Crystal Structures of $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ and $[ClLi{\cdot}O{=}P(NMe_2)_3]_4$; Discrete Tetrameric Pseudo-cubane Clusters with Bridging of Li_3 Triangles by Nitrogen and by Chlorine Atoms

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X-Ray crystallographic studies of the title compounds $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$, (**1**), and $[ClLi{\cdot}O{=}P(NMe_2)_3]_4$, (**2**), show them to have pseudo-cubane tetrameric structures in which triply-bonding methyleneamino-nitrogen atoms [(**1**)] or chlorine atoms [(**2**)] hold together the tetrahedral Li_4 frameworks.

We report the structure of $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$, (**1**), a pyridine complex of diphenylmethyleneaminolithium (Figure 1), and of $[ClLi{\cdot}O{=}P(NMe_2)_3]_4$, (**2**), a hexamethylphosphoramide (HMPA) complex of lithium chloride (Figure 2). Both have pseudo-cubane arrangements of Li_4X_4 cluster units (X = N, Cl) in which the atoms X bridge Li_3 triangles.

Complex (**1**) was prepared by reaction of the insoluble polymeric imidolithium $(LiN{=}CPh_2)_n$ with pyridine in hot toluene solution; cooling at −10 °C afforded the deep red crystals (m.p. 108—110 °C).† Complex (**2**) was isolated from a reaction of a 1:1 mixture of $LiN{=}CBu^t_2$ and HMPA $[O{=}P(NMe_2)_3]$ in hexane solution with a one-third molar equivalent of $AlCl_3$ in ether, in an attempt to prepare imidoaluminium complexes. Surprisingly, no precipitation of LiCl occurred, and cooling of the yellow solution at 0 °C gave colourless crystals of (**2**) (m.p. 142 °C; found 0.0% Al).† The relative ease of this utterly fortuitous *in situ* preparation in high yield (*ca.* 85%) contrasts with subsequent attempts to prepare (**2**) directly from LiCl and HMPA in various solvent media; such attempts were hindered by the difficulty of obtaining completely anhydrous LiCl substrate, and by the need for extensive refluxing to effect dissolution of even some of the LiCl.

While organolithium clusters are known to contain electron-deficient C–Li bonds in which a C atom bridges three Li atoms [in tetramers, $(LiR)_4$, *e.g.*, R = Et;[1] in complexed

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† Satisfactory elemental analyses were obtained for (**1**) and (**2**). Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

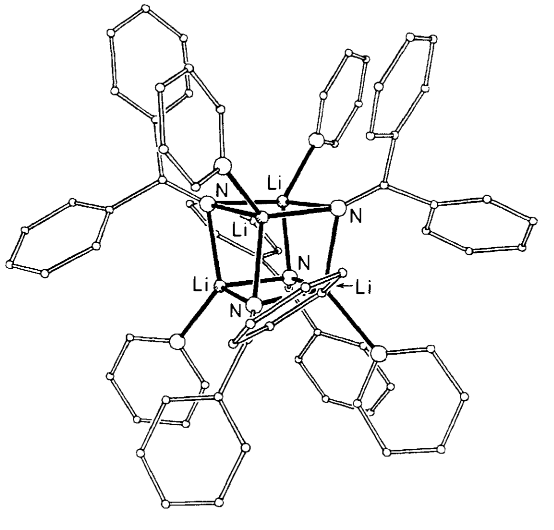

Figure 1. Molecular structure of $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$, (**1**); triclinic, space group $P\bar{1}$, a = 12.764(3), b = 13.134(2), c = 21.750(3) Å, α = 83.47(2), β = 79.82(2), γ = 61.30(2)°, Z = 2, R = 0.056 for 8194 reflections with $F > 3\sigma(F)$. *Key dimensions*: Li–N(imino) 2.019(4)—2.171(4), Li–N(pyridine) 2.075(5)—2.114(6), Li–Li 2.571(8)—2.746(8), N(imino)···N(imino) 3.123(5)—3.315(5), C=N 1.260(3)—1.264(3) Å; Li–N–Li 75.3(2)—83.3(2), N(imino)–Li–N(imino) 94.1(2)—104.7(2), N(imino)–Li–N(pyridine) 100.6(2)—130.9(2)°.

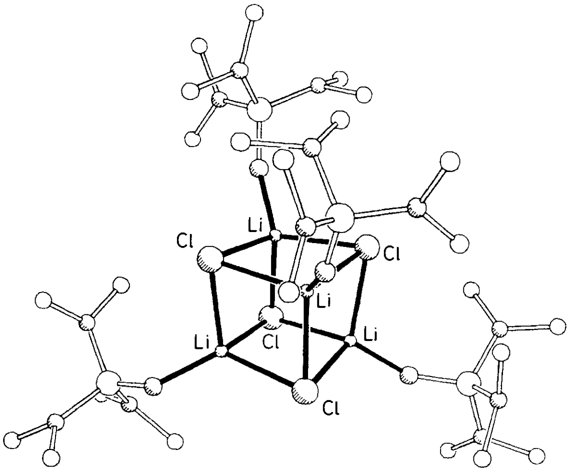

Figure 2. Molecular structure of $[ClLi{\cdot}O{=}P(NMe_2)_3]_4$, (**2**); triclinic, space group $P\bar{1}$, a = 12.574(2), b = 13.898(2), c = 15.696(2) Å, α = 93.04(1), β = 102.17(1), γ = 109.14(1)°, Z = 2, R = 0.076 for 6533 reflections with $F > 4\sigma(F)$. *Key dimensions*: Li–Cl 2.357(10)—2.441(12), Li–O 1.858(11)—1.877(13), Li–Li 3.064(15)—3.121(15), Cl···Cl 3.660(6)—3.688(6), O=P 1.460(5)—1.469(4) Å; Li–Cl–Li 78.5(4)—81.2(4), Cl–Li–Cl 98.4(4)—100.7(5), Cl–Li–O 112.8(5)—127.9(6)°.

tetramers, $(LiR)_4(L)_2$, *e.g.*, R = Me, L = tetramethylethylenediamine (tmeda)[2] and R = PhC≡C, L = tetramethylhexamethylenediamine (tmhda);[3] and in hexamers $(LiR)_6$, *e.g.*, R = cyclohexyl[4]], oligomeric organonitrogen–lithium compounds, increasingly used as alternatives to CLi species in organic syntheses requiring selective proton abstraction, had appeared to be electron-precise Li_xN_x ring species, with N atoms bridging Li_2 units in the tetramer $[LiNCMe_2(CH_2)_3CMe_2]_4$,[5] in trimers $(LiNR_2)_3$, *e.g.*, R = Me_3Si;[6] $PhCH_2$,[7] and in dimers $[(LiNR_2)(L)]_2$ *e.g.*, L = OEt_2, R = Me_3Si;[5] $PhCH_2$.[7] However, the recent structural characterisation of several imidolithium *hexamers* $(LiN{=}CRR')_6$, (R = R′ = Me_2N, Bu^t;[8] R = Ph, R′ = Me_2N, Bu^t[7]) demonstrated that imino N atoms can also bridge Li_3 triangles. Complex (**1**) represents a further link between NLi and CLi structural chemistry, being the first example of an $(LiN)_4$ *tetramer* with such electron-deficient bonding.

The structure of (**2**) is entirely novel for a lithium halide complex. Such complexes, of high solubility in organic solvents, have been almost exclusively studied in solution,[9] and (**2**) is the first known example of a solid state structure in which Cl → Li_3 bridge bonding occurs in a lithium cluster. Thus (**1**) and (**2**), together with the $(CLi)_4$ species noted above[1—4] and known $(OLi)_4$ enolates, *e.g.*, the tetrahydrofuran (thf) complex $[Li(thf){\cdot}O(Bu^t)C{=}CH_2]_4$,[10] demonstrate that tetrameric pseudo-cubane structures are possible, indeed likely, for complexes of lithium with Group 4—7 ligand atoms.

The relative sizes of these and related Li_4X_4 clusters, made up of two interpenetrating Li_4 and X_4 tetrahedra, can largely be rationalised in terms of the increasing size of the bridging atom X (some bond distances and angles are given in the captions to Figures 1 and 2). Thus, mean Li···X bond lengths increase from X = O {*e.g.*, 1.97 Å in $[Li(thf){\cdot}O(Bu^t)C{=}CH_2]_4$[10]}, to X = N [2.090 Å in (**1**)], to X = C [*e.g.*, 2.262 Å in $(LiMe)_4{\cdot}(tmeda)_2$[2]], to X = Cl [2.410 Å in (**2**)], to X = Si [2.68 Å in the hexameric cluster $(LiSiMe_3)_6$[11]]. The Li_4 tetrahedron of (**1**) [mean Li···Li, 2.663 Å] is of similar size to those found in $(CLi)_4$ tetramers [*e.g.*, 2.568 Å in $(LiMe)_4{\cdot}(tmeda)_2$;[2] 2.72 Å in $(LiC{\equiv}CPh)_4{\cdot}(tmhda)_2$[3]], but a large expansion (*ca.* 0.4 Å) is required when Cl is the bridging atom [thus in (**2**), mean Li···Li 3.096 Å]. Such expansion of the Li_4 core, yet with Li_4X_4 structure retention, might imply that Li···Li interactions are not essential for aggregate formation. Indeed, the skeletal cubane bonding in (**2**) could be explained in terms of twelve 2-centre electron-pair Li–Cl bonds (and no Li–Li bonds) if each Cl atom were to act as a 5 electron ligand. Distances alone are a poor guide here, as evidenced by unquestionably 'bonded' values in molecular Li_2 (2.67 Å) and in metallic Li (3.04 Å); from the latter, (**2**) could even be regarded as a small piece of lithium metal with added ligands.

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