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Conversion of a Cyclotriphosphazene to a Cyclohexaphosphazene by Ring Expansion

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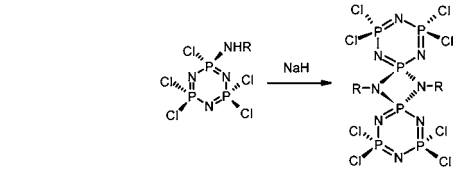
Supporting Information

ABSTRACT: Deprotonation of a cyclotriphosphazene with a *tert*-butylamino group in the side chain results in ring expansion to a very stable, planar cyclohexaphosphazene derivative that still contains eight P−Cl bonds suitable for forming macromolecular structures.

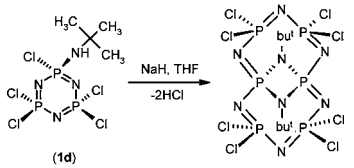
Cyclophosphazenes have many reactive P−halogen bonds, which are important in the preparation of a wide range of derivatives having diverse applications.[1−8] Although substitution reactions of cyclophosphazenes are well-known, there are fewer studies on deprotonation reactions. In our previous work, we investigated deprotonation reactions in the presence of a strong base of cyclotriphosphazenes containing P−NHR groups in the side chain [R = $(CH_2)_5CH_3$, $CH(CH_3)_2$, Ph] and obtained stable bicyclophosphazenes linked with cyclophosphazane rings in a spiro arrangement in different relative yields (68%, 49%, and 19%, respectively).[9]

In order to understand the role of the steric effect on the formation of spiro-bridged compounds, we treated cyclotriphosphazene derivatives having butylamino groups in the side chain [$N_3P_3Cl_5$(NHR), where R = *n*-butyl, *i*-butyl, *sec*-butyl, *tert*-butyl] directly with sodium hydride in a 1:1 molar ratio in tetrahydrofuran at room temperature for 2 h under an argon atmosphere. The expected spiro-bridged compounds consisting of cyclophosphazene−cyclophosphazane−cyclophosphazene rings (**2a−2c**) were formed with *n*-butyl-, *i*-butyl-, and *sec*-butylaminocyclophosphazene derivatives (Scheme 1), whereas the *tert*-butylaminocyclotriphosphazene reactant formed a novel type of cyclohexaphosphazene derivative (**3**) because of ring expansion as a result of the deprotonation reaction (Scheme 2). The proton-decoupled ^{31}P NMR spectra of compounds **2a** and **2b** consist of two

Scheme 1. Synthesis of Compounds 2a−2c



Scheme 2. Synthesis of Compound 3



multiplets corresponding to one P−spiro group and two PCl_2 groups similar to analogous compounds formed previously,[9] whereas those for **2c**, which contains a chiral center in each side chain, consist of two sets of similar multiplets corresponding to meso and racemic diastereisomers.[10] The proton-decoupled ^{31}P NMR spectrum of compound **3** is observed as a very complex spin system because of very similar chemical shifts and multiple coupling paths.

The molecular structures of compounds **2a−2c** and **3** were established by X-ray structure analysis. The crystallographic data (Table S1) and selected bond lengths, bond angles, and conformational parameters (Table S2) are summarized in the Supporting Information. In all structures, the molecule sits on an inversion center.

The molecular structures of compounds **2a−2c** (Figure 1) are similar to the analogous spiro-bridged cyclotriphosphazene compounds,[9] in that the two nearly planar cyclophosphazene (P_3N_3) rings are linked in a spiro arrangement by the 4-membered planar cyclophosphazane (P_2N_2) ring to form dispirane compounds, in which the two cyclophosphazene rings are coplanar and perpendicular to the planes of the cyclophosphazane (P_2N_2) rings. The bond lengths and angles of the cyclophosphazene rings are similar to those reported for many other cyclotriphosphazene structures in the literature,[1−8] and the structural parameters for spiro-bridged cyclotriphosphazene compounds **2a−2c** (Table S2 in the Supporting Information) are similar to those of the spiro-bridged dispirane cyclotriphosphazene compounds in the literature.[4e,9]

The molecular structure of compound **3** (Figure 2a) shows that the 12-membered cyclohexaphosphazene ring (P_6N_6) is bridged by the 4-membered cyclophosphazane (P_2N_2) rings to form a novel type of bicyclic compound. The P−N bond lengths of the cyclohexaphosphazene are in the range of 1.5497(13)−1.5843(11) Å (Table S2 in the Supporting

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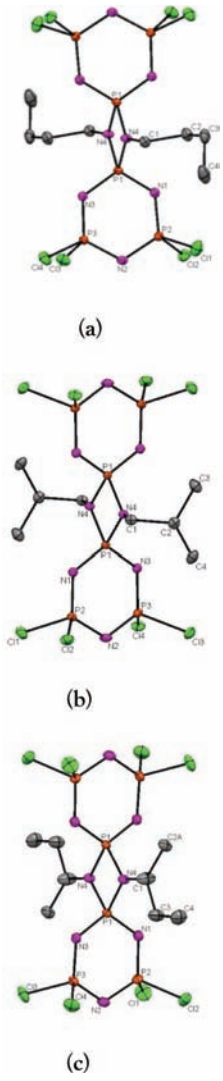

Figure 1. Crystal structures of compounds (a) **2a**, (b) **2b**, and (c) **2c**. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted, and only one orientation of the disordered C2 atom in compound **2c** has been presented for clarity. All three molecules sit on a center of symmetry. Symmetry codes (#) are $-x + 1, -y + 1, -z + 1$ for **2a**, $-x + 1, -y + 1, -z + 2$ for **2b**, and $-x + 1, -y, -z + 2$ for **2c**.

Information), which are similar to those in the crystal structures of the two cyclohexaphosphazene derivatives ($P_6N_6R_{12}$, where R = Me, OMe) in the literature.[11] In these structures, the 12-membered cyclohexaphosphazene (P_6N_6) ring has a double-tub conformation,[11] in contrast to compound **3**, where the cyclohexaphosphazene is nearly planar. The maximum deviation from the mean plane of the P_6N_6 ring in compound **3** is only 0.0983(4) Å (P3 atom), and this planarity is supported by the mean plane of the P_6N_6 ring being perpendicular to the planar P_2N_2 ring; the angle between the two planes is 89.93° (Figure 2b). The molecular parameters of the P_2N_2 cyclophosphazane ring of compound **3** (Table S2 in the Supporting Information) are similar to those of analogous compounds in the literature,[4e,9] in that the bond angles within the ring are close to right angles [N4−P1−N4# is 85.29(5)° and P1−N4−P1# is 94.71(5)°], the N4 atom is trigonal planar (the sum of the bond angles around N4 is 359.87°), and the

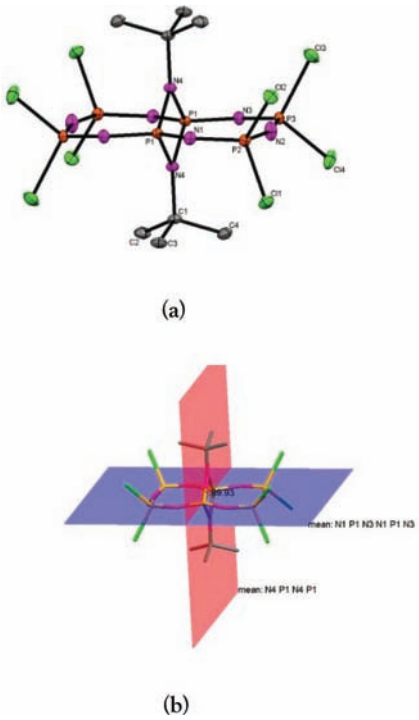

Figure 2. (a) Crystal structure of compound **3** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity. (b) Angle between planes of the 12-membered cyclohexaphosphazene (P_6N_6) and 4-membered cyclophosphazane (P_2N_2) rings in compound **3**. The molecule is centrosymmetrical. The symmetry code (#) is $-x, -y + 2, -z$.

P1−N4 and P1#−N4 bonds are 1.6764(12) and 1.6763(11) Å, respectively.

The yields of spiro-bridged compounds **2a**−**2c** formed by deprotonation reactions depend on the properties of the carbon atom (α) bonded to the P−NHR group. If the α-carbon is a primary carbon atom, the spiro-bridged compound is obtained with the highest yield (for **2a**, 72%, R = *n*-butyl; for **2b** 69%, R = *i*-butyl), but when the α-carbon is a secondary carbon atom, the spiro-bridged compound has a much lower yield (for **2c**, 40%, R = *sec*-butyl). These results are in line with those found for the analogous spiro-bridged compounds by deprotonation reactions of cyclophosphazene derivatives with secondary amino groups in that a higher yield was obtained when the α-carbon was a primary carbon atom (68%, R = *n*-hexyl) and a lower yield for the secondary carbon derivative (49%, R = *i*-propyl).[9] On the other hand, when the α-carbon is a tertiary carbon atom (R = *tert*-butyl), ring expansion occurs to form the cyclohexaphosphazene derivative, compound **3**. It has been suggested that, if there is a bulky substituent on the cyclotriphosphazene ring, then ring expansion probably occurs during the polymerization process and that tetramer or higher ring compounds may be formed,[12] whereas in this work, a new type of bicyclic cyclophosphazene compound was synthesized and the ring expansion phenomenon was proven by X-ray crystallography. In the formation of compound **3** (Scheme 3), it is likely that the intermediate spiro-bridged cyclotriphosphazene derivative is first formed by a proton abstraction/chloride ion elimination mechanism, as with the other the P−NHR derivatives,[9,13] and then the P−N bond of the cyclophosphazene ring in the spiro-bridged compound is broken

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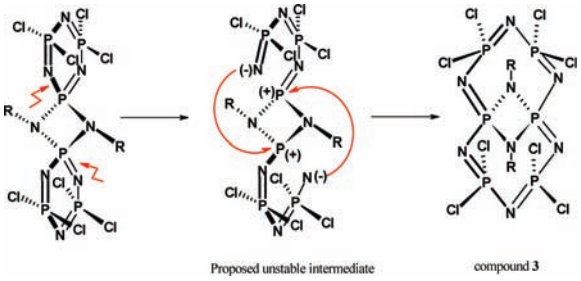
Scheme 3. Possible Mechanism for the Formation of Compound 3 (R = *tert*-Butyl)



because of ring strain. It is possible that, in order to minimize the strain in the whole molecule, the very reactive positive P^+ and negative N^- terminal groups can then mutually attack the neighboring N_3P_3 rings and form the N_6P_6 rings, which are stabilized by the interlocked N_2P_2 ring (Scheme 3). Compound **3** is very stable (melting point 303 °C) and has four PCl_2 groups at the corners of a planar rectangle, which make it a good precursor for the formation of different macromolecular and dendrimeric systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, analyses, X-ray diffraction, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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