry	R	R′	Entry	R	R′
a	NMe_2	H	**i**	NMe_2	3-Br
b	NMe_2	4-Me	**j**	NMe_2	3-OMe
c	NMe_2	4-OMe	**k**	NMe_2	3-NMe_2
d	NMe_2	4-NMe_2	**l**	NMe_2	3-CF_3
e	NMe_2	4-CF_3	**m**	NMe_2	2,3-$(CH)_4$
f	NMe_2	2-Me	**n**	5-IMID[a]	H
g	NMe_2	2-Cl	**o**	*t*-Bu	H
h	NMe_2	3-Me	**p**	1-Ad	H

[a] 2-Dimethylamino-1-methylimidazol-5-yl.

Compound **4b** was studied by single-crystal X-ray diffraction (Fig. 1). It exists in the solid state as the *Z*-isomer. The aromatic ring is rotated relative to the N1PN2 plane by 61.9°. While the C8–P1 bond is elongated (1.888 Å), the C8–N2 and C8–N1 bond lengths (1.365Å and 1.290Å, respectively) are typical for single and double bonds.

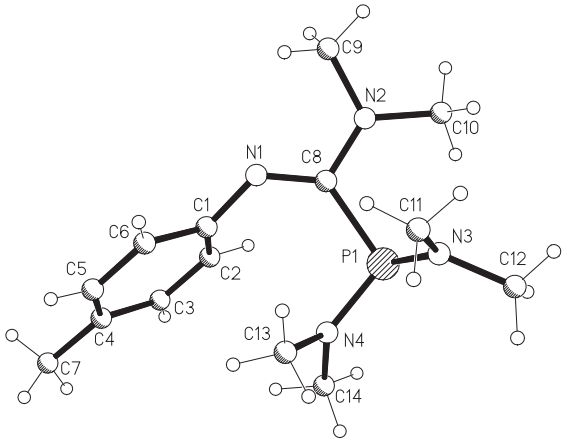
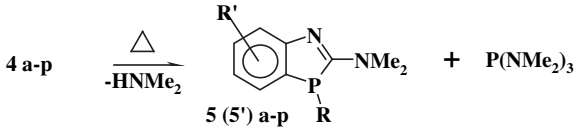


Fig. 1. Crystal structure of the amidine **4b**.

It was found that amidine **4k**, containing a Me_2N group at the *meta* position of the benzene ring, cannot be separated in pure form and cyclized spontaneously to **5k**. At 20 °C formation of **4k** can be monitored spectroscopically (δ_P=95.9 ppm), but after 10 min only the signal of the corresponding benzazaphosphole **5k** (δ_P=59.5 ppm) was present (Scheme 2). Other *C*-phosphorylated amidines **4**, with the exception of the naphthyl derivative **4m** (vide infra), are distilled in vacuo intact, and do not transform into 3*H*-1,3-benzazaphospholes.



Scheme 2. Synthesis of 3*H*-1,3-benzazaphospholes **5**.

Noteworthy, while the phenyl-derivative **4a** can be distilled without change, distillation of naphthyl-substituted amidine **4m** caused complete transformation into the corresponding benzazaphosphole **5m**. Thus, the ease of cyclization depends on the nature of the substituent and its position in the benzene ring.

To make a preliminary assessment of the propensity of *C*-phosphorylated arylformamidines **4** to cyclization, we heated their benzene solutions in a sealed tube at 170 °C, monitoring the reactions by ^{31}P NMR spectroscopy after 0.5 and 15 h. Amidines **4b** (4-methyl) and **4h** (3-Me) completely converted to **5b** and **5h**, respectively. In contrast, only partial transformation was found for isomer **4f** (2-methyl), probably because it has only one free *ortho* position at the benzene ring. In the most cases, along with the cyclization, a competitive reaction leading to the formation of hexamethylphosphorus triamide takes place (Scheme 2, Table 2).

Table 2
Ratio of signal intensities of $P(NMe_2)_3$ and compounds **5**+**5′** after heating **4** in a sealed tube at 170 °C

4→**5**,**5′**	0.5 h	15 h	**4**→**5**,**5′**	0.5 h	15 h
a	0/0	13/30	**h**	1/11	20/80
b	3/6	33/67	**j**	4/96	
c	0/0	21/64	**k**	0/100	
d	4/20	30/70	**l**	0/0	0/0
e	0/0	0/0	**m**	0/100	
f	0/0	15/48	**o**	0/0	0/0
g	0/0	36/42	**p**	0/0	0/0

The introduction of an electron-withdrawing trifluoromethyl group at the *para* or *ortho* positions of the benzene ring (compounds **4e**,**l**) hampers the cyclization. For instance, heating benzene solutions of amidines **4e**,**l** (4- and 3-CF_3) at 200 °C for 15 h does not afford even traces of benzazaphospholes **5e**,**l**.

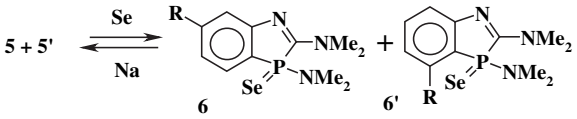
The results obtained allow us to rank the substituents in the following order by decreasing property to promote the cyclization: *m*-$Me_2NC_6H_4$>>α-naphthyl>*m*-$MeOC_6H_4$>*p*-$Me_2NC_6H_4$>*m*-MeC_6H_4>*p*-MeC_6H_4>*p*-$MeOC_6H_4$>*m*-BrC_6H_4>*o*-ClC_6H_4>*o*-MeC_6H_4>C_6H_5>>*p*-$F_3CC_6H_4$≈*m*-$F_3CC_6H_4$. Thus, with the exception of **5e**,**l**, heating amidines **4** in vacuum at 170 °C was found to be a convenient approach for the preparative synthesis of benzazaphospholes **5** (Table 3). All the isolated 2-dimethylamino-3*H*-1,3-benzazaphospholes **5** are bright yellow crystalline compounds, stable in an inert atmosphere. The structure and composition were proved by standard methods, such as ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

For *meta*-substituted amidines **4** the cyclization can afford mixtures of isomeric benzazaphospholes **5** and **5′**. As these compounds are moisture-sensitive, crude reaction mixtures were treated with selenium to afford the corresponding benzazaphosphole mixtures **6**+**6′**, which were separated chromatographically into the individual isomers. Thus, compounds **6h**, **6′h**, **6j**, **6′j**, **6′i**, **6l**, and **6′l** were isolated individually. Benzazaphospholes **6h**, **e**, **l** and **6′l** were reduced back to the pure benzazaphospholes **5** by boiling them with sodium in toluene (Scheme 3). Compounds **6′h** and **6j** were reduced by hexamethylphosphorus triamide.

Table 3
Reaction conditions and yields of benzazaphospholes **5**+**5′**

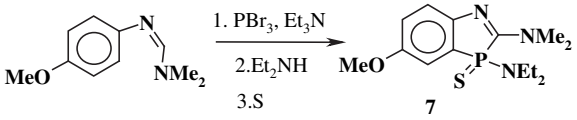
4	*T*, °C	Time, min	Pressure, Torr	Yield **5**+**5′**, % (ratio of 6 to 4 isomers)
a	220	30	150	76
b	220	20	150	88
c	200	20	20	83
d	200	10	20	78
e[a]	230	30	150	40
f	220	30	150	60
g	220	30	150	41
h	200	30	20	91 (1:1)
i	220	20	150	75 (1:2)
j	200	10	20	77 (10:1)
k	20	10	760	73
l[a]	230	30	150	56 (1:3)
m	150	10	0.2	89
n	200	10	20	61
o	250	1 h	150	0
p	250	1 h	150	0

[a] Experiments were carried out with catalytic amounts of salts (vide infra).



Scheme 3. Separation of isomers **5** and **5′**.

The corresponding sulfur derivative **7** was prepared by the one-pot method given in Scheme 4; its identity was confirmed by single-crystal X-ray investigation (Fig. 2). There are two independent molecules in the asymmetric unit, but these are closely similar (r.m.s. deviation of all non-H atoms is 0.16 Å overall and only 0.05 Å if ethyl and methyl groups are neglected). Molecular dimensions may be regarded as normal.



Scheme 4. Synthesis of benzazaphosphole **7**.

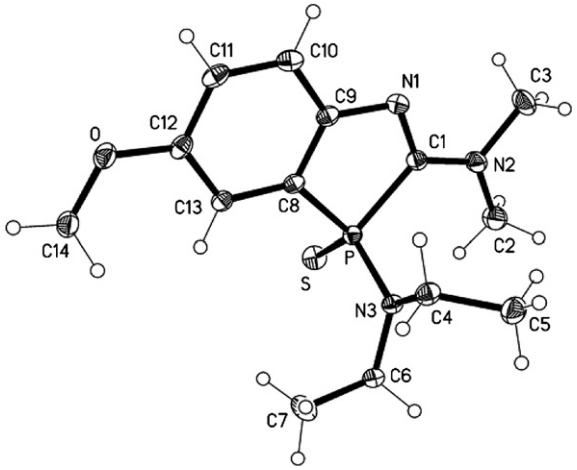
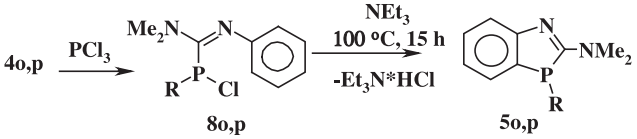


Fig. 2. Thermal ellipsoid representation (50% level) of one of the two independent molecules of compound **7** in the crystal. Bond lengths and angles at phosphorus for both independent molecules (Å,°): P–N(3) 1.6545 (15), 1.6452 (15), P–C(8) 1.792 (2), 1.797 (2), P–C(1) 1.865 (2), 1.8681 (19), P–S 1.9396 (7), 1.9408 (7); N(3)–P–C(8) 112.25 (8), 112.39 (8), N(3)–P–C(1) 106.19 (8), 107.04 (8), C(8)–P–C(1) 88.23 (9), 88.67 (9), N(3)–P–S 114.38 (7), 114.92 (6), C(8)–P–S 115.60 (6), 115.07 (6), C(1)–P–S 117.25 (6), 115.79 (6).

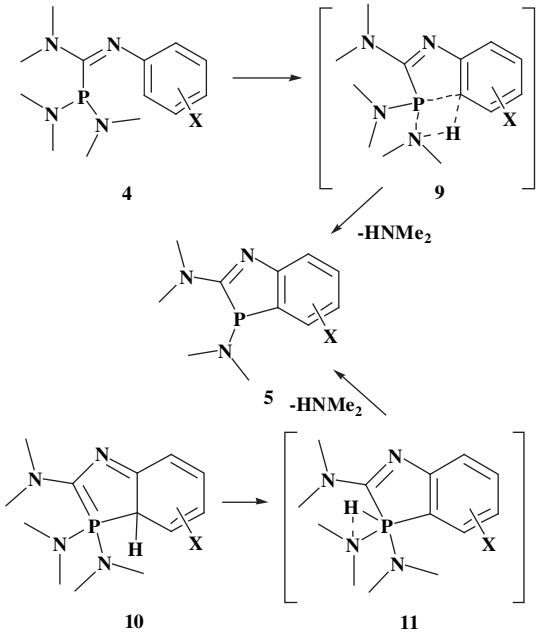


Scheme 5. Synthesis of benzazaphospholes **5o**,**p**.

The influence of steric effects at the phosphorus atom was studied by an example of amidines **4n**–**p**. Amidine **4n** bearing the electron-donating imidazol-2-yl substituent, undergoes a facile thermal cyclization. Thus, even its vacuum distillation is accompanied by a partial (9%) cyclization affording benzazaphosphole **5n**. In contrast, amidines **4o**,**p** bearing bulky substituents (*t*-Bu, 1-Ad) at the phosphorus atom do not give benzazaphospholes even on prolonged heating (250 °C/20 h). Compounds **4o**,**p** react with phosphorus trichloride affording chlorophosphines **8o**,**p**, which are viscous liquids, distillable at high vacuum. It is worth noting that compounds **8o**,**p** are the first known representatives of phosphorus acid chlorides bearing a *C*-formamidine residue. In a benzene solution in the presence of triethylamine these compounds undergo cyclization affording benzazaphospholes **5o**,**p** in 68% and 82% yields, respectively. The reaction proceeds probably via an S_N2-mechanism at the phosphorus atom.

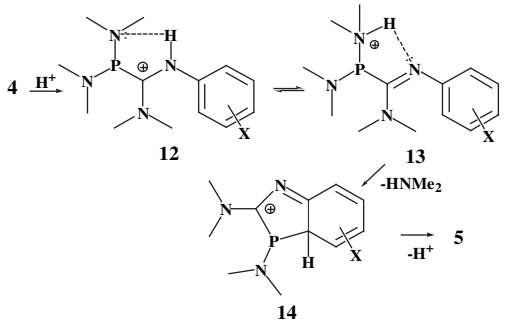
2.1. Theoretical investigation of the reaction

One of the most reliable methods of elucidating a mechanism of cyclization is the complete quantum-chemical investigation of a potential energy surface (PES) along the reaction pathway. Plausible cyclization routes for amidines **4** are given in Scheme 6. The formation of **5** is overall exothermic (Δ*E* for **5a**, **5k**, and **5l** are −10.0, −11.2, and −9.4 kcal/mol, respectively, approximation level II, see Details of Calculations). The absence of major differences in the Δ*E* values indicates that the rate of the cyclization is probably determined not by thermodynamic stability of the final reaction products, but by the different activation energies in the cyclization reactions. In particular, for considered concerted cyclization process, the P–C^{arom} bond is formed with the elimination of dimethylamine (Scheme 6). According to our calculations, such a pathway implies high activation energies for transition states **9**. Moreover, the activation energies in cases **9a**



Scheme 6. Some mechanisms suggested for cyclization of **4**.

(X=H) and **9k** (X=NMe_2) are almost equal (55.2 and 55.4 kcal/mol, respectively), which do not agree with the different reaction rates found for **4a** and **4k**. The reaction via the intermediary cyclic product **10** (X=H) is unlikely because **10** does not correspond to a real energy minimum on the PES. Proton transfer from the carbon atom to the phosphorus atom leading to structure **11** (X=H) is also characterized by very high activation energy (58.6 kcal/mol). The only possibility that excludes high activation energies is protonation of the nitrogen atom at the bis(dimethylamino)phospino group with the formation of intermediary products **13**, followed by elimination of dimethylamine and cyclization (Scheme 7).



Scheme 7.

It should be noted that the proton transfer reaction proceeds with a low activation energy (see Supplementary data) and the products **13** are only slightly less favorable compared to derivatives **12** (by 2.5 kcal/mol for X=NH_2 and 1.2 kcal/mol for X=H) and are characterized by almost identical total energies for X=CF_3. Thus, **13** can be considered as the first intermediate structure in the studied cyclization reaction.

2.2. Cyclization mechanisms

Our calculations indicate that cleavage of dimethylamine from protonation products **13** and the subsequent cyclization to the intermediate cyclic cations **14** (reaction (1)) are overall endothermic reactions. However, it should be noted that cyclization of **13k** into **14k** (X=NMe_2) requires considerably less energy (ΔE^1=+8.0 kcal/mol), than in the formation of **14a** (X=H) and **14l** (X=CF_3) (Fig. 3) with the endothermic reaction energy values 21.8 and 24.0 kcal/mol, respectively (the detailed quantitative description of the two-step cyclization reaction of **13a** the reader can find in the Supplementary data).

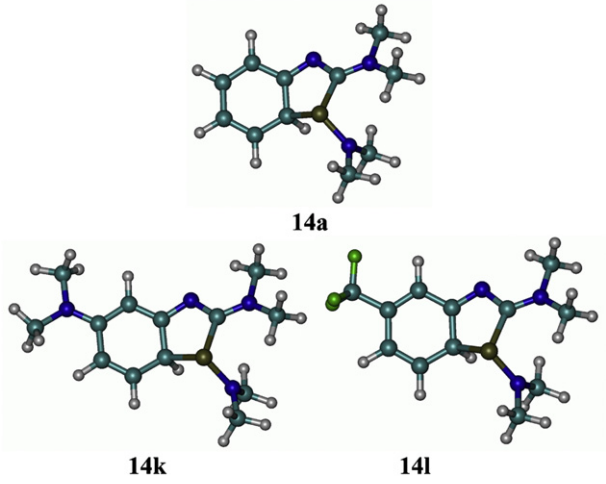
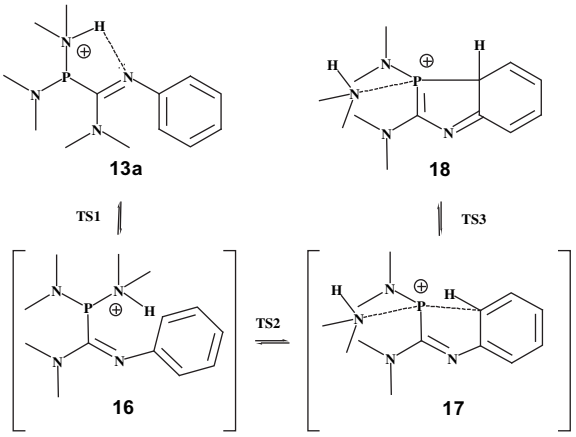


Fig. 3. VMD views for optimized (RI-BP86/TZVP) structures **14a**, **14k**, and **14l**.

$$\mathbf{13} \rightarrow \mathbf{14} + Me_2NH + \Delta E^1 \quad (1)$$

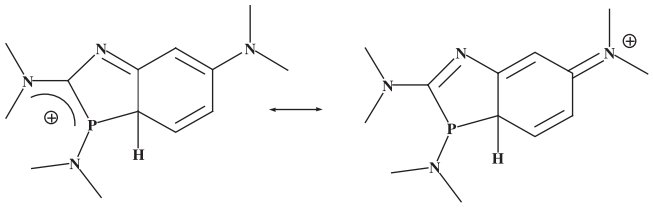
We have investigated the cyclization by a concerted mechanism calculating total energy values for **13a** along the IRC. Shortening the C^{ipso}–P distance is accompanied by increasing the P–$NHMe_2$ distance, forming the cyclic structure **18**, a loosely bound complex of **14a** with dimethylamine (Scheme 8). Probably, the reaction begins with inversion around the imine nitrogen atom with the formation of the isomeric cation **16** (see Supplementary data for more structural details and total energy values). Cation **16**, which can also be considered as a phosphenium cation **15a** stabilized by a molecule of dimethylamine, converts into a more stable form **17**, where the π-system of the aromatic ring formally donates into the vacant p-orbital at the phosphorus atom. The corresponding transition state **TS2** possesses the highest total energy at the reaction coordinate (+24.0 kcal/mol for **13a**, calculation level II), and in fact corresponds to the P–N bond dissociation. Finally, the last stage is the cyclization with the formation of **18**. The corresponding transition state **TS3** is 16.7 kcal/mol higher in energy with respect to **13a**. Thus, according to the calculations, the cyclization process of **13a** is accompanied by a gradual weakening of the P–N bond until it completely dissociates. Then **18** loses a dimethylamine molecule giving the cyclic cation **14** (Scheme 7). According to calculations based on the total energy values and ignoring the influence of the entropy factor, this process also seems to be slightly endothermic (ΔE^3=3.3 and 7.4 kcal/mol). The shift of the reaction equilibrium to the right is probably promoted by the removal of gaseous dimethylamine from the reaction mixture by heating under reduced pressure.



Scheme 8. Concerted mechanism of cyclization.

Cyclization products **14** (Fig. 3) are characterized by a mutual cis-orientation of the hydrogen atom in the six-membered ring and the dimethylamino group at the phosphorus atom (the corresponding trans-isomers are less stable by 2.3–2.6 kcal/mol). It should be noted that **14a**, **14k**, and **14l** are markedly different in C^{ipso}–P bond length (C^{ipso} indicates the carbon atom, attacked by or bound to the phosphorus atom). The shortest C^{ipso}–P distance has been found for **14k** (1.982 Å), which is, however, still noticeably longer than the corresponding value in the final product **5k** (1.834 Å).

On going to **14a** and **14l** the C^{ipso}–P bond elongates even more (to 2.056 and 2.067 Å, respectively). In the last two cyclic cations the positive charge is to a greater extent localized on the phosphorus atom, and they can be better represented as donor–acceptor complexes of aminophosphenium cations with the π-system of the aromatic ring. In contrast, the experimentally observed easy cyclization of **4k** we refer to the high relative stability of the intermediate cyclic cation **14k**, that is probably referred to the mesomeric equilibrium shown in Scheme 9.



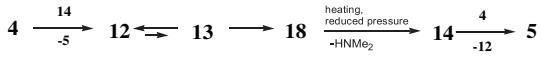
Scheme 9. Stabilization of **14k**.

2.3. Acid catalysis

As noted above, for the initiation of the reaction protonation of amidine **4** is necessary. Probably, traces of acid are present in the solution, for example, as dimethylammonium salts (reaction (2)).

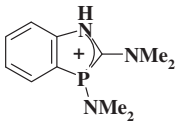
$$\mathbf{4} + Me_2NH_2^+ \rightarrow \mathbf{12} + Me_2NH + \Delta E^2 \quad (2)$$

The protonation proceeds most easily for **12k** (ΔE^2=−26.0 kcal/mol), then the exothermicity consistently decreases in going to **12a** (ΔE^4=−20.6 kcal/mol) and **12l** (ΔE^4=−15.7 kcal/mol). Therefore, all amidines **4** are stronger bases than dimethylamine. For facilitating the reaction it is important that the cyclic products **14a**,**k**,**l** are weaker bases than the corresponding amidines **4a**,**k**,**l**. The latter are exothermically protonated by the former initiating a new cycle of cyclization. The complete process is depicted in Scheme 10.

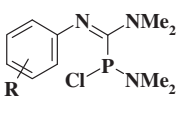


Scheme 10.

In contrast to the reaction with the dimethylammonium cation, the greatest exothermic effect was observed in the case of deprotonation of **14l** by amidine **4l** (−25.2 kcal/mol), and the smallest effect for the pair **14k** and **4k** (−13.7 kcal/mol). Reaction of **14a** with **4a** leading to the formation of **13a** and **5a** is characterized by the intermediate ΔE^2 value (−22.8 kcal/mol). The observed trend is not unexpected and determined by the relative stabilities of cyclic intermediates **14**: the most stable is **14f** and the least stable is **14l**. An additional remark should be made about Scheme 9. Deprotonation of the CH proton can also proceed via cyclic salt **19**, which is the protonated form of **5a** and is significantly (by 21.1 kcal/mol) more stable than **14a**. Therefore, the former can stand as an intermediate in the studied cyclization processes.



19a



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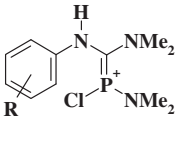

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2.4. Cyclization of 4b,e,l in the presence of ammonium salts

Taking into account the proposed reaction mechanism discussed above, we decided to study the cyclization of amidines **4** to benzazaphospholes **5** in the presence of catalytic amounts of triethylamine salts of hydrochloric and triflic acids. Heating a mixture of amidine **4b** and triethylammonium chloride or triethylammonium triflate (5 mol %) in benzene at 170 °C resulted in formation of benzazaphosphole **5b** already in 2–5 min. In the both cases the ratio of hexamethylphosphorus triamide to benzazaphosphole was the same as in the experiments without catalyst (Table 2). While amidines **4e**,**l** (4- and 3-CF_3) do not cyclize without addition of the salts (vide supra), the rate of the cyclization on heating them neat with the salts at 170 °C strongly depends on the nature of the anion. The formation of benzazaphospholes **5e** (4-CF_3) and **5** (**5′**)**l** (3-CF_3) was complete in 10 h for the chloride salt and in 10 min/5 min for the triflate salt. We therefore postulate different catalytic effects for these salts. The reaction can be accelerated by the substitution of the dimethylamino group with the nucleophilic chloride anion forming intermediary phosphorus chlorides of type **8** (Scheme 5) or product of its protonation **20**. As it was already mentioned above, the most energy-consuming step in the cyclization of **4** is the elimination of dimethylamine. Similarly to **4a** and **12a**, no direct cyclization pathways have been found for **8a** and **20a**, therefore the P–Cl bond dissociation is again an obliged reaction stage. The direct comparison of **12a** (**12**, X=H) and **20a** as the reactants yielding **14a**, demonstrates no thermodynamic advantages for HCl elimination (Eq. 3, ΔE^3=26.8 kcal/mol, Level I) compared to dimethylamine as leaving group (Eq. 4, ΔE^4=25.9 kcal/mol). Therefore, using triethylammonium chloride as the catalyst, the formation of benzazaphospholes is mainly accelerated by increasing of the corresponding protonated forms **12** and **13**.

$$\mathbf{20a} \rightarrow \mathbf{14a} + HCl + \Delta E^3 \quad (3)$$

$$\mathbf{12a} \rightarrow \mathbf{14a} + Me_2NH + \Delta E^4 \quad (4)$$

The increased reactivity of **4e**,**l** in the cyclization reaction by using ammonium triflate as a catalyst, can be explained by more pronounced dissociation of the P–O bond resulting from the high stability of the isolated triflate anion in nonpolar solvents, such as benzene. In this case a reactive phosphenium cation[7] is formed. The positively charged phosphorus attacks the electron-rich carbon atom in the aromatic ring resulting in the cyclic products **14**. A similar mechanism we recently envisaged for the formation of tris[2-(dimethylamino)-1-methyl-1*H*-imidazol-5-yl] phosphine selenide.[8]

3. Conclusion

We have developed a convenient approach to 3*H*-1,3-benzazaphospholes starting from readily available *C*-phosphorylated arylformamidines. The proposed method allows varying substituents both at the aryl ring and at the phosphorus atom. It has been shown that electron-donating substituents, especially at the *meta* position of the aromatic ring, markedly enhance the cyclization, whereas electron-withdrawing substituents hampers the reaction. Sterically demanding substituents at the phosphorus atom also have a negative effect on the cyclization. The first representatives of chlorophosphines bearing a formamidine substituent were synthesized. These compounds can also be used for the synthesis of 3*H*-1,3-benzazaphospholes. Quantum chemical calculations let us to leave out the direct cyclization pathways for amidines **4** and to propose an acid catalyzed concerted mechanism proceeding via intermediate cyclic cations. The addition of ammonium chloride or triflate to the reaction mixtures significantly increases the cyclization rate due to the higher concentration of the protonated forms of **4** and (in the case of triflate) by intermediary formation of highly reactive phosphenium cation which further cyclizes to benzazaphosphole **5**.

3.1. Calculation details

All the structures corresponding to the energy local minima were fully optimized without symmetry constraints using the TURBOMOLE 6.02 program packet[9] The RI-BP86//TZVP approach[10,11] was

used for geometry optimization. The used TZVP bases were the variant of TZV triple-zeta basis sets[12] extended by adding polarization functions. This approximation is noticed in the text as Level I. A fine SCF convergence criterion (SCFConv=1.0×10^{-8} Hartree) was used for the geometry optimization. The finest grids were used for all calculations (grid=5). Cartesian coordinates for all optimized structures are collected in the Supplementary data. The vibration frequencies calculated numerically checked the optimized structures to be the real minima in energy. All the IRC calculations were carried out using the GAUSSIAN-03 program set[13] within the DFT approximation. A hybrid functional B3LYP[14,15] was chosen, in combination with the 6-31G* basis sets[16] (Level II). The loose geometry convergence and middle integration grid was used for a higher performance. All the transition states were localized at approximation Level II using the structures derived from the IRC calculations, corresponding to energy maxima, as starting geometries. The tight optimization convergence criteria and fine grid (Int=UltraFine) were used for the calculations. For comparison, all the local minima structures were recalculated using approximation Level II. The calculations of the molecular vibrations were performed using Level II, calculating analytically the first and second derivatives. These calculations yielded no imaginary vibration for the local minima and one imaginary vibration for every transition state. The program VMD[17] was used for the graphical presentation of the optimized structures.

4. Experimental section

4.1. General

Syntheses and spectral characteristics of compounds **2a**–**c**,**e**,**i**–**h**; **3a**–**c**,**e**,**i**–**h**; **4a**–**c**,**e**,**i**,**j**,**l**–**h** are given in our previous work.[6] Previously unknown compounds **2d**, **f**–**h**, **3d**, **f**–**h**, and **4d**, **f**–**h** were synthesized by analogy.

*4.1.1. N′-[4-(Dimethylamino)phenyl]-N,N-dimethyl-P-(trichloromethyl)phosphonoselenoic diamide **2d**.* Yield 75%, white crystals, mp 95–96 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (2H, d, J=9.0 Hz, 2,6-H), 6.71 (2H, d, 3,5-H), 4.88 (1H, d, J=11.4 Hz, NH), 3.09 (6H, d, J=10.5 Hz, $PNMe_2$), 2.91 (6H, s, 4-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.83, 127.65, 122.84 (d, J=5.0 Hz), 113.59, 99.0 (d, J=62.8 Hz), 41.02, 39.95(d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 72.8. MS (APCI): m/z=408 [M+1]. [Found: C, 32.13; H, 4.09; N, 10.25; P, 7.72. $C_{11}H_{17}Cl_3N_3PSe$ requires C, 32.42; H, 4.20; N, 10.31; P, 7.60].

*4.1.2. N,N-Dimethyl-N′-(2-methylphenyl)-P-(trichloromethyl)phosphonoselenoic diamide **2f**.* Yield 83%, white crystals, mp 111–113 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (1H, d, J=8.4 Hz, 3-H), 7.21–7.16 (2H, m, 5,6-H), 7.00 (1H, dt, J=7.5, 1.2 Hz, 4-H), 5.11 (1H, d, J=11.0 Hz, NH), 3.09 (6H, d, J=10.5 Hz, $PNMe_2$), 2.29 (3H, s, 2-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.03, 130.89, 127.56 (d, J=8.8 Hz), 127.13, 123.39, 119.00 (d, J=3.8 Hz), 99.01 (d, J=65.4 Hz), 39.89 (d, J=5.0 Hz), 17.65; ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.8. MS (APCI): m/z=408 [M+1]. [Found: C, 31.83; H, 3.92; N, 7.25; P, 8.10. $C_{10}H_{14}Cl_3N_2PSe$ requires C, 31.73; H, 3.73; N, 7.40; P, 8.18].

*4.1.3. N′-[2-Chlorophenyl]-N,N-dimethyl-P-(trichloromethyl)-phosphonoselenoic diamide **2g**.* Yield 69%, white crystals, mp 90–91 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (1H, dd, J=8.1, 1.5 Hz, 3-H), 7.39 (1H, dd, J=8.1, 1.5 Hz, 6-H), 7.24 (1H, dt, J=8.1, 1.5 Hz, 5-H), 6.99 (1H, dt, J=7.8, 1.2 Hz, 4-H), 6.04 (d, 1H, J=10.8 Hz, NH), 3.08 (6H, d, J=10.8 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.76, 129.52, 127.82, 123.55 (d, J=8.8 Hz), 123.34, 118.52 (d, J=4.0 Hz), 98.47 (d, J=67.9 Hz), 39.8 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 70.0. [Found: C, 27.30; H, 2.96; N, 7.05; P, 7.82. $C_9H_{11}Cl_4N_2PSe$ requires C, 27.10; H, 2.78; N, 7.02; P, 7.76].

*4.1.4. N,N-Dimethyl-N′-(3-methylphenyl)-P-(trichloromethyl)phosphonoselenoic diamide **2h**.* Yield 93.6%, white crystals, mp 119–120 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (1H, t, J=7.50 Hz, 5-H), 6.94–6.90 (3H, m, 2,4,6-H), 5.12 (1H, d, J=11.0 Hz, NH), 3.10 (6H, d, J=10.5 Hz, $PNMe_2$), 2.36 (3H, s, 3-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.42, 138.49, 129.29, 124.10, 120.24 (d, J=7.5 Hz), 116.33 (d, J=6.3 Hz), 98.75 (d, J=65.4 Hz), 39.83 (d, J=4.0 Hz), 21.60; ^{31}P NMR (81 MHz, $CDCl_3$) δ 70.2. MS (APCI): m/z=377 [M−1]. [Found: C, 31.86; H, 3.86; N, 7.45; P, 8.09. $C_{10}H_{14}Cl_3N_2PSe$ requires C, 31.73; H, 3.73; N, 7.40; P, 8.18].

*4.1.5. 1,1-Bis(dimethylamino)-N′-[4-(dimethylamino)phenyl]-N,N-dimethyl phosphinecarboximidamide selenide **3d**.* Yield 94%, yellow crystals, mp 88–89 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (2H, d, J=7.0 Hz, 2,6-H), 6.68 (2H, d, J=6.5 Hz, 3,5-H), 2.89 (6H, s, $CNMe_2$), 2.84 (6H, s, 4-NMe_2), 2.80 (12H, d, J=10.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.85 (d, J=153.4 Hz), 146.40, 140.20 (d, J=21.4 Hz), 121.58, 113.36, 41.32, 41.19 (d, J=2.5 Hz), 38.1 (d, J=1.25 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 67.5. MS (APCI): m/z=390 [M+2]. [Found: C, 46.13; H, 7.43; N, 17.95; P, 8.10. $C_{15}H_{28}N_5PSe$ requires C, 46.39; H, 7.27; N, 18.03; P, 7.98].

*4.1.6. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(2-methylphenyl) phosphinecarboximidamide selenide **3f**.* Yield 95%, light yellow crystals, mp 86–87 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10–7.05 (2H, m, 3,5-H), 6.84 (1H, t, J=7.0 Hz, 4-H), 6.64 (1H, d, J=7.5 Hz, 6-H), 2.83 (12H, d, J=11.0 Hz, $PNMe_2$), 3.84 (6H, s, $CNMe_2$), 2.18 (3H, s, 4-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.96 (d, J=150.9 Hz), 149.20 (d, J=21.4 Hz), 129.92, 127.96, 125.81, 121.59, 119.16, 40.93 (d, J=4.0 Hz), 38.12 (d, J=2.5 Hz), 18.92; ^{31}P NMR (81 MHz, $CDCl_3$) δ 66.2. MS (APCI): m/z=361 [M+2]. [Found: C, 46.53; H, 6.92; N, 15.35; P, 8.40. $C_{14}H_{25}N_4PSe$ requires C, 46.80; H, 7.01; N, 15.59; P, 8.62].

*4.1.7. N′-(2-Chlorophenyl)-1,1-bis(dimethylamino)-N,N-dimethyl-phosphinecarboximidamide selenide **3g**.* Yield 79%, light yellow crystals, mp 77–78 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (1H, d, J=8.0 Hz, 3-H), 7.12 (1H, t, 5-H), 6.84 (1H, t, J=7.5 Hz, 6-H), 6.80 (1H, d, J=8.0 Hz, 4-H), 2.91 (6H, s, $CNMe_2$), 2.83 (12H, d, J=11.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.43 (d, J=145.9 Hz), 147.81 (d, J=20.1 Hz), 129.25, 126.77, 124.68, 122.12, 121.44, 40.80 (d, J=2.5 Hz), 38.25 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 66.4. [Found: C, 41.03; H, 6.02; N, 14.35; P, 8.10. $C_{13}H_{22}ClN_4PSe$ requires C, 41.12; H, 5.84; N, 14.75; P, 8.16].

*4.1.8. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(3-methylphenyl) phosphinecarboximidamide selenide **3h**.* Yield 90%, light yellow crystals, mp 104–105 °C (pentane); IR (KBr) 2880, 1573, 1480, 1437, 1222, 1179, 1148, 972, 691, 601 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (1H, t, J=7.5 Hz, 5-H), 6.71 (1H, d, J=7.5 Hz, 6-H), 6.58 (1H, s, 2-H), 6.56 (1H, d, J=7.5 Hz, 4-H), 2.87 (6H, s, $CNMe_2$), 2.79 (12H, d, J=11.8 Hz, $PNMe_2$), 2.29 (3H,s, 3-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.48 (d, J=148.4 Hz), 149.97 (d, J=20.1 Hz), 138.09, 128.22, 122.29, 121.03, 117.39, 41.30 (d, J=2.5 Hz), 38.1 (d, J=4.0 Hz), 21.5; ^{31}P NMR (81 MHz, $CDCl_3$) δ 66.6. MS (APCI): m/z=361 [M+2]. [Found: C, 46.39; H, 7.09; N, 15.45; P, 8.36. $C_{14}H_{25}N_4PSe$ requires C, 46.80; H, 7.01; N, 15.59; P, 8.62].

*4.1.9. 1,1-Bis(dimethylamino)-N′-[4-(dimethylamino)phenyl]-N,N-dimethylphosphinecarboximidamide **4d**.* Yield 93%, yellow oil, bp 155–157 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.06 (2H, d, J=9.0 Hz, 2,6-H), 6.77 (2H, d, J=9.0 Hz, 3,5-H), 2.87 (6H, s, 4-NMe_2), 2.71 (6H, s, $CNMe_2$), 2.65 (12H, d, J=7.5 Hz, $PNMe_2$); ^{13}C NMR

(125 MHz, C_6D_6) δ 162.50 (d, J=23.9 Hz), 145.6, 142.8 (d, J=2.5 Hz), 121.36 (d, J=2.5 Hz), 113.8, 41.64 (d, J=15.0 Hz) 41.32, 39.75 (d, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.5. [Found: C, 58.13; H, 9.33; N, 22.55; P, 10.10. $C_{15}H_{28}N_5P$ requires C, 58.23; H, 9.12; N, 22.64; P, 10.01].

4.1.10. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(2-methylphenyl) phosphinecarboximidamide ***4f***. Yield 94%, light yellow oil, bp 140–143 °C/0.05 Torr; ^{1}H NMR (300 MHz, C_6D_6) δ 7.11 (1H, d, J=7.5 Hz, 3-H), 7.06 (1H, t, J=7.2 Hz, 5-H), 6.80 (1H, t, 4-H), 6.72 (1H, d, J=7.5 Hz, 6-H), 2.68 (6H, br s, $CNMe_2$), 2.51 (12H, d, J=8.7 Hz, $PNMe_2$), 2.26 (3H, s, 2-Me); ^{13}C NMR (125 MHz, C_6D_6) δ 161.21 (d, J=22.6 Hz), 150.68 (d, J=1.3 Hz), 129.68, 127.59, 126.96, 119.96, 119.75, 41.29 (d, J=15.1 Hz), 39.21 (d, J=8.8 Hz), 18.99; ^{31}P NMR (81 MHz, C_6D_6) δ 94.5. [Found: C, 60.13; H, 9.13; N, 20.15; P, 10.97. $C_{14}H_{25}N_4P$ requires C, 59.98; H, 8.99; N, 19.98; P, 11.05].

4.1.11. N′-(2-Chlorophenyl)-1,1-bis(dimethylamino)-N,N-dimethyl-phosphinecarboximidamide ***4g***. Yield 99%, oil, bp 150–155 °C/0.05 Torr; ^{1}H NMR (300 MHz, C_6D_6) δ 7.29 (1H, dd, J=7.8, 1.5 Hz, 3-H), 6.92 (1H, dt, J=7.5, 1.2 Hz, 5-H), 6.73 (1H, dd, J=7.8, 1.5 Hz, 6-H), 6.54 (1H, dt, J=7.5, 1.5 Hz, 4-H), 2.74 (6H, s, $CNMe_2$), 2.45 (12H, d, J=8.7 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 162.31 (d, J=27.7 Hz), 149.08 (d, J=1.2 Hz), 129.01, 127.60, 124.22 (d, J=1.2 Hz), 121.63 (d, J=1.2 Hz)119.83, 41.34 (d, J=16.3 Hz), 38.97 (d, J=8.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 93.8. [Found: C, 52.14; H, 7.45; N, 18.75; P, 10.23. $C_{13}H_{22}ClN_4P$ requires C, 51.91; H, 7.37; N, 18.63; P, 10.30].

4.1.12. 1,1-Bis(dymethylamino)-N,N-dimethyl-N′-(3-methylphenyl) phosphinecarboximidamide ***4h***. Yield 94%, bp 125–126 °C/0.05 Torr; ^{1}H NMR (300 MHz, C_6D_6) δ 7.08 (1H, t, J=7.5 Hz, 5-H), 6.71–6.73 (2H, m, 2,6-H), 6.63 (1H, d, J=7.2 Hz, 4-H), 2.73 (6H, s, $CNMe_2$), 2.46 (12H, d, J=8.7 Hz, $PNMe_2$), 2.20 (3H, s, 3-Me); ^{13}C NMR (125 MHz, C_6D_6) δ 162.1 (d, J=28.9 Hz), 151.87 (d, J=6.3 Hz),137.07, 127.91, 121.24 (d, J=1.2 Hz), 120.59, 117.69 (d, J=1.2 Hz), 41.51 (d, J=16.3 Hz), 39.6 (d, J=7.5 Hz), 21.37; ^{31}P NMR (81 MHz, C_6D_6) δ 96.4. [Found: C, 59.75; H, 9.16; N, 19.75; P, 10.86. $C_{14}H_{25}N_4P$ requires C, 59.98; H, 8.99; N, 19.98; P, 11.05].

4.1.13. Reduction of 1,1-bis(dimethylamino)-N′-[3-(dimethylamino) phenyl]-N,N-dimethylphosphine carboximidamide selenide ***3k***. To a solution of compound **3k** (2.41 g, 6.2 mmol) in benzene (2 mL), a solution of trismorpholidophosphite (1.80 g, 6.2 mmol) in benzene (10 mL) was added. The reaction mixture was stirred for 30 min at 20 °C. ^{31}P NMR monitoring of the reaction mixture showed the gradual disappearance of the resulting **4k** (δ_p=95.9) and formation of the corresponding benzazaphosphole **5k** (δ_p=59.5 ppm). The benzene was evaporated in vacuo, ether (20 mL) was added, the solution was filtered and the solvents were evaporated. The residue was crystallized from pentane yielding (1.2 g, 73%) benzazaphosphole **5k**. *N,N,N′,N′,N″,N″-hexamethyl-3H-1,3-benzazaphosphonole-2,3,6-triamine* **5k**, bright orange crystals mp 104–105 °C (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.48–7.46 (1H, m, 4–H), 6.99 (1H, s, 7-H), 6.30–6.28 (1H, m, 5-H), 2.81 (3H, br s, 2-NMe_2), 3.01 (3H, br s, 2-NMe_2), 2.56 (6H, s, 6-NMe_2), 2.41 (6H, d, J=9.5 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 177.09 (d, J=22.6 Hz), 161.77 (d, J=7.5 Hz), 153.63, 129.98 (d, J=25.1 Hz), 115.16 (d, J=11.3 Hz), 106.23 (d, J=7.5 Hz), 104.31, 41.22 (d, J=12.5 Hz), 40.40(br s), 39.95, 37.19 (br s); ^{31}P NMR (81 MHz, C_6D_6) δ 59.7. [Found: C, 58.99; H, 8.33; N, 21.33; P, 11.80. $C_{13}H_{21}N_4P$ requires C, 59.07; H, 8.01; N, 21.20; P, 11.72].

4.2. General procedure of thermal cyclization of phosphorylated (P^{III}) formamidines 4a–d,f–j,m,n

A sample of amidine **4** (1–3 g) was heated under reduced pressure (temperature, pressure, time and yield are given in Table 2), and then the product was distilled at 0.05 Torr. In the case of compounds **4a**,**b**,**m**,**n** the residue was extracted with hot hexane, the solvent was evaporated and the residue was crystallized. In case of compounds **4c**,**d**,**f**–**j** the residue was dissolved in benzene and an equivalent of finely ground selenium was added. The reaction mixture was refluxed for 2–5 h until oxidation of the P(III) compound was complete. The reaction was monitored by ^{31}P NMR. The unreacted selenium was separated by filtration. The filtrate was evaporated in vacuo. The residue was crystallized. The mixture of selenides **6** and **6′h**–**j** was separated chromatographically.

4.2.1. N,N,N′,N′-Tetramethyl-3H-1,3-benzazaphosphonole-2,3-diamine ***5a***. Yield 76%, bright yellow crystals mp 52–54 °C (pentane), bp 143–146 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 (1H, d, J=8.0 Hz, 7-H), 7.49 (1H, m, 4-H), 7.20 (1H, t, J=8.0 Hz, 6-H), 6.87 (1H, m, 5-H), 2.94 (3H, br s, 2-NMe_2), 2.70 (3H, br s, 2-NMe_2), 2.31 (6H, d, J=9.5 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 175.90 (d, J=21.4 Hz), 159.41 (d, J=8.8 Hz), 131.12, 129.08 (d, J=7.5 Hz), 129.08 (d, J=25.2 Hz), 121.40 (d, J=7.5 Hz), 119.73, 41.55 (d, J=11.3 Hz), 40.20 (br s), 37.27 (br s); ^{31}P NMR (81 MHz, C_6D_6) δ 61.0. [Found: C, 59.42; H, 7.45; N, 19.17; P, 13.85. $C_{11}H_{16}N_3P$ requires C, 59.72; H, 7.29; N, 18.99; P, 14.00].

4.2.2. N,N,N′,N′,5-Pentamethyl-3H-1,3-benzazaphosphonole-2,3-diamine ***5b***. Yield 88%, bright yellow crystals mp 107–108 °C (pentane); bp 145–147 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (1H, d, J=7.5 Hz, 7-H), 7.32 (1H, br s, 4-H), 7.02 (1H, d, J=8.0 Hz, 6-H), 2.94 (3H, br s, 2-NMe_2), 2.76 (3H, br s, 2-NMe_2), 2.35 (6H, d, J=9.5 Hz, 3-NMe_2), 2.16 (3H, s, 5-Me); ^{13}C NMR (125 MHz, C_6D_6) δ 175.37 (d, J=22.6 Hz), 157.18 (d, J=8.8 Hz), 131.86, 130.35 (d, J=6.3 Hz), 129.63 (d, J=23.9 Hz), 129.13 (d, J=7.5 Hz), 191.51, 41.57 (d, J=12.6 Hz), 40.13 (br s), 37.17 (br s), 20.77; ^{31}P NMR (81 MHz, C_6D_6) δ 60.8. [Found: C, 61.52; H, 7.56; N, 17.93; P, 13.10. $C_{12}H_{18}N_3P$ requires C, 61.26; H, 7.71; N, 17.86; P, 13.17].

4.2.3. N,N,N′,N′-Tetramethyl-3H-naphtho[2,1-d][1,3]-azaphosphonole-2,3-diamine ***5m***. Yield 89%, yellow crystals mp 81–82 °C (pentane), bp 150–160 °C/0.02 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 9.09 (1H, d, J=8.5 Hz, 9-H), 7.71 (1H, d, J=8.0 Hz, 6-H), 7.63–7.59 (1H, m, 4-H), 7.44–7.38 (2H, m, 7,8-H), 7.33 (1H, t, J=7.5 Hz, 5-H), 3.01 (3H, br s, 2-NMe_2), 2.69 (3H, br s, 2-NMe_2), 2.31 (6H, d, J=9.5 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 177.18 (d, J=21.4 Hz), 155.78 (d, J=10.1 Hz), 136.24, 128.11, 127.72, 126.54, 125.96 (d, J=1.3 Hz), 125.37 (d, J=23.9 Hz), 124.95, 121.71 (d, J=10.1 Hz), 120.86 (d, J=7.5 Hz), 41.65 (d, J=12.6 Hz), 40.37 (br s), 37.21 (br s); ^{31}P NMR (81 MHz, C_6D_6) δ 64.5. [Found: C, 66.33; H, 6.72; N, 15.73; P, 11.40. $C_{15}H_{18}N_3P$ requires C, 66.41; H, 6.69; N, 15.49; P, 11.42].

4.2.4. 3-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethyl-3H-1,3-benzazaphosphonol-2-amine ***5n***. Yellow oil yield 61%, ^{1}H NMR (300 MHz, C_6D_6) δ 7.68 (1H, d, J=8.1 Hz, 7-H), 7.60 (1H, d, J=2.1 Hz, 4-H-imidazol), 7.33 (1H, m, 4-H), 7.24 (1H, d, J=7.8 Hz, 6-H), 6.83 (1H, m, 5-H), 2.87 (3H, br s, 2-NMe_2) 2.67 (3H, s, 1-Me–imidazol), 2.45 (3H, br s, 2-NMe_2), 2.36 (6H, s, 2-NMe_2–imidazol); ^{13}C NMR (125 MHz, C_6D_6) δ 175.92 (d, J=12.6 Hz), 160.14 (d, J=8.8 Hz), 158.92 (d, J=2.5 Hz), 141.78 (d, J=46.5 Hz), 130.13, 129.15 (d, J=11.3 Hz), 128.24 (d, J=23.9 Hz), 121.60 (d, J=7.5 Hz), 119.81, 114.09 (d, J=36.5 Hz), 41.96, 36.94 (d, J=3.8 Hz), 29.40; ^{31}P NMR (81 MHz, C_6D_6) δ −43.9. [Found: C, 60.03; H, 6.85; N, 23.22; P, 10.10. $C_{15}H_{20}N_5P$ requires C, 59.79; H, 6.69; N, 23.24; P, 10.28].

4.2.5. 5-Methoxy-N,N,N′,N′-tetramethyl-3H-1,3-benzazaphosphole-2,3-diamine 3-selenide ***6c***. Yield 73%, bright yellow crystals mp 132–135 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (1H, dd,

J=8.4, 4.8 Hz, 7-H), 6.91 (2H, m, 4,6-H), 3.79 (3H, s, 5-OMe), 3.25 (6H, br s, 2-NMe_2), 2.77 (6H, d, J=12.3 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16339 (d, J=73.0 Hz), 156.35 (d, J=16.3 Hz), 147.63 (d, J=28.9 Hz), 122.05 (d, J=115.7 Hz), 121.04 (d, J=7.5 Hz), 120.49 (d, J=2.5 Hz), 112.00 (d, J=15.1 Hz), 55.85, 38.85, 36.63 (d, J=3.80 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 57.1. MS (APCI): m/z=332 [M+2]. [Found: C, 43.51; H, 5.43; N, 12.55; P, 9.27. $C_{12}H_{18}N_3OPSe$ requires C, 43.65; H, 5.49; N, 12.72; P, 9.38].

4.2.6. N,N,N′,N′,N′,N″-Hexamethyl-3H-1,3-benzazaphosphole-2,3,5-triamine 3-selenide ***6d***. Yield 70%, bright orange crystals mp 86–87 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.02 (1H, dd, J=8.4, 5.1 Hz, 7-H), 6.78 (2H, m 4,6-H), 3.24 (6H, br s, 2-NMe_2), 2.92 (6H, s, 5-NMe_2), 2.72 (6H, d, J=12.0 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.25 (d, J=81.7 Hz), 148.06 (d, J=13.8 Hz), 144.90 (d, J=30.2 Hz), 121.49 (d, J=124.5 Hz), 120.86 (d, J=7.5 Hz), 118.84 (d, J=2.5 Hz), 111.50 (d, J=15.1 Hz), 41.35, 38.67 (d, J=3.8 Hz), 35.00 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 57.6. [Found: C, 45.43; H, 5.96; N, 16.57; P, 9.12. $C_{13}H_{21}N_4PSe$ requires C, 45.49; H, 6.17; N, 16.32; P, 9.02].

4.2.7. N,N,N′,N′,7-Pentamethyl-3H-1,3-benzazaphosphole-2,3-diamine 3-selenide ***6f***. Yield 52%, bright yellow crystals mp 93–94 °C (pentane); IR (KBr) 2920, 2803, 1562, 1462, 1394, 1266, 1173, 1138, 1065, 968, 835, 748, 703, 668, 559 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (2H, m, 4,6-H), 6.91 (1H, dt, J=7.5, 3.9 Hz, 6-H), 3.37 (3H, br s., 2-NMe_2), 3.25 (3H, br s, 2-NMe_2), 2.76 (6H, d, J=12.3 Hz, 3-NMe_2), 2.34 (3H, s, 7-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.28 (d, J=70.4 Hz), 152.34 (d, J=28.9 Hz), 135.47 (d, J=1.2 Hz), 129.23 (d, J=6.3 Hz), 124.86 (d, J=10.1 Hz), 123.04 (d, J=12.6 Hz), 121.0 (d, J=117.0 Hz), 38.69 (br s), 36.68 (d, J=5.0 Hz), 16.60 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 56.9. MS (APCI): m/z=316 [M+2]. [Found: C, 45.63; H, 5.69; N, 13.56; P, 9.63. $C_{12}H_{18}N_3PSe$ requires C, 45.87; H, 5.77; N, 13.37; P, 9.86].

4.2.8. 7-Chloro-N,N,N′,N′-tetramethyl-3H-1,3-benzazaphosphole-2,3-diamine 3-selenide ***6g***. Yield 27%, bright yellow crystals mp 114–115 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (1H, d, J=7.8 Hz, 6-H), 7.25 (1H, m, 4-H), 6.93 (1H, dt, J=7.5, 5.1 Hz, 5-H), 3.39 (3H, br s, 2-NMe_2), 3.31 (3H, br s, 2-NMe_2), 2.77 (6H, d, J=12.3 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.50 (d, J=70.4 Hz), 150.63 (d, J=28.9 Hz), 134.50, 125.81 (d, J=13.8 Hz), 124.92 (d, J=7.5 Hz), 123.83 (d, J=13.8 Hz), 123.54 (d, J=113.2 Hz), 38.93, 36.63 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 57.4. MS (APCI): m/z=336 [M+2]. [Found: C, 39.43; H, 4.59; N, 12.56; P, 9.22. $C_{11}H_{15}ClN_3PSe$ requires C, 39.48; H, 4.52; N, 12.56; P, 9.26].

4.2.9. N,N,N′,N′,6-Pentamethyl-3H-1,3-benzazaphosphonole-2,3-diamine 3-selenide ***6h***. R_f (CH_2Cl_2) 0.2. Yield 35%, bright yellow crystals mp 84–85 °C(hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (1H, dd, J=7.2, 9.9 Hz, 4-H), 6.94 (1H, d, J=3.9 Hz, 7-H), 6.84 (1H, dd, J=7.5, 3.6 Hz, 5-H), 3.38 (3H, br s, 2-NMe_2), 3.32 (3H, br s, 2-NMe_2), 2.75 (6H, d, J=12.3 Hz, 3-NMe_2), 2.34 (3H, s, 6-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.73 (d, J=70.4 Hz), 154.66 (d, J=30.2 Hz), 145.31 (d, J=2.5 Hz), 127.43 (d, J=13.8 Hz), 124.28 (d, J=12.5 Hz), 121.00 (d, J=6.3 Hz), 118.12 (d, J=118.12 Hz), 38.92, 36.66 (d, J=3.8 Hz), 21.98; ^{31}P NMR (81 MHz, $CDCl_3$) δ 54.5. MS (APCI): m/z=316 [M+2]. [Found: C, 46.06; H, 6.01; N, 13.03; P, 9.95. $C_{12}H_{18}N_3PSe$ requires C, 45.87; H, 5.77; N, 13.37; P, 9.86].

4.2.10. 6-Bromo-N,N,N′,N′-tetramethyl-3H-1,3-btnzazaphosphonole-2,3-diamine 3-selenide ***6i***. R_f (CH_2Cl_2)=0.4. Yield 9%, bright yellow crystals mp 112–113 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29–7.11 (3H, m, 4,5,7-H), 3.39 (3H, br s, 2-NMe_2), 3.23 (3H, br s, 2-NMe_2), 2.76 (6H, d, J=12.3 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.05 (d, J=70.4 Hz), 155.87 (d, J=30.2 Hz) 128.82 (d, J=3.8 Hz), 128.53 (d, J=15.1 Hz), 126.17 (d, J=12.6 Hz), 123.48 (d, J=5.0 Hz), 120.30 (d, J=118.2 Hz), 38.93 (d, J=3.8 Hz), 36.59 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 54.2. MS (APCI): m/z=381 [M+2]. [Found: C, 34.66; H, 4.05; N, 11.03; P, 8.08. $C_{11}H_{15}BrN_3PSe$ requires C, 34.85; H, 3.99; N, 11.08; P, 8.17].

4.2.11. 6-Methoxy-N,N,N′,N′-tetramethyl-3H-1,3-benzazaphosphonole-2,3-diamine 3-selenide ***6j***. R_f (CH_2Cl_2 : EtOAc=4:1) 0.1. Yield 40%, bright yellow crystals mp 123–124 °C (hexane); ^1H NMR (300 MHz, DMSO-d_6) δ 7.21 (1H, dd, J=9.3, 7.8 Hz, 4-H), 6.58 (2H, m, 5,7-H), 3.78 (3H, s, 6-OMe), 3.30 (3H, br s, 2-NMe_2), 3.14 (3H, br s, 2-NMe_2), 2.67 (6H, d, J=12.9 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.14 (d, J=66.7 Hz), 164.61 (d, J=2.5 Hz), 156.64 (d, J=31.4 Hz), 128.71 (d, J=15.1 Hz), 112.01 (d, J=124.5 Hz), 109.01 (d, J=12.6 Hz), 104.97 (d, J=6.3 Hz), 55.29, 39.5, 35.92 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, DMSO-d_6) δ 54.4. MS (APCI): m/z=332 [M+2]. [Found: C, 43.55; H, 5.65; N, 12.75; P, 9.33. $C_{12}H_{18}N_3OPSe$ requires C, 43.65; H, 5.49; N, 12.72; P, 9.38].

4.2.12. N,N,N′,N′,4-Pentamethyl-3H-1,3-benzazaphosphonole-2,3-diamine 3-selenide ***6′h***. R_f (CH_2Cl_2) 0.45. Yield 38%, bright yellow crystals mp 90–91 °C(hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (1H, dd, J=7.8, 1.3 Hz, 6-H-Ar), 6.93 (1H, dd, J=8.1, 4.2 Hz, 7-H), 6.75 (1H, dd, J=7.5, 4.2 Hz, 5-H), 3.38 (3H, br s, 2-NMe_2), 3.22 (3H, br s., 2-NMe_2), 2.81 (6H, d, J=12.3 Hz, 3-NMe_2), 2.43 (3H, s, 4-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.13 (d, J=71.7 Hz), 154.52 (d, J=30.2 Hz), 1140.26 (d, J=12.6 Hz), 134.20, 124.88 (d, J=10.1 Hz), 118.93 (d, J=144.4 Hz), 117.83 (d, J=5.0 Hz), 38.77, 36.50 (d, J=5.0 Hz), 18.60 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 53.9. MS (APCI): m/z=316 [M+2]. [Found: C, 45.93; H, 5.89; N, 13.22; P, 9.78. $C_{12}H_{18}N_3PSe$ requires C, 45.87; H, 5.77; N, 13.37; P, 9.86].

4.2.13. 4-Bromo-N,N,N′,N′-tetramethyl-3H-1,3-benzazaphosphonole-2,3-diamine 3-selenide ***6′i***. R_f (CH_2Cl_2)=0.15. Yield 32%, bright yellow crystals mp 131–132 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (1H, t, 6-H), 7.08–7.01 (2H, m, 5,7-H), 3.41 (3H, br s, 2-NMe_2), 3.24 (3H, br s, 2-NMe_2), 2.84 (6H, d, J=12.3 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.43 (d, J=81.7 Hz), 156.20 (d, J=30.2 Hz), 135.08, 126.51 (d, J=7.5 Hz), 122.76 (d, J=10.1 Hz), 121.34 (d, J=117.0 Hz), 119.11 (d, J=5.0 Hz), 39.14 (br s), 38.50 (br s), 36.50 (d, J=5.0 Hz,); ^{31}P NMR (81 MHz, $CDCl_3$) δ 56.5. MS (APCI): m/z=380 [M+1]. [Found: C, 34.63; H, 4.12; N, 11.05; P, 8.10. $C_{11}H_{15}BrN_3PSe$ requires C, 34.85; H, 3.99; N, 11.08; P, 8.17].

4.2.14. 4-Methoxy-N,N,N′,N′-tetramethyl-3H-1,-benzazaphosphonole-2,3-diamine 3-selenide ***6′j***. R_f (CH_2Cl_2/EtOAc=4 :1) 0.3. Yield 12%, bright yellow crystals mp 132–135 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (1H, t, J=8.1 Hz, 6-H), 6.73 (1H, dd, J=7.8, 3.9 Hz, 7-H), 6.49 (1H, dd, J=8.1, 6.0 Hz, 5-H), 3.87 (3H, s, 4-OMe), 3.41 (3H, br s, 2-NMe_2), 3.23 (3H, br s, 2-NMe_2), 2.77 (6H, d, J=12.9 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.94 (d, J=76.7 Hz), 160.40 (d, J=7.5 Hz), 155.77 (d, J=27.7 Hz), 135.88, 113.29 (d, J=3.8 Hz), 106.91 (d, J=113.2 Hz), 105.78 (d, J=6.3 Hz), 55.91, 39.09 (br s), 38.63(br s), 36.80 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 54.4. Found: C, 43.43; H, 5.59; N, 12.56; P, 9.22. $C_{12}H_{18}N_3OPSe$ requires C, 43.65; H, 5.49; N, 12.72; P, 9.38.

4.2.15. N^3,N^3-Diethyl-5-methoxy-N^2,N^2-dimethyl-3H-1,3-benzazaphosphole-2,3-diamine 3-sulfide ***7***. To a mixture of *N′*-(4-methoxyphenyl)-*N*,*N*-dimethylmethanimidoformamide (10 g, 56 mmol) and NEt_3 (5.7 g, 57 mmol) in pyridine (40 mL) cooled to 0 °C a solution of PBr_3 (15.20 g, 56 mmol) in methylene chloride

(40 mL) was added dropwise with stirring. The reaction mixture was stirred for 15 h at room temperature and then cooled to −30 °C. $HNEt_2$ (25.0 g, 0.34 mol) was added and the mixture was kept stirring for 1h. The solvents and volatile products were distilled off and the residue was kept at 100 °C in vacuo (10 Torr) for 1 h. To the residue benzene (50 mL) and sulfur (1.79 g, 56 mmol) were added and the reaction mixture was refluxed for 3 h. The reaction mixture was filtered and evaporated, leaving an oily residue that was triturated with methanol (5 mL). The crude solid product was recrystallized from heptane giving 5.06 g of **7**. (29%); bright orange crystals mp 85–86 °C (heptane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.07–7.02 (1H, m, 7-H), 6.94–6.86 (2H, m, 4-H+6-H), 3.79 (3H, s, 5-OMe), 3.35–2.91 (10H, m, 2-NMe_2+3-CH_2), 1.07 (6H, t, J=7.0 Hz, 3-CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 62.8. Found: C, 53.95; H, 7.18; N, 13.33; P, 10.06. $C_{14}H_{22}N_3OPS$ requires C, 54.00; H, 7.12; N, 13.49; P, 9.95.

4.2.16. N,N,N′,N′-Tetramethyl-5-(trifluoromethyl)-3H-1,3-benzazaphosphole-2,3-diamine 3-selenide ***6e****.* A mixture of **4e** (1.67 g, 5 mmol) and $Et_3NH^+TfO^-$ (0.025 g, 0.1 mmol) was heated at 170 °C (12 Torr) over 15 min while distilling off hexamethylphosphorus triamide and *N,N*-dimethyl-*N′*-[4-(trifluoromethyl)phenyl]methanimidamide. The residue was dissolved in benzene (5 mL) and Se (0.4 g, 5 mmol) was added. The reaction mixture was stirred for 1 h at 65 °C. The reaction mixture was placed on SiO_2 and chromatographed (eluent CH_2Cl_2). R_f 0.35–0.45; 0.74 g (40%); yellow crystals mp 70–71 °C(pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.55 (2H, m, 4-H+6-H), 7.15 (1H, dd, J=8.1, 4.2 Hz, 7-H), 3.41 (3H, br s, 2-NMe_2), 3.27 (3H, br s, 2-NMe_2), 2.77 (6H, d, J=12.6 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.73 (d, J=70.4 Hz), 157.50 (d, J=30.2 Hz), 131.46 (q, J=2.5 Hz), 125.25 (m), 124.78 (qd, J=15.1, 3.8 Hz), 124.05 (q, J=245.2 Hz), 122.23 (d, J=116.9 Hz), 120.17 (d, J=6.3 Hz), 39.00 (br s), 36.54 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 54.4; ^{19}F NMR (188 MHz, $CDCl_3$) δ −62.1. MS (APCI): m/z=370 [M+2]. Found: C, 39.22; H, 4.09; N, 11.22; P, 8.31. $C_{12}H_{15}F_3N_3PSe$ requires C, 39.14; H, 4.11; N, 11.41; P, 8.41.

4.2.17. N,N,N′,N′-Tetramethyl-6-(trifluoromethyl)-3H-1,3-benzazaphosphole-2,3-diamine 3-selenide ***6l*** *and N,N,N′,N′-tetramethyl-4-(trifluoromethyl)-3H-1,3-behzazaphosphole-2,3-diamine 3-selenide* ***6′l****.* This was prepared analogously to **6e**. Isomers **6l** and **6′l** were separated chromatographically on plates (eluent CH_2Cl_2). *N,N,N′,N′-Tetramethyl*-6-(*trifluoromethyl*)-3*H*-1,3-*benzazaphosphole*-2,3-*diamine* 3-*selenide* **6l**. R_f 0.48–0.53; 0.25 g (15%); yellow crystals mp 115–116 °C (pentane); IR (KBr) 2927, 1614, 1574, 1476, 1419, 1381, 1326, 1273, 1253, 1163, 1123, 1050, 974, 889, 820, 722, 698, 675, 623 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (1H, t, J=8.5 Hz, 4-H), 7.32 (1H, d, J=2.5 Hz, 7-H), 7.22 (1H, m, 5-H), 3.37 (3H, br s, 2-NMe_2), 3.23 (3H, br s, 2-NMe_2), 2.76 (6H, d, J=12.5 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.89 (d, J=70.4 Hz), 154.93 (d, J=30.2 Hz), 135.78 (qd, J=32.7, 2.5 Hz), 125.51 (d, J=115.7 Hz), 123.68 (q, J=272.9 Hz), 119.69 (dq, J=12.69, 2.5 Hz), 116.89 (m), 38.88 (d, J=3.8 Hz), 36.19 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 55.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ −63.7. MS (APCI): m/z=370 [M+2]. Found: C, 39.22; H, 4.04; N, 11.36; P, 8.52. $C_{12}H_{15}F_3N_3PSe$ requires C, 39.14; H, 4.11; N, 11.41; P, 8.41. *N,N,N′,N′-Tetramethyl*-4-(*trifluoromethyl*)-3*H*-1,3-*behzazaphosphole*-2,3-*diamine* 3-*selenide* **6′l**. R_f 0.35–0.48; 0.70 g (41%); mp 126–127 °C (pentane); IR (KBr) 1565, 1399, 1320, 1173, 1117, 973, 892, 799, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (1H, t, J=8.0 Hz, 6-H), 7.26 (1H, dd, J=8.0, 3.0 Hz, 7-H), 7.18 (1H, m, 5-H), 3.36 (3H, br s, 2-NMe_2), 3.23 (3H, br s, 2-NMe_2), 2.75 (6H, d, J=12.0 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.32 (d, J=85.5 Hz), 155.63 (d, J=27.7 Hz), 134.14, 130.13 (qd, J=32.7, 10.0 Hz), 124.14 (d, J=5.0 Hz), 123.61 (q, J=275.4 Hz), 120.30 (m), 118.49 (d, J=105.6 Hz), 39.22 (br s), 38.25 (br s), 36.02 (d, J=6.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 54.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ −60.1. MS (APCI): m/z=370 [M+2]. Found: C, 39.25; H, 4.23; N, 11.55; P, 8.37. $C_{12}H_{15}F_3N_3PSe$ requires C, 39.14; H, 4.11; N, 11.41; P, 8.41.

4.3. General method of reducing *N,N,N′,N′*-tetramethyl-3*H*-1,3-benzazaphosphole-2,3-diamine 3-selenides 6h, e, l and 6′l with metallic sodium

A mixture of the corresponding selenide **6** (0.6 mmol) and sodium (1.2 mmol) dispersed in toluene (3 mL) was refluxed for 2 h. The solution was filtered, the toluene was evaporated and the residue was distilled.

4.3.1. N,N,N′,N′,6-Pentamethyl-3H-1,3-benzazaphosphonole-2,3-diamine ***5h****.* Yield 90%, yellow oil, bp 110 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.46 (1H, s, 7-H), 7.43 (1H, dd, J=7.5, 4.0 Hz, 4-H), 6.73 (1H, m, 5-H), 2.95 (3H, br s, 2-NMe_2), 2.71 (3H, br s, 2-NMe_2), 2.34 (6H, d, J=9.0 Hz, 3-NMe_2), 2.16 (3H, s, 6-Me); ^{13}C NMR (125 MHz, C_6D_6) δ 176.24 (d, J=21.4 Hz), 159.69 (d, J=8.8 Hz), 141.03, 128.83 (d, J=25.1 Hz), 125.57 (d, J=7.5 Hz), 122.35 (d, J=6.3 Hz), 120.49, 41.30 (d, J=12.6 Hz), 41.35 (br s), 38.23 (br s), 21.46; ^{31}P NMR (81 MHz, C_6D_6) δ 60.4. Found: C, 61.42; H, 7.45; N, 18.17; P, 13.05. $C_{12}H_{18}N_3P$ requires C, 61.26; H, 7.71; N, 17.86; P, 13.17.

4.3.2. N,N,N′,N′-Tetramethyl-5-(trifluoromethyl)-3H-1,3-benzazaphosphole-2,3-diamine ***5e****.* Yield 90%, yellowish liquid; bp 120 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.78 (1H, m, 4-H), 7.39 (1H, d, J=8.5 Hz, 6-H), 7.35 (1H, d, J=8.0 Hz, 7-H), 2.87 (3H, br s, 2-NMe_2), 2.60 (3H, br s, 2-NMe_2), 2.18 (6H, d, J=9.0 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 177.70 (d, J=22.6 Hz), 161.99 (d, J=8.8 Hz), 129.41 (d, J=5.0 Hz), 128.35 (d, J=3.8 Hz), 125.86 (dq, J=25.1, 3.8 Hz), 125.52 (q, J=271.6 Hz), 122.80 (dd, J=25.1, 6.3 Hz), 119.14, 41.26 (d, J=12.6 Hz), 39.94 (d, J=13.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 58.9; ^{19}F NMR (188 MHz, C_6D_6) δ −61.1. Found: C, 49.52; H, 5.56; N, 14.33; P, 10.62. $C_{12}H_{15}F_3N_3P$ requires C, 49.83; H, 5.23; N, 14.53; P, 10.71.

4.3.3. N,N,N′,N′-Tetramethyl-6-(trifluoromethyl)-3H-1,3-benzazaphosphole-2,3-diamine ***5l****.* Yield 89%, yellowish crystals, mp 52–53 °C, bp 102 °C/0.05 Torr; ^{1}H NMR (300 MHz, C_6D_6) δ 7.79 (1H, s, 7-H), 7.29 (1H, dd, J=7.5, 3.6 Hz, 4-H), 7.03 (1H, dm, J=7.5 Hz, 5-H), 2.87 (3H, br s, 2-NMe_2), 2.61 (3H, br s, 2-NMe_2), 2.21 (6H, d, J=9.3 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 176.68 (d, J=22.6 Hz), 159.41 (d, J=10.1 Hz), 133.18 (d, J=5.0 Hz), 132.79 (q, J=35.7 Hz), 129.07 (d, J=23.9 Hz), 124.96 (q, J=272.9 Hz), 117.32 (m), 115.71(q, J=3.8 Hz), 41.39 (d, J=13.8 Hz), 39.90 (br s), 37.11 (br s); ^{31}P NMR (81 MHz, C_6D_6) δ 59.7; ^{19}F NMR (188 MHz, C_6D_6) δ −62.6. Found: C, 49.65; H, 5.27; N, 14.76; P, 10.47. $C_{12}H_{15}F_3N_3P$ requires C, 49.83; H, 5.23; N, 14.53; P, 10.71.

4.3.4. N,N,N′,N′-Tetramethyl-4-(trifluoromethyl)-3H-1,3-benzazaphosphole-2,3-diamine ***5′l****.* Yield 90%, yellowish crystals, mp 39–40 °C; bp 100 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.49 (1H, d, J=7.5 Hz, 7-H), 7.68 (1H, m, 5-H), 7.01 (1H, t, 6-H), 2.90 (3H, br s, 2-NMe_2), 2.67 (3H, br s, 2-NMe_2), 2.39 (6H, d, J=11.7 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 176.16 (d, J=12.6 Hz), 160.01 (d, J=8.8 Hz), 131.06 (qd, J=31.4, 16.3 Hz), 131.01, 126.05 (d, J=8.8 Hz), 124.97 (q, J=272.8 Hz), 122.78, 117.66 (m), 41.33 (br s), 39.60 (br s), 37.42 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 60.2; ^{19}F NMR (188 MHz, C_6D_6) δ −62.33 (d, J=24.4 Hz). Found: C, 49.99; H, 5.33; N, 14.37; P, 10.80. $C_{12}H_{15}F_3N_3P$ requires C, 49.83; H, 5.23; N, 14.53; P, 10.71.

4.3.5. N,N,N′,N′,4-Pentamethyl-3H-1,3-benzazaphosphole-2,3-diamine ***5′h****.* A solution of compound **6′h** (0.17 g, 0.54 mmol) and (0.1 g, 0.6 mmol) of hexamethylphosphorus triamide in benzene (1 mL) was stirred at 20 °C for 10 min. The solvent was evaporated, the residue was kept at 120 °C for 10 min in vacuo (0.05 Torr) and then

recrystallized from hexane to give the product (0.07 g, 58%), yellow crystals mp 32–34 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.49 (1H, d, J=7.8 Hz, 7-H), 7.19 (1H, m, 6-H), 6.72 (1H, dd, J=7.5, 4.8 Hz, 5-H), 2.95 (3H, br s, 2-NMe_2), 2.73 (3H, br s, 2-NMe_2), 2.38 (3H, br s, 4-Me), 2.32 (6H, d, J=8.7 Hz, 3-NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 175.65 (d, J=17.6 Hz), 159.06 (d, J=10.1 Hz), 139.27 (d, J=20.1 Hz), 131.26, 128.52 (d, J=7.5 Hz), 122.38 (d, J=3.8 Hz), 117.33, 41.44, 37.60 (d, J=3.8 Hz), 21.37 (d, J=6.3 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 58.1. [Found: C, 61.35; H, 7.83; N, 17.63; P, 13.80. $C_{12}H_{18}N_3P$ requires C, 61.26; H, 7.71; N, 17.86; P, 13.17].

4.3.6. 6-Methoxy-N,N,N′,N′-tetramethyl-3H-1,3-benzazaphosphole-2,3-diamine ***5j***. A solution of hexamethylphosphorus triamide (1.04 g, 3.6 mmol) in benzene (8 mL) was added to a solution of compound **6j** (1.19 g, 3.6 mmol) in solvent (10 mL). The reaction mixture was stirred at 50 °C for 0.5 h. The solvent was evaporated in vacuo and the residue was extracted with hot hexane (3×10 mL). The hexane was evaporated and the residue was distilled. Yellowish oil bp 159–160 °C/0.05 Torr (0.83 g, yield 92%); ^{1}H NMR (300 MHz, C_6D_6) δ 7.43 (1H, dd, J=8.1, 3.6 Hz, 4-H), 7.24 (1H, dd, J=2.4, 1.2 Hz, 7-H), 6.58 (1H, m, 5-H), 3.34 (3H, s, 6-OMe), 2.96 (3H, br s, 2-NMe_2), 2.70 (3H, br s, 2-NMe_2), 2.45 (6H, d, J=9.3 Hz, 3-NMe_2); ^{31}P NMR (81 MHz, C_6D_6) δ 59.7. [Found: C, 57.79; H, 7.33; N, 16.47; P, 12.60. $C_{12}H_{18}N_3OP$ requires C, 57.36; H, 7.22; N, 16.72; P, 12.33].

4.3.7. tert-Butyl[(Z)-(dimethylamino)(phenylimino)methyl]phosphinous chloride ***8o***. To a solution of compound **4o** (1.11 g, 4.0 mmol) in benzene (2 mL) cooled to 0 °C, a solution of phosphorus trichloride (0.55 g, 4.0 mmol) in benzene (2 mL) was added. The reaction mixture was stirred at 20 °C for 10 min. The solvent was evaporated in vacuo (10 Torr), and the residue was distilled. Yellowish oil bp 110–112 °C/0.05 Torr, oil, yield 75%. ^{1}H NMR (300 MHz, C_6D_6) δ 7.12 (2H, t, J=7.8 Hz, 3,5-H), 6.85 (1H, t, J=7.5 Hz, 4-H), 6.87 (2H, d, J=7.8 Hz, 2,6-H), 2.44 (6H, s, NMe_2), 1.27 (9H, d, J=13.5 Hz, CMe_3); ^{13}C NMR (125 MHz, C_6D_6) δ 160.08 (d, J=41.5 Hz), 150.68 (d, J=9.0 Hz), 128.61, 121.63, 121.19 (d, J=2.5 Hz), 40.75 (d, J=7.5 Hz), 36.24 (d, J=35.2 Hz), 26.54 (d, J=16.4 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 100.8. [Found: C, 57.95; H, 7.87; N, 10.63; P, 11.67. $C_{13}H_{20}ClN_2P$ requires C, 57.67; H, 7.45; N, 10.35; P, 11.44].

4.3.8. 1-Adamantyl[(Z)-(dimethylamino)(phenilimino)methyl]phosphinous chloride ***8p***. To a solution of compound **4p** (0.91 g, 2.5 mmol) in benzene (2 mL) cooled to 0 °C was added a solution of phosphorus trichloride (0.34 g, 2.5 mmol) in benzene (2 mL). The reaction mixture was stirred at 20 °C for 30 min in vacuo (10 Torr). The residue was washed with pentane (2×3 mL) and dried to give a yellowish oil (0.8 g, 90%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.18 (3H, m, 3,4,5-H), 6.90 (2H, d, J=7.0 Hz, 2,6-H), 2.59 (6H, s, NMe_2), 2.03 (6H, s, $PC(CH_2)_3$), 1.89 (3H, s, CH–Ad), 1.60 (6H, s, CH_2–Ad); ^{13}C NMR (125 MHz, C_6D_6) δ 159.27 (d, J=47.8 Hz), 150.60 (d, J=12.5 Hz), 128.47 (d, J=35.2 Hz), 121.59 (d, J=7.5 Hz), 121.55, 40.78 (d, J=6.3 Hz), 39.87 (d, J=40.2 Hz), 38.14 (d, J=12.6 Hz), 36.66, 28.66 (d, J=8.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 94.23. [Found: C, 65.72; H, 7.71; N, 8.15; P, 8.91. $C_{19}H_{26}ClN_2P$ requires C, 65.42; H, 7.51; N, 8.03; P, 8.88].

4.3.9. 3-tert-Butyl-N,N-dimethyl-3H-1,3-benzazaphosphonol-2-amine ***5o***. A solution of compound **8o** (0.27 g, 1.0 mmol) and NEt_3 (0.2 g, 1.98 mmol) in benzene (2 mL) was heated with stirring in a thoroughly capped flask (or sealed ampoule) at 100 °C for 20 h. The reaction mixture was cooled and the solvent was evaporated. Pentane (10 mL) was added to the residue. The solution was filtered; the solvent was evaporated to ¼ of the original volume and was left at −20 °C for 24 h. The precipitated solid was collected by filtration to give the product (0.15 g, 68%), yellow crystals mp=84–85 °C (pentane). ^{1}H NMR (500 MHz, C_6D_6) δ 7.65 (1H, d, J=8.0 Hz, 7-H), 7.44–7.42 (1H, m, 4-H), 7.23 (1H, t, J=8.0 Hz, 6-H), 6.88 (1H, m, 5-H), 2.80 (6H, br s, 2-NMe_2), 0.95 (9H, d, J=12.5 Hz, CMe_3); ^{13}C NMR (125 MHz, C_6D_6) δ 178.08 (d, J=24.0 Hz), 161.38, (d, J=2.5 Hz), 130.92 (d, J=1.2 Hz), 130.06, 129.28 (d, J=22.6 Hz), 121.19 (d, J=7.5 Hz), 119.58, 34.16 (d, J=17.6 Hz), 27.90 (d, J=12.75 Hz), 22.48; ^{31}P NMR (81 MHz, C_6D_6) δ 13.2. [Found: C, 66.96; H, 8.31; N, 11.65; P, 13.27. $C_{13}H_{19}N_2P$ requires C, 66.65; H, 8.17; N, 11.96; P, 13.22].

4.3.10. 3-(1-Adamantyl)-N,N-dimethyl-3H-1,3-benzazaphosphonol-2-amine ***5p***. A solution of compound **8p** (0.5 g, 1.4 mmol) and triethylamine (0.14 g, 1.4 mmol) in benzene (3 mL) was heated with stirring in a well-stoppered flask (or a sealed ampoule) at 100 °C for 20 h. The precipitated solid was separated and the filtrate was evaporated. The residue was dissolved in pentane (15 mL) at 100 °C. The solution was filtered and the solvent was evaporated to give a viscous yellow oil (0.36 g, 82%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.63 (1H, d, J=8.0 Hz, 7-H), 7.43–7.46 (1H, m, 4-H), 7.23 (1H, t, J=8.0 Hz, 6-H), 6.88–6.94 (1H, m, 4-H), 2.86 (6H, br s, 2-NMe_2), 1.73 (6H, s, $PC(CH_2)_3$), 1.64 (3H, s, CH–Ad), 1.45 (6H, m, CH_2–Ad); ^{13}C NMR (125 MHz, C_6D_6) δ 176.76 (d, J=25.1 Hz), 161.48, 129.93, 129.46 (d, J=21.4 Hz), 121.05 (d, J=6.3 Hz),119.37, 39.54 (d, J=8.8 Hz), 38.38 (d, J=18.9 Hz), 36.55, 29.08 (d, J=7.5 Hz), 28.11 (dd, J=127.0, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 11.1. [Found: C, 73.00; H, 8.16; N, 9.05; P, 9.83. $C_{19}H_{25}N_2P$ requires C, 73.05; H, 8.07; N, 8.97; P, 9.92].

4.4. X-ray crystallography

Numerical details are presented in Table 4. *Data collection*: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART CCDC for **4b**, Siemens P3 for **7**). Measurements were performed with monochromated Mo-$K\alpha$ radiation. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97, G.M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model except for methyl hydrogens, for which idealized rigid groups were employed.

Table 4
Details of X-ray structure analyses of **4b** and **7**

Compound	**4b**	**7**
Formula	$C_{14}H_{25}N_4P$	$C_{14}H_{22}N_3OPS$
M_r	280.35	311.38
Habit	Yellow plate	Yellow prism
Crystal size/mm	0.4×0.15×0.04	0.7×0.55×0.45
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Cell constants:		
a/Å	9.8191 (4)	50.310 (8)
b/Å	13.8618 (6)	9.3053 (16)
c/Å	11.5729 (6)	13.748 (2)
α/°	90	90
β/°	94.939(2)	91.083(10)
γ/°	90	90
V/Å^3	1569.34	6435.0
Z	4	16
D_x/Mg m^{-3}	1.187	1.286
μ/mm^{-1}	0.17	0.30
F(000)	608	2656
T/°C	−100	−100
$2\theta_{max}$	50	50
No. of reflections:		
Measured	11,200	9640
Independent	2680	5647
R_{int}	0.036	0.029
Parameters	179	371
$wR(F^2$, all refl.)	0.116	0.086
$R(F, >4\sigma(F))$	0.041	0.034
S	0.95	1.03
Max. $\Delta\rho$/e Å^{-3}	0.32	0.30

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC 807930 (**4b**), 709630 (**7**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Supplementary data includes Tables S1 and S2 with the calculated total and relative energy values, a short discussion of the two-step mechanism of cyclization of **4**, Fig. S2 with the VMD representation of the optimized structures **8** and **20** and a complete set of Cartesian coordinates for all optimized structures. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.007.

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