DALTON
FULL PAPER

The synthesis and structure of lithium derivatives of the sterically encumbered β-diketiminate ligand [{(2,6-Pr$^i_2$H$_3$C$_6$)N(CH$_3$)C}$_2$CH]$^-$, and a modified synthesis of the aminoimine precursor

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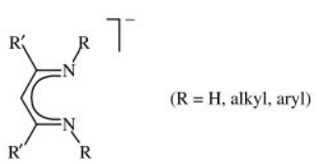
The reaction of the β-aminoimine compound (2,6-Pr$^i_2$H$_3$C$_6$)NC(CH$_3$)CHC(CH$_3$)N(C$_6$H$_3$-2,6-Pr$^i_2$)H (**1**, Dipp$_2$nacnacH; Dipp = C$_6$H$_3$-2,6-Pr$^i_2$) with *n*-BuLi in diethyl ether or tetrahydrofuran afforded the solvates Dipp$_2$nacnacLi(Et$_2$O) (**2**) and Dipp$_2$nacnacLi(THF) (**3**), respectively, which crystallized as monomers featuring the Li$^+$ ions in a distorted trigonal planar environment and an essentially planar arrangement for the LiN$_2$C$_3$ ring. The lithiation of **1**, in the absence of a donor solvent, afforded a Dipp$_2$nacnacLi product that crystallized in two different types of associated structures, **4a** and **4b**. In the dimer **4a**, the Li$^+$ ion is coordinated to the two nitrogens of the Dipp$_2$nacnac ligand, and it is associated by coordination of lithium to a carbon of the Dipp ring of the other Dipp$_2$nacnac unit of the dimer. In the dodecamer **4b**, the asymmetric unit consists of a chain of six LiDipp$_2$nacnac units associated by interactions of the Li$^+$ ions with one or two carbons from a Dipp ring of the next molecule in the chain. The hexamer is linked to an identical one (generated through an inversion center) by Li$^+$–Dipp interactions involving the first and third lithium atoms from each hexamer, thereby generating an overall dodecameric structure of a type that was previously unknown for lithium salts. An improved yield synthesis for **1** was also developed.

Over the past few years there has been a revival of interest in the bidentate, β-diketiminate ligands[1] which may be illustrated by the formula [{RNC(R′)}$_2$CH]$^-$.



A major portion of the new work has focussed on more crowded ligands that involve bulky substituents at the nitrogens.[2–26] These have been used to synthesize a variety of transition metal,[2–14] main group element,[15–25] and lanthanide[26] complexes, a significant number of which have been shown to be effective as either olefin polymerization catalysts[2,5,7,16,18] or structural models for the metal sites in metalloproteins.[13,14] In addition, these ligands have been applied successfully to the stabilization of low-coordinate, and low oxidation state main group metal complexes.[23,24] The readily synthesized, sterically encumbering [Dipp$_2$nacnac]$^-$,†[7] *i.e.* [{(2,6-Pr$^i_2$H$_3$C$_6$)-N(CH$_3$)C}$_2$CH]$^-$, ligand has played a prominent rôle in this work. Although it is possible to use the parent β-diketimine, Dipp$_2$nacnacH, as a ligand source in the preparation of some complexes, the lithium derivatives of the [Dipp$_2$nacnac]$^-$ anion, generated in diethyl ether, tetrahydrofuran or hydrocarbon solution, are the most widely used, and the most important, transfer agents for this ligand. In spite of this, very little is known about the spectroscopic and structural details of these key species. A recent report has described the monomeric structure of the related very crowded lithium salt [{(2,6-Pr$^i_2$-H$_3$C$_6$)N(Bu^t)C}$_2$CH]Li(THF)[8] which has *tert*-butyl instead of methyl substituents on the ring carbons. The structures of the less hindered dimers [({(Me$_3$Si)N(Ph)CH}$_2$CH)Li]$_2$[27] and [{(Me$_2$N)$_3$PO}Li{(Ph)NCH}CH]$_2$[28] have also been published, but, as will be shown, their structures are quite different from those described in this paper. The only currently known structure of a group 1 element derivative of the [Dipp$_2$nacnac]$^-$ ligand is its potassium salt (Dipp$_2$nacnac)K, which exists as a polymer *via* η^5-association of the K$^+$ ion with a Dipp group of a neighboring unit.[29] We now report an improved yield (>75%) synthesis of the parent ligand Dipp$_2$nacnacH (**1**), as well as the structural characterization of **1**, its lithium derivatives Dipp$_2$nacnacLi(Et$_2$O) (**2**) and Dipp$_2$nacnacLi(THF) (**3**), as well as the base free dimer (LiDipp$_2$nacnac)$_2$ (**4a**) and dodecamer (LiDipp$_2$nacnac)$_{12}$ (**4b**).

Experimental

General procedures

All manipulations, except those involving the synthesis of **1**, were carried out by using modified Schlenk techniques under an atmosphere of N$_2$ or in a Vacuum Atmospheres H-43 drybox. All solvents were distilled from Na–K alloy and degassed twice immediately before use. Diisopropylaniline (ACROS), 2,4-pentanedione (ACROS) and *n*-BuLi (as a 1.6 M solution in hexanes) were purchased commercially and used as received. ^{1}H, ^{13}C{^{1}H} and ^{7}Li NMR spectra were recorded near 300 K on a Bruker 300 MHz or a Varian 400 MHz instrument and referenced to the deuterated solvent.

CCDC reference numbers 162354–162358.

See http://www.rsc.org/suppdata/dt/b1/b103149j/ for crystallographic data in CIF or other electronic format.

† The designation [nacnac]$^-$ for the unsubstituted species [HC{C(Me)NH}$_2$]$^-$, by comparison with [acac]$^-$ for [HC{C(Me)O}$_2$]$^-$, was first proposed by Theopold and co-workers.[7]

Dipp$_2$nacnacH, 1. Concentrated, 12 M HCl (5 mL) was added to a solution of 2,4-pentanedione (4.45 g, 44.4 mmol) and 2,6-diisopropylaniline (19.1 g, 107 mmol) in ethanol (200 mL). The solution was heated to reflux for 3 days, after which, the solvent was removed to leave a dark pink solid residue. This solid was then refluxed with 300 mL of hexane for 1 h. The slurry was filtered, and the solid hydrochloride salt was placed in a 1 L flask where it was treated with 200 mL of a saturated aqueous Na_2CO_3 solution and 300 mL of dichloromethane. The slurry was stirred until the solid dissolved. The organic layer was separated, dried with $MgSO_4$, and filtered. The solvent was then removed to leave a white solid residue. The almost pure (by ^{1}H NMR) product **1** was washed with cold (*ca.* 0 °C) methanol (50 mL). The pure Dipp$_2$nacnacH was dried under reduced pressure to remove any residual methanol. The yield was 14.5 g or 78%. The product afforded a mp and ^{1}H and ^{13}C NMR spectra that were identical to those reported in the literature.[2]

Dipp$_2$nacnacLi(Et$_2$O), 2. With cooling in an ice bath, Dipp$_2$nacnacH (8.0 g, 19.1 mmol) was dissolved in rapidly stirred Et_2O (70 mL), and treated dropwise with 12.0 mL of a 1.6 M *n*-BuLi solution in hexanes. Upon completion of the addition, the solution was allowed to come to room temperature and stirred for 12 h. The Et_2O was removed under reduced pressure until the product precipitated. It was redissolved with gentle heating. Cooling for 24 h in a *ca.* −20 °C freezer afforded the product **2** as colorless crystals. Mp 138–139 °C. The yield obtained ranged between 75–90% in several preparations. The ^{1}H and ^{13}C NMR spectra were identical to those reported earlier.[30] ^{7}Li NMR (C_6D_6): δ 1.61.

Dipp$_2$nacnacLi(THF), 3. Dipp$_2$nacnacH (8.00 g, 19.1 mmol) was dissolved in THF (60 mL) with rapid stirring and 12.0 mL of a 1.6 M *n*-BuLi solution in hexanes was added while cooling in an ice bath. The solution was stirred overnight at room temperature and the THF was removed under reduced pressure until the product precipitated. It was redissolved by heating, and subsequent cooling in a *ca.* −20 °C freezer afforded the product **3** as colorless crystals. Mp 194–197 °C. Yield: 6.9 g, 73%. ^{1}H NMR (C_6D_6): δ 7.2–7.1 (m, 6H, C_6H_3), 5.01 (s, 1H, γ-CH), 3.42 (sept, 4H, J = 6.8 Hz, C*H*Me$_2$), 2.70 (t, 4H, OC*H*$_2$CH$_2$), 1.91 (s, 6H, Me), 1.27 (d, 12H, J = 6.8 Hz, CH*Me*$_2$), 1.20 (d, 12H, J = 6.8 Hz, CH*Me*$_2$), 0.87 (t, 4H, OCH$_2$C*H*$_2$); ^{13}C NMR (C_6D_6): δ 163.4 (CN), 150.3, 141.4, 123.4, 123.1 (C_6H_3), 92.7 (γ-C), 28.4 (*C*HMe$_2$), 24.8 (CH*Me*$_2$), 24.0 (CH*Me*$_2$), 23.3 (Me); ^{7}Li NMR (C_6D_6): δ 1.67.

(Dipp$_2$nacnacLi)$_n$ [n = 2 (4a), 12 (4b)]. Dipp$_2$nacnacH (8.00 g, 19.1 mmol) was dissolved in hexane (70 mL) with rapid stirring and 12.0 mL of a 1.6 M *n*-BuLi solution in hexanes was added dropwise while cooling in an ice bath. The solution was stirred overnight at room temperature and the hexane was removed under reduced pressure until the product precipitated. It was redissolved by heating. Colorless crystals of **4a** and **4b** were obtained by cooling to *ca* 5 °C for 24 h. Mp 150–152 °C (turns yellow above 120 °C). Yield: 6.3 g, 77%. ^{1}H NMR (C_6D_6): δ 7.2–7.1 (m, 6H, C_6H_3), 4.81 (s, 1H, γ-CH), 3.05 (sept, 4H, J = 6.8 Hz, C*H*Me$_2$), 1.75 (s, 6H, Me), 1.13 (d, 12H, J = 6.8 Hz, CH*Me*$_2$), 1.10 (d, 12H, J = 6.8 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 164.0 (CN), 149.2, 140.7, 127.7, 123.3 (C_6H_3), 93.0 (γ-C), 28.2 (*C*HMe$_2$), 24.2 (CH*Me*$_2$), 23.9 (CH*Me*$_2$), 23.3 (Me); ^{7}Li NMR (C_6D_6): δ −1.90.

Crystallography

Crystals of **1**–**4** were coated with hydrocarbon oil, mounted on a glass fiber, and quickly placed in a cold N_2 stream.[31] Data for **1** and **2** were collected on a P4 RA diffractometer at 130 and 140 K, respectively, using Cu-Kα radiation. Data for **3**, **4a** and **4b** were collected at 90 K using a Bruker SMART 1000 system (Mo-Kα radiation and a CCD area detector). The Bruker SHELXTL 5.11 program package was used for the structure solutions and refinement.[32] An absorption correction was applied using the program SADABS.[33] The structures of **2** and **4b** displayed minor disorder problems that affected some of the methyls of the Pr^i groups. These were refined satisfactorily by using partial occupancies of 50% for the two methyl sites. In addition, the hexane solvate molecule in **4b** displayed more severe disorder problems with the result that the hexane hydrogen atoms were not added. Some details of the data collection and refinement are given in Table 1.

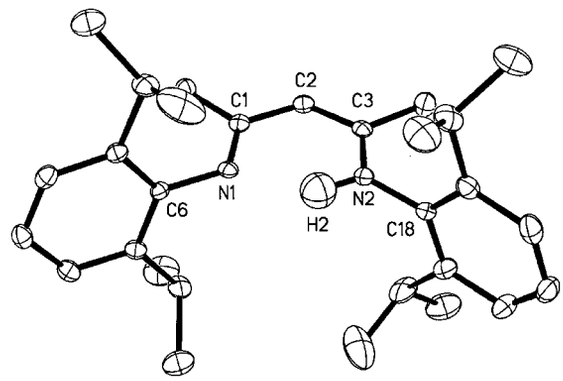


Fig. 1 Thermal ellipsoid plot of **1**. H atoms, except N–H, are not shown for clarity.

Results and discussion

Synthesis and spectroscopy

The aminoimine **1** was synthesized in a manner similar to that previously described by Feldman and co-workers.[2] However, we found that refluxing the crude hydrochloride, **1**·HCl, in hexane significantly increased the ultimate yield of the product **1**. Apparently, the use of hexane, in which **1**·HCl is insoluble, to remove contaminants minimizes the loss of product. In the previously published method, cold MeOH was used to wash the dehydrochlorinated product **1** (in which solvent it has some solubility) and this may account for the somewhat lower yield obtained by this method.

Treatment of **1** with *n*-BuLi in Et_2O, THF or hexane results in the products **2**, **3** or **4** in high yield. These lithium reagents have been generated *in situ* in several previous publications employing these solvents, however, only the ^{1}H and ^{13}C NMR spectra of **2** have been previously reported.[30] All products crystallize well from their respective solutions. In the synthesis of **4**, the products crystallized in dimeric and dodecameric forms, **4a** and **4b**. However, in solution at room temperature the products have identical ^{1}H, ^{13}C and ^{7}Li NMR spectra. Furthermore, the observed melting points are the same. The ^{1}H NMR spectra are characterized by distinct magnetic environments for the isopropyl methyl groups and a γ-H chemical shift in the range 4.8–5.1 ppm. the ^{7}Li NMR shifts of **2** and **3** feature peaks at δ 1.61 and 1.67 whereas the unsolvated **4a** and **4b** appear at δ −1.91.

Structures

The structure of **1** is shown in Fig. 1. Dipp$_2$nacnacH crystallized with two crystallographically independent, but structurally similar, molecules in the asymmetric unit. In each case, the nitrogen hydrogen was located and refined. They were found to be bonded primarily at one nitrogen in each molecule. The N(2)–H(2) and N(3)–H(3) distances are 0.97(4) and 0.92(4) Å, respectively. Furthermore, each hydrogen is located close to the plane formed by the two nitrogens and their three connecting carbons, with the result that there are long N ··· H contacts to N(1) [1.86(4) Å] and N(4) [1.89(4) Å]. In effect, N(2) and N(3) can be designated the amine nitrogens, and this is supported by

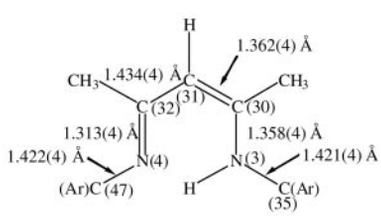
Table 1 Crystal and experimental data for compounds **1**–**4**

Compound	**1**	**2**	**3**	**4a**	**4b**·hexane
Formula	$C_{29}H_{42}N_2$	$C_{33}H_{51}LiN_2O$	$C_{33}H_{49}LiN_2O$	$C_{29}H_{41}N_2Li$	$C_{354}H_{506}Li_{12}N_{24}$
Fw	418.65	498.70	496.68	424.58	5181.11
Cryst. syst.	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
a/Å	15.053(5)	47.323(6)	13.936(5)	12.4708(14)	32.839(1)
b/Å	17.944(6)	10.1697(9)	14.757(5)	14.046(2)	16.7836(6)
c/Å	20.034(5)	19.933(1)	15.720(5)	15.124(2)	33.375(1)
α/°				90.765(3)	
β/°	97.40(2)	94.366(7)	106.498(6)	91.189(3)	112.275(1)
γ/°				102.979(3)	
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
Z	8	12	4	4	2
μ/mm^{-1}	0.44	0.46	0.06	0.06	0.06
Obs. data [$I > 2\sigma(I)$]	5195	5149	2707	4630	15015
*R*1	0.0628	0.0474	0.075	0.0769	0.0899
*wR*2	0.1659	0.1313	0.2159	0.2406	0.2932

Table 2 Selected bond distances (Å) and angles (°) for **1**–**4**

1		**2**		**3**		**4a**		**4b**	
N(1)–C(1)	1.318(3)	N(1)–C(1)	1.324(3)	N(1)–C(1)	1.325(3)	N(1)–C(1)	1.323(4)	N(1)–C(1)	1.321(5)
N(2)–C(3)	1.341(3)	N(2)–C(3)	1.325(3)			N(2)–C(3)	1.325(4)	N(2)–C(3)	1.337(5)
C(1)–C(2)	1.418(4)	C(1)–C(2)	1.402(3)	C(1)–C(2)	1.410(2)	C(1)–C(2)	1.413(5)	C(1)–C(2)	1.412(5)
C(2)–C(3)	1.386(4)	C(2)–C(3)	1.402(3)			C(2)–C(3)	1.388(5)	C(2)–C(3)	1.396(5)
N(1)–C(6)	1.431(3)	N(1)–C(6)	1.428(3)	N(1)–C(6)	1.421(3)	N(1)–C(6)	1.442(4)	N(1)–C(6)	1.433(5)
N(2)–C(18)	1.429(4)	N(2)–C(18)	1.424(3)						
		N(1)–Li(1)	1.917(4)	N(1)–Li(1)	1.958(5)	N(1)–Li(1)	1.894(7)	N(1)–Li(1)	1.892(7)
		N(2)–Li(1)	1.912(4)			N(2)–Li(1)	1.919(7)	N(2)–Li(1)	1.903(7)
		O(1)–Li(1)	1.911(4)	O(1)–Li(1)	1.790(7)	C(22) ··· Li(1)	2.834(7)	C(50) ··· Li(1)	2.407(8)
		Li(1)–N(1)–C(1)	120.9(2)	Li(1)–N(1)–C(1)	124.4(2)	Li(1)–N(1)–C(1)	119.5(3)	Li(1)–N(1)–C(1)	121.6(3)
		Li(1)–N(1)–C(6)	120.6(2)	Li(1)–N(1)–C(4)	115.7(2)	Li(1)–N(1)–C(6)	121.3(3)	Li(1)–N(1)–C(6)	119.4(3)
C(1)–N(1)–C(6)	121.1(2)	C(1)–N(1)–C(6)	118.4(2)	C(1)–N(1)–C(4)	119.8(2)	C(1)–N(1)–C(6)	118.8(3)	C(1)–N(1)–C(6)	119.0(3)
N(1)–C(1)–C(2)	120.6(2)	N(1)–C(1)–C(2)	124.3(2)	N(1)–C(1)–C(2)	123.4(2)	N(1)–C(1)–C(2)	123.7(3)	N(1)–C(1)–C(2)	123.5(3)
C(2)–C(1)–C(4)	117.5(2)	C(2)–C(1)–C(4)	116.3(2)	C(2)–C(1)–C(3)	116.6(2)	C(2)–C(1)–C(4)	115.9(3)	C(2)–C(1)–C(4)	116.9(3)
N(1)–C(1)–C(4)	121.9(2)	N(1)–C(1)–C(4)	119.4(2)	N(1)–C(1)–C(3)	120.0(2)	N(1)–C(1)–C(4)	120.3(3)	N(1)–C(1)–C(4)	119.5(3)
C(1)–C(2)–C(3)	126.3(3)	C(1)–C(2)–C(3)	129.5(2)	C(1)–C(2)–C(1A)	128.6(3)	C(1)–C(2)–C(3)	130.0(3)	C(1)–C(2)–C(3)	129.8(4)
C(2)–C(3)–N(2)	121.0(3)	C(2)–C(3)–N(2)	123.2(2)			C(2)–C(3)–N(2)	124.3(3)	C(2)–C(3)–N(2)	122.6(3)
C(2)–C(3)–C(5)	120.0(3)	C(2)–C(3)–C(5)	116.7(2)			C(2)–C(3)–C(5)	116.1(3)	C(2)–C(3)–C(5)	116.9(3)
C(5)–C(3)–N(2)	119.0(2)	C(5)–C(3)–N(2)	120.1(2)			C(5)–C(3)–N(2)	119.6(3)	C(5)–C(3)–N(2)	120.5(3)
		Li(1)–N(2)–C(3)	122.0(2)			Li(1)–N(2)–C(3)	118.2(3)	Li(1)–N(2)–C(3)	121.8(3)
		Li(1)–N(2)–C(18)	118.6(2)			Li(1)–N(2)–C(18)	120.8(3)	Li(1)–N(2)–C(18)	116.6(3)
C(3)–N(2)–C(18)	123.7(2)	C(3)–N(2)–C(18)	119.4(2)			C(3)–N(2)–C(18)	119.9(3)	C(3)–N(2)–C(18)	121.0(3)
		N(1)–Li(1)–N(2)	99.9(2)	N(1)–Li(1)–N(1A)	95.5(3)	N(1)–Li(1)–N(2)	102.3(3)	N(1)–Li(1)–N(2)	100.1(3)
		N(1)–Li(1)–O(1)	132.4(2)	N(1)–Li(1)–O(1)	132.3(2)				
		N(2)–Li(1)–O(1)	127.7(2)						

the pattern of N–C and C–C bond lengths in both molecules, as exemplified by the diagram below.



These distances and, to a lesser extent, those of the other molecule in the asymmetric unit (see Table 2) indicate that localization of the double bonds is far advanced. Extensive localization and comparable C–N and C–C distances are also observed in the structure of the corresponding N-phenyl-substituted compound H(Ph)NC(Me)CHC(Me)N(Ph), which seems to be the only other structurally characterized *β*-aminoimine.[34] However, in this species, the nitrogen hydrogen was found to bond equally strongly to each nitrogen (N–H = 1.42 Å). At present, it is not clear if the difference between the two structures is due to some chemical difference or to the larger standard deviations in the structure of the phenyl-substituted species.[34] However, the latter explanation appears to be more plausible.

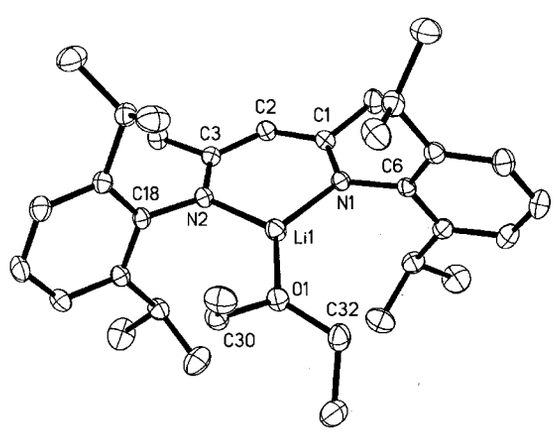


Fig. 2 Thermal ellipsoid plot of **2**. H atoms are not shown for clarity.

The addition of *n*-BuLi to **1** in Et_2O or THF solution afforded the lithium salts **2** (Fig. 2) and **3** (Fig. 3) as their solvent adducts. The etherate **2** crystallized with 1.5 crystallographically independent molecules in the asymmetric unit. These molecules have very similar structures so that data for only one of these are given in Table 2. Replacement of hydrogen by lithium leaves the planarity of the C_3N_2 ring unaffected.

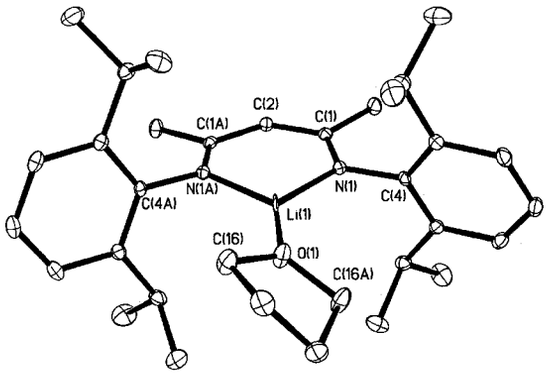


Fig. 3 Thermal ellipsoid plot of **3**. H atoms are not shown for clarity.

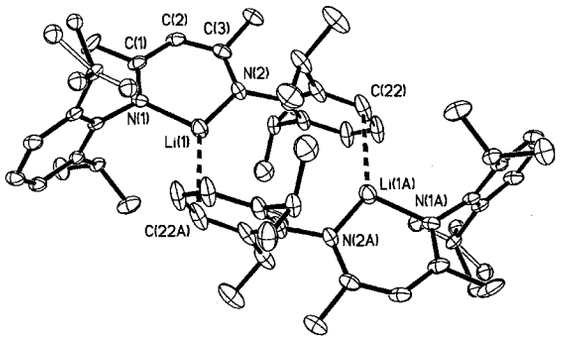


Fig. 4 Thermal ellipsoid plot of **4a**. H atoms are not shown for clarity.

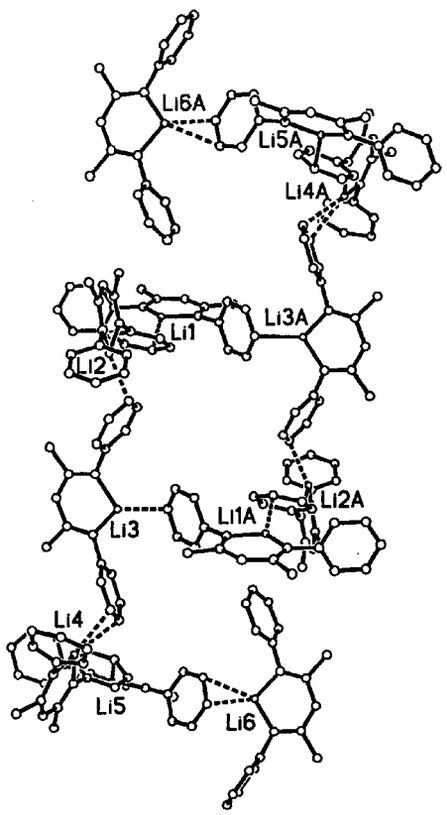


Fig. 5 Thermal ellipsoid plot of **4b**. H atoms and Pr^i groups are not shown for clarity.

However, it can be seen (Table 2) that the two C–C and two N–C distances within the C_3N_2Li ring become symmetric upon lithium substitution, indicating that the π-bonding is now delocalized. In effect, it may be described as a diazapentadienide alkali metal complex.[29] The lithium ion has a trigonal planar coordination that has angles which are grossly distorted from idealized values; *e.g.* N(1)–Li(1)–N(2) = 99.9(2)°. The Li–N and Li–O bond lengths are within the range of those previously observed for three coordinate lithium bound to amide ligands and ether ligands.[35,36]

The THF solvate **3** has a very similar structure to **2**. In this case, however, there is an imposition of planarity on the C_3N_2Li ring due to the crystallographic two-fold axis that passes through O(1), Li(1) and C(2) which has N–C and C–C distances that are very similar to those observed in **2**. The lithium ion has three coordinate planar geometry with a narrower N(1)–Li–N(1A) angle [95.5(3)°] than that seen in **2**. The lithium nitrogen distance in **3** is *ca.* 0.04 Å longer than the corresponding ones in **2**. In contrast, the Li(1)–O(1) bond length to the THF oxygen in **3** is *ca.* 0.12 Å shorter than the Li–O (Et_2O) bond in **2**. These changes reflect the greater donor strength of the THF molecule in comparison to Et_2O. Apparently, the increased donation by the solvating molecule in **3** increases electron density at lithium. This would be expected to lead to a weaker Li–N interaction, which is what is experimentally observed.

The change from an Et_2O to a THF donor does not appear to affect the $Dipp_2$nacnac ligand geometry to any great extent. Furthermore, the angles between the Dipp and LiN_2C_3 planes, 83.7 and 85.8° in **2** and 82.8° in **3** are very similar. The confinement of the aryl rings to an essentially perpendicular orientation with respect to the *β*-diketiminate ring results in magnetically distinct environments for the methyls of the Pr^i substituents, which is reflected in the ^1H and ^{13}C NMR spectra of **2**, **3**, and **4**, as well as numerous other derivatives of this ligand. Significant geometrical differences are observed between the structure of **3** and that of the related species [{(2,6-$Pr^i_2H_3C_6$)N(Bu^t)}$_2$CH]Li(THF).[8] This molecule differs from **3** in that Bu^t groups replace the methyl substituents on the central C_3N_2Li ring. The consequent steric conflict between the Bu^t and –C_6H_3-2,6-Pr^i_2 substituents is manifested in the wider C(2)–N(1)–C(6) and C(4)–N(2)–C(18) angles of 129.5(3) and 127.0(3)°, respectively, *cf.* 119.8(2)° for the corresponding angles in **3**. In effect, the flanking –C_6H_3-2,6-Pr^i_2 substituents are displaced toward the Li(THF) moiety as reflected in the narrower Li–N–C(*ipso*) angles of 110.3(3) and 107.9(3)°, respectively, *cf.* 115.7(2)° in **3**. This results in a more crowded and protected environment at lithium in the Bu^t substituted species. The greater crowding at lithium also results in a weakening of the THF coordination Li–O = 1.910(6) Å, *cf.* 1.790(7) Å in **3**. These structural differences are in agreement with previous findings on the reactivity of the lithium salt of the bulkier Bu^t species which did not react with $MCl_3(THF)_3$ (M = Ti or V) to afford the metal dihalide derivatives, whereas the corresponding derivatives $Dipp_2$nacnacMCl_2 were readily formed when the $MCl_3(THF)_3$ salts were treated with **3**.[8]

The unsolvated structures of **4a** and **4b** are shown in Fig. 4 and 5. The compound **4a** crystallized with two structurally similar half dimers in the asymmetric unit. Selected structural data for one of these dimers are given in Table 2. There are only slight deviations from planarity in the C_3N_2Li ring, which has an N(1)–Li(1)–N(2) angle of 102.3(3)°. The average Li–N distance of 1.910(8) Å is shorter than that in **3**, but not significantly different from those in **2**. The dimerization of the $Dipp_2$nacnacLi units is effected by a long interaction of 2.834(7) Å, (it is 2.732(6) Å in the other crystallographically independent dimer) between lithium and one of the aromatic carbons C(22A) of the –$C_6H_3Pr^i_2$-2,6 ring from the partner $Dipp_2$nacnac group. The lithium environment is similar to that observed for one of lithiums in the centrosymmetric structure of the dilithium *β*-diamide [LiN(Dipp)CH_2CH_2(Dipp)NLi]$_2$, where lithium is also bound to two nitrogens (Li–N = 1.940(9) Å) substituted by Dipp groups, and has an interaction of 2.15(1) Å to one of the carbons of the Dipp ring.[37] Clearly, the Li ··· C interactions in **4a** are significantly weaker on the basis

of their much longer Li ··· C interactions. Interestingly, the C(*β*)–N–C(*ipso*) angles in the structures of **4a** and **4b** are very similar to those observed in **2** and **3** in spite of the fact that they coordinate no ether molecules. In addition, the Li–N–C(*ipso*) angles are very similar to those in **2** (and only marginally narrower than that in **3**), suggesting that the wedge-shaped space between the flanking aryl groups is sufficient to accommodate molecules such as Et_2O or THF without strain. The dimerization in **4a** differs from that previously observed in $[(\{(Me_3Si)N(Ph)CH\}_2CH)Li]_2$[27] and $[\{(Me_2N)_3PO\}Li\{(Ph)NCH\}]_2$.[28] The former compound involves association through the behavior of one of the *β*-diketiminate nitrogens of each monomeric unit as bridging atoms to afford a central LiNLiN rhombus with Li–N distances of 1.965(9) and 2.095(2) Å.[27] Owing to their bridging character, these bonds are appreciably longer than those in **4a**. In the $(Me_2N)_3PO$ complexed dimer, the oxygens bridge the lithium ions to afford an Li_2O_2 core. The higher coordination number (4) of the Li^+ ion is reflected in longer Li–N distances of 2.038(4) and 2.052(4) Å.[28]

The unsolvated lithium derivative may also crystallize from the same solvent (hexane) as the dodecameric form **4b** which is illustrated in Fig. 5. This structure is of a new type which has not been previously reported.[35,36] It may be described as a slipped ladder structure. At present, it is not known what conditions favor the crystallization as a dodecamer in preference to the dimer. The asymmetric unit involves six $Dipp_2$nacnacLi molecules linked in a chain-like fashion by Li ··· C interactions between neighboring molecules, from which the dodecamer is generated by an inversion center. The "hexamers" are linked to each other by two Li ··· C interactions involving the Li(1) and Li(3) $Dipp_2$nacnacLi units. Inspection of the structural data in Table 2 indicates that there are no dramatic changes in the structural parameters within the individual $Dipp_2$nacnacLi molecules in comparison to those in **4a**. As in the case of **4a**, the Li ··· C interactions involve a carbon of an aryl ring of the C_6H_3-2,6-Pr_2 substituent of an adjacent molecule. These interactions have the values: Li(1)–C(5) = 2.407(8), Li(2)–C(79) = 2.387(7), Li(3)–C(21) = 2.357(7), Li(4)–C(68) = 2.652(10), Li(5)–C(98) = 2.383(7), Li(6)–C(137) = 2.358(7) Å. Clearly, these distances [with the exception of Li(4)–C(68)] are a good deal (*ca.* 0.4 Å) shorter than the corresponding interactions in **4a**. Even so, the anomalously "long" Li(4) ··· C(68) interaction does not result in any shortening of the Li(4)–N distances which might be expected if the Li ··· C interactions had a large effect on the electron density at lithium. The differences between the Li ··· C interactions in the two compounds are probably the result of the different modes of association. In the dimer **4a**, the association of the $Dipp_2$nacnacLi units is "face to face", in which the lithiums interact with the faces of the aryl rings oriented toward the wedge. In contrast, in **4b**, the lithiums interact with the back side of the aryl rings which makes for a less crowded environment. This permits a closer Li ··· C, which leads to the shorter observed distances. In view of the very slight effect of the different degrees of association on the geometries within the units, it seems likely that the aggregation of the $Dipp_2$nacnacLi units in **4a** and **4b** is relatively weak and this is confirmed by molecular weight studies that show the existence of monomers in solution. The degree of association in crystalline **4b** is a very rare example of a dodecameric structure for a s-block element molecule. The only previous example appears to be the magnesium species $\{EtMgN(H)C_6H_3Pr^i_2\text{-}2,6\}_{12}$ which has a ring of twelve magnesiums bridged by Et and –NHDipp ligands.[38]

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