Connecting cyclophosphazenes *via* ring N-centres with covalent linkers

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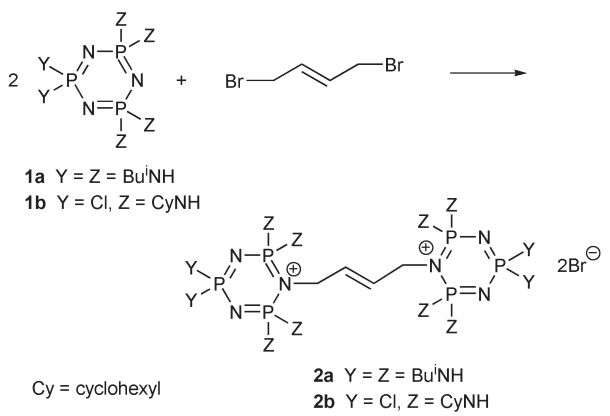
Two cyclotriphosphazene rings can be covalently linked *via* ring N-centres by a 2-butene-1,4-diyl unit and *vice versa* a cyclotriphosphazene molecule is able to bridge two cinnamyl groups *via* two ring N-centres yielding in either case dicationic assemblies which offers a route to novel polycations.

Polyphosphazenes have played an important role in the development of inorganic polymers due to the ease of introducing a wide variety of substituents onto P-centres.[1] Additionally, cyclophosphazenes can be used as building blocks for macromolecular and polymeric species. This is achieved by connecting two or more cyclophosphazene units *via* P-centres using di- or poly-functional linkers.[2] However, owing to the multitude of potential anchoring sites, linking cyclophosphazenes *via* P-centres is a rather unselective route.[3]

Herein we show that two cyclophosphazene molecules can be connected *via* ring N-centres with covalent linkers resulting in distinct products. So far only non-covalent linkages between phosphazenes have been described, in which ring N-centres play a role. These include hydrogen bonding[4] and metal coordination.[5] Nonetheless, it has been reported that cyclotriphosphazenes carrying electron-donating substituents are quaternised by methyl iodide at ring N-sites.[6] We assumed that equivalent reactions with bifunctional electrophiles provide a convenient route to link phosphazenes in covalent fashion.

Both hexakis(*iso*-butylamino) cyclotriphosphazene, **1a**,[4] and dichloro tetrakis(cyclohexylamino) cyclotriphosphazene, **1b**,[7] were treated with 1,4-dibromo-2-butene yielding compounds **2a** and **2b**, which contain dications comprising two cyclophosphazenes linked by a 2-butene-1,4-diyl unit (Scheme 1). **2a** is obtained after heating a freshly ground mixture of **1a** and 1,4-dibromo-2-butene in a 2 : 1 molar ratio to 90 °C for 1 h. The ^{31}P NMR spectrum of **2a** in chloroform displays an AX_2 signal {δ 12.9 (t), 16.8 (d), $^2J_{P-P}$ = 45.3 Hz}. Single crystals for X-ray structure analysis† were obtained from slow evaporation of a methanol solution giving crystals of the solvate **2a**·2CH_3OH.



Scheme 1

The dication in **2a** (Fig. 1) exhibits inversion symmetry, thus both phosphazene rings are aligned in parallel; their mean planes are displaced by 2.15 Å. The phosphazene ring is slightly puckered, adopting a half-chair conformation. The quaternisation of one ring N-atom has a notable effect on the P–N bonds in the ring: the bonds associated with the quaternised N atom measure 1.688(5) and 1.689(5) Å. This is rather long for cyclophosphazene bonds, which are on average 1.60 Å in the parent phosphazene **1a**.[4] Fairly long bonds were also found in cyclophosphazenes featuring protonated ring N-centres (~ 1.67 Å).[8] On the other hand, the remaining ring P–N bonds in **2a** range between 1.577(5) and 1.591(5) Å and are slightly shorter than those found in **1a**.[4] The supramolecular structure of **2a**·2CH_3OH consists of a two-dimensional assembly held together by an extensive network of hydrogen bonds (Fig. 2). All six NH groups and two ring N-atoms of each phosphazene unit are involved in H-bonding either towards bromide ions or methanol molecules.

The dichloro derivative **2b** was obtained after refluxing a solution of **1b** and 1,4-dibromo-2-butene (2 : 1 ratio) in thf for 12 h. The ^{31}P NMR spectrum of **2b** shows an AX_2 signal pattern {δ 13.3 (d), 18.9 (t), $^2J_{P-P}$ = 45.5 Hz}. The solvate **2b**·2$CHCl_3$

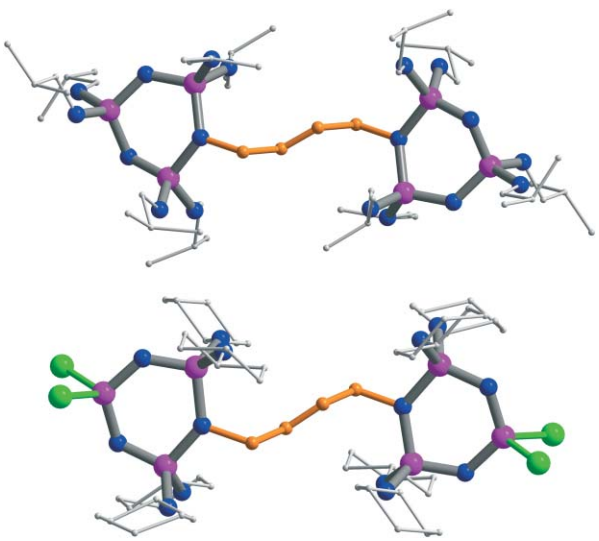


Fig. 1 Crystal structures of the dications in **2a** (top) and **2b** (bottom). H-atoms are omitted; the bridging 2-butene-1,4-diyl unit is highlighted in orange; blue: N, purple: P, green: Cl.

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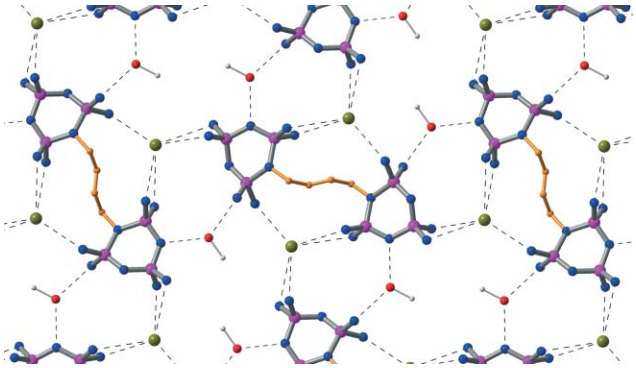
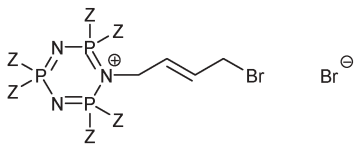


Fig. 2 Supramolecular structure of **2a**·2CH_3OH in the solid state. H-bonds are drawn as dashed lines, H-atoms and Bu^i-groups are omitted; red: O; green: Br.

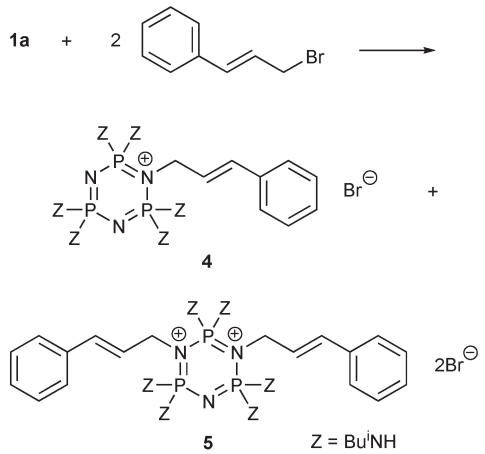
crystallised from chloroform solution containing three molecules in the asymmetric unit. The X-ray crystal structure† reveals that the ring N-centre opposite the PCl_2 unit is quaternised exclusively (Fig. 1). Evidently, the electron withdrawing effect of the PCl_2 unit prevents quaternisation of the adjacent ring N-centres.

It is interesting to note that heating a 1 : 1 mixture of **1a** and 1,4-dibromo-2-butene to 90 °C produces exclusively **2a**. There is no trace of the supposed monocationic species **3a** apparent in the ^{31}P NMR. However, reacting **1a** in the presence of 10 equivalents of 1,4-dibromo-2-butene in refluxing chloroform leads to a product mixture that contains **2a** and **3a** in a 1 : 2 molar ratio as inidcated by ^{31}P NMR which exhibits a set of AX_2 signals for each species {**3a** resonates at δ 13.1 (t) and 16.0 (d), $^2J_{P-P}$ = 43.3 Hz}. The cations of **2a** and **3a** were identified by electrospray mass spectrometry. We are currently investigating the mechanism leading to the preferential formation of **2a** over **3a**. The dicationic species **2a** is stable towards mild nucleophiles such as water, alcohols and dilute mineral acids. However, in the presence of alkali metal hydroxides and alkoxides the bridging 2-butene-1,4-diyl unit slowly ($t_{½}$ ~ 24 h) cleaves off the phosphazene rings yielding **1a**.



3a Z = Bu^iNH

In order to probe whether not only 2-butene-1,4-diyl, but also the cyclotriphosphazenes, can act as linkers, **1a** was mixed with excess cinnamyl bromide and the mixture was heated to 90 °C yielding the mono- and the di-quaternised species **4** and **5**, respectively (Scheme 2). The product ratio of **4** and **5** is 3 : 1 after 2 h, however, **5** is the main product after heating for 24 h accompanied by only traces of **4**. Solutions of both **4** and **5** in chloroform display AX_2 signals in the ^{31}P NMR spectrum {**4**: δ 12.7 (t), 17.6 (d), $^2J_{P-P}$ = 40.5 Hz; **5**: δ 15.6 (d), 32.1 (t), $^2J_{P-P}$ = 29.3 Hz}. While **4** shows ^{31}P NMR shifts similar to **2a** and **3a**, the triplet signal of **5** appears at lower field owing to the direct neighbourhood of two quaternised N-centres. Correspondingly, the P–P coupling constant in **5** is lower, since coupling occurs across a quaternised N-atom.



Scheme 2

Single crystals of **5** for X-ray structure analysis† were obtained from hexane/thf. The crystal structure confirms that the phosphazene ring binds two cinnamyl groups *via* two ring N-atoms (Fig. 3). There are two dications in the asymmetric unit, one of which contains a disordered phosphazene core. In the following only the bonding parameters of the non-disordered dication are discussed. The quaternisation of the two ring N-centres results in elongation of the adjacent P–N bonds. The P–N bonds between quaternised N-atoms and the two chemically equivalent P-atoms are longer (av. 1.684 Å) than the P–N bonds associated with the quaternised N-atom and the chemically unique P-atom (av. 1.635 Å). In contrast, the P–N bonds involving the unreacted N-atom are short (av. 1.573 Å). **5** forms an extensive network of hydrogen bonds in the solid state. The supramolecular structure consists of a double sheet arrangement of dications, which are connected by hydrogen bonding across bromide ions (Fig. 4). Again, all NH-units engage in hydrogen bonding. The phenyl groups of the cinnamyl groups are facing towards the inside of the double sheet arrangement.

Polycations find applications in many areas including polyelectrolytes, membranes, drug delivery and there is an on-going search for new and improved systems.[9] The potential to link phosphazenes with alkylene groups and to use phosphazenes as linkers *via* ring N-sites offers a route towards novel polycations consisting of alternating arrangements of phosphazenes and alkylene groups.

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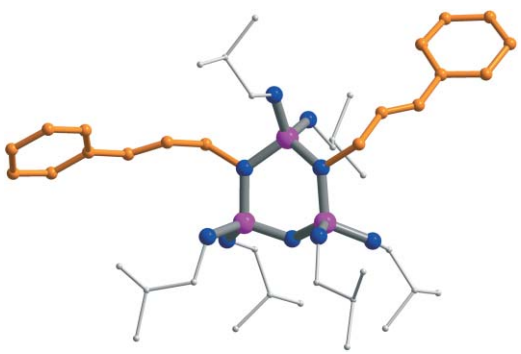

Fig. 3 Crystal structure of the dication in **5**. H-atoms are omitted; cinnamyl groups are highlighted in orange; blue: N, purple: P.

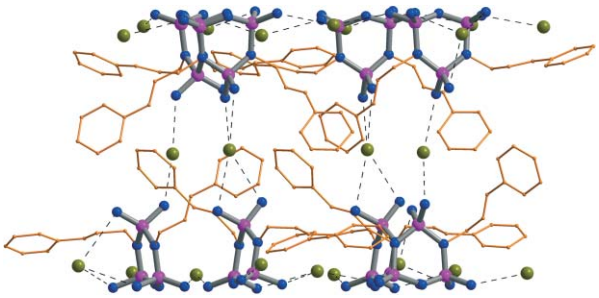

Fig. 4 Fraction of the supramolecular structure of **5** in the solid state. H-bonds drawn as dashed lines, H-atoms and Bu^i groups omitted.

Notes and references

† Crystallographic data were recorded on a Bruker Apex diffractometer using MoK_α-radiation ($\lambda = 0.71073$ Å), $T = 100$ K, structures were refined by full-matrix least squares against F^2 using all data (SHELXTL). Apart from disordered atoms, non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed geometrically. **2a**·$2CH_3OH$: $C_{54}H_{134}Br_2N_{18}O_2P_6$, $M = 1413.43$, $P2_1/c$, $a = 12.8506(8)$, $b = 16.7507(10)$, $c = 19.3666(12)$ Å, $\beta = 108.3600(10)^\circ$, $V = 3956.6(4)$ Å^3, $Z = 2$, μ(Mo-K_α) = 1.192, 5127 independent reflections, R_1 [$I > 2\sigma(I)$] = 0.060, wR_2 (all data) = 0.174; **2b**·$2CHCl_3$: $C_{54}H_{104}Br_2Cl_{10}N_{14}P_6$, $M = 1649.65$, P-1, $a = 15.580(3)$, $b = 26.870(5)$, $c = 28.283(6)$ Å, $\alpha = 90.25(3)$, $\beta = 92.69(3)$, $\gamma = 94.36(3)^\circ$, $V = 11792(4)$ Å^3, $Z = 6$, μ(Mo-K_α) = 1.537, 23661 independent reflections, R_1 [$I > 2\sigma(I)$] = 0.078, wR_2 (all data) = 0.230; **5**: $C_{42}H_{78}Br_2N_9P_3$, $M = 961.86$, $C2/c$, $a = 49.929(6)$, $b = 15.2205(17)$, $c = 30.940(3)$ Å, $\beta = 118.633(2)^\circ$, $V = 20637(4)$ Å^3, $Z = 16$, μ(Mo-K_α) = 1.701, 10705 independent reflections, R_1 [$I > 2\sigma(I)$] = 0.106, wR_2 (all data) = 0.310. All three crystal structures show disorder of one or more R-groups. In addition, **2b** contains disordered chloroform molecules and in **5** one bromide ion and one $P(NHR)_2$ unit in one of the two unique dications are disordered. Disordered atoms were split on two positions and refined isotropically using similar-distance and similar-U restraints. Crystals of both **2b** and **5** were of small size and diffracted to only low resolution. In both cases the datasets were truncated at $2\theta = 40^\circ$. CCDC 280844–280846. See http://dx.doi.org/10.1039/b510898e for crystallographic data in CIF or other electronic format.

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