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Stable P−N Bridged Cyclophosphazenes with a Spiro or Ansa Arrangement

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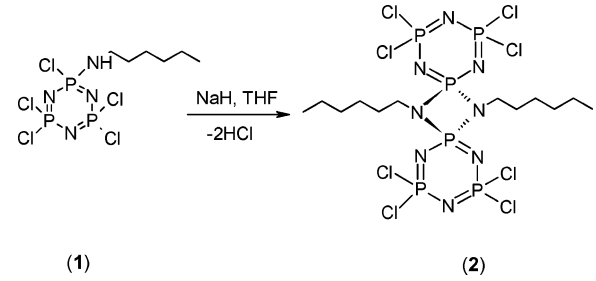
Deprotonation reactions of cyclophosphazenes containing secondary amino groups in the side chain lead to a doubly bridged tricyclophosphazene structure or to a cyclophosphazene−cyclophosphazane−cyclophosphazene compound, which are very stable and could be used as building blocks for larger structures.

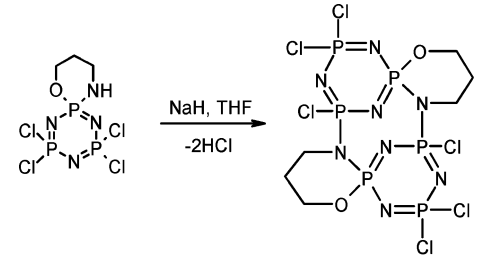
Cyclophosphazenes are multifunctional and usually have many reactive P−Cl bonds offering great potential in terms of facile synthetic manipulations.[1] For example, they are used as core units in the synthesis of dendrimers and as nodal ligands in coordination polymers.[2–4] Most reactions of cyclophosphazenes involve nucleophilic or electrophilic substitution, whereas deprotonation reactions are less common.[5] We have investigated the reactions of cyclotriphosphazenes containing P−NHR groups in the side chain in the presence of a strong base and obtained, with a linear secondary amine, a stable bis-cyclophosphazene bridged with a four-membered cyclophosphazane ring in a spiro arrangement and, with a cyclic secondary amine, obtained a bis-cyclophosphazene bridged with an eight-membered cyclophosphazene ring in an ansa arrangement.

Scheme 1. Synthesis of Compound **2**



(**1**) (**2**)

Scheme 2. Synthesis of Compound **4**



(**3**) (**4**)

The cyclotriphosphazene compound containing one aminoalkyl side chain, $N_3P_3Cl_5[NH(CH_2)_5CH_3]$ (**1**), was directly treated with sodium hyride in a 1:1 molar ratio in tetrahydrofuran (THF) at room temperature for 2 h under an argon atmosphere. A spiro-bridged compound consisting of cyclophosphazene−cyclophosphazane−cyclophosphazene rings, **2**, was formed in high yield from this reaction (Scheme 1).

Another example was to react NaH with a monospiro cyclotriphosphazene derivative containing one NH moiety, $N_3P_3Cl_4[O(CH_2)_3NH]$ (**3**), to form the ansa-bridged compound (**4**), in which two cyclotriphosphazene rings are joined

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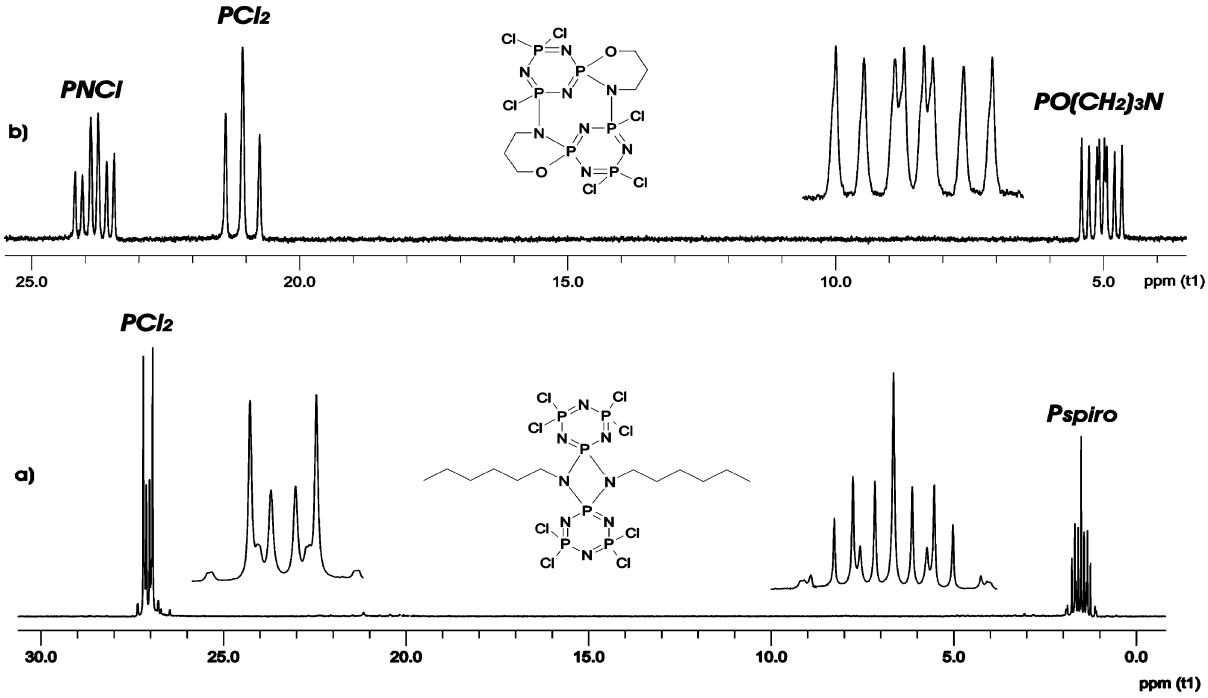

Figure 1. (a) Proton-decoupled ^{31}P NMR AA′B$_2$B′$_2$-type spectrum of compound **2**, exhibiting an additional two-bond coupling constant ($^2J_{P-P}$ = *ca.* 46 Hz) resulting from two equivalent coupling paths between the >P-spiro groups of different cyclophosphazene rings. (b) Proton-decoupled ^{31}P NMR AA′BB′XX′-type spectrum of compound **4** exhibiting an additional two-bond coupling constant ($^2J_{P-P}$ = 27.3 Hz) between the >P-spiro and >P(N)Cl groups of different cyclophosphazene rings. Coupling constants were obtained by simulation of the spectra.

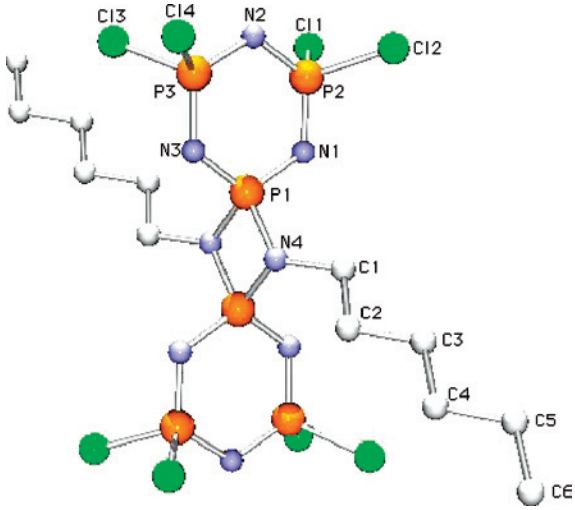

Figure 2. Crystal structure of compound **2**.

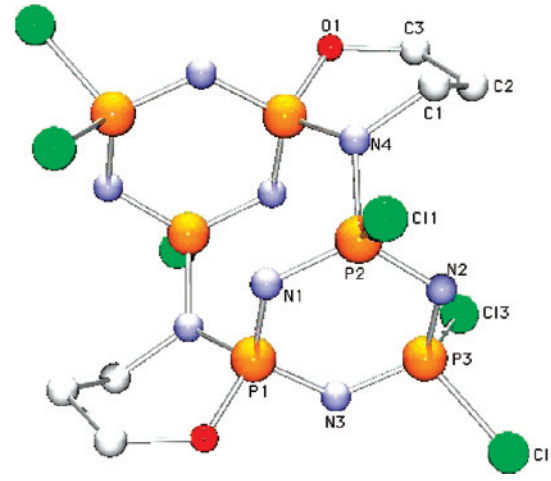

Figure 3. Crystal structure of the compound **4**.

by an eight-membered cyclophosphazene-type of ring system (Scheme 2).

The proton-decoupled ^{31}P NMR spectrum of compound **2** consists of two sets of multiplets corresponding to the P-spiro groups (δ 1.5 ppm) and the PCl_2 groups (δ 27.1 ppm), and the spectrum of compound **2** is shown in Figure 1a. The AA′B$_2$B′$_2$-type multiplets are very complex because of the multiple coupling paths. On the other hand, the proton-decoupled ^{31}P NMR spectrum of compound **4** (Figure 1b) is observed as a basic AA′BB′XX′ type of spin system with further coupling on the two multiplets, P(NR)Cl and P-spiro, due to geminal coupling of *ca.* 27 Hz across the cyclophosphazane ring, similar to that observed (23−35 Hz) for other P−N−P bridged cyclophosphazenes.[6]

The X-ray structual analyses of the spiro-bridged compound, **2**, and the ansa-bridged compound, **4**, are discussed with respect to related cyclotriphosphazene and cyclodiphosphazane compounds.[1b,5d,7] Single crystals of **2** were obtained from dichloromethane/petroleum ether, and the molecular structure (Figure 2) shows that the two cyclophosphazene rings are linked in a spiro arrangement by the four-membered substituted cyclophosphazane ring to form a novel dispirane compound, in which the two cyclophosphazene rings are coplanar.

Although compound **2** is achiral due to symmetry, various substituted derivatives could be used to explore the chiral properties of dispiranes. The cyclophosphazene ring of

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compound **2** is nearly planar; the maximum deviation from the mean plane is only 0.034 (atom P1), and the average bond lengths (P−N of 1.582 and P−Cl of 1.998 Å) and bond angles (N−P−N of 117.4 and P−N−P of 122.3 °) are similar to those for many phosphazene compounds in the literature.[1b,7] The cyclophosphazane ring compound, **2**, is also nearly planar, having bond angles within the ring that are close to right angles (84.3° at P and 95.7° at N); the nitrogen atom in the ring is approximately trigonal-planar (the sum of the bond angles around N4 is 346.8°), and the average P−N bond length in the phosphazane ring is 1.664 Å. The molecular parameters for the four-membered cyclophosphazane ring of compound **2** are also similar to those in the literature.[5d,7]

Single crystals of **4** were obtained from THF, and the molecular structure (Figure 3) confirms a five-ring structure, in which the two cyclotriphosphazene rings are linked via the N atoms of the two spirocyclic moieties to form a new type of eight-membered P−N ring. The molecule has four stereogenic centers, two pairs of two different centers of chirality [P-spiro (P1 = S, P1′ = R) and P(NR)Cl (P2 = R, P2′ = S)], but is not chiral itself due to the center of inversion.

The six-membered phosphazene rings of compound **4** are slightly puckered, with the maximum deviation from the mean plane = 0.098 Å (for atom N2); the planes of the phosphazene rings are parallel, and the distance between the P atom of the P-spiro group of one ring and the P atom of the P(NR)Cl group of the other ring is 2.905 Å, compared to the distance of 2.772 Å between those atoms in the same phosphazene ring. The P−N bond lengths of the central eight-membered P−N ring falls into two types; the N−P bonds in the cyclophosphazene moiety have an average length of 1.586 Å, whereas the N−P bonds of the cyclophosphazane bridge are longer, being 1.664 Å on average. The sum of the bond angles around the N4 atom is 356.7°, and the nitrogen atom is trigonal planar.

It is likely that the new spiro- and ansa-bridged compounds are formed by a proton abstraction/chloride ion elimination mechanism,[8] in which the spiro-bridged compound is formed from the condensation reaction of a monoamino-substituted derivative, and an ansa-bridged compound is formed from the condensation reactions of the mono spiro derivatives. The new spiro- and ansa-bridged cyclotriphosphazenes are quite rigid and very stable, for example, mpt of **4** is 338 °C, and as they still contain many P−Cl bonds, they might be used as precursors in the synthesis of macromolecular and supramolecular systems.

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Supporting Information Available: Material, methodological, preparative, and spectroscopic data for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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