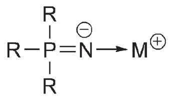
Zwitterionic phosphazenium phosphazenate ligands

Mark A. Benson, Joanne Ledger and Alexander Steiner*

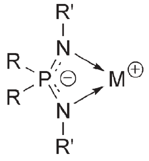
Received (in Cambridge, UK) 14th June 2007, Accepted 31st July 2007
First published as an Advance Article on the web 9th August 2007
DOI: 10.1039/b708993g

Zwitterionic ligands are readily prepared from phosphazenes $(RNH)_6P_3N_3$ by successive alkylation of ring nitrogen sites and deprotonation of exocyclic NH sites.

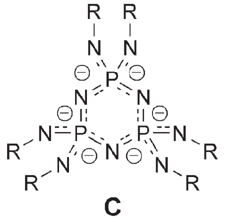
Phosphine imides (**A**)[1] and bis(imino) phosphinates (**B**)[2] are prominent monoanionic phosphorus(V) nitrogen ligands, which have been used as electron-rich and sterically demanding ligands for both olefin polymerisation catalysts and the stabilisation of low coordinated or high oxidation state metal centres. Over recent years we have studied multianionic poly(imino) cyclophosphazenate ligands, such as the hexaanion **C**. These ligands exhibit multidentate coordination surfaces that are able to accommodate large numbers of metal ions.[3] They are prepared by multiple deprotonation of poly(amino) cyclophosphazenes, such as $(RNH)_6P_3N_3$. Very recently, we reported that amino substituted phosphazenes react with alkyl halides at one or two ring N sites yielding *N*-alkyl and *N*,*N*′-dialkyl phosphazenium ions, respectively.[4] In view of the selective deprotonation pathways of $(RNH)_6P_3N_3$, we became interested in the deprotonation behaviour of the resulting mono and dicationic phosphazenium species. Here we show that selective deprotonation of *N*-methyl and *N*,*N*′-dimethyl phosphazenium cations give novel zwitterionic ligand systems.



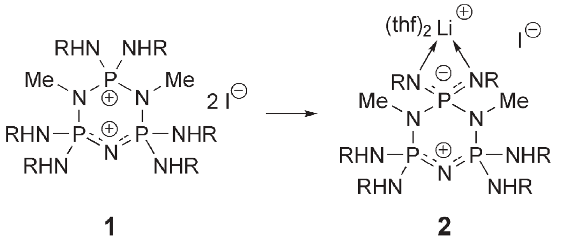
A



B



C



Scheme 1 Synthesis of **2**. *Reagents and conditions*: 2 Bu^nLi, thf, r.t., -2 Bu^nH, $-$LiI; R = cyclohexyl.

The reaction of the *N*,*N*′-dimethyl phosphazenium salt **1** with *n*-butyllithium in thf was monitored by ^{31}P NMR.† The addition of two equivalents of Bu^nLi gave a clean product as indicated by the sole appearance of two peaks at δ 6.8 and 24.6 showing an intensity ratio of 2 : 1. We attributed these to an AX_2 signal with a very low coupling constant, which could not be resolved.[5] Single crystals of the product were obtained from a thf solution at 2 °C. The X-ray crystal structure‡ revealed the formation of the lithium iodide complex **2** featuring a zwitterionic ligand system (Scheme 1 and Fig. 1).

Deprotonation occurred at two geminal amino sites attached to the phosphorus atom that is bounded by the two methylated N centres. The deprotonated N–P–N unit chelates the lithium ion in a bidentate fashion. Two thf molecules complete the coordination sphere of the tetrahedrally coordinated lithium ion. The P–N bond lengths associated with the N–P–N chelate are very short (av. 1.57 Å) and equal those found in the corresponding lithium complexes of **B** (av. 1.58 Å).[2b] The average N–Li distance of 2.03 Å also compares well with that observed in **B** (av. 2.06 Å). By

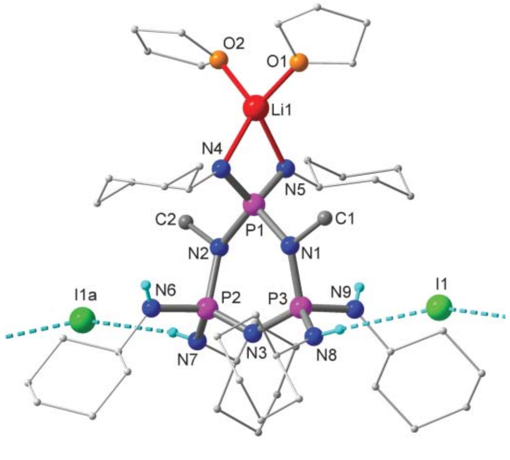
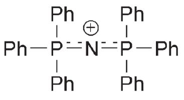


Fig. 1 Crystal structure of **2**. C-bound H-atoms and lattice bound thf molecules are omitted for clarity. Dashed lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (°): Li1–N4 2.046(8), Li1–N5 2.006(8), P1–N4 1.571(3), P1–N5 1.570(3), P1–N1 1.717(3), P1–N2 1.715(3), P2–N2 1.660(3), P2–N3 1.575(3), P2–N6 1.631(3), P2–N7 1.619(3), P3–N1 1.658(3), P3–N3 1.577(3), P3–N8 1.621(3), P3–N9 1.633(3), N1–C1 1.490(4), N2–C2 1.487(4), N8···I1 3.636(3), N7···I1a 3.620(3); N4–P1–N5 105.5(2), N1–P1–N2 99.97(14), N2–P2–N3 109.9(2), N1–P3–N3 109.7(2), P1–N1–P3 130.8(2), P2–N2–P1 130.6(2), P2–N3–P3 128.6(2). Additional ‘a’ letters indicate equivalent positions (1 + *x*, *y*, *z*).

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, UK L69 7ZD. E-mail: a.steiner@liv.ac.uk

contrast, the P–N ring bonds adjacent to the chelate are rather long (av. 1.72 Å) when compared to the corresponding ring bonds of the precursor **1**, which amount to 1.65 Å. The next pair of P–N bonds further along the ring are 1.66 Å on average, while the two P–N bonds located opposite in the ring to the chelating N–P–N unit measure only 1.58 Å. Similarly short P–N bonds of 1.58 Å are found in the bis(triphenylphosphine)iminium cation, PPN$^+$, which has been widely applied as a counterion to facilitate crystallisation of a range of anions.[6]



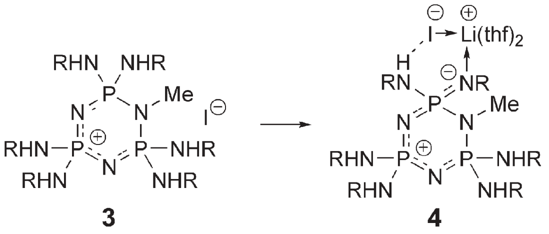
$[\mathrm{Ph_3P{=}N{=}PPh_3}]^{+}$

PPN$^+$

Formally the zwitterion in complex **2** is assembled from the anionic metal chelating unit N4–P1–N5, which resembles the monoanionic bis(imino)phosphinate ligand **B**, and the cationic backbone unit P2–N3–P3, which relates to bis(phosphine)iminium cations like PPN$^+$. The anionic phosphazenate and the cationic phosphazenium moieties are linked by long P–N bonds *via* the two methylated nitrogen centres. The equivalence of bonding parameters in the anionic N4–P1–N5 unit and the strongly basic ligand **B** suggest that the chelate of the zwitterion exhibits a strongly binding ligand site. Weak acids such as ethanol protonate the ligand suggesting that both ligand N sites are fairly basic. In the solid state the iodide ion interacts with the zwitterionic ligand *via* hydrogen bonds to two RNH groups resulting in a supramolecular chain structure arranged alternately of zwitterions and iodide ions. In addition to both lithium-coordinating thf ligands, the crystal structure contains two lattice bound thf molecules per formula unit.

We have also investigated the deprotonation of the N-methyl phosphazenium derivative **3**, which bears one methylated ring N site. It reacts with one equivalent of Bu^{n}Li to give the lithium iodide complex **4**.† The X-ray crystal structure‡ shows again the presence of a zwitterionic ligand system (Scheme 2 and Fig. 2). Deprotonation occurred at one exocyclic N atom in direct neighbourhood of the methylated N site. The resulting monodentate ligand binds the lithium ion, which is further coordinated by the iodide ion and two thf molecules.

The P–N bond associated with the monodentate ligand site is short (P1–N4 1.571(5) Å) and comparable to the P–N bonds of the chelate in **2**. The N–Li distance in **4** (Li1–N4 1.973(11) Å) is slightly shorter than in **2**, which reflects the interaction of the lithium ion with only one negatively charged N centre. Both P–N bonds in the ring involving the methylated N site are long. Here the P1–N1 bond that joins the P-centre carrying the deprotonated N site is with 1.715(5) Å substantially longer than the P2–N1 bond which measures 1.653(4) Å. All the other P–N ring bonds are short (<1.60 Å) showing some degree of multiple bond character typical of cyclophosphazene ring bonds.[7]



Scheme 2 Synthesis of **4**. *Reagents and conditions*: Bu^{n}Li, thf, r.t., −Bu^{n}H; R = cyclohexyl.

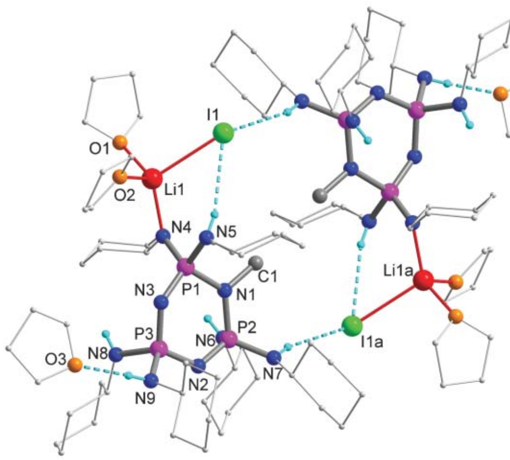


Fig. 2 Crystal structure of **4**. C-bound H-atoms are omitted for clarity. Dashed lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (°): I1–Li1 2.805(9), Li1–N4 1.973(11), P1–N4 1.571(5), P1–N1 1.715(5), P1–N3 1.590(4), P1–N5 1.639(4), P2–N1 1.653(4), P2–N2 1.565(4), P2–N6 1.654(5), P2–N7 1.604(5), P3–N2 1.594(5), P3–N3 1.583(4), P3–N8 1.657(4), P3–N9 1.632(5), N1–C1 1.479(6), N5···I1 3.689(4), N7···I1a 3.679(5); N1–P1–N3 105.8(2), N1–P2–N2 111.7(2), N2–P3–N3 115.0(2), P1–N1–P2 127.8(2), P2–N2–P3 124.2(3), P1–N3–P3 128.0(3). Additional 'a' letters indicate inversion related sites $(1 - x, 2 - y, 1 - z)$.

The RNH function geminal to the deprotonated N centre forms a hydrogen bond with the lithium bonded iodide ion. The close proximity of H-bonding and metal coordination sites enables the ligand to bind the lithium iodide unit *via* both N–Li and NH···I interactions. This synergistic anion/cation coordination to lithium halide aggregates is an interesting feature of phosphazenes containing N–P–NH units.[8] The lithium iodide complex in **4** forms a centrosymmetric dimer *via* additional NH···I interactions to an RNH group of a neighbouring zwitterion. A further RNH group binds a thf molecule *via* H-bonding.

Zwitterionic ligands featuring strongly binding, electron rich chelates for metal ions are of great interest in many areas, particularly in homogenous catalysis and coordination polymers.[9] Phosphazene based zwitterions have been reported, but they lack metal binding ligand sites.[10] Here we have shown that zwitterionic phosphazenium phosphazenate ligands are easily accessible from amino substituted cyclophosphazenes by successive alkylation of N ring sites and deprotonation of exocyclic NH groups. This reverses the polarity of the phosphazene by transferring the negative charge from the ring onto the exocyclic N sites. The resulting zwitterions show a ligand behaviour that is similar to conventional anionic phosphorus(V) nitrogen ligands.

We gratefully acknowledge the EPSRC for financial support.

Notes and references

† *Synthesis*. **2**. Upon addition of two molar equivalents of Bu^{n}Li in hexane to a suspension of **1** (0.5 g) in 20 ml thf the reaction mixture became clear. After stirring for 3 h the solution was filtered. The filtrate was stored at 2 °C giving colourless crystals. ^{1}H NMR (400 MHz, d$_8$-thf, SiMe$_4$ ext.)

δ 2.02–2.07 (m, 60H, CH_2(cyclohexyl)), 2.54 (m, 6H, CH(cyclohexyl)), 3.89 (m, 6H, NH), 3.89 (m, 3H, NCH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, d_8-thf, $SiMe_4$ ext.) δ 25.8, 35.7, 51.7, 67.6; $^{31}P\{^1H\}$ NMR (162.0 MHz, d_8-thf, 85% H_3PO_4 in D_2O ext.) δ 6.8, 24.6; IR (nujol) ν [cm^{-1}] = 3198 (N–H), 1283, 1143, 1105, 1045, 936, 889, 762, 723, 691. Elemental analysis: $C_{46}H_{92}LiN_9O_2P_3$ (1030.07): calc.: C 53.64, H 9.00, N 12.24; found: C 53.22, H 8.45, N 12.71%. **4**: Addition of one equivalent of Bu^nLi in hexane to a suspension of **3** (0.5 g) in 20 ml thf gave a clear reaction mixture. The solution was stirred for 3 h and filtered. The filtrate was stored at room temperature giving colourless crystals. ^1H NMR (400 MHz, d_8-thf, $SiMe_4$ ext.) δ 1.85–2.12 (m, 60H, CH_2(cyclohexyl)), 2.49 (m, 6H, CH(cyclohexyl)), 3.48 (br, 3H, NCH_3), 3.81 (m, 3H, NH); $^{13}C\{^1H\}$ NMR (100.6 MHz, d_8-thf, $SiMe_4$ ext.) δ 24.5, 34.8, 48.0, 65.7, 75.8; $^{31}P\{^1H\}$ NMR (162.0 MHz, d_8-thf, 85% H_3PO_4 in D_2O ext.) δ 10.2, 17.3; IR (Nujol) ν/cm^{-1}: 3224 (N–H), 1253, 1209, 1101, 1049, 889, 803, 723. Elemental analysis: $C_{45}H_{90}LiN_9O_2P_3$ (1016.04): calc.: C 53.20, H 8.93, N 12.41; found: C 52.70, H 8.52, N 12.82%.

‡ Crystallographic data were recorded on a Bruker Apex diffractometer using Mo-Kα-radiation (λ = 0.71073 Å). Both structures were refined by full-matrix least squares against F^2 using all data (SHELXTL).[11] Apart from disordered atoms, non-hydrogen atoms were refined anisotropically. C-bonded hydrogen atoms were fixed geometrically, N-bonded hydrogen atoms were refined freely using similar distance restraints for N–H distances. **2**: $C_{54}H_{108}ILiN_9O_4P_3$, M = 1174.24, $P2_1/c$, a = 11.9616(6), b = 22.3804(10), c = 24.1793(12) Å, β = 102.583(1)°, V = 6317.5(5) Å^3, Z = 4, 11095 independent reflections, R_1 [$I > 2\sigma(I)$] = 0.057, wR_2 (all data) = 0.141; **4**: $C_{49}H_{96}ILiN_9O_3P_3$, M = 1086.10, $P\bar{1}$, a = 13.190(2), b = 14.277(2), c = 17.645(2) Å, α = 100.961(2), β = 100.643(2), γ = 113.484(2)°, V = 2864.0(6) Å^3, Z = 2, 9863 independent reflections, R_1 [$I > 2\sigma(I)$] = 0.068, wR_2 (all data) = 0.185. CCDC 650739 and 650740. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708993g

1 (*a*) K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19–65; (*b*) K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103–169; (*c*) K. Dehnicke and A. Greiner, *Angew. Chem., Int. Ed.*, 2003, **42**, 1340–1354; (*d*) D. W. Stephan, *Organometallics*, 2005, **24**, 2548–2560.

2 (*a*) A. Steiner, S. Zacchini and P. I. Richards, *Coord. Chem. Rev.*, 2002, **227**, 193–216; (*b*) A. Steiner and D. Stalke, *Inorg. Chem.*, 1993, **32**, 1977–1981; (*c*) R. Fleischer and D. Stalke, *Inorg. Chem.*, 1997, **36**, 2413–2419; (*d*) B. F. Straub, F. Rominger and P. Hofmann, *Chem. Commun.*, 2000, 1611–1612; (*e*) R. Vollmerhaus, P. Shao, N. J. Taylor and S. Collins, *Organometallics*, 1999, **18**, 2731–2733.

3 (*a*) A. Steiner and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 636–637; (*b*) G. T. Lawson, F. Rivals, M. Tascher, C. Jacob, J. F. Bickley and A. Steiner, *Chem. Commun.*, 2000, 341–342; (*c*) F. Rivals and A. Steiner, *Chem. Commun.*, 2001, 1426–1427; (*d*) R. Boomishankar, P. I. Richards and A. Steiner, *Angew. Chem., Int. Ed.*, 2006, **45**, 4632–4634.

4 (*a*) M. A. Benson, S. Zacchini, R. Boomishankar, Y. Chan and A. Steiner, *Inorg. Chem.*, DOI: 10.1021/ic7009463, in press; (*b*) M. A. Benson and A. Steiner, *Chem. Commun.*, 2005, 5026–5028.

5 The addition of more than two equivalents of Bu^nLi gave ill-defined product mixtures.

6 The Cambridge Crystal Structure Database (CSD) contained 1147 structures featuring PPN^+ ions. An average P–N distance of 1.58 Å was calculated from 364 structures that were not disordered and showed R values below 5%.

7 (*a*) H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315–356; (*b*) V. Chandrasekhar and V. Krishnan, *Adv. Inorg. Chem.*, 2002, **53**, 159–211; (*c*) for phosphazenes $(RNH)_6P_3N_3$, see: J. F. Bickley, R. Bonar-Law, G. T. Lawson, P. I. Richards, F. Rivals, A. Steiner and S. Zacchini, *Dalton Trans.*, 2003, 1235–1244.

8 (*a*) P. I. Richards, M. A. Benson and A. Steiner, *Chem. Commun.*, 2003, 1392–1393; (*b*) J. F. Bickley, M. C. Copsey, J. C. Jeffery, A. P. Leedham, C. A. Russell, D. Stalke, A. Steiner, T. Stey and S. Zacchini, *Dalton Trans.*, 2004, 989–995.

9 See, for example: (*a*) Q.-Z. Yang, A. Kermagoret, M. Agostinho, O. Siri and P. Braunstein, *Organometallics*, 2006, **25**, 5518–5527; (*b*) R. V. Parish, Z. Salehi and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 251; (*c*) Z. Fei, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 6331–6337; (*d*) R. Chauvin, *Eur. J. Inorg. Chem.*, 2000, 577–591.

10 E. Rivard, P. J. Ragogna, A. R. McWilliams, A. J. Lough and I. Manners, *Inorg. Chem.*, 2005, **44**, 6789–6798.

11 G. M. Sheldrick, SHELXTL, Program for X-ray Crystal Structure Determination, Universität Göttingen, 1997.