Structures and Reactions of 1,3-Diamidodilithium Complexes: the Hemisolvated *l*-[$CMe_2\{CHMeN(R)\}_2Li_2\cdot OEt_2$], the Unsolvated 1:1 Mixed Organo-amidolithium *u*-[$CMe_2\{CHMeN(R')\}_2\cdot Li_2\cdot(nBuLi)_2$], and the Product of Oxidative Ring Closure, the Pyrazolidine *l*-[$(RNCHMe)_2CMe_2$] ($R = 2\text{-}i\text{Pr-}C_6H_4$; $R' = 2,6\text{-}i\text{Pr}_2\text{-}C_6H_3$)

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In memory of Ron Snaith, an inspired teacher, an inspiring researcher, and a humorous, kind and generous man.

Keywords: Solid-state structures / Lithium / N ligands / Carbanions

The hemi-solvated C_2-symmetric 1,3-diamidolithium *l*-[$CMe_2\{CHMeN(R)\}_2Li_2\cdot OEt_2$] has been crystallographically characterized. It reacts with oxygen to form the N-N ring-closed pyrazolidine *l*-[$(RNCHMe)_2CMe_2$]. The slightly bulkier C_s-symmetric amidolithium *u*-[$CMe_2\{CHMeN(R')\}_2\cdot Li_2$] forms an unsolvated 1:2 heterocubane complex with *n*BuLi in the solid state and in solution, as determined by X-ray crystallography and multinuclear NMR spectroscopy ($R = 2\text{-}i\text{Pr-}C_6H_4$; $R' = 2,6\text{-}i\text{Pr}_2\text{-}C_6H_3$).

Introduction

The basis for the solid-state study of the aggregation behaviour of secondary amidolithium and organolithium compounds was set in two major reviews some years ago.[1,2] Given the massive growth of interest in the intervening years, it comes as little surprise that investigation of mixed aggregates containing each of these two key weapons in the modern arsenal of synthetic chemistry has developed rapidly. There are now a good number of mixed lithium aggregates containing both carbanions and secondary amido groups. Seminal solution-phase studies[3] have been augmented by theory[4] and by a number of X-ray crystallographically characterized examples. The solution-phase studies indicate that a complicated, equilibrating mixture, containing some unmixed homo-aggregate of one or both components, is commonly in existence, such that attempts to crystallise components of the mixture offer no guarantee of isolation of a mixed aggregate. Most crystallographic studies circumvent this problem by placing the carbanion and nitrogen-anion centres on the same covalent framework.[5] There are only a very small number of solid-state studies not invoking such C/N dianions in order to isolate mixed species.[6] We present here an additional example, different in a number of key respects from those reported previously. We have isolated this first solid-sate unsolvated 2:2 amido/organolithium tetralithium cluster by lithiation of a new class of diamine ligand. Diamines,[7] including, as in our examples, 1,3-diamines,[8] have also enjoyed much previous interest from lithium structural chemists, but ours differ from almost all previous structurally characterized examples in that they are C_2 or C_s symmetric, as opposed to the common C_{2v} case, and incorporate a higher degree of substitution into the chain linking the two amido centres than has previously been the case. There is but a single precedent for a crystallographically characterized C_2-symmetric dilithiodiamide.[7c] We report a hemi-solvated dilithiated diamine, and its novel oxidative ring-closure reaction to yield a C_2-symmetric pyrazolidine. The isolation of this product has implications for the mechanism of formation of the remarkable "inverse crown ether" class of compounds developed by Mulvey and coworkers.[9]

In addition to the above-cited precedents in organo/amido mixed aggregates, there are increasing numbers of examples where *n*BuLi is incorporated into P-N, As-N, Al-N and other main-group cluster species.[10] These have yet to mirror the synthetic utility of more conventional secondary amidolithiums, though,[3d,4b,11] and so it is secondary amidolithium compounds which remain our focus.

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DOI: 10.1002/ejic.200300373

Results and Discussion

Lithiation in hexane of *l*-(2-*i*Pr-C_6H_4NHCHMe)$_2$CMe$_2$, an amine derived from a diastereoselective hydroboration[12] of a 1,3-diimine,[13] produced a pale cream precipitate, which would only redissolve upon addition of a coordinating solvent. From a solution containing diethyl ether, crystals of *l*-[(2-*i*Pr-C_6H_4NHCHMe)$_2$CMe$_2$Li$_2$·OEt$_2$] (**1**·OEt$_2$), deposited. Its structure was determined by X-ray crystallography, and is depicted in Figure 1; selected geometric parameters are listed in Table 1.

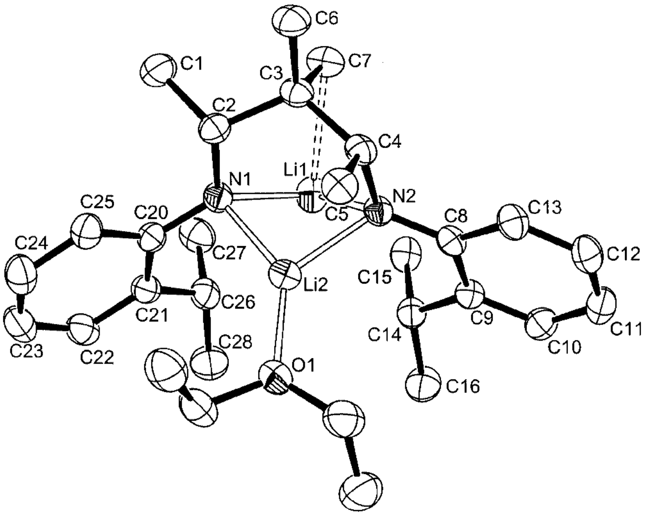
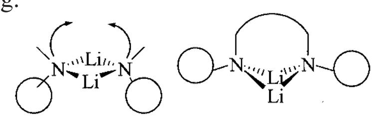


Figure 1. Molecular structure of **1**·OEt$_2$; hydrogen atoms are omitted

Table 1. Selected bond lengths [Å] and angles [°] for **1**·OEt$_2$

N(1)−Li(1)	1.945(3)	C(20)−N(1)−C(2)	115.89(11)
N(1)−Li(2)	2.029(3)	C(20)−N(1)−Li(1)	136.55(12)
N(2)−Li(1)	1.953(3)	C(2)−N(1)−Li(1)	106.73(11)
N(2)−Li(2)	2.008(3)	C(20)−N(1)−Li(2)	100.04(11)
Li(2)−O(1)	1.865(3)	C(2)−N(1)−Li(2)	105.74(11)
Li(1)−C(7)	2.487(3)	Li(1)−N(1)−Li(2)	75.21(11)
Li(2)−C(4)	2.593(3)	C(8)−N(2)−C(4)	115.92(11)
Li(2)−C(20)	2.652(3)	C(8)−N(2)−Li(1)	130.13(11)
Li(2)−C(5)	2.669(3)	C(4)−N(2)−Li(1)	107.47(11)
N(1)−C(2)	1.4754(17)	C(8)−N(2)−Li(2)	121.63(11)
N(1)−C(20)	1.3901(17)	C(4)−N(2)−Li(2)	95.03(10)
N(2)−C(4)	1.4742(17)	Li(1)−N(2)−Li(2)	75.51(11)
N(2)−C(8)	1.3778(17)	N(1)−Li(1)−N(2)	95.61(12)
C(1)−C(2)	1.537(2)	O(1)−Li(2)−N(2)	130.62(14)
C(2)−C(3)	1.5640(19)	O(1)−Li(2)−N(1)	137.21(14)
C(3)−C(6)	1.5393(19)	N(2)−Li(2)−N(1)	91.31(11)
C(3)−C(7)	1.545(2)	N(1)−C(2)−C(1)	110.50(12)
C(3)−C(4)	1.566(2)	N(1)−C(2)−C(3)	111.79(11)
C(4)−C(5)	1.541(2)	C(1)−C(2)−C(3)	111.12(12)
O(1)−C(31)	1.439(2)	C(6)−C(3)−C(7)	106.97(12)
O(1)−C(30)	1.4509(19)	C(6)−C(3)−C(2)	108.39(12)
C(6)−C(3)−C(4)	106.83(12)	C(7)−C(3)−C(2)	111.79(12)
C(2)−C(3)−C(4)	114.09(11)	C(7)−C(3)−C(4)	108.42(12)
N(2)−C(4)−C(5)	111.18(11)	C(3)−C(7)−Li(1)	80.05(10)
C(5)−C(4)−C(3)	112.79(11)	N(2)−C(4)−C(3)	112.43(11)

Only a single diethyl ether molecule is incorporated into the structure, which is comprised of a single diamido unit with a central Li$_2$N$_2$ ring. This most common motif[1] is in this case rather puckered [torsion angle Li(1)−N(3)−Li(2)−N(1) = −34°]. This butterfly conformation is characteristic of *di*amides,[7,8] where the linking group draws together the two N-vertices of the Li$_2$N$_2$ ring, pushing the lithium atoms downwards as shown below. Also apparent from this scheme is the reason that cyclic diamidolithium complexes often defy the ring-laddering prediction, since the projection of one of the substituents of the secondary amine into an axial position, which prevents ring stacking, thus favouring ring laddering,[1] is converted into an equatorial projection by the constraint of the diamido ring.



Evident from a comparison of the structures of **1**·OEt$_2$ and its protonated secondary amine precursor[12] is the fact that the conformational preferences of the organic portion are dominant. The organic portions of the structures map closely, since in the diamine, an H-bonded ring is present. The N−N distance of 2.89 Å in **1**·OEt$_2$ matches that of 2.84 Å in the NH precursor.[12] Because of the two lithium atoms bonded to each nitrogen atom, the ring in **1** can at once be described as both a boat and a chair. The axial/equatorial arrangement of the methyls attached to the two chiral centres is also identical in metallated and unmetallated forms. Crystallographic symmetry generates the molecule of opposite polarity in this racemic crystal. In the only other dilithiated C_2-symmetric diamine,[7c] the 1,2 diamidolithium *l*-[Li{*t*BuN(CHMe)$_2$N*t*Bu}Li], which, like most dilithiated diamines, defies Snaith's laddering principle by adopting a stacked, dimeric structure, disorder of both enantiomers confused the issue of conformation, and of whether in its dimeric structure, like or unlike enantiomers aggregated. It was synthesised by the rather different route of diastereoselective double carbolithiation[7c] of the parent 1,2-diimine *t*BuN(CH)$_2$N*t*Bu. The parent 1,3-diimines from which **1** is derived do not undergo similar carbolithiation or carbozincation reactivity.[14]

Included in the previous examples of stacked diamidolithium structures is a case involving a 1,3-diamine linkage: [Li{Me$_3$SiN(CH$_2$)$_3$NSiMe$_3$}Li]$_2$ was obtained as an unsolvated stack, reminiscent of the 1,2 cases discussed above.[8b] Complex **1** differs from all of these cases in the fact that it precipitates as an insoluble (presumably polymeric) powder from hexane. In this behaviour, it mimics the less-bulky amides which gave rise to the ring laddering principle.[1] The possibility that **1** aggregates in a ladder form is supported by close inspection of its structure. Unusually for an arylamidolithium,[15] the aryls are almost coplanar with the CNC planes (dihedral angles of −16.4° on the side bearing the equatorial methyl, and 2.1° on the axial methyl side). This facilitates π-interaction of the amido density into the aromatic ring, as shown by the relatively short (aryl)C−N bonds (mean 1.38 Å, cf. 1.43 Å for orthogonal rings; see later). This coplanarity is optimal for lateral packing (laddering), while both isopropyl groups are in a position which would make stacking difficult. This perhaps explains the insolubility of **1** in non-donor solvents, despite its relative bulk.

Nevertheless, **1** crystallizes with only a single molecule of diethyl ether coordinated to Li(2), rendering it three-coordinate, while Li(1) remains merely two-coordinate. A fairly close CH···Li interaction is present across the boat-ring. This sort of interaction is quite frequently found to low-coordination number lithium atoms,[16] but it is more usually a C_α or C_β interaction, as in [(*n*BuLi)$_6$], for example (see later).[17] To find a C···Li distance of 2.49 Å to a C_δ carbon is without precedent.[16] However, we tend toward the view that the short "δ-agostic" interaction is a consequence of the high degree of puckering of the boat conformation in the C_2N_2Li ring, rather than a cause of it. The hemisolvated nature of the Li_2N_2 ring has some precedent; in [$C_{10}H_6$(N{Li(THF)}SiMe$_3$){N(Li)SiMe$_3$}], also a 1,3-diamidolithium, though one with a planar aromatic core, a single lithium is coordinated by THF, while the other engages in π-interactions with a neighbouring molecule.[8a] Similar situations obtain in doubly lithium-reduced diazadiene complexes.[7e] In **1**, the only such stabilizing interaction is the aforementioned "δ-agostic" one.

The exposed nature of the low-coordinate lithium may be a factor in the reactivity of compound **1**. Interestingly, a similarly exposed, bent two-coordinate lithium is present in [LiMg{N(SiMe$_3$)$_2$}$_3$],[9a] which has been shown to be extremely sensitive to traces of oxygen, generating the first case of the remarkable oxo-centred "inverse crown ether" cluster class.[9b] It has, however, never been established without doubt that the oxo-centre of the clusters was a result of reduction of dioxygen, because it was not possible to unambiguously identify the partner product of oxidation, the presumed substituted hydrazine {N(SiMe$_3$)$_2$}$_2$, in the reaction mixtures.

We find the opposite scenario to pertain for **1**: significant amounts of the stable, crystalline product of oxidative N-N ring closure, the substituted pyrazolidine **2**, were found in aged solutions of **1**, and in reaction products where **1** was employed as an intermediate, whereas we have not isolated oxide-containing aggregates. It was subsequently shown that exposure of solutions of **1** to dry oxygen generated significant yields of **2**. While we have yet to identify oxo-centred lithium clusters in our products, this first clear proof of oxidative N-N coupling of secondary amidolithium compounds is strong indirect evidence supporting the mechanism proposed by Mulvey and co-workers for the generation of inverse crown ethers.[9]

Normal routes to pyrazolidines involve additions across an N−N π-bond.[18] In 1994, Nelsen et al. reported a curious reaction in which two molar equivalents of *t*BuLi were reacted with a polycyclic secondary bis(chloroamine) to yield an N−N bonded species,[19] but in this case the rings formed in the ring closure were four- and six-membered. The mechanism of this reaction was not discussed. It seems that our route to pyrazolidines is new. Structurally (see Figure 2), there is little remarkable in **2**; the conformation and bonding parameters (Table 2) are as expected; an approximate C_2 axis passes through the mid-point of the N−N bond and the C(3) atom. C(2), C(3), and C(4) are coplanar; the ring puckers above and below this plane at the pyramidalized N(1) and N(2) centres, in which the neighbouring lone pairs adopt an antiperiplanar arrangement.[19] This allows both methyls on the chiral carbon to adopt equatorial positions. The crystals are racemic.

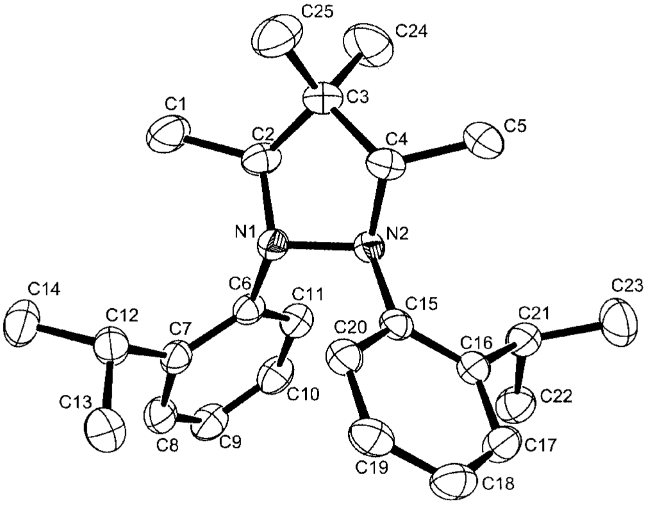


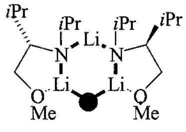
Figure 2. Molecular structure of **2**; hydrogen atoms are omitted

Table 2. Selected bond lengths [Å] and angles [°] for **2**

N(1)−C(6)	1.4505(17)	C(15)−N(2)−C(4)	111.52(10)
N(1)−C(2)	1.4757(17)	C(15)−N(2)−N(1)	109.79(9)
N(1)−N(2)	1.4846(15)	C(4)−N(2)−N(1)	100.94(10)
N(2)−C(15)	1.4510(17)	N(1)−C(2)−C(1)	111.25(13)
N(2)−C(4)	1.4773(17)	N(1)−C(2)−C(3)	104.44(11)
C(1)−C(2)	1.507(2)	C(1)−C(2)−C(3)	116.97(13)
C(2)−C(3)	1.543(2)	C(25)−C(3)−C(24)	109.35(15)
C(3)−C(25)	1.518(2)	C(25)−C(3)−C(2)	114.47(14)
C(3)−C(24)	1.522(2)	C(24)−C(3)−C(2)	108.18(14)
C(3)−C(4)	1.5450(19)	C(25)−C(3)−C(4)	109.23(13)
C(4)−C(5)	1.504(2)	C(24)−C(3)−C(4)	113.02(14)
		C(2)−C(3)−C(4)	102.55(11)
C(6)−N(1)−C(2)	111.75(10)	N(2)−C(4)−C(5)	111.67(12)
C(6)−N(1)−N(2)	109.17(10)	N(2)−C(4)−C(3)	104.36(10)
C(2)−N(1)−N(2)	100.97(10)	C(5)−C(4)−C(3)	116.61(12)

Turning now to mixed aggregates containing amido units akin to **1**, by far the most common means of achieving mixed carbanion/N-aggregation in the solid state is to tie both anionic centres together in the same molecule, i.e. to use heterodentate C/N dianions.[5a−5e] Rather less common are genuine mixed aggregates of independent carbanion and amido anion, where the thermodynamic balance between homo-aggregates and mixed aggregates is often a fine one, as evidenced by the observance of mixtures in solution.[3] The enthalpy-neutrality of the formation of mixed dimer over homodimer has been demonstrated computationally for simple amido and carbanion groups.[4a] However, by appropriate choice of ancillary donor atoms and/or steric bulk, it has proven possible in a few cases to isolate heterocomponent amidolithium/*n*-butyllithium aggregates.[6] In addition, there are two examples where C/N dianions are co-aggregated with Ph_2N monoanions and/or *n*-butyl carbanions in a large cluster,[5f,5g] and another example where an anti-fluorite-like cluster of $(C_6H_5C_6H_4)NLi_2$ is stabilized by a methanide anion.[20] All of these are ether-solvated.

We restrict our discussion to simple cases of solid-state co-aggregation of secondary amidolithium species with organolithium species. In this category there are only two structural types in existence (see below), **3** and **4**.[6] Isostructural analogues of **3** containing *sec*- and *tert*-butyllithium are also known.[6a] The structure of the homoaggregate, $[(n\text{BuLi})_6]$ (**5**) is shown for comparison.[17]



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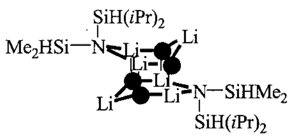

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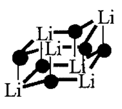


5

● = Butyl vertex

Use of an excess of *n*BuLi in the metallation of the bulkier, C_s-symmetric *u*-$(2,6\text{-}i\text{Pr}_2\text{-}C_6H_3NHCHMe)_2CMe_2$ in hexane afforded a solution from which the mixed organo/amidolithium compound **6** crystallized. Its structure (Table 3 and Figure 3) is that of a heterocubane, in which a dimer of *n*BuLi stacks with a diamidodilithium unit similar to that in **1**. The incorporation of bulk in both *ortho* positions on the phenyl rings, and the *u*-(*meso*) diastereochemistry of the diamide, results in conformational differences: both of the chiral carbons can now direct their methyl substituents into equatorial positions while maintaining the dual boat/chair character of the ring. This forces both aryls to pack in an approximately orthogonal disposition with respect to the average plane of the $N_2C_3Li_2$ pair of rings. In turn, this facilitates a stacked packing arrangement. However, key to the isolation of a mixed organo-amido complex is the fact that the extreme bulk of the 2,6-diisopropylphenyl substituents still precludes such a stacking arrangement in a homo-aggregate of amidolithium units; in order to relieve steric strain, it is the less demanding *n*BuLi units which are pressed into service to complete the stable, heterocubane arrangement. Looking from the other perspective, this is a case where the extra bulk of the amido unit forces *n*BuLi to adopt a role in a tetrameric aggregate, whereas in a homo-aggregate of *n*BuLi a hexameric stack of two trimeric rings is preferred.[17]

Table 3. Selected bond lengths [Å] and angles [°] for **6**

N(1)−Li(2)	1.997(3)	C(3)−C(7)−Li(1)	77.58(10)
N(1)−Li(1)	2.041(3)	N(2)−C(8)−Li(3)	66.40(9)
N(1)−Li(4)	2.180(3)	N(1)−C(20)−Li(4)	64.62(9)
N(2)−Li(1)	1.977(3)	C(33)−C(32)−Li(4)	75.60(11)
N(2)−Li(2)	2.031(3)	Li(4)−C(32)−Li(2)	68.21(10)
N(2)−Li(3)	2.182(3)	C(33)−C(32)−Li(3)	121.69(13)
C(2)−N(1)	1.4851(18)	Li(4)−C(32)−Li(3)	69.42(11)
C(2)−C(3)	1.5715(19)	Li(2)−C(32)−Li(3)	67.57(10)
C(3)−C(4)	1.581(2)	C(32)−C(33)−Li(4)	64.66(10)
C(4)−N(2)	1.4916(18)	C(37)−C(36)−Li(4)	126.78(13)
C(7)−Li(1)	2.402(3)	Li(1)−C(36)−Li(4)	65.20(10)
C(8)−N(2)	1.4267(18)	C(37)−C(36)−Li(3)	140.59(13)
C(8)−Li(3)	2.318(3)	Li(1)−C(36)−Li(3)	66.19(10)
C(20)−N(1)	1.4301(18)	Li(4)−C(36)−Li(3)	68.83(10)
C(20)−Li(4)	2.369(3)	C(20)−N(1)−C(2)	113.94(11)
C(21)−Li(4)	2.500(3)	C(20)−N(1)−Li(2)	104.58(11)
C(32)−Li(4)	2.178(3)	C(2)−N(1)−Li(2)	110.26(11)
C(32)−Li(2)	2.185(3)	C(20)−N(1)−Li(1)	144.50(11)
C(32)−Li(3)	2.222(3)	C(2)−N(1)−Li(1)	97.41(11)
C(33)−Li(4)	2.334(3)	Li(2)−N(1)−Li(1)	77.95(11)
C(36)−Li(1)	2.182(3)	C(20)−N(1)−Li(4)	79.04(10)
C(36)−Li(4)	2.209(3)	Li(2)−N(1)−Li(4)	71.53(10)
C(36)−Li(3)	2.224(3)	Li(1)−N(1)−Li(4)	68.09(10)
		N(1)−Li(2)−N(2)	93.23(11)
C(8)−N(2)−C(4)	116.82(11)	C(8)−N(2)−Li(1)	136.84(11)
C(4)−N(2)−Li(2)	91.95(10)	C(4)−N(2)−Li(1)	101.78(11)
Li(1)−N(2)−Li(2)	78.66(11)	C(32)−Li(4)−C(33)	39.74(7)
C(8)−N(2)−Li(3)	76.79(10)	N(1)−Li(4)−C(36)	108.66(12)
Li(1)−N(2)−Li(3)	70.51(11)	C(32)−Li(4)−C(36)	105.74(12)
Li(2)−N(2)−Li(3)	71.05(10)	C(32)−Li(4)−N(1)	104.85(11)
N(2)−Li(1)−N(1)	93.54(11)	C(32)−Li(3)−C(36)	103.73(12)
N(2)−Li(1)−C(36)	114.41(13)	N(2)−Li(3)−C(36)	105.07(12)
N(1)−Li(1)−C(36)	115.20(12)	N(2)−Li(3)−C(32)	106.22(12)
N(2)−Li(1)−C(7)	87.03(10)	N(2)−Li(2)−C(32)	113.31(12)
N(1)−Li(1)−C(7)	94.07(11)	N(1)−Li(2)−C(32)	111.28(12)

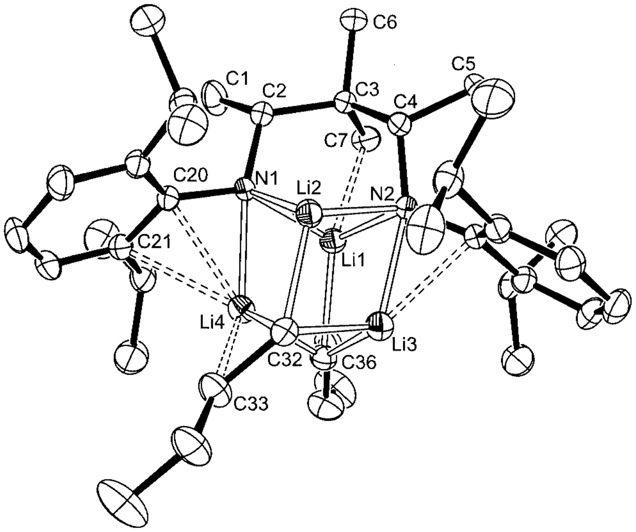
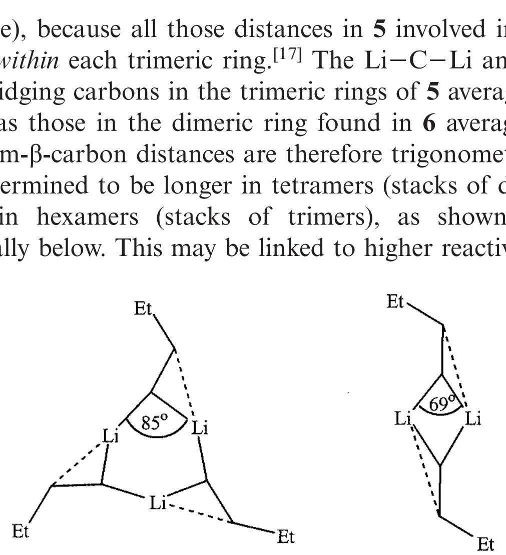


Figure 3. Molecular structure of **6**; hydrogen atoms are omitted

Unfortunately, attempts to isolate a homoaggregate of the 1,3-diamido unit in **6** resulted only in isolation of oils, though a similar 1,2-diamidolithium, with identical 2,6-diisopropylphenyl substituents, has been characterized.[7b] It is a rare example of an unsolvated four-runged step-ladder (the extreme bulk limits growth of the ladder in this case), and it seems reasonable to assume a similar arrangement would occur for the 1,3 analogue. In such an aggregation mode, only two lithiums attain three coordination, the other two having to limit themselves to two-coordination, augmented by aryl-Li interactions. Just such a situation occurs in an arched unsolvated limited ladder attained by lithiation of a trimethylsilyl-substituted benzyldiamine.[8c] Incorporation of *n*BuLi into the aggregate **6** allows for more stabilizing electrostatic interactions, all four lithium atoms attaining three coordination. The energetic cost of this to the *n*BuLi fragment is modest. It finds itself in a very similar arrangement to that of its homoaggregate, capping a triangular face of lithium atoms, to use the traditional terminology for the description of organolithium structures.[17] In this mode of description, **5** is viewed as an octahedral array of lithium atoms with six of its faces capped by butyl anions. In the same way, the mixed aggregate **4** is described as an octahedron in which four faces are capped by butyl anions, and two edges are capped by amido anions. We prefer to describe the structures on the basis of the electrostatic interaction which hold them together, rather than the Li−Li framework, which has been shown not to be involved in bonding.[21] Re-examination of **5** in this way reveals a view of it as a stack of cyclic trimers. The inter-trimer distances are systematically longer than the intra-trimer ones.[22] Each six-membered ring adopts a flattened chair conformation. The extra bulk of the amido groups in **4** is inconsistent with stacking, but they can be accommodated without distorting the structure unduly simply by flipping one corner of each six-membered ring, so that each is in a boat, rather than a chair, conformation. This generates room for all four butyl groups to direct their secondary interaction to the two lithium atoms that are left two-coordinate by the cleavage of the two stacking interactions. Further stabilization through SiH−Li interactions help to favour the mixed aggregate **5**, despite the fact that the stoichiometry employed in its preparation was far from 1:2.[6b] In the synthesis of **6**, we originally employed a 2:1 N:*n*Bu ratio, hoping to isolate unsolvated versions of compound **3**, but in our hands also, there was no stoichiometric control over the product identity. This is generally true of all mixed aggregate syntheses in s-block chemistry. The key to the unusual stoichiometry of **3** is clearly in the internal solvation and high degree of bulk, which destabilize the homoamide aggregate in favour of incorporation of a single unit of organolithium.[6a] All of these factors must be considered for the successful isolation of solid state mixed aggregates. Though in ether solutions, cubic amido-organoaggregates similar to **6** have been previously characterized by NMR spectroscopy,[3b,3c,3e] they are generally components of mixtures. Synthetic studies have shown that incorporation of *n*BuLi into the mixed aggregates often increases its reactivity, and where the amidolithium unit is chiral, asymmetric induction can be observed in additions of *n*BuLi across carbonyl bonds.[11]

This might be partially explained by a closer inspection of the structure of **6**. It has a δ-agostic interaction between C(7) and Li(1) even shorter (2.40 Å) than that in **1**, possibly as a result of flattening of the butterfly (torsion = −31°, a decrease of 3° with respect to $\mathbf{1}\cdot\mathrm{OEt_2}$) by the steric influence of the $(n\mathrm{BuLi})_2$ ring, and a more conventional β-agostic interaction between C(33) and Li(4), separated by 2.33 Å. This is longer than the β-agostic distances in **5** (2.28 Å on average), because all those distances in **5** involved interactions *within* each trimeric ring.[17] The Li−C−Li angles at the bridging carbons in the trimeric rings of **5** average 85°, whereas those in the dimeric ring found in **6** average 69°. Lithium-β-carbon distances are therefore trigonometrically predetermined to be longer in tetramers (stacks of dimers) than in hexamers (stacks of trimers), as shown schematically below. This may be linked to higher reactivity.



Similar β-agostic distances to that in **6** are found in $[(n\mathrm{BuLi})_4(t\mathrm{BuOLi})_4]$, in which $(n\mathrm{BuLi})_2$ units cap either end of a folded (*t*BuOLi) octagon.[23] In fact, there is only a single conventional β-agostic interaction in **6**, shown in Figure 4. The other butyl chain is excluded by the bulky substituents, a result of the C_s symmetry of the backbone, telegraphed via the conformation of the aryl rings, and the δ-agostic interaction to C(7) differentiating either side of the $(n\mathrm{BuLi})_2$ unit. Aryl-Li interactions are probably more important in stabilizing the structure of **6**: *ipso*-C(aryl)···Li distances of 2.318(3) and 2.369(3) Å are in the normal range for such interactions.[7b] Despite the fact that in all structures the hydrogen atoms were freely refined, no statistically meaningful systematic lengthening of C−H bonds is seen for hydrogens with short H···Li contacts.[16]

The above discussion presupposes that **6** can be rationalized as a stack of amidolithium dimers with butyllithium dimers. The Li−N distances support this view, those within the $\mathrm{Li_2N_2}$ butterfly [1.977(3)−2.041(3) Å] being systematically shorter than the stacking N−Li distances [2.180(3) and 2.182(3) Å].[1] However, the Li−C distances involving the carbanionic centres of the $(n\mathrm{BuLi})_2$ unit are in the range 2.178(3)−2.224(3) Å, and the stacking interactions lie within the *lower* part of that range [2.182(3) and 2.185(3) Å]. There is, therefore, little basis for viewing the $(n\mathrm{BuLi})_2$ unit as an independent entity within the cluster. Rather, the molecule is an integrated whole. The rather longer-than-expected C−Li distances within the $(n\mathrm{BuLi})_2$ "dimer" might be explained by a slight elongation of the Li(3)···Li(4) distance {2.506(4) Å, cf 2.42 Å in $[(n\mathrm{BuLi})_4(t\mathrm{BuOLi})_4]$ and 2.43 Å in **5** for the equivalent distances}[17,23] in order for those two lithium atoms to engage most effectively in the stacking interactions with N(1) and N(2).

Given the extent of previous interest in the solution-phase behaviour of mixed amidolithium/butyllithium aggregates,[3] and the fact that reactions of such aggregates have hitherto been performed only in solution,[11] a limited NMR investigation of **6** was undertaken. The signals in the NMR spectra are broad at room temperature. The best-

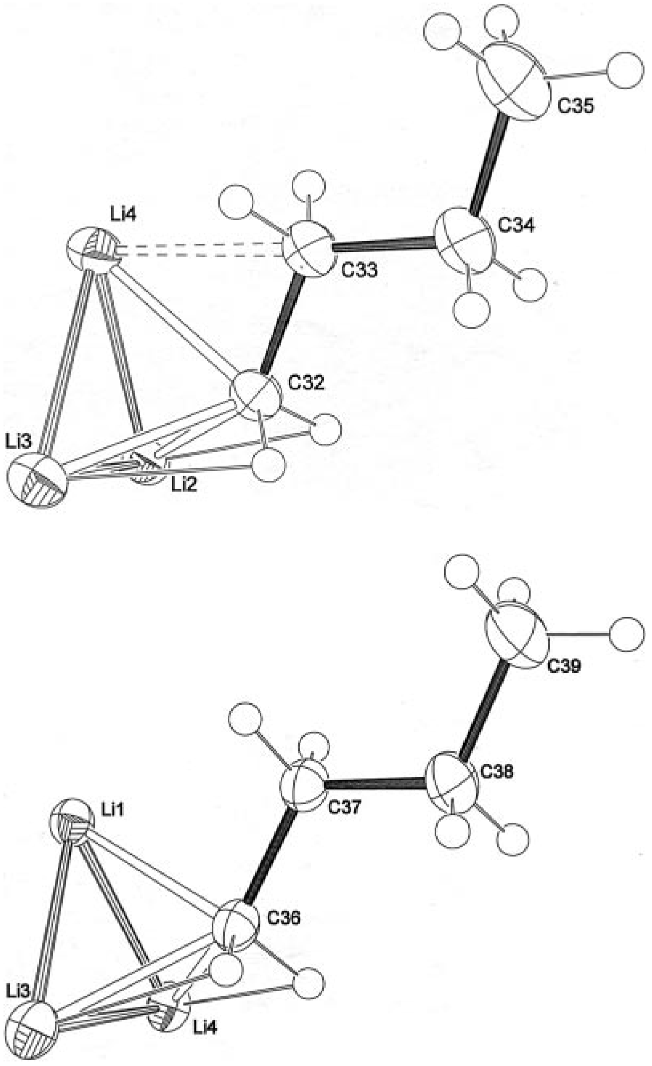


Figure 4. Views of the two butyl anions (top) including normal Cβ interaction to the lithium with shortest bond to Cα and (bottom) lacking Cβ interaction due to steric effect of C(7)

resolved data were obtained at −40 °C. It is reasonable to assume that the puckering of the central $C_3N_2Li_2$ ring is maintained, since flexing into the alternative conformation [C(7) equatorial] would place a total of three methyl groups and one lithium atom, as well as the isopropyl substituents on each aryl, into axial positions. It is deemed highly unlikely that this conformation would be populated to any appreciable extent. Therefore, the environments of Li(1) and Li(2) should remain well-distinguished. Li(3) and Li(4), being related by the approximate molecular C_s symmetry plane, are less likely to exhibit distinct chemical shifts. At −40 °C a ^{7}Li NMR spectrum consistent with this model, i.e. three signals in the ratio 1:1:2, is observed. In the ^{1}H NMR spectrum at −40 °C, two high-field signals in the *n*BuLi C_α region are observed. Both show a characteristic non-first-order envelope which has previously been associated with restricted rotation about the $C_\alpha-C_\beta$ bond of the butyl anions.[24] It is observed here at significantly higher temperature than in the other studies, which were performed in ether solvents.[3,24] It may be that the bulky amide substituents help to hinder such rotation. In any case, the presence of two types of butyl is consistent with the molecular symmetry of **6**. The other butyl signals are partially obscured by the methyl region, but the integrals of the resolved peaks match for two distinct α-carbons for each amido ligand, of which there is only one type. The observance of two distinct isopropyl methine resonances in the ratio 1:1 shows that the aryl-N bonds are fixed. An interesting feature of the ^{1}H NMR spectrum is the observance of a quintet at $\delta = 0.2$ ppm. This is tentatively assigned (attempts at ^{1}H-^{1}H COSY failed for these broad, weak peaks) to the β-carbon of an atypical butyl group. For **5** in toluene, and for $(n\mathrm{BuLi})_4$ in THF, this proton environment resonates around $\delta = 1.5$ ppm. The marked shift in what must either be the β- or the γ-proton environment into a region which is silent in all other observed spectra of *n*BuLi fragments suggests an unusual situation.[3,24] Given that close β-C(H)···Li contacts are reported in all other *n*BuLi fragments discussed above, but are absent in one of the butyls in **6**, we tentatively ascribe the anomalous shift to the absence of the agostic-type interaction. More normal β, γ and δ environments were also observable, but not all eight expected butyl peaks could be identified due to crowding in the $\delta = 0.9-1.7$ ppm region. The different butyl environments were less-easily distinguished in the ^{13}C NMR spectrum, but such resonances as could be discerned were consistent with the maintenance of the structure **6** in solution. It should be stressed, however, that alternative models of behaviour, such as expulsion of one *n*BuLi unit from **6** to form one sixth of an equivalent of **5** (matching of some of the butyl resonances to **5** in toluene was quite close, but not identical), and reversion of the remaining cluster to a structure analogous to **3**,[6a] cannot be ruled out. There was fluxionality evident (e.g. coalescence of the different butyl environments at 0 °C), but detailed solution studies lie outside the scope of this predominantly solid-state investigation.

Unfortunately, the *l*-diastereomer of the bulkier amine used in **6** is inaccessible due to the difficulty in deboronating the hydroboration intermediate,[12] but, given the encouraging results that have been obtained by others in enantioselective syntheses using mixed aggregates of chiral amines,[11] we feel justified in pressing on with resolution of the amine used in **1**, and its employment in mixed aggregate synthesis. There may yet prove to be a role for the C_s-symmetric amine used in **6** in the promotion of syndiotacticity in alkene polymerization, where titanium complexes of 1,3-diamido ligands identical to that in **6** but for the de-symmetrizing methylene backbone substituents, have shown promise.[25]

Experimental Section

All manipulations were carried out under a protective argon blanket, either in a double manifold argon/vacuum line or argon-filled recirculating glovebox. Argon was dried over phosphorus pentoxide supported on vermiculite. Toluene and diethyl ether were used freshly distilled under argon from sodium-benzophenone ketyl; in the case of hexane, approximately 5% tetraglyme was added in order to dissolve the sodium-benzophenone ketyl. $CDCl_3$, C_6D_6,

C_7D_8 and [D_8]THF were stored over freshly activated 4 Å molecular sieves. The hexane solution of *n*BuLi was used as received and standardised using *N*-benzylbenzamide.[26] *u*-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,3′-dimethylpentane-2,4-diamine and *l*-*N*,*N*′-bis(2-isopropylphenyl)-3,3′-dimethylpentane-2,4-diamine were prepared by literature methods.[12] All other reagents were obtained from standard commercial vendors and used as received.

Melting points were determined in sealed glass capillaries under argon. Elemental analyses were performed by the microanalytical group in the Chemistry Department at UMIST.

Chemical shifts are given in ppm and referenced to residual solvent shifts for ^{13}C and ^{1}H; ^{7}Li spectra were referenced to 0.1 M LiCl in D_2O. Assignments were made with the aid of DEPT and HMQC experiments. Infrared spectra were recorded on a Nicolet Nexus-FTIR/Raman spectrometer using NaCl plates and nujol mulls.

***l*-[(2-*i*Pr-C_6H_4NCHMe)$_2$CMe$_2$Li$_2$·OEt$_2$] (1·OEt$_2$):** *n*BuLi (16.0 mL of a 1.51 M hexane solution, 24.16 mmol) was added to a stirring solution of *l*-[(2-*i*Pr-C_6H_4NHCHMe)$_2$CMe$_2$ (4.03 g, 11.0 mmol) in hexane (30 mL) at room temperature. Initially, a pale orange solution was obtained, but over a stirring period of 5 minutes, a cream precipitate deposited. Heating to boiling did not induce re-dissolution. To the cream precipitate was added diethyl ether (65 mL, in 5 mL volumes) over a 10 minute period until the precipitate had dissolved. The resulting dark orange solution was cooled to −45 °C yielding crystals of dilithiated amido complex **1**·OEt$_2$. Isolation by filtration in vacuo resulted in a decrease in crystal quality, associated with loss of coordinated diethyl ether. Isolated material (2.84 g, 57% based on the formulation [2-*i*Pr-C_6H_4NCHMe)$_2$CMe-$_2$Li$_2$.OEt$_2$]) was poorly soluble in deuterobenzene. M.p. 160−163 °C dec. $C_{29}H_{46}Li_2N_2O$ (452.6): calcd. C 77.0, H 10.2, N 6.2; found C 79.0, H 10.1, N 6.6. Poor agreement due to diethyl ether loss. ^{1}H NMR (300 MHz; [D_8]THF, 35 °C): δ = 1.08 [br. s, 6 H, NCHMeC(*Me*)$_2$CHMeN],1.12 (d, 6 H, *Me*CHMe), 1.17 [d, 6 H, NCH*Me*C(Me)$_2$CH*Me*N], 1.31 (d, 6 H, MeCH*Me*), 2.69 (sept., 2 H, MeC*H*Me), 3.96 [q, 2 H, NC*H*MeC(Me)$_2$C*H*MeN], 7.00 (dd, 2 H), 7.10 (td, 2 H), 7.20 (td, 2 H) and 7.35 (dd, 2 H, aromatic C*H*) ppm. ^{13}C NMR (75 MHz; [D_8]THF, 35 °C): δ = 15.6 [NCH*Me*C(Me)$_2$CH*Me*N], 21.3 [NCHMeC(*Me*)$_2$CHMeN, broad; accidental coincidence], 23.4 and 24.6 [CH(*Me*)$_2$], 29.8 [*C*H(Me)$_2$], 42.7 [NCHMe*C*(Me)$_2$CHMeN], 65.3 [N*C*HMeC(Me)$_2$*C*HMeN], 114.0, 118.4, 127.2 and 129.1 (aromatic CH), 133.2 (*C*-N, aromatic C), 151.9 {*C*[CH(Me)$_2$], aromatic C}. Peaks due to free Et$_2$O could also be observed at substoichiometric levels.

1,2-(2-Isopropylphenyl)-3,4,4,5-tetramethylpyrazolidine (2): *n*BuLi (1.6 mL of a 1.51 M hexane solution, 2.42 mmol) was added to a stirring solution of *l*-[(2-*i*Pr-C_6H_4NHCHMe)$_2$CMe$_2$] (0.40 g, 1.1 mmol) in hexane (5 mL) at room temperature. The suspension was vented to the atmosphere via a drying tube freshly charged with anhydrous CaCl$_2$, and stirred for 12 h. Removal of solvent yielded a brown oil. Its NMR spectrum was dominated by peaks listed below, but contained some other unidentified impurities. Flash column chromatography on silica (eluting with hexane) yielded **2** as the major fraction, $R_f = 0.7$. Large colourless crystals of 1,2-(2-isopropylphenyl)-3,4,4,5-tetramethyl pyrazolidine (**2**) were grown from a hexane solution at −25 °C. M.p.: 118−120 °C. Yield: 0.19 g, 48%. ^{1}H NMR (300 MHz. CDCl$_3$): δ = 0.97 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, *Me*CHMe), 0.91 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, NCH*Me*C(Me$_2$)CH*Me*N], 1.10 [s, 6 H, NCHMeC(*Me*$_2$)CHMeN], 1.19 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, MeCH*Me*), 2.80 [q, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, NC*H*MeC(Me$_2$)C*H*MeN], 3.94 (septet, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, MeC*H*Me), 6.96−7.11 and 7.76−7.82 (8 H, non-first-order m, aromatic protons) ppm. ^{13}C NMR (75 MHz; C_6D_6): δ = 14.4 [NCH*Me*C(Me$_2$)CH*Me*N], 24.3 [NCHMeC(*Me*$_2$)CHMeN], 24.4 (*Me*CHMe), 25.5 (MeCH*Me*), 25.9 (Me*C*HMe), 42.6 [NCHMe*C*(Me$_2$)CHMeN], 73.7 [N*C*HMeC(Me$_2$)*C*HMeN], 125.6, 126.1, 126.2 and 126.4 (aromatic CH), 147.4 and 147.8 {*C*-N, aromatic C and *C*[CH(Me)$_2$]}. $C_{25}H_{36}N_2$ (364.6): calcd. C 82.4, H 10.0, N 7.7; found C 82.7, H 10.2, N 7.8. IR: $\tilde{\nu}$ = 1521 cm^{-1}, 1485 cm^{-1} and 1445 cm^{-1} (s, aromatic C−C stretch), 1345 cm^{-1} [s, ν(C−N)].

{*N*,*N*′-Bis(2,6-diisopropylphenyl)-3,3′-dimethylpentane-2,4-diamido}dibutyltetralithium (6): *n*BuLi (4.2 mL of a 1.58 M hexane solution, 6.7 mmol) was added dropwise to a stirring solution of *N*,*N*′-bis(2,6-diisopropylphenyl)-3,3′-dimethylpentane-2,4-diamine (1.00 g, 2.2 mmol) in toluene (20 mL) at 22 °C and the solution was stirred for 2 h. Large, colourless crystals were grown overnight from the solution at −4 °C. The crystals were filtered from the solution and dried under vacuum. Yield: 0.42 g, 32%. M.p. 80−83 °C dec. The UMIST microanalysis facility could not handle this extremely sensitive compound; results indicated hydrolysis. Large crystal size and reproducibility and purity of NMR spectroscopic data indicated acceptable sample purity and homogeneity. ^{1}H NMR (200 MHz; [D_8]toluene, −40 °C): δ = −1.6 [br. m, 2 H, CH$_3$(CH$_2$)$_2$C*H*$_2$Li], −0.9 [br. m, 2 H, CH$_3$(CH$_2$)$_2$C*H*$_2$Li], 0.2 (br. quint., 2 H, CH$_3$CH$_2$C*H*$_2$CH$_2$Li or CH$_3$C*H*$_2$CH$_2$CH$_2$Li), 0.75 [t, $^{3}J_{H,H}$ = 7.2 Hz, 3 H, C*H*$_3$(CH$_2$)$_2$CH$_2$Li], 1.0 [two broad d overlapped, 6 H +6 H, NCH*Me*C(Me$_2$)CH*Me*N and *Me*C$_A$HMe], 1.1 [s, 3 H +3 H, unresolved NCHMeC(*Me*$_2$)CHMeN], 1.31 (br. d, 6 H, MeC$_B$H*Me*), 1.45 (apparent br. d, two d overlapped, 6 H +6 H, *Me*C$_A$HMe and MeC$_B$H*Me*), 1.75 [non-first-order br. m, 4 H, CH$_3$(C*H*$_2$)$_2$CH$_2$Li], 3.01 (br. septet, 2 H, MeC$_A$*H*Me), 3.89 [br. q, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, NC*H*MeC(Me$_2$)C*H*MeN], 4.16 (br septet, 2 H, MeC$_B$*H*Me), 7.02−7.22 (non-first-order br. m, 6 H, aromatic protons) ppm. ^{7}Li NMR (78 MHz, [D_8]toluene, −40 °C): δ = 1.0 (br. s, 2 Li), 2.6 (br. s, 1 Li), 3.3 (br. s, 1 Li) ppm. ^{13}C NMR (75 MHz; C_6D_6, 22 °C): δ = 10 [br. overlapped m, Me(CH$_2$)$_2$*C*H$_2$Li], 14.2 [NCHMeC(*Me*$_2$)CHMeN], 20.4 [NCH*Me*C(Me$_2$)CH*Me*N], 25.6, 26.5 and 30.8 (*Me*CH*Me*), 27.1 and 31.2 (Me*C*HMe), 32 [br. overlapped m, Me(*C*H$_2$)$_2$CH$_2$Li], 44.1 [NCHMe*C*(Me$_2$)CHMeN], 69.7 [N*C*HMeC(Me$_2$)*C*HMeN], 123.2, 126.0 and 128.0 (aromatic CH), 145.6, 149.1 and 151.4 [*C*(CHMe$_2$) and *C*-N, aromatic C] ppm.

X-ray Structure Determinations: Low-temperature X-ray diffraction data for **1**·OEt$_2$, **2** and **6** were recorded from perfluoropolyether-coated crystals on a Nonius KappaCCD instrument fitted with an Oxford Instruments Cryostream (**1**·OEt$_2$ and **6**), or a Nonius MACH 3 diffractometer (**2**) fitted with a liquid-nitrogen boil-off device. Collection and solution methods and programs have been detailed elsewhere.[14] All hydrogens were found in difference maps and freely refined. Collection and refinement summaries are shown in Table 4. CCDC-212782 (**1**·OEt$_2$), -212783 (**2**) and -212784 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are indebted to the EPSRC for studentships (RJW, JEW) and NMR and X-ray diffraction equipment grants, to the Royal Society (FSM) for small equipment and consumables, and to Creators Ltd for Total Technology support (JEW).

Table 4. Crystal data

Compound	$1\cdot OEt_2$	2	6
Formula	$C_{29}H_{46}Li_2N_2O$	$C_{25}H_{36}N_2$	$C_{39}H_{66}Li_4N_2$
M_w	452.56	364.56	590.70
Crystal system	Monoclinic	Triclinic	Monoclinic
a (Å)	13.8928(3)	10.352(2)	19.8740(6)
b (Å)	12.9728(3)	10.791(2)	13.0540(5)
c (Å)	15.5382(4)	11.134(3)	30.2390(11)
α (°)	(90)	63.35(2)	(90)
β (°)	98.1100(10)	79.18(2)	98.9750(10)
γ (°)	(90)	84.357(18)	(90)
Space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2	$C2/c$, No. 15
Z	4	2	8
Temp. (K)	150(2)	203(2)	123(2)
μ (mm^{-1})	0.063	0.064	0.056
Reflns. measd.	27311	3995	9366
Reflns. obsd[a] (R_{int})	6158 (0.0469)	3770 (0.0421)	9366 (0.000)
R_1(observed)	0.0505	0.0391	0.0542
wR_2(all data)[b]	0.1237	0.0964	0.1327

[a] $I > 2\sigma(I)$. [b] $wR_2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{1/2}$.

[1] K. Gregory, P. v. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47.

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

[3] [3a] G. Hilmersson, Ö. Davidsson, *J. Organomet. Chem.* **1995**, *489*, 175. [3b] G. Hilmersson, Ö. Davidsson, *Organometallics* **1995**, *14*, 912. [3c] G. Hilmersson, P. I. Arvidsson, Ö. Davidsson, M. Håkansson, *Organometallics* **1997**, *16*, 3352. [3d] P. I. Arvidsson, G. Hilmersson, Ö. Davidsson, *Chem. Eur. J.* **1999**, *5*, 2348. [3e] P. I. Arvidsson, P. Ahlberg, Ö. Davidsson, *Chem. Eur. J.* **1999**, *5*, 1348. [3f] A. Johansson, G. Hilmersson, Ö. Davidsson, *Organometallics* **2002**, *21*, 2283. [3g] A. Corruble, J.-Y. Valnot, J. Maddaluno, Y. Iprgnet, D. Davoust, P. Duhamel, *J. Am. Chem. Soc.* **1997**, *119*, 10042. [3h] A. Corruble, D. Davoust, S. Desjardins, C. Fressigné, C. Giessner-Prettre, A. Harrison-Marchand, H. Houte, M.-C. Lasne, J. Maddaluno, H. Oulyadi, J.-Y. Valnot, *J. Am. Chem. Soc.* **2002**, *124*, 15267.

[4] [4a] C. Fressigné, A. Corruble, J.-Y. Valnot, J. Maddaluno, C. Giessner-Prettre, *J. Organomet. Chem.* **1997**, *549*, 81. [4b] Y. Balamraju, C. D. Sharp, W. Gammill, L. M. Pratt, *Tetrahedron* **1998**, *54*, 7357. [4c] C. Fressigné, J. Maddaluno, A. Marquez, C. Giessner-Prettre, *J. Org. Chem.* **2000**, *65*, 8899. [4d] O. Parisel, C. Fressigné, J. Maddaluno, C. Giessner-Prettre, *J. Org. Chem.* **2003**, *68*, 1290.

[5] [5a] D. Barr, W. Clegg, S. M. Hodgson, R. E. Mulvey, D. Reed, R. Snaith, D. S. Wright, *J. Chem. Soc., Chem. Commun.* **1988**, 367. [5b] S. Harder, M. Lutz, T. Kremer, *Organometallics* **1995**, *14*, 2133. [5c] M. Konemann, G. E. Erker, R. Frohlich, E.-U. Wurthwein, *J. Am. Chem. Soc.* **1997**, *119*, 11155. [5d] P. C. Andrews, S. M. Calleja, M. Maguire, *J. Chem. Soc., Dalton Trans.* **2002**, 3640. [5e] P. G. Williard, M. A. Jacobsen, *Org. Lett.* **2000**, *2*, 2753. [5f] R. P. Davies, P. R. Raithby, R. Snaith, *Angew. Chem.* **1997**, *109*, 1261; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1215. [5g] G. B. Deacon, C. M. Forsyth, N. M. Scott, *J. Chem. Soc., Dalton Trans.* **2001**, 2494.

[6] [6a] P. G. Williard, C. Sun, *J. Am. Chem. Soc.* **1997**, *119*, 11693. [6b] J. Schneider, E. Popowski, H. Reinke, *Z. Anorg. Allg. Chem.* **2002**, *628*, 719.

[7] [7a] D. J. Brauer, H. Bürger, G. R. Liewald, *J. Organomet. Chem.* **1986**, *308*, 119. [7b] H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1991**, *30*, 2487. [7c] M. G. Gardiner, C. L. Raston, *Inorg. Chem.* **1995**, *34*, 4206. [7d] M. G. Gardiner, C. L. Raston, *Inorg. Chem.* **1996**, *35*, 4047. [7e] M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millerolte, M. Denk, R. West, *J. Am. Chem. Soc.* **1998**, *120*, 12714.

[8] [8a] K. W. Hellmann, C. Galka, L. H. Gade, A. Steiner, D. S. Wright, T. Kottke, D. Stalke, *Chem. Commun.* **1998**, 549. [8b] K. W. Hellmann, A. Bergner, L. H. Gade, I. J. Scowen, M. McPartlin, *J. Organomet. Chem.* **1999**, *573*, 156. [8c] R. M. Gauvin, N. Kyritsakas, J. Fischer, J. Kress, *Chem. Commun.* **2000**, 965. [8d] S. Danielle, C. Drost, B. Gerhus, S. M. Hawkins, P. B. Hitchcock, M. F. Lappert, P. G. Merle, S. G. Bott, *J. Chem. Soc., Dalton Trans.* **2001**, 3179.

[9] [9a] A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816. [9b] R. E. Mulvey, *Chem. Commun.* **2001**, 1049.

[10] [10a] J. K. Brask, T. Chivers, G. P. A. Yap, *Chem. Commun.* **1998**, 2543. [10b] J. K. Brask, T. Chivers, G. Schatte, G. P. A. Yap, *Organometallics* **2000**, *19*, 5683. [10c] M. A. Beswick, B. R. Elvidge, N. Feeder, S. J. Kidd, D. S. Wright, *Chem. Commun.* **2001**, 379. [10d] M. C. Copsey, J. C. Jeffery, A. P. Leedham, C. A. Russell, J. M. Slattery, *Dalton Trans.* **2003**, 2103.

[11] [11a] M. B. Eleveld, H. Hogeveen, *Tetrahedron Lett.* **1984**, *25*, 5187. [11b] A. Corruble, J.-Y. Valnot, J. Maddaluno, P. Duhamel, *J. Org. Chem.* **1998**, *63*, 8266. [11c] P. I. Arvidsson, Ö. Davidsson, G. Hilmersson, *Tetrahedron: Asymmetry* **1999**, *10*, 527. [11d] K. Flinois, Y. Yuan, C. Bastide, A. Harrison-Marchand, J. Maddaluno, *Tetrahedron* **2002**, *58*, 4707. [11e] J. Granander, R. Sott, G. Hilmersson, *Tetrahedron* **2002**, *58*, 4717.

[12] D. T. Carey, F. S. Mair, R. G. Pritchard, J. E. Warren, R. J. Woods, *Dalton Trans.* in press.

[13] D. T. Carey, E. K. Cope-Eatough, E. Vilaplana-Mafé, F. S. Mair, R. G. Pritchard, J. E. Warren, R. J. Woods, *Dalton Trans.* **2003**, 1083.

[14] E. K. Cope-Eatough, F. S. Mair, R. G. Pritchard, J. E. Warren, R. J. Woods, *Polyhedron* **2003**, *22*, 1447.

[15] D. K. Kennepohl, S. Brooker, G. M. Sheldrick, H. W. Roesky, *Chem. Ber.* **1991**, *124*, 2223.

[16] D. Braga, F. Grepioni, K. Biradha, G. R. Desiraju, *J. Chem. Soc., Dalton Trans.* **1996**, 3925.

[17] T. Kottke, D. Stalke, *Angew. Chem.* **1993**, *105*, 619; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 580.

[18] See, for example: K. N. Zelenin, A. V. Dovgilevich, I. P. Bezhan, G. A. Golubeva, L. A. Sviridova, *Chem. Heterocycl. Compd.* **1984**, *20*, 529; J. L. Vennerstrom, T. J. Holmes, *J. Med. Chem.* **1987**, *30*, 563; A. R. Katritzky, G. Qiu, B. Yang, *J. Org. Chem.* **1997**, *62*, 8210.

[19] S. F. Nelsen, M. R. Willi, *J. Org. Chem.* **1984**, *49*, 1.

[20] C. Neumann, A. Schulz, T. Siefert, W. Storch, M. Vosteen, *Eur. J. Inorg. Chem.* **2002**, 1040.

[21] J. P. Ritchie, S. M. Bachrach, *J. Am. Chem. Soc.* **1987**, *109*, 5909.

[22] R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167.

[23] M. Marsch, K. Harms, L. Lochmann, G. Boche, *Angew. Chem.* **1990**, *102*, 334; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 308.

[24] [24a] J. F. McGarrity, C. A. Ogle, *J. Am. Chem. Soc.* **1984**, *107*, 1805. [24b] W. Bauer, T. Clark, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1987**, *109*, 970.

[25] J. D. Scollard, D. H. McConville, N. C. Payne, J. J. Vittal, *Macromol.* **1996**, *29*, 5241; J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc.* **1996**, *118*, 10008; J. Jin, S. Tsubaki, T. Uozumi, T. Sano, K. Soga, *Makromol. Chem. Rapid Commun.* **1998**, *19*, 597.

[26] A. F. Burchatt, J. M. Chong, N. Nielsen, *J. Organomet. Chem.* **1997**, *542*, 281.

Received June 17, 2003