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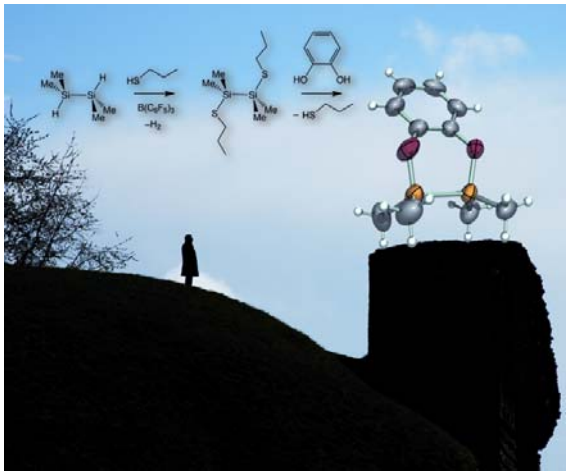

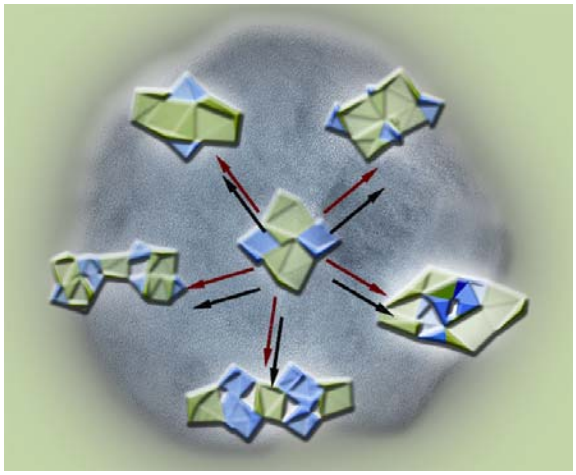

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Phosphazene *vs.*diazaphospholene PN-bond cleavage in spirocyclic cyclodiphosphazenes†

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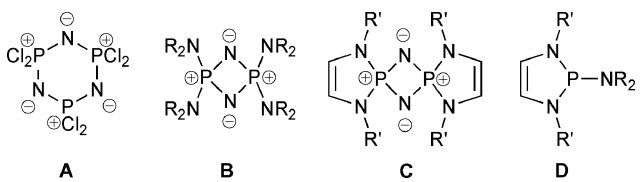
Thermolysis of 2-azido-1,3,2-diazaphospholenes offers access to novel and rare spirocyclic cyclodiphosphazenes. The spectroscopic data and X-ray structure of one representative of the 2-azido-1,3,2-diazaphospholenes reveals an ionic bonding situation explaining sufficiently its rather high thermal stability. The cyclodiphosphazenes were characterised by NMR, mass spectrometry, and X-ray diffractometry. The results of ESI-FT-ICR studies demonstrate the potential of these compounds to undergo reductive elimination at a phosphazene unit *via* [1,4]-cycloreversion of a λ^5-diazaphospholene ring, as well as symmetrical cleavage of the P_2N_2-unit. The unexpected inclusion of benzene in the crystal of one of the cyclodiphosphazenes was interpreted in terms of molecular recognition. Chemical reaction studies comprise the proof of double N-protonation at a phosphazene ring, and hydrolytic degradation *via* selective cleavage of a phosphazene P–N bond.

Introduction

Stable phosphazenes are composed of alternating R_2P- and N-moieties that form either rings with sizes between two or up to forty, or polymers with as much as 15 000 repeating units.[1] The first reported procedure for the synthesis of such polymers started from the cyclotriphosphazene **A** (Scheme 1) which was prepared by reaction of NH_4Cl and PCl_5, and was the first phosphazene to be ever made.[2] This cyclic trimer whose structure was first proposed in 1895 by Stokes[3] is since then used to access polyphosphazenes *via* ring-opening polymerisation in the molten state[4] or in the presence of cationic catalysts.[5] Subsequent displacement of the chlorine substituents on the polymer backbone offers access to a broad range of inorganic polymers with adjustable properties which make useful functional materials for various applications.[6]



Scheme 1

The most simple building block for polyphosphazenes is obviously not the cyclotriphosphazene **A** but rather the phosphinonitrene monomer, R_2PN.[7] However, species of this type are unstable toward oligomerisation, and it was predicted that cyclotrimerisation of transient phosphinonitrenes is thermodynamically favoured over cyclodimerisation.[8] Nonetheless, cyclodiphosphazenes **B** can be obtained when sterically bulky ligands on the phosphorus atoms are present, and the first derivative was prepared more than two decades ago *via* thermolysis or photolysis of a diamino–azido phosphine and dimerisation of the transient phosphinonitrene formed.[7] Although some further stable cyclodiphosphazenes became known later on,[9] compounds of this type remain scarce until today, and their chemical properties have not been studied in depth.

Some time ago we reported on the synthesis of 2-amino-1,3,2-diazaphospholenes **D** and provided quantum chemical evidence for a perceptible weakening of the *endocyclic* PN-bonds in these compounds[10] that is in stark contrast to the observed polarisation of exocyclic bonds in *P*-hydrogen-,[11] *P*-cyclopentadienyl-,[12] and *P*-phosphinyl-substituted 1,3,2-diazaphospholenes.[13] This effect was explained by hyperconjugation between the lone-pair at the exocyclic nitrogen atom and the σ*-orbitals of the endocyclic PN-bonds and resulted at the same time in relative strengthening of the exocyclic PN-bond.[10] In principle, this interaction should facilitate [1,4]-cycloreversion of the heterocycle in **D** to afford a 1,4-diazabutadiene and a (transient) phosphinidene[14] which has a reputation as a highly reactive intermediate.[15] By analogy to this process, fragmentation of a five-membered ring in a cyclodiphosphazene **C** might afford new σ^2,λ^3-phosphines, or, when both diazaphospholene rings are cleaved, the elusive molecule P_2N_2[16] or polymeric $(PN)_x$-materials.[17]

These considerations prompted us to investigate this chemistry in more detail. We report here on the synthesis and characterisation of spirocyclic representatives of rare cyclodiphosphazenes, and on mass spectrometric studies which were carried out to establish the fragmentation pathway of the spirocyclic assembly. The results are expected to provide insight if compounds of type **C** may undergo selective PN-bond activation to yield new types of phosphorus–nitrogen compounds.

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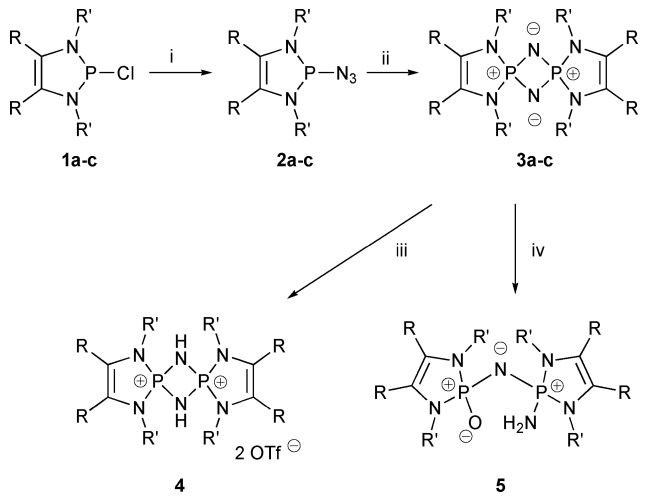
Results and discussion

Syntheses

Thermal decomposition of azidophosphines is a useful method for the generation of cyclodiphosphazenes (Scheme 2).[7,9] The appropriate 2-azido-1,3,2-diazaphospholenes **2a–c** were easily accessed by salt metathesis between the 2-chloro-1,3,2-diazaphospholenes **1a–c** and sodium azide in the presence of a catalytic amount of LiCl to increase the solubility of the azide ion in THF. ^{31}P NMR spectra indicated that the conversion was complete after the reaction mixtures had been stirred for 16 h at ambient temperature. The solvents were then evaporated, and the residues dissolved in toluene, followed by filtration of the insoluble parts. Further purification of the products **2a–c** is not necessary for the consecutive reaction, but **2a** was isolated in pure form in 91% yield after removal of the solvent, and recrystallisation from diethylether/THF at −20 °C.



Scheme 2 Synthesis of 2-azido-1,3,2-diazaphospholenes **2a–c**, cyclodiphosphazenes **3a–c**, and **4**, **5** (**a**: R′ = 2,6-$Me_2C_6H_3$, R = H; **b**, **4**: R′ = 2,4,6-$Me_3C_6H_2$, R = H; **c**, **5**: R′ = 2,6-$^i Pr_2C_6H_3$, R = Me). *Reagents and conditions*: i. NaN_3, LiCl, 16 h; ii. 6 h at 110 °C, iii. excess HOTf, CH_2Cl_2, iv. neat DMF, 2 h at 145 °C.

For the transformation of **2a–c** into cyclophosphazenes, the toluene solutions were heated to 110 °C for several hours until the ^{31}P NMR spectra showed that the reaction was complete. Careful inspection of the ^{31}P NMR spectra of the reaction mixtures showed no signals indicating the formation of side-products and, furthermore, mass spectra of the residues obtained after evaporation of the solvent gave no evidence for the presence of cyclotriphosphazenes or polymeric products. Crystallisation from concentrated reaction mixtures finally afforded the cyclodiphosphazenes **3a–c** in 75–95% yield.

Characterisation of the *P*-azido-1,3,2-diazaphospholene 2a

The pure 2-azido-1,3,2-diazaphospholene **2a** was isolated as colourless, air- and moisture-sensitive crystalline material and was characterised by spectroscopic techniques and an X-ray diffraction study. As already known for bulkily substituted diamino azidophosphines, **2a** is a stable and non-explosive solid,[18] but should nevertheless always be handled with suitable safety precautions. The ^{31}P NMR signal of **2a** (δ 118.3) is more shielded than in other diamino azidophosphines,[18] and the ^{1}H and ^{13}C NMR data are similar to those of the corresponding 2-chloro-1,3,2-diazaphospholene, **1a**.[19] The IR spectrum displays an intense band attributable to ν_{NN} at 2080 cm^{-1} in the typical region for azidophosphines.[20]

The crystals of **2a** contain isolated molecules without significant intermolecular interactions (Fig. 1). The five-membered ring displays a flat envelope conformation with an angle between the PN_2 and C_2N_2 planes of 12°. The P1–N2/N5 bond distances in the ring (1.682(1), 1.683(1) Å) match those in 2-chloro-1,3,2-diazaphospholenes (1.66–1.68 Å[19]). The P1–N11 bond to the azide substituent (1.862(1) Å) is significantly longer than both the endocyclic PN bonds in **2a** and the corresponding P–N(azide) bonds in known acyclic derivatives $(R_2N)_2P–N_3$ (1.78–1.79 Å[21]) but compares to the bond length in a tricyclic azidophosphine reported by Schranz *et al.*[22] The azide substituent shows a quasi linear arrangement with an NNN-angle of 177.8(2)°, and the N11–N12 (1.228(2) Å) and N12–N13 distances (1.135(2) Å) are normal. The relation between the endocyclic P1–N2/N5 and the exocyclic P1–N11 bonds in **2a** suggests the presence of a similar n(P–N)–σ*(P–X) (X = N_3) interaction as in 2-chlorodiazaphospholenes[19,23] and may explain the relatively high thermal stability of **2a**.

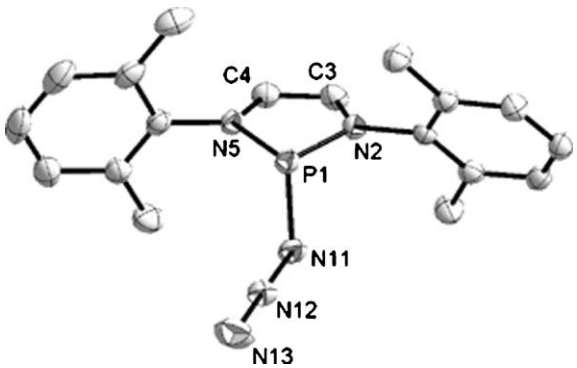


Fig. 1 Molecular structure of **2a** in the crystal. Thermal ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N5 1.682(1), P1–N2 1.683(1), P1–N11 1.862(1), N11–N12 1.228(2), N12–N13 1.135(2), N2–C3 1.415(2), C3–C4 1.329(2), C4–N5 1.409(2); N5–P1–N2 89.4 (1), N5–P1–N11 103.0(1), N2–P1–N11 98.7(1), N12–N11–P1 113.0(1), N13–N12–N11 177.8(2).

Characterisation of the cyclodiphosphazenes 3a–c

The ^{31}P NMR-spectra of the cyclodiphosphazenes **3a–c** display singlets with a chemical shift of 33 ppm which is very similar to that reported for $[(^iPr_2N)_2PN]_2$.[7] The ^{1}H NMR spectra of **3a**,**b** display AA′XX′-type multiplets for the olefinic protons in the five-membered heterocycles; all other data are normal.

Suitable crystals for X-ray diffraction studies of **3a**,**b** were grown from cooled toluene solutions. The structure of **3a** is shown in Fig. 2. Surprisingly, **3b** was found to crystallise as a 1 : 1 solvate with one molecule of benzene (see Fig. 3) which was present as a trace impurity in the solvent used. The molecules occupy sites with crystallographic C_i (**3a**) and C_{2h} symmetry (**3b**). Selected bond lengths and angles are summarised in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) of **3a**,**b**

	3a	**3b**
P1–N1	1.642(2)	1.641(2)
P1–N1#[a]	1.639(2)	1.642(2)
P1–N2	1.666(2)	1.661(2)
P1–N5	1.666(2)	
N2–C3	1.405(3)	1.414(2)
N5–C4	1.408(3)	
C3–C4[b]	1.325(3)	1.326(4)
P1–N1–P1#[a]	85.0(1)	84.9(1)
N1–P1–N1#[a]	95.0(1)	95.1(1)
N2–P1–N5(N2#)	91.4(1)	91.8(1)

[a] N1, N1# and P1, P1# indicate pairs of atoms related by crystallographic C_i symmetry. [b] C3–C3# in the case of **3b**.

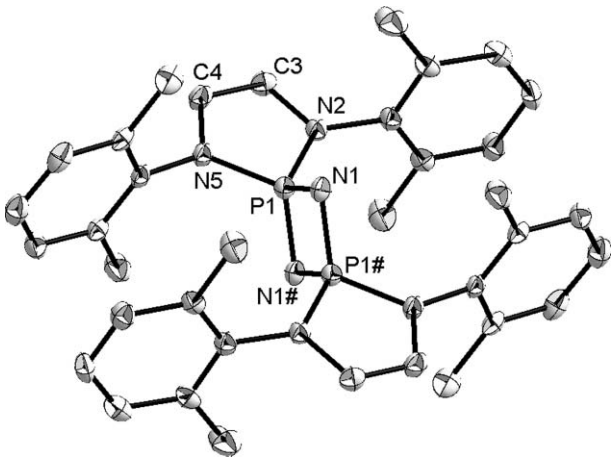


Fig. 2 Molecular structure of **3a**. Thermal ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity.

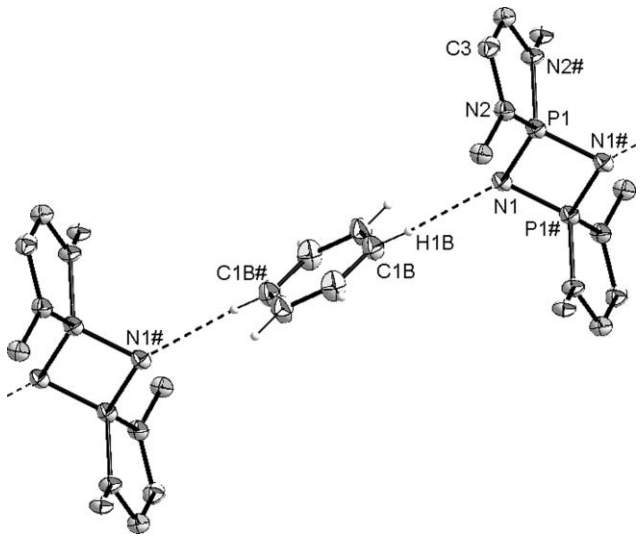


Fig. 3 Representation of the intermolecular interactions between two molecules of **3b** and one benzene molecule in the solvate **3b**·C_6H_6. The carbon atoms in the aryl rings of **3b** that are not directly attached to the ring nitrogen atoms and all hydrogen atoms of **3b** have been omitted for clarity. Intermolecular distances (Å) and angle (°): N1–C1B 3.580(4), N1–H1B 2.63; N1–H1B–C1B 176.0.

The molecular structures of both compounds show very similar features. The 1,3,2-diazaphospholene rings and the central phosphazene ring are all planar and are arranged mutually orthogonal. The flanking aryl rings lie perpendicular to the diazaphospholene rings and are nearly parallel to each other. The special ring stacking motif allows the methyl groups in 2,6-position of opposite aromatic rings to evade both each other and the adjacent nitrogen atoms in the phosphazene ring and yields thus minimal steric repulsion. Looking at the arrangement of the different building blocks, it is easily envisaged that attachment of six peripheral aryl rings to a cyclotriphosphazene unit must result in greater crowding, suggesting that the observed preference for the cyclodiphosphazene structure owes mainly to steric constraints.

The phosphorus nitrogen bonds in the central phosphazene rings display values around 1.64 Å and are by some 2 pm shorter than the PN-bonds in the five-membered rings. All PN distances are shorter than typical single bond lengths[24] and resemble the values reported for known tetraamino-cyclodiphosphazenes.[7,9] The NC and CC bond lengths are similar as in **2a** and in other 1,3,2-diazaphospholenes.[11,19]

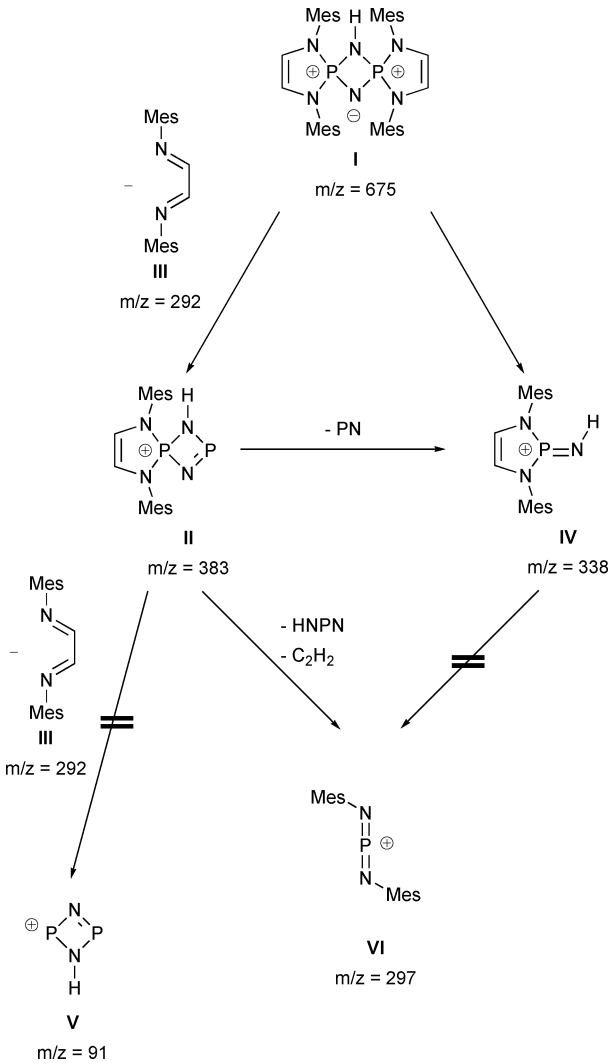
The inclusion of one molecule of benzene per formula unit of **3b** results in an interesting packing structure as shown in Fig. 3. The phosphazene nitrogen atoms N1, N1# display short intermolecular distances of 3.580(4) Å to the C1B and C1B# atoms in the benzene molecule that are interpreted as a sign of weak C–H···donor hydrogen bonds[25] which link phosphazene and benzene molecules in a one-dimensional strand parallel to the crystalline *c*-axis.

The inclusion of benzene molecules in the solvate **3b**·C_6H_6 owes presumably to both the presence of appropriately sized cavities between molecules of **3b** and the possibility to form hydrogen bridges, which is facilitated by the increased charge density at the nitrogen atoms of a cyclodiphosphazene.[7,9] If one considers that neither incorporation of the bulk solvent (toluene) nor the occurrence of a similar inclusion phenomenon in crystalline **3a** was observed, it is clear that the inclusion is a highly selective process which can be described as molecular recognition.[26]

Mass spectrometric studies of the cyclodiphosphazenes 3a–c

The EI mass spectra of **3a–c** show beside the peaks of the molecular radical cations those of characteristic fragment ions arising from elimination of 1,4-diazabutadienyl radicals. The fragmentation process can be explained by cleavage of a diazabutadiene unit under simultaneous shift of a hydrogen atom from the *ortho*-methyl group of a *N*-aryl substituent and concomitant formation of a fragment ion with an even electron number; the loss of a neutral diazabutadiene is not observed as this would end up in the formation of another radical cation and is obviously energetically less favourable.

To obtain more detailed information on the decay of cyclodiphosphazenes in the gas phase, compound **3b** was studied also by ESI-FT-ICR mass spectrometry using MS^2/MS^3-CID and double resonance experiments. The use of the ESI technique was considered as a particular advantage as it allows to suppress the formation of radical ions. The ESI mass spectrum of **3b** shows a peak at *m*/*z* 675.3 corresponding to a protonated molecular ion **I** (*cf*. Scheme 3) and an additional peak of a fragment ion at *m*/*z* 383.2 (Fig. 4(a)).



Scheme 3 Fragmentation pathway of N-protonated monocation **I**.

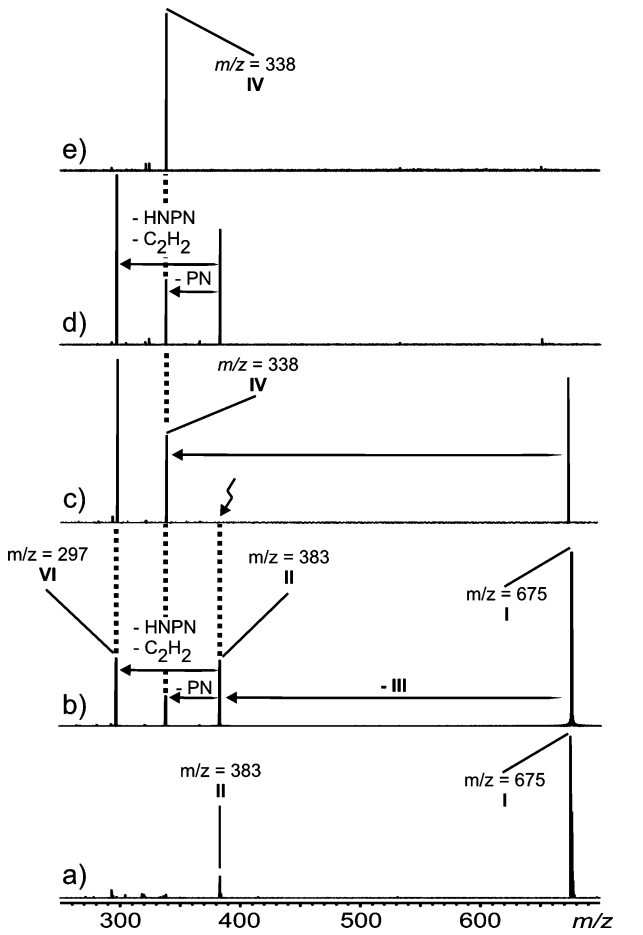


Fig. 4 ESI-MS spectra of **3b** recorded in the positive ion mode sprayed from a 50 μM methanol solution: (a) only two peaks attributable to the protonated cation **I** and a fragment ion **II** are visible; (b) CID-spectrum of the mass selected monocation **I**; (c) double resonance experiment of the mass selected cation **I** with all ions with $m/z = 383$ being removed from the collision cell during the fragmentation period; (d) MS^3 experiment with mass selected **II** which results from previous fragmentation of mass selected **I**; (e) MS^3 experiment with mass selected **IV** resulting from previous fragmentation of mass selected **I**.

Additional information on the fragmentation mechanism was secured from the CID and double resonance experiments. Upon mass selection of the parent ion followed by collisional activation, cation **I** shows two different decay pathways (Fig. 4(b) and (c)). The first one proceeds by the loss of a 1,4-diazabutadiene **III** in a [1,4]-cycloreversion and affords cation **II**. The second fragmentation pathway involves cleavage of the phosphazene unit by loss of a neutral phosphinonitrene and gives the N-monoprotonated phosphinonitrene **IV**. The same ion is also obtained *via* further fragmentation of **II** under extrusion of PN. An alternative decay pathway of **II** involves the loss of a neutral fragment of composition $C_2H_3N_2P$ to give the phosphorus analogue of a carbodiimide **VI** (Fig. 4(d)). In contrast, decay of the protonated monophosphazene cation **IV** by loss of HN/C_2H_2 which would likewise give **VI** was not observed (Fig. 4(e)). Likewise, a second [1,4]-cycloreversion of **II** resulting in the formation of a diazabutadiene **III** and a cation HN_2P_2 (**V**) could not be detected.

These gas-phase studies reveal that breaking phosphorus nitrogen bonds is the favourite decay channel for protonated **3b**. Support for the initial protonation occurring at a phosphazene nitrogen atom comes from the fact that a stable cation of this type has been isolated (see below). The observed fragmentation processes are conclusively interpreted by assuming that both types of P–N bonds are accessible for cleavage, thus giving way to two possible decay mechanisms. The breaking of bonds in the phosphazene ring recovers a phosphinonitrene and reverses thereby the formation of **3b**. To the best of our knowledge there is no evidence for an equilibrium between cyclo- or poly-phosphazenes and a monomeric phosphinonitrene building block in solution. As an alternative, the observed loss of 1,4-diazabutadiene provides evidence that the postulated [1,4]-cycloreversion of a diazaphospholene unit can actually take place. Fragmentation *via* reductive elimination at phosphorus has not yet been reported for cyclophosphazenes whose dominant decay process in the gas phase involves the loss of a negatively charged exocyclic substituent.[27] The previously reported finding of a biphenyl radical anion being produced in the reduction of $P_3N_3Ph_6$ with alkali metals may be explained by a reductive elimination pathway, but this interpretation is questionable as the fate of the phosphorus compound in this reaction remains unknown.[28] The proposed molecular structure of **VI** is supported by the fact that isolable Lewis-base adducts

of such cations are known.[29] Likewise, iminophosphenium ions of type **IV** are known, although they are only marginally stable.[18a,30] In contrast, there is no precedence for the spirocyclic skeleton of **II**; if one considers that the overall mass loss during the formation of a daughter ion **VI** can be rationalised by elimination of a stable 1,3,2-diazaphosphole, it may be speculated that the creation of the fragment ions **II**, **VI** is accompanied by extensive rearrangement processes.

Reactivity of cyclodiphosphazene 3c

That the phosphazene nitrogen atoms constitute the most basic site in the cyclodiphosphazenes under study is demonstrated by reaction of **3b** with excess triflic acid to give the salt **4** (Scheme 2). The product was isolated after work-up in 89% yield and characterised by NMR data and a single-crystal X-ray diffraction study of a solvate **4**·2HOTf that was obtained by crystallisation from CH_2Cl_2 at −20 °C. The ^{31}P NMR signal of **4** (δ 5.0) exhibits an upfield shift as compared to both **3b** and known tetraaminophosphonium ions which display signals between 20 and 45 ppm.[31] The crystalline solvate contains cations (Fig. 5) that feature crystallographic C_2 symmetry and are connected with the two triflate anions *via* NH···O hydrogen bridges. The overall disposition of the spirocyclic skeleton of the cation is similar as in **3b** but the two structures differ in a lengthening of the P1–N1/N1# bonds in the phosphazene ring by approx. 2 pm and a concomitant shortening of the P1–N2/N5 distances in the diazaphospholene moiety by approx. 1 pm. Since at the same time the N–C bonds are by 2–3 pm shorter and the C–C bonds in the diazaphospholene ring by 2 pm shorter than in **3b**, the structural data point to a more pronounced bond localisation.

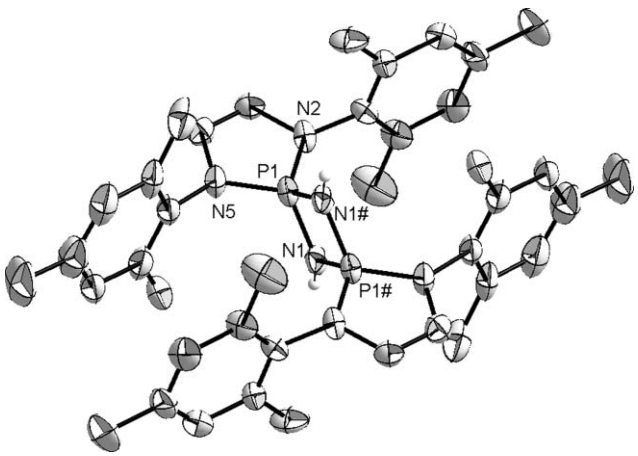


Fig. 5 Representation of the cation in the solvate **4**·2HOTf. Thermal ellipsoids are drawn at 50% probability level and H atoms except those at N1 and N1# to N have been omitted for clarity. N1, N1# and P1, P1# indicate pairs of atoms in symmetry equivalent halves of the molecules related by a symmetry operation $0.5 - x$, $1.5 - y$, $1 - z$. Selected bond lengths (Å): N1–P1 1.666(5), P1–N2 1.601(6), P1–N5 1.607(5), P1–N1# 1.657(5)

By heating of **3c** in wet DMF a product **5** arising from hydrolytic cleavage of one P–N bond in the phosphazene ring was obtained. The ^{31}P NMR spectrum shows two doublets of an AB-type spin system with chemical shifts at 5.2 and 3.0 ppm and a coupling of 31.7 Hz. Besides the signals attributable to two distinguishable N-substituted 1,3,2-diazaphospholene moieties, the ^{1}H NMR spectrum displays an additional doublet with a splitting by $^2J_{PH}$ = 2.9 Hz that is assigned to an NH_2-group. The proposed structure of **5** is confirmed by the results of an X-ray diffraction study that was carried out on a crystal of a toluene solvate obtained from toluene solution at low temperature (Fig. 6). The O1–P1–P1′–N1′ torsional angle is 45°. One of the NH_2-hydrogen atoms (H1′B) is connected by an intramolecular hydrogen bridge with the oxygen atom O1 (H1′B···O1 2.44(4) Å), thus forming a twisted six-membered ring. The P–N bonds in the 1,3,2-diazaphospholene moieties are in the range 1.68–1.70 Å and are only slightly longer than in **3a**,**b**. The bridging N1 atom features distances of 1.565(4) and 1.617(4) Å to the adjacent phosphorus atoms of which the one to the P1′ atom bearing the amino group is clearly shorter. The P1′–N1′ bond in the NH_2 substituent of 1.633(4) Å is likewise shorter than the corresponding bond in an NH_2-substituted 1,3,2-diazaphospholene.[10] The P1–O1 bond of 1.489(3) Å lies in the typical range for phosphine oxides.[32]

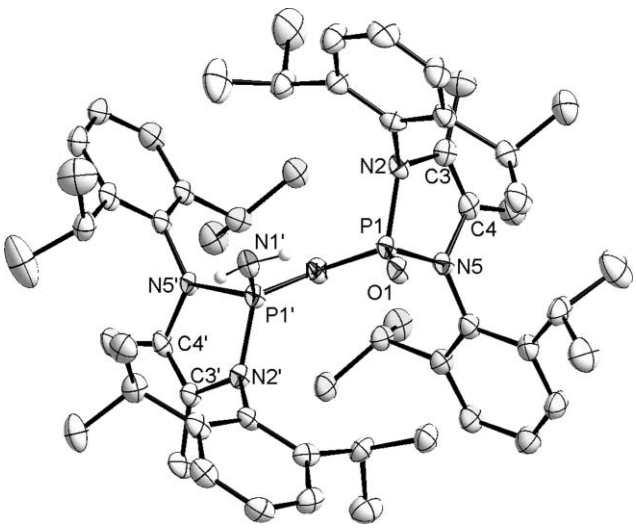


Fig. 6 Representation of the molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability level and H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°). O1–P1 1.489(3), N1–P1′ 1.565(4), N1–P1 1.617(4), P1–N5 1.675(4), P1–N2 1.697(3), N2–C3 1.435(5), C3–C4 1.329(6), C4–N5 1.438(5), N1′–P1′ 1.633(4), N1′–H1′A 0.91(2), N1′–H1′B 0.91(2), P1′–N5′ 1.670(3), P1′–N2′ 1.682(4), N2′–C3′ 1.443(5), C3′–C4′ 1.324(5), C4′–N5′ 1.446(5); P1′–N1–P1 132.0(2), N5–P1–N2 91.5(2), N5′–P1′–N2′ 91.6(2).

The reaction of **3c** with water is remarkable since the preferred reaction mode of cyclophosphazenes involves cleavage of exocyclic bonds with conservation of the heterocyclic ring.[33] A similar hydrolytic ring opening was, however, reported for a diazadiphosphetidinium salt.[34] A plausible reason for the particular reactivity of **3c** lies in the combination of high ring strain in the P_2N_2-ring with efficient protection of the PN-bonds in the 1,3,2-diazaphospholene rings by the flanking 2,6-diisopropylphenyl groups.

Conclusions

The selective synthesis of novel and rare spirocyclic cyclodiphosphazenes is achieved by thermolysis of 2-azido-1,3,2-diazaphospholenes that were obtained by salt metathesis from

readily available 2-chloro-1,3,2-diazaphospholenes and sodium azide. Although the NMR and crystal structural data show no significant differences to known monocyclic cyclodiphosphazenes, the highly specific inclusion of benzene present as trace impurity in the solvent in crystalline **3b** is a surprising result which can be interpreted as an example for molecular recognition in the solid state. A comprehensive mass spectrometric study reveals the accessibility of both types of PN-bonds for fragmentation reactions of N-protonated cations in the gas phase. Two observable decay patterns include the splitting of the diphosphazene unit into monomeric phosphinonitrenes and the rupture of the diazaphospholene rings by [1 + 4]-cycloreversion under formal reductive elimination at phosphorus and are both highly unusual for cyclophosphazenes. Realising these fragmentations with neutral molecules (in the gas phase or even in solution) rather than protonated cations would make the cyclodiphosphazenes under study suitable precursors for the generation for phosphinonitrenes or novel $(PN)_x$-compounds. Finally, the hydrolytic ring opening reaction reveals a highly unusual reaction mode for a cyclophosphazene which is presumably owed to the sterical protection of the peripheral P–N bonds by the bulky N-aryl substituents.

Experimental

General considerations

All manipulations were carried out under protective gas atmosphere (argon) and in flame dried glassware. Solvents were dried prior to use by common procedures. **1a–c** were synthesised according to reported procedures.[19] All other chemicals were purchased from commercial suppliers. NMR Spectra: Bruker Avance 400 (^{1}H: 400.13 MHz, ^{31}P: 161.9 MHz, ^{13}C: 100.4 MHz) at 30 °C; chemical shifts referred to external TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P); positive signs of chemical shifts denote shifts to lower frequencies; coupling constants are given as absolute values; prefixes *ipso*-, *o*-, *m*-, *p*- denote atoms of aryl-substituents. ESI mass spectra were recorded on a Bruker APEX IV Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70° spray needle. Analyte solutions were introduced into the ion source with a syringe pump (Cole–Parmers Instruments, Series 74900) at flow rates of ca. 3 − 4 μL/min. For CID experiments, the monoisotopic parent ions of interest were mass-selected in the FT-ICR cell and then collided with argon in order to increase the internal energy of the ions and provoke their decomposition. EI-MS: Varian MAT 711, 70 eV. Elemental analysis: Perkin Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

Syntheses

2-Azido-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholene (2a). 4 mmol (1.32 g) **1a**, 4 mmol (0.26 g) sodium azide and 0.1 mmol (4 mg) lithium chloride were dissolved in THF (50 mL) and stirred for 24 h at room temperature. The reaction mixture was then evaporated to dryness, the residue taken up in toluene (50 mL) and the inorganic solids filtered off. The solution was again evaporated to dryness and the residue dissolved in a mixture of Et_2O (15 mL) and THF (10 mL). Storage at −20 °C afforded colourless crystals which were filtered of and dried in vacuum. Yield: 1.22 g (91%), mp 126 °C; ^{1}H NMR (C_6D_6): δ 6.94 (s, 6 H, *m*/*p*-CH), 5.60 (d, 2 H, $^3J_{PH}$ = 1.9 Hz, N–CH), 2.33 (s, br, 12 H, *o*-CH_3); ^{13}C{^{1}H} NMR (C_6D_6): δ 138.3 (d, $^2J_{PC}$ = 12.6 Hz, *ipso*-C), 129.1 (s, br, *o*-C), 128.3 (s, *p*-C), 127.8 (d, $^4J_{PC}$ = 2.3 Hz, *p*-C), 117.9 (d, $^2J_{PC}$ = 7.6 Hz, N–CH), 18.8 (s, *o*-CH_3), 18.7 (s, *o*-CH_3); ^{31}P{^{1}H} NMR (C_6D_6): δ 118.3 (s); MS (EI, 70 eV; 405 K) *m*/*z* (%) = 327.1 ([M]$^+$, 5.4), 295.1 ([M − N_3]$^+$, 100.0), 249.1 ([M − $C_3H_{10}N_3$]$^+$, 14.1). Calc. for $C_{18}H_{20}N_5P$: C 64.08, H 5.98, N 20.76. Found: C 64.24, H 6.04, N 20.19%; IR (KBr, Nujol): $\tilde{\nu}$/cm^{-1} = 2081 (s).

General procedure for the synthesis of 3a–c. 10 mmol of the appropriate 2-chloro-1,3,2-diazaphospholene **1a–c**, 10 mmol (0.65 g) sodium azide, and 1 mmol (0.04 g) lithium chloride were dissolved in THF (100 mL) and stirred for 12 h at room temperature. The reaction mixture was then evaporated to dryness, the residue dissolved in toluene (100 mL) and the insoluble parts filtered off. The solution was then heated to 110 °C for 2 h. After cooling to room temperature the solution was concentrated to a volume of 15 mL and stored at −20 °C for crystallisation. The colourless crystals formed were filtered off and dried in vacuum.

1,4,8,11-Tetrakis(2,6-dimethylphenyl)-1,4,6,8,11,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-2,9-diene (3a). Yield: 2.31 g (75%); mp 313 °C; ^{1}H NMR ($CDCl_3$): δ 6.95–6.70 (m, 12 H, *m*/*p*-CH), 5.62 (m, 4 H, N–CH), 2.20 (s, 24 H, *o*-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.0 (dd, $^{2/4}J_{PC}$ = 1.2 Hz, *ipso*-C), 135.6 (dd, $^{3/5}J_{PC}$ = 1.7 Hz, *o*-C), 128.6 (s, *m*-CH), 128.2 (s, *p*-CH), 115.4 (dd, $^{3/4}J_{PC}$ = 7.6 Hz, N–CH), 19.8 (s, *o*-CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.3 (s); MS: (EI, 70 eV, 430 K): *m*/*z* (%) = 618.3 ([M]$^+$, 100.0), 571.2 ([M − C_3H_{11}]$^+$, 33.5), 474.2 ([M − $C_{10}H_{10}N$]$^+$, 15.0), 355.1 ([M − $C_{18}H_{19}N_2$]$^+$, 82.9), 300.0 ([M − $C_{18}H_{19}N_3P$]$^+$, 11.6), 295.1 ([M − $C_{18}H_{20}N_4P$]$^+$, 15.8), 262.2 ([M − $C_{18}H_{20}N_4P_2$]$^+$, 32.9). Calc. for $C_{36}H_{40}N_6P_2$: C 69.89, H 6.52, N 13.58. Found: C 69.93, H 6.44, N 13.12%.

1,4,8,11-Tetramesityl-1,4,6,8,11,12-hexaaza-5λ^5,7λ^5-diphosphadispiro[4.1.4.1]dodeca-2,9-diene (3b). Yield: 3.22 g (95%); mp 315 °C; ^{1}H NMR ($CDCl_3$): δ 6.56 (s, 8 H, M–CH), 5.92 (m, 4 H, N–CH), 2.30 (s, 12 H, *p*-CH_3), 2.17 (s, 24 H, *o*-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 133.3 (pseudo-t, $^{4/6}J_{PC}$ = 1.2 Hz, *m*-CH), 131.4 (pseudo-t, $^{3/5}J_{PC}$ = 0.8 Hz, *o*-C), 127.8 (pseudo-t, $^{2/4}J_{PC}$ = 1.7 Hz, *ipso*-C), 123.5 (s, *p*-C), 110.0 (pseudo-t, $^{3/5}J_{PC}$ = 7.8 Hz, N–CH), 16.1 (s, *p*-CH_3), 13.3 (s, *o*-CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.4 (s); MS: (EI, 70 eV, 450 K) *m*/*z* (%) = 674.3 ([M]$^+$, 100.0), 383.1 ([M − $C_{20}H_{23}N_2$]$^+$, 95.2). Calc. for $C_{40}H_{48}N_6P_2$: C 71.20, H 7.17, N 12.45. Found: C 71.01, H 7.04, N 12.28%.

1,4,8,11-Tetra(2,6-diisopropylphenyl)-2,3,9,10-tetramethyl-1,4,6,8,11,12-hexaaza-5λ^5,7λ^5-diphospha-dispiro[4.1.4.1]-dodeca-2,9-diene (3c). Yield: 4.18 g (93%); mp 298 °C; ^{1}H NMR (C_6D_6): δ 7.01 (s, 8 H, M–CH), 6.98 (s, 4 H, *p*-CH), 3.34 (sep, 4 H, $^3J_{HH}$ = 6.8 Hz, CH), 1.18 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.17 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.12 (s, 12 H, CH_3); ^{13}C{^{1}H} NMR (C_6D_6): δ 149.2 (pseudo-t, $^{2/4}J_{PC}$ = 1.3 Hz, *ipso*-C), 135.2 (pseudo-t, $^{3/5}J_{PC}$ = 1.6 Hz, *o*-C), 129.3 (s, *o*-C), 128.5 (s, *m*-CH), 125.6 (s, *m*-CH), 124.5 (s, *p*-CH), 118.9 (pseudo-t, $^{2/4}J_{PC}$ = 7.0 Hz, N–C), 28.6 (s, CH), 24.8 (s, CH_3), 24.0 (s, CH_3), 12.2 (pseudo-t, $^{3/5}J_{PC}$ = 2.1 Hz, N–CCH_3); ^{31}P{^{1}H} NMR (C_6D_6): δ 33.7 (s); MS: (EI, 70 eV, 450 K) *m*/*z* (%) = 898.6 ([M]$^+$, 4.8), 495.3 ([M − $C_{28}H_{39}N_2$]$^+$, 10.3), 452.3 ([M − $C_{28}H_{40}N_4P$ + OH]$^+$, 100.0), 435.4 ([M − $C_{28}H_{40}N_4P$]$^+$,

12.3), 361.3 ([M − $C_{25}H_{33}N_4P_2$]$^+$, 43.2), 202.2 ([M − $C_{42}H_{60}N_5P_2$]$^+$, 81.5). Calc. for $C_{56}H_{60}N_6P_2$: C 74.80, H 8.97, N 9.35. Found: C 74.86, H 9.05, N 8.98%.

1,4,8,11-Tetramesityl-1,4,6,8,11,12-hexaaza-5,7-diphosphoniadispiro[4.1.4.1]dodeca-2,6,9-triene bis(trifluormethanesulfonate) (4). A solution of 1 mmol (674 mg) of **3b** in toluene (30 mL) was cooled to −78 °C. Triflic acid (2 mmol, 300 mg) was added dropwise. The solution was stirred for additional 15 min and then allowed to warm to ambient temperature. The solvent was evaporated in vacuum and the residue dissolved in 30 mL of CH_2Cl_2. Storage of the solution at −20 °C produced colourless crystals which were filtered off and dried in vacuum. Yield 869 mg (89%); ^{1}H NMR ($CDCl_3$): δ 7.13 (s, br, 2H, NH), 6.68 (s, br, 8H, M–CH), 6.08 (s, br, 4 H, N–CH), 2.29 (s, br, 12 H, *p*-CH_3), 2.04 (s, br, 24 H, *o*-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.1 (pseudo-t, $^{2/4}J_{PC}$ = 1.0 Hz, *ipso*-C), 137.1 (pseudo-t, $^{3/5}J_{PC}$ = 1.7 Hz, *o*-C), 130.4 (s, *m*-CH), 126.7 (s, *p*-C), 119.5 (q, $^1J_{CF}$ = 317.8 Hz, CF_3), 118.4 (pseudo-t, $^{2/4}J_{PC}$ = 11.8 Hz, N–CH), 21.6 (s, *p*-CH_3), 17.9 (s, *o*-CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.0 (s). Due to the highly hygroscopic nature no elemental analysis could be obtained.

1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl-2-[1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl-2-oxo-2λ^5-1,3,2-diazaphospholenylimino]-2λ^5-1,3,2-diazaphospholenylamine (5). 5 mmol (450 mg) of **3c** were dissolved in DMF (15 mL) and heated to 150 °C for 8 h. After cooling to room temperature all volatiles were removed in vacuum and the remaining solid was taken up in toluene (5 mL). Storage at −20 °C afforded colourless crystals that were filtered off and dried in vacuum. Yield: 437 mg (95%); mp 324 °C; ^{1}H NMR (C_6D_6): δ 4.18 (sep, 1 H; $^3J_{HH}$ = 6.7 Hz, CH), 4.06 (sep, 1 H; $^3J_{HH}$ = 6.7 Hz, CH), 3.96 (sep, 1 H; $^3J_{HH}$ = 6.8 Hz, CH), 3.82 (sep, 1 H; $^3J_{HH}$ = 6.9 Hz, CH), 3.38 (sep, 1 H; $^3J_{HH}$ = 6.7 Hz, CH), 3.35 (sep, 1 H; $^3J_{HH}$ = 6.7 Hz, CH), 3.08 (sep, 1 H; $^3J_{HH}$ = 6.9 Hz, CH), 2.70 (sep, 1 H; $^3J_{HH}$ = 6.7 Hz, CH), 2.29 (d, 2 H, $^2J_{PH}$ = 2.9 Hz, NH_2), 1.62 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, CH_3) 1.59 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.58 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.50 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.37 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.30 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.23 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.13 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.00 (dd, 3 H, $^4J_{PP}$ = 6.8 Hz, $^6J_{PP}$ = 1.6 Hz, CH_3), 0.95 (dd, 3 H, $^3J_{HH}$ = 6.4 Hz, $^6J_{PP}$ = 5.1 Hz, CH_3), 0.84 (dd, 3 H, $^3J_{HH}$ = 6.6 Hz, $^6J_{PH}$ = 1.4 Hz, CH_3), 0.50 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, CH_3); ^{31}P{^{1}H} NMR (C_6D_6): δ 5.3 (d, $^2J_{PP}$ = 31.7 Hz, PO), 2.0 (d, $^2J_{PP}$ = 31.7 Hz, PNH_2); MS (EI, 70 eV, 590 K) *m*/*z* (%) = 916.6 ([M]$^+$, 100.0), 512.2 ([M − $C_{28}H_{40}N_2$]$^+$, 17.2), 202.1 ([M − $C_{28}H_{42}N_4P_2O$]$^+$, 7.0). Calc. for $C_{56}H_{82}N_6P_2O{\cdot}C_4H_8O$: C 72.84, H 9.17, N 8.49. Found: C 72.74, H 9.04, N 8.74%.

Crystal structure determinations

All single-crystal X-ray diffraction studies were carried out on a Nonius Kappa-CCD diffractometer at 123(2) K using Mo-Kα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97[35]) were used for structure solution and refinement (SHELXL-97,[36] full-matrix least squares on F^2). No absorption corrections were applied, and H atoms were localized by difference electron density determination and refined using a riding model (except the NH_2 group in **5**, in which H(N) were refined free).

2a. Colourless crystals, $C_{18}H_{20}N_5P$, M = 337.4, crystal size 0.45 × 0.40 × 0.35 mm, monoclinic, space group $P2_1/n$ (no. 14): a = 12.7383(8), b = 10.8003(8), c = 12.8025(6) Å, β = 90.415(4)°, V = 1761.3(2) Å^3, Z = 4, D_c = 1.272 Mg m^{-3}, F(000) = 712, μ = 0.165 mm^{-1}, 16649 reflections ($2\theta_{max}$ = 55°), 4028 unique (R_{int} = 0.048), 221 parameters, $R1$ ($I > 2\sigma(I)$) = 0.040, $wR2$ (all data) = 0.108, largest diff. peak/hole 0.212/−0.318 e Å^{-3}.

3a. Colourless crystals, $C_{36}H_{40}N_6P_2$, M = 618.7, crystal size 0.25 × 0.15 × 0.06 mm, monoclinic, space group $P2_1/n$ (no. 14): a = 8.3779(3), b = 17.0975(7), c = 11.4017(6) Å, β = 96.728(2)°, V = 1622.0(1) Å^3, Z = 2, D_c = 1.267 Mg m^{-3}, F(000) = 656, μ = 0.170 mm^{-1}, 9486 reflections ($2\theta_{max}$ = 50°), 2855 unique (R_{int} = 0.054), 203 parameters, $R1$ ($I > 2\sigma(I)$) = 0.040, $wR2$ (all data) = 0.090, largest diff. peak and hole 0.275/−0.387 e Å^{-3}.

3b·C_6H_6. Yellowish crystals, $C_{46}H_{54}N_6P_2$ ($C_{40}H_{48}N_6P_2{\cdot}C_6H_6$), M = 752.9, crystal size 0.30 × 0.15 × 0.05 mm, orthorhombic, space group *Cmca* (no. 64): a = 22.6662(8), b = 14.4954(5), c = 12.2951(4) Å, V = 4039.6(2) Å^3, Z = 4, D_c = 1.238 Mg m^{-3}, F(000) = 1608, μ = 0.149 mm^{-1}, 13927 reflections ($2\theta_{max}$ = 50°), 1829 unique (R_{int} = 0.067), 130 parameters, $R1$ ($I > 2\sigma(I)$) = 0.039, $wR2$ (all data) = 0.098, largest diff. peak/hole 0.287/−0.354 e Å^{-3}.

4. Colourless crystals, $C_{44}H_{52}F_{12}N_6O_{12}P_2S_4$ ($[C_{40}H_{50}N_6P_2]^{2+}$-$2[CF_3SO_3]^-{\cdot}2CF_3SO_3H$), M = 1275.1, crystal size 0.30 × 0.15 × 0.10 mm, monoclinic, space group $C2/c$ (no. 15), a = 31.662(2), b = 12.3344(13), c = 16.2491(17) Å, β = 108.536(3)°, V = 6016.6(10) Å^3, Z = 4, D_c = 1.408 Mg m^{-3}, F(000) = 2624, μ = 0.307 mm^{-1}, 13155 reflections ($2\theta_{max}$ = 50°), 5235 unique (R_{int} = 0.061), 368 parameters, $R1$ ($I > 2\sigma(I)$) = 0.096, $wR2$ (all data) = 0.309, largest diff. peak/hole 1.458/−0.721 e Å^{-3}.

5·2$C_6H_5CH_3$. Colourless crystals, $C_{70}H_{98}N_6OP_2$ ($C_{56}H_{82}N_6$-$OP_2{\cdot}2C_6H_5CH_3$), M = 1101.5, crystal size 0.20 × 0.15 × 0.10 mm, triclinic, space group $P\bar{1}$ (no. 2), a = 13.279(3), b = 14.542(3), c = 17.751(4) Å, α = 102.26(3), β = 103.09(3), γ = 99.46(3)°, V = 3180.2(12) Å^3, Z = 2, D_c = 1.150 Mg m^{-3}, F(000) = 1196, μ = 0.115 mm^{-1}, 37376 reflections ($2\theta_{max}$ = 50°), 11069 unique (R_{int} = 0.103), 692 parameters, 92 restraints, $R1$ ($I > 2\sigma(I)$) = 0.080, $wR2$ (all data) = 0.219, largest diff. peak/hole 0.475/−0.474 e Å^{-3}.

CCDC reference numbers 664556 (**2a**), 664557 (**3a**), 664558 (**3b**), 664559 (**4**) and 664560 (**5**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717219b

Notes and references

1 (*a*) R. T. Oakley, S. J. Rettig, N. L. Paddock and J. Trotter, *J. Am. Chem. Soc.*, 1985, **107**, 6923; (*b*) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, 1965, **87**, 4216.
2 (*a*) J. H. Gladstone and J. D. Holmes, *J. Chem. Soc.*, 1864, **17**, 225; (*b*) J. H. Gladstone and J. D. Holmes, *Ann. Chim. Phys.*, 1864, **3**, 465.
3 H. N. Stokes, *Chem. Ber.*, 1895, **28**, 437.
4 H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, 1965, **87**, 4216.
5 R. De Jaeger and M. Gleria, *Prog. Polym. Sci.*, 1998, **23**, 179.
6 (*a*) J. E. Mark, H. R. Allcock and R. West, *Inorganic Polymers*, Prentice-Hall, New Jersey, 1992; (*b*) H. R. Allcock, *Chemistry and Applications of Polyphosphazenes*, Wiley, Hoboken, 2003; (*c*) M. Gleria, R. De Jaeger, *Phosphazenes - A World Wide Insight*, Nova Science, New York, 2004; (*d*) M. Gleria, R. De Jaeger, *Applicative Aspects of Poly(organophosphazenes)*, Nova Science, New York, 2004; (*e*) M. Gleria, R. De Jaeger, *Top. Curr. Chem.*, 2005, 250, 165.

7 A. Baceiredo, G. Bertrand, J.-P. Majoral, G. Sicard, J. Jaud and J. Galy, *J. Am. Chem. Soc.*, 1984, **106**, 6088.
8 G. Trinquier, *J. Am. Chem. Soc.*, 1986, **108**, 568.
9 (*a*) R. Reau, A. Baceiredo and G. Bertrand, *Phosphorus Sulfur Silicon Relat. Elem.*, 1994, **93–94**, 1; (*b*) J. Tirreé, D. Gudat, M. Nieger and E. Niecke, *Angew. Chem., Int. Ed.*, 2001, **40**, 3025; (*c*) R. J. Wehmschulte, M. A. Khan and S. I. Hossain, *Inorg. Chem.*, 2001, **40**, 2756.
10 S. Burck, D. Gudat, F. Lissner Nättinen, M. Nieger and T. Schleid, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2738.
11 (*a*) D. Gudat, A. Haghverdi and M. Nieger, *Angew. Chem., Int. Ed.*, 2000, **39**, 3084; (*b*) S. Burck, D. Gudat, M. Nieger and W.-W. du Mont, *J. Am. Chem. Soc.*, 2006, **128**, 3946.
12 S. Burck, D. Gudat, M. Nieger and J. Tirreé, *Dalton Trans.*, 2007, 1891.
13 (*a*) S. Burck, D. Gudat and M. Nieger, *Angew. Chem., Int. Ed.*, 2004, **43**, 4801; (*b*) S. Burck, D. Förster and D. Gudat, *Chem. Commun.*, 2006, 2810; (*c*) S. Burck, D. Gudat and M. Nieger, *Angew. Chem., Int. Ed.*, 2007, **46**, 2919.
14 Z. Benkő, D. Gudat and L. Nyulaszi, *Chem.–Eur. J.*, 2008, **14**, 902.
15 (*a*) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 523; (*b*) F. Mathey, in *Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, p. 33.
16 (*a*) O. Kwon, P. M. Almond and M. L. McKee, *J. Phys. Chem. A*, 2002, **106**, 6864; (*b*) H. Schnöckel, T. Mehner, H. S. Plitt and S. Schunck, *J. Am. Chem. Soc.*, 1989, **111**, 4578.
17 (*a*) Y. Furukawa, O. Mikami, M. Okamura and Y. Hirota, *Proc. Electrochem. Soc.*, 1986, **86**, 34; (*b*) Y. Hirota and T. Kobayashi, *J. Appl. Phys.*, 1982, **53**, 5037; (*c*) O. Mikami, M. Okamura, E. Yamaguchi, Y. Hirota and Y. Furukawa, *Jpn. J. Appl. Phys.*, 1984, **23**, 1408; (*d*) Y. H. Jeong, S. Takagi, F. Arai and T. Sugano, *J. Appl. Phys.*, 1987, **62**, 2370; (*e*) Y. Matsumoto, T. Hanajiri, T. Sugano, Le. T. T. Tuyen and T. Katoda, *Thin Solid Films*, 1995, **269**, 4146.
18 (*a*) G. Alcaraz, A. Baceiredo, F. Dahan and G. Bertrand, *J. Am. Chem. Soc.*, 1994, **116**, 1225; (*b*) G. Sicard, A. Baceiredo, G. Bertrand and J.-P. Majoral, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 459; (*c*) A. Baceiredo, G. Bertrand, J.-P. Majoral, F. El Anba and G. Manuel, *J. Am. Chem. Soc.*, 1985, **107**, 3945; (*d*) J. Tejeda, R. Reau, F. Dahan and G. Bertrand, *J. Am. Chem. Soc.*, 1993, **115**, 7880.
19 S. Burck, D. Gudat, K. Nättinen, M. Nieger, M. Niemeyer and D. Schmid, *Eur. J. Inorg. Chem.*, 2007, 5112.
20 (*a*) O. J. Scherer and N. Kuhn, *Chem. Ber.*, 1974, **107**, 2123; (*b*) I. Yu. Budilova, N. I. Gusar' and Yu. G. Gololobov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1984, **54**, 1771; (*c*) R. Kalgutkar, A. S. Ionkin, L. D. Quin and P. M. Lahti, *Tetrahedron Lett.*, 1994, **35**, 3889.
21 (*a*) U. Englert, P. Paetzold and E. Eversheim, *Z. Kristallogr.*, 1993, **208**, 307; (*b*) A. H. Cowley, F. B. Gabbai, G. Bertrand, C. J. Carrano and M. R. Bond, *J. Organomet. Chem.*, 1995, **493**, 95.
22 I. Schranz, L. P. Grocholl, L. Stahl, R. J. Staples and A. Johnson, *Inorg. Chem.*, 2000, **39**, 3037.
23 D. Gudat, A. Haghverdi, H. Hupfer and M. Nieger, *Chem.–Eur. J.*, 2000, 3414.
24 B. F. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, in *International Tables for Crystallography*, ed. A. J. C. Wilson, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992, 685.
25 G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565.
26 (*a*) D. J. Cram, *Science*, 1988, **240**, 760; (*b*) J. D. Dunitz and A. Gavezzotti, *Angew. Chem., Int. Ed.*, 2005, **44**, 1766; (*c*) F. Toda, *Adv. Supramol. Chem.*, 1992, **2**, 141.
27 (*a*) S. Daolio, P. Traldi, E. Vecchi and M. Gleria, *Org. Mass Spectrom.*, 1985, **20**, 492; (*b*) M. Gleria, S. Daolio, A. M. Maccioni, E. Vecchi and P. Traldi, *Org. Mass Spectrom.*, 1985, **20**, 686; (*c*) M. Gleria, G. Audisio, S. Daolio, P. Traldi and E. Vecchi, *Macromolecules*, 1984, **17**, 1230; (*d*) M. Gleria, G. Audisio, P. Traldi, S. Daolio and E. Vecchi, *J. Chem. Soc., Chem. Commun.*, 1983, 1380.
28 D. Chapman, S. H. Glarum and A. G. Massey, *J. Chem. Soc.*, 1963, 3140.
29 M. Blättner, M. Nieger, A. Ruban, W. W. Schoeller and E. Niecke, *Angew. Chem.*, 2000, **112**, 2876.
30 M. Mulliez, J.-P. Majoral and G. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1984, 284.
31 G. N. Koidan, A. P. Marchenko, A. A. Kudryatsev and A. M. Pinchuk, *J. Gen. Chem. USSR*, 1982, **52**, 1779.
32 Result of a query in the CSD on P–O bond length in phosphine oxides of type $(R_2N)_3PO$: 1.474 ± 0.016 Å.
33 (*a*) H. R. Allcock and T. J. Fuller, *J. Am. Chem. Soc.*, 1981, **103**, 2250; (*b*) D. G. Gabler and J. F. Haw, *Inorg. Chem.*, 1990, **29**, 4018.
34 H. Thönnessen, P. G. Jones and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1265.
35 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
36 G. M. Sheldrick, University of Göttingen, 1997.