

## Supplementary information

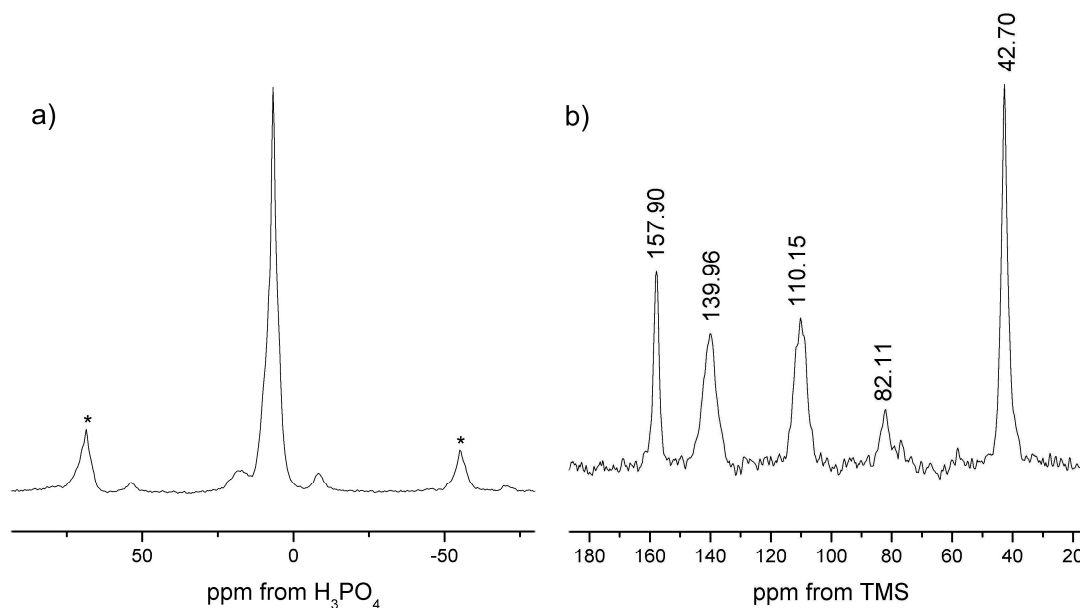
### The N-donor stabilised cyclotriphosphazene hexacation $[P_3N_3(DMAP)_6]^{6+}$

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#### Solid state NMR spectra of 2:



a)  $^{31}P\{^1H\}$  MAS NMR (6.7 ppm)

b)  $^1H$ - $^{13}C$  CP/MAS NMR (CH<sub>3</sub> 42.70, CHCl<sub>3</sub> 82.11, *m*-C 110.15, *o*-C 139.90, *p*-C 157.90 ppm)

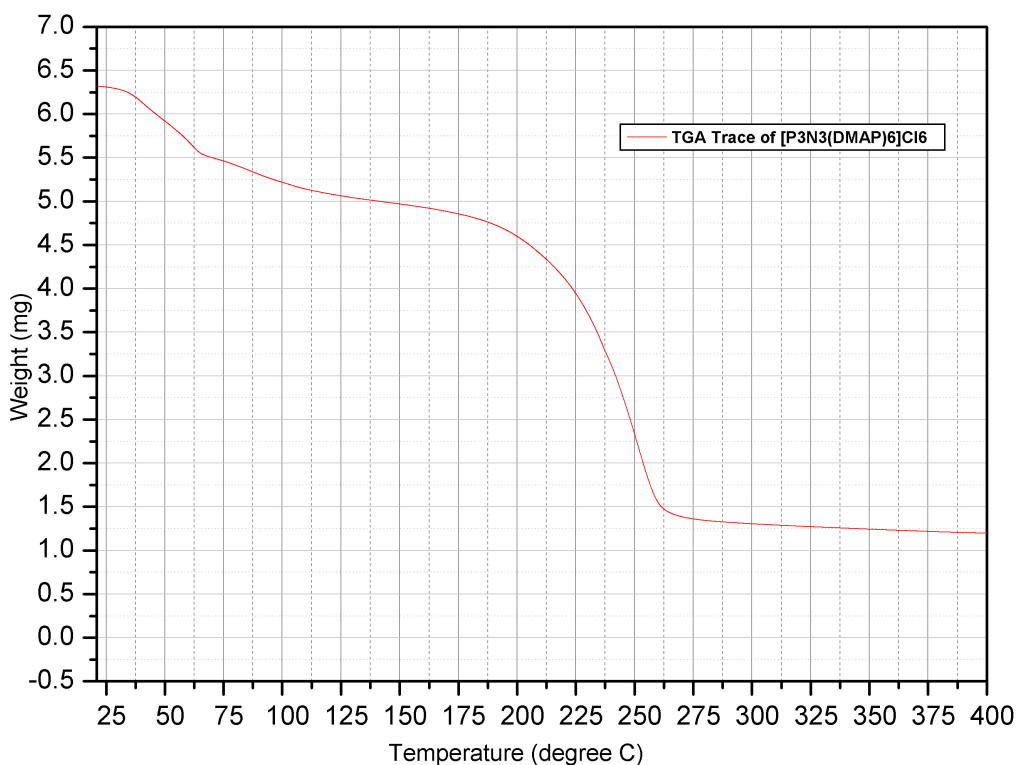
Both spectra were recorded at a spinning rate of 10 kHz, \* denotes spinning sidebands.

The solid-state NMR spectra were measured on a Bruker Avance DSX 400 spectrometer operating at 100.61 MHz for  $^{13}C$ , 161.98 MHz for  $^{31}P$  and 400.13 MHz for  $^1H$ . All spectra were collected using a 4 mm triple resonance probe and zirconia rotors. The  $^1H \rightarrow ^{13}C$  cross-polarisation magic-angle spinning (CP/MAS) NMR spectra were measured at MAS rate of 10.0 kHz. The  $^1H \pi/2$  pulse was 3.0  $\mu s$ . The two pulse phase modulation (TPPM) decoupling<sup>1</sup> was used during the acquisition at an *rf* field of *ca.* 83 kHz. The Hartmann-Hahn condition was set using glycine. The recycle delay was 10 s and the contact time was set to 2.0 ms. The  $^{31}P\{^1H\}$  MAS NMR spectra were measured at a MAS rate of 10 kHz with  $^1H$  TPPM decoupling during acquisition at an *rf* field of *ca.* 83 kHz. A  $^{31}P \pi/3$  pulse length of 2.1  $\mu s$  with a recycle delay of 120.0 s was used.

1 A. E. Bennett, C. M. Rienstra, M. Auger, K. V. Lakshmi, R. G. J. Griffin, *Chem. Phys.*, 1995, **103**, 695; A. K. Khitrin, T. Fujiwara, H. Akutsu, *J. Magn. Reson.*, 2003, **162**, 46.

### Thermogravimetric analysis of 2:

The sample was heated at a rate of 5°/min. in a flow of N<sub>2</sub> (Seiko SII-TGA/DTA 6300 Thermal Analyzer).



This TGA trace correlates well with the loss of 5 chloroform and 6 DMAP molecules from [P<sub>3</sub>N<sub>3</sub>(DMAP)<sub>6</sub>]Cl<sub>6</sub>·5CHCl<sub>3</sub> (MW = 1677.6) yielding a material of the composition PNC<sub>l</sub><sub>2</sub> (MW = 347.7 for P<sub>3</sub>N<sub>3</sub>Cl<sub>6</sub>) when heated above 260°C, which corresponds to a weight loss of 79%. Below 260°C the trace displays a gradual weight loss and lacks distinct steps. This indicates the absence of a pure desolvated compound [P<sub>3</sub>N<sub>3</sub>(DMAP)<sub>6</sub>]Cl<sub>6</sub> (MW = 1080.7) at any given temperature during the heating process. At around 200°C the weight loss accelerates. At this point the weight loss amounts to 27%, which corresponds the molecular weight of [P<sub>3</sub>N<sub>3</sub>(DMAP)<sub>6</sub>]Cl<sub>6</sub>·CHCl<sub>3</sub> (MW = 1200.1).

**Experimental geometries for B3LYP/6-31G\* NPA charges** were obtained from coordinates of the following crystal structures:

P<sub>3</sub>N<sub>3</sub>Cl<sub>6</sub>: Ref. Code KAGKUY01, S. W. Bartlett, S. J. Coles, D. B. Davies, M. B. Hursthouse, H. Ibisoglu, A. Kilic, R. A. Shaw and I. Un, *Acta Crystallogr.*, 2006, **B62**, 321

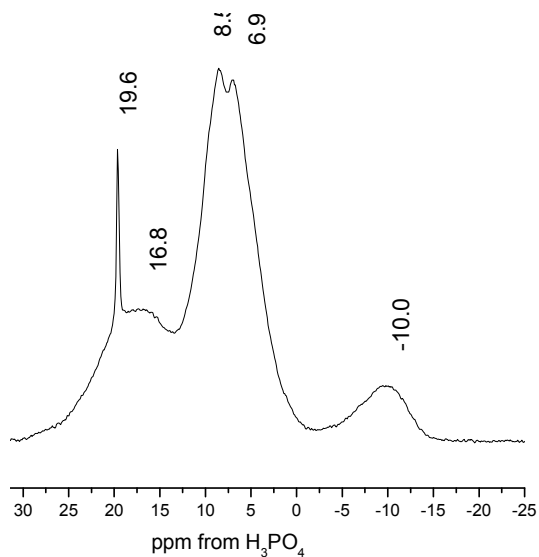
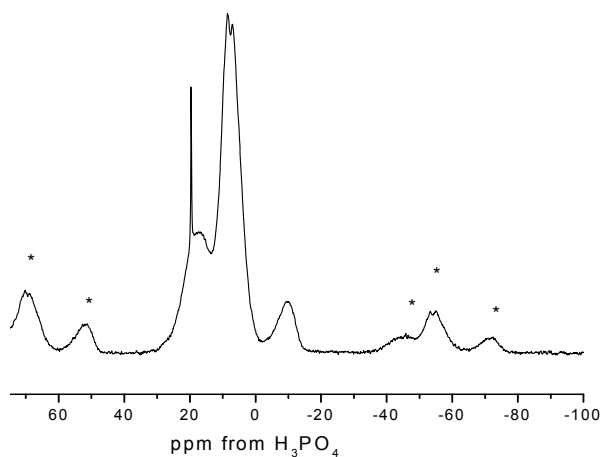
[P<sub>3</sub>N<sub>3</sub>(DMAP)<sub>6</sub>]Cl<sub>5</sub><sup>+</sup>: Compound **1**, this work

P<sub>3</sub>N<sub>3</sub>F<sub>6</sub>: Ref. Code VARYES02, R.P.Singh, A.Vij, R.L.Kirchmeier and J.M.Shreeve, *Inorg.Chem.*, 2000, **39**, 375

P<sub>3</sub>N<sub>3</sub>(NH<sub>2</sub>)<sub>6</sub>: Ref. Code HEKCUV, F.Golinski and H.Jacobs, *Z.Anorg.Allg.Chem.*, 1994, **620**, 965

NPA charges and electrostatic potential maps were produced with Spartan (Wavefunction, Inc.).

**Reproduction of the alleged synthesis of  $[P_3N_3(DMAP)_6]Cl_6$**  reported by Vapirov et al.<sup>2</sup> The described procedure entails the reaction of  $P_3N_3Cl_6$  and DMAP in a 1:6 ratio in toluene. The resulting precipitate was worked-up as described. The  $^{31}P\{^1H\}$  MAS NMR spectrum of the product is shown below (recorded using the same parameters as discussed above). It indicates that the reaction formed a product mixture. The sharp signal at 19.6 ppm is due to unreacted  $P_3N_3Cl_6$ . Evidently under the conditions described, the reaction is leading to premature precipitation of partially substituted products  $[P_3N_3Cl_{6-x}(DMAP)_x]Cl_x$ .



2 A. E. Shumeiko, G. D. Titskii, L. P. Kurchenko, V. V. Vapirov, *Zh. Obshch. Khim.*, 1986, **56**, 2275.