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MELDOLA MEDAL LECTURE*

Ring-Stacking and Ring-Laddering in Organonitrogenlithium Compounds: The Development of Concepts with Wide Applicability throughout Lithium Structural Chemistry

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1 Introduction

It is appropriate that the reaction vessels used for inert-atmospheric work, and in which many modern organolithium preparations are carried out, honour the name of the pioneer of these air- and moisture-sensitive compounds, Wilhelm *Schlenk*, who died in 1943. His epochal paper (with Johanna Holtz) announcing the discovery of methyllithium, ethyllithium, and phenyllithium was published in *Berichte der Deutschen Chemischen Gesellschaft* back in 1917.[1] Since then the numbers and types of lithium organic derivatives have greatly multiplied, as indeed have their uses in chemical synthesis, which are based upon their ability to act as either nucleophilic reagents or basic reagents. But our knowledge and understanding of the principles governing their reactions has not developed to the same extent. Often these reactions cannot be rationalized, particularly in stereoselective applications, even though the precise conditions—choice of solvents, concentration of reactants, reaction temperature *etc.*—needed to harvest a specific product have been meticulously worked out. Therefore, to gain insight into the mechanistic behaviour of these reagents, many research groups have now turned their attention to gathering structural information on the lithium species themselves. When employed in synthesis, such species are almost exclusively prepared and used in an *in situ* manner. But this current quest for structural knowledge often necessitates their isolation from solution. This new trend, in turn, has led over the past decade to a dramatic rise in the number of lithium organometallic crystal structures determined by *X*-ray diffraction. Schleyer and Setzer's excellent general review of this topic[2] covers the literature to 1983. Two subsequent reviews focus on structural aspects of lithium enolates (by Seebach)[3] and of lithium compounds of sulphones, sulphoximides, sulphoxides, thioethers

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* The present text is based upon the lecture delivered on 16 October 1989 at the symposium 'New Directions in Organometallic Chemistry' held by the Royal Society of Chemistry at the Scientific Societies' Lecture Theatre, London W1

[1] W. Schlenk and J. Holtz, *Chem. Ber.*, 1917, **50**, 262.

[2] W. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353.

[3] D. Seebach, *Angew. Chem.*, 1988, **100**, 1685; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1624.

and 1,3-dithianes, nitriles, nitro-compounds, and hydrazones (by Boche).[4] From these structural studies, it has emerged that lithium organic derivatives adopt a bewildering diversity of geometrical arrangements.

It is a series of lithium organonitrogen structures within this rich variety, which follow a discernible structural and bonding pattern, that form the basis of this review. Two types of compound are involved. Section 2 is dedicated to lithium imides (or imidolithiums), $(R^1R^2C{=}NLi)_n$, derived from ketimines. Section 3 is dedicated to lithium amides (amidolithiums), $(R^1R^2NLi)_n$, derived from secondary amines. A comprehensive review of lithium organonitrogen structures is not necessary here as Gregory, Schleyer, and Snaith have recently collated such information.[5] Instead, this is very much a personalized account of the key studies by co-workers and myself that have brought to light these structural and bonding patterns. Cited work that has been carried out in other laboratories is duly acknowledged in the text with the principal author's name in parentheses. Here, general synthetic aspects are touched on, but, by and large, the review has a structural theme. Emphasis is placed on how molecular 'building-blocks' [small $(NLi)_n$ rings] can associate either in a vertical, face to face manner in lithium imides or in a lateral, edge to edge manner in lithium amides. These alternative ways of aggregating have been labelled 'ring-stacking' and 'ring-laddering', respectively. Lithium imide structures exhibiting ring-stacking—tetramers composed of two $(NLi)_2$ stacked rings, hexamers composed of two $(NLi)_3$ stacked rings, and polymers composed of many stacked rings—are described in detail. Lithium amide ladder-type structures displaying either a stepped or a cyclized arrangement of $(NLi)_2$ rungs are also discussed. In Section 4 excursions are made into other areas of lithium structural chemistry to show how extensions of these ring-stacking and ring-laddering concepts can rationalize many other structures including ones derived from alkanes, alkynes, aromatics, alkoxides, aryloxides, enols, and halogens. The applicability of these concepts to recently-established structural types in sodium chemistry is discussed in Section 5.

2 Lithium Imides

A. Background.—Organic ketimine synthesis began a century ago with the introduction of the diphenyl compound $Ph_2C{=}NH$.[6] About seventy years then passed before significant research was carried out on their lithium derivatives, $R^1R^2C{=}NLi$. Ironically, lithium imides were initially prepared to provide an alternative method of synthesizing ketimines, specifically of the *N*-organosilyl type.[7] In this procedure, generated lithium reagents were not isolated but used *in situ* on organohalosilanes (equation 1). Wade and co-workers exploited this imido-

$$R^1R^2C{=}NLi + ClSiR_3 \longrightarrow R^1R^2C{=}NSiR_3 + LiCl \qquad (1)$$

transfer capability to make imido-derivatives of a range of main group

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[4] G Boche, *Angew Chem*, 1989, **101**, 286, *Angew Chem, Int Ed Engl*, 1989, **28**, 277

[5] K Gregory, P v R Schleyer, and R Snaith, *Adv Inorg Chem*, 1991, in the press

[6] A Hantzsch and F Kraft, *Chem Ber*, 1891, **24**, 3511

[7] L-H Chan and E G Rochow, *J Organomet Chem*, 1967, **9**, 231

elements.[8–17] As in the previous example, the lithium imido-transporters were generally not isolated but made *in situ*, then reacted with suitable halides. In this way, one, two, or three imido ligands can be attached to B, Al, and P; one or two to Be; and up to four to Si, Ge, and Sn; in a similar way, many imido-transition metal derivatives have proved accessible.[18]

B. Synthesis and Classification of Compounds and Complexes.—The two standard ways of preparing lithium imides involve either addition of an organolithium compound across the triple bond of a nitrile (equation 2) or lithiation of a ketimine by an organolithium reagent, commonly Bu^nLi (equation 3).

$$R^1Li + R^2C{\equiv}N \longrightarrow R^1R^2C{=}NLi \tag{2}$$

$$RLi + R^1R^2C{=}NH \longrightarrow R^1R^2C{=}NLi + RH \tag{3}$$

In both cases, and indeed in all reactions leading to or employing lithium organic derivatives, an inert atmosphere is mandatory. An alternative method, replacing the organolithium R^1Li in equation 2 with a Grignard reagent R^1MgX, requires further hydrolysis and lithiation steps, and therefore offers no general advantage over the two direct routes. That notwithstanding, an early study (Kilner *et al.*)[19] did make use of the Grignard option as a preliminary to preparing imidomolybdenum species. However, the lithium imides now discussed have all been successfully prepared in high yield (typically, in excess of 75%) following either one or both of the standard procedures noted by equations 2 and 3.

Dealing first with lithium imides of formula $(R^1R^2C{=}NLi)_n$, where n indicates the state of association, this set falls into two distinct categories depending on the nature of the substituents attached to the imido-carbon (*C*=N) atom. Diaryl types (*e.g.*, $R^1 = R^2 =$ Ph or p-MeC_6H_4; $R^1 =$ Ph, $R^2 = p$-MeC_6H_4 or p-ClC_6H_4) have so far proved to be amorphous solids which, once made in hydrocarbon solution, readily precipitate on account of their poor solubility.[20,21,7] On the other hand, those lithium imides with no aryl substituents (*e.g.*, $R^1 = R^2 = Bu^t$ or Me_2N) or with only one aryl substituent (*e.g.*, $R^1 =$ Ph,

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[8] M R Collier, M F Lappert, R Snaith, and K Wade, *J Chem Soc*, *Dalton Trans*, 1972, 370

[9] G J Bullen and K Wade, *J Chem Soc*, *Chem Commun*, 1971, 1122

[10] J R Jennings, R Snaith, M M Mahmoud, S C Wallwork, S J Bryan, J Halfpenny, E A Petch, and K Wade, *J Organomet Chem*, 1983, **249**, C1

[11] R Snaith, C Summerford, K Wade, and B K Wyatt, *J Chem Soc A*, 1970, 2635

[12] H M M Shearer, R Snaith, J D Sowerby, and K Wade, *J Chem Soc*, *Chem Commun*, 1971, 1275

[13] B Hall, J Keable, R Snaith, and K Wade, *J Chem Soc*, *Dalton Trans*, 1978, 986

[14] J B Farmer, H M M Shearer, J D Sowerby, and K Wade, *J Chem Soc*, *Chem Commun*, 1976, 160

[15] B Hall, J B Farmer, H M M Shearer, J D Sowerby, and K Wade, *J Chem Soc*, *Dalton Trans*, 1979, 102

[16] J B Farmer, R Snaith, and K Wade, *J Chem Soc*, *Dalton Trans*, 1972, 1501

[17] J Keable, D G Othen, and K Wade, *J Chem Soc*, *Dalton Trans*, 1976, 1

[18] H R Keable, Ph D Thesis, University of Durham, 1972

[19] M Kilner and C Midcalf, *J Chem Soc*, *Dalton Trans*, 1974, 1620

[20] R E Mulvey, Ph D Thesis, University of Strathclyde, 1984

[21] I Pattison, K Wade, and B K Wyatt, *J Chem Soc A*, 1968, 837

R^2 = Bu^t or Me_2N) dissolve well in arene solvents, from which they crystallize as hexamers $(R^1R^2C{=}NLi)_6$ (see Section 2C for a detailed analysis of their structures) [22–24]

Complications have been noted to occur in some attempts to synthesize lithium imides *via* nitrile insertion (equation 2) For example, $[Me_2N(Ph)C{=}NLi]_n$ can be satisfactorily prepared in high yield and high purity *via* the reactants $Me_2NLi/PhC{\equiv}N$, but switching the 'R' groups to the alternative combination $PhLi/Me_2NC{\equiv}N$ sometimes leads to substantial amounts of an amorphous, insoluble, polymeric powder [20 24] Complex competing reactions with $Me_2NC{\equiv}N$ acting as a protic acid towards the lithio-reagent are thought to be the cause Earlier efforts to obtain lithium imides by the action of alkyllithiums on $MeC{\equiv}N$ or on $EtC{\equiv}N$ were thwarted by similar protic acid behaviour, believed ultimately to give solids containing $>C{=}C{=}N-$ linkages [21]

Turning to complexed lithium imides of formula $[R^1R^2C{=}NLi\,(L)_x]_n$, where L represents the Lewis base (electron donor), these owe their existence to the pronounced Lewis acidity (electron-accepting nature) of the metal Table 1 lists the L molecules referred to throughout this text and explains their abbreviations $(Ph_2C{=}NLi)_\infty$, the most studied diaryl system thought to typify this group, gives isolable adducts of this type on treatment with the L molecules THF,[21] HMPA,[25] DABCO,[20] and pyridine[26 27] [its crystal structure, $(Ph_2C{=}NLi\,NC_5H_5)_4$, is described in Section 2D] In contrast, the hexameric lithium imides are recovered intact and donor-free, after treatment with various proportions of various L ligands including diethylether, pyridine, TMEDA, and PMDETA [20] Only HMPA, an oxygen donor with a strong affinity for lithium, forms complexes with these systems, though just in two cases While the first complex $(Bu^t_2C{=}NLi\,HMPA)_n$[27 28] has been structurally elucidated in both solution (see Section 2E) and the solid state (see Section 2D), the second, $[(Me_2N)_2C{=}NLi\,(HMPA)_x]_n$,[20] has not yet been fully characterized as the precise value of x (possibly $\frac{2}{5}$ or $\frac{1}{3}$) remains uncertain Both complexes were nevertheless synthesized in the same manner, by the addition of one molar equivalent of the donor to hydrocarbon solutions of their parent lithium imides

Complexation studies on another lithium imide $[Bu^n(Bu^t)C{=}NLi]_n$[29] have revealed that it rearranges to an aza-allyl isomeric form $[CH_3CH_2CH_2C(H)\cdots C(Bu^t)\cdots N(H)Li\,(L)_x]_n$ on contact with Lewis bases L(L = HMPA or THF) This behaviour is attributed to the R group (Bu^n) attached to the C=N link having α-

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[22] W Clegg, R Snaith, H M M Shearer, K Wade, and G Whitehead *J Chem Soc Dalton Trans* 1983, 1309

[23] D Barr, W Clegg, R E Mulvey, R Snaith, and K Wade, *J Chem Soc*, *Chem Commun* 1986, 295

[24] D R Armstrong, D Barr, R Snaith, W Clegg, R E Mulvey, K Wade, and D Reed, *J Chem Soc Dalton Trans*, 1987, 1071

[25] D Barr, W Clegg, R E Mulvey, and R Snaith, *J Chem Soc Chem Commun*, 1984, 226

[26] D Barr, W Clegg, R E Mulvey, and R Snaith, *J Chem Soc*, *Chem Commun*, 1984 79

[27] D Barr, R Snaith, W Clegg, R E Mulvey, and K Wade, *J Chem Soc*, *Dalton Trans* 1987 2141

[28] D Barr, W Clegg, R E Mulvey, D Reed, and R Snaith, *Angew Chem* 1985 **97** 322 *Angew Chem*, *Int Ed Engl*, 1985, **24**, 328

[29] P C Andrews, D R Armstrong, M MacGregor, R E Mulvey, and D Reed *J Chem Soc Chem Commun*, 1989, 1341

Table 1 *Characteristics of the Lewis base (L) molecules mentioned in the text*

Common name	*Abbreviation*	*Molecular formula*	*Donor atom/s*	*Normal denticity*
Tetrahydrofuran	THF	C_4H_8O	O	1
Diethylether	Ether	$(C_2H_5)_2O$	O	1
Hexamethylphosphoramide	HMPA	$(Me_2N)_3P{=}O$	O	1
12-crown-4	—	$C_8H_{16}O_4$	O	4
Pyridine	C_5H_5N	C_5H_5N	N	1
Diazabicyclo[2,2,2]octane	DABCO	$N(CH_2CH_2)_3N$	N	1
Di-t-butylketimine	$Bu^t_2C{=}NH$	$(C_4H_9)_2C{=}NH$	N	1
2-anilinopyridine	Ph(2-Pyr)NH	$C_6H_5(C_5H_4N)NH$	N	1
Tetramethylhexanediamine	TMHDA	$Me_2N(CH_2)_6NMe_2$	N	1
Tetramethylethylenediamine	TMEDA	$Me_2NCH_2CH_2NMe_2$	N	2
Pentamethyldiethylenetriamine	PMDETA	$(Me_2NCH_2CH_2)_2NMe$	N	3

C–H units. L molecules facilitate proton transfer from this C–H unit to the imido-N atom with concomitant formation of an aza-allyl $C{\cdots}C{\cdots}N^-$ anion. The driving force appears to lie with the increase in metal coordination number (c.n.) from complexed imide to aza-allyl species. None of the lithium imides now discussed possesses such α-C–H units.

C. Crystal Structures of Lithium Imide Hexamers $(R^1R^2C{=}NLi)_6$.—*X*-Ray crystallographic studies on the lithium imides $[Ph(Bu^t)C{=}NLi]_n$ (1), $[Me_2N(Ph)C{=}NLi]_n$ (2), $[(Me_2N)_2C{=}NLi]_n$ (3), and $(Bu^t_2C{=}NLi)_n$ (4), have established that they belong to the same hexameric ($n = 6$) structural family.[22–24] Their common molecular structure consists of a highly-puckered, chair-shaped Li_6 ring centre (Figure 1a), surrounded by six triplybridging imido-nitrogen atoms (Figure 1b). The 'R' groups attached to the imido-carbon atoms point away from the hexanuclear core (Figure 1c). Figure 2 shows the typical orientation taken up by an imido ligand. Its terminal nitrogen binds to a Li_3 triangle. In total, there are six such units and two distinctly larger triangular lithium faces (unbridged by nitrogen atoms) within the gross structure.

(i) *Introduction to the Ring-stacking Bonding Concept.* In keeping with lithium organometallics generally, lithium imides are highly polar in nature. However, the interactions that hold their structures together are not exclusively electrostatically based. Reinforcing this point, the hexameric $(R^1R^2C{=}NLi)_6$ clusters can be rationalized by a directional bonding approach that can accommodate the fact that the core-atoms involved carry significant charge. An alternative view of their $(NLi)_6$ core looking down through its three-fold axes (Figure 3) illustrates the crux of the approach. That is, the hexamers are best regarded as pairs of stacked

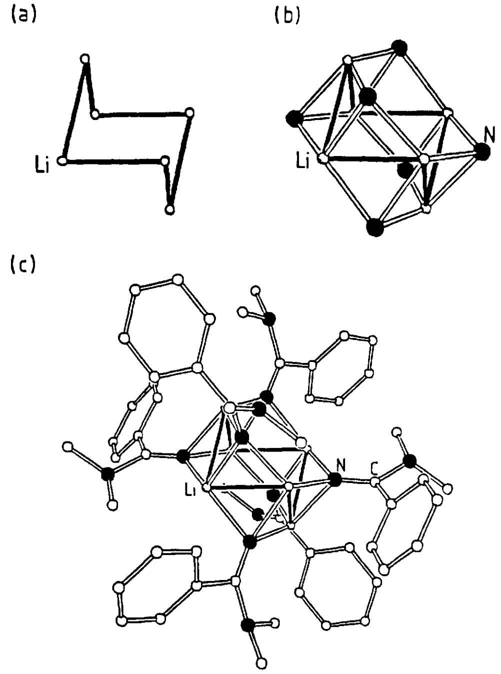

Figure 1 *Building up the molecular structure of a representative hexameric lithium imide,* $[Me_2N(Ph)C{=}NLi]_6$, (2)

cyclic $(NLi)_3$ ring trimers. Each six-membered ring is puckered and is positioned so that the metal atoms in one ring almost eclipse the nitrogen atoms of the other. While this ring-stacking phenomenon is clearly perceptible to the eye, the real strength of the concept is that each individual well-refined hexamer [the structure of (4) is considerably disordered and thus does not come into this category] displays precisely the same pattern in both its imido ligand orientations and nitrogen–lithium interatomic distances. On the basis of the regularity of the former, depicted in Figure 2, the N–Li bonds can be divided into either *two-centre* links, or *three-centre* links, depending on whether the ligand skeletal plane (and by implication one N sp^2 lobe) is oriented either directly towards a Li atom [Li(1)] or between two Li atoms [Li(2) and Li(3′)]. The refined bond lengths (*e.g.*, see Figure 2b) fully support this interpretation as the expected two-centre link [N(1)–Li(1)] is indeed the shortest, while the expected three-centre links [N(1)–Li(2) and N(1)–Li(3′)] are both longer, but unequally so. All six distinct NLi_3 bridges within each of the hexamers (1A), (1B) [two independent molecules were found in the unit cell of (1)], (2), and (3), twenty-four bridges in total, conform to this pattern. The overall effect produced by these three distinct sets of N–Li interatomic distances (shown pictorially and numerically in Figure 4 and Table 2, respectively) is that each constituent trimeric ring exhibits short (two-

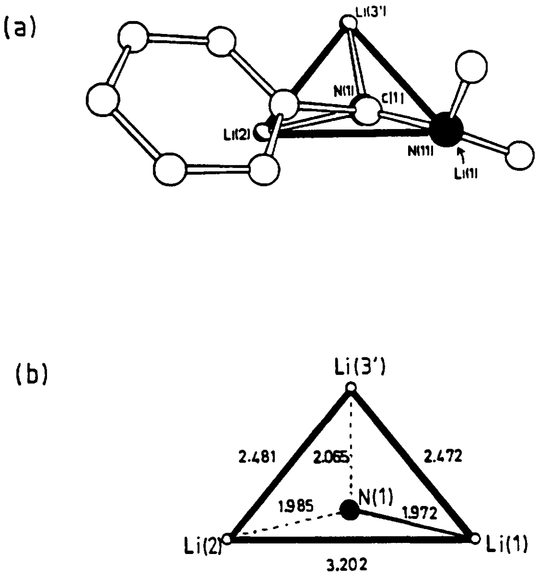

Figure 2 *Typical orientation of an imido ligand over a* Li$_3$ *triangle. The interatomic distances are in* Å

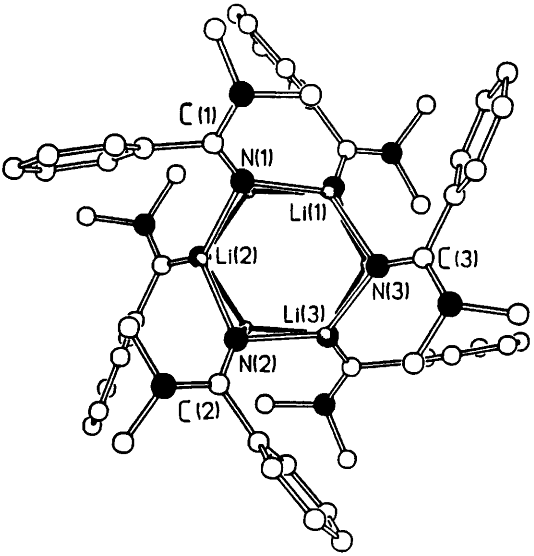

Figure 3 *Alternative view of hexamer* (2) *looking through the vertically-associated ('stacked')* (NLi)$_3$ *trimeric rings*

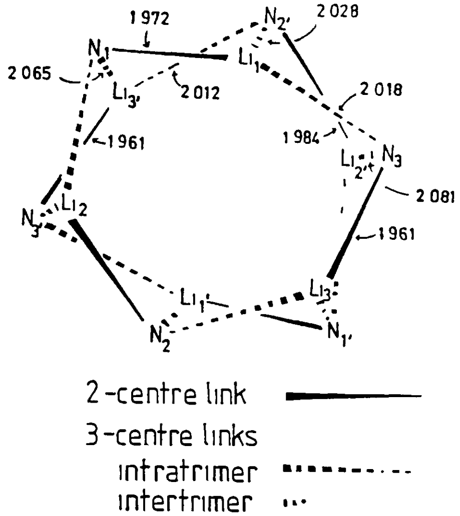

Figure 4 *Classification of* N–Li *bonds in accord with the ring-stacking treatment: lengths are in* Å

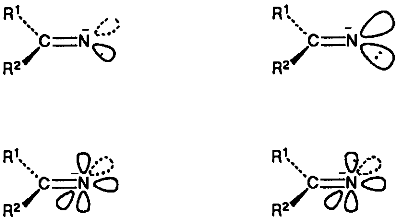

Figure 5 *Stereochemistry of the imido-ligand showing the localized centres of electron density at the imido-nitrogen*

centre) bonds and long (three-centre) bonds in alternation. The weaker (three-centre) bonds between the trimers (*inter*trimer as opposed to *intra*trimer) are even longer. Also, 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′)], in order to minimize R^1,R^2 group repulsions within and between trimers. One can visualize that, were the two trimeric $(R^1R^2C{=}NLi)_3$ rings making up the hexamers separated, the primary atoms of each R group, the imido-carbons, the imido-nitrogens, and the metal cations to which they are electrostatically bound, would sit in the same plane (see Figure 5). Imidolithium $[\alpha\text{-}C^1(\alpha\text{-}C^2)C{=}NLi]_3$ ring units, in being flat in this way, are thus primed for stacking: the advantage of doing so lies in the increased coordination numbers (c.n.) experienced by the metal cations [*i.e.*, from 2 (to nitrogen) in an isolated trimer, to 3 (to nitrogen) in the double stack]. Of course, to stack together the two trimeric $(NLi)_3$ rings must revert to a slightly-puckered state as their imido-ligands have to twist to effect association of

Table 2 *Average lengths in Å of the three distinct groups of* N–Li *bonds in hexameric lithium imide crystals* (*X-ray diffraction data*)

			Three-centre bonds	
Hexamer	*Text number*	*Two-centre bonds*	*Intratrimer*	*Intertrimer*
$[\mathrm{Ph(Bu^t)C{=}NLi}]_6$	(1A)[a]	1.986	2.017	2.047
	(1B)[a]	1.990	2.005	2.069
$[\mathrm{Me_2N(Ph)C{=}NLi}]_6$	(2)	1.972	2.005	2.058
$[\mathrm{(Me_2N)_2C{=}NLi}]_6$	(3)	1.979	2.004	2.022

[a] Two independent molecules co-exist in the unit cell

the trimers, *i.e.*, in order that the imido-nitrogens can convert from a di-bridging role to a tri-bridging role with respect to lithium. Average summed angles within the three sets of trimeric rings making up hexamers (1A), (2), and (3) reflect this loss of ideal planarity in being 699.0, 695.7, and 697.5° respectively, *i.e.*, in being less than the 720° predicted by an *ab initio* geometrical optimization of fully planar $(\mathrm{H_2C{=}NLi})_3$.[24]

(ii) *Implications of the Ring-stacking Model for the Structures of Diaryl Lithium Imides* $[\mathrm{Aryl(Aryl)C{=}NLi}]_n$. Structural characterization has not yet proved possible in the case of those lithium imides having two aryl substituents, $[\mathrm{Aryl(Aryl)C{=}NLi}]_n$. *X*-Ray crystallography cannot be used on account of the amorphous nature of these compounds. However, one can deduce their basic structural types by evoking similar ring-stacking ideas. Central to this approach are the contrasting physical properties of the two types of uncomplexed lithium imides involved: the hexamers exhibit hydrocarbon solubility and crystallinity in the solid state, while the diaryls exhibit hydrocarbon insolubility and they are amorphous in the solid state. Having established that the molecular 'building-blocks' of lithium imides are six-membered $(\mathrm{NLi})_3$ cyclic rings and that two such rings form the oligomeric stacks of the hexamers, it is proposed that the discordant features of the diaryls reflect more highly associated structures composed of extended stacks of such cyclic trimers (Figure 6). This stack propagation is valid from a coordination viewpoint. Each lithium atom in the two trimeric rings of the hexameric stacks (which actually are end-rings from which further stacking can ensue) possesses a vacant coordination site, *i.e.*, with c.n. of 3, rather than of 4, the most common c.n. found in organolithium chemistry.[2] Supporting evidence for the existence of higher order stacks is discussed elsewhere in the review: thus, Section 2D deals with the oligomeric adducts formed when diaryls are treated with Lewis bases, while Section 2E focuses on solution NMR spectroscopic studies of lithium imides.

D. Crystal Structures of Lithium Imide Complexes $[\mathrm{R^1R^2C{=}NLi.(L)}_x]_n$.—To date, three lithium imide complexes have been crystallographically characterized. Two of them, $(\mathrm{Bu^t_2C{=}NLi.HMPA})_2$ (5)[27,28] and $(\mathrm{Ph_2C{=}NLi.NC_5H_5})_4$ (6),[26,27] adopt distinct structural types that can be rationalized by ring-stacking considerations.

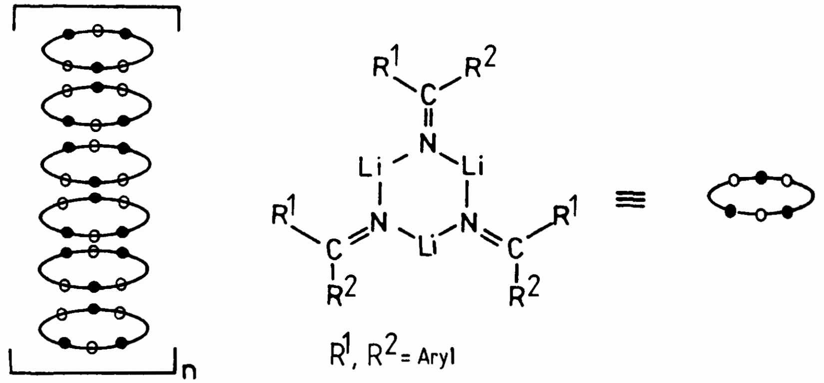

Figure 6 *Extended stacks in* [Aryl(Aryl)C=NLi]$_n$ *systems*

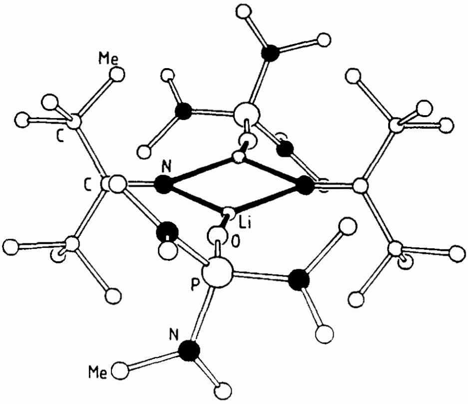

Figure 7 *Molecular structure of complex* (5) *with a central* $(NLi)_2$ *ring sterically prevented from stacking*

From its empirical formula, the third complex, $[Ph_2C{=}NLi.(HMPA)_{5/6}]_6$, (7),[25] appears closely related to this pair, but, in fact, it belongs to another category altogether in being an alkali metal lithiate made up of discrete $[Li.(HMPA)_4]^+$ $[(Ph_2C{=}N)_6Li_5.(HMPA)]^-$ ion pairs. Each crystal structure is now reviewed in turn.

(i) *Analysis of Structures in terms of Ring-stacking.* At first glance, the *four*-membered $(NLi)_2$ ring structure of (5) (Figure 7) appears to conflict with the ring-stacking model proposed for its parent lithium imide $(Bu^t_2C{=}NLi)_6$, (4), and for other lithium imide hexamers, as these are based on the association of *six*-membered $(NLi)_3$ rings. However, consideration must be given to the respective coordination arcs (Figure 8) offered to the incoming HMPA donor molecules. Van der Waals repulsions would clearly be greater on complexation of the

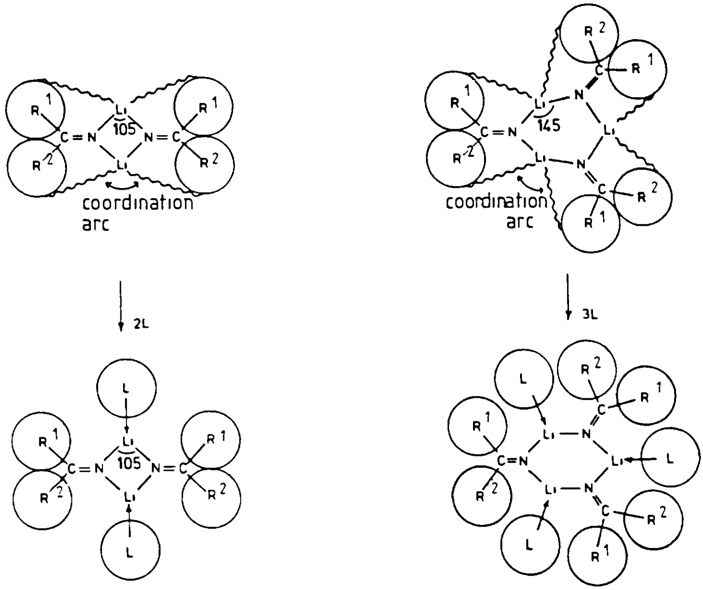

Figure 8 *The steric and geometric effects of complexing* $(\text{imido-Li})_2$ *and* $(\text{imido-Li})_3$ *rings*

Table 3 (*Imido*)*nitrogen–lithium interatomic distances* (*in* Å) *in the pseudo-cubane structure of* $(Ph_2C{=}NLi.NC_5H_5)_4$ (X-*ray diffraction data*)

Two-centre bonds		*Three-centre bonds* *Intradimer*		*Interdimer*	
Li(1)–N(111)	2.035(4)	Li(1)–N(211)	2.171(4)	Li(1)–N(411)	2.096(6)
Li(2)–N(211)	2.034(5)	Li(2)–N(111)	2.152(4)	Li(2)–N(311)	2.067(6)
Li(3)–N(411)	2.034(4)	Li(3)–N(311)	2.154(5)	Li(3)–N(211)	2.079(6)
Li(4)–N(311)	2.019(4)	Li(4)–N(411)	2.165(5)	Li(4)–N(111)	2.068(6)
Average	2.03	Average	2.16	Average	2.08

$(NLi)_3$ ring in view of its significantly smaller coordination arc (reflected by the large, internal, ring bond angle at lithium of 145°); hence, the preferred building units of *complexed* lithium imides are $(NLi)_2$ rings (with internal, ring bond angles at lithium of only 105°). That notwithstanding, (5) is still a sterically congested structure, so much so that the $C_2C{=}N$ imido planes must twist 58.6° out of their ideal orientation in the plane of the $(NLi)_2$ ring to avoid touching the HMPA ligands. It is this loss of planarity that precludes ring-stacking. To compensate for the lack of the extra connectivity that ring-stacking would provide the nitrogen–lithium ring bonds are both short [1.923(6) and 1.948(6) Å] and strong. Tri-coordination of each metal atom is completed by the oxygen donor atom of HMPA.

Imido ligands with flat phenyl substituents are not restricted by the same steric constraints as their di-t-butyl counterparts. Consequently the basic dimeric

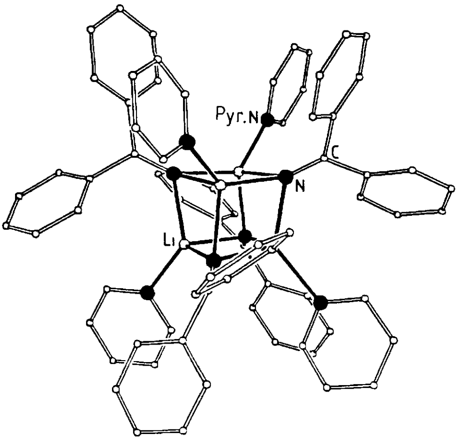

Figure 9 *Distorted cubic molecular structure of the imidolithium pyridine complex* (6)

building unit $(Ph_2C{=}NLi.NC_5H_5)_2$,[26,27] can form a stacked structure with another ring unit of the same type to give $(Ph_2C{=}NLi.NC_5H_5)_4$, (6), a pseudo-cubane structure of interpenetrating Li_4 and N_4 tetrahedra (Figure 9). The twelve N–Li cube edges have lengths that fall into three well-defined, distinct categories: four short [Li(1)–N(111), Li(2)–N(211), Li(3)–N(411), and Li(4)–N(311), mean 2.03 Å], four intermediate [Li(1)–N(411), Li(2)–N(311), Li(3)–N(211), and Li(4)–N(111), mean 2.08 Å], and four long [Li(1)–N(211), Li(2)–N(111), Li(3)–N(311), and Li(4)–N(411), mean 2.16 Å] (see Table 3). Ring-stacking theory, in viewing the cubane as made up of two identical dimeric rings, interprets the short bonds to be intradimer, two-centre links [*i.e.*, those originally two-centre in the (theoretical) isolated dimers and which remain so in the cubane-stack], the intermediate bonds to be interdimer, three-centre links [*i.e.*, the new bonds created between the two original $(NLi)_2$ rings], and the long bonds to be intradimer, three-centre links [*i.e.*, those originally two-centre in the dimers which convert into three-centre on formation of the tetramer (Figure 10a)]. Notice also that the short and long bonds alternate within the dimeric rings, while the short bonds in one dimer approximately eclipse the long bonds in the other. In this approach the stacking direction is defined as passing through faces $\overline{\text{Li(1)N(111)Li(2)N(211)}}$ and $\overline{\text{Li(3)N(311)Li(4)N(411)}}$ (Figure 10b). Treating the imido-ligands as anions $Ph_2C{=}N^-$ allows each imido-N to have two lone-pairs of electrons available for coordination to the metal atoms. These lone pairs lie in the $C_2C{=}N$ skeletal plane of the ligand (*i.e.*, in concert with sp^2 hybridization at N), so their orientations are eclipsed, in Figure 10c, by the bonds from the imido-C atom to the *ipso*-phenyl-C atoms. A metal atom [Li(3) in Figure 10c] that is eclipsed, or nearly eclipsed, by these bonds is therefore suitably positioned to form a two-centre, two-electron NLi bond to the imido-N atom, while pairs of metal atoms [Li(1) and Li(4)] that straddle the ligand plane are suitably positioned to engage in three-centre NLi_2 interactions. Pyridine, though *exo*-

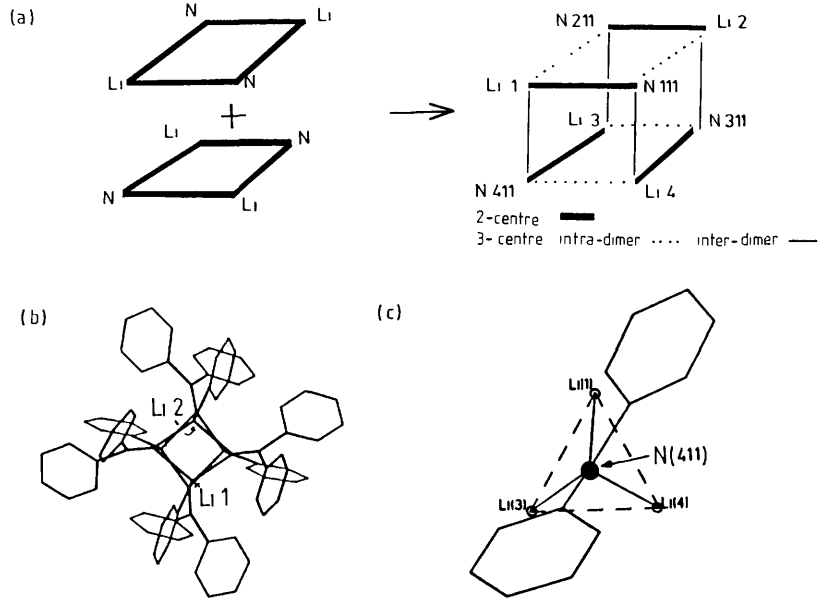

Figure 10 *(a) Classification of the* N–Li *bonds in* (6) *according to the ring-stacking treatment, (b) the stacking direction, (c) orientation of the* C_2C=N *skeletal plane over a* Li_3 *triangle*

orientated with respect to the cubane core, still influences the core-bonding as the three-centre links within each parent ring are longer and weaker than those between the rings—the reverse of the trend found in the hexameric stacked arrangements. This distinction is attributed to the increased c.n. experienced by the metal atoms upon pyridine attachment, which reduces the need for strong intramolecular association within a parent ring, and to differences in the imido-ligand orientations.

From structural considerations, the third complex (7)[25] truly deserves the epithet 'novel', being composed of discrete $[Li.(HMPA)_4]^+$ cations and $[(Ph_2C{=}N)_6Li_5.(HMPA)]^-$ anions (Figure 11). Although the ring-stacking model does not appear directly applicable in this case, it is significant that all the structural features present in (7) [*i.e.*, Li–O(HMPA) dative bonds, μ_2N–Li bridges, and μ_3N–Li pyramids] turn up (though not combined into one structure as here) in other crystalline lithium imides [*e.g.*, (1)—(6)] that can be rationalized by this approach. As alluded to earlier, the uncomplexed precursor of (7), $(Ph_2C{=}NLi)_\infty$, is thought to exist as an infinitely stacked array of six-membered $(NLi)_3$ rings; thus, a possibility is that the powerful Lewis base HMPA abstracts a metal cation from each two-tiered section of the polymeric stack to leave the penta-lithium clustered anion $[(Ph_2C{=}N)_6Li_5]^-$, which then re-organizes to accommodate the remaining HMPA molecule.

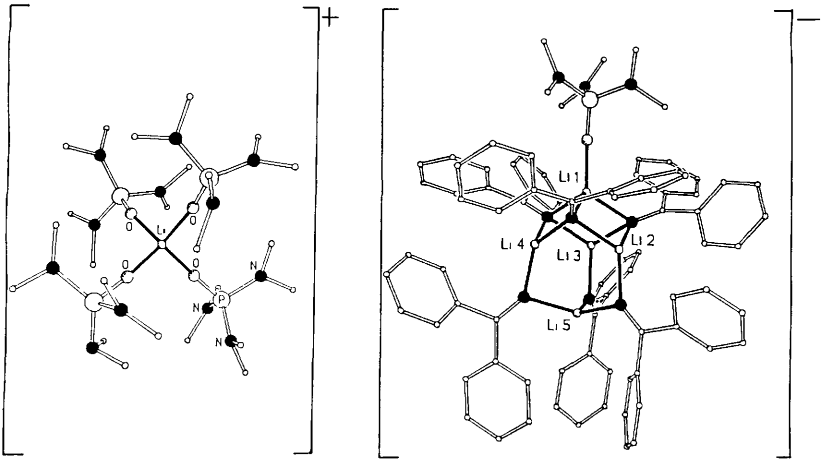

Figure 11 *Ion pairs in the lithium lithiate complex* (7)

E. Solution Studies.—Lithium organonitrogen derivatives behave as typical organolithium compounds in showing a marked tendency to engage in complicated dynamic processes in solution. We have used NMR spectroscopic studies, linked to cryoscopic relative molecular mass measurements, to probe the nature of the solution species involved in both uncomplexed and complexed lithium imide systems.

In the former category, limited arene solubility negates such studies of diaryl species so only the hexameric solids (1)—(4) have been investigated in this phase.[30,31] On the basis of cryoscopy in benzene, dissolution appears to have little effect on their hexameric constitutions with calculated *n* (the state of association) values being consistently close to 6 [range 5.9—6.1, bar a 0.03 M solution of (4) with a lower value of 5.1]. However, ^{7}Li NMR spectra recorded in [$^2H_8$]toluene over temperature and concentration ranges not accessible to cryoscopy reveal that an assortment of species actually co-exist within solutions of both compounds (2) and (3), *i.e.*, those with Me_2N substituents. Resolution of the separate resonances concerned is best achieved at temperatures as low as −105 °C. Figure 12 emphasizes both this point and the pronounced effect that dilution has on the relative abundances of the distinct lithium species present: a five-fold fall in the concentration of (2) increases the number of major signals detected from 1 to 7! Additional ill-defined peaks, apparently engaged in exchange processes, provide further complication. Nevertheless, the basic spectra can still be interpreted, albeit in qualitative terms, by applying ring-stacking ramifications that can be summarized as follows. The stacked hexamer (assigned to the one prominent signal in the concentrated solution at +0.71 ppm) breaks

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[30] D. Reed, D. Barr, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1986, 557.

[31] D. Barr, R. Snaith, R. E. Mulvey, K. Wade, and D. Reed, *Magn. Res. Chem.*, 1986, **24**, 713.

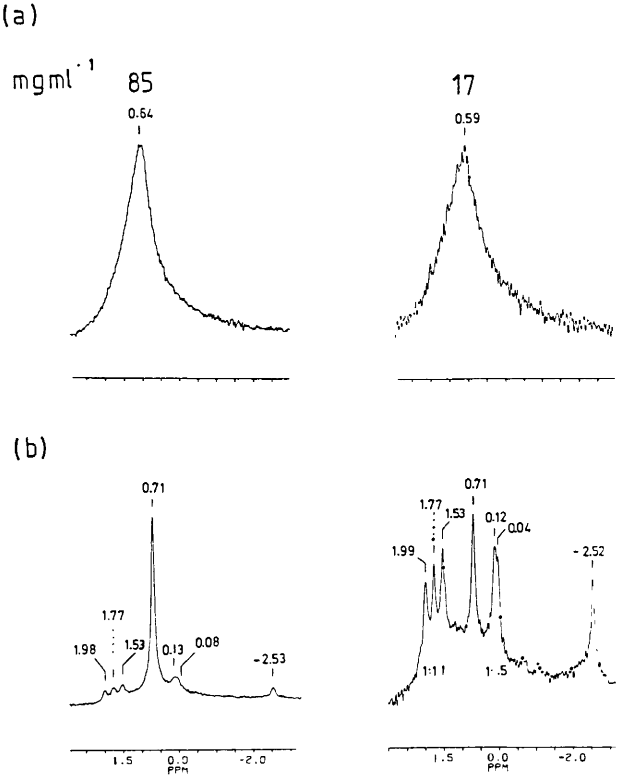

Figure 12 ^{7}Li *NMR spectra of relatively concentrated and dilute* [$^{2}H_8$]*toluene solutions of hexamer* (2), (*a*) −60 °C, (*b*) −105 °C

down at its weakest points, the intermolecular ring to ring bonds. The basic trimeric rings (assigned to the signal at *ca.* −2.5 ppm, distinct from the crowded group of signals, in the dilute solution) are released. These, in turn, re-associate to generate new higher order stacks (assigned to the two signals at +0.12 and 0.04 ppm, and to the three signals at +1.99, 1.77, and 1.53 ppm, in the respective integration ratios 1:0.5 and 1:1:1, in the dilute solution). These ratios are taken to reflect the numbers of positionally distinct trimeric rings $(R^1R^2C{=}NLi)_3$ in the higher stacked aggregates. They are consistent with a triple stack $(R^1R^2C{=}NLi)_9$, having an ABA ring arrangement (*i.e.*, A:B ratio, 1:0.5), and a sextuple stack $(R^1R^2C{=}NLi)_{18}$, having an ABCCBA ring arrangement (*i.e.*, A:B:C ratio, 1:1:1). A cogent factor in this assessment is that dilution would favour cleavage of the hexamer to give the trimer: a concomitant growth in the 'Li_3' signal, as the 'Li_6' signal diminishes, bears this out. The corresponding ^{7}Li spectra of (3) display the same general characteristics. Those of (1) and (4) do not. Over the same variable-temperature range, only one major signal is detectable in dilute solutions of each of these samples, though three minor peaks are also visible in the case of (4). Since (1)—(4) belong to the same structural family, the point is made[31] that complicated solution processes akin to those described above for (2) may be observable for both (1) and (4) on further cooling.

The solution structures generated by dissolution of the complex (Bu^t_2-C=NLi.HMPA)$_2$, (5),[27,28] are more clear-cut. Molecular weight measurements intimate that the dimeric molecules retained in benzene solution readily cleave to a monomeric form, in a dynamic process strongly dependent on concentration [*i.e.*, monomer (m):dimer (d) ratio, 2:1 (0.04 M solution) *cf.* 6:1 (0.02 M solution)]. NMR spectroscopy additionally shows that the m:d ratio, *ca.* 1:3 under the more concentrated conditions of these experiments, falls to *ca.* 1:1.4 on five-fold dilution: this can be ascertained by examining either the distinct lithium sites concerned (in the ^{7}Li spectra) or their associated t-butyl substituents (in the ^{1}H spectra) (see Figure 13—note that the order of the m and d signals depends on the nucleus being observed).

Solutions of complex (6) provide greater scope for intermolecular exchange phenomena on account of the more associated tetrameric ($n = 4$) structure of the solid.[26,27] But, two weak signals apart, its ^{7}Li NMR spectra in [$^2H_8$]toluene show similar characteristics to those of (5). Two interdependent resonances dominate. Integration ratios, *ca.* 4:1 in a relatively concentrated solution (0.41 mol dm^{-3}), switch to *ca.* 0.7:1 under more dilute conditions (0.05 mol dm^{-3}). Values of n, cryoscopically determined in benzene, range from 2.2 to 1.4 on increasing dilution. A tetramer ↔ monomer equilibrium is implied. The monomer, assigned to the NMR resonance that grows on dilution, must retain co-ordinated pyridine as the parent lithium imide ($Ph_2C{=}NLi)_n$ is polymeric and almost totally insoluble in benzene.

3 Lithium Amides Derived from Secondary Amines

A. Introduction.—Historically, Titherley's preparation of lithamide, $(LiNH_2)_n$, in 1894,[32] launched lithium amide chemistry, though due recognition must go to Gay-Lussac and Thénard for their pioneering work on the sodium and potassium congeners nearly a century earlier.[33] Since then, a variety of compounds belonging to this class have risen to prominence on account of their synthetic applicability. This section of the review deals specifically with the structural natures of the organonitrogen-metal compounds formed on replacing hydrogen by lithium in secondary amines of formula R^1R^2NH. Both R^1 and R^2 denote simple organic ligands. Other types of lithium amide, *e.g.*, functionalized ones containing *additional* electronegative N, O, or S centres (or a combination of such centres), are thus not covered here.

'Bulky' lithium amides tend to be synonymous with proton abstraction reactions because of their strong Lowry–Brønsted basicity coupled with their relatively low nucleophilicity. This latter feature gives them an advantage over

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[32] A. W. Titherley, *J. Chem. Soc.*, 1894, **65**, 504.

[33] J. L. Gay-Lussac and L. J. Thénard, 'Recherches Physicochimiques (I)', pp. 337, 341, 354, 356, Paris, 1811.

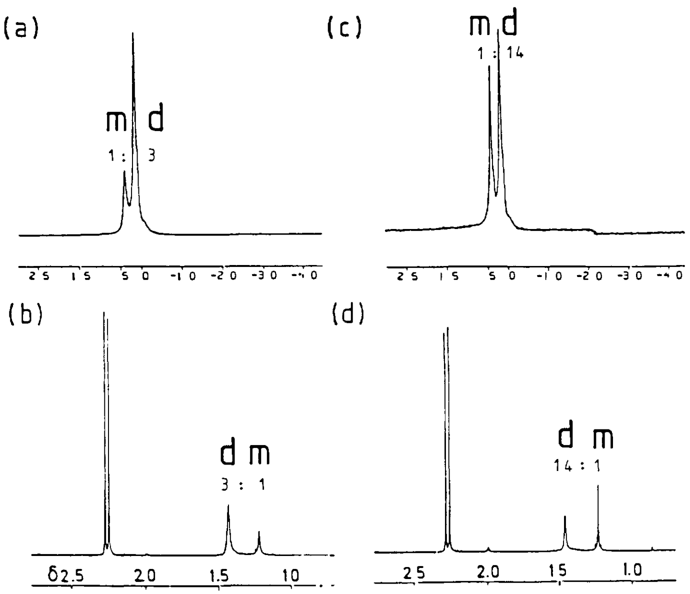

Figure 13 *NMR spectra* (25 °C, [$^2H_8$]*toluene*) of solutions of complex (5): (*a*) ^7Li, 0.25M, (*b*) ^1H, 0.25 M, (*c*) ^7Li, 0.05 M, (*d*) ^1H, 0.05 M. *Monomer* = *m*, *dimer* = *d*

C–Li reagents such as n-butyllithium or methyllithium. The leading amido-reagent in this connection, lithium di-isopropylamide (LDA), $(Pr^i_2NLi)_n$, in common with a few others, *e.g.*, lithium dicyclohexylamide $[(c\text{-}C_6H_{11})_2NLi]_n$ and lithium bis(trimethylsilyl)amide $[(Me_3Si)_2NLi]_n$, is commercially available (however, such convenience does not extend to any lithium imide compound). General information regarding the preparations and uses of lithium amides can be found elsewhere.[34–36] Aside from regioselectivity, many lithium amide reactions can exhibit stereoselectivity, so an important and developing use worthy of mention concerns their role in asymmetric synthesis, which has been discussed separately.[37]

The lithium amide compounds focused on here are generally accessible *via* lithiation of the parent mono-amine in an aromatic solvent. They can be represented by the formula $(R^1R^2NLi)_n$, or, in the additional presence of a donor co-solvent (L), by $[R^1R^2NLi.(L)_x]_n$. Considerable effort has been directed

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[34] G. B. Gill and D. A. Whiting, *Aldrichimica Acta*, 1986, **19**, 31.

[35] J. L. Wardell in 'The Chemistry of the Metal–Carbon Bond', ed. F. R. Hartley, 1987, Vol. 4, 'The Use of Organometallic Compounds in Organic Synthesis', Wiley, Chichester.

[36] L. Brandsma and H. D. Verkruijsse, 'Preparative Polar Organometallic Chemistry Vol. 1', Springer, Berlin, 1987.

[37] C. H. Heathcock in 'Asymmetric Synthesis', ed. J. D. Morrison, 1984, Vol. 3B, Academic Press, New York.

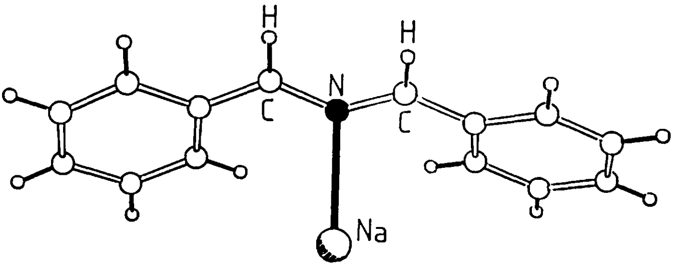

Figure 14 *Crystal and molecular structure of the mono-hapto aza-allyl sodium complex,* [PhC(H)NC(H)Ph.Na.(PMDETA)]. *The PMDETA ligand has been omitted*

towards coaxing crystals from solutions of these reagents, so that they can be properly identified (*i.e.*, to establish x and n values) and, in some cases, structurally characterized. Studies on sodium dibenzylamide, $[(PhCH_2)_2N\text{-}Na]_n$,[38,39] emphasize the wisdom in isolating such alkali metal organics. In principle, this could be employed *in situ* as a dibenzylamido transfer agent. A donor such as PMDETA is needed to effect dissolution. But examination of its crystal [by *X*-ray diffraction (Figure 14)] and of solutions of it (by NMR spectroscopy), show in fact that the 2-aza-allyl monomer [PhC(H)NC(H)Ph.Na.(PMDETA)], not the amido species, exists under these conditions. It has also been pointed out[40] that isolation can ensure reagent purity and enable pre-weighing of lithium amide solids, so giving better stoicheiometric control in reactions with substrates.

B. Fundamental Geometrical Differences between Lithium Amide and Lithium Imide Parent Rings: Ring-laddering *versus* Ring-stacking.—Associated structures in lithium amide chemistry, like their imido counterparts, are based on cyclic $(NLi)_n$ rings. But the orientations of the organic substituents emanating from the ring-nitrogens [R^1,R^2 in the former; $R^1(R^2)C=$ in the latter] are inherently different in the two cases. Approximate tetrahedral geometries at the amide N centres dictate that the R^1 and R^2 groups project above and below the $(NLi)_n$ plane (Figure 15a). In localized-bonding parlance, these N centres exhibit sp^3 hybridization. Imide N centres, on the other hand, prefer sp^2-type geometries that place the α-C units of the 'R' groups in the same plane as the $(NLi)_n$ ring, as explained in Section 2C(i). Ring-stacking (face to face association) can thus occur owing to the 'two-dimensional' nature of the parent imido rings. The antithesis is that ring-stacking is prohibited in amido ring systems because of their 'three-dimensional' nature. Nevertheless, amido rings can still 'self-associate', not face to face (vertically), but edge to edge (laterally) (Figure 15c). This type of association

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[38] P. C. Andrews, D. R. Armstrong, R. E. Mulvey, and D. Reed, *J. Am. Chem. Soc.*, 1988, **110**, 5235.

[39] P. C. Andrews, R. E. Mulvey, W. Clegg, and D. Reed, *J. Organomet. Chem.*, 1990, **386**, 287.

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

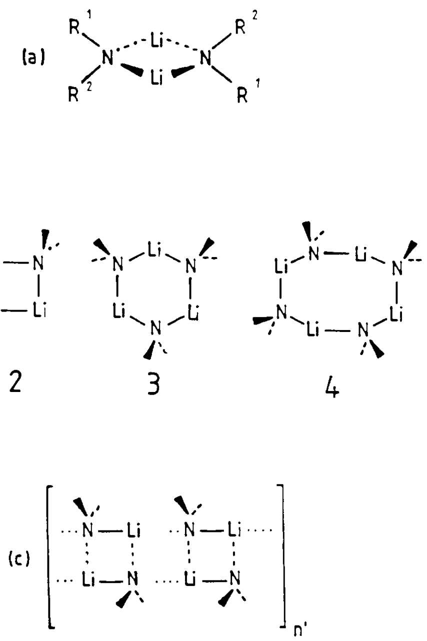

Figure 15 *Basic structural types in uncomplexed lithium amides*

has been termed *ring-laddering*.[41,42] Specific lithium amide structures are now discussed.

C. Uncomplexed Lithium Amides ($R^1R^2NLi)_n$.—This section considers the structural natures of unsolvated lithium amides.

(i) *Solid-state Structures*. Four of the five known crystal structures in this category are based on planar, singular $(NLi)_n$ rings. The exception, $[H_2\overline{C\ (CH_2)_5N}Li]_6$, (8),[43] adopts a cyclic ladder arrangement consisting of three joined $(NLi)_2$ rings and is therefore discussed with other ladders in Section 3E. Laddering is sterically prevented in the other cases. Their relatively bulky R groups occupy much of the lateral space surrounding the rings. The ring size depends on the sizes of the R groups. Lappert *et al.* have found that the large tetramethylpiperidinato anions keep apart in a tetrameric ring structure, $[Me_2\overline{C\ (CH_2)_3CMe_2N}Li]_4$, (9) (Figure 15b).[40] With less sterically demanding

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[41] D. R. Armstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1986, 869.

[42] D. R. Armstrong, D. Barr, W. Clegg, S. M. Hodgson, R. E. Mulvey, D. Reed, R. Snaith, and D. S. Wright, *J. Am. Chem. Soc.*, 1989, **111**, 4719.

[43] R. Snaith, D. Barr, D. S. Wright, W. Clegg, S. M. Hodgson, G. R. Lamming, A. J. Scott, and R. E. Mulvey, *Angew. Chem.*, 1989, **101**, 1279; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1241.

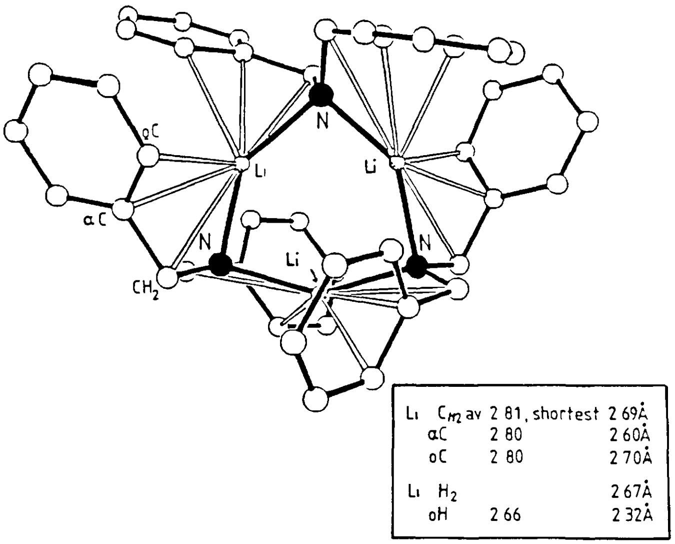

Figure 16 *Molecular structure of dibenzylamidolithium,* (10), *highlighting the close* Li•••HC *contacts*

groups, trimeric rings (Figure 15b) are the norm: $[(PhCH_2)_2NLi]_3$, (10),[44,45] $[(Me_3Si)_2NLi]_3$, (11) (Atwood *et al.*[46] and Mootz *et al.*[47]), and $[(Me_3Ge)_2NLi]_3$, (12) (Weidlein *et al.*[48]). Average NLiN ring angles (144°, 147°, and 149° respectively) are distinctly smaller than that in (9) (169°); N–Li interatomic distances, however, show little variation (1.95, 2.00, and 1.92 Å *c.f.* 2.00 Å). Compound (10) is noteworthy for displaying additional, intramolecular Li•••HC interactions. These stem from the close proximity of the lithium centres and benzyl $C(H_2)$–*ipso*-C–ortho-C(H) edges (Figure 16). Molecular orbital bond index (MOBI) calculations show that these interactions alleviate the coordinatively unsaturated nature of the metal atoms (formal c.n. 2), in constituting 40% of the total lithium valency. Related calculations probing similar Li•••HC bonding contacts in selected organolithium and lithium 'ate species have also appeared.[49]

Laddering can occur in lithium amides with relatively small or flat R^1 and R^2 groups.[41,42] Association occurs laterally by joining N–Li ring edges (Figure 15c). As in ring-stacking, the driving force behind this process is the increased c.n.

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[44] D R Armstrong, R E Mulvey, G T Walker, D Barr, and R Snaith, *J Chem Soc*, *Dalton Trans*, 1988, 617

[45] D Barr, W Clegg, R E Mulvey, and R Snaith, *J Chem Soc*, *Chem Commun*, 1984, 285, 287

[46] R D Rogers, J L Atwood, and R Gruning, *J Organomet Chem*, 1978, **157**, 229

[47] D Mootz, A Zinnius, and B Bottcher, *Angew Chem*, 1969, **81**, 398, *Angew Chem*, *Int Ed Engl*, 1969, **8**, 378

[48] M Rannenberg, H -D Hausen, and J Weidlein, *J Organomet Chem*, 1989, **376**, C27

[49] D Barr, R Snaith, R E Mulvey, and P G Perkins, *Polyhedron*, 1988, 7, 2119

experienced by the metal atoms (from 2 in the parent ring to 3 for an internal position in the ladder). Furthermore, in theory, rings primed for laddering can associate *ad infinitum* to give ladders of infinite length (*cf.* stacks of infinite height). Many unsolvated lithium amides (*e.g.*, R^1 = Ph, R^2 = Ph, naphthyl, $PhCH_2$, and Me)[44,50] share physical characteristics (*e.g.*, amorphousness, arene insolubility, high melting points >250 °C) that would be expected of such extended ladders. Although a crystal structure is still awaited, such evidence proving the existence of polymeric ladder structures can be found in a sodium amide analogue (see Section 5).

(ii) *Solution Studies.* Most uncomplexed lithium amide solids possess negligible arene/hydrocarbon solubility. Studies on such compounds in this medium are therefore very rare.

An exception is $[(PhCH_2)_2NLi]_3$, (10), one of the few oligomeric lithium amide solids.[44,45] It dissolves in arene solvents to give pink solutions. Association state values (n) in benzene, determined cryoscopically, intimate that the trimer (with $n = 3$) is in equilibrium with a lower association species. The value of n dips under 3 (2.87 for a 0.033 M solution), and falls further on dilution (2.66 for a 0.025 M solution). ^{7}Li NMR spectra concur with this interpretation in showing two distinct resonances, the weaker of which only exists under dilute conditions. Experimental electronic spectra, linked to predicted ones based on configuration interaction MO calculations, established that the secondary species is monomeric. As already noted, in the crystal structure of (10) the benzyl groups bend in towards the two-coordinate Li centres of the trimer (Figure 16). In the monomer with a one-coordinate Li centre, Li···benzyl interactions are thought to be magnified. These stronger interactions allow a charge transfer mechanism to operate, producing the solution colour (which intensifies on dilution, *i.e.*, when more monomer is present).

D. Complexed Lithium Amides $[R^1R^2NLi.(L)_x]_n$.—This section considers the structural natures of solvated lithium amides. Excluded are complexed ladder structures which are discussed separately in Section 3E.

(i) *Solid-state Structures.* Lithium amide reagents are usually generated in Lewis base (donor) solvents (L). Such polar solvents effect dissolution of the normally arene/hydrocarbon-insoluble solids. Concomitantly, the long ladder structures often break down into smaller units. To compensate the metal for the loss of bonding that occurs on de-aggregation, new dative bonds, denoted by Li.L, are formed. The smaller structures are therefore complexes of general formula $[R^1R^2NLi.(L)_x]_n$. Their degrees of association, n, are limited by the steric natures of both the R groups and the attached donor molecules (L). Reaction rates,

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[50] D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 716.

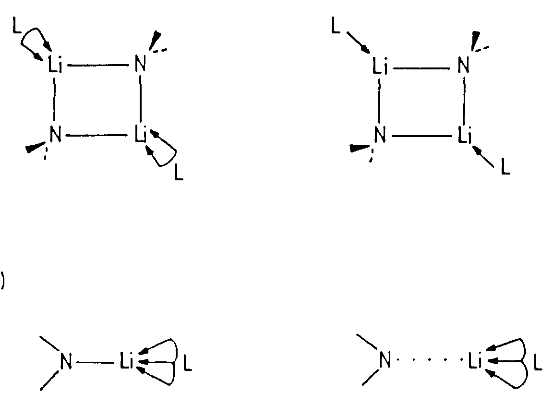

Figure 17 *General structures of (a) dimeric and (b) monomeric lithium amide complexes*

particularly metallation rates, tend to be greatly enhanced when lithium amide reagents are employed in the presence of donor solvents. It is thought that the low association states of the complexes produced have a major bearing on this increased reactivity. In some cases, solid complexes can be isolated from solution. Often they exhibit good solubility in arene/hydrocarbon media, *i.e.*, polar solvents are no longer required to bring about dissolution. Crystalline ones, successfully characterized by *X*-ray diffraction, are now discussed.

Non-ladder lithium amide complexes can be either dimeric ($n = 2$) or monomeric ($n = 1$). Identified structural options within each of these categories are shown in Figure 17. Table 4 lists key structural parameters of those complexes made in our own laboratory. A complete list of dimeric and monomeric crystal structures of this type has appeared elsewhere.[5]

Dimeric $(NLi)_2$ rings occur when the Li:L ratio is 1:1. $[(PhCH_2)_2NLi.L]_2$, L = OEt_2, (13) or HMPA, (14),[44,45] are representative of this group in having monodentate, terminally bound L molecules. HMPA can also bridge between Li^+ centres, though such bonding is rare. The two structural isomers (1A, 1B in Figure 18) adopted by $[Ph(2\text{-}Pyr)NLi.HMPA]_2$, (15),[51] exemplify this versatility. Oxygen, the donating atom of HMPA, attaches to the metal in a terminal manner in 1A, but in a bridging manner in 1B. Additional interactions with the *amido-* and *pyridyl*-N centres increase the metal c.n. to four in each isomer. It is for another reason that the Li^+ centres in $[Ph(Me)NLi.TMEDA]_2$, (16),[50] attain this same coordination state: the L molecule is bidentate. More usually, Li^+ centres within ring dimers attain c.n. of only three. Potential ways of achieving higher association, that would increase c.n., are sterically blocked.

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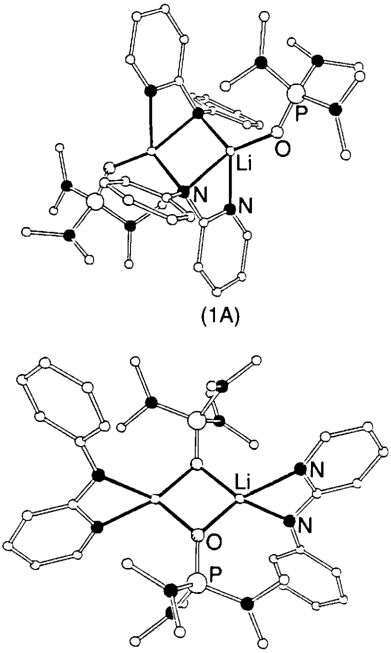
[51] D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 700.

Table 4 *Representative monomeric and dimeric lithium amide complexes: key dimensions from* X*-ray diffraction data*

Monomer	*Text number*	(amido)N–Li *distance* (Å)	Li–L^a *distances* (Å)	N–Li–N *ring angle* (°)	*Ref.*
Ph(Naphthyl)NLi.PMDETA	(20)	2.00	2.18, 2.21, 2.22	—	50
Ph(Naphthyl)NLi.TMEDA	(21)	1.97	2.12, 2.13	—	54
Ph(2-Pyr)NLi.HMPA.[Ph-(2-Pyr)NH]	(22)	2.09	2.11,^{b} 2.08,^{b} 1.82^c	—	55
Dimer					
[$(PhCH_2)_2$NLi.OEt_2]$_2$	(13)	1.98—1.99	2.01	104.0	44
[$(PhCH_2)_2$NLi.HMPA]$_2$	(14)	2.00—2.01	1.85	102.7	45
[Ph(2-Pyr)NLi.HMPA]$_2$	(15) 1A^d	2.14	2.05,^{b} 1.87^c	104.4	51
	1B^d	1.98^e	2.17,^{b} 1.92^c	—	
[Ph(Me)NLi.TMEDA]$_2$	(16)	2.08	2.30	97.6	50

^{a} L = Lewis base molecule. ^{b} Li–(*pyridyl*)N. ^{c} Li–(*HMPA*)O. ^{d} One of two structural isomers. ^{e} A terminal N–Li bond



(1A)

(1B)

Figure 18 *Molecular isomers in the crystal of* [Ph(2-Pyr)NLi.HMPA]$_2$, (15)

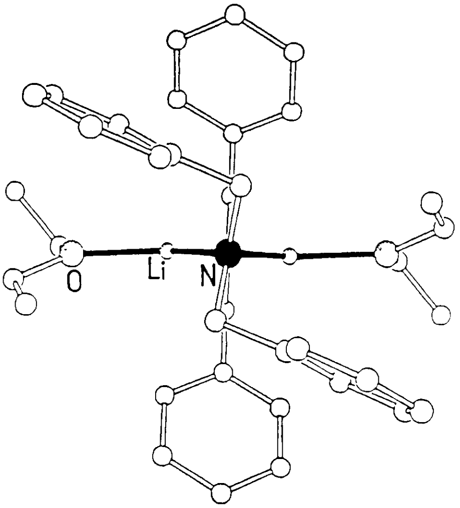


Figure 19 *Dimeric ring structure of the lithium amide ether complex,* (13), *showing the intrusion of atoms into lateral space around the ring*

Ring-stacking, for reasons stressed in Section 3B, is not an option open to lithium amides. Ring-laddering, on the other hand, can be possible, but is denied in these cases by L molecules protruding into lateral areas around the ring (Figure 19). The L molecules themselves must be offered sufficiently wide coordination arcs to 'dock' at the metal centres. Trimeric rings like that adopted by the uncomplexed analogue of (13) and (14), $[(PhCH_2)_2NLi]_3$, (10) have large, internal angles at Li (*ca.* 145°) and therefore concomitantly small external angles (the coordination arcs).[44] In contrast, in a $(R^1R^2NLi)_2$ dimer the internal ring angle at Li is expected to be *ca.* 100° {as found for gaseous $[(Me_3Si)_2NLi]_2$, (17) (Lappert *et al.*) (Figure 15b)[52]}. Hence more space is available at Li to accommodate an incoming L molecule. For the same reason, the preferred building blocks of complexed lithium *imides* are also dimeric, not trimeric, rings, as discussed earlier (Section 2D).

Monomers come in two types: contact ion pairs (CIPs) and solvent-separated ion pairs (SSIPs). The former type, each with an (*amido*)N–Li bond, are the most common. Complexes remain monomeric due to steric factors. Dimerization (or higher oligomerization) is always prevented when there are two or more monodentate L molecules per Li [*e.g.*, $Mes_2B(Ph)NLi.2Et_2O$, (18) (Power *et al.*)[53]]. This also is usual with bidentate donors [*e.g.*, $(Me_3Si)_2NLi.TMEDA$, (19)

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[52] T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 822.

[53] R. A. Bartlett, X. Feng, M. M. Olmstead, P. P. Power, and K. J. Weese, *J. Am. Chem. Soc.*, 1987, **109**, 4851.

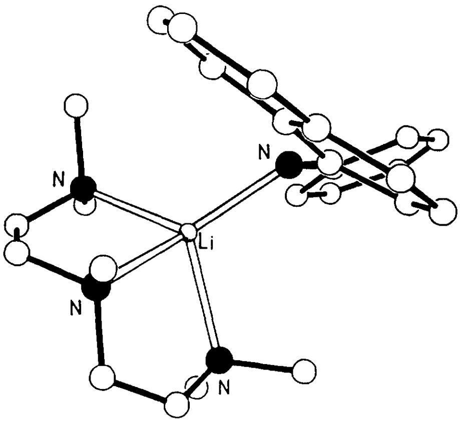

Figure 20 *Crystal structure of monomeric* (20)

(Lappert *et al.*)[54]], and is mandatory when donors have higher denticity. Even when the R groups are flat and free to rotate about the C–(*amido*)N bonds, the bulk of a tridentate donor prevents association. The structure of Ph(Naphthyl)NLi.PMDETA, (20) (Figure 20),[50] illustrates this point. Its TMEDA analogue Ph(Naphthyl)NLi.TMEDA, (21),[51] is unique in adopting a compromise structure, between that of a monomer and that of a dimer. In monomeric units the aryl groups lie in very different positions with respect to the N–Li bond, with naphthyl roughly perpendicular and phenyl roughly parallel (Figure 21a). This set-up enables two units to associate in 'slipped' vertical pairs; each unit is displaced opposite to the other (Figure 21b). Loose dimerization is thus facilitated through *intermolecular* Li•••*ortho*-C(Ph) (distance 3.12 Å) and Li•••*meta*-C(Ph) (distance 3.15 Å) contacts (*cf.* the normal situation where dimerization occurs through amido-N bridges).

The crystal structure of Ph(2-Pyr)NLi.HMPA.[HN(2-Pyr)Ph], (22),[55] is also unusual. An amine ligand with an intact N–H bond is connected to the lithium centre through an anchimeric (*pyridyl*)N-Li coordination (Figure 22). This model compound for the study of lithiation mechanisms was isolated from a mixture of Bu^{n}Li, HMPA, and *excess* amine. In 1:1:1 reaction mixtures, all the N–H bonds are converted into N–Li ones, to afford the more conventional lithium amide, $[\text{Ph(2-Pyr)NLi.(HMPA)}]_2$, (15), mentioned earlier.

Li^+ coordination spheres in SSIPs *e.g.*, $[\text{Mes}_2\text{B(Ph}_3\text{Si)N}]^-.[\text{Li.(12-Crown-4)}_2]^+$, (23) (Power *et al.*),[56] are filled exclusively by L molecules, *i.e.*, direct (*amido*)N–Li bonding is absent. This situation is extremely rare.

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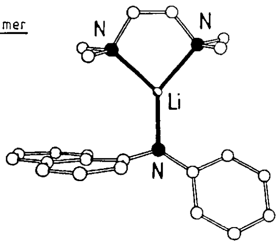
[54] J. L. Atwood, M. F. Lappert, W.-P. Leung, and H. Zhang, unpublished results.
[55] D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 469.
[56] P. P. Power, *Acc. Chem. Res.*, 1988, **21**, 147.

(a) Monomer



(b) 'Loose Dimers'

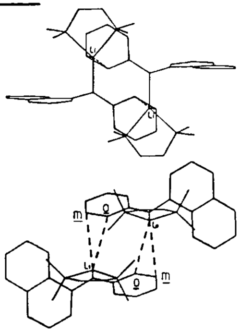


Figure 21 *Molecular structure of* Ph(Naphthyl)NLi.TMEDA, (21): (*a*) *the monomeric component,* (*b*) *loose association of these monomers into dimers,* via Li···*o*-Ph *and* Li···*m*-Ph *interactions*

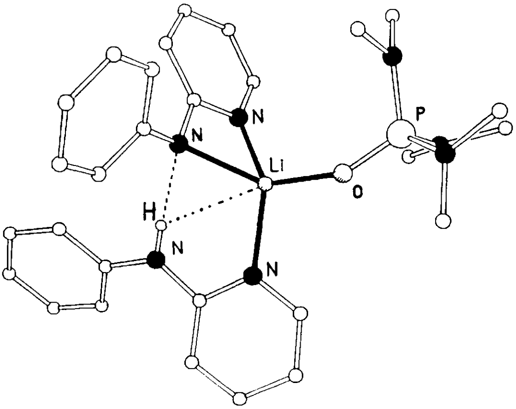


Figure 22 *A rare example of a protonated amine ligand complexing to* Li^+ *in the molecular structure of the amidolithium* Ph(2-Pyr)NLi.HMPA.[HN(2-Pyr)Ph], (22)

(ii) *Solution Studies.* A large number of groups are carrying out research in this area. The attraction is that lithium reagents operate in this medium and to understand fully their chemistry we must elucidate their solution natures. Identification of solid-state structures is of fundamental interest, but more importantly it provides a foundation from which solution information can be rationalized. Our strategy in this connection has been to link variable-concentration and -temperature NMR spectroscopic results to those from cryoscopic RMM values. Ideally, the number of solution species, and their association states (*n*), can be ascertained.

A study of the solid-state dimer $[(PhCH_2)_2NLi.OEt_2]_2$, (13), is given here to illustrate these points.[44,45] Cryoscopically determined *n* values, 1.20 and 1.07 (for benzene solutions of concentration 3.1×10^{-2} and 1.8×10^{-2} mol dm^{-3}, respectively), rule out the possibility that (13) simply remains dimeric on dissolution. Rather, a dynamic equilibrium between species of different association states is implicated. ^7Li NMR spectroscopic experiments further establish that two species are involved, as only two signals are detected. Moreover, their chemical shifts coincide with those found for the dual signals observed in the spectra of the uncomplexed $[(PhCH_2)_2NLi]_3$, (10). In solutions of (10), a trimer $\leftrightarrow$ monomer equilibrium is discernible [Section 3C(ii)]. By piecing together all this information, the solution picture of (13) becomes clear: on dissolution, the $Li.OEt_2$ bonds cleave to leave unsolvated dimers which subsequently rearrange to trimers and monomers.

E. Structurally Characterized Lithium Amide Ladders.—The concept of ring-laddering was introduced earlier in Section 3B. Evidence for the existence of extended ladder molecules followed in Section 3C(i). Here, discussion centres on three compounds identified as oligomeric ladders by *X*-ray diffraction studies: two complexed ladders and an uncomplexed type.

(i) *Solid-state Structures.* Lithiation of the cyclic amine pyrrolidine, $H_2\overline{C(CH_2)_3N}H$, affords the lithium amide $[H_2\overline{C(CH_2)_3N}Li]_n$, (24).[41,42] This is the parent compound of the crystalline complexes $\{[H_2\overline{C(CH_2)_3N}Li]_2.TMEDA\}_2$, (25), and $\{[H_2\overline{C(CH_2)_3N}Li]_3.PMDETA\}_2$, (26). Both adopt ladder structures of four (N–Li) rungs in length (Figures 23 and 24, respectively; the insets show their basic skeletons). The central rings of the ladders, N(1)Li(1).N(1′)Li(1′), and the N atoms of the outer rungs [N(2),N(2′)] are approximately co-planar, but the Li atoms of the outer rungs [Li(2),Li(2′)] straddle this plane [by 1.01 Å in (25) and 0.71 Å in (26)]. Since TMEDA and PMDETA differ in terms of denticity and steric size, complexation affects the ends of each ladder in a different way (the inner rung, three-coordinate Li atoms remain uncomplexed). In (25), each outer rung Li atom carries a bidentate TMEDA molecule and so attains four-coordination. However, the Li atoms in the same position in (26) are not complexed. Instead, they carry one additional N–Li unit, which makes them three-coordinate. It is these terminal lithium atoms

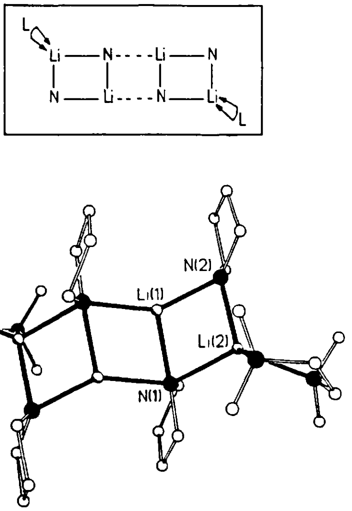


Figure 23 *Ladder molecular structure of* $\{[H_2\overline{C(CH_2)_3N}Li].TMEDA\}_2$, (25)

[Li(3),Li(3′)] that carry the PMDETA molecules. Were the terminal N–Li units outer rungs of the ladder, PMDETA tri-nitrogen complexation would render the Li atoms five-coordinate. Steric hindrance negates this possibility [*cf.* the structures of the analogous PhLi complexes: with TMEDA, a $(CLi.L)_2$ ring dimer;[57] with PMDETA, a (C–Li.L) terminal monomer;[58] (both Weiss *et al.*)]. For PMDETA to form an effective complex, an N–Li rung with a bridging Li must change into a form with a terminal Li. This restricts the c.n. of the Li atoms involved to four. Hence, (26) can be regarded as a six-runged ladder, whose two end rungs have been partially broken off to accommodate the bulky L ligands.

Bond lengths within both structures clearly illustrate that laddering is achieved by the lateral connection of two $(N–Li)_2$ rings. In the isolated rings, two N sp^3-type lobes point directly to two Li atoms to give four bonds of equal length. To effect the lateral joining of two such rings, one N lobe from each ring must move into a bridging position between two Li atoms. In this way, a new, central $(NLi)_2$ ring made up entirely of three-centre interactions is generated. Rings either side of this central one retain their original two-centre interactions (along the ladder edges). The pattern in the bond lengths expected to accompany this laddering process, three-centre ‘interdimer’ bonds being longer than two-centre ‘interdimer’ ones, is indeed that observed (Figure 25).

Bond angles in the ladder frameworks also vary. Within the central planar ring they average 108.2° at Li and 71.8° at N. But in the outer rings their sum is only

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[57] D. Thoennes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157.

[58] U. Schümann, J. Kopf, and E. Weiss, *Angew. Chem.*, 1985, **97**, 222; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 215.

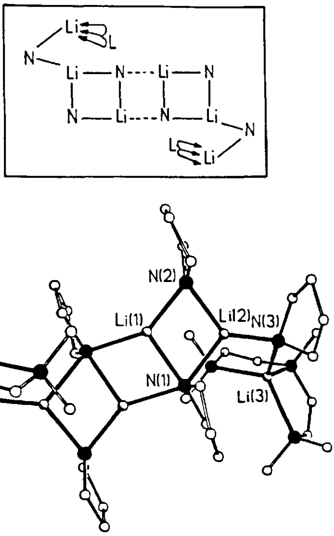

Figure 24 *Ladder molecular structure of* $\{[H_2\overline{C(CH_2)_3N}Li]_3.PMDETA\}_2$, (26)

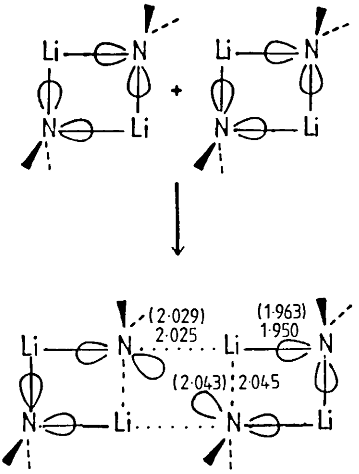

Figure 25 *Classification of* N–Li *bonds in the ladder molecules* (25) *and* (26) *according to the ring-laddering treatment; lengths in* Å *are shown with and without parentheses, respectively*

347.7° for (25) and 352.6° for (26) and there is a wider angle at the inner Li atoms (av. 105.0°) than at the outer ones (av. 99.3°). This deviation from planarity is due to the attachment of TMEDA and the NLi.PMDETA unit in (25) and (26) respectively. All-planar ladders of continuous length would be expected in the absence of such coordinating molecules. This type of ladder framework has now

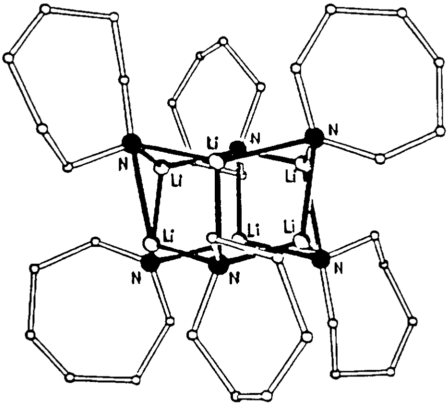

Figure 26 *Cyclic ladder molecular structure of* $[H_2C(CH_2)_5NLi]_6$, (28)

been crystallographically identified in the polymeric sodium amide (2,3,4,5-tetramethyl-1-sodiopyrrole), (27) (see Section 5). The structures of (25) and (26) provide indirect proof that their parent uncomplexed compound (24) is also a polymeric ladder. Both L molecules TMEDA and PMDETA intercept this polymeric ladder, and the latter, in doing so, causes its partial fragmentation.

Hexamethyleneimine $H_2C(CH_2)_5NH$, a higher homologue of pyrrolidine, affords the crystalline, arene-soluble amide $[H_2C(CH_2)_5NLi]_n$, (28), on lithiation. *X*-Ray diffraction studies revealed $n = 6$, making (28) the first structurally characterized uncomplexed lithium amide with $n > 4$.[43] Hexameric lithium imides achieve this aggregation state by ring-stacking [Section 2C(i)]. For steric reasons detailed earlier (Section 3B), this mode of association is inaccessible to lithium amides. Hence, a structure exhibiting ring-laddering was anticipated and indeed found for (28): not a stepped ladder like those of (25) and (26), but rather one cyclic in nature (Figure 26). Following N-orbital reorientation ideas akin to those outlined for the simpler $(NLi)_2 \times 2$ stepped ladder frameworks, an alternating set of relatively short and long bonds along edges, and medium bonds in rung positions, would be expected for cyclic ladder molecules (Figure 27). Hexameric structures interpreted in terms of two stacked trimeric rings show a quite different pattern: alternating shorter and medium length bonds are found within each ring and longer bonds between the rings [see lithium imides (1)—(4), Section 2C(i); Table 2]. Bond lengths in (28) clearly follow the first pattern (Figure 27) and its $(NLi)_6$ framework is therefore better regarded as a cyclized ladder of six (NLi) rungs, rather than as a stack of two $(NLi)_3$ ring trimers.

(ii) *Solution Studies.* The solid-state ladders $\{[H_2C(CH_2)_3NLi]_2.TMEDA\}_2$, (25), $\{[H_2C(CH_2)_3NLi]_3.PMDETA\}_2$, (26), and $[H_2C(CH_2)_5NLi]_6$, (28), can dissolve in non-polar solvents on account of their oligomeric nature. Interestingly, the

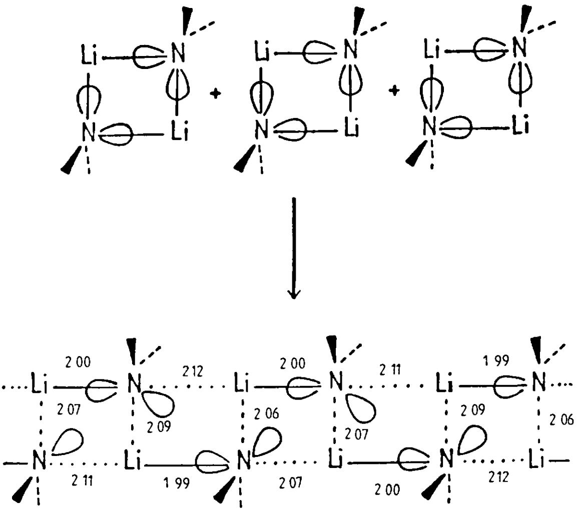

Figure 27 *Classification of* N–Li *bonds in the cyclic ladder* (28) *according to the ring-laddering treatment; lengths are in* Å

solutions produced exhibit markedly different behaviours. The chemistry involved is straightforward only in the case of (25). Concentration-dependent processes occur in the two other cases; these are most prominent, and especially complicated, in solutions of (26). Each system is now discussed in turn.

The complexed ladder molecule of solid (25) appears to remain intact in hydrocarbon solutions over the concentration range studied.[42] Association state values, *n*, determined cryoscopically in benzene, consistently approach the solid-state value (2) over a spread of concentrations (2.02 ± 0.06 and 2.10 ± 0.06 for solutions of 3.4×10^{-2} and 9.0×10^{-2} mol dm^{-3} concentrations, respectively). Furthermore, the ^{7}Li NMR spectra of [$^{2}H_{8}$]toluene solutions at −95 °C all exhibit essentially just two resonances, though both are relatively broad. In the corresponding ^{6}Li (natural abundance) NMR spectra, better signal definition allows more accurate integration measurements. Since the 1:1 ratio obtained matches that expected for the solid-state ladder, the signals can be assigned to Li inner rung and outer rung environments.

Cryoscopic and NMR spectroscopic results from solutions of the second complexed ladder (26) present a more challenging problem.[41,42] Values of *n* in benzene, initially low (1.77 ± 0.12), steadily rise until peaking at 6.5 ± 0.31, then fall again (5.26 ± 0.32) on increasing the concentration from 2.0×10^{-2} to 6.5×10^{-2} and finally to 8.0×10^{-2} mol dm^{-3}. This fluctuation is thought to stem from the PMDETA ligands, amending their role from tridentate within each ladder to bi- or even mono-dentate {its ambidentate nature has recently been demonstrated in the crystal structure of the sodium amide [Ph(2-Pyr)NNa.-PMDETA]$_2$, (29), Section 5}. Donor nitrogen atoms dangling free from such 'partially attached' ligands are thus available to complex to Li$^+$ centres in other

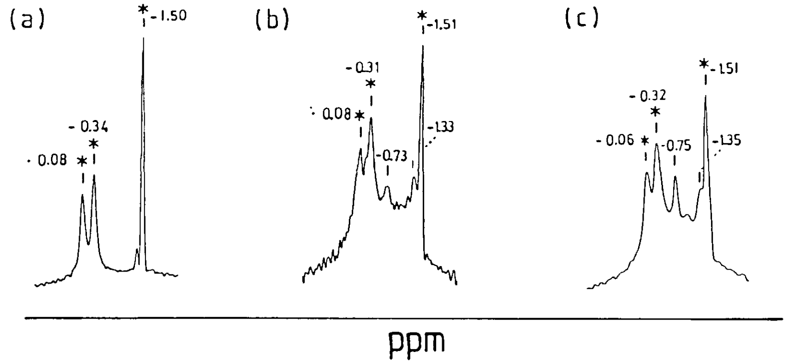

Figure 28 *Variable concentration* ^{7}Li NMR *spectra of* [$^2H_8$]*toluene solutions of the ladder molecule* (26)*:* (*a*) 1.8×10^{-1} mol dm^{-3}, (*b*) 9.0×10^{-2} mol dm^{-3}, (*c*) 4.0×10^{-2} mol dm^{-3}

ladders. Molecules with x ladder units (when $x = 1$, $n = 2$ as in the solid-state structure) giving n values of 4 ($x = 2$), 6 ($x = 3$) ... *etc*., could then result. Both processes are concentration dependent, but PMDETA amendment is encouraged under more dilute conditions, whereas association of resultingly coordinatively unsaturated ladders is favoured by more concentrated conditions. Variable concentration ^{7}Li NMR spectra of [$^2H_8$]toluene solutions at −95 °C are consistent with this interpretation. Three signals of equal integral are found for solutions more concentrated than those employed in the cryoscopic experiments (Figure 28a). These can be assigned to the three Li environments of the intact dimeric ladder (see Figure 24); at this high concentration, PMDETA amendment is suppressed. At an intermediate concentration, a clutter of new signals appears, though the three signals (asterisked) attributed to dimeric (26) can still be identified (Figure 28b). Further dilution causes the signals to merge into an indistinguishable mass. However, under even more dilute conditions, the three aforementioned signals re-emerge (*i.e.*, the dimeric ladder structure again dominates) (Figure 28c). This final observation is central to the interpretation as at very low concentrations the joining of ladders would be suppressed even though ligand amendment could still occur.

As noted above, the presence of the L ligand is fundamental to the concentration dependency of solutions of (26). Compound (28), $[H_2\overline{C(CH_2)_5N}Li]_6$, is unsolvated, yet its solution chemistry is also concentration dependent.[43] On the basis of cryoscopy in benzene, higher aggregates than the hexamer ($n = 6$; the association in the solid state) are implicated. Values of n as large as 10.1 ± 0.5 (for a 0.14 M solution) have been recorded. Lower values are obtained on dilution (*e.g*., 5.4 ± 0.2 for a 0.06 M solution). A relatively dilute [$^2H_8$]toluene solution gives two sharp singlets (ratio 1:1) in the ^{7}Li NMR spectrum. Gradually increasing the concentration causes the growth of the higher field resonance and the diminution of the second one. Eventually, at very high concentrations, the higher field resonance is the only one present. Presumably, this corresponds to an aggregate with $n > 6$, while the other signal belongs to the cyclic hexamer.

4 Ring-stacking and Ring-laddering: General Applications to Lithium Structural Chemistry

The architecture in all lithium organic derivatives is primarily dictated by the need of the polar Li^+ cations to attract as many negative centres (anions) or negative poles (polar ligands) as possible. Often the metal is encapsulated within a tetrahedron (or pseudo-tetrahedron) of such centres. The Li^+ centres are thus four-coordinate. However, the preponderance of such structures does not arise because lithium has a natural tendency to attain four-coordination (*i.e.*, in valence-bond parlance, to satisfy the 'octet rule' by involving its four sp^3 orbitals in bonding), as is often stated in the literature. Rather, since electrostatic forces dominate their structures, the maximum number of metal–ligand contacts will prevail. But steric factors (van der Waals repulsions between ligands) compete, and limit the number of such contacts. Bulkier ligands tend to restrict c.n. to less than four: there are many examples of structures with two- or three-coordinate Li^+ centres. Less sterically demanding ligands can give even higher c.n. than four: a significant number of crystal structures feature such coordinatively rich Li^+ centres. We have shown that Li^+ centres in imides and in amides can increase their c.n. by forming $(NLi)_n$ rings which can then stack (in imides) or ladder (in amides). Ring-stacking and ring-laddering therefore provide means by which coordinatively unsaturated NLi molecules [the basic $(NLi)_n$ rings] can associate to maximize electrostatic interactions.

Other types of lithium compound with ligands orientationally compatible to these organonitrogen ones also exhibit ring-stacking and ring-laddering phenomena. An impressive number come into this category. Examples are known where lithium is bound to carbon-, phosphorus-, oxygen-, sulphur-, or halogen-centres. A representative sample is given here to illustrate the principles involved (another review gives a complete survey[5]). Crystal structures exhibiting ring-stacking, which significantly outnumber those exhibiting ring-laddering, are discussed first.

A. Ring-stacking in other Types of Lithium Compound.—In lithium imides the steric criterion for ring-stacking is that the $C^1(C^2)C{=}N$ units are essentially coplanar with the $(NLi)_{2,3}$ rings (Figure 29, inset). Compatible stereochemistries occur in a series of organolithium ring systems involving alkynyl ($RC{\equiv}C^-$), alkoxy/aryloxy (RO^-), and enolato [$RC(=CH_2)O^-$] anions [Figure 29a, b, c]. Rings need not necessarily be dimeric (as pictured); trimers are also common. The ring size depends largely on the bulk of the anion, *i.e.*, the size of the R substituents. However, the stereochemistry of the anion–lithium attachment remains fixed, irrespective of ring size variations. Aryl and alkyl anions in $(CLi)_{2,3}$ ring systems (Figure 29d, e) have more flexibility than the other anions mentioned. Their α-C^- centres each offer just one lobe, of pseudo-cylindrical symmetry, for ring bonding. For this reason, R groups *exo*-orientated from the

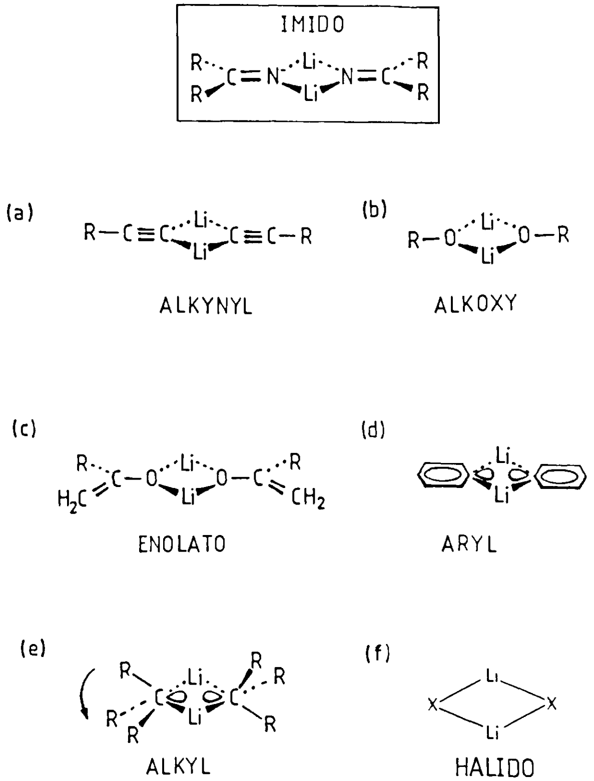

Figure 29 *Lithium ring systems compatible or pseudo-compatible, in stereochemical terms, to* (imido-Li)$_n$ *rings*

rings have scope for rotation without detrimentally affecting the strength of ring bonding. Several orientations can thus be assumed, but the preferred one will be that which most favours ring-stacking (*i.e.*, with stereochemistries resembling, as closely as possible, those of imido ligands). Lithium ring systems ideal for stacking are not confined to those with organic based anions. Atomic anions such as halides, Hal$^-$, perfectly fulfil both the electronic and steric requirements in having high charge densities and no substituents *exo* the ring (Figure 29f). Key examples covering each type of anion are now presented.

The most widely known organolithium crystal structure is probably that of methyllithium, (30), (Weiss *et al.*).[59] Its pseudo-cubane tetrameric structure (Figure 30a) can be classified as a stack of two $(MeLi)_2$ dimeric rings. The small size of the anion permits the close packing of cubes in the lattice. Each cube is

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[59] E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, 1964, **2**, 197; E. Weiss and G. Hencken, *J. Organomet. Chem.*, 1970, **21**, 265.

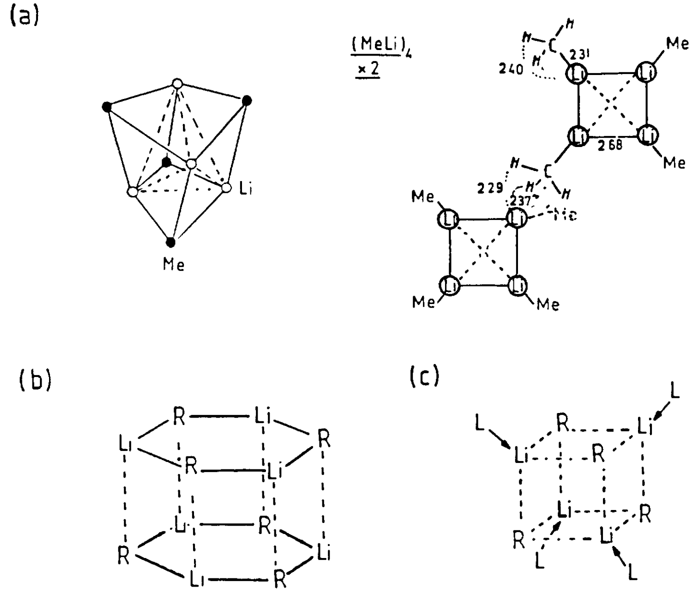

Figure 30 *Examples of stacked structures based on* $(CLi)_{2,3}$ *ring systems:* (*a*) MeLi, (30); (*b*) $(c\text{-}C_6H_{11}Li)_6$, (31), R = $c\text{-}C_6H_{11}$; (*c*) $(PhLi.OEt_2)_4$, (32), R = Ph, L = OEt_2

positioned so that its three-coordinate Li corners can interact with CH_3 corners of a neighbouring cube. This is an example of *inter*molecular Li•••HC bonding {*cf.* the *intra*molecular type in the lithium amide (10) [Section 3C(i)]}. Methyllithium is insoluble in hydrocarbon solvents on account of the three-dimensional network produced by this bonding. Uncomplexed alkyllithiums with larger anions are hexamers, *e.g.*, $(c\text{-}C_6H_{11}Li)_6$, (31) (Stucky *et al.*);[60] these are stacks of two $(RLi)_3$ trimeric rings (Figure 30b). In contrast, no uncomplexed *oligomeric* aryllithium species are known. An examination of Figure 29d shows why—the aryl anions can be co-planar with the $(CLi)_{2,3}$ rings. Rings of this ilk can therefore stack indefinitely, so extended stack structures are predicted. Significantly, the simplest aryllithium, phenyllithium, exhibits the same characteristics as polymeric lithium imide stacks [Section 2C(ii)]: amorphousness and hydrocarbon-insolubility. Complexing (L) solvents can break down extended stack structures. Ether reduces phenyllithium to an isolated cubane-type stack $(PhLi.OEt_2)_4$, (32) (Power *et al.*) (Figure 30c).[61] The largest oligomeric organolithium stack yet identified belongs to an alkynyllithium species. Dodecameric $[(Bu^tC{\equiv}CLi)_{12}.(THF)_4]$, (33) (Schleyer, Weiss *et al.*) boasts six-fold

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[60] R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, 1974, **96**, 6048.

[61] H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 5320.

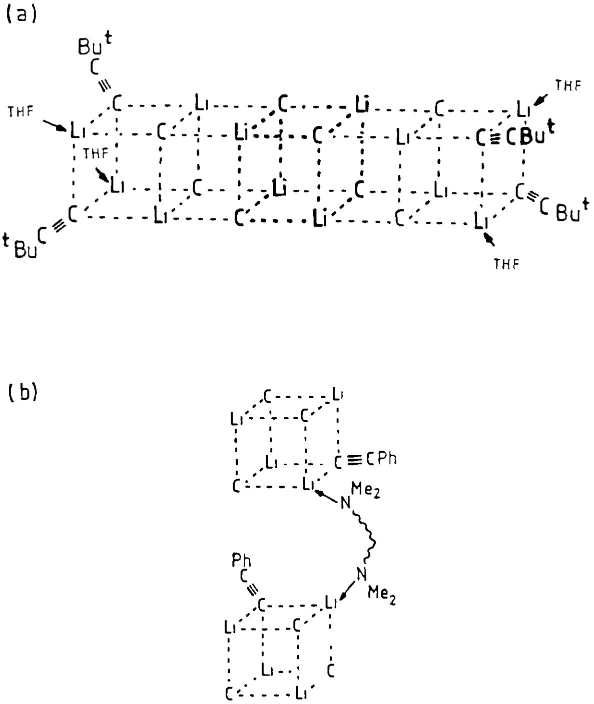

Figure 31 *Selected stacked structures in alkynyl-Li chemistry* (*a*) *dodecameric* (33), (*b*) *pseudo-tetrameric* (35)

stacking of $(CLi)_2$ rings, terminated by L molecules (Figure 31a).[62,63] The deficiency of THF molecules (Li:L ratio, 3:1) is critical to its construction. Addition of more THF (Li:L ratio, 1:1) reduces the structure to a two-fold stack, $(Bu^tC{\equiv}CLi.THF)_4$, (34) (Schleyer, Weiss *et al.*),[62,63] similar to the cubane of (32). The structure of $(PhC{\equiv}CLi)_4.(TMHDA)_2$, (35) (Weiss *et al.*) consists of two such cubic tetramers linked by the N-head and N-tail of the snake-like L ligand TMHDA (Figure 31b).[64] In this case the complexing atoms belong to an 'external' L molecule. 'Internal' complexing sources, *i.e.*, donor centres which are part of the anion moiety, are also known. Tetrameric (36), $[Bu^t_2Si(NH_2)OLi]_4$ (Klingebiel *et al.*),[65] illustrates this point (Figure 32a). Although it exhibits dative

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[63] M Geissler, J Kopf, B Schubert, E Weiss, W Neugebauer, and P v R Schleyer, *Angew Chem*, 1987, **99**, 569, *Angew Chem*, *Int Ed Engl*, 1987, **26**, 587

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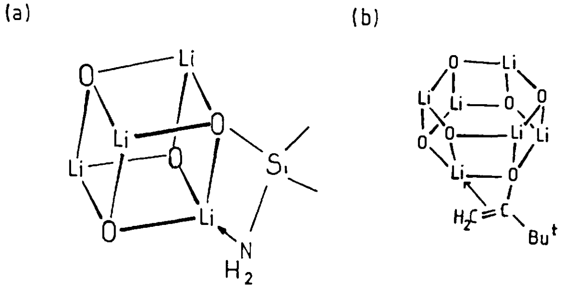

Figure 32 *Selected stacked structures in oxyanion* Li *chemistry:* (*a*) *the 'internal' complex* (36), (*b*) *the* π*-bonded complex* (37)

Li.N bonding it is not a complex in the normal sense, since no (external) L molecules are present. The nitrogen atom attached to the silyl group does the complexing. This ability to complex from an internal position is not confined to atoms with lone pairs. Unsaturated groups can do likewise. For example, each $C{=}CH_2$ unit in the lithium enolate $[Bu^tC({=}CH_2)OLi]_6$, (37) (Williard *et al.*), appears to π-bond to Li (Figure 32b).[66,67] This feature precludes further stacking. Ring-stacking can also occur in mixed-anion systems. For example, in $[(PhLi.OEt_2)_3.LiBr]$, (38) (Power *et al.*), two different four-membered rings make up the distorted-cubane structure (Figure 33a).[61] Three of its Li^+ cations are four-coordinate (those complexed by Et_2O); the unique three-coordinate Li^+ cation is the one bound exclusively to three Ph^- anions. Structure (38) can be viewed as a complexed organolithium cubane from which one RLi.L unit has been removed and replaced by a lithium halide molecule [*cf.* the structure of (32); Figure 30c]. Another cubane, $(LiCl.HMPA)_4$, (39), (Figure 33b) is made up entirely of Li^+, Hal^- ion pairs.[26,68,69] Here, two $(LiCl)_2$ ring dimers stack. The metal coordination sites *exo* the core are filled by HMPA ligands. *Laddering* as well as further stacking is precluded by their presence. Uncomplexed $(LiHal)_2$ rings are perfectly set up to both stack and ladder. The three-dimensional 'rock-salt' lattices they adopt can therefore be classed as composite continuous-stack and continuous-ladder structures.

B. Ring-laddering in other Types of Lithium Compound.—Crystal structures of lithium compounds exhibiting laddering are scarce (*cf.* the rich collection of stacks). This reflects the paucity of lithium ring systems that have a stereochemistry akin to that of lithium amides, $(R^1R^2NLi)_n$. Only three lithium amide ladders [(25), (26), and (28)] have been crystallographically identified. However, laddering is thought to be general in this class for relatively small or flat R^1 and

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[67] P. G. Williard and G. B. Carpenter, *J. Am. Chem. Soc.*, 1986, **108**, 462.

[68] D. Barr, R. Snaith, D. S. Wright, R. E. Mulvey, and K. Wade, *J. Am. Chem. Soc.*, 1987, **109**, 7891.

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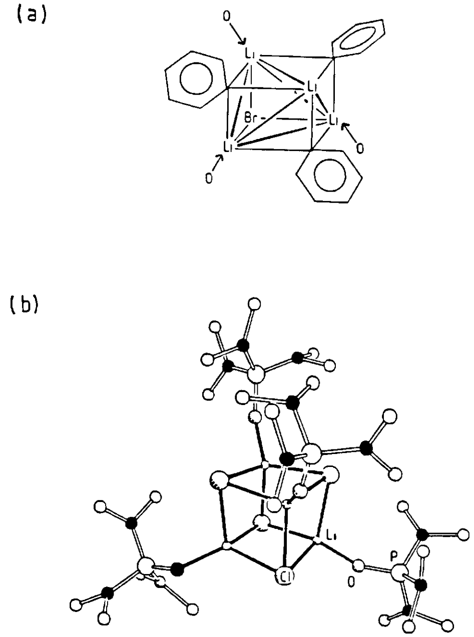

Figure 33 *Selected stacked structures involving halide anions:* (*a*) *the mixed organo-bromo-lithium aggregate* (38), (*b*) *the lithium chloride* HMPA *complex* (39)

R^2 substituents. Long ladders of indeterminate lengths are formed. Full characterization has so far proved elusive on account of their amorphous nature.

Lithium phosphide rings, $(R^1R^2PLi)_n$, do belong to the same select stereochemical family as $(R^1R^2NLi)_n$ ones. The projection of the R^1PR^2 planes perpendicular to the $(PLi)_n$ ring plane prohibits ring-stacking. Figure 34a illustrates this point through the crystal structure of dimeric $(Ph_2PLi.TMEDA)_2$, (40).[70] On the other hand, this set-up can facilitate laddering. The bulk of the bidentate L ligands prevent this possibility in complex (40) (Figure 34b). But it is realised in the complexes $[(Me_3Si)_2PLi]_4.2THF$, (41) (Lappert *et al.*)[71] and $(Bu^t_2PLi)_4.2THF$, (42) (Jones *et al.*).[72] Their common ladder framework is essentially planar and of four PLi rungs in length (Figure 35a). Monodentate L ligands, one on each end Li^+ cation, prevent further laddering. In principle, removal of the L ligands would give continuous ladder structures (Figure 35b). This type of structure has been proposed for $(Ph_2PLi)_\infty$, (43),[70] the uncomplexed analogue of (40).

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[70] R. E. Mulvey, K. Wade, D. R. Armstrong, G. T. Walker, R. Snaith, W. Clegg, and D. Reed, *Polyhedron*, 1987, **6**, 987.

[71] E. Hey, P. B. Hitchcock, M. F. Lappert, and A. K. Rai, *J. Organomet. Chem.*, 1987, **325**, 1.

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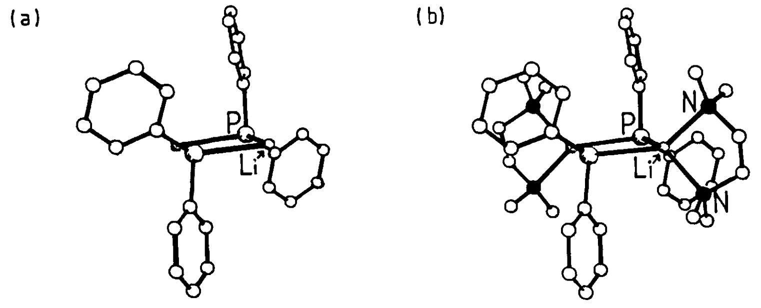

Figure 34 *Crystal and molecular structure of* $(Ph_2PLi.TMEDA)_2$, (40), *shown with* (*b*) *and without* (*a*) *TMEDA*

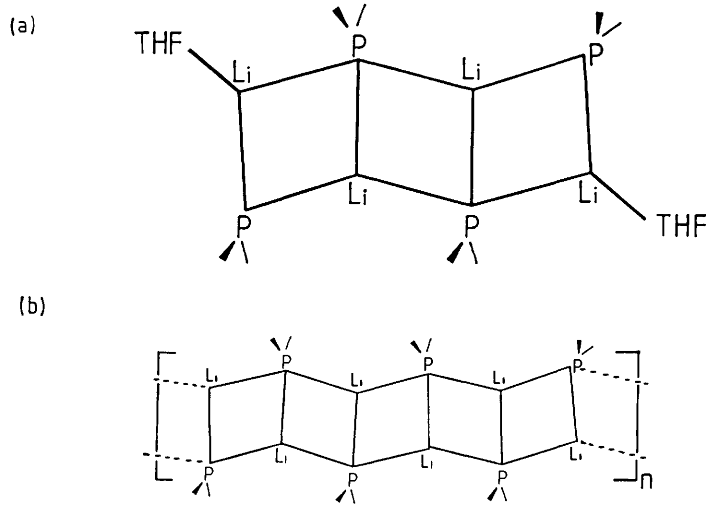

Figure 35 *Limited-length ladders* (*a*) *and extended-length ladders* (*b*) *in phosphidolithium chemistry*

5 Sodium Amides and Sodium Imides: Structural Links with Stacks and Ladders of Lithium Congeners

Relatively few crystal structures of heavier alkali metal organic derivatives are known (*cf.* the extensive library of organolithiums). Those available pre-1987 have been reviewed (by Schade and Schleyer[73]). Structural studies on sodium amides and sodium imides are particularly meagre in quantity. However, over the past year or so this area has begun to prosper. Similarities to stacking and laddering aspects of lithium chemistry have already been established. These form the basis of this final section.

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[73] C. Schade and P. v. R. Schleyer, *Adv. Organomet Chem*, 1987, **27**, 169

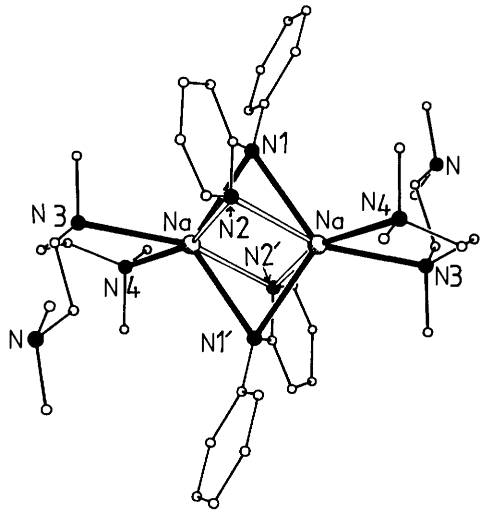

Figure 36 *Molecular structure of a representative sodium amide dimer* $[Ph(2\text{-}Pyr)NNa \; PMDETA]_2$, (29)

A number of sodium amide complexes $(R^1R^2NNa \; L)_n$ share the same dimeric ($n = 2$) structural type, *e g*, $(N\text{-sodioindole} \; TMEDA)_2$, (44), and $(N\text{-sodioindole} \; PMDETA)_2$, (45) (both Schleyer, Weiss *et al*),[74] $\{Bu^t[F(Bu^t_2)Si]NNa \; THF\}_2$, (46) (Stalke *et al*),[75] $[Ph(2\text{-}Pyr)NNa \; PMDETA]_2$, (29)[76] Each displays a planar $(NNa)_2$ ring with R groups projected above and below this plane these are isostructural with lithium amide $(NLi)_2$ rings (see Figure 17a) Bond lengths within the rings reflect the larger Na^+ radius (*cf* Li^+ radius) being generally *ca* 0 5 Å longer Hence N–Na bonds are weaker than corresponding N–Li ones But the larger and more polar cation can attract more electronegative centres Attached R groups occupy *transoid* positions (*i e*, R^1 and R^1 lie on opposite sides of the ring plane) The structure of (29) (Figure 36) illustrates all of these points Its Na^+ cations interact with six N centres [two amido N(1) and N(1′), two pyridyl N(2) and N(2′), and two from PMDETA N(3) and N(4)] PMDETA is usually a tridentate donor Its bidentate role here is sterically imposed Complexes (44), (45), and (46), exhibit Na^+ cations with c n of six, five, and four, respectively This sequence reflects the increasing steric demands of their anion/ligand combinations Laddering, not stacking, is feasible for $(NNa)_2$ rings in view of their kinship with $(NLi)_2$ rings Complexation by L molecules rules out this possibility in the cases above But a ladder structure has been

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[74] K Gregory, M Bremer, W Bauer P v R Schleyer N P Lorenzen J Kopf and E Weiss *Organometallics* 1990, **9** 1485

[75] U Pieper, D Stalke, S Vollbrecht, and U Klingebiel, *Chem Ber*, 1990, **123** 1039

[76] P C Andrews, W Clegg, and R E Mulvey, *Angew Chem*, 1990 **102** 1480, *Angew Chem Int Ed Engl*, 1990, **29**, 1440

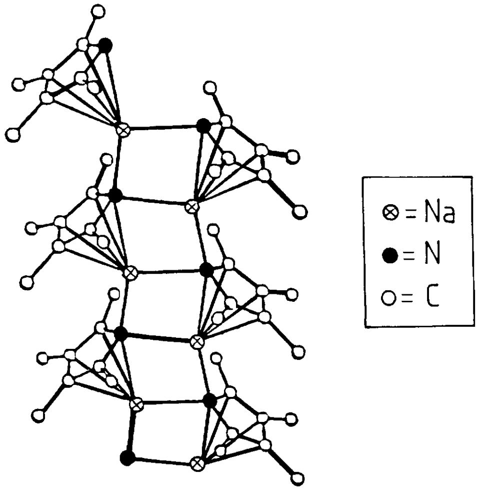

Figure 37 *The polymeric ladder structure of the uncomplexed sodiopyrrole,* (27)

identified for the uncomplexed sodium amide (2,3,4,5-tetramethyl-1-sodiopyrrole), (27) (Kuhn *et al.*).[77] Significantly, its anion is a five-membered cyclic ring [a pyrrole derivative *cf.* the pyrrolidine anions of the intercepted lithium ladders (25) and (26) (Section 3E)]. In the absence of complexing L ligands, lateral association can occur indefinitely, so a continuous ladder is produced (Figure 37). Its framework is essentially planar. With respect to N, the Na^+ cations are merely three-coordinate. However, additional interactions with the π-systems of the pyrrole rings render them seven-coordinate. Each pyrrole anion is thus penta-hapto bonded to one particular Na^+ cation and mono-hapto bonded (through N) to two others. Overall, this structure is a landmark as it provides crystallographic proof of the existence of a basic structural type predicted by ring-laddering theory, namely, polymeric ladders.

Sodium imide structural chemistry is at an even earlier stage of its development. Smith and Bergstrom reported the synthesis of the first sodium imide, an impure form of $(\mathrm{Ph_2C{=}NNa})_n$, over fifty-five years ago.[78] Since then, only one such species, $[(\mathrm{Bu^t_2C{=}NNa})_4.(\mathrm{HN{=}CBu^t_2})_2]$, (47), has been structurally characterized.[79] Two bimetallic imido crystal structures are also known. Complex $\{[(\mathrm{Me_2N})_2\mathrm{C{=}N}]_4\mathrm{LiNa_3}.(\mathrm{HMPA})_3\}$, (48) is rich in sodium, while uncomplexed $\{[\mathrm{Ph(Bu^t)C{=}N}]_6\mathrm{Li_4Na_2}\}$, (49), is rich in lithium.[80,81] The reasons for their

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[77] N. Kuhn, G. Henkel, and J. Kreutzberg, *Angew. Chem.*, 1990, **102**, 1179; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1143.

[78] G. E. P. Smith and F. W. Bergstrom, *J. Am. Chem. Soc.*, 1934, **56**, 2095.

[79] R. E. Mulvey, W. Clegg, and M. MacGregor, unpublished results.

[80] W. Clegg, R. E. Mulvey, R. Snaith, G. E. Toogood, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1986, 1740.

[81] D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1989, 57.

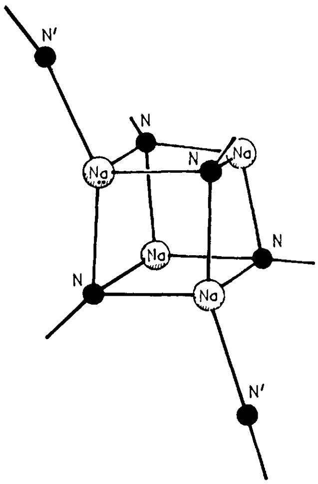

Figure 38 *Molecular structure of* [$(Bu^t_2C{=}NNa)_4.(HN{=}CBu^t_2)_2$], (47)*:* N′ *denotes protonated imine-nitrogen centres*

conflicting stoicheiometries (1:1, Li:Na ratios were used in the reaction mixtures) have not yet been ascertained.

All three crystal structures exhibit stacking. In all-sodium (47), two dimeric $(NNa)_2$ rings stack to form a tetramer (Figure 38). Imine (L) molecules complex to only two of the four Na^+ centres causing the $(NNa)_4$ core to be markedly distorted from cubic. Protonated ketimine molecules, as here, have never before been noted as L ligands to alkali metal cations [*cf.* the protonated *amine* bound to lithium in the amide (22)]. Only preliminary studies have been conducted on the synthetic route to (47) *via* PhNa and $Bu^t_2C{=}NH$ reactants. 1:1 mixtures appear to afford the same L complexed product, so the composition of (47) may not be stoicheiometrically controlled. The structure of the monolithium–trisodium complex (48) is also based on a cubanoid core.[80] Here, stacking involves a $(NNa)_2$ ring with a (NLiNNa) one (Figure 39a). The asymmetry in the $(NM)_4$ tetrameric core, a consequence of the presence of one unique metal cation (Li^+), negates an analysis of the N–M bond lengths similar to that carried out for the lithium imides (1)—(4) and (6). Interestingly, complexation is restricted to the three larger Na^+ centres. Short Li•••HC distances appear to signify that the Li^+ cation gains compensation for the lack of a L(HMPA) molecule by interacting with methyl groups on the $(Me_2N)_2C{=}N–$ substituents. A new stacking option is revealed in the final structure (49).[81] Four-membered $(NM)_2$ rings occupy the tiers of a triple stack (Figure 39b). Significantly both sodium cations sit preferentially in the central ring. It is this arrangement that facilitates three-fold stacking. The longer N–Na bonds (*cf.* N–Li ones) projecting perpendicularly from the central ring allow stacking on either side to a $(NLi)_2$ ring. $Ph(Bu^t)$ units between tiers are further apart than they would be in an $(NLi)_2$ × 3 stack.

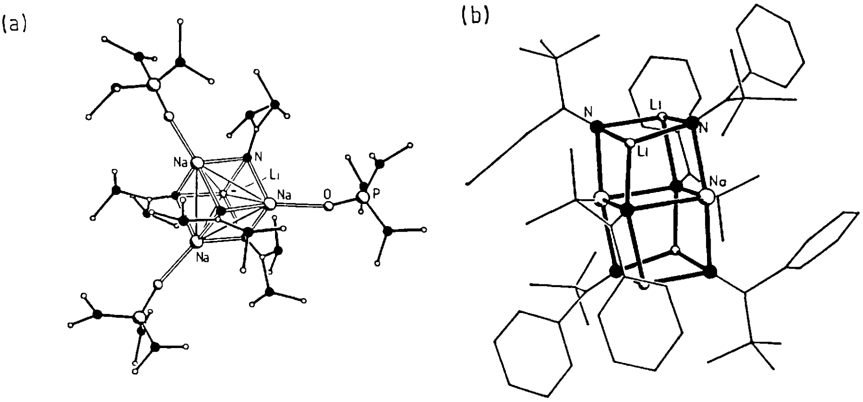

Figure 39 *Two-fold and three-fold stack structures in mixed alkali metal aggregates* (*a*) $\{[(Me_2N)_2C{=}N]_4LiNa_3.(HMPA)_3\}$, (48), (*b*) $\{[Ph(Bu^t)C{=}N]_6Li_4Na_2\}$, (49)

Consequently, steric repulsions would be considerably greater in the lithium case, which is why stacking is limited to two tiers in the crystal of $[Ph(Bu^t)C{=}NLi]_6$, (1) (see Section 2C). Uncomplexed sodium imides, for similar reasons, may adopt polymeric stack structures. Many more experiments need to be performed before sodium imide structural chemistry can be made intelligible; it is envisaged that further ramifications of ring-stacking theory will unfold along the way.

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