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$\{Li[P(N^tBu)_2]\}_4 \cdot 0.25P_4(N^tBu)_6$: Solvent and Substituent Effects on the Structures and Reactivity of 1,3-Diaza-2-phosphaallyllithium Complexes

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The addition of 2 equiv of ^nBuLi to a solution of $^tBuN(H)P(\mu\text{-}N^tBu)_2PN(H)^tBu$ (**1**) in toluene produces the adduct $[LiP(N^tBu)_2]_4 \cdot 0.25P_4(N^tBu)_6$ (**2**·0.25**3**), but the reverse addition yields only **2**. The structure of **2**·0.25**3** has been determined by X-ray crystallography: monoclinic, $P2_1/a$, $a = 17.649(5)$ Å, $b = 18.272(4)$ Å, $c = 20.295(5)$ Å, $\beta = 111.92(2)°$, $V = 6072(3)$ Å^3, and $Z = 4$. The tetrameric cluster **2** consists of two P_2N_2 rings bridged by a tub-shaped, eight-membered Li_4N_4 ring. The mean P−N distance in the P_2N_2 rings (1.78 Å) is significantly longer than the corresponding value of 1.65 Å for the P−N bonds linking the P_2N_2 rings to the Li_4N_4 unit. The $P_4(N^tBu)_6$ cage **3** in the adduct is formed as the isomer in which two P_2N_2 rings are bridged by two N^tBu groups. The same tetracyclic isomer of **3** is prepared in 71% yield by the reaction of $^tBuN(Li)P(\mu\text{-}N^tBu)_2PN(Li)^tBu$ with $ClP(\mu\text{-}N^tBu)_2PCl$ in toluene. Variable temperature $^{31}P\{^1H\}$ NMR studies of the 16-atom cluster $[LiP(N^tBu)_2]_4$ (**2**) at different concentrations in C_7D_8 indicate that facile dissociation into two molecules of the dimer $[LiP(N^tBu)_2]_2$ occurs above ca. 295 K.

Introduction

Cluster compounds have played an important role in the development of main group element chemistry.[1] This topic has been enriched by recent studies of ternary systems containing homoleptic polyimido anions of the p-block elements, as their lithium derivatives.[2−9] In addition to the interest in the structures of these ternary clusters, and related quaternary systems,[10] the polyimido anions themselves have been investigated as ligands that provide unusual environments for both main group[5,11] and transition metal centers.[11,12]

Coordinating solvents such as THF have an important influence on the structures of these clusters. For example, the unsolvated dimer $\{Li_2[C(N^tBu)_3]\}_2$ has a cyclic ladder structure,[13a] whereas the THF adduct $\{Li_2[C(NPh)_3]\}_2 \cdot 6THF$ has a step-shaped arrangement of four-membered rings.[13b] In effect the coordination of THF to lithium ions results in unravelling of the cyclic ladder.[13a] For group 15 derivatives the solvated dimer $\{Li[Bi(N^tBu)_2]\}_2 \cdot 2THF$ has a cubane structure,[4] but the unsolvated congener $\{Li[Sb(NCy)_2]\}_4$ is tetrameric.[2] In the former case solvation apparently prevents the dimerization of the cubic building blocks.

The first example of a 1,3-diaza-2-phosphaallyl anion, Li[RNPNR′] (R = R′ = Mes* = 2,4,6-$(^tBu)_3C_6H_2$) was reported in 1986.[14a] Although the reaction of this symmetrical reagent with ClP═NMes* was subsequently investigated,[14b] the solid-state structure was not determined.[14a] However, a solvated unsymmetrical derivative $[Li(OEt_2)][Mes^*NPNCPh_3]$ was shown to be monomeric whereas the solvent-free dimers $\{Li[RNPNMes^*]\}_2$ (R = 1-Ad, ^tBu) consist of eight-membered $Li_2P_2N_4$ rings.[15] After the original submission of this manuscript, a cubic structure was reported for the dimeric THF adduct $\{Li[P(N^tBu)_2]\}_2 \cdot 2THF$.[16]

We describe here the preparation and structural characterization of the adduct $\{Li[P(N^tBu)_2]\}_4 \cdot 0.25P_4(N^tBu)_6$ (**2**·0.25**3**) from the reaction of 2 equiv of ^nBuLi with $^tBuN(H)P(\mu\text{-}N^tBu)_2PN(H)^tBu$ (**1**) *in toluene*. The identity of the product(s) of this reaction is shown to be dependent on both the solvent and the order of addition of the reagents. The behavior of the tetrameric $Li_4P_4N_8$ cluster (**2**) in solution is investigated by $^{31}P\ \{^1H\}$ NMR

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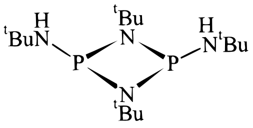
spectroscopy. The tetracyclic $P_4(N^tBu)_6$ isomer **3** is obtained in good yields by the reaction of $^tBuN(Li)P(\mu\text{-}N^tBu)_2PN(Li)^tBu$ and $ClP(\mu\text{-}N^tBu)PCl$.



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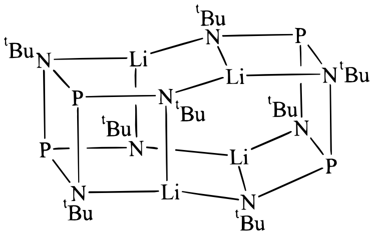

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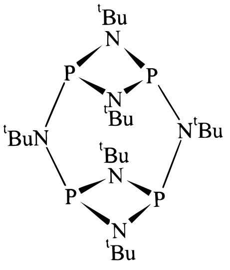

3

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled before use: tetrahydrofuran, toluene, pentane, hexane, diethyl ether (Na/benzophenone). *n*-Butyllithium (in hexanes), $^tBuNH_2$, Mes^*NH_2, and $^tBu(Me_3Si)NH$ were commercial samples (Aldrich) used as received. PCl_3 (Aldrich) was distilled before use. The compounds **1**,[17] $ClP(\mu\text{-}N^tBu)_2PCl$[18] [$^1H$ NMR (in C_6D_6 at 23 °C): δ 1.17 (t, $^4J(^{31}P-{}^1H) = 1.0$ Hz); $^{31}P\{^1H\}$ NMR (in C_6D_6 at 23 °C): δ 207.5 (s)], and $P[N(H)Mes^*][NMes^*]$[14c] were prepared by the literature procedures. The adduct $\{Li[P(N^tBu)_2]\}_2\cdot 2THF$ was obtained in 77% yield by the literature method.[16] The ^1H NMR chemical shifts were in good agreement with the reported values. ^7Li NMR (in C_6D_6 at 23 °C): δ −0.48 ($\Delta\nu_{1/2} = 17$ Hz). $^{31}P\{^1H\}$ NMR (in C_6D_6 at 23 °C): δ 161.1. The handling of air and moisture-sensitive reagents was performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

Instrumentation. $^{31}P\{^1H\}$ and ^7Li NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 161.98 and 155.51 MHz, respectively; chemical shifts are relative to 85% H_3PO_4 in D_2O and 4 M LiCl in D_2O, respectively. ^1H NMR spectra were collected on a Bruker AM-200 spectrometer and chemical shifts are reported relative to Me_4Si in $CDCl_3$. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, The University of Calgary.

Preparation of $[LiP(N^tBu)_2]_4\cdot 0.25P_4(N^tBu)_6$ (2·0.253). A 2.5 M solution of ^nBuLi in hexanes (3.45 mL, 8.62 mmol) was added dropwise via a stainless steel transfer needle to a stirred solution of $^tBuN(H)P(\mu\text{-}N^tBu)_2PN(H)^tBu$ (1.50 g, 4.31 mmol) in toluene (50 mL) cooled to −78 °C. After 0.5 h the cooling bath was removed and the reaction mixture was stirred for a further 1.5 h at 23 °C. Upon removal of all volatiles in vacuo, the white residue was dissolved in hexane and filtered through a fine sintered glass frit. The resulting clear, colorless solution was subjected to vacuum yielding white microcrystalline **2**·0.25**3** (1.32 g, 1.54 mmol, 89%); the product decomposes at about 200 °C. Anal. Calcd for $C_{38}H_{85.5}Li_4N_{9.5}P_5$: C, 53.18; H, 10.04; N, 15.50. Found: C, 53.29; H, 9.97; N, 15.11. ^1H NMR [in C_6D_6 at 23 °C]: δ 1.58 (br, 18H, ^tBu), 1.51 (br, 180H, ^tBu), 1.46 (s, 144H, ^tBu). ^7Li NMR [in C_6D_6 at 23 °C]: δ −0.68. $^{31}P\{^1H\}$ NMR [in C_7D_8 at −60 °C]: δ 124.5 (s) and 117.1 (s).

Table 1. Crystallographic Data for **2**·0.25**3**

formula	$[LiP(NC_4H_9)_2]_4\cdot$ $0.25[P_4(NC_4H_9)_6]$	*Z*	4
fw	858.29	*T*, °C	−103.0
space group	$P2_1/a$ (No. 14)	λ, Å	0.71069
a, Å	17.649(5)	d_{calcd}, g cm^{-3}	0.939
b, Å	18.272(4)	μ, cm^{-1}	1.80
c, Å	20.295(5)	R^a	0.138
β, deg	111.92(2)	$R_w{}^b$	0.352
V, Å^3	6072(3)		

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w\Delta^2/\Sigma wF_o2]^{1/2}$.

Preparation of $[LiP(N^tBu)_2]_4$ (2). A solution of $^tBuN(H)P(\mu\text{-}N^tBu)_2PN(H)^tBu$ (1.83 g, 5.25 mmol) in toluene (35 mL) was added dropwise to a stirred solution of ^nBuLi (10.50 mmol, 4.20 mL of a 2.5 M solution in hexanes) in toluene (5 mL) cooled to 0 °C. After 0.5 h the clear, colorless reaction mixture was stirred for a further 2 h at 23 °C. Removal of all volatiles in vacuo and subsequent washing of the resulting white residue with cold pentane (2 × 5 mL) yielded, upon drying, white microcrystalline **2** (1.67 g, 2.32 mmol, 88%); mp 195 °C (decomp.). Anal. Calcd for $C_8H_{18}LiN_2P$: C, 53.34; H, 10.07; N, 15.55. Found: C, 53.16; H, 10.12; N, 15.90. ^1H NMR [in C_7D_8 at 23 °C]: δ 1.49 (s, 36H, ^tBu), 1.45 (s, 36H, ^tBu). ^7Li NMR [in C_6D_6 at 23 °C]: δ −0.68 ($\Delta\nu_{1/2} = 78$ Hz). VT $^{31}P\{^1H\}$ NMR data are presented in the Results and Discussion section.

Preparation of $P_4(N^tBu)_6$ (3). A solution of $ClP(\mu\text{-}N^tBu)_2PCl$ (0.89 g, 3.23 mmol) in toluene (15 mL) was added via a stainless steel transfer needle to a stirred solution of $\{Li[P(N^tBu)_2]\}_2\cdot 2THF$ (1.63 g, 3.23 mmol) in toluene (45 mL) at 0 °C. The reaction mixture was heated at reflux for 3.5 h, during which the precipitation of LiCl occurred. Filtration followed by removal of all volatiles in vacuo and subsequent washing of the yellow residue with cold *n*-pentane (8 mL) yielded, upon drying, $P_4(N^tBu)_6$ (1.26 g, 2.29 mmol, 71%) as a white, amorphous solid. Crystalline material was obtained from a THF solution (24h at 23 °C); mp 230 °C (decomp.). Anal. Calcd for $C_{24}H_{54}N_6P_4$: C, 52.35; H, 9.88; N, 15.26. Found: C, 53.25; H, 10.33; N. 14.73. ^1H NMR [in C_6D_6 at 23 °C]: δ 1.57 (m, 18H, ^tBu), 1.53 (s, 36H, ^tBu). $^{31}P\{^1H\}$ NMR [in C_6D_6 at 23 °C]: δ 117.2 (s). EI-MS (70 eV): 550 (M^+, 60%).

Preparation of $LiP(NMes^*)_2$ (4). A 2.5 M solution of ^nBuLi in hexanes (0.36 mL, 0.89 mmol) was added dropwise to a stirred solution of $P[N(H)Mes^*][NMes^*]$ (0.49 g, 0.89 mmol) in hexane (45 mL). The resulting yellow precipitate was allowed to settle and the hexane layer was decanted. The residue was washed with hexane (10 mL) to give, upon drying in vacuo, yellow amorphous **4** (0.45 g, 0.81 mmol, 91%); mp 235 °C (decomp.). Anal. Calcd for $C_{36}H_{58}LiN_2P$: C, 77.66; H, 10.50; N, 5.03. Found: C, 77.26; H, 10.32; N, 5.19. ^1H NMR [in C_6D_6 at 23 °C]: δ 7.64 (s, 4H, *m*-H), 1.66 (s, 36H, *o*-^tBu), 1.41 (s, 18H, *p*-^tBu). ^7Li NMR [in C_6D_6 at 23 °C]: δ −3.56. $^{31}P\{^1H\}$ NMR [in C_6D_6 at 23 °C]: δ 341.3 (cf. lit: 337.0).[14a] Dark yellow crystals of $\mathbf{4}\cdot C_7H_8$ suitable for X-ray crystallography were obtained by recrystallization from toluene/hexane (5:1) at 23 °C.

X-ray Analyses. All measurements were made on a Rigaku AFC6S diffractometer. Crystallographic data are summarized in Table 1.

2·0.253. Crystals of $[LiP(N^tBu)_2]_4\cdot 0.25P_4(N^tBu)_6$ were obtained from benzene-d_6 at 23 °C. A colorless prismatic crystal (0.38 × 0.29 × 0.25 mm) was coated with epoxy and mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $13.38 < 2\theta < 19.39°$. The systematic absences of $h0l$, $h = 2n + 1$ and $0k0$, $k = 2n + 1$ uniquely determined the space group to be $P2_1/a$ (No. 14). Scans of $(1.10 + 0.34 \tan \theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 55.1°. The intensities of 13 661 unique reflections were measured, of which 2671 had $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects. The structure was solved by and expanded using Fourier techniques.[19] Some of the non-hydrogen atoms were refined anisotropically. Several C atoms of ^tBu groups were disordered and were allowed isotropic displacement parameters with partial occupancy factors. Some of the hydrogen atoms were included but not refined. For both structures scattering factors

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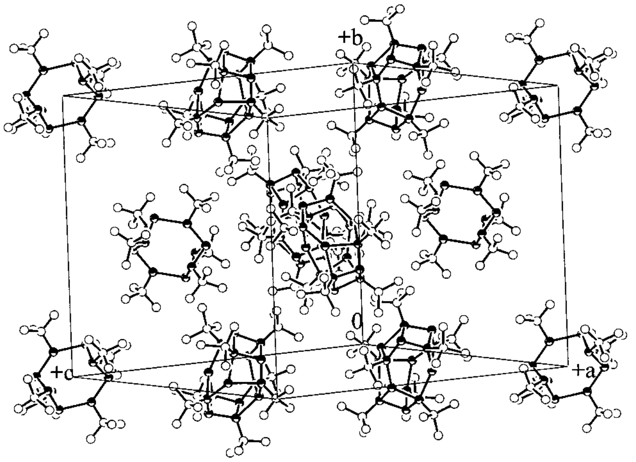

Figure 1. Unit cell diagram for $\{Li[P(N^tBu)_2]\}_4{\cdot}0.25P_4(N^tBu)_6$. For clarity only the occupation of four corner sites by $P_4(N^tBu)_6$ molecules is shown. The site occupancy factor for all $P_4(N^tBu)_6$ molecules is 50%.

were those of Cromer and Waber,[20] and allowance was made for anomalous dispersion.[21] All calculations were performed using teXsan.[22] The structure of **2**·0.25**3** was refined with SHELX97.[23]

Results and Discussion

Preparation and X-ray Structure of $\{Li[P(N^tBu)_2]\}_4{\cdot}0.25P_4(N^tBu)_6$. Although the cyclodiphosph(III)azane **1** has been known for many years,[17] the *cis*-arrangement of the exocyclic $N(H)^tBu$ groups was only established by X-ray crystallography very recently.[16,24] As part of our interest in homoleptic polyimido anions of the p-block elements, we became interested in the dilithio derivative of **1** from the viewpoint of cluster structures obtained from *noncoordinating* solvents.[5,7,13a] We have investigated the reaction of **1** with *n*-butyllithium in toluene under a variety of reaction conditions. We find that the identity of the product(s) depends not only on the solvent, but also on the order of addition of the reagents and the stoichiometry.

The addition of two equivalents of *n*-butyllithium to **1** in toluene at −78 °C produced a white microcrystalline solid, which exhibited two singlets in the $^{31}P\{^1H\}$ NMR spectrum (in C_7D_8 at −60 °C) at δ 124.5 and 117.1 in the approximate ratio of 5:1 and a singlet in the ^7Li NMR spectrum. The ^1H NMR spectrum (in C_6D_6) consists of three peaks at δ 1.58, 1.51, and 1.46 with approximate relative intensities of 1:10:8. The reason for these puzzling observations became apparent when an X-ray structural determination revealed this product to be an adduct of the tetrameric cluster $[LiP(N^tBu)]_4$ (**2**) and the cage molecule $P_4(N^tBu)_6$ (**3**). The $P_4(N^tBu)_6$ molecules lie on inversion centers and occupy the eight corner positions and two opposite faces of the unit cell (see Figure 1). The site occupancy factor for all $P_4(N^tBu)_6$ molecules is 50%. Thus each unit cell contains four molecules of **2** and one molecule of **3**, which gives the molecular formula $\{LiP(N^tBu)_2\}_4{\cdot}0.25P_4(N^tBu)_6$. Both the $^{31}P\{^1H\}$ NMR spectrum and the integrated values of the N^tBu resonances in the ^1H NMR spectrum are consistent with this stoichiometry.

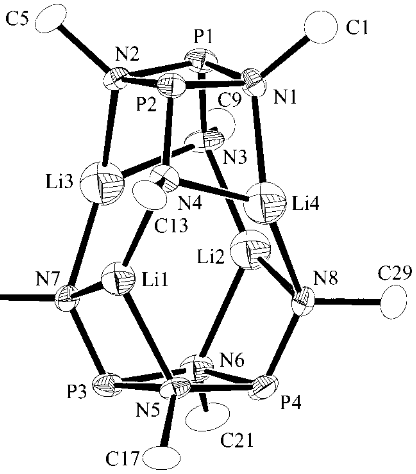

Figure 2. Molecular structure of $\{Li[P(N^tBu)_2]\}_4$. For clarity, only the α-carbon atoms of ^tBu groups are shown. Displacement ellipsoids are plotted at 30% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[LiP(N^tBu)_2]_4$

P(1)−N(1)	1.743(9)	Li(1)−N(4)	2.08(2)
P(1)−N(2)	1.791(9)	Li(1)−N(5)	2.19(3)
P(1)−N(3)	1.655(9)	Li(1)−N(7)	2.02(2)
P(2)−N(1)	1.782(9)	Li(2)−N(3)	2.05(3)
P(2)−N(2)	1.794(9)	Li(2)−N(6)	2.24(3)
P(2)−N(4)	1.644(9)	Li(2)−N(8)	1.99(3)
P(3)−N(5)	1.797(9)	Li(3)−N(2)	2.15(2)
P(3)−N(6)	1.774(10)	Li(3)−N(3)	2.05(2)
P(3)−N(7)	1.648(9)	Li(3)−N(7)	2.09(3)
P(4)−N(5)	1.762(9)	Li(4)−N(1)	2.10(3)
P(4)−N(6)	1.794(10)	Li(4)−N(4)	2.09(3)
P(4)−N(8)	1.654(10)	Li(4)−N(8)	2.03(3)
N(1)−P(1)−N(2)	82.9(4)	P(1)−N(3)−Li(2)	132.1(10)
N(1)−P(2)−N(2)	81.7(4)	P(1)−N(3)−Li(3)	92.1(10)
N(5)−P(3)−N(6)	82.9(4)	Li(2)−N(3)−Li(3)	86.5(13)
N(5)−P(4)−N(6)	83.3(6)	P(2)−N(4)−Li(1)	134.9(8)
N(1)−P(1)−N(3)	105.9 (3)	P(2)−N(4)−Li(4)	89.9(9)
N(2)−P(1)−N(3)	102.8(5)	Li(1)−N(4)−Li(4)	84.8(11)
N(1)−P(2)−N(4)	103.9(4)	P(3)−N(7)−Li(1)	93.1(8)
N(2)−P(2)−N(4)	104.8(4)	P(3)−N(7)−Li(3)	135.4(10)
N(5)−P(3)−N(7)	103.0(4)	Li(1)−N(7)−Li(3)	85.7(1)
N(6)−P(3)−N(7)	105.0(5)	P(4)−N(8)−Li(2)	93.6(9)
N(5)−P(4)−N(8)	104.1(4)	P(4)−N(8)−Li(4)	134.9 (10)
N(6)−P(4)−N(8)	104.0(5)	Li(2)−N(8)−Li(4)	81.2(12)
P(1)−N(1)−P(2)	98.2(5)	N(4)−Li(1)−N(5)	130.8(11)
P(1)−N(2)−P(2)	96.0(4)	N(4)−Li(1)−N(7)	132.1(12)
P(3)−N(5)−P(4)	96.5(4)	N(5)−Li(1)−N(7)	79.4(8)
P(3)−N(6)−P(4)	96.2(5)	N(3)−Li(2)−N(6)	131.4(15)
P(1)−N(1)−Li(4)	115.6(9)	N(3)−Li(2)−N(8)	134.4(15)
P(2)−N(1)−Li(4)	85.8(9)	N(6)−Li(2)−N(8)	79.7(11)
P(1)−N(2)−Li(3)	85.2(9)	N(2)−Li(3)−N(3)	79.7(12)
P(2)−N(2)−Li(3)	118.0(9)	N(2)−Li(3)−N(7)	133.8(16)
P(3)−N(5)−Li(1)	83.7(7)	N(3)−Li(3)−N(7)	130.5(16)
P(4)−N(5)−Li(1)	119.9(7)	N(1)−Li(4)−N(4)	80.3(11)
P(3)−N(6)−Li(2)	117.0(8)	N(1)−Li(4)−N(8)	138.6(16)
P(4)−N(6)−Li(2)	82.2(8)	N(4)−Li(4)−N(8)	132.3(16)

An ORTEP drawing of the tetramer $[LiP(N^tBu)_2]_4$ with the atomic numbering scheme is shown in Figure 2. Selected bond distances and bond angles are summarized in Table 2. The sixteen atom $Li_4N_8P_4$ cluster in **2** can be viewed to result from the dimerization of two $Li_2N_4P_2$ cubes via their Li_2N_2 faces with concomitant cleavage of one pair of antipodal Li−N bonds on each face (Scheme 1). Similar structures have been observed for the octameric iminoalanes $(RAlNR')_8$ (R = H, R′ = ^{i}Pr;[25] R = R′ = Me[26]) and the antimony analogue of **2**, {Li[Sb-

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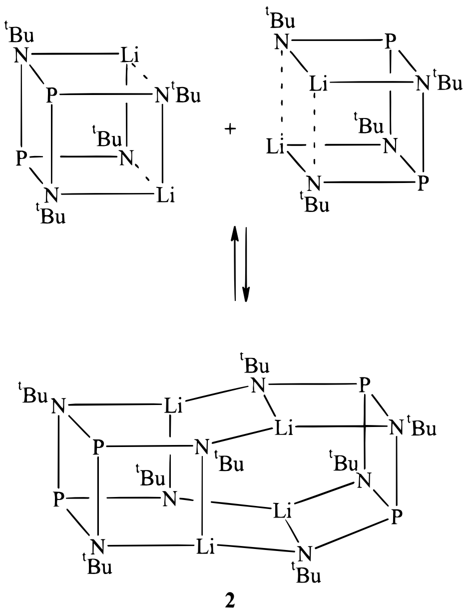
Scheme 1



$(NCy)_2]\}_4$.[2] Alternatively, the structure of **2** can be described as two four-membered P_2N_2 rings linked by an eight-membered, tub-shaped Li_4N_4 ring. The P_2N_2 rings are planar to within ca. 0.065 Å. The mean P−N bond length within these rings [1.780(9) Å] is significantly longer than the mean distance of 1.650(9) Å for the P−N bonds linking the P_2N_2 rings to the Li_4N_4 unit. A similar observation has been reported for $[LiP(N^tBu)_2]_2\cdot 2THF$ [1.725(2) vs 1.664(2) Å].[16] The mean bond angles within the P_2N_2 rings are $|{<}NPN| = 82.7°$, $|{<}PNP| = 96.7°$ (cf. $|{<}NSbN| = 79.7°$, $|{<}SbNSb| = 98.6°$ for $[LiSb(NCy)_2]_4{}^2$). The mean value of the sum of the bond angles at the three-coordinate phosphorus atoms is ca. 291°, *cf. ca.* 261° in $\{Li[Sb(NCy)_2]\}_4$,[2] implying substantially higher p character for the lone pairs on the Group 15 centers in **2**. As a result of disorder the four lithium atoms were refined isotropically. Consequently, the metrical parameters involving these atoms have high esds. Nevertheless, some generalizations can be made. The mean Li−N bond length within the Li_4N_4 ring (2.05 Å) is significantly shorter than the mean value of 2.17 Å observed for the Li−N bonds connecting this unit to the P_2N_2 rings, as found for the antimony analogue of **2**.[2] The distorted geometry at the three-coordinate Li atoms in **2** is reflected in the bond angles, which range from 79.4 to 138.6°. The mean value of the sum of the bond angles at these Li atoms is 345.8°, significantly less than the value of 353.8° found for the antimony analogue,[2] presumably as a result of the constraints imposed by the shorter P−N compared to Sb−N bonds in the cluster.

Structure and Formation of the $P_4(N^tBu)_6$ Cage. The structure of the cage compound **3** found in the adduct $[LiP(N^tBu)_2]_4\cdot 0.25P_4(N^tBu)_6$ consists of two P_2N_2 rings bridged by two N^tBu groups (see Figure 3). Because of disorder all of the heavy atoms in $P_4(N^tBu)_6$ were refined isotropically and it is not appropriate to discuss the structural parameters. This is only the second example of a P_4N_6 cage with this structure. The only previous example, $P_4(N^iPr)_6$, was obtained in 25% yield from $ClP(\mu\text{-}N^iPr)_2PN(^iPr)(SiMe_3)$ by a condensation reaction.[27] It isomerizes to the thermodynamically more stable isomer with an adamantane-type structure upon prolonged heating at ca. 160 °C. No further studies of this isomer have been reported although the admantane P_4N_6 cage has been investigated extensively.[28,29] Interestingly, the reaction of primary amines with PCl_3 in the absence of solvent yields adamantane-type cages $P_4(NR)_6$ when R = Me, Et, ^{i}Pr, but not in the case of R = ^{t}Bu.[30] Consequently, we have prepared **3** by a procedure analogous to that reported by Veith et al. for the corresponding isomer of $As_4(N^tBu)_6$.[31] The reaction of $^tBuN(Li)P(\mu\text{-}N^tBu)_2PN(Li)^tBu$ with $ClP(\mu\text{-}N^tBu)_2PCl$ in toluene produces **3** in 71% yield (Scheme 2). The product **3** exhibited two resonances for N^tBu groups at δ 1.53 and 1.57 with relative intensities in the ratio 2:1 consistent with the formation of the isomer shown in Figure 3. The EI mass spectrum showed a strong parent ion at $m/z = 550$ and the $^{31}P\{^1H\}$ NMR spectrum consisted of a singlet at δ 117.2 ppm (cf. 117.1 ppm in the adduct of **2**$\cdot$0.25**3**).[32] Unlike the ^{i}Pr derivative,[27] the tetracyclic cluster **3** showed no signs of isomerization to the adamantane isomer (^{31}P NMR) after 24 days at 150 °C. In contrast to other derivatives of the type $P_4(NR)_6$ (R = Me, Et, ^{i}Pr),[27,30] for which the most stable isomer has an adamantane structure, the bulky ^{t}Bu groups in **3** appear to favor the isomer with four-membered P_2N_2 rings. In the context of homoleptic polyimido anions of p-block elements, the nonadamantane structure of **3** can be viewed as a dimeric P(III) derivative of the tripodal trianion $P(N^tBu)_3{}^{3-}$, isoelectronic with $PO_3{}^{3-}$.

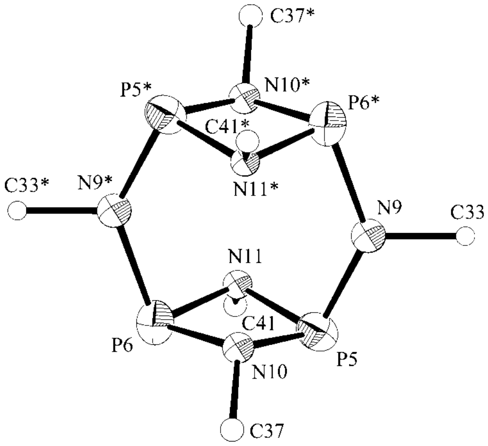


Figure 3. Molecular structure of $P_4(N^tBu)_6$. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown. Displacement ellipsoids are plotted at 30% probability level.

The formation of the cage **3** from the addition of ^{n}BuLi to a solution of **1** is an interesting observation. Significantly, it is accompanied by the production of $LiN(H)^tBu$ (^{1}H and ^{7}Li NMR). Thus two possible routes leading to the cage molecule **3** should be considered (eqs 1 and 2).

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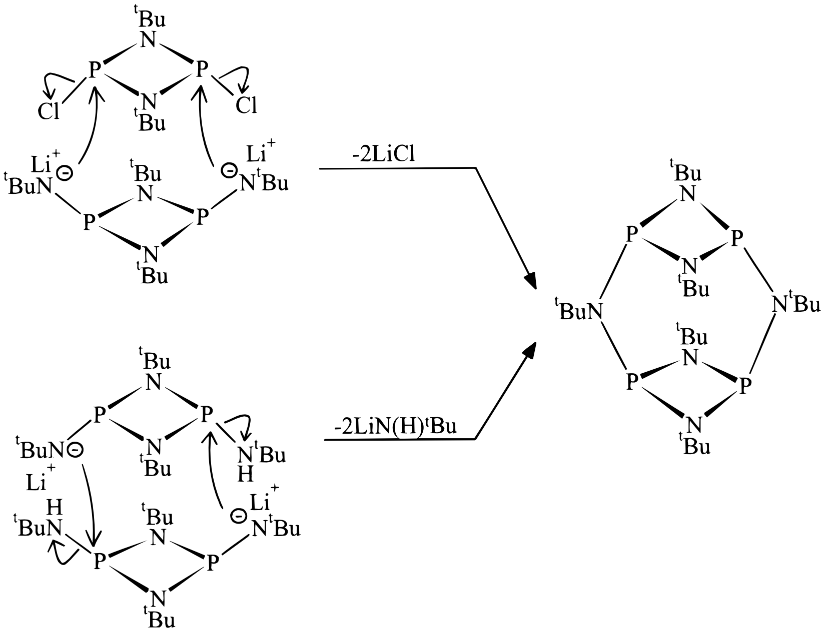
(32) An X-ray structural determination of **3** was carried out, but satisfactory refinement could not be achieved owing to severe disorder problems. Crystals of **3** obtained from THF are monoclinic, space group *C*2/*m* (No. 12), $a = 28.632$ (5) Å, $b = 16.889$ (3) Å, $c = 9.816$ (5) Å, $\beta = 95.00$ (3)°, $V = 4728$ (3) Å^3.

Scheme 2



$$\{Li[P(N^tBu)_2]\}_2 + \mathbf{1} \rightarrow P_4(N^tBu)_6 + 2LiN(H)^tBu \tag{1}$$

$$2^tBuN(Li)P(\mu\text{-}N^tBu)_2PN(H)^tBu \rightarrow P_4(N^tBu)_6 + 2LiN(H)^tBu \tag{2}$$

The following observations indicate that the prevailing pathway is eq 2. The tetramer **2** dissociates into two dimeric units in solution above room temperature (vide infra). However, no reaction occurred when **2** was heated with 2 equiv of **1** in toluene at 50 °C for 2 h (eq 1). Furthermore, the generation of the dilithiated derivative of **1** by the addition of **1** to 2 equiv of ^{n}BuLi in toluene (i.e. *reverse addition*) produces only **2**. Hence, the condensation reaction involving two molecules of the monolithiated derivative of **1** is the most likely source of **3** (Scheme 2). However, an attempt to generate **3** in high yields by the slow addition of *one equivalent* of ^{n}BuLi to **1** at −78 °C produced a mixture of **2**, **3** and unreacted **1**. Apparently, the dilithiation of **1** competes with the condensation reaction and it is not possible to adapt this method to an exclusive synthesis of **3**. Finally, we note that the addition of ^{n}BuLi to **1** *in THF* produces only $\{Li[P(N^tBu)_2]_2 \cdot 2THF\}$.[16] Apparently the solvation of Li ions inhibits the condensation reaction and, consequently, the formation of **3**.

Solution Behavior of $\{Li[P(N^tBu)_2]\}_4$ (2). The dissociation of the sixteen atom cluster $\{Li[Sb(NCy)_2]\}_4$ into two cubic units $\{Li[Sb(NCy)_2]\}_2$ has been inferred on the basis of cryoscopic measurements in benzene at different concentrations and supported by ^{7}Li NMR studies.[4] In the case of **2** the ^{31}P nuclei provide a more incisive NMR probe of solution behavior than the quadrupolar ^{7}Li nuclei. Variable temperature $^{31}P\{^1H\}$ NMR spectra of solutions of **2** in C_7D_8 at two concentrations are illustrated in Figure 4. The tetrameric cluster exhibits a singlet at δ ca. 125 ppm at 273 K, consistent with the S_4 symmetry of the solid-state structure. Upon warming the solution this resonance broadens and collapses at 323 K and then resolves into two distinct singlets at δ ca. 124 ppm (tetramer) and ca.128 ppm (dimer) consistent with the dissociation of the tetrameric cluster into two cubic units (Scheme 1). Since the resonance at δ ca. 128 ppm predominates at the lower concentration [Figure 4b], it is assigned to the dimer $[LiP(N^tBu)_2]_2$.

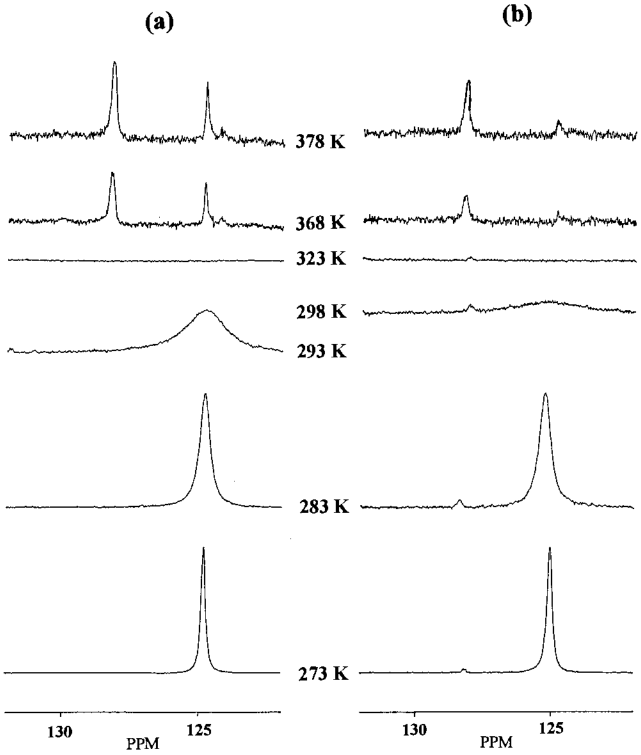
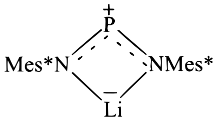


Figure 4. Variable temperature $^{31}P\{^1H\}$ NMR spectra of $[LiP(N^tBu)_2]_4$ in C_7D_8 (a) 1.15×10^{-1} M; (b) 2.7×10^{-2} M.

The ^{1}H NMR spectrum of the tetramer **2** in C_7D_8 at 23 °C exhibits partially resolved shoulders ca. 0.01 ppm to high field of the two main resonances at δ 1.49 and 1.45. These additional resonances are tentatively assigned to the cubic dimer formed by dissociation of **2** (Scheme 1). The ^{7}Li NMR spectrum of **2** in C_6D_6 at 23 °C consists of a broad resonance ($\nu_{1/2} = 78$ Hz) centered at δ −0.68, cf. δ −0.48 ($\nu_{1/2} = 17$ Hz) for $[LiP(N^tBu)_2]_2 \cdot 2THF$. Apparently the ^{7}Li NMR resonance for the unsolvated dimer $[LiP(N^tBu)_2]_2$ is hidden under the resonance for **2**.

Structure of Li[Mes*NPNMes*]·$C_6H_5CH_3$ (4·C_7H_8). The influence exerted by the steric characteristics of the groups attached to the N atoms in $\{Li[RNPNR']\}_n$ is illustrated by the structure of the unsymmetrical derivative (R = ${}^tBu$, R′ = Mes*), in which the dimeric $Li_2P_2N_4$ units form eight-membered rings with two-coordinate lithium ions.[15] Apparently the bulky *ortho*-^{t}Bu groups of the Mes* substituent inhibit the formation of a cubic structure. Thus it was of interest to determine the structure of the symmetrical derivative (R = R′ = Mes*). The structure of **4**·C_7H_8 is highly disordered,[33] but the data do confirm the previously assumed monomeric arrangement.[14a] Apparently, the four *ortho*-^{t}Bu substituents prevent aggregation of PN_2Li units.

Crystalline samples of this complex are dark yellow rather than green as first reported.[14a] The observed ${}^{31}P\{{}^1H\}$ NMR chemical shift of ca. 340 ppm is close to the values found for the solvated monomer $[Li(OEt_2)][Mes^*NPNCPh_3]$ (361.0 ppm) and the eight-membered rings $\{Li[RNPNMes^*]\}_2$ (R = 1-Ad, ^{t}Bu) (356.7 ppm).[15] However, the ^{7}Li chemical shift for **4** (−3.6 ppm) indicates that the lithium atom is significantly shielded compared to those in either the solvated monomer [$\delta({}^7Li) = -0.5$ ppm][15] or the eight-membered rings [R = 1-Ad, $\delta({}^7Li) = -0.7$ ppm, R = ^{t}Bu, $\delta({}^7Li) = -0.9$ ppm],[15] which also contain two-coordinate lithium atoms. This shielding effect provides some support for the charge distribution implied by Lappert et al. in their structural representation of **4** (vide infra).[14a]



4

Conclusions

The *unsolvated* complexes $[Li(RNPNR')]_n$ may be monomeric, dimeric or tetrameric depending on the steric requirements of the R and R′ groups. The formation of the tetrameric cluster $[LiP(N^tBu)_2]_4$ involves the aggregation of two $Li_2P_2N_4$ cubes via Li_2N_2 faces. Investigations of the formation of $P_4(N^tBu)_6$ from the reaction of ^{n}BuLi with **1** have revealed that the identity of the product(s) is influenced by the order of addition of reagents as well as by the coordinating ability of the solvent. This finding may be an important consideration for other polyimido anions of the p-block elements.

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Supporting Information Available: Listings of crystal data and data collection and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **2**·0.25**3** (10 pages). Ordering information is given on any masthead page.

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(33) The complex lies on a 2-fold axis and a mirror plane, which requires the P and Li atoms to occupy the same position with a site occupancy factor of 0.60P. The toluene molecule is also disordered with the methyl group located over two sites. *Crystal data*: orthorhombic, space group *Cmca* (No. 64), $a = 13.934(4)$ Å, $b = 11.845(3)$ Å, $c = 23.974(3)$ Å, $V = 3957(1)$ Å^3, and $Z = 4$.