Azomethine Derivatives. Part 20.[1] Crystal and Molecular Structures of the Lithioketimine $[\{Li(N{=}CBu^t_2)\}_6]$ and Lithioguanidine $[\{Li[N{=}C(NMe_2)_2]\}_6]$; † Electron-deficient Bridging of Li_3 Triangles by Methyleneamino-nitrogen Atoms

William Clegg
Institut für Anorganische Chemie der Universität Göttingen, Tammanstrasse 4, D-3400 Göttingen, West Germany
Ronald Snaith *
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL
(The late) Harrison M. M. Shearer, Kenneth Wade,* and Graham Whitehead
Chemistry Department, Durham University, South Road, Durham DH1 3LE

The lithioketimine $Li(N{=}CBu^t_2)$ (1) and lithioguanidine $Li[N{=}C(NMe_2)_2]$ (2) have remarkably similar hexameric structures $[\{Li(N{=}CR_2)\}_6]$ (R = Bu^t or NMe$_2$) in the crystal phase, based on slightly folded chair-shaped Li_6 rings held together by triply-bridging methyleneamino-groups, $N{=}CR_2$, thus providing examples of electron-deficient bridging by the nitrogen atoms of organonitrogen ligands. The mean distance between adjacent metal atoms in the Li_6 rings is 2.35(2) Å in (1), and 2.445(2) Å in (2), and the mean dihedral angles between Li_6 chair seats and backs are 85 and 78° respectively. The nitrogen atoms of the bridging methyleneamino-groups are approximately equidistant from the three bridged metal atoms, the mean Li–N distance being 2.06(1) Å in (1) and 2.00(1) Å in (2). The N=C distances of 1.30(1) and 1.244(3) Å respectively lie within the range expected for carbon–nitrogen double bonds. Features of these structures are compared with those of related compounds, and some bonding implications are discussed.

Electron-deficient bridging of pairs or triangles of metal atoms by carbon-attached organic groups such as alkyls or aryls is an established feature of the organometallic chemistry of such metals as lithium, beryllium, magnesium, and aluminium.[2-6] Bridging of these same metals by N-attached organic groups, for example amino-groups, NR_2,[7-9] or methyleneamino-groups, $N{=}CR_2$,[1,10-14] is normally electron-precise in that the number of bonding contacts is equal to the number of electron pairs available for bonding. However, electron-deficient bridging of two lithium atoms and one nickel atom by diphenylmethyleneamino-ligands has recently[15] been found in crystals of composition $Ni_2[Li(N{=}CPh_2)]_3(HN{=}CPh_2)_2{\cdot}(OEt_2)_2$ (for details of bonding and bridging see ref. 15).

Multicentre Li_3N bonding involving a dinitrogen ligand has been detected previously[16] in another mixed-metal system, $[\{Ni_2(N_2)(OEt_2)_2(LiPh)_6\}_2]$. Here, we describe what are believed to be the first examples of electron-deficient bridging of Li_3 triangles by nitrogen-attached organic ligands which have been revealed by *X*-ray crystallographic studies of the compounds $Li(N{=}CBu^t_2)$ (1) and $Li[N{=}C(NMe_2)_2]$ (2). A preliminary account of the structure of (1) has already been published.[17] Our subsequent study of (2) has shown it to have a remarkably similar structure in which the dimethylamino-nitrogen atoms surprisingly do not co-ordinate to the metal atoms.

Results and Discussion

Preparation and Characterization of the Lithio-derivatives.—Both lithio-derivatives have found frequent use in our laboratories as reagents for the synthesis of methyleneamino-derivatives of various metals and metalloids, for which purpose they have normally been prepared *in situ* and used without being isolated (see for example, refs. 1, 10—12 and work cited therein). In the present work, di-t-butylmethyleneamidolithium, $Li(N{=}CBu^t_2)$, was prepared from equimolar proportions of t-butyl-lithium and t-butyl cyanide in a hydrocarbon solvent [pentane, hexane, light petroleum (b.p. 40—60 °C), toluene or mixtures of these]. For example, a convenient synthesis on a 20 mmol (3 g) scale employs addition, by syringe, of a solution of LiBu^t (20 mmol) in hexane (10 cm^3) to a frozen (−196 °C) solution of Bu^{t}CN (20 mmol) in hexane (20 cm^3). Subsequent warming to room temperature affords a pale yellow-green solution of $Li(N{=}CBu^t_2)$. If the reaction is carried out in an i.r. cell, it can be followed by the disappearance of the nitrile stretching frequency, $\nu(C{\equiv}N)$, at 2 220 cm^{-1} and the development of the azomethine stretching frequency, $\nu(C{=}N)$, at 1 593 cm^{-1}, a change that occurs as the temperature of the mixture of reagents rises from *ca.* −40 to −20 °C. Evaporation of the solvent affords the lithioketimine as a white microcrystalline powder that can be recrystallised from pentane, hexane, or other hydrocarbon solvents as very pale yellow transparent needles or plates that decompose immediately on exposure to the atmosphere due to hydrolysis to lithium hydroxide and di-t-butylketimine $Bu^t_2C{=}NH$, readily identified by their O–H and N–H stretching absorptions which rapidly develop in the region >3 300 cm^{-1} in the i.r. spectra of moist samples.

The lithioguanidine $Li[N{=}C(NMe_2)_2]$, (2), was prepared on a 20 mmol scale by reaction of the commercially available tetramethylguanidine $HN{=}C(NMe_2)_2$ and n-butyl-lithium in pentane or hexane. It too is very moisture sensitive, forming LiOH and $HN{=}C(NMe_2)_2$ immediately on exposure to moist air.

Description of the Molecular Structures.—Both (1) (Figure 1) and (2) (Figure 2) have structures based on slightly folded

---

† *Supplementary data available* (No. SUP 23573, 26 pp.): structure factors, anisotropic thermal parameters for (1) and (2); H-atom co-ordinates, isotropic thermal parameters for (2). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

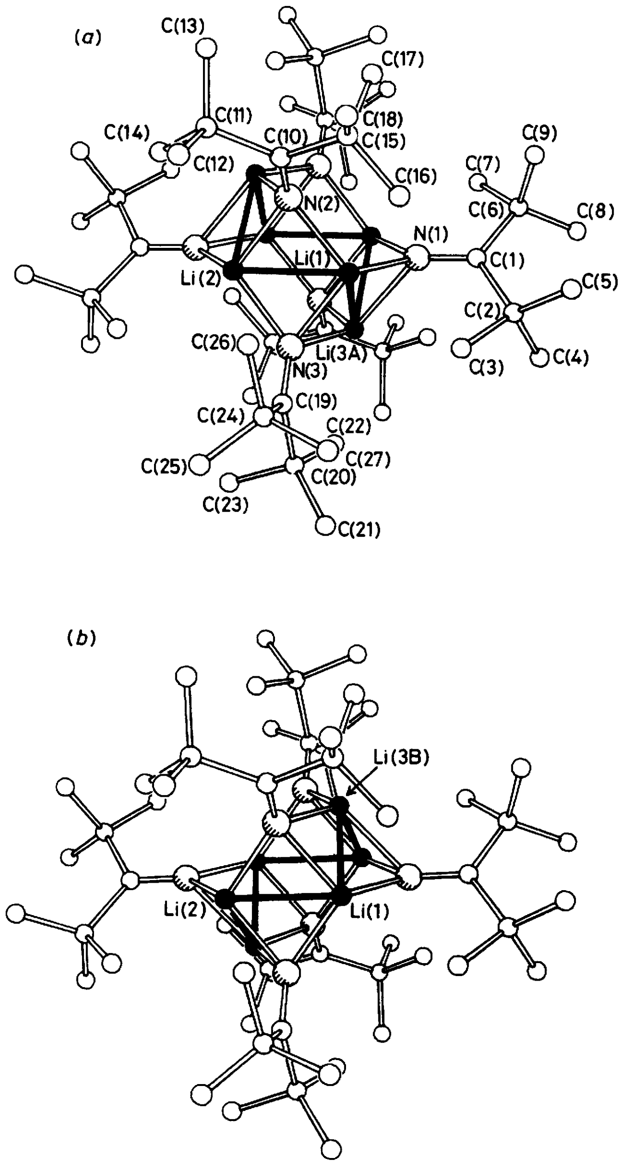


Figure 1. Molecular structure of (1), [{Li(N=CBu$^t_2$)}$_6$], showing the alternative Li$_6$ ring orientations, (*a*) A and (*b*) B

chair-shaped Li$_6$ rings (Figure 3) held together by triply bridging N=CR$_2$ (R = Bu^t or NMe$_2$) ligands. The mean dihedral angle between the Li$_6$ chair seat and back is 85° for (1) and 78° for (2). The N=CR$_2$ ligands bridge the six smaller of the eight triangular faces of the Li$_6$ core, which can be regarded as derived from a regular Li$_6$ octahedron by expansion of two opposed, unbridged faces. The view through these faces is illustrated in the case of (2) in Figure 4. The ligand N=CR$_2$ planes are perpendicular to the bridged Li$_3$ faces, each of which (Figure 5) has one long edge [range 3.13(5)—3.31(4) Å, mean 3.21(1) Å for (1) and 3.126(5)—3.192(6) Å, mean 3.166(2) Å for (2)] and two short edges [range 2.23(5)—2.44(3) Å, mean 2.35(1) Å for (1) and 2.440(5)—2.449(7) Å, mean 2.445(2) Å for (2)], one roughly parallel to the ligand NCR$_2$ plane, the other perpendicular to, and roughly bisected by, that plane. The bridging nitrogen atoms are approximately equidistant from the three bridged metal atoms (Figure 5), the mean Li–N distance being 2.06(1) Å in (1) and 2.00(1) Å in (2).

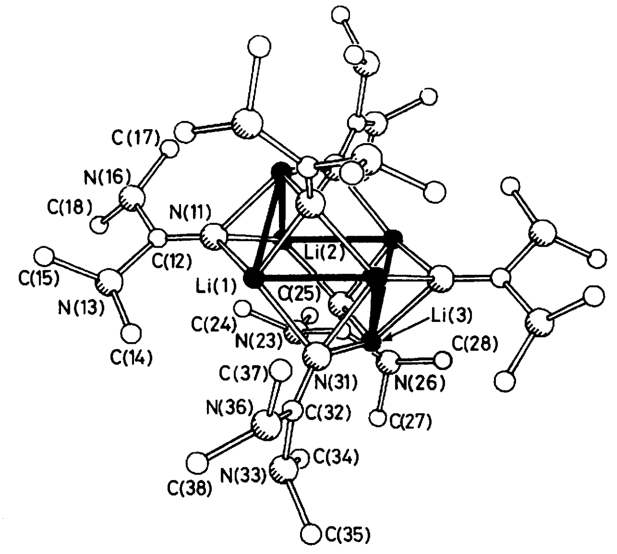


Figure 2. Molecular structure of (2), [{Li[N=C(NMe$_2$)$_2$]}$_6$]

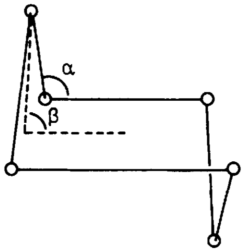


Figure 3. The slightly folded chair-shaped Li$_6$ rings of (1) (α = 86.1, β = 84.9°) and (2) (α = 80.7, β = 77.8°); α is the average ring bond angle in the Li$_6$ chair-shaped ring and β is the average dihedral angle between ' seat ' and ' back ' in the Li$_6$ chair-shaped ring

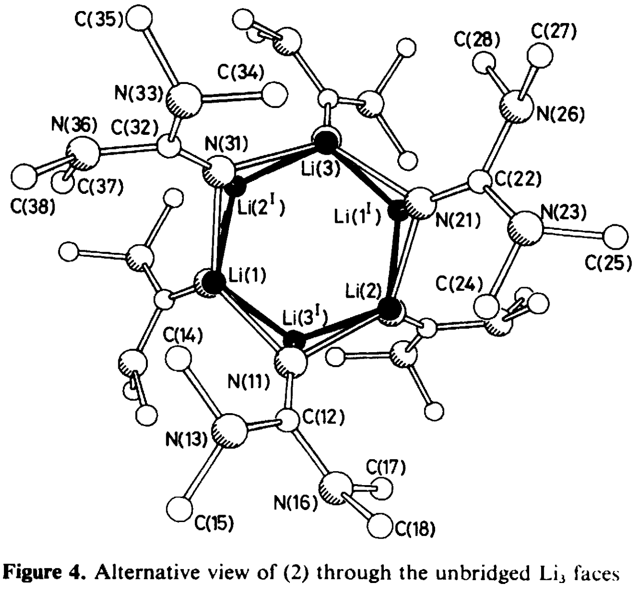


Figure 4. Alternative view of (2) through the unbridged Li$_3$ faces

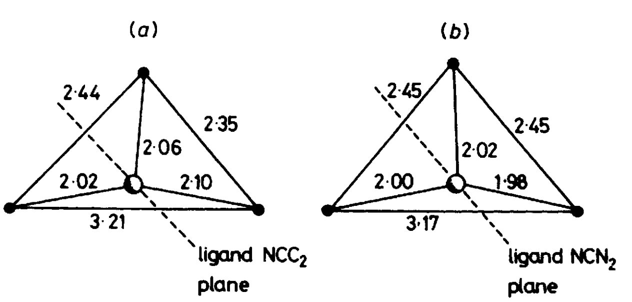
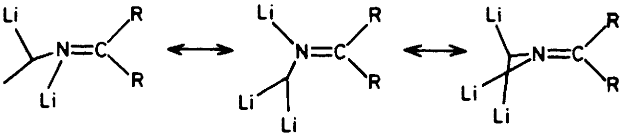
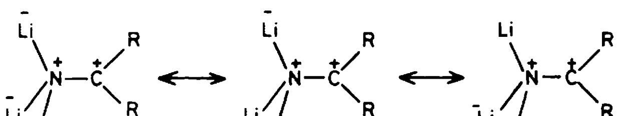


Figure 5. Ligand N=CR$_2$ orientations with respect to the bridged Li$_3$ triangles in (*a*) [{Li(N=CBu$^t_2$)}$_6$] (1) and (*b*) [{Li[N=C(NMe$_2$)$_2$]}$_6$] (2); bond distances are in Å

The bond orders of these lithium–nitrogen bonds may be inferred from other structural and spectroscopic features as follows. Two extreme types of behaviour can be envisaged for the methyleneamino-ligands, N=CR$_2$. On the one hand, each such ligand might function as a source of three electrons for metal–ligand bonding by using the three formally non-bonding electrons associated with the nitrogen atom in the neutral ligand. Together with the one electron each metal atom can supply, this would give a total of 24 electrons to distribute among the 18 Li–N bonding contacts in each hexameric molecule. Locally, each ligand nitrogen atom would have altogether two electron pairs to bond to the three neighbouring lithium atoms, allowing a valence-bond description that involves one two-centre bond and one three-centre bond resonating between the three possible positions (see below). The mean Li–N bond order would thus be 0.66′.



On the other hand, the electron deficiency in the metal–ligand bonding might in principle be relieved by transfer of electronic charge from the ligand azomethine link, N=C. Reduction of the carbon–nitrogen bond order from two to one would allow each methyleneamino-ligand to function as a source of five electrons, providing then enough electrons to make each Li–N link a single bond. This could be represented in valence-bond terms as shown below.



We believe that the former mode of bonding, with Li–N bonds of order 0.66′ and N=C double bonds in the ligands, provides the better rationale for the observed structures. For example, the mean N=C bond lengths in the ligands [1.30(1) Å in (1) and 1.244(3) Å in (2)] although apparently differing slightly, nevertheless fall within the range expected for carbon–nitrogen double bonds, which typically have lengths 1.27(1) Å. Neither shows the degree of lengthening that would be expected if there were considerable reduction in bond order. Moreover, their i.r. stretching frequencies at 1 593 and 1 625 cm^{-1} respectively also show that these bonds are essentially double bonds, as they lie in the range (1 590—1 650 cm^{-1}) usually found for azomethine linkages *e.g.*, for the parent imines themselves, HN=CBu$^t_2$ and HN=C(NMe$_2$)$_2$, at 1 603 and 1 590 cm^{-1} respectively. Both these features are inconsistent with a bonding model that treats the ligands as five-electron ligands. A further factor making it unlikely that each ligand supplies five electrons is the extent to which that would require electronic charge to be transferred from ligand to metal, leaving the ligand highly positively charged, a feature illustrated by the canonical forms above. Such a charge distribution would be exceedingly unlikely for the ketimino-ligand N=CBu$^t_2$, and only slightly less unlikely for the guanidino-ligand N=C(NMe$_2$)$_2$, in which the dimethylamino-groups could in principle stabilise the carbocationic centre generated. The N–C distances involving the *pyramidally* co-ordinated amino-nitrogen atoms of (2), however, give no indication of such charge stabilisation, which would be optimised by the adoption of a *planar* geometry about these same nitrogen atoms anyway.

Table 1. Comparison of various six-membered ring systems

Species	Ring bond angle α [a]/°	Dihedral angle β [a]/°	Ratio y/x [b]
Octahedron	60	54.7	1.0
[{Li(SiMe$_3$)}$_6$] [33,34]	74.6	70.5	1.21 [c]
[{Li(C$_6$H$_{11}$)}$_6$] [31]	76.8	72.9	1.24 [d]
[{Li[N=C(NMe$_2$)$_2$]}$_6$]	80.7	77.8	1.29 [e]
[{Li(N=CBu$^t_2$)}$_6$]	86.1	84.9	1.37 [f]
' Upright chair '	90	90	1.41
Cyclohexane	111.6	130.7	1.64
Benzene	120	180	1.73

[a] See Figure 3. [b] x = Shortest edge length (Å); y = longest edge length (Å). [c] x = 2.70(3), y = 3.27(4) Å. [d] x = 2.39(1), y = 2.97(1) Å. [e] x = 2.445(4), y = 3.16(1) Å. [f] x = 2.35(1), y = 3.21(1) Å.

In our preliminary report of the structure of (1) we suggested that the length of the Li · · · N bonds [2.06(1) Å] provided a further clear indication of their low bond order. Single Li–N bonds are expected to be *ca.* 1.96 Å, although the unprecedented state of co-ordination of the nitrogen atoms in (1) makes it difficult to estimate the Li · · · N bond orders from their lengths. In the mixed-metal ketimino-derivative Ni$_2$-[Li(N=CPh$_2$)]$_3$(HN=CPh$_2$)$_2$·(OEt$_2$)$_2$,[15] which contains both single and fractional order Li · · · N bonds, the former are 1.96 Å, while the latter lie in the range 2.00—2.17 Å. In the related dinitrogen complex [{Ni$_2$(N$_2$)(OEt$_2$)$_2$(LiPh)$_6$}$_2$], the Li–N single bonds are 1.95 Å, while the fractional order Li · · · N bonds lie in the range 1.99—2.16 Å. The formally single Li–N bonds in the compounds [{Li[N(SiMe$_3$)$_2$]}$_3$],[13,18] [{Li[N(SiMe$_3$)$_2$](OEt$_2$)}$_2$],[13] and [{Li[NCMe$_2$(CH$_2$)$_3$CMe$_2$]}$_4$],[13] however, have lengths 2.00(2), 2.06(1), and 2.00(2) Å respectively. Rather longer formally single Li–N bonds are to be found in tetramethylethylenediamine (tmed) complexes of organolithium compounds, for example, [{Li(tmed)}$_2$(np)] (np = dianion of 1,4-dihydronaphthalene), 2.09—2.13 Å; [19] [Li(tmed)(in)] (in = indenyl) 2.11 Å;[20] [{Li(tmed)}$_2$(an)] (an = dianion of 9,10-dihydroanthracene), 2.07—2.12 Å;[21] [{Li(tmed)}$_2$(bife)] (bife = 9,9′-bifluorenyl), 2.08 Å;[22] and [{Li(tmed)}$_2$(st)] (st = stilbene), 2.10 Å.[23]

The lengths of the Li–N bonds found for compound (2), [{Li[N=C(NMe$_2$)$_2$]}$_6$], in the present work [mean 2.00(1) Å] thus do not provide a clear indication of their bond order,

Table 2. Atomic co-ordinates ($\times$ 10^4)[a] for [{Li(N=CBu$^t_2$)}$_6$]

Atom	*x*	*y*	*z*
Li(1)	1 750(22)	−3(13)	500(22)
Li(2)	253(19)	−675(11)	−998(17)
Li(3A)	483(32)	877(16)	−375(31)
Li(3B)	788(43)	−237(19)	1 555(39)
N(1)	1 488(10)	700(6)	1 463(9)
N(2)	1 333(9)	−929(5)	700(8)
N(3)	970(10)	154(5)	−1 211(9)
C(1)	2 323(12)	1 030(6)	2 264(11)
C(2)	3 434(7)	1 329(5)	2 094(8)
C(3)	3 446(7)	987(5)	1 056(8)
C(4)	3 171(7)	2 049(5)	1 823(8)
C(5)	4 673(7)	1 250(5)	3 138(8)
C(6)	2 279(9)	1 167(5)	3 458(7)
C(7)	963(9)	1 059(5)	3 232(7)
C(8)	2 681(9)	1 847(5)	3 948(7)
C(9)	3 093(9)	665(5)	4 330(7)
C(10)	1 991(11)	−1 432(7)	1 176(11)
C(11)	1 555(11)	−2 134(4)	676(10)
C(12)	2 398(11)	−2 405(4)	207(10)
C(13)	1 544(11)	−2 593(4)	1 593(10)
C(14)	270(11)	−2 074(4)	−307(10)
C(15)	3 250(10)	−1 340(6)	2 277(10)
C(16)[b]	3 673(10)	−656(6)	2 185(10)
C(17)[b]	2 887(10)	−1 376(6)	3 255(10)
C(18)[b]	4 335(10)	−1 785(6)	2 543(10)
C(160)[b]	3 631(10)	−1 889(6)	3 162(10)
C(170)[b]	3 602(10)	−830(6)	3 226(10)
C(180)[b]	4 246(10)	−1 195(6)	1 918(10)
C(19)	1 444(10)	271(6)	−1 896(10)
C(20)	1 071(10)	922(4)	−2 657(8)
C(21)	2 107(10)	1 234(4)	−2 821(8)
C(22)	567(10)	1 412(4)	−2 100(8)
C(23)	63(10)	720(4)	−3 830(8)
C(24)	2 446(7)	−184(4)	−1 969(8)
C(25)	2 120(7)	−387(4)	−3 204(8)
C(26)	2 553(7)	−787(4)	−1 247(8)
C(27)	3 660(7)	175(4)	−1 458(8)

[a] In all the Tables, estimated standard deviations in the last place of figures are given in parentheses. [b] Carbon atoms C(16)—C(18) and C(160)—C(180) represent alternative possible orientations of the t-butyl group centred on C(15), and were assigned site occupation factors of 0.5.

being within the ranges known both for single bonds and for bonds of fractional order. Nevertheless for the reasons outlined above, we prefer to regard these bonds as of formal order 0.66′, although possibly strengthened a little relative to those in (1) by the influence of the dimethylamino-substituents as outlined above. Detailed consideration of the relationships between the length and order of these lithium–nitrogen bonds must await the accumulation of more precise data, preferably on systems with less variation in the metal and nitrogen co-ordination states than is shown by the presently known examples.

A further pointer to the fractional bond order of the metal–nitrogen bonds is provided by the metal–metal distances between the bridged metal atoms, which reflect the metal–metal bonding component of the metal–ligand bonding. The distance between metal atoms that are not directly bonded to each other, but are held in close proximity by electron-precise bridge bonding, is characteristically greater than that between metal atoms held together by electron-deficient bridges, since the latter systems necessarily contain some metal–metal bonding.[3,5,24] The short Li–Li distance in (1) and (2) (the edge lengths of the puckered Li_6 rings) average 2.35(1) and 2.445(2) Å respectively. These may be compared with the Li · · · Li distance of 2.87, 2.50 and 3.12 Å in the compounds [{Li[N(SiMe$_3$)$_2$]}$_3$],[13,18] [{Li[N(SiMe$_3$)$_2$](OEt$_2$)}$_2$],[13] and [{Li[NCMe$_2$(CH$_2$)$_3$CMe$_2$]}$_4$][13] respectively, all of which contain electron-precise Li–N–Li bridging.

When compared with systems containing electron-deficient bridging between lithium atoms by the carbon atoms of alkyl or aryl groups, the Li · · · Li distances in (1) and (2) are still seen to be remarkably short. For example, in unsolvated methyl-lithium, [{LiMe}$_4$], in which equilateral Li_3 triangles are bridged by methyl carbon atoms, the Li · · · Li distance is *ca.* 2.68 Å;[25] similar structural units in the tmed adduct [(LiMe)$_4$(tmed)$_2$] have Li · · · Li links of 2.56 Å.[26] The metal–metal distances in some other organolithium systems containing electron-deficient Li · · · C · · · Li bonding are as follows: [{LiPh(tmed)}$_2$], 2.49 Å;[27] [{Li(tmed)L}$_2$] (L = bicyclo[1.1.0]butane-1,1-diyl), 2.74 Å;[28] [{LiEt}$_4$], 2.42 Å;[29] [{Li$_2$[Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe$_2$]Fe(C$_5$H$_4$)$_2$}$_2$], 2.37 Å;[30] and [{Li(C$_6$H$_{11}$)}$_6$], 2.40 Å.[31] In metallic lithium, the atoms are 3.04 Å apart.[32] In [{Li(SiMe$_3$)}$_6$], in which there is electron-deficient bridging of lithium atoms by trimethylsilyl groups, the Li · · · Li distance is 2.72 Å.[33,34]

Table 3. Interatomic distances (Å) in [{Li(N=CBu$^t_2$)}$_6$]

Configuration A		Configuration B	
Li(1)–Li(2)	2.444(30)	Li(1)–Li(2)	2.440(30)
Li(1)–Li(3A)	2.349(41)	Li(1)–Li(3B)	2.250(71)
Li(1)–Li(2$^{\mathrm{I}}$)	3.173(30)	Li(1)–Li(2$^{\mathrm{I}}$)	3.173(30)
Li(1)–Li(3A$^{\mathrm{I}}$)	3.258(40)	Li(1)–Li(3B$^{\mathrm{I}}$)	3.129(48)
Li(2)–Li(3A)	3.309(37)	Li(2)–Li(3B)	3.232(46)
Li(2)–Li(3A$^{\mathrm{I}}$)	2.392(38)	Li(2)–Li(3B$^{\mathrm{I}}$)	2.225(46)
	Li(3A)–Li(3B$^{\mathrm{I}}$)	2.110(53)	
N(1)–Li(1)	2.051(33)	N(1)–Li(1)	2.051(33)
N(1)–Li(2$^{\mathrm{I}}$)	1.965(21)	N(1)–Li(2$^{\mathrm{I}}$)	1.965(21)
N(1)–Li(3A)	2.187(33)	N(1)–Li(3B)	2.160(45)
N(2)–Li(1)	2.042(29)	N(2)–Li(1)	2.042(29)
N(2)–Li(2)	2.083(21)	N(2)–Li(2)	2.083(21)
N(2)–Li(3A$^{\mathrm{I}}$)	2.102(33)	N(2)–Li(3B)	2.114(43)
N(3)–Li(1)	2.025(28)	N(3)–Li(1)	2.028(28)
N(3)–Li(2)	2.018(27)	N(3)–Li(2)	2.018(27)
N(3)–Li(3A)	2.103(43)	N(3)–Li(3B$^{\mathrm{I}}$)	2.029(44)
	N(1)–C(1)	1.292(15)	
	N(2)–C(10)	1.301(16)	
	N(3)–C(19)	1.299(21)	
	C(1)–C(2)	1.618(20)	
	C(1)–C(6)	1.616(20)	
	C(10)–C(11)	1.591(16)	
	C(10)–C(15)	1.591(15)	
	C(19)–C(20)	1.620(20)	
	C(19)–C(24)	1.601(17)	

Superscript I refers to the position $-x$, $-y$, $-z$.

The shape of the Li_6 ring in (1) and (2) (Figure 3) is a further feature that deserves comment. Puckered Li_6 rings were already known in lithium chemistry in the hexameric structures of cyclohexyl-lithium[31] and trimethylsilyl-lithium.[33,34] The Li_6N_6 frameworks in (1) and (2) in fact resemble surprisingly closely the Li_6C_6 and Li_6Si_6 frameworks in these other hexamers, even though (1) and (2) contain twice as many electrons for framework bonding (12 pairs per hexamer)

Table 4. Bond angles (°) in [{Li(N=CBu$^t_2$)}$_6$]

Li(2)–Li(1)–Li(3A)	86.9(15)	Li(1)–N(1)–Li(2^I)	105.5(10)	C(1)–N(1)–Li(3B)	129.1(15)
Li(2)–Li(1)–Li(3B)	87.0(20)	Li(1)–N(2)–Li(3A^I)	103.8(13)	C(10)–N(2)–Li(1)	132.8(11)
Li(1)–Li(2)–Li(3B^I)	84.1(20)	Li(2)–N(2)–Li(3B)	100.7(16)	C(10)–N(2)–Li(2)	132.8(12)
Li(1^I)–Li(2^I)–Li(3A)	84.9(15)	Li(1)–N(3)–Li(3B^I)	100.8(21)	C(10)–N(2)–Li(3A^I)	148.4(12)
Li(1)–Li(3A)–Li(2^I)	84.0(13)	Li(2)–N(3)–Li(3A)	106.8(15)	C(10)–N(2)–Li(3B)	125.2(15)
Li(1^I)–Li(3B^I)–Li(2)	89.8(17)	Li(1)–N(1)–Li(3A)	67.2(12)	C(19)–N(3)–Li(1)	130.9(12)
N(1)–Li(1)–N(2)	118.3(16)	Li(1)–N(1)–Li(3B)	64.5(18)	C(19)–N(3)–Li(2)	128.5(12)
N(1^I)–Li(2)–N(3)	118.3(14)	Li(2^I)–N(1)–Li(3B)	65.2(18)	C(19)–N(3)–Li(3A)	123.5(14)
N(2^I)–Li(3A)–N(3)	117.8(18)	Li(2^I)–N(1)–Li(3A)	70.3(14)	C(19)–N(3)–Li(3B^I)	142.5(16)
N(2)–Li(3B)–N(3^I)	120.7(17)	Li(1)–N(2)–Li(2)	72.7(10)	C(2)–C(1)–N(1)	121.1(14)
N(1)–Li(1)–N(3)	115.8(12)	Li(1)–N(2)–Li(3B)	65.5(16)	C(6)–C(1)–N(1)	120.9(14)
N(2)–Li(1)–N(3)	105.7(14)	Li(2)–N(2)–Li(3A^I)	69.7(13)	C(6)–C(1)–C(2)	118.0(9)
N(1^I)–Li(2)–N(2)	114.5(11)	Li(1)–N(3)–Li(2)	74.3(10)	C(11)–C(10)–N(2)	121.1(9)
N(2)–Li(2)–N(3)	104.6(12)	Li(1)–N(3)–Li(3A)	69.3(18)	C(15)–C(10)–N(2)	119.1(11)
N(1)–Li(3A)–N(3)	107.3(15)	Li(2)–N(3)–Li(3B^I)	66.5(16)	C(15)–C(10)–C(11)	119.8(10)
N(1)–Li(3A)–N(2^I)	105.1(13)	C(1)–N(1)–Li(1)	125.8(13)	C(20)–C(19)–N(3)	119.3(11)
N(1)–Li(3B)–N(2)	110.6(17)	C(1)–N(1)–Li(2^I)	140.6(11)	C(24)–C(19)–N(3)	122.5(10)
N(1)–Li(3B)–N(3^I)	109.3(14)	C(1)–N(1)–Li(3A)	131.0(14)	C(24)–C(19)–C(20)	118.2(11)

than [{Li(C$_6$H$_{11}$)}$_6$] or [{Li(SiMe$_3$)}$_6$] (six pairs per hexamer). In describing the structures of (1) and (2) above, we noted that the folded-chair arrangement of the metal atoms could be regarded as derived from a regular octahedral Li$_6$ core by expansion of two opposed, unbridged faces. This point is underlined by the data collected in Table 1, which lists the ring and dihedral angles (see Figure 3) for the lithium hexamers together with the related angles in the more familiar chair-shaped ring of cyclohexane and in three further related systems, a regular octahedral arrangement of the six metal atoms, a planar arrangement of the six skeletal atoms as in benzene, and an ' upright chair ' arrangement in which chair seat and back are mutually perpendicular. The Li$_6$ chairs in (1) and (2) are seen to be significantly less folded than in [{Li(C$_6$H$_{11}$)}$_6$] and [{Li(SiMe$_3$)}$_6$], though distinctly more so than in benzene. The figures in the final column of Table 1 show that the M$_6$ structure becomes progressively more open as the M$_3$ faces change from equilateral to isosceles triangles of progressively more disparate edge lengths.

In our discussion of these molecules, we have focused attention on the ' folded-chair ' shapes defined by the Li$_6$ arrangements. An alternative way of viewing these molecules that helps one to understand the metal atom disorder in compound (1) is to focus attention on the azomethine nitrogen atom positions. In both (1) and (2), the six azomethine nitrogen atoms in each molecule define an octahedron, distorted only slightly from a regular octahedron by expansion of two opposed faces. In (2) for example, the longer N$_6$ octahedral edges have a mean length of 3.57 Å, while the shorter edges have a mean length of 3.16 Å. Of the eight triangular N$_3$ faces of the N$_6$ octahedra, the six smaller are ' capped ' (from inside, not outside) by lithium atoms, leaving the two larger faces open. Since the difference between the ' capped ' and ' uncapped ' N$_3$ faces is small, the disorder in the lithium atom positions is not surprising.

Experimental

Standard inert-atmosphere techniques and scrupulously dried solvents were used for the preparation, recrystallisation and characterisation of compounds (1) and (2). The sample of (1) used for crystallographic study crystallised from hexane as pale yellow transparent plates (Found: C, 72.7; H, 12.8; Li, 4.6; N, 9.5. C$_9$H$_{18}$LiN requires C, 73.5; H, 12.2; Li, 4.8; N, 9.5%). The sample of (2) used for crystallographic study crystallised from a hexane–toluene (2 : 1) mixture in the form of very pale yellow chunky crystals (Found: C, 49.7; H, 9.3; Li, 5.9; N, 34.5. C$_5$H$_{12}$LiN$_3$ requires C, 49.6; H, 9.9; Li, 5.8; N, 34.7%).

Crystals of each compound suitable for *X*-ray analysis were transferred in a nitrogen-filled glove-box to quartz capillary tubes which were subsequently sealed prior to data collection. All computer programs except for standard Hilger and Watts control software were written by W. C. and Professor G. M. Sheldrick. Calculations were performed on the NUMAC IBM 370/168 computer and in Göttingen on a Data General Eclipse S/250, which also controlled the Stoe-Siemens diffractometer.

X-Ray Crystal Structure of Compound (1), Li(N=CBu$^t_2$).—*Crystal data.* C$_9$H$_{18}$LiN, $M = 147$, Monoclinic, space group $P2_1/c$, $a = 12.429(1)$, $b = 20.794(2)$, $c = 13.099(1)$ Å, $\beta = 116.78(2)^\circ$, $U = 3\,022.3$ Å^3, $D_m = 0.98$ g cm^{-3}, $Z = 12$, $D_c = 0.970$ g cm^{-3}, μ(Mo-K_α) = 0.51 cm^{-1}.

The intensities of the hkl and $\bar{h}kl$ reflections were measured on a Hilger and Watts four-circle diffractometer, using zirconium-filtered Mo-K_α radiation and a $2\theta/\omega$ scan. The data were corrected for Lorentz and polarisation effects and for absorption. A total of 2 817 unique reflections were obtained, of which 1 625 were classed as observed, having net counts $\geqslant 2\sigma$.

The hexameric structure, illustrated in Figure 1(*a*) and (*b*), was solved by the symbolic addition procedure using a multi-solution program. Disordering or extensive libration of some of the t-butyl groups prevented location of the hydrogen atoms and accounts for the rather high final *R* value (0.16). During refinement, alternative positions [(3A) and (3B)] were found for one of the three lithium atoms in the asymmetric unit [Li(N=CBu$^t_2$)]$_3$. These were assigned site occupation factors of 0.5, and correspond to two possible orientations of the slightly folded chair-shaped Li$_6$ rings. Table 2 gives the atomic co-ordinates, Table 3 selected interatomic distances, Table 4 selected bond angles, and Table 5 the equations of some key planes, with perpendicular distances of selected atoms therefrom.

X-Ray Crystal Structure of Compound (2), Li[N=C(NMe$_2$)$_2$].—*Crystal data.* C$_5$H$_{12}$LiN$_3$, $M = 121$, Monoclinic, $P2_1/c$, $a = 11.492(2)$, $b = 20.257(4)$, $c = 11.322(2)$ Å, $\beta = 117.86(2)^\circ$, $U = 2\,330.2$ Å^3, $D_m = 0.99$ g cm^{-3}, $Z = 12$, $D_c = 1.036$ g cm^{-3}, $F(000) = 792$, μ(Mo-K_α) = 0.61 cm^{-1}.

Table 5. Equations of mean planes, and perpendicular distances *p* (Å) of atoms therefrom, in $[\{\mathrm{Li(N{=}CBu^t_2)}\}_6]$

Plane (1): $-10.0468x - 3.0993y + 11.4313z = -1.1850$

Atom	Li(1)	Li(2)	Li(3A)	N(3) *
p	0	0	0	−1.22

Plane (2): $5.5059x + 10.5840y + 6.0156z = -0.0389$

Atom	N(3)	C(19)	C(20)	C(24)	Li(1) *	Li(2) *	Li(3A) *
p	0.01	−0.02	0.01	0.01	1.30	−1.14	1.01

Plane (3): $-6.3575x + 16.3822y - 0.9923z = -1.1672$

Atom	Li(1)	Li(2)	Li(3A^{I})	N(2) *
p	0	0	0	−1.27

Plane (4): $-9.9898x - 2.0719y + 11.6033z = -0.3270$

Atom	N(2)	C(10)	C(11)	C(15)	Li(1) *	Li(2) *	Li(3A^{I}) *
p	0.00	0.00	0.00	0.00	−0.84	−0.94	1.43

Plane (5): $5.5759x + 12.8850y + 4.8832z = 1.2160$

Atom	Li(1)	Li(2^{I})	Li(3A)	N(1) *
p	0	0	0	1.23

Plane (6): $-4.9284x + 17.3727y - 2.1086z = 0.1731$

Atom	N(1)	C(1)	C(2)	C(6)	Li(1) *	Li(2^{I}) *	Li(3A) *
p	0.00	−0.01	0.00	0.00	−1.15	0.91	1.19

Plane (7): $-5.8271x + 16.6201y - 1.6291z = -1.1063$

Atom	Li(1)	Li(2)	Li(3B)	N(2) *
p	0	0	0	−1.33

Plane (8): $-9.7260x - 4.0458y + 11.5351z = -1.1234$

Atom	Li(1)	Li(2)	Li(3B^{I})	N(3) *
p	0	0	0	−1.28

Plane (9): $5.0183x + 9.8567y + 6.7670z = 1.2137$

Atom	Li(1)	Li(2^{I})	Li(3B)	N(1) *
p	0	0	0	1.21

Plane (10): $-2.6580x - 14.6006y + 9.2041z = 0.0000$

Atom	Li(1)	Li(2)	Li(1^{I})	Li(2^{I})	Li(3A) *	Li(3B) *	N(1) *
p	0	0	0	0	−1.75	1.57	−0.07

Plane (11): $8.6118x - 2.9528y + 4.1769z = 0.0000$

Atom	Li(2)	Li(3A)	Li(2^{I})	Li(3A^{I})	Li(1) *	N(3) *
p	0	0	0	0	1.72	0.28

Plane (12): $-3.4599x + 7.0928y + 12.1425z = 0.0000$

Atom	Li(1)	Li(3A)	Li(1^{I})	Li(3A^{I})	Li(2) *	N(2) *
p	0	0	0	0	−1.78	−0.27

Plane (13): $-0.9782x + 19.9930y + 3.5444z = 0.0000$

Atom	Li(1)	Li(3B)	Li(1^{I})	Li(3B^{I})	Li(2) *	N(3) *
p	0	0	0	0	−1.73	−0.21

Plane (14): $10.8460x + 9.9390y - 3.9784z = 0.0000$

Atom	Li(2)	Li(3B)	Li(2^{I})	Li(3B^{I})	Li(1) *	N(2) *
p	0	0	0	0	1.70	0.24

* Atoms not included in the mean plane calculations.

Angles (°) between normals to planes

	Ligand plane–Li$_3$ face			Chair seat–chair back					
				Configuration A			Configuration B		
Planes	1—2	3—4	5—6	1—11	3—12	5—10	7—14	8—13	9—10
Angle	89.2	82.5	84.6	82.2	84.1	84.6	86.3	88.3	83.6
Mean		85.4			83.6			86.1	

Planes 1, 3, and 5 relate to the Li$_3$ triangles bridged by the methyleneamino-ligands in configuration A.
Planes 7—9 relate to the Li$_3$ triangles bridged by the methyleneamino-ligands in configuration B.
Planes 2, 4, and 6 are the planes of the bridging methyleneamino-ligands.
Planes 10—14 are the five possible ' seats ' of the Li$_6$ chair in the two configurations.

Table 6. Atomic co-ordinates (× 10^4) for $[\{Li[N{=}C(NMe_2)_2]\}_6]$

Atom	x	y	z	Atom	x	y	z
Li(1)	6 344(5)	514(2)	6 522(5)	C(24)	4 451(3)	1 291(2)	1 717(3)
Li(2)	5 301(4)	246(2)	3 474(4)	C(25)	2 492(4)	1 030(2)	−313(3)
Li(3)	3 249(4)	424(2)	4 599(4)	N(26)	1 264(2)	741(1)	1 272(2)
N(11)	6 895(2)	558(1)	5 106(2)	C(27)	552(4)	1 367(2)	905(4)
C(12)	7 671(2)	954(1)	5 007(3)	C(28)	702(3)	291(2)	1 846(4)
N(13)	8 073(2)	1 565(1)	5 700(3)	N(31)	4 577(2)	742(1)	6 360(2)
C(14)	7 417(4)	1 738(2)	6 463(4)	C(32)	4 583(3)	1 249(1)	6 975(3)
C(15)	9 488(4)	1 699(2)	6 415(5)	N(33)	3 825(3)	1 830(1)	6 415(2)
N(16)	8 297(3)	870(1)	4 195(3)	C(34)	3 093(4)	1 822(2)	4 983(3)
C(17)	8 150(4)	234(2)	3 576(4)	C(35)	3 045(4)	2 076(2)	7 026(4)
C(18)	8 269(4)	1 417(2)	3 336(4)	N(36)	5 359(3)	1 347(1)	8 382(3)
N(21)	3 421(2)	443(1)	2 916(2)	C(37)	6 035(4)	786(2)	9 143(3)
C(22)	2 660(3)	747(1)	1 879(3)	C(38)	6 058(5)	1 966(2)	8 896(4)
N(23)	3 055(2)	1 161(1)	1 116(2)				

Table 7. Interatomic distances (Å) in $[\{Li[N{=}C(NMe_2)_2]\}_6]$

Li(1)–Li(2)	3.126(5)	C(12)–N(13)	1.423(4)	N(21)–Li(2)	1.987(2)	N(23)–C(25)	1.458(4)
Li(1)–Li(3)	3.192(6)	C(12)–N(16)	1.418(5)	N(21)–Li(3)	2.006(6)	N(26)–C(27)	1.460(5)
Li(2)–Li(3)	3.181(6)	N(13)–C(14)	1.430(6)	N(21)–Li(1^1)	2.019(5)	N(26)–C(28)	1.436(5)
Li(1)–Li(2^1)	2.440(5)	N(13)–C(15)	1.463(5)	N(31)–Li(1)	2.006(6)	C(32)–N(33)	1.425(4)
Li(1)–Li(3^1)	2.449(7)	N(16)–C(17)	1.438(6)	N(31)–Li(3)	1.968(4)	C(32)–N(36)	1.431(4)
Li(2)–Li(3^1)	2.446(4)	N(16)–C(18)	1.465(6)	N(31)–Li(2^1)	2.010(2)	N(33)–C(34)	1.436(4)
N(11)–Li(1)	1.982(7)	C(22)–N(23)	1.421(4)	N(11)–C(12)	1.244(4)	N(33)–C(35)	1.453(7)
N(11)–Li(2)	2.001(2)	C(22)–N(26)	1.420(4)	N(21)–C(22)	1.250(3)	N(36)–C(37)	1.417(4)
N(11)–Li(3^1)	2.036(5)	N(23)–C(24)	1.445(4)	N(31)–C(32)	1.239(4)	N(36)–C(38)	1.456(5)

Superscript 1 refers to the position $1 - x, -y, 1 - z$.

Table 8. Bond angles (°) in $[\{Li[N{=}C(NMe_2)_2]\}_6]$

Li(2^1)–Li(1)–Li(3^1)	81.2(2)	Li(1)–N(31)–Li(2^1)	74.8(2)	C(17)–N(16)–C(18)	113.2(4)
Li(1^1)–Li(2)–Li(3^1)	81.6(2)	Li(3)–N(31)–Li(2^1)	75.9(1)	N(21)–C(22)–N(23)	125.4(3)
Li(1^1)–Li(3)–Li(2^1)	79.4(2)	C(12)–N(11)–Li(1)	128.0(2)	N(21)–C(22)–N(26)	125.9(3)
N(11)–Li(1)–N(31)	127.5(2)	C(12)–N(11)–Li(2)	120.4(2)	N(23)–C(22)–N(26)	108.7(2)
N(11)–Li(2)–N(21)	128.4(1)	C(12)–N(11)–Li(3^1)	139.6(3)	C(22)–N(23)–C(24)	114.9(2)
N(21)–Li(3)–N(31)	125.6(3)	C(22)–N(21)–Li(2)	125.3(3)	C(22)–N(23)–C(25)	117.7(3)
N(11)–Li(1)–N(21^1)	104.6(3)	C(22)–N(21)–Li(3)	124.4(3)	C(24)–N(23)–C(25)	112.0(3)
N(31)–Li(1)–N(21^1)	103.3(3)	C(22)–N(21)–Li(1^1)	134.5(2)	C(22)–N(26)–C(27)	119.1(2)
N(11)–Li(2)–N(31^1)	103.5(1)	C(32)–N(31)–Li(1)	113.5(2)	C(22)–N(26)–C(28)	115.6(2)
N(21)–Li(2)–N(31^1)	104.3(1)	C(32)–N(31)–Li(3)	129.7(2)	C(27)–N(26)–C(28)	111.7(3)
N(21)–Li(3)–N(11^1)	103.1(2)	C(32)–N(31)–Li(2^1)	142.3(2)	N(31)–C(32)–N(33)	126.4(2)
N(31)–Li(3)–N(11^1)	103.7(2)	N(11)–C(12)–N(13)	125.0(3)	N(31)–C(32)–N(36)	125.3(2)
Li(1)–N(11)–Li(2)	103.4(2)	N(11)–C(12)–N(16)	125.7(3)	N(33)–C(32)–N(36)	108.3(3)
Li(2)–N(21)–Li(3)	105.6(1)	N(13)–C(12)–N(16)	109.3(3)	C(32)–N(33)–C(34)	114.0(3)
Li(1)–N(31)–Li(3)	106.9(2)	C(12)–N(13)–C(14)	114.7(3)	C(32)–N(33)–C(35)	117.2(3)
Li(1)–N(11)–Li(3^1)	75.1(2)	C(12)–N(13)–C(15)	117.1(3)	C(34)–N(33)–C(35)	112.0(3)
Li(2)–N(11)–Li(3^1)	74.6(1)	C(14)–N(13)–C(15)	112.6(3)	C(32)–N(36)–C(37)	116.5(3)
Li(2)–N(21)–Li(1^1)	75.1(2)	C(12)–N(16)–C(17)	116.3(3)	C(32)–N(36)–C(38)	120.3(3)
Li(3)–N(21)–Li(1^1)	74.9(2)	C(12)–N(16)–C(18)	118.7(3)	C(37)–N(36)–C(38)	113.8(3)

Unit-cell dimensions were obtained from 40 strong reflections. Intensity data were measured in the θ/ω scan mode by a profile-fitting procedure,[35] with a Stoe-Siemens AED diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). No absorption corrections were applied. 2 416 Unique reflections with $2\theta \leqslant 50°$ and $I > 2\sigma(I)$ were used for structure determination.

The structure was solved by direct methods, and refined to $R = 0.064$ ($R' = 0.076$). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.001F^2$. Hydrogen atoms were located in a difference synthesis, and included in the refinement with constraints on geometry (C–H = 0.96 Å, H–C–H = 109.5°) and on isotropic thermal parameters [$U(\mathrm{H}) = 1.2\ U_{\mathrm{eq.}}(\mathrm{C})$, where $U_{\mathrm{eq.}}$ is the equivalent isotropic thermal parameter]. Anisotropic thermal parameters were refined for all other atoms. There was no evidence of disorder or of extinction effects.

The hexameric structure, $[\{Li[N{=}C(NMe_2)_2]\}_6]$ (Figure 2) is very similar to that of (1) [Figure 1(*a*), with the Li_6 chair in orientation A]. The dimethylamino-nitrogen atoms quite clearly make no direct contribution, either intra- or intermolecularly, to the lithium-nitrogen bonding. Atomic co-ordinates are given in Table 6. Table 7 lists key interatomic distances, Table 8 gives selected bond angles, and Table 9 lists equations of some mean planes, with distances of selected atoms therefrom.

Despite the close similarity between the hexameric molecules of (1) and (2), illustrated by Figures 1 and 2, there is a difference between their orientations with respect to the crystal lattices. In compound (2), the normal to the mean plane of the Li_6 arrangement is inclined at 10.4° to the y axis. In compound (1), the corresponding angle is 103.2° for configuration A, and 27.2° for configuration B.

Table 9. Equations of mean planes, and perpendicular distances p (Å) of atoms therefrom, in $[\{Li[N{=}C(NMe_2)_2]\}_6]$

Plane (1): $10.1301x + 9.5375y - 4.3037z = 4.1100$

Atoms	Li(1)	Li(2)	Li(3$^{\rm I}$)	N(11) *
p	0	0	0	1.209

Plane (2): $5.3741x - 9.2860y + 5.0907z = 5.7866$

Atoms	N(11)	C(12)	N(13)	N(16)	Li(1) *	Li(2) *	Li(3$^{\rm I}$) *
p	0.000	−0.001	0.000	0.000	0.466	−1.398	0.985

Plane (3): $3.3763x - 7.2722y + 7.3131z = 4.1515$

Atoms	Li(1$^{\rm I}$)	Li(2)	Li(3)	N(21) *
p	0	0	0	−1.186

Plane (4): $-3.1234x + 15.9339y + 6.9878z = 1.6744$

Atoms	N(21)	C(22)	N(23)	N(26)	Li(1$^{\rm I}$) *	Li(2) *	Li(3) *
p	0.001	−0.002	0.001	0.001	−1.205	−0.510	1.200

Plane (5): $-5.7738x + 12.5311y + 8.7048z = 2.6587$

Atoms	Li(1)	Li(2$^{\rm I}$)	Li(3)	N(31) *
p	0	0	0	1.165

Plane (6): $10.5167x + 7.5875y - 6.3344z = 1.3483$

Atoms	N(31)	C(32)	N(33)	N(36)	Li(1) *	Li(2$^{\rm I}$) *	Li(3) *
p	−0.001	0.001	0.000	0.000	1.582	−0.727	−0.523

Plane (7): $7.0824x - 15.3283y - 1.0769z = 3.0028$

Atoms	Li(1)	Li(2)	Li(1$^{\rm I}$)	Li(2$^{\rm I}$)	Li(3) *	N(11) *
p	0	0	0	0	−1.847	0.476

Plane (8): $3.2843x + 16.7324y + 3.3510z = 3.3176$

Atoms	Li(2)	Li(3)	Li(2$^{\rm I}$)	Li(3$^{\rm I}$)	Li(1) *	N(21) *
p	0	0	0	0	1.812	−0.475

Plane (9): $5.0806x + 12.6813y - 8.7691z = -1.8442$

Atoms	Li(1)	Li(3)	Li(1$^{\rm I}$)	Li(3$^{\rm I}$)	Li(2) *	N(31) *
p	0	0	0	0	1.803	−0.466

* Atoms not included in the mean plane calculations.

Angles (°) between normals to planes

	Ligand plane–Li$_3$ face			Chair seat–chair back		
Planes	1—2	3—4	5—6	1—7	3—8	5—9
Angle	77.1	82.6	71.4	78.8	77.4	77.1
Mean		77.0			77.8	

Planes 1, 3, and 5 relate to the Li$_3$ triangles bridged by the ligands.
Planes 2, 4, and 6 are the planes of the bridging ligands.
Planes 7—9 are the three possible ' seats ' of the Li$_6$ chair.

Acknowledgements

We thank the S.E.R.C. and the Verband der Chemischen Industrie for financial support.

References

1 Part 19, B. Hall, J. B. Farmer, H. M. M. Shearer, J. D. Sowerby, and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1979, 102.

2 G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds. Vol. 1. The Main Group Elements,' 3rd edn., Methuen, London, 1967.

3 K. Wade, ' Electron Deficient Compounds,' Nelson, London, 1971.

4 B. J. Wakefield, ' Chemistry of Organolithium Compounds,' Pergamon, Oxford, 1974.

5 J. P. Oliver, *Adv. Organomet. Chem.*, 1977, **15**, 257.

6 M. E. O'Neill and K. Wade, ' Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, E. J. Abel, and F. G. A. Stone, Pergamon, Oxford, 1982, vol. 1, ch. 1.

7 K. Jones and M. F. Lappert, *J. Organomet. Chem.*, 1965, **3**, 295.

8 D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.

9 M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, ' Metal and Metalloid Amides,' Ellis Horwood-John Wiley, Chichester, 1980.

10 R. Snaith, C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc. A*, 1970, 2635.

11 H. M. M. Shearer, R. Snaith, J. D. Sowerby, and K. Wade, *Chem. Commun.*, 1971, 1275.

12 K. Manning, E. A. Petch, H. M. M. Shearer, K. Wade, and G. Whitehead, *J. Chem. Soc., Chem. Commun.*, 1976, 107.

13 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.

14 J. C. Halfpenny, H. M. M. Shearer, and K. Wade, unpublished work.

15 H. Hoberg, V. Götz, R. Goddard, and C. Krüger, *J. Organomet. Chem.*, 1980, **190**, 315.

16 C. Krüger and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 998.

17 H. M. M. Shearer, K. Wade, and G. Whitehead, *J. Chem. Soc., Chem. Commun.*, 1979, 943.

18 R. D. Rogers, J. L. Atwood, and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229.

19 J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7346.

20 W. E. Rhine and G. D. Stucky, *J. Am. Chem. Soc.*, 1975, **97**, 737.
21 W. E. Rhine, J. Davis, and G. D. Stucky, *J. Am. Chem. Soc.*, 1975, **97**, 2079.
22 M. Walczak and G. D. Stucky, *J. Organomet. Chem.*, 1975, **97**, 313.
23 M. Walczak and G. D. Stucky, *J. Am. Chem. Soc.*, 1976, **98**, 5531.
24 R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, 1973, **50**, 53.
25 E. Weiss and G. Hencken, *J. Organomet. Chem.*, 1970, **21**, 265.
26 H. Köster, D. Thoennes, and E. Weiss, *J. Organomet. Chem.*, 1978, **160**, 1.
27 D. Thoennes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157.
28 R. P. Zerger and G. D. Stucky, *J. Chem. Soc., Chem. Commun.*, 1973, 44.
29 H. Dietrich, *Acta Crystallogr.*, 1963, **16**, 681.
30 M. Walczak, K. Walczak, R. Mink, M. D. Rausch, and G. D. Stucky, *J. Am. Chem. Soc.*, 1978, **100**, 6382.
31 R. Zerger, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, 1974, **96**, 6048.
32 A. F. Wells, ' Structural Inorganic Chemistry,' 4th edn., Oxford Universit7 Press, 1975.
33 T. F. Schaaf, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 1974, **96**, 7593.
34 W. H. Ilsley, T. F. Schaaf, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 1980, **102**, 3769.
35 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22, 437.

Received 27th September 1982; *Paper* 2/1646