β-*trans*-$[N_4\{P(Ph)(C_6H_{11}N)\}_4]^{4-}$; a tetraanionic ligand system exhibiting two separated tetradentate coordination sites of concave-shaped cavities

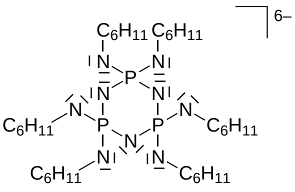
Alexander Steiner* and Dominic S. Wright

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

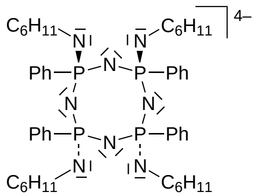
β-*trans*-$[N_4\{P(Ph)(C_6H_{11}NH)\}_4]$ can be deprotonated at all four N–H functions with BuLi in toluene yielding $Li_4\{$β-*trans*-$[N_4\{P(Ph)(C_6H_{11}NH)\}_4]\}$, using an excess of BuLi in the presence of thf, the lithium enolate co-complex $Li_6\{$β-*trans*-$[N_4\{P(Ph)(C_6H_{11}N)\}_4](CH_2{=}CHO)_2\}\cdot4thf$ is formed, in which the tetraanionic ligand β-*trans*-$[N_4\{P(Ph)(C_6H_{11}N)\}_4]^{4-}$ exhibits two separated coordination sites; both act in a tetradentate way and form concave-shaped cavities.

Multianionic ligand systems have scarcely been investigated in metallo-organic coordination chemistry.[1] Their high reactivity and low solubility, due to their exceptional high polarity, limit their synthetic applications in aprotic solvents. Recently we discovered, that highly charged ligand systems can be stabilized by introducing cyclophosphazene backbones into the ligand cores as shown in the hexaanionic $[N_3P_3(C_6H_{11}N)_6]^{6-}$ **A** (C_6H_{11} = cyclohexyl).[2] Its structural and spectroscopic features suggest, that the negative charge is stabilised by delocalisation from the terminal amido onto the central ring-nitrogen functions. The dimeric lithium complex $Li_{12}[N_3P_3(CyN)_6]_2\cdot4thf$ **1** (Cy = C_6H_{11}) is soluble in aprotic solvents and therefore a potential transfer reagent for introducing this ligand system into a wide range of diverse metal complexes. In systems such as **A**, where there is an extensive surface of donating N-centres, a variety of metal coordination modes is expected. This paper is concerned with manipulating the ligand sphere of these systems by partial substitution of donating centres with organic substituents. The introduction of non-coordinating substituents should provide steric control and therefore a specific design of the ligand surface. Consequently the overall equatorial arrangement of the phosphorus-bonded phenyl substituents in the novel tetraanionic ligand system β-*trans*-$[N_4\{P(Ph)(C_6H_{11}N)\}_4]^{4-}$ **B**, presented here, should provide a sterically controlled separation of coordination sites within this ligand system.

The β-*trans* isomer of 2,4,6,8-tetraphenyl-2,4,6,8-tetrakis(cyclohexylamino)cyclotetraphosphazene **1** can be obtained with retention of configuration by the aminolysis reaction of the corresponding nongeminal tetrachlorotetraphenylcyclotetraphosphazene[3] with cyclohexylamine in the presence of triethylamine in diethyl ether in 50% yield. Further reaction with 4 equiv. of BuLi in toluene gives almost quantitatively the tetrametallated derivative $Li_4\{$β-*trans*-$[N_4\{P(Ph)(CyN)\}_4]\}$ **2**. Carrying out the reaction in thf by using an excess of BuLi yielded a colourless crystalline material, which was suitable for X-ray structure analysis‡ and could be identified as $Li_6\{$β-*trans*-$[N_4\{P(Ph)(C_6H_{11}N)\}_4](CH_2{=}CHO)_2\}\cdot4thf$ **3**. The presence of two equivalents of lithium enolate in **3** is derived from the reaction of excess BuLi with thf. However, this is a common decomposition pathway of thf in the presence of strong bases and inclusion of $CH_2{=}CHOLi$, caused by fragmentation of thf, has been reported recently.[4]



A



B

The molecular structure of **3** exhibits C_i symmetry and is composed of the centrally arranged tetraanionic ligand encapsulated by two triangular Li_3 faces, each capped by an O-donor function of the monoanionic enolate moieties (Fig. 1). The equatorial configuration of all four phenyl substituents and the overall axial arrangement of the cyclohexylamido substituents at the puckered chair-shaped P_4N_4 ring separate the donating ligand surface into two coordination spheres. Both form concave-shaped cavities, due to the shielding arrangement of the surrounding organic substituents, and act in a tetradentate way *via* two terminal and two ring-nitrogen centres. Fig. 2 illustrates the central core of **3**, which approximately can be described as three interlocked distorted hexagonal prisms, in which the central one is surrounded by the P_4N_4 ring. Each N(r)-function (r = ring) coordinates one and each N(t)-function (t = terminal) coordinates two Li centres, resulting in three different coordination patterns towards the three crystallo-

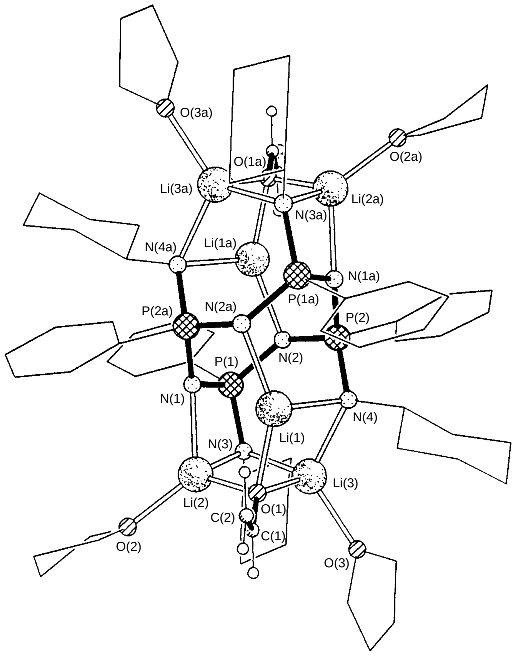


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.626(6), P(1)–N(2) 1.635(6), P(1)–N(3) 1.624(6), P(2)–N(2) 1.603(6), P(2)–N(4) 1.622(6), P(2)–N(1a) 1.660(6), Li(1)–N(2a) 2.07(1), Li(1)–N(4) 2.10(1), Li(1)–O(1) 1.94(1), Li(2)–N(1) 2.08(1), Li(2)–N(3) 2.06(1), Li(2)–O(1) 1.91(1), Li(2)–O(2) 1.96(1), Li(3)–N(3) 2.09(1), Li(3)–N(4) 2.08(1), Li(3)–O(1) 2.02(1), Li(3)–O(3) 2.06(1), O(1)–C(1) 1.339(9), C(1)–C(2) 1.28(1); N(1)–P(1)–N(2) 112.9(3), N(1)–P(1)–N(3) 103.0(3), N(2)–P(1)–N(3) 119.5(3), N(2)–P(2)–N(1a) 110.0(3), N(2)–P(2)–N(4) 111.5(3), N(4)–P(2)–N(1a) 115.9(3), P(1)–N(1)–P(2a) 124.0(3) P(1)–N(2)–P(2) 127.6(4), O(1)–C(1)–C(2) 128.9(9). Atoms labelled a are generated by a centre of inversion.

graphically independent Li centres; while Li(1) and Li(3) can be seen as parts of two different six-membered heterocycles [Li(1)–N(r)–P–N(r)–P–N(t) and Li(3)–N(t)–P–N(r)–P–N(t)], Li(2) is chelated by a N(r)–P–N(t) unit. Four- and six-membered heterocyclic P–N ring-systems containing s-block metals were observed also in the presence of monoanionic linear phosphazene ligands.[5] All Li centres in **3** are further saturated by an enolate O-function, in addition Li(2) and Li(3) are coordinated by thf donor molecules, resulting in trigonal-planar [Li(1)] and tetrahedral [Li(2) and Li(3)] metal environments.

Structural parameters of the central P_4N_8 unit are comparable with those of the P_3N_9 unit in **1** and suggest an equal distribution of the negative charge onto all eight N-functions. As observed in **1** there is no significant difference in bond lengths from the phosphorus atoms toward the ring [av. P–N(4) 1.63 Å] and those toward the terminally located nitrogen centres [av. P–N(t) 1.62 Å]. On the other hand, neutral amino-substituted cyclophosphazenes exhibit significantly shorter P–N-ring bond distances compared to their terminal located counterparts, as illustrated in the structurally related β-*trans*-[$N_4\{P(Ph)(MeNH)\}_4$] [P–N(r) 1.60 Å, P–N(t) 1.68 Å (av.)].[3b]

Ligand systems such as **A** and **B** show that there is a vast potential in multianionic ligand systems. Coordination mode and charge can be varied by formal successive substitution of donating centres with steric organic groups, thus introducing a specific design of the ligand surface. It would be interesting to investigate the nature of delocalisation of the negative charge throughout the P–N cores and its influence on coordination behaviour. There is also the possibility that anion **B** could accommodate two mixed-valent metal centres in its separate cavities, interacting electronically *via* the P–N core.[6]

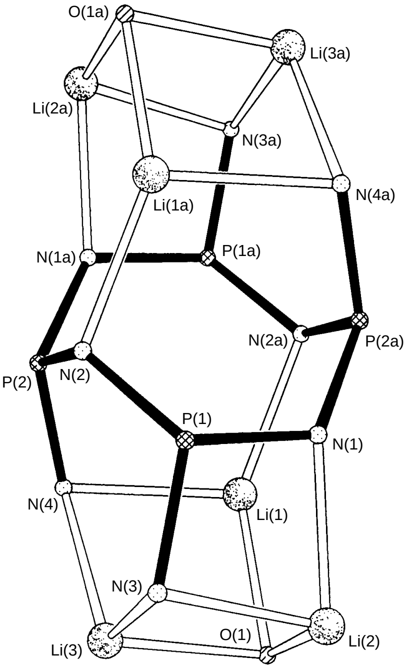


Fig. 2 Core structure of **3**

We thank Dr J. M. Rawson for providing a sample of [$N_4\{P(Ph)Cl\}_4$]. A. S. gratefully acknowledges the EU Human Capital and Mobility Program for a research fellowship.

Footnotes

† *Selected NMR data* (25 °C): **1**: ^1H NMR (C_6D_6) δ 0.8–1.6 (m, CH_2, C_6H_{11}, 40 H), 2.6 (m, CH, C_6H_{11}, 4 H), 7.0–7.4 (m, Ph, 12 H), 8.3 (m, Ph, 8 H); ^{31}P NMR (C_6D_6, relative to H_3PO_4) δ 3.2. **2**: ^1H NMR (C_6D_6) δ 1.0–2.0 (m, CH_2, C_6H_{11}, 40 H), 2.8 (m, CH, C_6H_{11}, 4 H), 7.1–7.5 (m, Ph, 12 H), 8.6 (m, Ph, 8 H); ^{31}P NMR (C_6D_6, relative to H_3PO_4 δ 24.6. **3**: ^1H NMR (C_6D_6) δ 0.8–1.8 (m, CH_2, C_6H_{11}, 40 H), 1.5 (m, thf, 16 H), 2.4 (m, CH, C_6H_{11}, 4 H), 3.6 (t, thf, 16 H), 3.7–4.0 (m, CH_2, $OCH{=}CH_2$, 4 H), 7.0 (dd, CH, $OCH{=}CH_2$, 2 H), 7.2–7.5 (m, Ph, 12 H), 8.6 (m, Ph, 8 H); ^{31}P NMR (C_6D_6, relative to H_3PO_4) δ 24.3.

‡ *Crystal data* for **3**: $C_{68}H_{102}Li_6N_8O_6P_4$, $M_w = 1293.10$, triclinic, space group $P\bar{1}$, $a = 10.969(2)$, $b = 13.022(3)$, $c = 14.760(3)$ Å, $\alpha = 64.12(3)$, $\beta = 69.62(3)$, $\gamma = 86.52(3)°$, $U = 1767.7(6)$ Å^3, $Z = 1$, $\lambda = 0.71073$ Å, $T = 153(2)$ K, $D_c = 1.215$ Mg m^{-3}, μ(Mo-Kα) = 0.161 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer (θ–$\bar{\omega}$ method, $8 \leqslant 2\theta \leqslant 45°$) using an oil-coated rapidly cooled crystal[7] of dimensions 0.4 × 0.5 × 0.5 mm. Of a total of 5662 reflections, 4574 were independent ($R_{int} = 0.14$). The structure was solved by direct methods[8] and refined by full-matrix least squares on F^2 using all data to final values of $R1 = 0.084$ [$F > 4\sigma F$ (3471 reflections)], $wR2 = 0.300$ (all data). [$R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2\}^{0.5}$].[9] Largest features in the final difference map, 0.491 and −0.754 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/335.

References

1 *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2.

2 A. Steiner and D. S. Wright, *Angew. Chem.*, 1996, **108**, 712; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 636.

3 (*a*) B. Grushkin, A. Berlin, J. McClanahan and R. G. Rice, *Inorg. Chem.*, 1966, **5**, 172; (*b*) G. J. Bullen and P. R. Mallinson, *Chem. Commun.*, 1969, 691.

4 S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1994, 2467.

5 M. Witt and H. W. Roesky, *Chem. Rev.*, 1994, **94**, 1163; A. Steiner and D. Stalke, *Inorg. Chem.*, 1993, **32**, 1977; R. Hasselbring, S. K. Pandey, H. W. Roesky, D. Stalke and A. Steiner, *J. Chem. Soc., Dalton Trans.*, 1994, 3447; S. K. Pandey, A. Steiner, H. W. Roesky and D. Stalke, *Angew. Chem.*, 1993, **105**, 625; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 596; J. F. van der Maelen Uria, S. K. Pandey, H. W. Roesky and G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 1994, **50**, 671.

6 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086.

7 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615.

8 G. M. Sheldrick, SHELXS-86, crystal structure solution program, Göttingen, 1986.

9 G. M. Sheldrick, SHELXL-93, crystal structure refinement program, Göttingen, 1993.

Received, 16th October 1996; Com. 6/07055H