cis-Trihydrogen cyclotriphosphazenates—acidic anions in strongly basic media

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Exclusively *cis*-protonation occurs at axial N-atoms of chair shaped P_3N_9 ring cores in the protolysis of the lithium salt of hexaanionic cyclotriphosphazenate $[(CyN)_6P_3N_3]^{6-}$ with three equivalents of butan-1-ol and *cis*-deprotonation takes place at the hexaprotic cyclotriphosphazene $(PhNH)_6P_3N_3$ with three equivalents of Bu^{n}Li, respectively, yielding both times lithium salts of *cis*-trihydrogen cyclotriphosphazenates $[(RNH)_3(RN)_3P_3N_3]^{3-}$.

The formal replacement of oxy and hydroxy units (=O, –OH) by isoelectronic imino and amino groups (=NR, –NHR), respectively, has led to novel compounds with unusual properties, due to both the increased electron donating capability of the nitrogen centre and the steric demand of the lipophilic organic substituent.[1] Imino analogues of the classic oxy-anions $[SO_3]^{2-}$,[2] $[SO_4]^{2-}$,[3] $[PO_4]^{3-}$ [4] and the kinetically unstable $[PO_3]^{-}$ [5] exist as molecular aggregates and are highly soluble in aprotic organic solvents. However, little is known about multistep protonation pathways between corresponding acid–base pairs. Recently, we have discovered that cyclophosphazenes carrying RNH groups act as multiprotic acids in the presence of strong bases yielding multianionic phosphazenates, a novel class of highly charged ligand systems.[6] The hexaprotic cyclotriphosphazene $(CyNH)_6P_3N_3$ **1a** is fully deprotonated by Bu^{n}Li generating the lithium salt of the hexaanionic cyclotriphosphazenate $[(CyN)_6P_3N_3]^{6-}$ **3a** which is highly soluble in non-polar aprotic solvents.[6a] Its central P_3N_9 core is electronically related to the cyclotrisilicate ion $[Si_3O_9]^{6-}$. We have now revealed protonation and deprotonation pathways between hexaprotic phosphazenes and hexaanionic phosphazenates by monitoring reactions using ^{31}P NMR spectroscopy and determining crystal structures of trianionic intermediates.

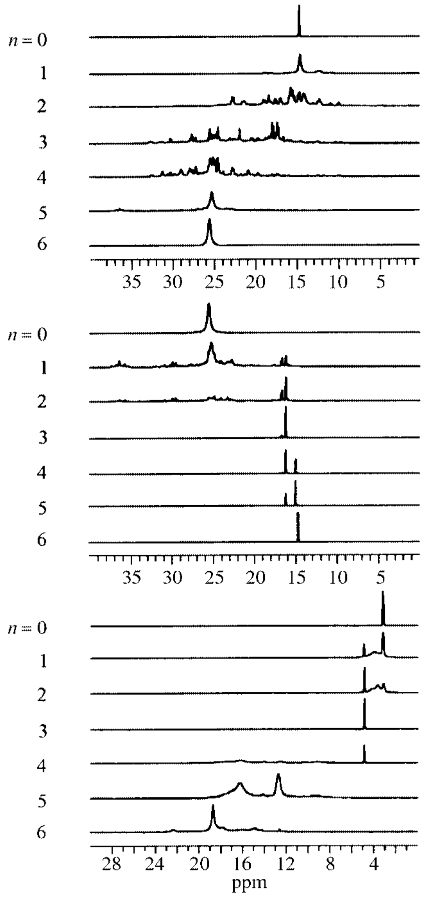
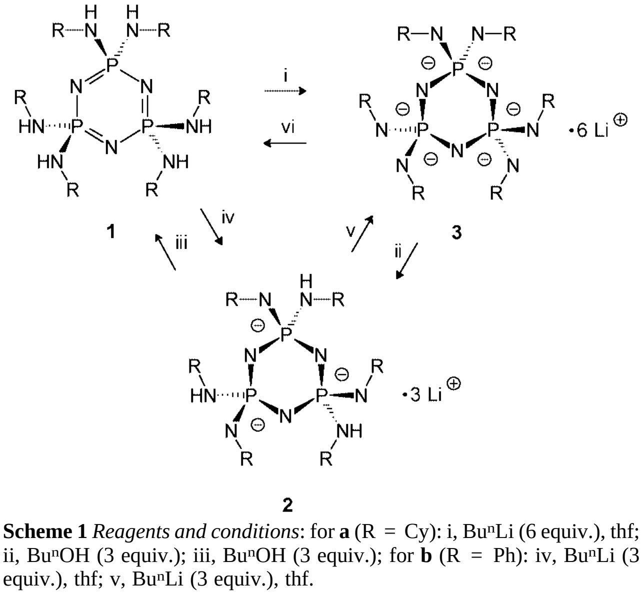


Fig. 1 ^{31}P NMR spectra (ppm) (161 MHz, thf, 25 °C) of stepwise reactions (a) **1a** + *n* Bu^{n}Li, (b) **3a** + *n* Bu^{n}OH and (c) **1b** + *n* Bu^{n}Li.



Scheme 1 *Reagents and conditions*: for **a** (R = Cy): i, Bu^{n}Li (6 equiv.), thf; ii, Bu^{n}OH (3 equiv.); iii, Bu^{n}OH (3 equiv.); for **b** (R = Ph): iv, Bu^{n}Li (3 equiv.), thf; v, Bu^{n}Li (3 equiv.), thf.

Stepwise addition of Bu^{n}Li to a solution of **1a** (14.9 ppm) in thf leads to a complex signal pattern in the ^{31}P NMR spectrum (Fig. 1) which finally gives a single peak at 25.3 ppm due to the formation of fully deprotonated **3a**. However, stepwise protolysis of **3a** with Bu^{n}OH gives a single peak at 16.2 ppm after addition of three equivalents of Bu^{n}OH indicating the existence of the trianionic intermediate $[(CyNH)_3(CyN)_3P_3N_3]^{3-}$ **2a**. In contrast, the hexaanilino derivative $(PhNH)_6P_3N_3$ **1b** (3.2 ppm) gives directly $[(PhNH)_3(PhN)_3P_3N_3]^{3-}$ **2b** upon addition of three equivalents of Bu^{n}Li as indicated by the appearance of a single peak at 5.0 ppm. Addition of six equivalents to **1b** results in one signal at 16.2 ppm which can be attributed to hexaanionic $[(PhN)_6P_3N_3]^{6-}$ **3b**. In both cases tri- and hexa-anionic species are levelled by excess of Bu^{n}OH yielding **1** and exist only in aprotic non-acidic media or very weakly protic solvents such as cyclohexylamine.

The X-ray structure† of **2a** reveals that exclusively axial N-atoms at the chair shaped P_3N_3 ring have been protonated (Fig. 2). The dimeric complex of **2a** is closely related to that of hexaanionic **3a** containing a centrally arranged polyhedral cage comprising six lithium cations which are encapsulated by two trianions. Each lithium cation is chelated by a bidentate N(eq)–P–N(ring) site of one of the anions and additionally coordinated by an equatorial N-atom of the other anion. The geometry of the central P_3N_9 core in **2a** is midway between those observed in **1a**

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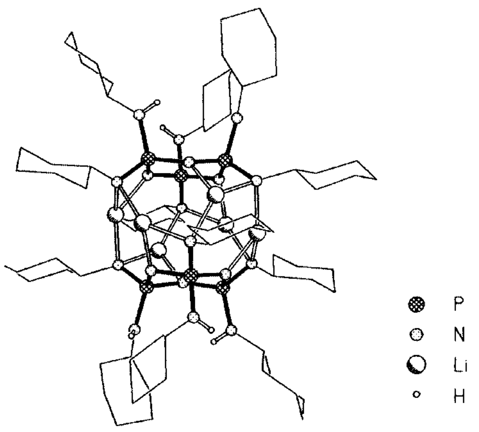

Fig. 2 Crystal structure of **2a**. Average bond lengths (Å) and angles (°): P–N(ring) 1.635, P–N(eq) 1.614, P–N(ax) 1.665, Li–N(ring) 1.99, Li–N(eq) 2.04, Li–N(eq) of the other trianion 2.03, N(ring)–P–N(ring) 112.3, N(eq)–P–N(ax) 111.3, P–N(ring)–P 121.9, av. P_3N_3 ring torsion = 33.2°.

and **3a**: torsion angles within the P_3N_3 ring show that the degree of ring puckering increases in the order **1a** (av. 3.6° ~ planar), **2a** (av. 33.2°) and **3a** (av. 43.7°). The P–N ring stretching frequency in the IR-spectra undergoes a considerable red shift from **1a** (1194 cm^{-1}), **2a** (1095 cm^{-1}) to **3a** (1031 cm^{-1}) suggesting a decrease in bond order, also shown by the increase in P–N(ring) bond lengths from 1.598 (**1a**), 1.635 (**2a**) to 1.660 Å (**3a**) and decrease in N–P–N(ring) angles [116.3° (**1a**), 112.3° (**2a**), 109.7° (**3a**)] causing puckering of the central six-membered ring. The difference in exocyclic P–N bond lengths in **2a** [P–N(eq) 1.614, P–NH(ax) 1.665 Å] indicates that multiple bond character is partly transferred from ring onto equatorial P–N bonds.

2b exists as the monomeric C_3-symmetric complex $[(thf)_6Li_3$ *cis*-$(PhNH)_3(PhN)_3P_3N_3]$ in the solid state. Each lithium cation is chelated by an N(eq)–P–N(ring) site of the ligand and in addition coordinated by two thf molecules. Structural parameters of the P_3N_9 core in **2b** resemble those in **2a** (Fig. 3) and deprotonation also occurred in *cis* fashion at equatorial N-atoms. The difference in P–N bond lengths (P–N(ring) 1.617 (av.), P–N(eq) 1.592(3), P–NH(ax) = 1.708(4) Å) shows the same tendency as **2a**. The *cis*-arrangement in both structures can be rationalised as follows: charge repulsion within the P_3N_9 core forces the six-membered ring into a chair conformation, due to distribution of charge over ring and equatorial N atoms. This leaves axial sites protonated and provides three N(ring)–P–N(eq) chelates complexing the lithium cations on the opposite side of the trianion.

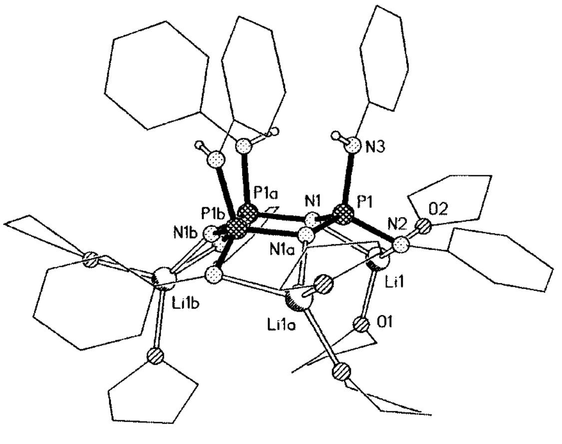

Fig. 3 Crystal structure of **2b**. Selected bond lengths (Å) and angles (°): P1–N1 1.621(3), P1–N1a 1.614(3), P1–N2 1.592(3), P1–N3 1.708(4), N1–Li1 2.054(8), N2–Li1 2.038(8); N1–P1–N1a 114.7(2), N2–P1–N3 112.3(2), P1–N1–P1a 119.8(2); P_3N_3 ring torsion = 32.3(4)°. Non-coordinated thf molecules have been omitted for clarity.

The successive protonation pattern of the above described $\{(RNH)_6P_3N_3/[(RNH)_3(RN)_3P_3N_3]^{3-}/[(RN)_6P_3N_3]^{6-}\}$ systems resembles that of mononuclear polyprotic oxy acids. It is, however, shifted towards the far basic region of the acidity scale and ion pairing seems to play a significant role. In contrast, condensed oxy acids lack corresponding acid–base reactions due to backbone cleavage in the presence of strong bases and related acidic oxy-anions such as $[H_3Si_3O_9]^{3-}$ are unknown. Another interesting feature of **2** is the site selective protonation pattern which is to our knowledge the first selective *cis*-trifunctionalisation of a cyclotriphosphazene.[7] This could lead to novel ligand systems equipped with a hexadentate coordination surface on one side and a non-polar surface on the other side of the molecule similar to calixarenes.

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Notes and references

† Crystal data were collected on a Stoe-IPDS at 200 K using Mo-Kα radiation (λ = 0.71073 Å). Full-matrix least square refinements on F^2 using all data (SHELX97). *Crystal data*: **1a**: $C_{36}H_{72}N_9P_3$, M = 723.94, triclinic, space group $P\bar{1}$, a = 11.039(4), b = 12.001(4), c = 16.651(6) Å, α = 95.81(4), β = 91.38(4), γ = 108.77(3)°, V = 2074(1) $Å^3$, Z = 2, μ(Mo-Kα) = 0.180 mm^{-1}, $R1[I > 2\sigma(I)]$ = 0.061, $wR2$ (all 5408 data) = 0.145. **2a**: $C_{72}H_{138}Li_6N_{18}P_6 \cdot C_7H_8$, M = 1575.60, monoclinic, space group $C2/c$, a = 25.993(5), b = 17.647(4), c = 20.639(4) Å, β = 109.81(3)°, V = 8920(3) $Å^3$, Z = 4, μ(Mo-Kα) = 0.172 mm^{-1}, $R1[I > 2\sigma(I)]$ = 0.068, $wR2$ (all 5676 data) = 0.210. **2b**: $C_{60}H_{81}Li_3N_9O_6P_3 \cdot 4C_4H_8O$, M = 1426.48, rhombohedral, space group $R\bar{3}c$, a = 21.620(3), c = 61.490(12) Å, V = 24891(7) $Å^3$, Z = 12, μ(Mo-Kα) = 0.129 mm^{-1}, $R1[I > 2\sigma(I)]$ = 0.059, $wR2$ (all 3619 data) = 0.166. Both coordinated and non-coordinated thf molecules in **2b** show disorder. CCDC 182/1530. See http//www.rsc.org/suppdata/cc/a9/a908954c/ for crystallographic files in .cif format.

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