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Structurally diverse organoamides and organoamido-, organometallic-lithium aggregates from reactions of *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine with LiBu^n†

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Deprotonation of *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine (L^1H) with a slight excess of LiBu^n in tetrahydrofuran (thf) or 1,2-dimethoxyethane (dme) yielded the solvated lithium organoamide complexes $[Li(L^1)(thf)]_n$ (**1**) and $[Li(L^1)(dme)]$ (**2**) ($L^1 = N(C_6H_4OPh\text{-}2)(SiMe_3)$), respectively. Reaction of L^1H with LiBu^n in hexane gave the solvent free lithium organoamide $[Li(L^1)]_n$ (**3**). Monomeric **2** was shown to have a four-coordinate lithium centre surrounded by chelating L^1 and dme ligands in a distorted tetrahedral environment. Utilisation of diethyl ether as the reaction solvent, followed by work up in hexane containing a trace of bis(2-methoxyethyl) ether (diglyme), gave a low yield of colourless crystals, shown by X-ray crystallography to be $[\{Li(OEt_2)(L^1)Li_2(L^{11})\}_2(\mu\text{-}\eta^3\text{-}O,O',O''\text{-diglyme})]$ (**4**) ($L^{11} = N(C_6H_4(OC_6H_4\text{-}2')\text{-}2)(SiMe_3)$), a hexalithium cluster having both singly deprotonated (L^1) and doubly deprotonated (L^{11}) ligands. In L^{11}, the proton of the phenyl substituent *ortho* to the oxygen has been removed in addition to the amine hydrogen. Deliberate attempts to prepare a pure double lithiated product by reaction of L^1H with 2 equivalents of LiBu^n in diethyl ether yielded two different $Li_2(L^{11})$ complexes depending upon the crystallisation solvent. From hexane, a hexalithium aggregate $[Li_2(L^{11})(OEt_2)Li(Bu^n)]_2$ (**5**) was obtained. The structure of **5** showed the presence of two doubly deprotonated $Li_2(L^{11})$ units but, surprisingly, also incorporation of two molecules of LiBu^n. Alternatively, a $Li_2(L^{11})$ complex free of LiBu^n, $[Li_2(L^{11})(dme)]_2$ (**6**) was obtained by crystallisation of the product, prepared in diethyl ether, from a hexane/dme mixture. Variable temperature solution NMR (^1H, ^7Li) data for **4**–**6** indicated the occurrence of dynamic exchange processes at room temperature, but **4** and **5** have the same number of lithium environments at −90 °C as in the solid state structures.

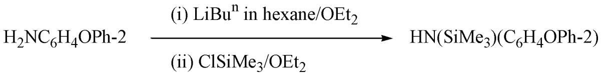
Introduction

Lithium organoamides are of major intrinsic interest because of their structural variety, as strong bases in organic synthesis, and as precursors of organoamidometallics of other elements.[1–6] On transfer to lanthanoid elements, diorganoamide groups provide an alternative to cyclopentadienyls as ligands for compound stabilisation and catalysts.[1,7–9] Bulky chelation supported amide ligands are of particular interest as they can eliminate coordination of ancillary solvent molecules leading to six-coordination which is low for lanthanoids.[10–13] As a prelude to the use of lithium derivatives of the recently prepared *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine[14] in metathesis reactions, we have studied the lithiation of this compound and discovered a rich synthetic and structural chemistry, which is now reported.

Results and discussion

Syntheses and crystal structures

N-(2-Phenoxyphenyl)-*N*-(trimethylsilyl)amine (L^1H), obtained by reaction of $LiNH(C_6H_4OPh\text{-}2)$ with $ClSiMe_3$ in diethyl ether (Scheme 1), is a colourless, moisture sensitive, low melting solid, which has been characterised by elemental analyses, IR and ^1H NMR spectroscopy.[14] Subsequently, single crystals have been obtained and the crystal structure determined (see ESI†).



$$H_2NC_6H_4OPh\text{-}2 \xrightarrow[\text{(ii) ClSiMe}_3\text{/OEt}_2]{\text{(i) LiBu}^n\text{ in hexane/OEt}_2} HN(SiMe_3)(C_6H_4OPh\text{-}2)$$

Scheme 1 Synthesis of L^1H.

Delocalisation of the nitrogen lone pair into the aromatic ring is indicated by the partial double bond character of the N–C bonds (1.389(2) Å) and is consistent with the near planar environment (Σ(°) 357°) of the nitrogen atom. The diaryl ether moiety has the phenyl substituent bent away from the arene backbone plane (torsion angle C(3)–C(2)–O(1)–C(11) 78.5°) and rotated near perpendicular to it (interplanar angle 76.64(4)°).

Lithium derivatives of L^1H are readily prepared by reaction of a slight excess of LiBu^n in hexane with L^1H in tetrahydrofuran (thf), 1,2-dimethoxyethane (dme), or hexane yielding $[Li(L^1)(thf)]_n$ (**1**), $[Li(L^1)(dme)]$ (**2**) and $[Li(L^1)]_n$ (**3**) respectively (Scheme 2), in high yield (>80%). The compositions of the colourless, crystalline products were established by elemental analyses (C, H, N). For **1** and **2**, a 1 : 1 ratio of coordinated thf or dme to the L^1 ligand, distinct ^1H NMR resonances for each of the backbone aromatic protons (H3–H6) and a typical phenyl pattern were evident in the room temperature ^1H NMR spectra for C_7D_8 solutions. In contrast, the room temperature ^1H NMR spectrum of **3** was poorly resolved, but at −90 °C, two unique ligand (L^1) environments at a ratio of *ca.* 1 : 3 were detected (see Experimental section). The ^7Li NMR spectra of **1** and **2** in C_7D_8 solution showed narrow ($\Delta\nu_{1/2}$ 20–30 Hz) single peaks at 1.68 and 1.43 ppm, respectively, consistent with the single Li environment in the structure of **2** (see below). For **3**, the comparable ^7Li resonance (1.65 ppm) is somewhat broader

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† Electronic supplementary information (ESI) available: table of selected bond distances and angles for L^1H. See http://www.rsc.org/suppdata/dt/b1/b103642b/

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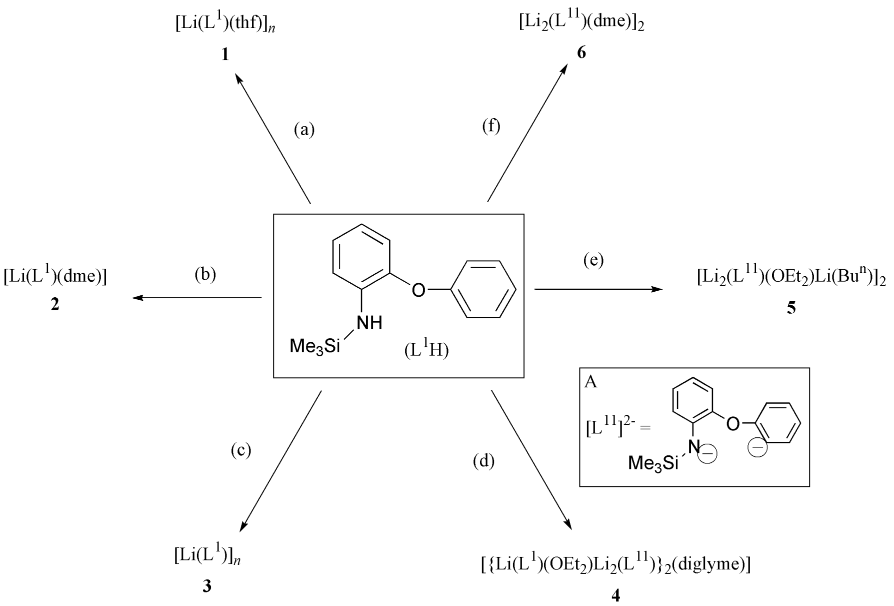


Scheme 2 Reagents and conditions: (a) L^{1}H, LiBu^n (1.6 M in hexane) (1 : 1 or 1 : 2), thf; (b) L^{1}H, LiBu^n (1.6 M in hexane) (1 : 1 or 1 : 2), dme; (c) L^{1}H, LiBu^n (1.6 M in hexane) (1 : 1 or 1 : 2), hexane; (d) i) L^{1}H, LiBu^n (1.6 M in hexane) (1 : 1.1), Et$_2$O, ii) diglyme (trace) hexane; (e) i) L^{1}H, LiBu^n (1.6 M in hexane) (1 : 2), Et$_2$O, ii) hexane; (f) i) as for (e), ii) hexane, dme.

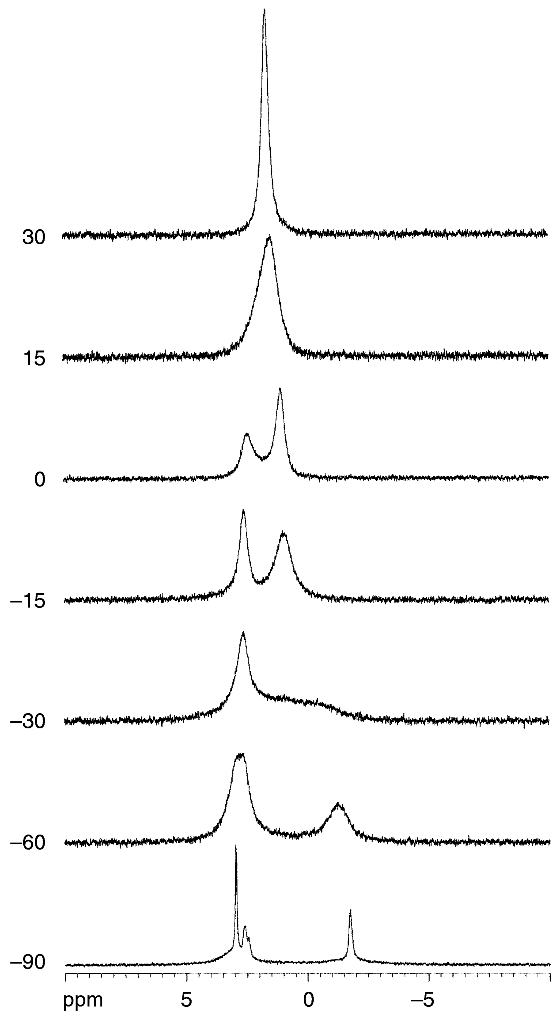


Fig. 1 ^{7}Li NMR spectra of [Li(L^1)]$_n$ in C_7H_8 at 30 to −90 °C.

($\Delta\nu_{1/2}$ 50 Hz) but is resolved into two broad peaks at 0 °C and three sharp resonances at −90 °C (Fig. 1). The NMR behaviour of solutions of **3** is typical of the presence of rapidly exchanging species at room temperature and of one or more aggregates with different Li environments at −90 °C (see below). Comparable data for the recently prepared [LiNPh(SiMe$_3$)]$_4$ showed two ^{7}Li resonances (0.9 and −4.6 ppm) at −110 °C, the low frequency peak being assigned to a terminal Li nucleus with an intramolecular η^6-π-phenyl interaction.[15]

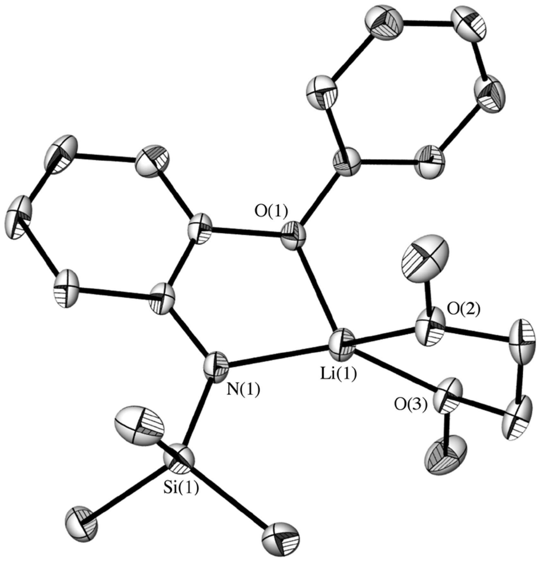


Fig. 2 The molecular structure of [Li(L^1)(dme)] **2**.

Table 1 The lithium environment in [Li(L^1)(dme)] (**2**)

Li(1)–N(1)	1.930(3)	N(1)–Li(1)–O(2)	117.2(1)
Li(1)–O(2)	1.963(3)	N(1)–Li(1)–O(3)	144.2(2)
Li(1)–O(3)	1.986(3)	O(2)–Li(1)–O(3)	83.4(1)
Li(1)–O(1)	2.062(3)	N(1)–Li(1)–O(1)	85.2(1)
		O(2)–Li(1)–O(1)	119.6(1)
		O(3)–Li(1)–O(1)	111.0(1)

The molecular structure of **2** (Fig. 2) shows a monomeric complex with lithium surrounded by chelating L^1 and dme ligands in a highly distorted tetrahedral arrangement (Table 1). The irregular geometry is presumably due to the narrow bite angles of the L^1 (85.2(1)°) and dme (83.4(1)°) ligands and to repulsion between the bulky SiMe$_3$ and OPh substituents. The Li–N distance (Table 1) is marginally smaller than that of monomeric and four-coordinate [Li{N(SiMe$_3$)$_2$}(pmdeta)] (pmdeta = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) (Li–

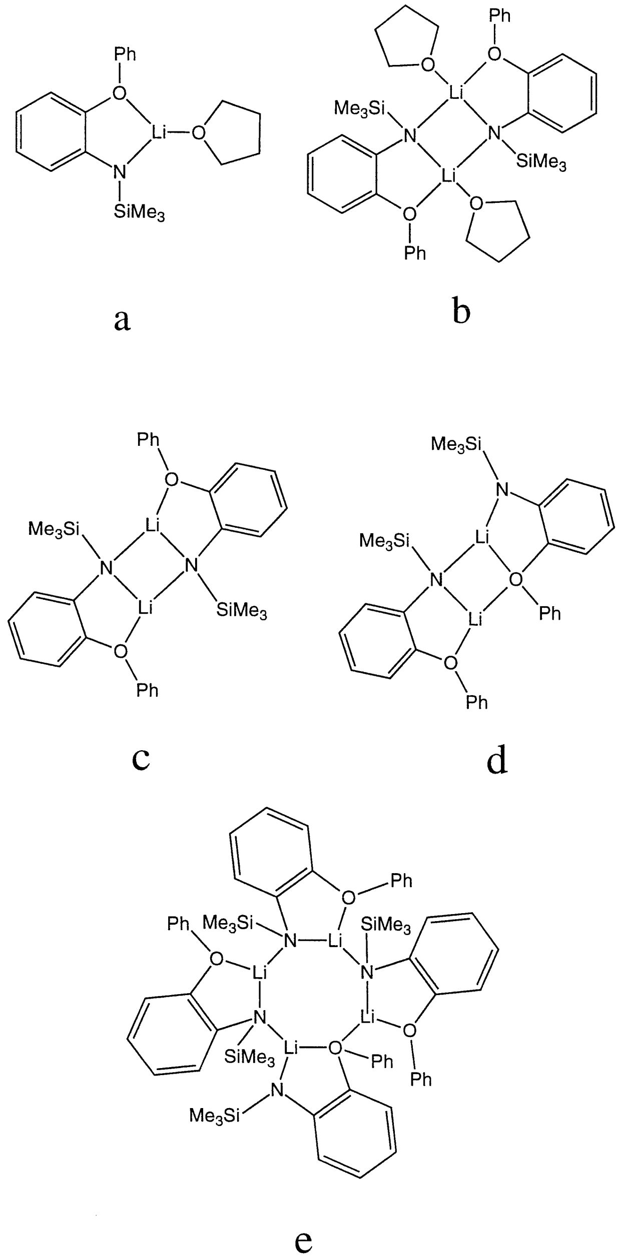


Fig. 3 Possible structures of **1** (a, b) and **3** (c–e).

N(amide) 1.988(6) Å).[16] The Li–O(OPh) bond length in **2** is significantly longer than Li–O(dme) owing to the bulkiness and the electron withdrawing character of the aryl groups. The relative disposition of the two arene rings is similar to that of L^1H (torsion angle C(3)–C(2)–O(1)–C(11) 55.5°; interplanar angle 67.6(5)°). Possible structures for **1** are a three-coordinate monomer (Fig. 3a) or a four-coordinate dimer (Fig. 3b). A dimeric $[Li(L)(S)]_2$ arrangement has precedents for Li complexes of bidentate amides, *e.g.* L = 8-quinolinyl(trimethylsilyl)amide, S = OEt_2,[17] but more sterically hindered systems display an unsymmetrical dinuclear $[Li(L)_2Li(OEt_2)]$ structure *e.g.* L = *N*,*N*-dimethyl-*N*′-trimethylsilylethane-1,2-diaminate.[10] Given the bulky diaryl ether moiety present in L^1, a dimeric structure would seem less probable than the monomer.

The structure of **3** is, reasonably, at least dimeric (Fig. 3c or d). The related complex $[Li(L)]_2$ (L = 8-quinolinyl(trimethylsilyl)amide) is a symmetrical dimer with three-coordinate Li centres bridged by two amido nitrogen atoms.[17] However, this arrangement has only a single Li environment in contrast to the three suggested by the low temperature NMR spectrum of **3** (Fig. 1). A mixture of the two possible dimeric structures (Fig. 3c and d) would show three Li environments (one from the symmetrical dimer 'c' and two from the unsymmetrical dimer 'd'). A higher aggregate is also possible and a tetramer (Fig. 3e) derived from combining 'c' and 'd' would approximate the number of Li and L^1 environments suggested by the NMR spectra. A tetranuclear structure was recently observed for unsolvated $[LiNPh(SiMe_3)]_4$.[18]

Table 2 The lithium environments in $[\{Li(L^1)(OEt_2)Li_2(L^{11})\}_2(diglyme)]$ (**4**)

Li(1)–O(1)	1.980(5)	O(1)–Li(1)–O(3)	106.1(2)
Li(1)–O(3)	1.979(5)	O(1)–Li(1)–N(1)	83.5(2)
Li(1)–N(1)	2.009(5)	O(3)–Li(1)–N(1)	139.4(3)
Li(1)–O(2)	2.033(5)	O(1)–Li(1)–O(2)	108.0(2)
		O(3)–Li(1)–O(2)	112.7(2)
		N(1)–Li(1)–O(2)	100.8(2)
Li(2)–N(1)	2.073(5)	N(1)–Li(2)–N(2)	139.7(2)
Li(2)–N(2)	2.020(5)	N(1)–Li(2)–O(2)	96.2(2)
Li(2)–O(2)	2.110(5)	N(1)–Li(2)–C(212)	120.3(2)
Li(2)–C(212)	2.254(5)	N(2)–Li(2)–O(2)	86.4(2)
Li(2)–C(211)	2.509(5)	N(2)–Li(2)–C(212)	97.9(2)
		O(2)–Li(2)–C(212)	67.4(2)
Li(3)–N(2)	2.060(6)	N(2)–Li(3)–C(212)	100.6(2)
Li(3)–C(212)	2.133(6)	N(2)–Li(3)–O(51)	121.7(3)
Li(3)–O(51)	2.032(7)	N(2)–Li(3)–O(53)	121.6(3)
Li(3)–O(52)	1.835(7)	C(212)–Li(3)–O(51)	117.9(3)
Li(3)–O(53)	2.181(7)	C(212)–Li(3)–O(53)	116.7(3)
		O(51)–Li(3)–O(53)	79.2(2)
		N(2)–Li(3)–O(52)	123.9(3)
		C(212)–Li(3)–O(52)	133.3(3)

In an attempt to generate a *crystalline* lithium salt of L^1 without co-ligands, L^1H was reacted with a 10% excess of $LiBu^n$ in diethyl ether (Scheme 2). Work up of the product in hexane that contained a trace of adventitious bis(2-methoxyethyl) ether (diglyme) gave a very low yield of colourless crystals which were subsequently shown to be the novel lithium aggregate $[\{Li(L^1)(OEt_2)Li_2(L^{11})\}_2(diglyme)]$ (**4**) (L^{11} = $N(C_6H_4-(OC_6H_4-2')-2)(SiMe_3)$), by X-ray crystallography (Fig. 4). There are two trilithium units, one comprising the asymmetric unit. Each contains the expected $Li(L^1)(OEt_2)$ moiety but, remarkably, each is bridging to an $Li_2(L^{11})$ fragment with a doubly deprotonated ligand (L^{11}) (**A**, Scheme 2). The two $Li(L^1)(OEt_2)Li_2(L^{11})$ units are linked by a diglyme, coordinated by two oxygen atoms to one lithium (Li(3)) and by one oxygen to the corresponding lithium atom (Li(3A)) of the neighbouring, symmetry generated, trilithium unit. The diglyme is disordered over the symmetry site with the ligation to the two lithium atoms (Li(3) and Li(3A)) reversed in the other component of the disorder. The lithium atom Li(1) of the $Li(L^1)(OEt_2)$ fragment is four-coordinate and is terminally bound by the Et_2O and L^1 oxygen atoms and bridges to Li(2) through the amide nitrogen (N(1)) of L^1 and the phenoxy oxygen (O(2)) of L^{11}. A diaryl ether bridging two lithium centres has previously been observed only *once* in lithium organoamides[19] and, as in **4**, was supported by further donor groups located on the aryl ether unit. Four-coordination of the central lithium atom Li(2) is completed by the amide nitrogen, N(2), and the *ortho* carbon C(212) of the phenoxy substituent of the L^{11} ligand. Both N(2) and C(212) also bridge to Li(3). The disordered diglyme coordinates to Li(3) which is thus four- and three-coordinate in the respective disordered components. The Li–N distances in **4** (Table 2) are longer than the corresponding terminal distance in **2** above, as expected for bridging atoms, and are comparable with the $Li–N_{br}$ bond length in $[Li\{N(SiMe_3)_2\}(OEt_2)]_2$ (2.055(5) Å).[20,21] The terminal Li(1)–O distances in **4** (to OAr_2, OEt_2) are virtually identical, whilst the bonding of the diglyme to Li(3)/Li(3A) is highly unsymmetrical (Table 2) due to the presence of both four- and three-coordinate lithium atoms. Not only is the terminal Li(1)–O(1)(OAr_2) bond (Table 2) shorter than the bridging Li–O(2)(OAr_2) distances, it is also shorter (by 0.08 Å) than the corresponding bond length in **2** (Table 1),

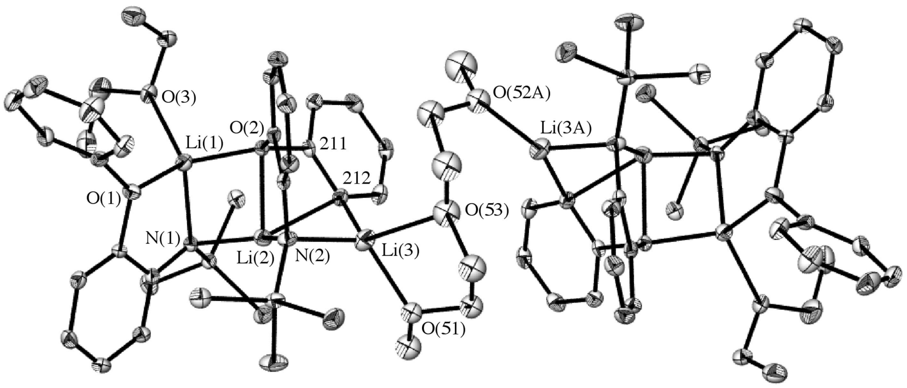
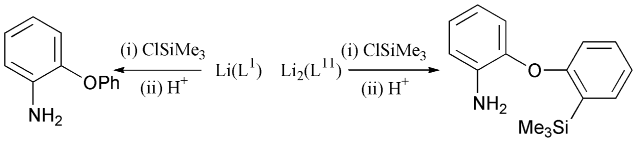


Fig. 4 The molecular structure of [{Li(L^1)(OEt_2)Li_2(L^{11})}$_2$(diglyme)] **4**.

possibly owing to weaker binding of the bridging amide nitrogen in **4** than the terminal nitrogen of **2**. A major feature of the structure of **4** is the presence of the Li_2(μ-η^1:η^1-Ph) unit resulting from deprotonation of the phenoxy substituent in L^{11} (Scheme 2). The Li–C(212) bonds are not equivalent. The shorter, Li(3)–C(212), is comparable with Li–C bond lengths previously reported for [Li(μ-η^1:η^1-Ar)]$_4$ (Ar = $C_6H_3(OBu^t)_2$-2,6 2.139(5)–2.160(6) Å)[22] whilst the longer, Li(2)–C(212), is in the range for dimeric [Li(μ-η^1:η^1-Ar)]$_2$ (Ar = C_6H_3(CH(Me)-$NMe_2)_2$-2,6 2.21(1)–2.26(2) Å).[23] Severe distortion of the Li(2) coordination geometry from tetrahedral, as evidenced by the narrow O(2)–Li(2)–C(212) angle (Table 2), results from attachment of the nitrogen, oxygen and *ortho*-carbon from the L^{11} ligand to the same lithium atom. To accommodate this configuration, the phenyl ring of the L^{11} ligand is pulled further out from the plane of the arene backbone (torsion angle C(23)–C(22)–O(21)–C(211) 89.7°; interplanar angle 53.04(9)°) than in L^1H (see above). In contrast, the L^1 ligand in **4** has the phenoxy group in line with the backbone (torsion angle C(3)–C(2)–O(1)–C(11) −2.8°) but the ring plane is rotated by 84.18(9)°. As a result of O(2), C(212) chelation of the phenoxy ring to Li(2), the *ipso* carbon C(211) is close (2.509(5) Å) to Li(2), but is probably not bonding.

An attempted deliberate preparation of a lithium derivative of the L^{11} ligand by reaction of 2 equivalents of $LiBu^n$ in hexane with L^1H in diethyl ether, followed by work up in hexane (free of donor impurities) generated a low yield of [Li_2(L^{11})-(OEt_2)Li(Bu^n)]$_2$ (**5**) (Scheme 2), with the desired Li_2(L^{11}) unit unexpectedly accompanied by a molecule of $LiBu^n$. Repeating this preparation followed by crystallisation from hexane containing a little dme eliminated residual $LiBu^n$ and gave pure [Li_2(L^{11})(dme)]$_2$ (**6**) in moderate yield (Scheme 2). Both **5** and **6** gave satisfactory elemental analyses and their compositions were further confirmed by single crystal X-ray studies (see below). The incorporation of organolithium reagents in the structures of lithiated products is novel and unusual but has occasionally been observed previously, the most closely related system being formation of [(Ph_2NLi){Ph(C_6H_4Li)NLi}$_2$-($LiBu^n$)$_2$(Et_2O)$_4$], on lithiation of diphenylamine.[24]

In contrast to the preparation of Li_2(L^{11}) complexes in diethyl ether, reaction of *two equivalents* of $LiBu^n$ with L^1H in either the *more polar* thf or dme or in the *less polar* hexane gave only complexes of the mono-deprotonated ligand, **1**–**3**. The presence of solely the L^1 ligand in the sample of **3** from the L^1H/$LiBu^n$ (mole ratio 1 : 2) reaction in hexane was proven by treatment of the product with $ClSiMe_3$ followed by hydrolysis. Only $H_2N(C_6H_4OPh$-2), derived from L^1, and no H_2N(C_6H_4-($OC_6H_4SiMe_3$-2′)-2), the product expected[25,26] from L^{11}, was detected (Scheme 3).



Scheme 3 Hydrolysis outcomes for Li(L^1) and Li(L^{11}).

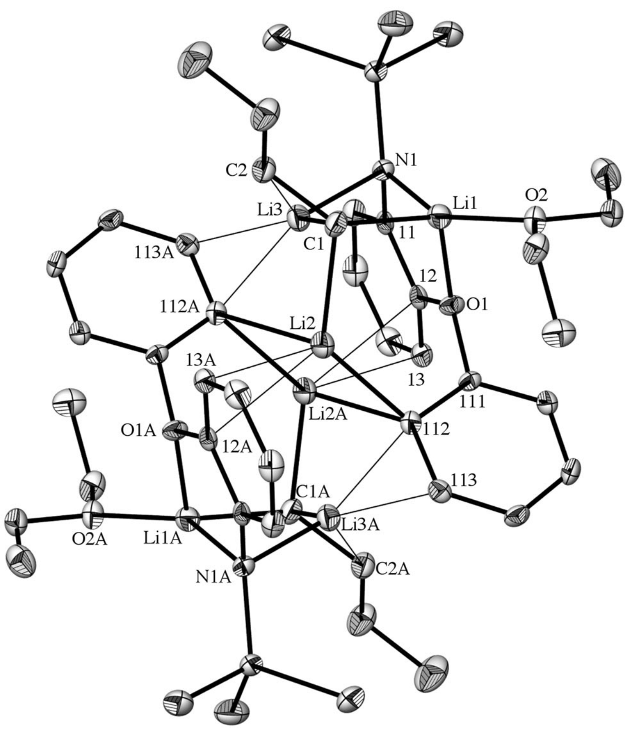


Fig. 5 The molecular structure of [Li_2(L^{11})(OEt_2)Li(Bu^n)]$_2$ **5**.

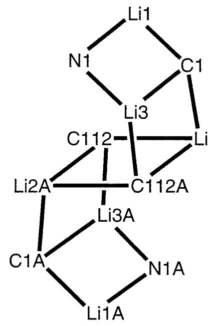


Fig. 6 The S-shaped ladder in **5**.

The structure of **5** (Fig. 5) shows a hexalithium aggregate derived from two Li_2(L^{11})(OEt_2) units and two molecules of $LiBu^n$. A distinctive feature of the structure is the central *organolithium* array (comprising Li(3), C(1), Li(2), C(112), C(112A), Li(2A), C(1A) and Li(3A)) which is sandwiched between two organoamidolithium units. The overall core can be described as an ‘S’ shaped ladder of Li, N and C atoms (Fig. 6)

Table 3 The lithium environments in $[Li_2(L^{11})(OEt_2)Li(Bu^n)]_2$ (**5**)

Li(1)–O(1)	1.948(4)	O(1)–Li(1)–O(2)	102.7(2)
Li(1)–O(2)	1.973(4)	O(1)–Li(1)–N(1)	82.8(1)
Li(1)–N(1)	2.057(4)	O(2)–Li(1)–N(1)	147.5(2)
Li(1)–C(1)	2.350(4)	O(1)–Li(1)–C(1)	116.1(2)
		O(2)–Li(1)–C(1)	105.3(2)
		N(1)–Li(1)–C(1)	100.5(2)
Li(2)–C(112)	2.189(4)	C(112)–Li(2)–C(112A)[a]	109.8(2)
Li(2)–C(112A)[a]	2.660(4)	C(1)–Li(2)–C(112)	128.9(2)
Li(2)–C(1)	2.226(4)	C(1)–Li(2)–C(112A)[a]	97.1(2)
Li(2)–C(12A)[a]	2.596(4)	C(112)–Li(2)–C(1C)[b]	115.7(5)
Li(2)–C(13A)[a]	2.583(4)	C(112A)–Li(2)–C(1C)[a,b]	79.9(5)
		C(1)–Li(2)–C(1C)[b]	111.1(5)
Li(3)–N(1)	2.016(4)	N(1)–Li(3)–C(1)	109.3(2)
Li(3)–C(1)	2.143(4)	N(1)–Li(3)–C(11C)[c]	121.8(5)
Li(3)–C(2)	2.419(4)	C(1)–Li(3)–C(11C)[c]	127.1(5)
Li(3)–C(112A)[a]	2.241(4)		
Li(3)–C(113A)[a]	2.304(4)		

Symmetry transformations used to generate equivalent atoms: [a] $-x,-y+1,-z$. [b] C(1C) = centre of C(12A) and C(13A). [c] C(11C) = centre of C(112A) and C(113A).

Table 4 Selected bond distances and angles for $[Li_2(L^{11})(dme)]_2$ (**6**)[a]

Li(1)–N(1)	2.04(1)	N(1)–Li(1)–C(112)	103.0(7)
Li(1)–C(112)	2.25(1)	N(1)–Li(1)–O(31)	115.0(5)
Li(1)–O(31)	1.96(1)	N(1)–Li(1)–O(32)	131.0(6)
Li(1)–O(32)	1.98(2)	C(112)–Li(1)–O(31)	114.7(5)
Li(2)–N(1)	2.01(1)	C(112)–Li(1)–O(32)	109.3(5)
Li(2)–O(1)	2.015(9)	O(31)–Li(1)–O(32)	83.7(6)
Li(2)–C(112)	2.30(1)	N(1)–Li(2)–O(1)	86.9(4)
Li(2)–C(212)	2.18(1)	N(1)–Li(2)–C(112)	102.3(5)
		N(1)–Li(2)–C(212)	130.0(5)
		O(1)–Li(2)–C(112)	67.7(3)
		O(1)–Li(2)–C(212)	139.5(7)
		C(112)–Li(2)–C(212)	111.3(4)

[a] For one of the independent molecules only (data for the remaining molecules are similar and are listed in the deposited CIF data. See http://www.rsc.org/suppdata/dt/b1/b103642b/).

and the central Li_2C_2 unit is situated on a crystallographic inversion centre.

There are three unique lithium atoms, with four-coordinate Li(1) surrounded by the phenoxy and diethyl ether oxygen atoms (O(1) and O(2)), the amide nitrogen atom (N(1)) and the α-carbon atom (C(1)) of the Bu^n group in an approximately tetrahedral geometry. The amide nitrogen is bridging to Li(3) whilst the α-carbon atom C(1) bridges all three lithium atoms. Surprisingly, the second lithium atom, Li(2), *is coordinated solely by carbon atoms* (Fig. 5) with the shortest interactions being to the α-carbon atom of the Bu^n group and the *ortho* carbon atom (C(112)) of L^{11}. The phenyl carbon C(112) and its symmetry equivalent C(112A) are bridging between Li(2) and Li(2A) (Fig. 5), as in **4** above, but in **5** the bridging is highly unsymmetrical. The Li(2)–C(112) distance (Table 3) is similar to those of **4** (Table 2), but Li(2)–C(112A) (Table 3) is exceptionally long for an Li–C σ-bond[2,3] and it even approaches the longer extreme of the range of neutral π-arene–Li interactions (see below).[27–29] Supporting the two primary C(1) and C(112) bonds to Li(2), there are also longer, similar length Li(2)–C interactions with two of the carbon atoms C(12A) and C(13A) from the symmetry generated L^{11} ligand (L^{11}A) (Table 3). Ligation is best described as a neutral π-η^2-arene–Li interaction since Li(2) is side on to the C(12A)–C(13A) bond (the angle defined by Li(2)–centre of the C(12A) and C(13A) bond–centre of the arene ring (C(11A)–C(16A)) is 98.7°). The Li(2)–C(12A,13A) lengths are in the range (2.28–2.77 Å) for this type of bonding,[27–29] and are shorter than Li(2)–C(112A).

The remaining lithium atom Li(3) is coordinated by the bridging amide nitrogen and the α-carbon atom of the Bu^n group. The amide bridge to Li(1) and Li(3) has near equivalent Li–N distances but Li(3)–C(1) is 0.207 Å shorter than Li(1)–C(1) (Table 3). As with Li(2) above, Li(3) further interacts with two arene carbon atoms (C(112A) and C(113A)), in this case from the phenyl substituent of L^{11}A. Thus C(112) and C(112A) each bridge three lithium atoms (Fig. 5). The Li(3)–C(112A)/C(113A) bond lengths are considerably shorter than π-bonded Li(2)–C(12A)/C(13A) (Table 3) and are close to the σ-bonded Li(2)–C(1) and Li(1)–C(1) distances. Significant σ-bond character in the Li(3)–C(112A)/C(113A) bonding may also be indicated by the Li(3)–centre C(112A)–C(113A) bond–centre of the phenyl ring (C(111A)–C(116A)) angle (131.9°) which is much larger than the expected 90° for a π-phenyl–Li interaction. A possible Li(3)–C(2) (β-C of the butyl chain) interaction (Table 3) is longer than in the parent $[Li(Bu^n)]_6$ (Li–β-C 2.287 Å)[30] but is presumably shorter than in the related aggregate $[(Ph_2NLi)\{Ph(C_6H_4Li)NLi\}_2(LiBu^n)_2(OEt_2)_4]$,[24] for which no Li–β-C interaction was suggested. Whilst **5** and $[Li(Bu^n)]_6$ both have a μ_3-α-C arrangement, the parent has two shorter (2.137(3)–2.175(3) Å) and one longer Li–α-C distances (2.227(3)–2.262(3) Å), whereas **5** has one in each of these ranges as well as one much longer.

Despite problems with the data collection for **6** (see Experimental section), sufficient data were obtained to establish unambiguously the atom connectivity of the complex (Fig. 7), which was the ultimate synthetic target. Thus, **6** consists of a $[Li_2(L^{11})(dme)]_2$ dimer with the $Li_4(L^{11})_2$ unit capped at each end by a chelated dme. The core consists of a four-rung ladder of Li, N, and C atoms. The dme ligand chelates to Li(1) and L^{11} binds in a tridentate manner (N, O, C) to Li(2), whilst the amide nitrogen is bridging between Li(2) and Li(1). The deprotonated phenyl substituents bridge three lithium atoms Li(1), Li(2) and Li(3) through C(112) and three Li(2), Li(3) and Li(4) through C(212). Thus each lithium atom is four-coordinate, consistent with coordinative saturation resulting from the presence of the strongly basic dme. Within the errors of the structure determination, the bond distances and lithium geometries (Table 4) are unexceptional. Furthermore, the tridentate L^{11} ligands display similar features to those of the L^{11} ligand in **4** (above), in contrast to **5**, with severe bending of the phenoxy substituent out of the plane of the arene backbone (torsion angles C(X3)–C(X2)–O(X)–C(X11) (X‡ = 1,2,5,6,9) 93.7–98.4°; interplanar angles 58.2(2)–65.3(2), *cf.* −18.5/88.51(6) for **5**) as a result of *ortho* carbon/oxygen bonding with the same lithium atom.

Solution NMR studies of 4–6

Room temperature solution NMR (^1H, ^7Li) data obtained for **4**–**6** in toluene-d_8 clearly indicated the occurrence of dynamic exchange phenomena. A single ^7Li resonance was observed for all, despite several unique lithium environments in the solid-state structures. Although the room temperature ^1H NMR spectrum of **4** exhibited many broad features, two distinct $SiMe_3$ resonances were observed, one from each of the amide ligands, L^1 and L^{11}. Cooling to −90 °C produced only a limited increase in resolution of the ^1H NMR spectrum, but the ^7Li resonance resolved into four separate peaks (see Experimental section), consistent with the four unique lithium atoms observed in the solid state structure of **4** (Fig. 4). For the butyllithium cluster **5**, the room temperature ^1H spectrum was broadened but at −90 °C was well resolved showing a single set of L^{11} resonances in line with one type of L^{11} ligand in the solid state. The protons of the α-C of the butyl group were evident as two broad multiplets at −1.16 and −1.02 ppm, close to the values observed for $LiBu^n$.[31] Whilst this is consistent with

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‡ These numbers refer to the unique torsion angles derived from the 2.5 dimers which comprise the asymmetric unit of the structure of **6**.

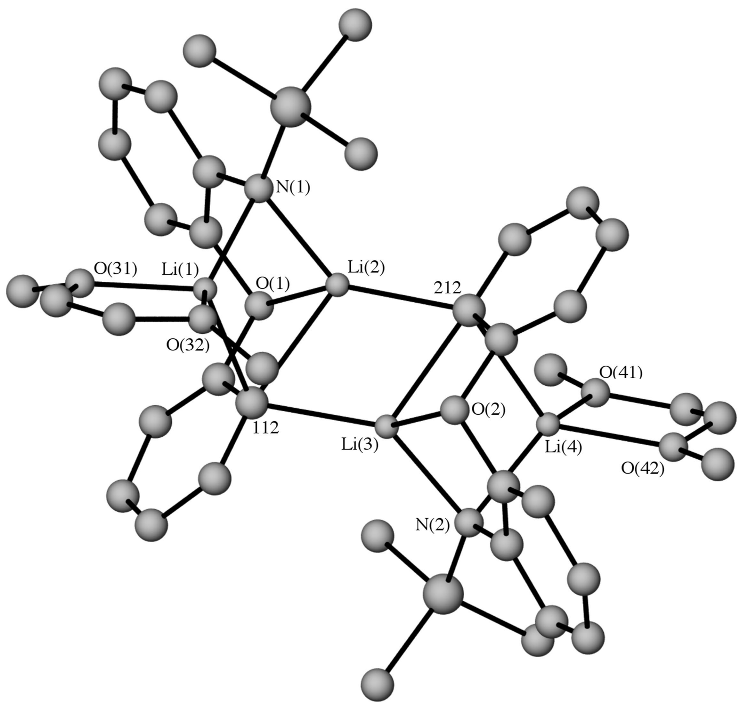

Fig. 7 The molecular structure of [Li(L^{11})(dme)]$_2$ **6**.

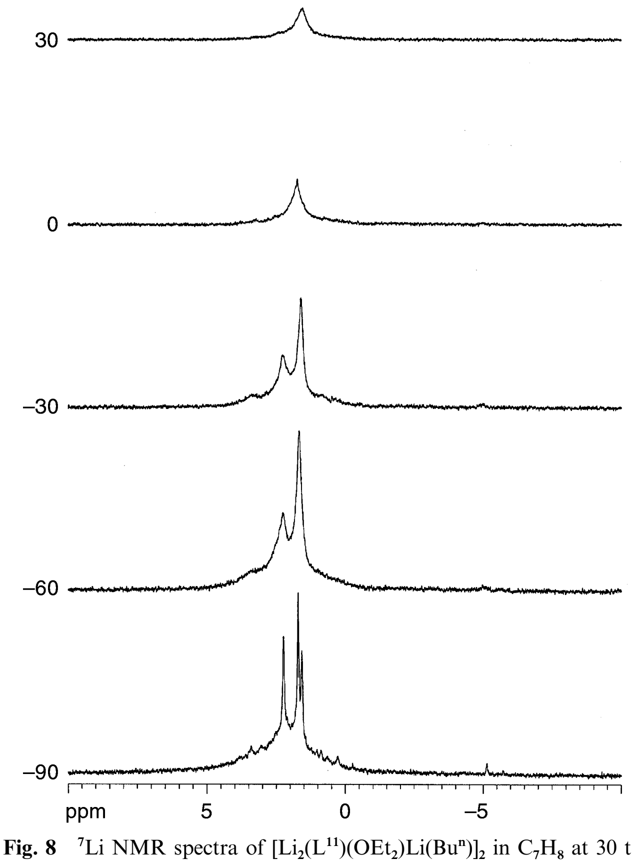

Fig. 8 ^{7}Li NMR spectra of [Li$_2$(L^{11})(OEt$_2$)Li(Bu^n)]$_2$ in C_7H_8 at 30 to −90 °C.

reversion of **5** into separate Li$_2$(L^{11}) and LiBu^n species in solution, the variable temperature ^{7}Li NMR spectra (Fig. 8) ultimately resolved into three peaks at −90 °C as expected for the three unique Li environments in the solid state structure of **5** (Fig. 5). The room temperature ^{1}H NMR spectrum of the dme complex **6** showed the expected L^{11} and dme resonances in a 1 : 1 ratio. Only a single ^{7}Li NMR resonance was observed at room temperature and also at −90 °C. Since two distinct lithium atoms are observed in the X-ray structure (Fig. 7), these data suggest either a very rapid exchange process or accidental coincidence of the two lithium resonances.

Conclusions

Lithiation of *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine is strongly solvent dependent with both the highly polar thf and dme and the non-polar hexane giving complexes (**1**–**3**) of the monodeprotonated ligand, L^1, whereas the intermediate polarity Et$_2$O allows formation of the doubly deprotonated L^{11}, as in **4** and **5** (Scheme 2). However in Et$_2$O, LiBu^n can compete with the solvent for coordination sites on Li$_2$L^{11} giving **5**. Although dme is unsuitable for the generation of L^{11}, it removes coordinated LiBu^n from **5** enabling isolation of [Li$_2$(L^{11}((dme)]$_2$ **6** in a conveniently accessible form (Scheme 2). Still greater lithium coordination versatility can be demonstrated by this system, since double deprotonation in Et$_2$O (*now established as leading to isolation of* **5**) followed by addition of LaCl$_3$ led to crystallisation of the remarkable, decalithium cage, [{Li$_2$(L^{11})}$_2$-(LiOEt)(OEt$_2$)]$_2$·hexane with carbanion, organoamide and alkoxide functionalities.[32]

Experimental

All operations were performed under dry nitrogen using dry box and standard Schlenk techniques. Solvents were dried by distillation from sodium wire/benzophenone. IR data (4000–650 cm^{-1}) were recorded for Nujol mulls sandwiched between NaCl plates with a Perkin-Elmer 1600 FTIR spectrometer. NMR spectra were obtained either on a Bruker AC 200 MHz (^{1}H) or a Bruker AC 400 MHz spectrometer (^{7}Li and ^{1}H) as indicated. Deuterated solvents were degassed and distilled from Na/K alloy prior to use. ^{1}H NMR spectra were referenced to the solvent (toluene-d_8) signals; chemical shifts for ^{7}Li spectra are given relative to external 0.1 M LiCl in D$_2$O at room temperature. Elemental analyses (C, H, N) were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Commercial LiBu^n in hexanes (1.6 M) and ClSiMe$_3$ (Aldrich) were used as received. *N*-(2-Phenoxyphenyl)-*N*-(trimethylsilyl)amine was prepared as previously reported.[14]

[Li(L^1)(thf)] (1)

LiBu^n (1.63 cm^3, 2.60 mmol) was added dropwise to a stirring solution of L^{1}H (0.63 g, 2.45 mmol) in thf (30 cm^3) at 0 °C. The resulting mixture was then stirred until it had warmed to room temperature (*ca.* 1 h) whereupon a white solid formed. This was washed with hexane (30 cm^3) and dried under vacuum giving the title compound (0.76 g, 87%) (Found: C, 67.2; H, 8.0; N, 4.4. C$_{19}$H$_{26}$LiNO$_2$Si requires C, 68.0; H, 7.8; N, 4.2%). Infrared (Nujol, ν/cm^{-1}): 1592 s, 1582 s, 1489 s, 1279 s, 1239 s, 1211 vs, 1170 s, 1102 vs, 1072 w, 1046 s, 947 vs, 868 s, 844 w, 824 vs, 769 m, 734 s, 694 vs, 663 w. NMR (400 MHz, C$_7$D$_8$, 298 K): ^{1}H, δ 0.35 (9 H, s, SiMe$_3$), 1.20 (4 H, br m, β-H (thf)), 3.46 (4 H, br m, α-H (thf)), 6.46–6.50 (1H, ddd, ^3J 7.2, ^4J 1.6 Hz, H4), 6.60–6.63 (1H, dd, ^3J 8.0, ^4J 1.6 Hz, H3), 6.67–6.69 (2H, br d, ^3J 7.8 Hz, H2′,6′), 6.73–6.78 (1H, tt, ^3J 7.4, ^4J 1.1 Hz, H4′), 6.84–6.88 (2H, br t, ^3J 7.4 Hz, H3′,5′), 6.96–7.03 (1H, ddd, ^3J 7.2, ^4J 1.7 Hz, H5), 7.15–7.20 (1H, dd, ^3J 8.0, ^4J 1.6 Hz, H6); ^{7}Li (155.51 MHz, 298 K), δ 1.68. An identical product (0.68 g, 60%) was obtained from a reaction of L^{1}H (0.63 g, 2.45 mmol) with two equiv. of LiBu^n (3.30 cm^3, 5.25 mmol) in thf (30 cm^3) followed by the same work up procedure.

[Li(L^1)(dme)] (2)

LiBu^n (2.44 cm^3, 3.90 mmol) was added dropwise to a stirring solution of L^{1}H (0.94 g, 3.66 mmol) in dme (30 cm^3) at 0 °C. The resulting mixture was then stirred until it had warmed to room temperature (*ca.* 1 h) whereupon a white solid formed. The solid was washed with hexane (30 cm^3) and dried under vacuum giving the title compound (1.24 g, 96%) (Found: C, 63.7; H, 7.7; N, 4.0. C$_{19}$H$_{28}$LiNO$_3$Si requires C, 64.6; H, 8.0; N, 4.0%). Infrared (Nujol, ν/cm^{-1}): 1594 s, 1585 s, 1458 s, 1444 s, 1366 s, 1332 vs, 1309 s, 1238 s, 1206 vs, 1168 vs, 1150 w, 1117 s, 1099 m, 1082 vs, 1037 m, 1025 w, 955 vs, 907 w, 892 w, 872 m, 825 s, 768 w, 734 s, 690 s, 665 s, 624 w, 596 w. NMR (400 MHz, C$_7$D$_8$, 298 K): ^{1}H, δ 0.41 (9 H, s, SiMe$_3$), 2.79 (6 H, s, Me(dme)), 2.80 (4 H, s, CH$_2$(dme)), 6.33–6.37 (1H, ddd, ^3J 7.2, ^4J 1.8 Hz, H4), 6.63–6.66 (1H, dd, ^3J 7.8, ^4J 1.6 Hz, H3), 6.75–6.79 (1H, br t, ^3J 6.6 Hz, H4′), 6.88–6.92 (4H, br m, H2′,3′,5′,6′), 6.96–7.02 (1H, ddd, ^3J 7.1, ^4J 1.6 Hz, H5), 7.14–7.16 (1H, dd, ^3J 8.0, ^4J 1.6 Hz, H6); ^{7}Li (155.51 MHz, 298 K), δ 1.43. An identical product (1.12 g, 70%) was obtained from a reaction of L ^{1}H (0.94 g, 3.66 mmol) with two equiv. of LiBu^n (4.88 cm^3, 7.80 mmol) in dme (30 cm^3) followed by the same work up procedure.

[Li(L^1)]$_n$ (3)

a) LiBu^n (1.2 cm^3, 1.9 mmol) was added slowly to a stirring solution of L^{1}H (0.39 g, 1.52 mmol) in hexane (40 cm^3) at 0 °C. The resulting mixture was stirred at room temperature for 6 h, and then heated until dissolution of the white precipitate occurred. On cooling colourless crystals of the title complex formed (0.36 g, 89%) with identical IR and ^{1}H NMR data to the product obtained from the 2 : 1 preparation below.

b) A similar procedure using LiBu^n (2.3 cm^3, 3.7 mmol) and L^{1}H (0.39 g, 1.52 mmol) in hexane afforded a white precipitate (0.34 g, 84%) (Found: C, 68.5; H, 7.2; N, 5.2. C$_{15}$H$_{18}$LiNOSi requires C, 68.4; H, 6.9; N, 5.3%). Infrared (Nujol, ν/cm^{-1}): 1586 s, 1560 s, 1490 s, 1444 s, 1267 s, 1230 br s, 1203 s, 1167 vs, 1100 vs, 1067 w, 1040 s, 1022 w, 1004 w, 931 vs, 914 s, 867 vs, 851 s, 825 vs, 803 s, 780 s, 741 s, 694 vs, 620 w, 600 w, 556 w. NMR (400 MHz, C$_7$D$_8$, 288 K): ^{1}H, δ 0.12 (9H, s, SiMe$_3$), 6.48–6.52 (1H, br dd, ^3J 7.9 Hz, H4), 6.57–6.59 (1H, br d, ^3J 7.9 Hz, H3), 6.65–7.00 (7H, vbr m, H5,6,2′–6′); (183 K; assignment based on two L^1 environments in the ratio of 1 : 3; major component*) 0.23–0.26 (36H, br d, SiMe$_3$*), 6.45–6.52 (1H, br t, H4), 6.55–6.59 (3H, br t, H4*), 6.62–6.73 (15H, br m, H3*, Ph), 6.79–6.90 (9H, br m, H3, Ph), 6.96–7.00 (1H, br d, H6*), 7.00–7.04 (3H br m, H6*), 7.05–7.09 (3H, br m, H5), 7.35–7.40 (1H br t, H5); ^{7}Li (155.51 MHz, 303 K), δ 1.65; (183 K) −1.77, 2.60, 2.96.

[{Li(L^1)(OEt$_2$)Li$_2$(L^{11})}$_2$(diglyme)] (4)

To a solution of L^{1}H (1.02 g, 3.9 mmol) in Et$_2$O (30 cm^3) was slowly added LiBu^n (2.7 cm^3, 4.3 mmol), and the mixture was stirred until it had warmed to room temperature (*ca.* 1 h). The solvent was removed under vacuum, and hexane (20 cm^3) was added. The volume was reduced to 10 cm^3 under vacuum and, after standing for 3 days undisturbed, colourless crystals of the title compound formed (0.09 g, yield 8%). Infrared (Nujol, ν/cm^{-1}) 1585 vs, 1562 w, 1404 s, 1286 vs, 1242 s, 1208 vs, 1166 vs, 1095 vs, 1065 s, 1044 s, 1028 s, 937 vs, 827 s, 802 s, 769 s, 748 s, 730 vs, 694 vs, 668 w. NMR (400 MHz, C$_7$D$_8$, 303 K): ^{1}H, δ 0.17 (18H, br s, SiMe$_3$), 0.24 (18H, s, SiMe$_3$), 1.00 (12H, t, ^3J 7.0 Hz, CH$_3$(OEt$_2$)), 2.68 (6H, br s, CH$_3$(diglyme)), 2.74 (8H, br s, CH$_2$(diglyme)), 3.23 (8H, q, ^3J 7.0 Hz, CH$_2$(OEt$_2$)), 6.46 (4H, br t, Ar), 6.60 (2H, d, ^3J 7.9 Hz, Ar), 6.73 (2H, br m, Ar), 6.85 (12H, vbr s, Ar), 6.96 (4H, t, ^3J 7.9 Hz), 7.05 (4H, vbr s, Ar), 7.12 (4H, br m, Ar), 7.80 (2H, vbr s, Ar); ^{7}Li (155.51 MHz, 303 K), δ 1.67; (183 K) 0.83, 1.50, 2.08, 3.50.

[Li$_2$(L^{11})(OEt$_2$)Li(Bu^n)]$_2$ (5)

To a solution of L^{1}H (0.77 g, 3.0 mmol), in Et$_2$O (30 cm^3) was slowly added LiBu^n (3.75 cm^3, 6.0 mmol), and the mixture was stirred until it had warmed to room temperature (*ca.* 1 h). The solvent was removed under vacuum, and hexane (20 cm^3) added. Upon standing for 2 h undisturbed, colourless crystals of the title compound formed (0.23 g, yield 19%) (Found: C, 67.0; H, 8.8; N, 3.7. C$_{46}$H$_{68}$Li$_6$N$_2$O$_4$Si$_2$ requires C, 67.8; H, 8.9; N, 3.4%). Infrared (Nujol, ν/cm^{-1}): 1583 s, 1572 s, 1545 m, 1408 s, 1311 w, 1288 s, 1244 vs, 1182 s, 1148 vs, 1105 vs, 1068 m, 1039 w, 994 w, 939 vs, 829 s, 769 w, 734 w, 668 s, 619 w. NMR (400 MHz, C$_7$D$_8$, 303 K): ^{1}H, δ −1.10 (4H, br s, α-CH$_2$(Bu^n)), 0.11 (18H, vbr s, SiMe$_3$), 0.85 (16H, br m, CH$_3$(OEt$_2$), γ-CH$_2$(Bu^n)), 0.91 (6H, br m, CH$_3$(Bu^n)), 1.35 (4H, br s, β-CH$_2$(Bu^n)), 3.12 (8H, br m, CH$_2$(OEt$_2$)), 6.40 (2H, br s, Ar), 7.05 (6H, br s, Ar), 7.16 (6H, br s, Ar), 7.88 (2H, br s, Ar); (183 K) −1.16 (2H, br m, α-CH$_2$(Bu^n)), −1.02 (2H, br m, α-CH$_2$(Bu^n)), 0.56 (12H, br t, CH$_3$(OEt$_2$)), 0.62 (18H, s, SiMe$_3$), 0.90 (4H, br m, γ-CH$_2$(Bu^n)), 1.05 (6H, br t, CH$_3$(Bu^n)), 1.50 (4H, br m, β-CH$_2$(Bu^n)), 2.75 (4H, br m, CH$_2$(OEt$_2$)), 2.89 (4H, br m, CH$_2$(OEt$_2$)), 6.61 (2H, t, ^3J 7.4 Hz, Ar), 6.90 (2H, d, ^3J 8.0 Hz, Ar), 6.92 (2H, t, ^3J 7.5 Hz, Ar), 6.97 (2H, d, ^3J 7.9 Hz, Ar), 7.16 (2H, t, Ar), 7.35 (2H, d, ^3J 6.9 Hz, Ar), 7.38 (2H, d, ^3J 8.3 Hz, Ar), 7.88 (2H, d, Ar); ^{7}Li (155.51 MHz, 303 K), δ 1.54; (183 K) 1.58, 1.71, 2.24.

[Li$_2$(L^{11})(dme)]$_2$ (6)

To a solution of L^{1}H (0.39 g, 1.52 mmol) in Et$_2$O (30 cm^3) was slowly added LiBu^n (1.90 cm^3, 3.04 mmol), and the mixture was stirred until it had warmed to room temperature (*ca.* 1 h). The solvent was removed under vacuum and hexane (20 cm^3) and dme (0.16 cm^3, 1.52 mmol) were then added and the resulting mixture was heated until dissolution of all the solid occurred. After standing overnight, colourless crystals of the title compound formed (0.26 g, yield 47%) (Found: C, 63.7; H, 7.7; N, 4.1. C$_{38}$H$_{54}$Li$_4$N$_2$O$_6$Si$_2$ requires C, 63.5; H, 7.6; N, 3.9%). Infrared (Nujol, ν/cm^{-1}): 1585 s, 1565 w, 1550 w, 1409 s, 1284 s, 1243 m, 1191 w, 1172 vs, 1130 vs, 1097 s, 1077 vs, 1034 w, 941 vs, 869 s, 826 vs, 797 s, 749 s, 722 w, 667 w. NMR (400 MHz, C$_7$D$_8$, 303 K): ^{1}H, δ 0.41 (18H, s, SiMe$_3$), 2.80 (12H, s, CH$_3$(dme)), 2.81 (8H, s, CH$_2$(dme)), 6.35 (2H, t, ^3J 7.0 Hz, Ar), 6.65 (2H, dd, ^3J 7.8 Hz, ^4J 1.6 Hz, Ar), 6.76 (2H, br t, Ar), 6.91 (6H, br m, Ar), 7.01 (2H, t, ^3J 7.6 Hz, Ar), 7.15 (2H, dd, ^3J 8.0 Hz, ^4J 1.5 Hz, Ar); (183 K) 0.72 (18H, s, SiMe$_3$), 2.27 (8H, s, CH$_2$(dme)), 2.54 (12H, s, CH$_3$(dme)), 6.55 (2H, t, ^3J 8.0 Hz, Ar), 6.76 (2H, t, ^3J 7.0 Hz, Ar), 6.86 (2H, dd, ^3J 7.8 Hz, ^4J 1.3 Hz, Ar), 6.94 (6H,

Table 5 Crystal and refinement parameters[a]

Compound	L^1H	**2**	**4**	**5**	**6**
Formula	$C_{15}H_{19}NOSi$	$C_{19}H_{28}LiNO_3Si$	$C_{74}H_{104}Li_6N_4O_9Si_4$	$C_{46}H_{68}Li_6N_2O_4Si_2$	$C_{38}H_{54}Li_4N_2O_6Si_2$
M	257.41	353.45	1347.62	810.84	718.78
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbcn*	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	21.4777(4)	10.1225(2)	40.3040(11)	12.9117(2)	22.1749(10)
b/Å	7.9215(2)	12.8885(2)	10.5611(3)	11.5166(3)	14.3421(6)
c/Å	16.9555(2)	16.4847(3)	18.7239(3)	16.9667(5)	34.5285(11)
β/°		107.395(1)	99.263(1)	100.243(2)	105.890(3)
V/Å^3	2884.7(2)	2052.3(7)	7866(3)	2482.7(9)	10562(4)
Z	8	4	4	2 (dimers)	10 (dimers)
μ(Mo-Kα)/mm^{-1}	0.151	0.130	0.129	0.111	0.126
N (R_{int})	3414 (0.058)	5063 (0.050)	9451 (0.047)	5851 (0.073)	14985 (0.069)
R, R_w [$I > 2\sigma(I)$]	0.045, 0.090	0.046, 0.100	0.070, 0.139	0.056, 0.126	0.110, 0.273
R, R_w (all data)	0.060, 0.095	0.082, 0.113	0.122, 0.162	0.100, 0.143	0.228, 0.343

[a] Measured at 123 K.

m, Ar), 7.30 (2H, t, ^3J 8.0 Hz, Ar), 7.43 (2H, d, ^3J 8.0 Hz, Ar); ^{7}Li (155.51 MHz, 303 K), δ 1.42; (183 K) 1.48.

X-Ray crystallography

Under an inert atmosphere, the air and moisture sensitive crystals were covered by viscous oil and mounted onto a glass fibre. Low temperature (≈123 K) data were collected on an Enraf-Nonius CCD area-detector diffractometer (Mo-Kα radiation, λ 0.7107$_3$ Å, frames comprised 1.0° increments in φ and ω yielding a sphere of data) using proprietary software (Nonius B.V., 1998). For **6**, loss of crystal integrity occurred after approximately 1 h exposure of the crystal to the X-ray beam (unexposed crystals from the same batch remained intact). Consequently data were collected from several specimens and the resulting data sets combined yielding an adequate but still limited amount of data. Each data set was merged (R_{int} as quoted) to N unique reflections and the structures were solved by conventional methods and refined with anisotropic thermal parameter forms for the non-hydrogen atoms by full matrix least-squares on all F^2 data using the SHELX97 software package.[33] Hydrogen atoms were included in calculated positions and allowed to ride on the parent carbon atom with isotropic thermal parameters. Crystal and refinement details for each compound are listed in Table 5.

CCDC reference numbers 163622–163626.

See http://www.rsc.org/suppdata/dt/b1/b103642b/ for crystallographic data in CIF or other electronic format.

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