The Ring-stacking Principle in Organolithium Chemistry: its Development through the Isolation and Crystal Structures‡ of Hexameric Iminolithium Clusters $(RR'C{=}NLi)_6$ ($R' = Ph$, $R = Bu^t$ or Me_2N; $R = R' = Me_2N$ or Bu^t)

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Synthetic and *X*-ray crystallographic studies on two new iminolithium compounds, $[Bu^t(Ph)C{=}NLi]_6$ (**1**) and $[Me_2N(Ph)C{=}NLi]_6$ (**2**), have revealed, in conjunction with previously reported work on $[(Me_2N)_2C{=}NLi]_6$ (**3**) and $(Bu^t_2C{=}NLi)_6$ (**4**), a family of hexameric iminolithium species. All four compounds have remarkably similar solid-state structures based on slightly folded chair-shaped Li_6 cores, the six smaller (isosceles) Li_3 triangular faces of which are bridged by three-electron imino ligands through electron-deficient bonds. The precise determination of the structures of (**1**) and (**2**) has revealed features which were not apparent in the earlier limited and less fully refined structural studies on (**3**) and (**4**). Recognition of such features and their detailed analysis leads to a ring-stacking principle which envisages the formation of these hexameric structures from two slightly puckered trimeric rings, $(RR'C{=}NLi)_3$, brought together in a staggered arrangement. Extension of this principle allows the rationalisation of many other structures in lithium chemistry and facilitates structural predictions.

The tendency for lithium to use its four valence-shell atomic orbitals (a.o.s) as fully as possible is reflected in the structures of its organo derivatives.[1–9] Lithium alkyls and aryls are normally associated species, $(RLi)_n$, adopting tetrameric [$n = 4$, *e.g.* $(EtLi)_4$[4]] or hexameric [$n = 6$, *e.g.* $(C_6H_{11}Li)_6$[5]] structures. In these, triangles of Li atoms are bridged by alkyl or aryl groups functioning as one-electron ligands and spreading the bonding power of these electrons as widely as possible in forming four-centre CLi_3 bonds [Figure 1, (**I**) and (**II**) for $n = 4$ and 6 respectively]. Such structures effectively use three of the four valence-shell a.o.s on each metal atom, leaving the fourth (*exo* oriented) a.o. for use by Lewis bases (B) which therefore, if they occupy just one donor site per Li, do not necessarily cause any deaggregation [Figure 1, (**III**); *e.g.* as in $(MeLi)_4{\cdot}2tmen$ (tmen = *NNN'N'*-tetramethylethylenediamine)[6]]. However, complexation by bidentate donors usually leads to dimeric ring structures [Figure 1, (**IV**)], though still with electron-deficient C–Li bonding, *e.g.* $(PhLi{\cdot}tmen)_2$.[7] Monomers, with terminal, so electron-precise C–Li linkages, result only when there are high steric demands from R groups and/or from donors (*e.g.* $Ph_3CLi{\cdot}tmen$[8]), or when tridentate donors are employed [Figure 1, (**V**); *e.g.* as in PhLi·pmdien (pmdien = *NNN'N'N''*-pentamethyldiethylenetriamine)[9]].

In contrast, the hitherto most studied crystalline organonitrogen–lithium compounds, amidolithiums $(RR'NLi)_n$ and their complexes $(RR'NLi{\cdot}xB)_n$, have been shown to adopt structures in which the amide ligands form N–Li bonds which

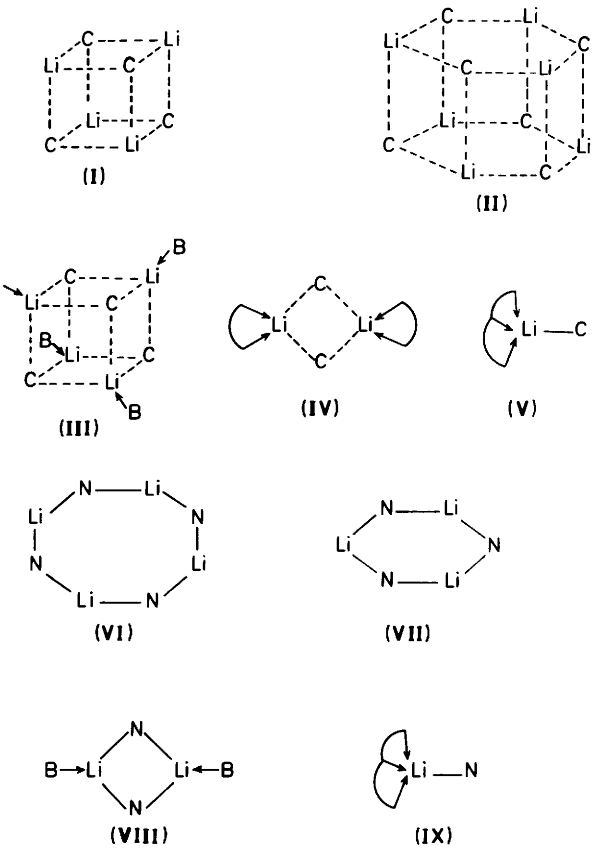

Figure 1. Structural types for organo- and amido-lithium compounds and their complexes, showing electron-deficient (— — —) and electron-precise bonds (——)

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‡ Hexa-μ_3-(phenyl-t-butylmethyleneamido)- and hexa-μ_3-[(dimethylamino)phenylmethyleneamido]-*cyclo*-hexalithium(6 *Li–Li*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Physical and analytical data for the iminolithium compounds $(\mathrm{RR'C{=}NLi})_6$

Complex	R	R′	Description	Melting/decomposition points (°C)	Analysis (%)* C	H	Li	N	Ref.
(1)	$\mathrm{Bu^t}$	Ph	Pale yellow hexagonal plates	Decomp. 119—121	79.0 (79.0)	8.6 (8.4)	4.4 (4.2)	8.2 (8.4)	This work
(2)	$\mathrm{Me_2N}$	Ph	Deep yellow hexagonal plates	Decomp. 129—131	70.4 (70.1)	7.4 (7.1)	4.3 (4.5)	17.8 (18.1)	This work
(3)	$\mathrm{Me_2N}$	$\mathrm{Me_2N}$	Colourless hexagonal plates	Decomp. 120	49.7 (49.6)	9.3 (9.9)	5.9 (5.8)	34.5 (34.7)	16
(4)	$\mathrm{Bu^t}$	$\mathrm{Bu^t}$	Very pale yellow needles or plates	Melts 192	72.7 (73.5)	12.8 (12.2)	4.6 (4.8)	9.5 (9.5)	16, 17

* Calculated values in parentheses.

are formally electron precise, *i.e.* the number of bonding contacts is equal to the number of electron pairs available for bonding. Thus, while many uncomplexed amidolithium compounds are insoluble powders seemingly with polymeric structures, crystalline ones are $(\mathrm{NLi})_n$ ring compounds with $n = 4$ [Figure 1, (**VI**)], as in $[\mathrm{Me_2C(CH_2)_3CMe_2NLi}]_4$,[10] or $n = 3$ [Figure 1, (**VII**)], as in $[(\mathrm{PhCH_2})_2\mathrm{NLi}]_3$[11] and $[(\mathrm{Me_3Si})_2\mathrm{NLi}]_3$.[12] Complexation with monodentate donors leads to smaller, four-membered rings [Figure 1, (**VIII**)], *e.g.* $[(\mathrm{PhCH_2})_2\mathrm{NLi{\cdot}hmpa}]_2$ (hmpa = hexamethylphosphoramide)[11] and $[(\mathrm{Me_3Si})_2\mathrm{NLi{\cdot}OEt_2}]_2$.[10,13] As for organolithium compounds, bulky R/R′ groups together with a large multidentate donor or a combination of monodentate ones force the adoption of monomeric structures with terminal N–Li bonds [Figure 1, (**IX**)], *e.g.* $(\mathrm{Me_3Si})_2\mathrm{NLi}$·12-crown-4 (12-crown-4 = 1,4,7,10-tetraoxacyclododecane)[14] and $\mathrm{Ph(C_5H_4N)NLi{\cdot}hmpa{\cdot}Ph(C_5H_4N)NH}$ ($\mathrm{C_5H_4N}$ = 2-pyridyl).[15]

In this paper we describe the syntheses and structures of a further class of organonitrogen–lithium compounds, namely iminolithiums, $(\mathrm{RR'C{=}NLi})_n$, and their complexes, $(\mathrm{RR'C{=}NLi}{\cdot}x\mathrm{B})_n$, which interestingly can exhibit the above noted bonding characteristics of both organolithium and amidolithium species. Here we present results on the parent crystalline iminolithium compounds $(\mathrm{RR'C{=}NLi})_n$ [R′ = Ph, R = $\mathrm{Bu^t}$ (**1**) or $\mathrm{Me_2N}$ (**2**); R = R′ = $\mathrm{Me_2N}$ (**3**) or $\mathrm{Bu^t}$ (**4**)], all of which have been shown to form remarkably similar hexameric ($n = 6$) clusters with electron-deficient bridging of $\mathrm{Li_3}$ triangles by imino ligands. Our report focuses on (*i*) the various methods available for the preparation of such compounds; (*ii*) *X*-ray crystallographic data on the new compounds $[\mathrm{Bu^t(Ph)C{=}NLi}]_6$ (**1**) and $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**) and a comparison of their structures with those previously published for $[(\mathrm{Me_2N})_2\mathrm{C{=}NLi}]_6$ (**3**)[16] and $(\mathrm{Bu^t_2C{=}NLi})_6$ (**4**);[16,17] and (*iii*) a discussion of the bonding within these hexameric clusters. In particular, the determination of the two new structures has revealed features which were not apparent in the earlier limited and less fully refined structural studies on (**3**) and (**4**). As noted in a preliminary communication,[18] recognition of such features permits the development of a ring-stacking principle which rationalises the formation of these hexameric structures (*cf.* organolithium compounds) in terms of two puckered $(\mathrm{RR'C{=}NLi})_3$ rings (*cf.* amidolithium compounds) brought together in a slightly staggered arrangement. Finally, we indicate briefly how this stacking principle can explain many of the structural patterns described above for organo- and amido-lithium species.

Results and Discussion

Preparation and Characterisation of the Iminolithium Compounds.—Iminolithium compounds, $(\mathrm{RR'C{=}NLi})_n$, used for many years as reagents for the syntheses of imino derivatives of many other metals and metalloids, have, with the notable exception of $[(\mathrm{Me_2N})_2\mathrm{C{=}NLi}]_n$ (**3**), which was first described in its own right in 1968,[19] usually been made in solution and employed without isolation (see for example refs. 20 and 21, and work cited therein). Recently we gave brief preparative details for $[(\mathrm{Me_2N})_2\mathrm{C{=}NLi}]_n$ (**3**) and $(\mathrm{Bu^t_2C{=}NLi})_n$ (**4**) as part of a report of their crystal structures,[16] but a re-examination of routes to these compounds, along with the subsequent isolation of the new iminolithiums $[\mathrm{Bu^t(Ph)C{=}NLi}]_n$ (**1**) and $[\mathrm{Me_2N(Ph)C{=}NLi}]_n$ (**2**), allows us now to present a more complete picture of the synthetic methods generally available for these lithio derivatives. Table 1 reports the physical characteristics and analyses of all four compounds which were prepared by addition reactions of organolithium reagents to nitriles [equation (1)] and/or by lithiation of appropriate imines [equation (2)].

$$\mathrm{RLi + R'C{\equiv}N \longrightarrow RR'C{=}NLi} \qquad (1)$$

$$\mathrm{LiBu^n + RR'C{=}NH \longrightarrow RR'C{=}NLi + Bu^nH} \qquad (2)$$

Compound $[\mathrm{Bu^t(Ph)C{=}NLi}]_n$ (**1**) was synthesised according to equation (1) by treating phenyl-lithium with t-butyl cyanide in benzene–hexane solution (R = Ph, R′ = $\mathrm{Bu^t}$) or t-butyllithium with benzonitrile in hexane alone (R = $\mathrm{Bu^t}$, R′ = Ph). Both reactions gave a yellow powder which could be recrystallised from toluene in similarly high yield (91 and 88% respectively) and purity so that, as both organolithium solutions are commercially available, both routes are equally convenient. Previously,[22] (**1**), used in the synthesis of molybdenum complexes, had been prepared by addition of $\mathrm{Bu^tCN}$ to the Grignard reagent PhMgBr followed by hydrolysis to the imine $\mathrm{Bu^t(Ph)C{=}NH}$ and its subsequent lithiation according to equation (2). The second new iminolithium compound, $[\mathrm{Me_2N(Ph)C{=}NLi}]_n$ (**2**), was prepared initially by reaction of phenyllithium with $\mathrm{Me_2NC{\equiv}N}$ [equation (1), R = Ph, R′ = $\mathrm{Me_2N}$] in pentane, recrystallisation of the microcrystalline powder so obtained giving deep yellow hexagonal plates in 78% yield. However, this method cannot always be reproduced successfully as it sometimes leads to substantial amounts of an amorphous, insoluble polymeric powder. Similar products, believed to contain $>$C=C=N– groups, have been described as ensuing from reaction of $\mathrm{Me_2NC{\equiv}N}$ as a protic acid towards methyllithium.[19] Given such complications, a more reliable method, though still following equation (1) (R = $\mathrm{Me_2N}$, R′ = Ph), is the addition of benzonitrile to a freshly prepared suspension of $\mathrm{Me_2NLi}$; compound (**2**) can thus be obtained consistently in *ca.* 80% yield.

As implied above, the organolithium–nitrile addition route [equation (1)] is usually preferred to the more tedious (though potentially cheaper) one of hydrolysis of a prepared Grignard reagent $\mathrm{RR'C{=}NMgX}$ to give the imine which is then lithiated

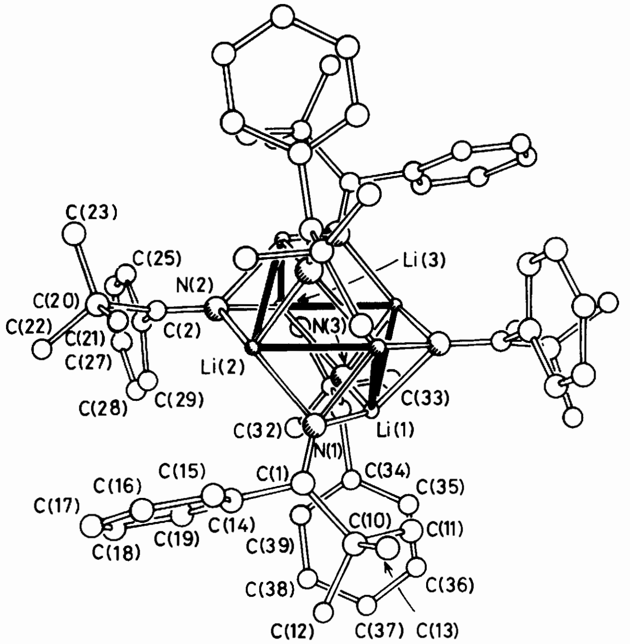


Figure 2. Molecular structure of $[\mathrm{Bu^t(Ph)C{=}NLi}]_6$, molecule (**1A**)

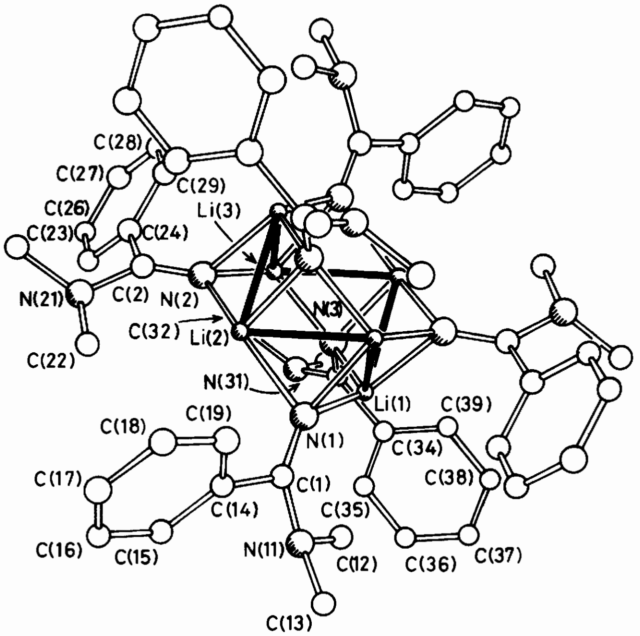


Figure 3. Molecular structure of $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**)

[equation (2)]; indeed methanolysis of iminolithiums (**1**) and (**2**) affords their respective imines in rather better yield than do previously described Grignard routes to $\mathrm{Bu^t(Ph)C{=}NH}$ [23] and $\mathrm{Me_2N(Ph)C{=}NH}$.[24] However, tetramethylguanidine, $\mathrm{(Me_2N)_2C{=}NH}$, is commercially available so, as described earlier,[16,19] its lithiation with n-butyl-lithium in hexane [equation (2), R = R′ = $\mathrm{Me_2N}$] is very convenient for the synthesis of $[\mathrm{(Me_2N)_2C{=}NLi}]_n$ (**3**). For completeness, reaction of $\mathrm{Me_2NLi}$ with $\mathrm{Me_2NC{\equiv}N}$ [equation (1), R = R′ = $\mathrm{Me_2N}$] has now been examined and shown to give (**3**) in comparably high yield (87%, *cf.* 95% from the lithiation reaction). The final iminolithium compound, $\mathrm{(Bu^t_2C{=}NLi)}_n$ (**4**), can be prepared by addition of a solution of t-butyl-lithium in hexane to t-butyl cyanide [equation (1), R = R′ = $\mathrm{Bu^t}$] to give a pale yellow solution, evaporation of which provides a microcrystalline powder in 87% yield.[16,17] Although previous reports have noted that this can be recrystallised from a variety of hydrocarbon solvents, we now find that much superior crystals are obtained using hexane to which a small amount of a donor such as triethylamine has been added. Here recrystallisation is possibly aided by formation of a weak iminolithium–amine complex (though none such is isolable from solution).

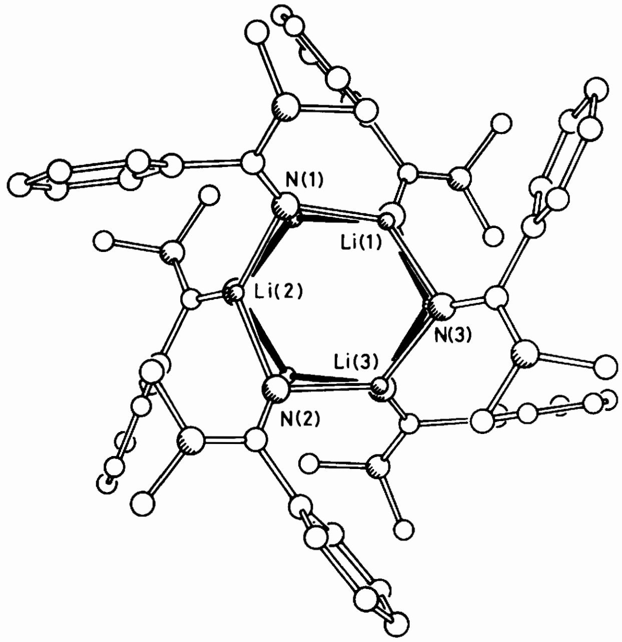


Figure 4. Alternative view of (**2**) through the unbridged $\mathrm{Li_3}$ faces

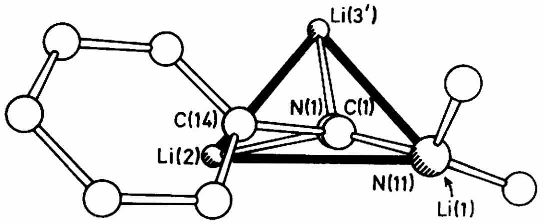


Figure 5. Orientation of an imino ligand over one $\mathrm{Li_3}$ face of $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**). The view direction is approximately along the C(1)–N(1) bond

Description of the Molecular Structures.—Preliminary accounts of the solid-state hexameric structures of (**3**)[16] and (**4**)[16,17] have already been published. Subsequent *X*-ray crystallographic studies of the new iminolithium compounds $[\mathrm{Bu^t(Ph)C{=}NLi}]_6$ (**1**) and $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**) have now established that they too belong to the same structural family.

In the *X*-ray analysis of (**1**), two independent molecules [(**1A**) and (**1B**)] were found in the unit cell. Figure 2 shows the highly puckered chair-shaped $\mathrm{Li_6}$ ring of molecule (**1A**) with six t-butyl(phenyl)imino ligands triply bridging to the six smaller of the eight triangular faces of this hexanuclear core, the two opposite expanded faces being left vacant. Although, as discussed below, there are minor differences in bond lengths and angles, precisely the same gross structural features are found for molecule (**1B**) and for that of compound (**2**) (Figure 3); an alternative view of the latter molecule through the unbridged

Table 2 Key averaged dimensions for the iminolithium compounds $(RR'C{=}NLi)_6$

Complex	R	R′	Ring bond angle in Li_6 chair (°)	Mean standard torsion angle in Li_6 chair (°)	Li···Li distances (Å)			Li–N distances (Å)[b]
					Short edge	Long edge	Cross-ring	
(**1**)[a]	Bu^t	Ph	80.9	98.0	2.511	3.257	4.112	2.016 [1.976(9)—2.054(9)]
(**2**)	Me_2N	Ph	80.6	98.1	2.480	3.207	4.054	2.012 [1.961(8)—2.081(8)]
(**3**)	Me_2N	Me_2N	80.7	102.2	2.445	3.166	4.001	2.002 [1.968(4)—2.036(5)]
(**4**)	Bu^t	Bu^t	86.1	95.1	2.395	3.247	4.036	2.064 [1.965(21)—2.187(33)]

[a] Values given for molecule (**1A**). [b] The range of values is given in parentheses.

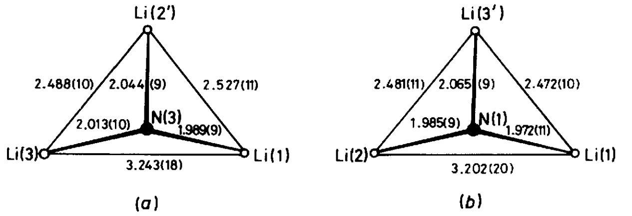


Figure 6. Typical N–Li and Li··· Li distances in bridged faces of (*a*) $[Bu^t(Ph)C{=}NLi]_6$, molecule (**1A**), and (*b*) $[Me_2N(Ph)C{=}NLi]_6$ (**2**)

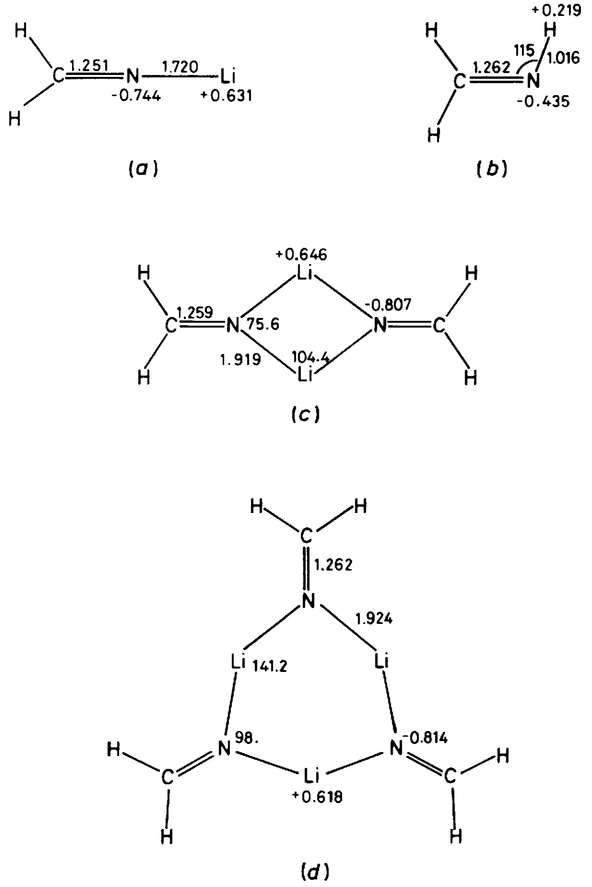


Figure 7. The optimised geometries (6-31 G level) of (*a*) $H_2C{=}NLi$, (*b*) $H_2C{=}NH$, (*c*) $(H_2C{=}NLi)_2$, and (*d*) $(H_2C{=}NLi)_3$; distances in Å, angles in °

Li_3 faces is shown in Figure 4. For all three molecules (**1A**), (**1B**), and (**2**), as for (**3**) and (**4**) reported earlier,[16] the normals to the ligand RR′C=N planes are on average *ca.* 103° from the normals of the Li_3 faces they bridge, and this is illustrated in Figure 5 which portrays a single imino-Li_3 unit in (**2**) viewed in the plane of the ligand. Figure 6 details N–Li and Li··· Li distances within typical bridged Li_3 faces for (**1A**) and (**2**), each such face having one long edge which forms part of one of the vacant faces [range 3.204(14)—3.325(13), mean 3.257 Å, for (**1A**) and 3.168(13)—3.252(14), mean 3.207 Å, for (**2**)] and two short edges [range 2.488(10)—2.527(11), mean 2.511 Å, for (**1A**) and 2.472(10)—2.487(16), mean 2.480 Å, for (**2**)]. The N–Li distances vary from 1.976(9) to 2.054(9) Å (mean 2.016 Å) in (**1A**) and from 1.961(8) to 2.081(8) Å (mean 2.012 Å) in (**2**).

The close similarity between the structures of all four iminolithium compounds so far investigated by *X*-ray crystallography is further emphasised when their detailed dimensions are considered in concert. Table 2 presents the averaged key dimensions for (**1**)—(**4**). Although there are some slightly disparate values for (**4**), these may well reflect the fact that its structure was less precisely determined because of disorder [*R* value 0.160, *cf.* 0.084, 0.078, and 0.064 for (**1**), (**2**), and (**3**) respectively]. For example, such a consideration could explain the noticeably larger average ring bond angle and the rather longer N–Li bond lengths found for (**4**). Such minor differences apart, it is clear that the Li_6 cores of all these iminolithium compounds are significantly less puckered (mean standard torsion angle 98.6°) than those of Group 4 ligand analogues such as $(C_6H_{11}Li)_6$[5] and $(Me_3SiLi)_6$[25] (torsion angles 107.1 and 109.5° respectively).

Bonding within the Iminolithium Clusters.—Turning to the bonding which holds these similar clusters together, our discussion first concerns the most useful way of viewing the nitrogen–lithium bonding. Secondly, from a consideration of ligand orientations and N–Li distances, we develop a ring-stacking principle which rationalises formation of these hexamers in terms of bringing together two trimeric rings, and which similarly helps to account for many of the structural features observed for lithium compounds in general.

The nature of N–Li *bonding in the iminolithium clusters.* It is clear that, on electronegativity grounds alone, the N–Li bonds in these organonitrogen–lithium species must be even more ionic than the C–Li bonds in organolithiums, whose structures, as illustrated by Streitwieser and co-workers,[26] can often be rationalised largely by electronic considerations. Reflecting this highly ionic nature, our CNDO-based molecular orbital (m.o.) calculations on a range of amido- and imino-lithium compounds give bond indices (a measure of the covalent contribution to the bonding[27]) for their N–Li bonds of only 0.25—0.45 even though the formal bond orders are often much greater and, in some cases, unity. Our *ab initio* calculations on $H_2C{=}NLi$, $(H_2C{=}NLi)_2$, and $(H_2C{=}NLi)_3$ [Figure 7(*a*), (*c*), and (*d*) respectively] also show that the bonding in these compounds is highly ionic. Indeed, it is likely that the C_{2v} structure of $H_2C{=}NLi$ with linear framework bonds at N [Figure 7(*a*)], in contrast to the C_s structure of $H_2C{=}NH$ with a C–N–H angle of 115° [Figure 7(*b*)], is due to the ionic nature of the N–Li bond. Analysis of the charge distribution for all three lithium compounds [Figure 7(*a*), (*c*), and (*d*)] shows that the charge on Li lies between $+0.62$ and $+0.65$ while N possesses extra charge of the order of -0.74 to -0.81 e. Thus the ionic nature of the N–Li bonds is also present in the associated compounds of $H_2C{=}NLi$. This can be elegantly illustrated for the case of the dimer [Figure 7(*c*)] by repeating the geometry optimisation calculation with only Li^+ species present (no 2*s* and 2*p* orbitals in the basis set). The resulting geometry has angles within 1° and bond lengths within 0.02 Å of those obtained from a full basis set calculation. Moreover, the resulting dimerisation energy is 73.3 kcal mol^{-1} (cal = 4.184 J), close to the value of 66.0 kcal mol^{-1} found by the full basis set calculation.

Furthermore, the variations in lengths of N–Li bonds from compound to compound do not always reflect the accompanying changes in their formal bond orders, although sufficient data are now available to allow some rationalisation according to N and Li co-ordination numbers for systems with similar ligands. Exemplifying this last point, the μ_3-N–Li distances in the hexamers (**1**)—(**3**) range from 1.961(8) to 2.081(8) Å, with a mean value of *ca.* 2.01 Å (Table 2), while in the clustered tetrameric complex $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ whose Li atoms bear additional donor ligands, the μ_3-N–Li distances are in general slightly longer [2.019(4)—2.171(4) Å, average 2.09 Å],[28] but in the dimeric complex $(Bu^t_2C{=}NLi{\cdot}hmpa)_2$ whose merely three-co-ordinate Li atoms are bridged by N ligands in a formally electron-precise manner, the N–Li distances are significantly shorter, averaging 1.936 Å.[29] However, on turning to amidolithium compounds having formally electron-precise N–Li bonds, it is possible to find bond lengths spanning those noted above for largely electron-deficiently bonded iminolithium clusters; citing the presently known most extreme examples, the N–Li distances in $[Ph(Me)NLi{\cdot}tmen]_2$, whose N and Li atoms are both four-co-ordinate, average 2.189 Å,[30] while that in monomeric $(2,4,6\text{-}Bu^t_3C_6H_2)(H)NLi{\cdot}tmen$, with three-co-ordinate N and Li atoms, is 1.895(8) Å.[31]

Nonetheless, having just given due regard to the highly ionic nature of bonds to lithium, it is equally clear that a fully electrostatic model cannot explain all the structural features found in lithium chemistry. For example, point-charge calculations fail to reproduce adequately the tetramerisation energies obtained by *ab initio* methods for LiX species (X = F, O, or NH_2) and, even more strikingly, predict planar ring structures for $(LiF)_4$ and $(LiOH)_4$ rather than the tetrahedral ones found by *ab initio* calculations at all levels of theory.[32] From this study, Schleyer and co-workers[32] concluded that there are significant covalent contributions to the bonding, particularly for $(LiOH)_4$ and $(LiNH_2)_4$; furthermore, they showed that lone-pair orientation arguments can be employed to explain structural preferences. Given these points, we have been encouraged to seek a simple localised valence-bond description of the bonding within the iminolithium hexamers reported here. Such a description is best served by considering imino ligands $RR'C{=}N$ bonding to Li atoms, rather than anionic ligands $RR'C{=}N^-$ interacting with Li^+ ions, though, as outlined above, we recognise that the true situation lies between these extremes.

Our earlier report[16] of the structures of (**3**) and (**4**) favoured viewing each of the six imino ligands $RR'C{=}N$ as three-electron donors to the six Li atoms (or, in fully ionic parlance, $RR'C{=}N^-$ anions as four-electron donors to Li^+ cations); hence each hexamer has only 24 electrons available for cluster bonding, giving a mean formal bond order of 0.66 for each of the 18 N–Li contacts (ignoring any Li • • • Li interactions) and so underlining the electron-deficient nature of the cluster bonding. However, we recognised (though doubted) that such electron deficiency might in principle be relieved by use of electronic charge from the ligand C=N link, as reduction of the carbon–nitrogen bond order from 2 to 1 would allow each ensuing $RR'^+C{-}N^-$ unit to function as a five-electron donor, leading to formally single N–Li bonds. This alternative bonding interpretation can now, given the additional results on (**1**) and (**2**), be rejected even more confidently on several counts. First, the mean azomethine bond lengths found in these ligands are typically those of C=N double bonds, as in Schiff bases and oximes (*ca.* 1.26 Å), being 1.255(6) for (**1A**), 1.261(7) for (**2**), 1.244(4) for (**3**), and, again slightly anomalously, 1.297(17) Å for (**4**). These values can be compared with the C–N bond lengths found in our *ab initio* calculations on $(H_2C{=}NLi)_2$ and $(H_2C{=}NLi)_3$ [Figure 7(*c*) and (*d*) respectively], 1.259 and 1.262 Å respectively; the calculated bond indices are 2.17 and 2.15 respectively. The absence of the bond lengthening that would be apparent had there been any significant reduction in carbon–nitrogen bond order is also reflected in the i.r. azomethine stretching frequencies, ν(C=N), which are similar for both the imino ligand within the cluster and for the parent imine, *e.g.* for (**2**) at 1 615 cm^{-1} and for $Me_2N(Ph)C{=}NH$ at 1 590 cm^{-1}. Secondly, although those clusters containing dimethylamino groups, namely (**2**) and (**3**), could best allow imino ligands to function as five-electron donors by stabilising canonical forms such as $(R')Me_2N{-}C{=}N \longleftrightarrow (R')Me_2N{\cdots}\overset{+}{C}{\cdots}N^-$, the $Me_2N{-}C$ bond distances observed give no indication of partial double bond character; indeed, the lack of such potentially stabilising groups in (**1**) (R′ = Ph, R = Bu^t) and in (**4**) (R = R′ = Bu^t), yet their adoption of such similar structures to those of (**2**) and (**3**), also mitigates against this interpretation of ligand bonding. It can also be noted for (**2**) and (**3**) that their Me_2N groups fail to participate *directly* in cluster bonding, the shortest Me_2N • • • Li distances in each case being > 3.3 Å, *cf.* 2.01 Å in the tetrameric cluster $(\overbracket{CH{=}CHCH{=}CH(Me_2N)C{=}C}Li)_4$, whose *exo*-$Me_2N$ groups co-ordinate to the Li atoms.[33]

A third and final valence-bond description of the bonding in these hexameric clusters would envisage that the lone pair on the N atom of the imino ligand does not engage in cluster bonding, so making each such ligand merely a one-electron donor. This view is given some credence by the general similarity between the $(NLi)_6$ clusters described here and the Group 4 ligand analogues $(C_6H_{11}Li)_6$[5] and $(Me_3SiLi)_6$,[25] whose C and Si atoms mimic the behaviour of the imino N atoms even though each can supply formally just a single electron to cluster bonding. However, such a bonding picture seems unlikely given that the whole tenor of the structural chemistry of lithium revolves around its need to acquire electron density. Moreover, if each imino ligand was functioning as a source of just one electron, one would then expect free rotation about the C=N bond axis whereas in reality the planes of these ligands are consistently related to the triangles of the lithium atoms they cap. The high barrier to such rotation is indicated by the fact that *ab initio* calculations show that the form of $(H_2C{=}NLi)_3$ with H_2C moieties perpendicular to the $(NLi)_3$ ring is 91.0 kcal mol^{-1} less stable than the fully planar molecule [Figure 7(*d*)].

We therefore believe that the best valence-bond model of the bonding within these iminolithium hexamers regards each nitrogen ligand as supplying three electrons.

Development of the ring-stacking principle. Having established, in valence-bond terms, the three-electron nature of the

Table 3. N–Li distances (Å) in the iminolithium hexamers (**1**) and (**2**)*

	N(1) to			N(2) to			N(3) to		
Complex	basal atoms		apical atom	basal atoms		apical atom	basal atoms		apical atom
(**1A**) $[Bu^t(Ph)C{=}NLi]_6$	Li(2)	Li(1)	Li(3′)	Li(3)	Li(2)	Li(1′)	Li(1)	Li(3)	Li(2′)
	1.976(9)	2.014(9)	2.042(9)	1.993(9)	2.024(9)	2.054(9)	1.989(9)	2.013(10)	2.044(9)
(**2**) $[Me_2N(Ph)C{=}NLi]_6$	Li(1)	Li(2)	Li(3′)	Li(2)	Li(3)	Li(1′)	Li(3)	Li(1)	Li(2′)
	1.972(11)	1.985(9)	2.065(9)	1.984(12)	2.012(10)	2.028(9)	1.961(8)	2.018(12)	2.081(8)

* Numbering schemes are shown in Figure 2 for molecule (1A), and in Figures 3 and 4 for molecule (**2**).

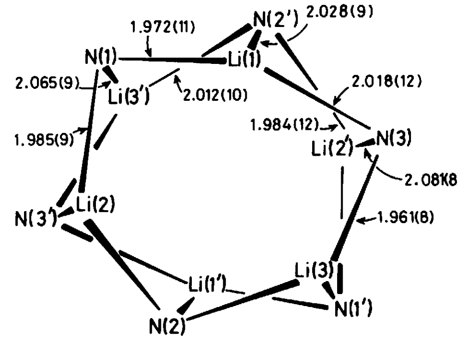


Figure 8. A view down the pseudo-three-fold axis of compound (**2**) with typical N–Li distances within and between the two puckered and slightly staggered N_3Li_3 stacked rings: N $\cdots$ N distances range 3.178(12)—3.187(12) Å, Li $\cdots$ Li distances range 2.472(10)—2.487(16) Å

imino ligands, we now develop a ring-stacking principle which shows that these hexamers are best regarded as pairs of cyclic trimers, stacked in a manner that has wide implications for many other associated lithium compounds.

Views of the molecular skeletons of these hexamers down through their three-fold axes [as exemplified in Figure 4 for compound (**2**)] suggest that the N_6Li_6 core of each consists of two puckered N_3Li_3 six-membered rings, the metal atoms of one almost eclipsing the nitrogen atoms of the other. An analysis of the imino ligand orientations and of the N–Li bond distances adds weight to this pictorial impression. For the first, the ligand orientation shown in Figure 5 for one μ_3-imino unit over one Li_3 triangle of hexamer (**2**) is typical for all the ligands and faces of hexamers (**1**), (**2**), and (**3**). Thus, one Li atom lies very near to the ligand skeletal atom plane [*e.g.* atom Li(1), obscured in Figure 5] in a direction [*e.g.* C(1)=N(1)–Li(1) angle *ca.* 120°] consistent with sp^2 hybridisation of the N atom; one lobe on this N atom thus points directly towards this Li atom, indicating formation of a two-centre N–Li link. The other two bridged Li atoms straddle the ligand plane in a direction implying that they engage the other lobe of the imino N atom in an unsymmetrical three-centre NLi_2 bonding interaction. The N–Li distances confirm fully the validity of this treatment. Figure 6(*b*) shows the same Li_3 face of hexamer (**2**) as depicted in Figure 5, and it is seen that the expected two-centre link [N(1)–Li(1)] is indeed the shortest and that the expected three-centre links [N(1)–Li(2) and N(1)–Li(3′)] are both longer but unequally so. Such an analysis can be extended to all the 12 Li_3 faces of the new hexamers (**1A**) and (**2**), and detailed N–Li bond lengths are given in Table 3. Thus, each of these hexamers exhibits three sets of quite distinct N–Li bond lengths, one of each set being found in each of its six bridged Li_3 faces, *viz.* a short bond [the two-centre linkage: range 1.976(9)—1.993(9) Å, average 1.986 Å for (**1A**); range 1.961(8)—1.984(12) Å, average 1.972 Å for (**2**)], a slightly longer one (by *ca.* 0.03 Å) to a second Li atom [the stronger part of the three-centre NLi_2 interaction: range 2.013(10)—2.024(9) Å, average 2.017 Å for (**1A**); range 1.985(9)—2.018(12) Å, average 2.005 Å for (**2**)], and an even longer one (by yet another 0.03—0.05 Å) to a third Li atom [the weaker component of the three-centre link: range 2.042(9)—2.054(9) Å, average 2.047 Å for (**1A**); range 2.028(9)—2.081(8) Å, average 2.058 Å, for (**2**)]. Although this pattern is obscured by the considerable disorder found in the structure of (**4**),[16,17] it emerges again for hexamers (**1B**) and (**3**), the three distinct sets of N–Li bond lengths averaging 1.990, 2.005, and 2.069 Å for (**1B**) and 1.979, 2.004, and 2.022 Å for (**3**).

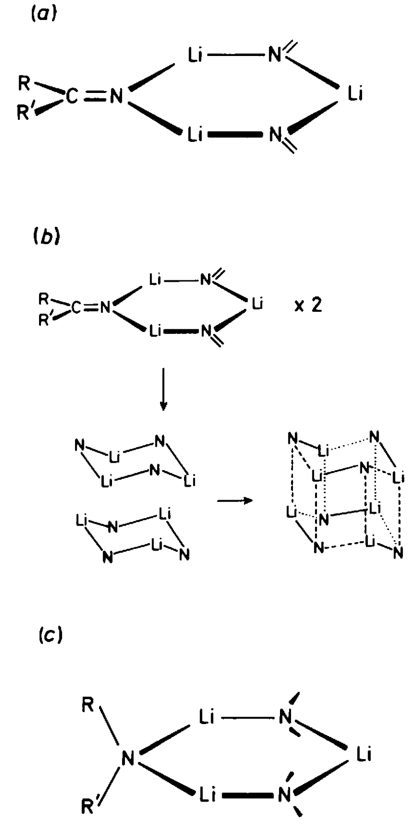
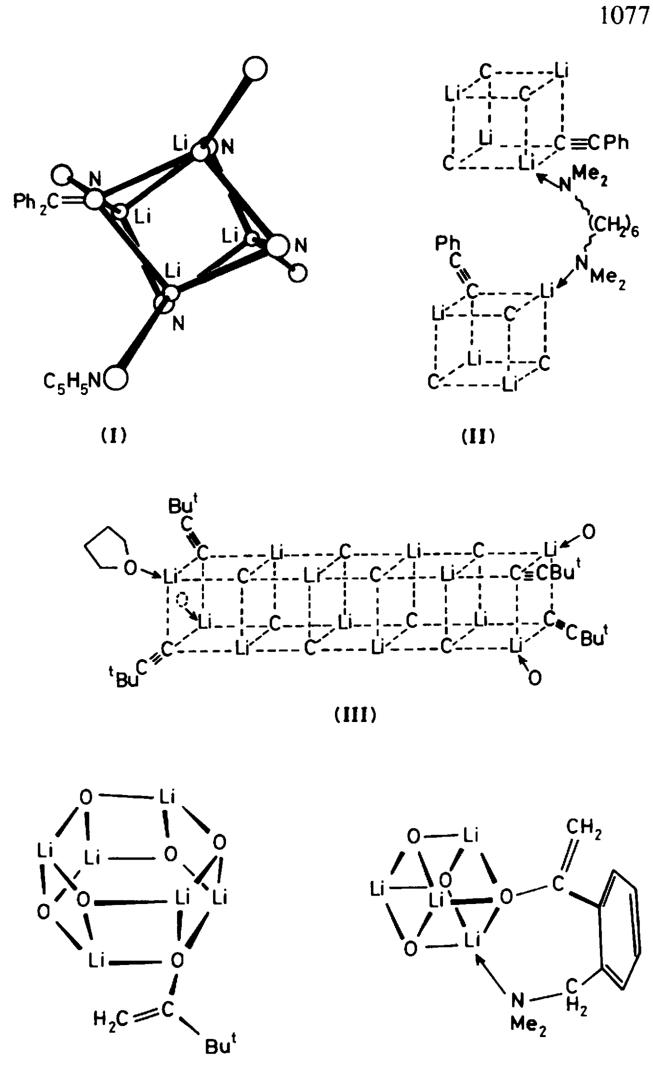


Figure 9. (*a*) The planar stereochemistry of $(RR'C{=}NLi)_3$ trimeric rings, (*b*) formation of the $(NLi)_6$ hexameric skeletons from two such trimeric rings; N–Li links are shown as two-centre (N–Li) or three-centre (N $\cdots$ Li), and (*c*) the perpendicular stereochemistry of $(RR'NLi)_3$ trimeric rings

The result of these interactions is shown in Figure 8 which depicts, for hexamer (**2**), a view from above the puckered and slightly staggered two six-membered N_3Li_3 rings (*cf.* Figure 4). Each μ_3-imino N atom forms a short bond to a Li atom (an intratrimer, two-centre bond), a slightly but distinctly longer one (the stronger, intratrimer, part of a three-centre link), and a longer one still (the weaker, intertrimer, part of the three-centre link). It is clear from Figure 8 that, going round each trimer, all the RR′C=N ligands are twisted the same way, but that this way is different on comparing the trimers; hence every short N–Li bond [*e.g.* N(1)–Li(1)] in one trimer lies above or below a longer one in the second trimer [*e.g.* N(2′)–Li(3′)], so helping to reduce R,R′ group repulsions within and between trimers to a minimum.

If separate, each N_3Li_3 ring would be planar [Figure 9(*a*)] and would be held together by electron-precise bonds, with merely two-co-ordinate metal atoms being bridged by three-co-ordinate nitrogen atoms. However, the *crucial feature* of such a ring is that the imino C atom and the primary atoms of the substituents R,R′ lie in the ring plane. Stacking of such rings, thereby increasing the co-ordination numbers of the Li atoms, is thus facilitated. Figure 9(*b*) shows how the N–Li bonding changes when one trimeric iminolithium molecule is stacked on another. Three alternate N–Li bonds of each trimer donate electronic charge to vacant metal orbitals of the other trimer, so being transformed into the six three-centre NLi_2 bonds *between* the trimers, leaving an alternating set of three two-centre N–Li bonds *within* each of the original trimers (adjacent to the equilateral Li_3 triangles of the hexamer). The six two-centre and six three-centre bonds holding together the N_6Li_6 cores of compounds (**1**)—(**4**) clearly make far more effective use of the available twelve skeletal pairs of electrons than would the twelve two-centre bonds of two trimers $(RR'C{=}NLi)_3$. Perhaps significantly, no iminolithium trimers are known experimentally (prevention of their dimerisation would require exceedingly bulky substituents R or R′), but amidolithium trimers, $(RR'NLi)_3$, are, with R = R′ = $PhCH_2$[11] or Me_3Si.[12] In these, the two-centre N–Li distances average 1.953 and 2.005 Å respectively, and such values compare favourably with average N–Li distances within the two trimers making up each of hexamer (**1A**) (2.002), (**2**) (1.989), and (**3**) (1.992 Å). The *ab initio* geometry optimised structure of $(H_2C{=}NLi)_3$ has N–Li bond lengths of 1.924 Å within the planar $(NLi)_3$ ring; the CH_2N portions are also fully coplanar with this framework ring [Figure 7(*d*)]. Clearly, the bonding *within* each trimer remains strong despite the loss of ideal planarity of the $(NLi)_3$ rings caused by the slight twistings of the RR′C=N ligands which are needed to effect association, and despite the concomitant conversion of three of the two-centre N–Li bonds into three-centre bonds. Furthermore, it is apparent that the N–Li bonds *between* the stacked trimers are also quite strong, not being excessively longer (0.03—0.07 Å) than those within the trimers; intertrimer N–Li lengths lie in the ranges 2.042(9)—2.054(9) (average 2.047), 2.028(9)—2.081(8) (average 2.058), and 2.010(2)—2.036(5) Å (average 2.022 Å) for (**1A**), (**2**), and (**3**) respectively. A similar analysis of the angles within the trimers making up each hexamer illustrates the puckered nature of each ring. Thus, average trimer angles at the formally sp^2 hybridised imino N atoms are 109.0, 107.5, and 105.3° for (**1A**), (**2**), and (**3**) respectively {*cf.* average Li–N(sp^3)–Li angles in the amidolithium trimers $(RR'NLi)_3$ of 95.2° (R = R′ = $PhCH_2$)[11] and 92.3° (R = R′ = Me_3Si);[12] the Li–N(sp^2)–Li angles in the optimised structure of $(H_2C{=}NLi)_3$ [Figure 7(*d*)] are all 98.8°}, while those at the Li atoms are 124.0, 124.4, and 127.2° respectively [*cf.* in $(RR'NLi)_3$, 143.8° when R = R′ = $PhCH_2$[11] and 147.6° when R = R′ = Me_3Si;[12] in optimised $(H_2C{=}NLi)_3$, 141.2°]. Average summed angles within the three sets of puckered trimeric rings making up hexamers (**1A**), (**2**), and (**3**) are thus 699.0, 695.7, and 697.5° respectively [*cf.* in the isolated, very planar, $(RR'NLi)_3$ rings, 721.7° when R = R′ = $PhCH_2$[11] and 719.7° when R = R′ = Me_3Si;[12] in optimised $(H_2C{=}NLi)_3$, exactly 720°].



(I) (II)

(III)

(IV) (V)

Figure 10. Other stacked-ring systems in imino-, alkynyl-, and alkoxy-lithium chemistry

From the above discussion, one can see why and how trimeric iminolithium rings $(RR'C{=}NLi)_3$ dimerise readily to form hexamers $(RR'C{=}NLi)_6$. Indeed, since one orbital remains unused on each metal atom even in the hexamers, further stacking of trimeric units to form nonamers $(RR'C{=}NLi)_9$, dodecamers $(RR'C{=}NLi)_{12}$, or even higher oligomers may occur. We have reported elsewhere low-temperature, high-field ^7Li n.m.r. spectroscopic evidence for such continued stacking in arene solutions of hexamer (**2**),[34] and higher oligomer/polymer formation of this type may explain the amorphous nature and insolubility in non-donor solvents of many diaryliminolithiums, *e.g.* when R = R′ = Ph or *p*-MeC_6H_4 and when R = Ph, R′ = *p*-MeC_6H_4 or *p*-ClC_6H_4.[19,35]

Further applications of the ring-stacking principle. The ring-stacking model developed above for uncomplexed iminolithium hexamers is equally applicable to complexed iminolithium species and to many other lithium compounds having, for example, alkynyl, alkyl, aryl, alkoxy, or halide ligands. Although we intend to elaborate on these extensions in future papers which will include full accounts of several preliminary communicated crystal structures, *e.g.* $(Ph_2C{=}NLi{\cdot}C_5H_5N)_4$,[28] $(Bu^t_2C{=}NLi{\cdot}hmpa)_2$,[29] and $(ClLi{\cdot}hmpa)_4$,[28] it is appropriate for completeness to give brief details here. Figure 10 illustrates the central cores of some of these stacked systems.

Hexamers (**1**), (**2**), and (**3**) fail to deaggregate in a range of donors of variable strengths and denticities, *e.g.* Et_2O, C_5H_5N, hmpa, tmen, or pmdien; only hexamer (**4**), which is considerably

Table 4. Atomic co-ordinates ($\times 10^4$) for $[Bu^t(Ph)C=NLi]_6$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Li(1)	5 404(7)	3 801(6)	−420(4)	Li(4)	4 635(7)	1 418(7)	5 082(4)
Li(2)	6 078(6)	6 419(6)	−407(4)	Li(5)	4 088(7)	−745(6)	4 226(4)
Li(3)	5 626(7)	5 030(7)	896(4)	Li(6)	4 133(6)	−966(6)	5 721(3)
N(1)	6 099(3)	5 171(3)	−920(2)	N(4)	4 131(3)	805(3)	4 240(2)
C(1)	6 813(4)	5 257(4)	−1 337(2)	C(4)	3 542(4)	1 163(4)	3 890(2)
C(10)	6 731(4)	4 327(4)	−1 810(2)	C(40)	3 608(4)	2 377(4)	3 869(2)
C(11)	6 004(5)	3 217(4)	−1 547(2)	C(41)	4 168(4)	2 978(4)	4 455(2)
C(12)	7 944(5)	4 292(5)	−1 955(3)	C(42)	2 414(5)	2 464(5)	3 786(3)
C(13)	6 144(5)	4 507(5)	−2 392(2)	C(43)	4 367(5)	2 930(5)	3 320(3)
C(15)	7 746(3)	7 103(4)	−1 846(2)	C(45)	3 192(3)	241(3)	2 842(2)
C(16)	8 663	8 107	−1 895	C(46)	2 489	−523	2 419
C(17)	9 654	8 336	−1 522	C(47)	1 333	−1 129	2 555
C(18)	9 726	7 561	−1 100	C(48)	880	−971	3 115
C(19)	8 808	6 557	−1 050	C(49)	1 582	−207	3 538
C(14)	7 818	6 328	−1 423	C(44)	2 738	399	3 402
N(2)	6 349(3)	6 498(3)	511(2)	N(5)	3 570(3)	−1 784(3)	4 929(2)
C(2)	7 239(4)	7 217(4)	750(2)	C(5)	2 659(4)	−2 633(4)	4 914(2)
C(20)	7 795(4)	8 421(4)	541(2)	C(50)	2 172(4)	−3 355(4)	4 339(2)
C(21)	7 462(5)	8 523(4)	−124(2)	C(51)	2 771(5)	−2 750(5)	3 763(2)
C(22)	9 125(4)	8 839(4)	599(3)	C(52)	865(5)	−3 610(6)	4 249(3)
C(23)	7 318(5)	9 137(4)	942(3)	C(53)	2 397(6)	−4 409(5)	4 403(3)
C(25)	7 621(3)	7 111(3)	1 888(2)	C(55)	2 361(3)	−3 654(3)	5 911(2)
C(26)	8 143	6 758	2 375	C(56)	1 829	−3 929	6 477
C(27)	8 871	6 166	2 260	C(57)	919	−3 578	6 633
C(28)	9 076	5 927	1 658	C(58)	541	−2 951	6 223
C(29)	8 554	6 280	1 172	C(59)	1 073	−2 675	5 657
C(24)	7 827	6 873	1 287	C(54)	1 984	−3 026	5 501
N(3)	5 605(3)	3 641(3)	475(2)	N(6)	4 193(3)	583(3)	5 845(2)
C(3)	6 158(3)	3 066(3)	672(2)	C(6)	3 538(4)	773(3)	6 233(2)
C(30)	6 208(4)	2 738(4)	1 342(2)	C(60)	3 243(4)	218(4)	6 860(2)
C(31)	5 942(5)	3 561(5)	1 766(2)	C(61)	3 421(4)	−880(4)	6 849(2)
C(32)	7 404(4)	2 713(5)	1 529(3)	C(62)	2 006(4)	31(5)	7 054(3)
C(33)	5 290(5)	1 602(5)	1 435(3)	C(63)	4 106(5)	975(5)	7 330(2)
C(35)	6 293(3)	1 577(3)	−52(2)	C(65)	3 652(3)	2 761(4)	6 237(2)
C(36)	6 891	1 217	−493	C(66)	3 206	3 569	6 068
C(37)	8 011	1 889	−657	C(67)	2 133	3 274	5 762
C(38)	8 533	2 919	−379	C(68)	1 506	2 170	5 624
C(39)	7 935	3 279	62	C(69)	1 952	1 362	5 792
C(34)	6 815	2 607	226	C(64)	3 025	1 657	6 099

disordered in the solid, does so, and then only with hmpa, giving the ring dimer $(Bu^t_2C=NLi\cdot hmpa)_2$.[29] Such usual hexamer retention, and even then without incorporation of donor molecules, might initially seem surprising on two counts. First, such donors could provide the two-co-ordinate Li atoms in trimeric $(RR'C=NLi)_3$ rings with an alternative to stacking as a means of increasing their co-ordination numbers [to three in $(RR'C=NLi\cdot$monodentate donor$)_n$ rings, to four in $(RR'C=NLi\cdot$bidentate donor$)_n$ rings and in $RR'C=NLi\cdot$pmdien monomers], while secondly, monodentate donors could in principle simply add on to the three-co-ordinate Li atoms within the hexamer, giving $(RR'C=NLi\cdot$donor$)_6$ species. That neither type of behaviour is generally observed presumably reflects, first, the strength and efficiency of intertrimer stacking alluded to earlier, and secondly, the fact that, as Figure 8 makes clear, the spare fourth orbital on each Li atom within the hexamers is far from being sterically available, being blocked by an outer ring of imino N atoms. However, both of these prohibitive factors might be assuaged in the case of highly oligomeric/polymeric diaryliminolithiums which, as outlined above, probably consist of more extensively stacked $(RR'C=NLi)_3$ trimeric rings. Significantly, treatment of $(Ph_2C=NLi)_n$ with pyridine (C_5H_5N) produces the pseudo-cubane tetramer $(Ph_2C=NLi\cdot C_5H_5N)_4$.[28] This example of a complexed iminolithium structure, together with that of $(Bu^t_2C=NLi\cdot hmpa)_2$,[29] makes it clear that the basic unit is now a dimeric ring rather than a trimeric one as in the uncomplexed analogues, *cf.* the similar behaviour of trimeric amidolithiums on complexation, as in $[(PhCH_2)_2NLi]_3$ becoming $[(PhCH_2)_2NLi\cdot hmpa]_2$[11] and $[(Me_3Si)_2NLi]_3$[12] becoming $[(Me_3Si)_2NLi\cdot OEt_2]_2$.[10,13] Two such dimers complexed with monodentate donors can themselves stack, and this is observed for $(Ph_2C=NLi\cdot C_5H_5N)_4$ [Figure 10, (**I**)]; such double stacking is prevented for $(Bu^t_2C=NLi\cdot hmpa)_2$ whose imino ligand $=CBu^t_2$ residues are twisted severely (by 58°) out of the $(NLi)_2$ ring plane.

Alkynyl (RC≡C–) and alkoxy and aryloxy (R–O–) ligands are, like imino ligands (RR′C=N–), compatible with ring stacking since the *exo* rings of type $(RC\equiv CLi)_3$, $(RC\equiv CLi\cdot$donor$)_2$ and $(ROLi)_3$, $(ROLi\cdot$donor$)_2$ of the ligand residues are reasonably coplanar with such $(CLi)_{3,2}$ and $(OLi)_{3,2}$ rings. For the former ligand type, examples such as the dimer $[PhC\equiv CLi\cdot Me_2N(CH_2)_3NMe_2]_2$,[36] whose donors can act in a bidentate manner towards each Li so preventing ring stacking, the cubane tetramer $(PhC\equiv CLi)_4\cdot 2[Me_2N(CH_2)_6NMe_2]$,[37] whose donor atoms link Li atoms in two separate doubly stacked four-membered rings [Figure 10, (**II**)], and the dodecamer $(Bu^tC\equiv CLi)_{12}\cdot 4$thf (thf = tetrahydrofuran), which consists of six stacked dimeric $(CLi)_2$ rings terminated by donors at each end [Figure 10, (**III**)],[38] serve to illustrate these ring-stacking principles. For alkoxylithiums one may similarly note the uncomplexed lithium enolate $[Bu^tC(=CH_2)OLi]_6$, which can be regarded as being composed of two near-planar $(OLi)_3$ trimeric

Table 5. Selected interatomic distances (Å) for $[\mathrm{Bu^t(Ph)C{=}NLi}]_6$ (**1**)*

N(1)–C(1)	1.250(6)	N(4)–C(4)	1.245(6)
N(2)–C(2)	1.265(5)	N(5)–C(5)	1.261(5)
N(3)–C(3)	1.250(7)	N(6)–C(6)	1.258(6)
Li(1)–N(1)	2.014(9)	Li(4)–N(4)	2.002(9)
Li(1)–N(3)	1.989(9)	Li(4)–N(6)	1.968(9)
Li(1)–N(2′)	2.054(9)	Li(4)–N(5″)	2.085(9)
Li(2)–N(1)	1.976(9)	Li(5)–N(4)	1.996(9)
Li(2)–N(2)	2.024(9)	Li(5)–N(5)	2.006(8)
Li(2)–N(3′)	2.044(9)	Li(5)–N(6″)	2.054(9)
Li(3)–N(2)	1.993(9)	Li(6)–N(5)	2.008(8)
Li(3)–N(3)	2.013(10)	Li(6)–N(6)	2.005(9)
Li(3)–N(1′)	2.042(9)	Li(6)–N(4″)	2.067(9)
Li(1)–Li(2′)	2.527(11)	Li(4)–Li(5″)	2.535(13)
Li(1)–Li(3′)	2.517(14)	Li(4)–Li(6″)	2.532(12)
Li(2)–Li(3′)	2.488(10)	Li(5)–Li(6″)	2.504(9)
Li(1)–Li(2)	3.204(14)	Li(4)–Li(5)	3.229(17)
Li(1)–Li(3)	3.243(18)	Li(4)–Li(6)	3.262(15)
Li(2)–Li(3)	3.325(13)	Li(5)–Li(6)	3.281(12)

* The prime denotes an atom related by the symmetry operation $1 - x, 1 - y, -z$; the double prime denotes an atom related by the symmetry operation $1 - x, -y, 1 - z$.

Table 6. Atomic co-ordinates ($\times 10^4$) for $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**)

Atom	x	y	z
Li(1)	5 804(8)	6 656(7)	3 939(7)
Li(2)	5 972(8)	4 140(7)	6 318(7)
Li(3)	5 755(8)	4 237(7)	3 816(7)
N(1)	6 356(4)	5 895(3)	5 451(3)
C(1)	7 220(5)	6 209(4)	5 702(4)
N(11)	8 036(4)	7 275(4)	4 880(4)
C(12)	7 953(5)	7 979(5)	3 603(5)
C(13)	8 124(6)	8 007(5)	5 435(6)
C(15)	9 011(4)	5 206(4)	6 737(4)
C(16)	9 365	4 379	7 795
C(17)	8 343	3 754	8 967
C(18)	6 967	3 955	9 082
C(19)	6 613	4 782	8 025
C(14)	7 635	5 408	6 852
N(2)	6 263(4)	3 206(3)	5 380(3)
C(2)	7 072(5)	2 367(4)	5 306(4)
N(21)	8 030(4)	1 863(3)	5 940(4)
C(22)	8 132(5)	2 437(5)	6 637(5)
C(23)	8 116(6)	548(4)	6 595(5)
C(25)	8 535(3)	1 785(3)	3 578(4)
C(26)	8 664	1 454	2 654
C(27)	7 496	1 232	2 539
C(28)	6 199	1 341	3 347
C(29)	6 070	1 672	4 270
C(24)	7 238	1 894	4 386
N(3)	6 138(4)	5 970(3)	2 732(3)
C(3)	6 886(5)	6 609(4)	1 595(4)
N(31)	7 763(4)	6 144(4)	755(3)
C(32)	7 867(6)	4 837(5)	1 316(5)
C(33)	7 713(7)	6 698(5)	−532(5)
C(35)	8 354(3)	8 497(4)	278(3)
C(36)	8 503	9 730	−181
C(37)	7 361	10 418	106
C(38)	6 070	9 872	853
C(39)	5 921	8 639	1 313
C(34)	7 063	7 951	1 025

Table 7. Selected interatomic distances (Å) for $[\mathrm{Me_2N(Ph)C{=}NLi}]_6$ (**2**)*

N(1)–C(1)	1.261(9)	N(2)–C(2)	1.258(6)
N(3)–C(3)	1.263(5)		
Li(1)–N(1)	1.972(11)	Li(1)–N(3)	2.018(12)
Li(1)–N(2′)	2.028(9)	Li(2)–N(1)	1.985(9)
Li(2)–N(2)	1.984(12)	Li(2)–N(3′)	2.081(8)
Li(3)–N(2)	2.012(10)	Li(3)–N(3)	1.961(8)
Li(3)–N(1′)	2.065(9)		
Li(1)–Li(2′)	2.487(16)	Li(1)–Li(3′)	2.472(10)
Li(2)–Li(3′)	2.481(11)		
Li(1)–Li(2)	3.202(20)	Li(1)–Li(3)	3.168(13)
Li(2)–Li(3)	3.252(14)		

* The prime denotes an atom related by the symmetry operation $1 - x, 1 - y, 1 - z$.

rings stacked together [and, perhaps significantly, in that it may deter further stacking, each $=\mathrm{CH_2}$ unit is close to, so 'π-bond paired with,' one specific Li atom, Figure 10, (**IV**)],[39] the tetramer $[o\text{-}\mathrm{Me_2NCH_2C_6H_4C({=}CH_2)OLi}]_4$, whose central $(\mathrm{OLi})_4$ cube has its Li atoms intramolecularly co-ordinated by the $\mathrm{NMe_2}$ units [Figure 10, (**V**)],[40] and the dimeric rings $(\mathrm{Bu^t{}_3COLi{\cdot}thf})_2$[41] and $[2,6\text{-}\mathrm{Bu^t{}_2\text{-}4\text{-}MeC_6H_2OLi{\cdot}OEt_2}]_2$,[42] for which stacking is prevented by the bulk of the alkoxy substituents. Finally, for alkyl- and aryl-lithiums, the situation is rather different as these organic ligands present just one lobe each for bonding within $(\mathrm{CLi})_{3,2}$ rings. Therefore, the disposition of R groups *exo* to the ring may not be crucial, so in principle they can rotate to allow interlocking, and therefore stacking, without disrupting ring bonding. Significantly, as noted in the Introduction, uncomplexed $(\mathrm{RLi})_2$ and $(\mathrm{RLi})_3$ rings are uncommon (indeed, possibly unknown experimentally), tetrameric $(\mathrm{RLi})_4$ (*e.g.* R = Et[4]), hexameric $(\mathrm{RLi})_6$ (*e.g.* R = $\mathrm{C_6H_{11}}$[5]), or higher oligomeric species $(\mathrm{RLi})_n$ being the norm. Monodentate donors allow double stacking to tetramers, *e.g.* $(\mathrm{PhLi{\cdot}OEt_2})_4$,[43] though bidentate ones preclude this, *e.g.* $(\mathrm{PhLi{\cdot}tmen})_2$.[7]

In stark contrast to the above ligand types, amidolithiums $(\mathrm{RR'NLi})_n$ cannot adopt stacked structures because in cyclic systems such as $[(\mathrm{PhCH_2})_2\mathrm{NLi}]_3$[11] the substituents project above and below the $(\mathrm{NLi})_n$ ring plane, inhibiting close approach of rings vertically [Figure 9(*c*)]. Nonetheless, the Li atoms in such isolated rings are merely two-co-ordinate and it can be noted that many amidolithiums are indeed amorphous, hydrocarbon-insoluble, and apparently polymeric materials. Clearly, this strong urge to associate can be relieved, but it now must be through *lateral* association, *i.e.* the linking together of N–Li ring edges [*cf.* in stacking, the joining of $(\mathrm{NLi})_n$ ring faces], and we have described recently the first example of such a laddered structure, that of $[(\mathrm{C_4H_8NLi})_3{\cdot}\mathrm{pmdien}]_2$ ($\mathrm{C_4H_8N}$ = pyrrolidin-1-yl).[44] Finally it can be noted that alkali-metal halide (X) rings, $(\mathrm{LiX})_n$, are primed to both stack and ladder: sterically, as there are *no* groups *exo* to the ring so that both vertical and lateral modes of association are achievable readily, and electronically, as halide ligands can operate as rich and flexible electron donors to effect interring associations. Indeed, continuous stacking and laddering is one way of viewing an ionic macrolattice which prompts the thought that the structure of $(\mathrm{LiCl})_4{\cdot}4\mathrm{hmpa}$, a compound formed by the *in situ* preparation of $(\mathrm{LiCl})_n$ at low temperature, represents that of a limited stack (of just two dimeric rings) prevented from further stacking, and from laddering, by the presence of donors.[28]

Experimental

Standard inert-atmosphere techniques were used for the preparation, recrystallisation, and characterisation of compounds (**1**)—(**4**). Analytical values (C, H, and N determined using a Perkin-Elmer 240 elemental analyser, Li on a 360 Perkin-Elmer atomic absorption spectrometer) are recorded in Table 1 together with melting or decomposition points.

Synthesis of $[Bu^t(Ph)C{=}NLi]_6$. (**1**).—A brief account of the isolation of (**1**) from reaction of Bu^tCN with PhLi in benzene–hexane solution [equation (1); R = Ph, R′ = Bu^t] has already been published.[45] As an alternative [equation (1); R = Bu^t, R′ = Ph], a hexane solution of t-butyl-lithium (7.1 cm^3 of a 1.40 mol dm^{-3} solution, 10 mmol) was added to a frozen solution of benzonitrile (1.03 g, 10 mmol) in the same solvent. Warming to room temperature produced a pale yellow solid which dissolved on addition of warm toluene (3 cm^3). Slow cooling then afforded pale yellow hexagonal plates of compound (**1**).

Synthesis of $[Me_2N(Ph)C{=}NLi]_6$ (**2**).—An earlier report[45] described the synthesis of (**2**) from reaction of Me_2NLi with PhCN in pentane [equation (1); R = Me_2N, R′ = Ph]. An alternative route [equation (1); R = Ph, R′ = Me_2N], though not always reproducible (see text), employed addition of a solution of phenyl-lithium (5.0 cm^3 of a 2.0 mol dm^{-3} solution in diethyl ether–benzene, 10 mmol) to a chilled (*ca.* 0 °C) solution of $Me_2NC{\equiv}N$ (0.70 g, 10 mmol) in pentane. Near room temperature a yellow solid was produced which dissolved on addition of warm toluene (5 cm^3). Cooling of the deep yellow solution to 0 °C gave yellow hexagonal plates of compound (**2**).

Synthesis of $[(Me_2N)_2C{=}NLi]_6$ (**3**).—The isolation of (**3**) from lithiation of $(Me_2N)_2C{=}NH$ with $LiBu^n$ [equation (2), R = R′ = Me_2N] has been reported in full.[16,19] Compound (**3**) was also obtained by reaction of Me_2NLi with Me_2NCN [equation (1), R = R′ = Me_2N] as follows. Dimethylamine (0.45 g, 10 mmol) in pentane was syringed onto a frozen solution of n-butyl-lithium (5.0 cm^3 of a 2.0 mol dm^{-3} solution in pentane, 10 mmol). Warming to room temperature gave a white precipitate of dimethylamidolithium. A solution of $Me_2NC{\equiv}N$ (0.70 g, 10 mmol) in hexane was then added dropwise to this suspension resulting in a clear, colourless solution which on cooling to 0 °C rapidly deposited large hexagonal plates of compound (**3**).

Synthesis of $(Bu^t_2C{=}NLi)_6$ (**4**).—Compound (**4**) was prepared by the reaction of equimolar amounts of t-butyl-lithium in hexane solution with t-butyl cyanide in the same solvent.[16,17] Although the white microcrystalline powder first produced can be recrystallised from pentane, hexane, or other hydrocarbon solvents, addition of a small quantity of a base such as NEt_3 or thf to such solutions has now been found to result in much better quality crystals, uncontaminated by the added base.

Crystal-structure Determinations.—Crystals of compounds (**1**) and (**2**) suitable for *X*-ray analysis were transferred in a nitrogen-filled glove-box to glass Lindemann capillary tubes which were then sealed prior to data collection. All *X*-ray diffraction computer programs used in this study were written by W. C. and Professor G. M. Sheldrick. Calculations were performed on a Data General Eclipse S/250 computer.

Crystal data for (**1**). $C_{66}H_{84}Li_6N_6$, M = 1 003.1, triclinic, a = 12.282(3), b = 12.998(3), c = 21.844(5) Å, α = 90.28(2), β = 90.79(2), γ = 110.79(2)°, U = 3 259.7 Å^3 (from 2θ values of 24 reflections centred at ±ω), T = 291 K, Mo-K_α radiation, λ = 0.710 69 Å, space group $P\bar{1}$, Z = 2 hexamers, D_c = 1.022 g cm^{-3}, $F(000)$ = 1 080. Pale yellow crystal, 0.4 × 0.4 × 0.55 mm, μ = 0.54 cm^{-1}.

Data collection and processing. Stoe-Siemens AED diffractometer, ω/θ scan mode with on-line profile-fitting,[46] $2\theta_{max.}$ = 50°, one hemisphere of data together with some equivalents, no absorption or extinction corrections, no significant variation in standard reflection intensities. 10 540 Reflections, 8 479 unique (merging R = 0.055), 4 701 with $F > 4\sigma(F)$.

Structure analysis and refinement. Random-start tangent refinement direct methods, difference synthesis, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.000\,76F^2$ optimised automatically, rigid ideal hexagons for Ph groups with C–C = 1.395 Å, C–H = 0.96 Å on C–C–C external bisectors, rigid methyl groups with C–H = 0.96 Å, H–C–H = 109.5°, $U_{iso}(H) = 1.2U_{eq}(C)$, anisotropic thermal parameters for other atoms. Final R = 0.084, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ = 0.092 (observed data only), 631 parameters, slope of normal probability plot = 1.65, max. peak in final difference synthesis = 0.19 e Å^{-3}, scattering factors from ref. 47.

Programs: SHELXTL,[48] diffractometer control program by W. C. Two independent molecules each have crystallographic inversion symmetry.

Crystal data for (**2**). $C_{54}H_{66}Li_{12}N_6$, M = 924.8, triclinic, a = 10.597(3), b = 12.720(2), c = 12.847(4) Å, α = 60.69(2), β = 67.08(3), γ = 79.45(3)°, U = 1 390.7 Å^3 (from 31 reflections), T = 291 K, Mo-K_α radiation, λ = 0.710 69 Å, space group $P\bar{1}$, Z = 1 hexamer with crystallographic inversion symmetry, D_c = 1.104 g cm^{-3}, $F(000)$ = 492. Colourless plate crystal, 0.4 × 0.4 × 0.15 mm, μ = 0.61 cm^{-1}.

Data collection and processing. As for (**1**), $2\theta_{max.}$ = 45°. 4 011 Reflections, 3 611 unique (merging R = 0.025), 2 139 with $F > 4\sigma(F)$.

Structural analysis and refinement. Multisolution direct methods, refinement as for (**1**), $w^{-1} = \sigma^2(F) + 0.000\,78F^2$. Final R = 0.078, R' = 0.084, 289 parameters, slope of normal probability plot = 1.49, max. peak = 0.24 e Å^{-3}.

Atomic co-ordinates for non-H atoms and selected interatomic distances are given for compound (**1**) in Tables 4 and 5 respectively, and for compound (**2**) in Tables 6 and 7 respectively.

The optimised geometries described were obtained from the *ab initio* computer program GAMESS[49] using the 6-31G basis set.[50]

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