Synthesis and Structure of $[\{(THF)_2Li\}_3Me_2Al\{(PhNH)_2(PhN)_4P_3N_3\}]$, the First Mixed-Metal Phosphazenate Complex

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In memory of Ron Snaith

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Reaction of the trilithium phosphazenate $[\{(THF)_2Li\}_3\{(PhNH)_3(PhN)_3P_3N_3\}]$ with one equivalent of trimethylaluminium yields the first mixed-metal phosphazenate complex $[\{(THF)_2Li\}_3Me_2Al\{(PhNH)_2(PhN)_4P_3N_3\}]$. X-ray structure analysis showed that the Me_2Al group is accommodated in an N(exo)–P–N(exo) chelation site of the phosphazenate ligand. Two lithium ions reside in N(ring)–P–N(exo) sites, while the third lithium ion interacts with the ligand solely via an N(ring) atom. NMR spectroscopic data obtained from THF solution indicate a fluxional behaviour of the lithium ions, which oscillate between mono- and bidentate coordination sites.

Introduction

Multianionic ligand systems containing extended arrays of coordination sites often enable the accommodation of well-defined and kinetically stable multinuclear metal ion and mixed-metal ion arrangements. Prominent examples are multianionic calixarinates[1] and calixpyrrolates[2] comprising cyclic structures of repeating monoanionic phenolate and pyrrolate units, respectively. Recently, we introduced phosphazenates as multianionic ligands. They are assembled from repeating tridentate dianionic $[\text{-N=P(NR)}_2\text{-}]^{2-}$ units and facilitate the accommodation of large numbers of metal ions around the ligand backbone in a variety of bi- and tridentate coordination sites.[3] The highly selective sequential deprotonation patterns of the multiprotic phosphazene precursors enable the synthesis of well-defined partially metallated phosphazenate complexes. For example, threefold deprotonation of the hexaprotic phosphazene $(PhNH)_6P_3N_3$ (**1**) by *n*BuLi occurs in a *cis*-fashion yielding the monomeric trilithium phosphazenate $[\{(THF)_2Li\}_3\{(PhNH)_3(PhN)_3P_3N_3\}]$ (**2**), which hosts three lithium ions in alternating N(ring)−P−N(exo) chelation sites on one face of the central phosphazenate ring.[4] The other face of the ring is equipped with three protonated N(exo) functions. Organoaluminium compounds were also applied as metallating agents. Trimethylaluminium fully deprotonates $(CyNH)_6P_3N_3$ to give the monomeric pentanuclear organoaluminium complex $[(THFMeAl)(Me_2Al)_4\{(CyN)_6P_3N_3\}]$ (**3**). All five Al atoms in **3** occupy bidentate chelation sites.[5] Threefold deprotonation generates the trinuclear complex $[(Me_2Al)_3\{(CyNH)_3(CyN)_3P_3N_3\}]$.[3a] The characteristic sequential metallation pattern leading to multinuclear metal phosphazenates is an ideal platform for the preparation of mixed-metal complexes by subsequent treatment of multiprotic phosphazenes with different metallating agents. Herein, we discuss further metallation of the trilithium complex **2** with Me_3Al. This reaction yields the complex $[\{(THF)_2Li\}_3Me_2Al\{(PhNH)_2(PhN)_4P_3N_3\}]$ (**4**), the first example of a mixed-metal phosphazenate.

Results and Discussion

The trilithium phosphazenate **2** reacts with one equivalent of trimethylaluminium in THF as indicated by the appearance of a doublet at $\delta = 3.7$ ppm and a triplet at $\delta = 7.9$ ppm, with an intensity ration of 2:1, in the ^{31}P NMR spectrum. The reaction product was crystallised from THF solution and an X-ray structure analysis showed the formation of the monomeric complex $[\{(THF)_2Li\}_3Me_2Al\{(PhNH)_2(PhN)_4P_3N_3\}]$ (**4**; Figure 1). In addition, the crystal lattice contains two non-bonded THF molecules per formula unit. The crystal structure reveals that one NH group of **2** has been deprotonated by Me_3Al, with evolution of methane (Scheme 1). One exocyclic N−P−N unit chelates the resulting Me_2Al group by forming a planar four-membered PN_2Al ring system. Both N−Al bonds are of equal length (selected bond lengths and angles are listed in Table 1). The chelation of an Me_2Al group in an exocyclic N−P−N site of a phosphazenate ligand also occurs in the solid-state structure of the pentaalu-

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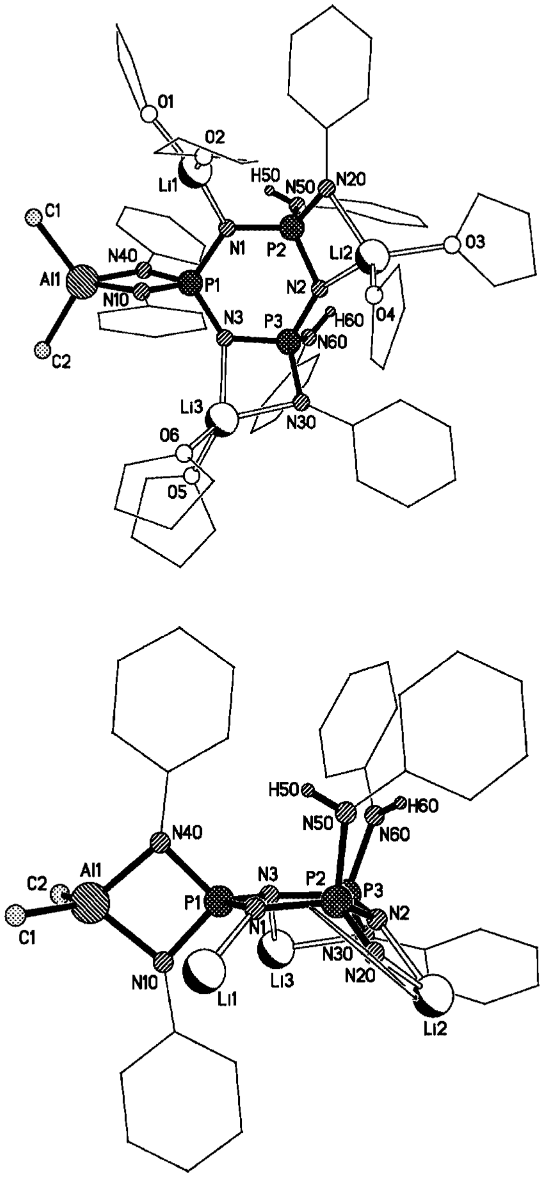
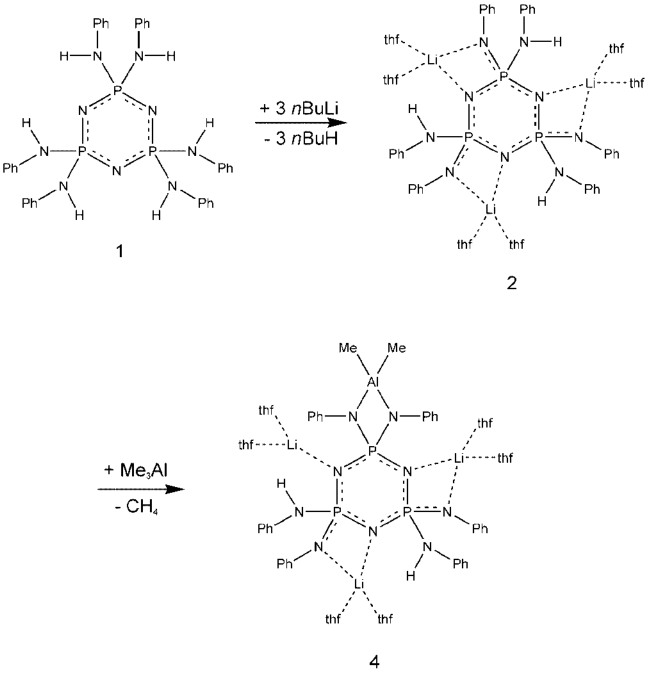


Figure 1. Two different orientations of the crystal structure of **4**; the THF molecules have been omitted from the bottom diagram for clarity



Scheme 1. Mixed metallation pathway leading to complex **4**

Table 1. Selected bond lengths [Å] and angles [°] for **4**

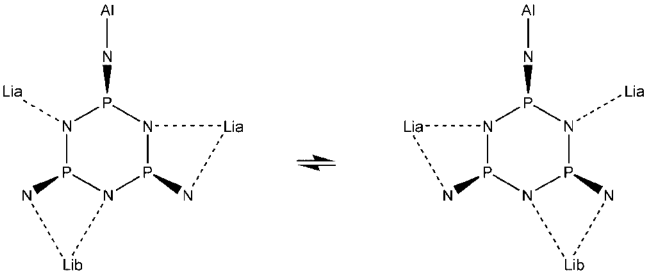
P1−N1	1.622(3)	N1−P1−N3	113.3(2)
P1−N3	1.605(3)	N10−P1−N40	89.8(2)
P1−N10	1.666(3)	N1−P1−N10	111.1(2)
P1−N40	1.659(3)	N1−P2−N2	113.9(2)
P2−N1	1.618(3)	N20−P2−N50	111.0(2)
P2−N2	1.618(3)	N2−P2−N20	102.6 (2)
P2−N20	1.593(3)	N2−P3−N3	114.2(2)
P2−N50	1.709(2)	N30−P3−N60	111.8(2)
P3−N2	1.611(3)	N3−P3−N30	102.7(2)
P3−N3	1.616(3)	P1−N1−P2	123.6(2)
P3−N30	1.595(3)	P2−N2−P3	118.5(2)
P3−N60	1.701(3)	P1−N3−P3	125.6(2)
Al1−N10	1.903(3)	N10−Al1−N40	76.2(2)
Al1−N40	1.900(3)	C1−Al1−C2	112.4(2)
Li1−N1	1.989(7)	P1−N10−Al1	96.7(2)
Li2−N2	2.065(6)	P1−N40−Al1	97.1(2)
Li2−N20	2.031(6)		
Li3−N3	2.099(7)		
Li3−N30	2.021(8)		

minium phosphazenate **3**.[5] The two lithium ions Li2 and Li3 reside in the N(ring)−P−N(exo) sites of **4**, while Li1 is interacting with the ligand solely via an N(ring) atom. In addition, each lithium ion is coordinated by two THF molecules. This results in a trigonal planar coordination at Li1 and distorted tetrahedral environments at Li2 and Li3. The Li−N(ring) distance at Li1 is shorter than the Li−N distances of Li2 and Li3, reflecting the low coordination number of Li1. Within the bidentate chelates Li−N(exo) bonds are slightly shorter than Li−N(ring) bonds. The coordination of Li2 and Li3 is similar to that of the lithium ions in the C_3 symmetrical precursor complex **2**.[4] In **4** there are no interactions between the Al-coordinated N(exo) centres and the lithium ions, presumably due to the strong acceptor behaviour of the aluminium atom. This reduces the number of N-donor sites available for Li coordination. As a result, the ligand provides only a monodentate interaction to one of the lithium ions.

The central P_3N_3 ring in **4** adopts a half-chair conformation. The ring atom N2 deviates by 0.43 Å from the planar arrangement of the other five ring atoms. The P−N(ring) bond lengths are similar throughout the ring, ranging from 1.605(3) to 1.622(3) Å. Conversely, the P−N(exo) bond lengths have a broader range: short P−N(exo) bonds are found at lithiated N(exo) positions [P−N(Li) 1.593(3), 1.595(3) Å], while P−N(exo) bonds within the chelate coordinating Al1 are of intermediate length [P−N(Al) 1.659(3), 1.666(3) Å] and P−N(exo) bonds associated with NH functions are relatively long [P−N(H) 1.701(3), 1.709(3) Å]. Equally short P−N(Li) bonds and long P−N(H) bonds were observed in **2**, but somewhat shorter P−N(H) bonds were found in the hexaprotic phosphazene **1**.[6] Interestingly, the average P−N bond length of the four P−N bonds surrounding one phosphorus atom is almost the same for all three P atoms (av. P−N at P1: 1.638, at P2: 1.635 and at P3: 1.631 Å). This cooperative "seesaw" effect suggests that the P−N bond orders within each PN_4 tetrahedron vary, but the overall sum of P−N bond orders around each P atom is finely balanced. A similar effect has been observed for the S−N bonds in iminosulfonate complexes.[7] The shortness of the P−N(Li) bonds indicates delocalisation of the negative charge from the P−N(Li) onto the P−N(ring) bond and a mainly ionic character of the N−Li interactions. This extra amount of negative charge around the PN_4 tetrahedra is compensated by an elongation of the P−N(H) bond. On the other hand the N−Al bonds in **4** are covalent, as indicated by P−N(Al) bonds of intermediate lengths. The range of exocyclic N−P−N angles mirrors the flexibility of the phosphazenate ligand towards metal coordination. The N−P−N angle of the exocyclic chelate hosting the aluminium centre is very sharp [89.9(2)°] compared to the other two exocyclic N−P−N angles [111.0(2), 111.8(2)°]. The N−P−N angles within the ring are similar and range from 113.3(2)° to 114.2(2)°. The two N(ring)−P−N(exo) angles of lithium binding chelates are identical [102.6(2), 102.7(2)°], but not as acute as that of the Al binding site.

A variety of complexes containing both lithium and aluminium centres have been described,[8] although the accommodation of three Li and one Al centre around one ligand system has not been reported so far. The coordination modes exhibited in **4** are closely related to those of other ligands containing N−P−N chelates.[3a] Several metal complexes have been described featuring four-membered PN_2M ring systems where M is either Li[9] or Al.[10] Monodentate coordination of N-donor ligands towards tricoordinate lithium ions in monomeric complexes, like Li1 in **4**, is usually achieved by bulky ligands with sterically demanding substituents.[11] On the contrary, the phosphazenate ligand **4** gains its steric demand by accommodating a larger number of metal ions rather than providing bidentate chelation sites.

In contrast to the solid-state structure, which contains three chemically different phosphorus nuclei, the ^{31}P NMR spectrum of a solution of complex **4** in THF exhibits an AX_2 system. Variable-temperature NMR studies were hampered by the low solubility of **4** in THF at low temperatures. However, NMR spectroscopic data obtained from measurements at room temperature suggest a fluctuating behaviour of the lithium ions in solution, as illustrated in Scheme 2. The three lithium ions oscillate in a concerted manner around the three N(ring) and the two lithiated N(exo) sites. The two chemically equivalent lithium ions, Li^a, oscillate between a bidentate N(ring)−P−N(exo) chelate and the monodentate N(ring) site, whilst Li^b oscillates between two neighbouring N(ring)−P−N(exo) sites. This mechanism is backed up by the ^7Li NMR spectrum, which consists of two signals at δ = 2.83 and 3.40 ppm displaying an intensity ratio of 2:1. Also, four sets of chemically distinct phenyl groups are evident from the ^{13}C NMR spectrum, reflecting the mirror symmetry of the fluctuating structure. These four sets consist of: (i) the two PhNH groups, (ii) the two PhNLi groups, (iii) the PhNAl group at the "NH face" of the phosphazenate ring, and (iv) the PhNAl group at the "NLi face" of the ring. The ^1H NMR spectrum exhibits one singlet at δ = −0.89 ppm for the Me_2Al, unit indicating the chemical equivalence of both methyl groups, and one signal at δ = 6.21 ppm for the two NH groups.



Scheme 2. Proposed mechanism of fluctuation of lithium ions within complex **4** in THF solution (for clarity, only P, Al, Li and coordinating N atoms are shown)

Further metallation of the phosphazenate ligand in **4** appears possible, since it holds two potentially acidic NH functions. The stepwise addition of excess Me_3Al to **2** was monitored by ^{31}P NMR spectroscopy (Figure 2). The familiar AX_2 pattern of **4** emerges upon addition of one equivalent Me_3Al. After further addition of Me_3Al several other species appear, exhibiting either an AX_2 or AXY pattern, indicating the presence of either two or three distinct phosphorus nuclei. So far, we have been unsuccessful in isolating mixed Li-Al complexes showing higher metallation grades than **4**. Moreover, complex **4** proved to be a rather stable member of a possible series of mixed Li-Al phosphazenates, since higher metallated species slowly degrade in THF solu-

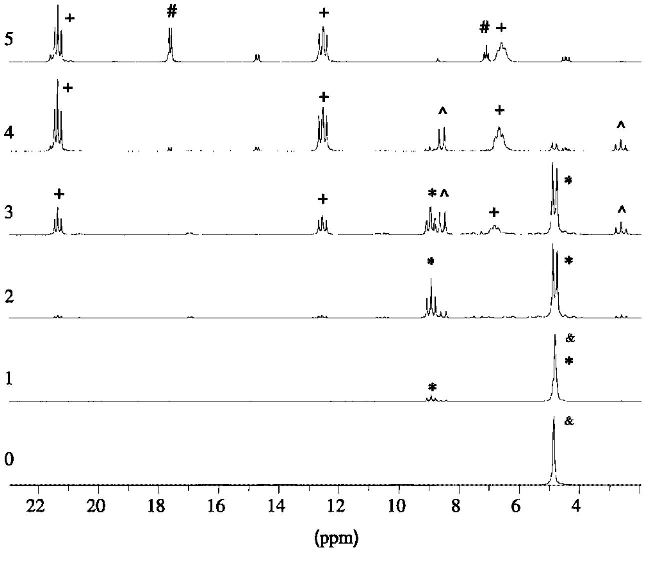


Figure 2. ^{31}P NMR spectrum of stepwise reaction of **2** with *n* equivalents of Me_3Al in THF at room temperature; & represents complex **2** and * complex **4**; +, ^ and # indicate further metalated species

tion to give **4**. The fluctuating behaviour of lithium ions could be a stabilising factor for **4**.

In summary, we have presented the first phosphazenate complex that accommodates a mixed-metal array. The synthesis of the mixed Li-Al complex was achieved by successive deprotonation of a hexaprotic phosphazene with *n*BuLi and Me_3Al. It looks as if a variety of other stable mixed-metal species can be generated by exploiting the selective metalation pattern of multiprotic phosphazenes. Metal ions and organometallic fragments occupy specific coordination sites around the phosphazenate core. The ligand provides both rigid metal chelation and allows a fluctuating behaviour of the metal ions within the ligand sphere. This concept could lead to tailor-made, mixed-metal complexes for homogeneous catalysis.

Experimental Section

All synthetic procedures were carried out under a dry N_2 atmosphere. Compounds **1**[6] and **2**[4] were prepared according to literature methods. Organometallic reagents were applied as standard solutions: *n*BuLi (1.6 M in hexane) and Me_3Al (2 M in hexane).

Synthesis of 4: *n*BuLi (0.85 mL, 1.35 mmol) was added at −78 °C to a solution of **1** (300 mg, 0.45 mmol) in 20 mL of THF. After stirring for one hour at room temperature, Me_3Al (0.22 mL, 0.45 mmol) was added dropwise and the solution was stirred overnight at room temperature. Subsequently the reaction solution was filtered and the volume of the filtrate reduced by half in vacuo. Single crystals were obtained after three days. In the absence of mother liquor the crystals degrade to give a white powder. Yield 215 mg (73%). ^1H NMR (300 MHz, $[D_8]$THF $SiMe_4$): $\delta = -0.87$ (s, 3 H, $AlCH_3$), 6.21 (br., 2 H, N*H*), 6.98−6.51 (m, 30 H, Ph) ppm. ^7Li NMR [97.16 MHz, THF, $(CD_3)_2CO$, LiCl in D_2O ext.] $\delta = 2.83$ (2 Li), 3.40 (Li) ppm. $^{13}C\{^1H\}$ NMR (75.46 MHz, $[D_8]$THF, $SiMe_4$): $\delta = -9.94$ (Me_2Al), 113.6, 114.7, 115.3, 116.7 (*ortho*), 117.4, 120.0, 120.1, 120.2 (*para*), 127.6, 127.7, 127.8 128.1, (*meta*), 143.8, 148.5, 148.7, 153.1 (*C*N) ppm. ^{31}P NMR (101.25 MHz, $[D_8]$THF, 85% H_3PO_4 in D_2O ext.): $\delta = 3.7$ (t, $^2J_{P,P} = 21.8$ Hz, 1 P), 7.9 (d, $^2J_{P,P} = 21.8$ Hz, 2 P) ppm. IR (nujol): $\tilde{\nu} = 3380.5$ (N−H), 1588.2, 1335.3, 1300.2, 1242.5, 1109.2 (P−N), 1073.5, 1030.9, 1005.9, 891.9, 860.8, 797.2, 748.6, 692 cm^{-1}. $C_{62}H_{86}AlLi_3N_9O_6P_3$ (1193.62): calcd. C 62.4, H 7.26, N 10.6; found C 62.0, H 7.01, N 11.1.

Crystal data for **4**·2THF were recorded on a Stoe-IPDS diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å), $T = 200$ K. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using all data (SHELX-97). $C_{70}H_{102}AlLi_3N_9O_8P_3$: $M = 1338.32$, triclinic, $P\bar{1}$, $a = 12.431(2)$, $b = 14.467(2)$, $c = 23.663(4)$ Å, $\alpha = 91.97(2)°$, $\beta = 101.62(2)°$, $\gamma = 114.46(2)°$, $V = 3760.9(9)$ Å^3, $Z = 2$, $D_c = 1.182$, μ(Mo-K_α) = 0.147, number of reflections: 23726 (total), 11018 (unique), $R_{int} = 0.057$, R_1 [$I > 2\sigma(I)$] = 0.057, wR_2 (all data) = 0.160. One THF molecule bonded to Li3 and the two non-bonded lithium ions are disordered over two positions and were refined using similar distance and similar *U* restraints. Non-hydrogen atoms were refined anisotropically, except for the disordered positions, which were treated isotropically. H-atoms were placed geometrically in accordance with the hybridisation of their parent atoms.

CCDC-208395 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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