Syntheses and Structural Studies of [2-(6-Methyl)pyridyl]- and (8-Quinolyl)-trimethylsilylamido-lithium Complexes *

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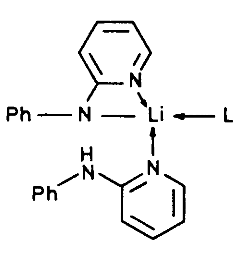
Reactions of 6-methyl-2-trimethylsilylaminopyridine (Hmtmsap) with LiBu^n in hexane–diethyl ether, [LiBu^n(tmen)] (tmen = *N,N,N',N'*-tetramethylethylenediamine), or LiBu^n in hexane, yield, respectively, [{Li(OEt$_2$)(mtmsap)}$_2$] (**1**), [Li(tmen)(mtmsap)] (**2**), and [{Li(mtmsap)}$_2$] (**3**). Mixtures (5:2) of Hmtmsap and 2-amino-6-methylpyridine (Hamp) yield the complex molecule [Li$_7$(mtmsap)$_5$(amp)$_2$] (**4**). Corresponding compounds, prepared *via* metallation of 8-trimethylsilylaminoquinoline (Htmsaq), are [{Li(OEt$_2$)(tmsaq)}$_2$] (**5**), [Li(tmen)(tmsaq)] (**6**), and [{Li(tmsaq)}$_2$] (**7**). Compounds (**1**), (**2**), and (**4**)—(**7**) are crystalline and have been characterized by *X*-ray structure determination. Compounds (**1**) and (**5**) are dimeric with four-co-ordinate lithium centres, the amido-N bridging; (**7**) is based on the structure of (**5**), but with a gap in the metal co-ordination spheres where the ether ligands reside in (**5**). Compounds (**2**) and (**6**) are monomeric with four-co-ordinate metal centres, and (**4**) has seven different metal environments, each either three- or four-co-ordinate and with both bridging amido-N and pyridine-N centres.

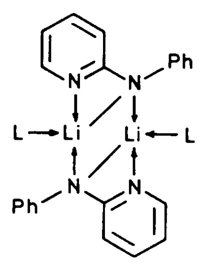
Lithium complexes containing anionic N-centred species, for example amides and imides, are of interest as transfer reagents for the anionic species in inorganic chemistry, as strong Brønsted bases or nucleophiles in organic synthesis,[1] and structurally with respect to the degree of aggregation and the nature of Li–N bonding. The high polarity of Li–N bonds causes compounds of lithium to associate[2] unless prevented by bulky substituents. In recent years there have been a number of structural studies dealing with amido-lithium and related complexes,[3–23] and some theoretical predictions.[3,24]

In this paper we report structural studies of N-functionalized amido-lithium complexes based on the new [2-(6-methyl)pyridyl]trimethylsilylamido (mtmsap) and (8-quinolyl)trimethylsilylamido (tmsaq) ligands, as part of a systematic study of the metallation of Hmtmsap and Htmsaq using LiBu^n in a variety of solvents, and to develop suitable transfer reagents of the respective anions. Both ligands are related to the ubiquitous bis(trimethylsilyl)amido ligand, N(SiMe$_3$)$_2$, in the sense that the amido centres bear a bulky trimethylsilyl group. Several Li complexes of this ligand have been authenticated, showing that the N-centres can bridge or be terminally bound to lithium.[9,14–17] The functional group in the present amido ligands is likely to perturb the nature of the metal–amido group bonding and also the state of aggregation. Novel structures established for phenyl(2-pyridyl)amido-lithium complexes, (**I**)—(**III**) [L = OP(NMe$_2$)$_3$],[18,19] give some insight into possible structures for at least mtmsap. The same amido group features in transition metal chemistry where it bridges or chelates.[25] Related to tmsaq is the ligand (**IV**) for which some complexes of boron and silicon have recently been reported.[26]

Studies on mtmsap are akin to our work on its C-centred analogue, 2-(CHSiMe$_3$)NC$_5$H$_4$$^-$, albeit lacking a methyl substituent on the pyridine ring,[27] and the more hindered 2-[C(SiMe$_3$)$_2$]NC$_5$H$_4$$^-$, both having yielded some unusual results. For lithium these include the formation of a two-co-ordinate lithium alkyl, (V), and lithium η^3-aza-allyls, *e.g.* (VI).[27] Moreover, it relates to our contemporary studies on hindered alkoxido-lithium complexes where the alkoxido group bears a P^{III} functional group.[28]



(I)



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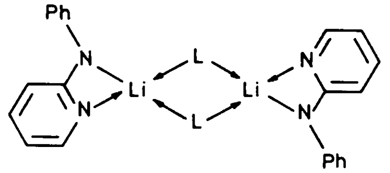

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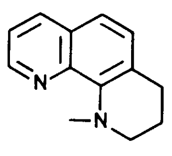

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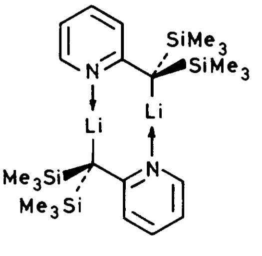

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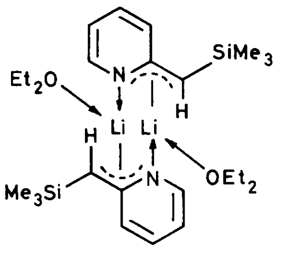

(VI)

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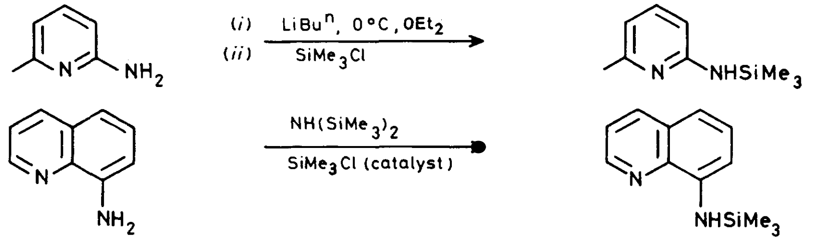
* *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Results and Discussion

6-Methyl-2-trimethylsilylaminopyridine (Hmtmsap) and 8-trimethylsilylaminoquinoline (Htmsaq) were respectively prepared in high yield by the method of Phillion *et al.*[29] For the silylation of aromatic amines,[20] equation (1), and the method used for the silylation of ethylenediamine,[30] equation (2). The latter when applied to 2-amino-6-methylpyridine (Hamp) gave a mixture of the desired product and unreacted amine which proved difficult to separate.



(1)

(2)

Treatment of Hmtmsap in OEt$_2$ with LiBu^n in hexane (*ca.* 1.6 mol dm^{-3}) yielded the binuclear complex [{Li(OEt$_2$)(mtmsap)}$_2$] (**1**), while [LiBu^n(tmen)] (tmen = *N,N,N',N'*-tetramethylethylenediamine) in hexane gave the mononuclear species [Li(tmen)(mtmsap)] (**2**); metallation in the absence of a donor solvent gave [{Li(mtmsap)}$_2$] (**3**). The silylated aminoquinoline, Htmsaq, under the same conditions yielded the corresponding compounds: [{Li(OEt$_2$)(tmsaq)}$_2$] (**5**), [Li(tmen)(tmsaq)] (**6**), and [{Li(tmsaq)}$_2$] (**7**).

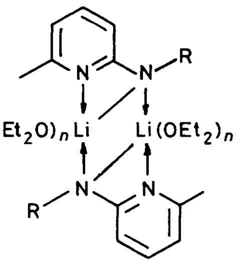
On treating Hmtmsap contaminated with 2-amino-6-methylpyridine (see above) with LiBu^n in hexane, the novel heptanuclear species [Li$_7$(mtmsap)$_5$(amp)$_2$] (**4**) was isolated, although its synthesis was subsequently shown to be reproducible using the appropriate ratio of amines.

Although n.m.r. data facilitate characterization of (**1**)—(**7**) at various temperatures, and benzene cryoscopy showed (**3**) to be binuclear, the substance of our understanding of the nature of the compounds rested heavily on the structural chemistry as defined by diffraction methods (see below). Compound (**7**) is only sparingly soluble in non-co-ordinating solvents and the only meaningful n.m.r. was for ^{7}Li nuclei. For both Hmtmsap and Htmsaq no adducts of the type Li(mtmsap)(Hmtmsap) or Li(tmsaq)(Htmsaq) were detected. Such adducts have been noted for 2-phenylaminopyridine, *viz.* (I),[18] and also for 2-[CH(SiMe$_3$)$_2$]NC$_5$H$_4$[27] where the active proton is attached to the carbon bearing the trimethylsilyl groups.

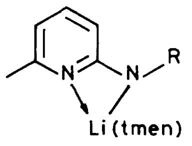
At 35 °C the ^{7}Li n.m.r. spectrum of (**4**) in toluene consisted of a sharp line at 1.99 p.p.m. Thus the seven distinct lithium environments in the solid (see below) are lost in solution. However, on cooling to *ca.* -80 °C a 14-line spectrum was obtained showing that whilst a Li$_7$ unit can be crystallized, in solution a mixture of complex species abounds. ^{29}Si N.m.r. chemical shifts for (**1**)—(**3**), (**5**), and (**6**) are *ca.* 10 p.p.m. to high field relative to the free amines. This is consistent with shielding from the negative charge on the anionic N centres. No ^{29}Si n.m.r. signal was detected for (**7**), a consequence of its low solubility in aromatic solvents. The *X*-ray structure of (**7**) and the recognised bridging capacity of amido-N centres,[2] suggest the structure of (**3**) to be that shown above.

Results of the *X*-ray crystal structure determinations of (**1**), (**2**), and (**4**)—(**7**) are given in Tables 1—9, and Figures 1—6 which show the numbering schemes used. The compounds comprise discrete mononuclear [(**2**) and (**6**)], binuclear [(**1**), (**5**), and (**7**)], or heptanuclear species, (**4**). The asymmetric unit in each is the complete molecule [(**2**), (**4**), and (**6**)], or one half of the molecule [(**1**), (**5**), and (**7**)], the other half being generated by a centre of inversion.

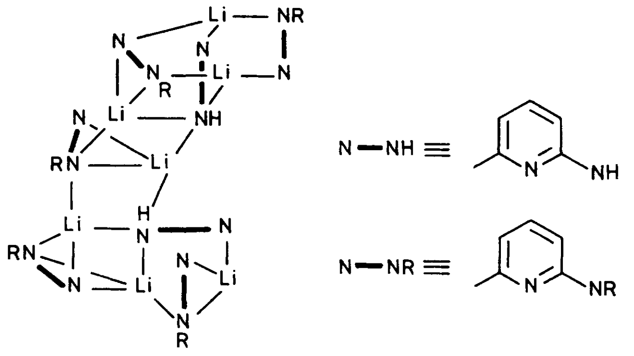
In (**1**), (**2**), and (**5**)—(**7**) the amido-group acts as a bidentate ligand to a lithium centre; in (**1**), (**5**), and (**7**) it also bridges through the amido-N to a second lithium. With an OEt$_2$ molecule attached to each metal centre in (**1**) and (**5**) the common four-fold co-ordination of lithium is attained, whilst in (**7**) the metal centres are three-co-ordinate. The presence of



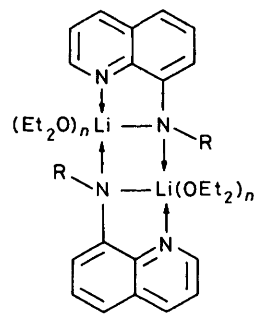
(**1**), n = 1
(**3**), n = 0



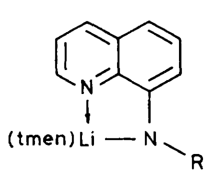
(**2**)



(**4**)



(**5**), n = 1
(**7**), n = 0



(**6**)

R = SiMe$_3$

bidentate tertiary amine groups in (**2**) and (**6**) gives four-fold co-ordination without the necessity for bridging. In (**4**) there is a mixture of three- and four-co-ordinate metal centres.

Table 1. The lithium and nitrogen environments:[a] distances (Å) in (**1**), (**2**), and (**5**)—(**7**)

(**1**)	Li–N(1)	2.08(1)	Li–N(1′)	2.08(2)
	Li–C(1)	2.45(2)	Li · · · Li′	2.53(1)
	Li–N(2)	2.08(1)	N–Si	1.705(5)
	Li–O	1.98(1)		
(**2**)[b]	Li–N(1)	2.00(3), 2.04(3)	Li–N(a)	2.11(3), 2.04(3)
	Li–C(1)	2.42(3), 2.44(3)	Li–N(b)	2.08(4), 2.09(4)
	Li–N(2)	2.07(3), 2.06(3)	N(1)–Si	1.69(1), 1.69(2)
(**5**)	Li–N(1)	2.07(2)	Li–O	1.94(3)
	Li–N(1′)	2.21(2)	N(1)–Si	1.735(7)
	Li–N(3)	2.03(2)	Li · · · Li′	2.69(4)
(**6**)[b]	Li–N(1)	1.94(1), 1.96(2)	Li–N(b)	2.12(1), 2.17(2)
	Li–N(3)	2.05(2), 2.05(2)	Si–N(1)	1.692(6), 1.691(7)
	Li–N(a)	2.16(1), 2.16(2)		
(**7**)	Li–N(1)	2.033(10)	N(1)–Si	1.715(5)
	Li–N(1′)	2.087(11)	Li · · · Li′	2.55(1)
	Li–N(3)	2.011(11)		

[a] Primed atoms are related to the others by inversion centres. [b] For molecules 1 and 2 respectively.

There are differences in structure of the OEt$_2$ adducts (**1**) and (**5**) which relate mainly to the unsymmetrical nature of the Li–N(amido) distances in (**5**) [Li–N(1), N(1′) 2.07(2), 2.21(2) Å], but not in (**1**) [Li–N(1), N(1′) 2.08(1), 2.08(2) Å], and angular variations arising from the difference in ligand 'bite', the metal centres in (**1**) being more distorted from regular tetrahedral by virtue of the smaller 'bite', mtmsap < tmsaq. Only the Li–N(1′) value of 2.21(2) Å departs from those reported for related systems.[11,16,17] The Li–O distances [1.98(1) in (**1**), 1.94(3) Å in (**5**)] are similar to those in related etherates, *e.g.* 1.943(6) Å in [{Li(OEt$_2$)[μ-N(SiMe$_3$)$_2$]}$_2$],[15] *cf.* 2.094(4) Å in [Li(12-crown-4){N(SiMe$_3$)$_2$}] (12-crown-4 = 1,4,7,10-tetraoxacyclododecane).[18] The Li–N(aromatic) bond lengths [2.08(1) in (**1**), 2.03(2) Å in (**5**)], are similar to those in (**II**) (2.055 Å) and (**VI**) [2.04(1) Å], and the corresponding values in (**2**) and (**6**) (see below). As expected they are much longer than in the highly electron deficient lithium-containing compound (**V**), Li–N 1.936(6) Å.[27]

Molecules of (**2**) and (**6**) are monomeric. They also differ in geometry about the metal centres in consequence of the difference in amido-ligand bite. Li–N(amido) distances differ [2.0$_2$ in (**2**), 1.9$_5$ Å in (**6**)], whereas Li–N(aromatic) distances are similar [2.0$_6$ in (**2**), 2.0$_5$ Å in (**6**)]. The cause of the former may be related to the presence of a strained four-membered chelate ring in (**2**). In support of this the value of 1.9$_5$ Å in the unstrained compound (**6**), agrees with 1.965(4) Å in [Li(12-crown-4)-{N(SiMe$_3$)$_2$}].[18] However, there is no apparent disparity of

Table 2. Lithium, nitrogen, and oxygen environments:[a] angles (°) for (**1**), (**2**), (**5**)—(**7**)

(**1**)	N(1)–Li–N(2)	66.8(5)	Li′–N(1)–Si	113.5(3)
	N(1)–Li–O	122.7(6)	C(1)–N(1)–Si	123.7(6)
	N(1)–Li–N(1′)	105.1(5)	Li–N(1)–Li′	74.9(5)
	N(2)–Li–O	117.4(6)	Li–N(2)–C(1)	88.8(5)
	N(2)–Li–N(1′)	116.2(6)	C(1)–N(2)–C(3)	120.3(7)
	O–Li–N(1′)	118.2(8)	Li–N(2)–C(3)	150.9(6)
	Li–N(1)–C(1)	89.0(5)	Li–O–C(11)	119.2(8)
	Li–N(1)–Si	134.1(4)	Li–O–C(13)	123.9(12)
	Li′–N(1)–C(1)	111.5(5)	C(11)–O–C(13)	112.6(12)
(**2**)[b]	N(1)–Li–N(2)	68(1), 67(1)	Li–N(1)–C(1)	91(1), 90(1)
	N(1)–Li–N(a)	133(2), 132(2)	Li–N(1)–Si	137(1), 136(1)
	N(1)–Li–N(b)	128(2), 126(2)	Si–N(1)–C(1)	132(1), 134(1)
	N(2)–Li–N(a)	122(2), 126(2)	C(1)–N(2)–Li	86(1), 89(1)
	N(2)–Li–N(b)	122(2), 123(2)	C(1)–N(2)–C(3)	120(1), 119(1)
	N(a)–Li–N(b)	88(1), 88(1)	Li–N(2)–C(3)	154(2), 152(1)
(**5**)	N(1)–Li–N(1′)	102.2(11)	Si–N(1)–Li′	110.8(6)
	N(1)–Li–N(3)	83.0(8)	Si–N(1)–C(1)	118.8(6)
	N(1)–Li–O	127.3(9)	Li′–N(1)–C(1)	108.2(9)
	N(1′)–Li–N(3)	113.0(9)	C(2)–N(3)–Li	112(1)
	N(1′)–Li–O	118.6(9)	C(2)–N(3)–C(4)	119(1)
	N(3)–Li–O	107.5(12)	Li–N(3)–C(4)	129(1)
	Li–N(1)–Si	123.8(7)	Li–O–C(11)	125(1)
	Li–N(1)–Li′	77.8(9)	Li–O–C(13)	122(1)
	Li–N(1)–C(1)	109.1(8)	C(11)–O–C(13)	111(1)
(**6**)[b]	N(a)–Li–N(b)	85.9(5), 84.3(6)	Li–N(1)–Si	127.1(5), 125.4(5)
	N(a)–Li–N(1)	141.8(7), 133.1(8)	Li–N(1)–C(1)	109.3(6), 109.6(6)
	N(a)–Li–N(3)	113.5(6), 113.9(7)	Si–N(1)–C(1)	123.1(5), 124.3(5)
	N(b)–Li–N(1)	121.1(7), 127.6(8)	Li–N(3)–C(2)	107.6(6), 107.5(6)
	N(b)–Li–N(3)	106.3(6), 114.6(8)	Li–N(3)–C(4)	132.4(7), 131.8(7)
	N(1)–Li–N(3)	86.3(6), 85.5(6)	C(2)–N(3)–C(4)	119.8(7), 120.6(7)
(**7**)	N(1)–Li–N(1′)	103.5(5)	Li′–N(1)–C(1)	109.0(4)
	N(1)–Li–N(3)	85.9(4)	Si–N(1)–Li′	113.9(4)
	N(1′)–Li–N(3)	118.4(5)	C(2)–N(3)–Li	108.8(5)
	Li–N(1)–Si	121.7(4)	C(2)–N(3)–C(4)	118.0(5)
	Li–N(1)–Li′	76.5(4)	Li–N(3)–C(4)	132.4(5)
	Li–N(1)–C(1)	106.2(4)		
	Si–N(1)–C(1)	120.9(4)		

[a] Primed atoms are related to the others by inversion centres. [b] For molecules 1 and 2 respectively.

Li–N(amido) distances in the structures of (**1**) and (**5**), although in these the amido-N centres bridge two lithium centres. In [Li(tmen)($NHC_6H_2Bu^t_3$-2,4,6)], which is the only other authenticated amido–lithium–tmen complex, the *three-co-ordinate* Li–N(amido) distance is much shorter, 1.895(8) Å.[9] Interestingly, the tridentate tertiary amine *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (pmdien) has yielded a complex hexanuclear amido-lithium species.[7] The Li–N(tmen) distances in (**2**) and (**6**) are comparable with those in other tertiary amine derivatives of amido-lithium complexes.[7,9]

Of particular significance in the structure of (**7**) is the large gap in the metal co-ordination spheres (Figure 6), the overall arrangement of ligands being similar to the non-ethereal part of molecules of (**5**). Relevant angles in (**5**) and (**7**) are respectively N(1)–Li–N(1′) 102.2(11), 103.5(5)°; N(1)–Li–N(3) 83.0(8), 85.9(4)°; N(1′)–Li–N(3) 113.0(9), 118.4(5)°. There is a few percent reduction in Li–N distances from (**5**) to (**7**) as expected. A dimer rather than a higher oligomer in which the lithium would have less departure from regular trigonal three-co-ordination is noteworthy, as is the presence of *naked* electron-deficient lithium centres in the absence of CH ··· Li contacts of the type commonly encountered in unsaturated lithium compounds.[27,31]

Table 3. Lithium environments in (**4**)*

	Atom	*r*	C(31)	N(32)	N(72)
Li(1)	N(31)	2.04(2)	35.2(6)	67.6(8)	114.9(10)
	C(31)	2.34(3)		34.4(6)	141.9(10)
	N(32)	2.08(3)			136.5(14)
	N(72)	2.00(3)			
Li(2)	Atom	*r*	N(12)	N(61)	N(71)
	N(11)	2.34(2)	64.3(7)	102.7(11)	106.5(9)
	N(12)	1.96(3)		117.5(13)	124.8(14)
	N(61)	2.14(3)			117.6(13)
	N(71)	1.96(3)			
Li(3)	Atom	*r*	N(21)	N(22)	N(61)
	N(11)	2.21(2)	138.8(10)	123.1(12)	109.6(12)
	N(21)	2.19(3)		65.0(8)	99.9(10)
	N(22)	2.07(3)			113.9(9)
	N(61)	2.07(2)			
	[C(21)	2.43(3)]			
Li(4)	Atom	*r*	N(52)	N(61)	
	N(21)	2.03(2)	141.4(16)	104.7(11)	
	N(52)	1.95(2)		112.6(11)	
	N(61)	2.10(3)			
Li(5)	Atom	*r*	N(41)	N(42)	N(71)
	N(31)	2.05(3)	132.8(14)	133.4(12)	115.1(9)
	N(41)	2.06(3)		63.9(7)	98.9(11)
	N(42)	2.24(2)			100.0(11)
	N(71)	2.28(3)			
	[C(41)	2.39(2)]			
Li(6)	Atom	*r*	N(41)	N(42)	N(71)
	N(11)	2.19(3)	135.8(13)	134.4(11)	108.3(10)
	N(41)	2.05(3)		61.0(8)	106.6(12)
	N(42)	2.41(3)			101.2(11)
	N(71)	2.07(2)			
	[C(41)	2.48(3)]			
Li(7)	Atom	*r*	N(51)	N(62)	
	N(22)	2.15(2)	119.7(14)	119.9(14)	
	N(51)	2.00(3)		115.6(12)	
	N(62)	2.03(3)			

* *r* is the Li–N distance (Å). Other entries are the angles subtended at the lithium atom by the atoms at the head of the relevant row and column. In N(*mn*), *m* is the ligand and *n* the atom number.

The salient features of the structure of (**4**) embrace the presence of (*i*) seven distinct lithium centres, either irregular three-co-ordinate, Li(1,4,7), or four-co-ordinate, Li(2,3,5,6), centres (Figure 3, Table 3); (*ii*) bridging as well as the usual terminal pyridine-N centres; (*iii*) doubly bridged and triply bridged amido-NH centres; and (*iv*) terminal, and doubly and triply bridged silylated amido-N centres. Unfortunately, the precision of this determination does not yield meaningful Li–N

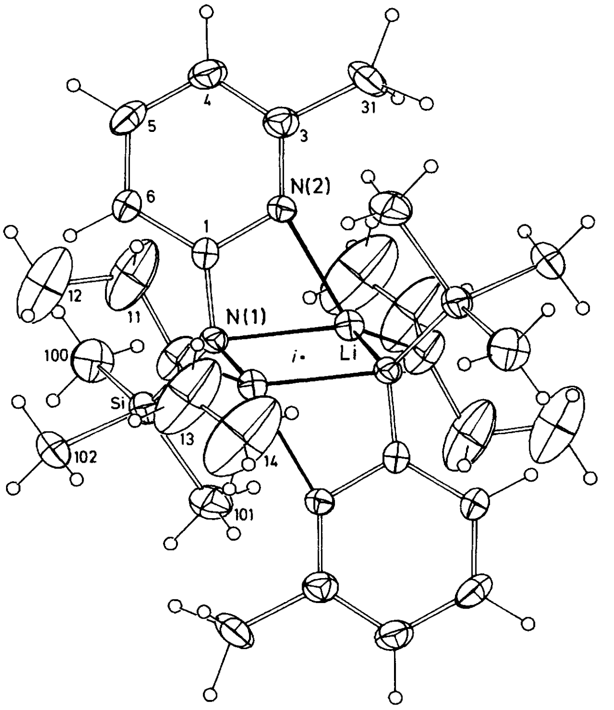


Figure 1. Projections of the binuclear unit in [{$Li(OEt_2)$(mtmsap)}$_2$] (**1**) perpendicular to the pyridine planes, showing 20% thermal ellipsoids for non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å

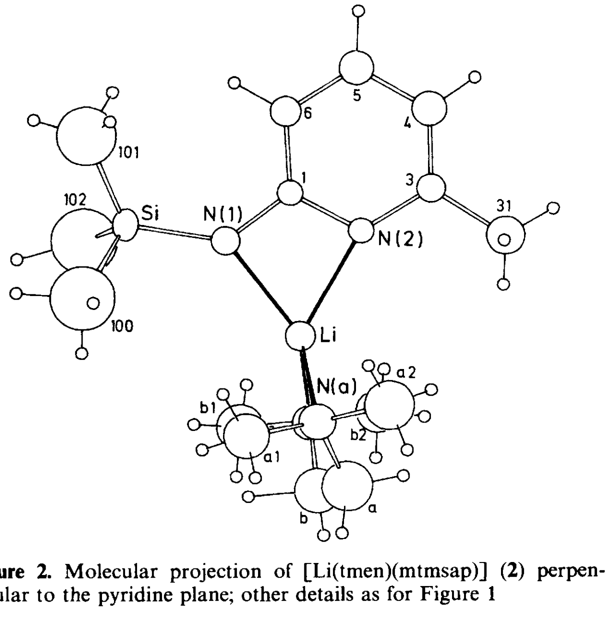


Figure 2. Molecular projection of [Li(tmen)(mtmsap)] (**2**) perpendicular to the pyridine plane; other details as for Figure 1

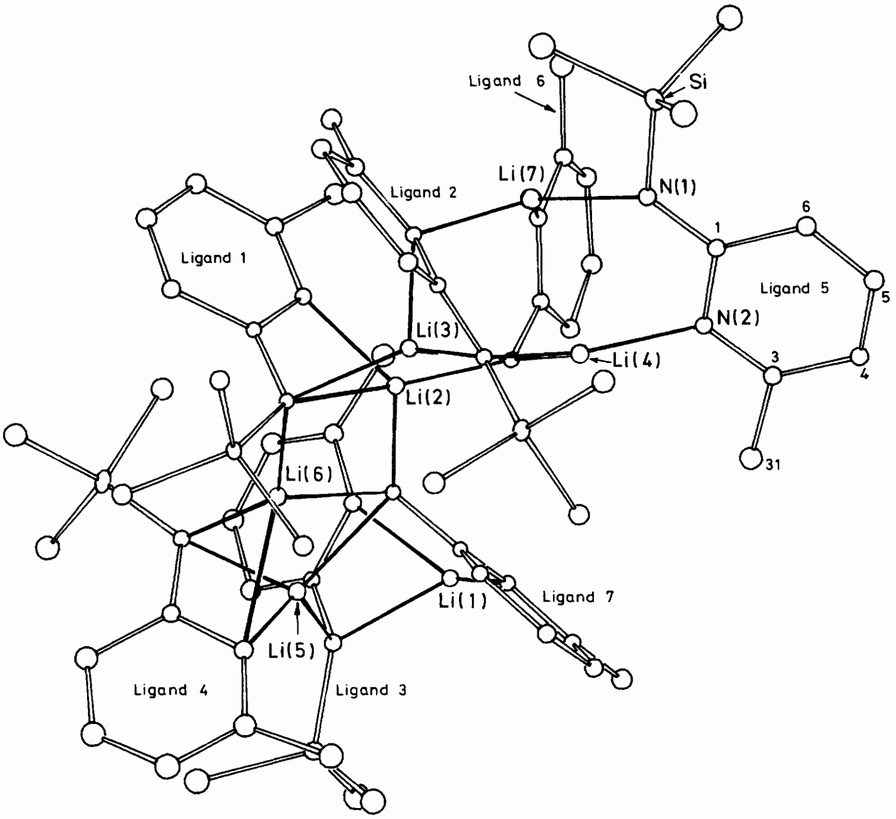


Figure 3. Molecular projection of $[Li_7(mtmsap)_5(amp)_2]$ (**4**); all atoms shown have arbitrary radii

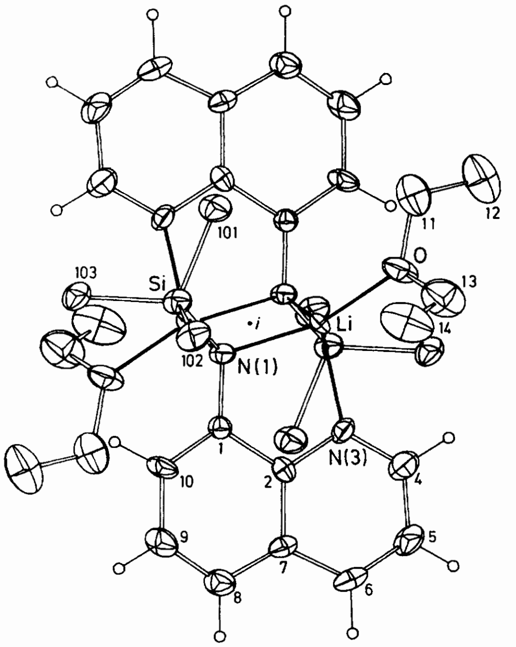


Figure 4. Projection of the binuclear unit of $[\{Li(OEt_2)(tmsaq)\}_2]$ (**5**) onto the quinoline plane; other details as for Figure 1

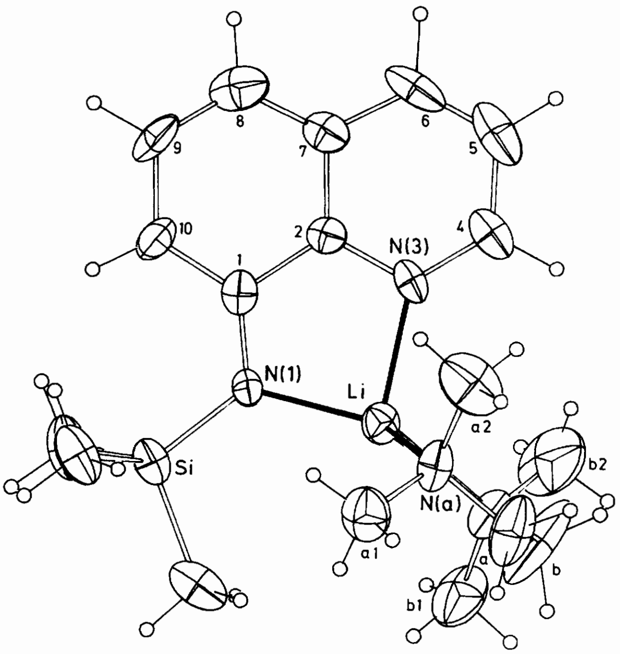


Figure 5. Molecular projection of [Li(tmen)(tmsaq)] (**6**); details as for Figure 1

distances and angles for a detailed comparison with other compounds, although the Li–N distances associated with the triply bridging centres are consistently longer [2.19(3), 2.21(2), and 2.34(2) Å for N(11)] or irregular [2.28(3), 2.07(2), and 1.96(3) Å for N(71)], than in other terminal and doubly bridged systems, as has been noted for hexanuclear species.[7,11] The presence of bridging pyridine-N centres may be accredited to the predominantly ionic character of lithium compounds,[2] and/or that the pyridine-N centre is engaged in multicentre electron-deficient bonding as commonly described for bridging aryl groups. This Li_7 cluster is unique to lithium chemistry; the previous highest aggregates for anionic N-centred compounds are hexanuclear species for both amides[7,11] and imides.[6,8]

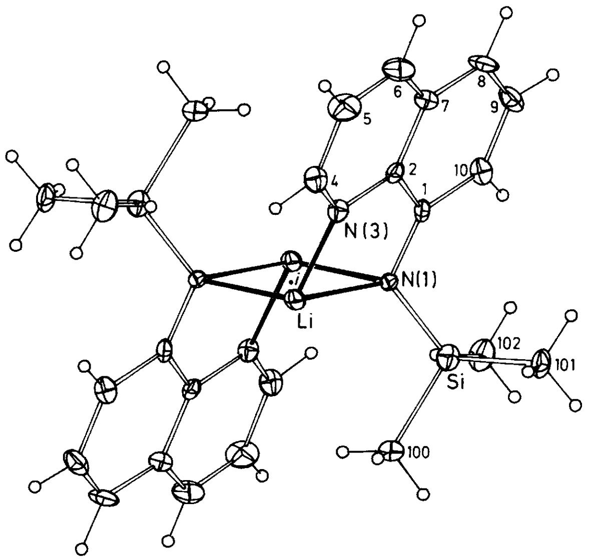


Figure 6. Projection of the binuclear unit in [{Li(tmsaq)}$_2$] (7); details as for Figure 1

The Si–N distances in the binuclear compounds where the nitrogens bridge are marginally longer than in the mononuclear species: 1.705(5) in (**1**), 1.735 in (**5**), 1.715(5) Å in (**7**); *cf.* 1.6_9 in (**2**), 1.69_1 Å in (**6**). Mainly on the basis of N–Si $p\pi$—$d\pi$ interactions, it has been proposed that longer Si–N distances in compounds of $N(SiMe_3)_2$ reflect a higher degree of covalency of the metal–nitrogen bonds.[32] If this is so for amido-N centres possessing only one trimethylsilyl group, the bridging amido-N centres in (**1**) and (**5**) have greater ionic character, but not as high as in [{K($C_4H_8O_2$)$_2$[N(SiMe$_3$)$_2$]}$_2$] (Si–N 1.64 Å), which represents the present upper limit of ionic character in compounds of $N(SiMe_3)_2$.[32] In compound (**4**) there is a spread of values for Si–N bonds [1.70(1)—1.723(9) Å], and no apparent correlation between distance and whether the nitrogen centres are terminal, or bridging.

Experimental

Materials.—All operations of the air- and moisture-sensitive silylamines and amido-lithium complexes were carried out under an argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from Na–benzophenone (diethyl ether), Na (benzene and toluene), $LiAlH_4$ (pentane), KOH (tmen), and CaH_2 (hexane) under a dinitrogen atmosphere prior to use.

Table 4. Non-hydrogen atom co-ordinates for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
N(1)	0.356 9(5)	0.531 9(5)	−0.029 4(5)	C(100)	0.107 2(8)	0.597 0(9)	−0.191 9(8)
C(1)	0.409 4(7)	0.637 0(7)	0.104 6(7)	C(101)	0.204 5(8)	0.424 3(9)	−0.357 2(7)
N(2)	0.564 8(6)	0.740 9(6)	0.174 8(6)	C(102)	0.023 7(8)	0.271 1(9)	−0.183 6(8)
C(3)	0.629 3(8)	0.849 6(8)	0.308 5(8)	O	0.654 7(6)	0.762 4(6)	−0.133 4(6)
C(31)	0.798 6(8)	0.961 9(8)	0.375 0(8)	C(11)	0.662(2)	0.690(1)	−0.265(2)
C(4)	0.549 2(9)	0.863 1(9)	0.383 6(8)	C(12)	0.807(2)	0.766(2)	−0.254(2)
C(5)	0.389 5(10)	0.756 2(10)	0.315 9(9)	C(13)	0.644(2)	0.896(2)	−0.146(2)
C(6)	0.320 5(7)	0.645 3(8)	0.178 8(8)	C(14)	0.580(2)	0.942(2)	−0.108(2)
Si	0.180 6(2)	0.460 2(2)	−0.180 0(2)	Li	0.583(1)	0.635(1)	−0.005(1)

Table 5. Non-hydrogen atom co-ordinates for (**2**)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.995(1)	0.781 7(7)	0.220 9(8)	0.484(1)	0.465 0(7)	0.233 9(6)
C(1)	0.960(2)	0.817 8(8)	0.153 8(10)	0.452(2)	0.428 1(8)	0.166 4(10)
N(2)	0.971(1)	0.884 1(7)	0.167 7(8)	0.454(1)	0.364 0(7)	0.181 0(8)
C(3)	0.941(2)	0.924(1)	0.106(1)	0.418(2)	0.321 5(9)	0.116 6(11)
C(31)	0.951(2)	0.996(1)	0.128(1)	0.423(2)	0.252(1)	0.139 1(1)
C(4)	0.896(2)	0.905(1)	0.025(1)	0.380(2)	0.343(1)	0.039(1)
C(5)	0.886(2)	0.842(1)	0.011(1)	0.373(2)	0.410(1)	0.023(1)
C(6)	0.913(2)	0.796(1)	0.071(1)	0.411(2)	0.452(1)	0.088(1)
Si	1.000 3(6)	0.700 5(3)	0.234 3(3)	0.493 9(6)	0.546 1(2)	0.250 4(4)
C(100)	0.853(3)	0.666(2)	0.223(2)	0.627(5)	0.560(3)	0.336(3)
C(101)	1.049(3)	0.652(2)	0.162(2)	0.525(4)	0.599(2)	0.176(3)
C(102)	1.104(3)	0.679(2)	0.333(2)	0.373(5)	0.574(3)	0.280(3)
C(a1)	1.241(2)	0.951(1)	0.338(2)	0.761(3)	0.399(2)	0.420(2)
C(a2)	1.282(3)	0.847(2)	0.399(2)	0.727(3)	0.297(2)	0.344(2)
N(a)	1.195(2)	0.898(1)	0.371(1)	0.678(2)	0.348(1)	0.383(1)
C(a)	1.151(3)	0.916(2)	0.442(2)	0.637(3)	0.308(2)	0.437(2)
C(b)	1.048(3)	0.920(1)	0.441(2)	0.538(3)	0.330(2)	0.451(2)
N(b)	0.953(2)	0.894(1)	0.372(1)	0.441(2)	0.351(1)	0.386(1)
C(b1)	0.863(3)	0.943(2)	0.338(2)	0.360(3)	0.305(1)	0.354(2)
C(b2)	0.900(3)	0.841(2)	0.401(2)	0.388(3)	0.406(2)	0.413(2)
Li	1.034(3)	0.861(1)	0.291(2)	0.523(3)	0.383(2)	0.304(2)

Hydrogen-1 and ^{13}C n.m.r., and mass spectra were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz), Bruker WP-80, and Hewlett Packard-4986 spectrometers respectively. Silicon-29 and ^{7}Li n.m.r. were obtained on a Bruker WM-300 spectrometer. Chemical shifts (δ) are recorded relative to $SiMe_4$ (^{1}H and ^{29}Si, external), $[^{2}H_6]$benzene (^{13}C), and aqueous $LiNO_3$ (^{7}Li, external). Concentrations for ^{7}Li n.m.r. spectroscopy were *ca.* 100 mg per cm^3 benzene.

n-Butyl-lithium in hexane (*ca.* 1.6 mol dm^{-3}) was purchased from Metallgesellschaft and $SiMe_3Cl$, $NH(SiMe_3)_2$, 2-amino-6-methylpyridine, and 8-aminoquinoline from Fluka.

Synthesis of 6-Methyl-2-trimethylsilylaminopyridine.—n-Butyl-lithium (23.8 cm^3, 1.6 mol dm^{-3}, 38.1 mmol) in hexane was added slowly to a solution of 2-amino-6-methylpyridine (4.1 g, 38.1 mmol) in OEt_2 (60 cm^3) at 0 °C, and stirred at room temperature for 90 min. Chlorotrimethylsilane (7.2 cm^3, 57.1 mmol) was then slowly added at 0 °C, and the resulting mixture stirred for 12 h, yielding a pale yellow solution. This was filtered, volatiles removed *in vacuo* and the resulting yellow oil distilled yielding the product as a colourless liquid (3.11 g, 75.6%), b.p. 38—40 °C (1 mmHg). ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.24 (9 H, s, $SiMe_3$), 2.27 (3 H, s, CCH_3), 4.14 (1 H, s, NH), 5.9—7.1 (3 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 0.1 ($SiMe_3$), 24.2 (CCH_3), 106.6, 112.2, 137.6 156.8, 159.7 (aromatic); ^{29}Si n.m.r. (59.63 MHz, $CDCl_3$), δ 2.21 (s); *m/e* (gas chromatography, g.c.) 180 (M^+, 13), 179 (7), 166 (14), 165 (100), 135 (16%).

Synthesis of 8-Trimethylsilylaminoquinoline.—A mixture of 8-aminoquinoline (2.0 g, 14.1 mmol), hexamethyldisilazane (2.3 g, 3.0 cm^3, 14.1 mmol) and chlorotrimethylsilane (4 drops) was heated at 120 °C for 12 h. The volatiles were then removed *in vacuo* yielding a red oil from which the product was distilled as a pale yellow oil (2.6 g, 86.2%), b.p. 110 °C (3 mmHg). ^{1}H N.m.r. (80 MHz, $CDCl_3$), δ 0.05 (9 H, s, $SiMe_3$), 6.0 (1 H, br s, NH), 6.40—7.60 (5 H, m, aromatic), 8.30—8.45 (1 H, m, H^2); ^{13}C n.m.r. (20.1 MHz, $CDCl_3$), δ −0.489 ($SiCH_3$), 145.0, 139.2, 128.8 (aromatic quaternary), 146.6, 135.7, 127.2, 120.9, 114.6, 109.1 (aromatic CH); ^{29}Si n.m.r. (59.63 MHz, $CDCl_3$), δ 1.58 (s); *m/e* (g.c.) 216.0 (M^+, 11.6), 201.1 (100), 171.1 (28%).

Synthesis of $[\{Li(OEt_2)(mtmsap)\}_2]$ **(1)**.—n-Butyl-lithium (6.6 cm^3, 1.6 mol dm^{-3}, 10.6 mmol) in hexane was added to Hmtmsap (1.9 g, 10.6 mmol) in OEt_2 (2 cm^3) at 0 °C, yielding a white precipitate of the product. This was filtered, washed with ice-cold pentane (2 × 5 cm^3) and dried *in vacuo* (1.6 g, 58.4%), m.p. 60 °C. ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.31 (9 H, s, $SiMe_3$), 0.90 (6 H, t, CH_2CH_3), 2.21 (3 H, s, CCH_3), 3.20 (4 H, q, OCH_2), 6.0—7.2 (3 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 1.7 ($SiMe_3$), 14.6 (CCH_3), 24.1 (CH_2CH_3), 65.3 (OCH_2), 108.6, 111.9, 137.8, 156.1, 170.0 (aromatic); ^{7}Li n.m.r. (116.64 MHz, C_6D_6), δ 1.51 (s); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −7.85 (s).

Synthesis of [Li(tmen)(mtmsap)] **(2)**.—A solution of $LiBu^n$ (3.0 cm^3, 1.7 mol dm^{-3}, 5.26 mmol) and tmen (0.79 cm^3, 5.26 mmol) in hexane (3 cm^3) was slowly added to a stirred solution of Hmtmsap (0.9 g, 5.26 mmol) in hexane at 0 °C. During 2 h at room temperature a white precipitate of the product formed. This was filtered, washed with ice-cold pentane (3 × 5 cm^3) and dried *in vacuo* (1.0 g, 60.5%), m.p. 102—105 °C (decomp.). ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.41 (9 H, s, $SiMe_3$), 1.80 (4 H, s, NCH_2), 1.89 (12 H, s, NCH_3), 2.12 (3 H, s, CCH_3), 5.9—7.2 (3 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 2.3 ($SiMe_3$), 24.6 (CCH_3), 45.1 (NCH_3), 56.4 (NCH_2), 104.4, 110.5, 126.4, 137.2, 154.7 (aromatic); ^{7}Li n.m.r. (116.64 MHz, C_6D_6), δ 2.04 (s); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −13.0 (s).

Synthesis of $[\{Li(mtmsap)\}_2]$ **(3)**.—n-Butyl-lithium (7.6 cm^3, 1.60 mol dm^{-3}, 12.1 mmol) in hexane was added slowly to a stirred solution of Hmtmsap (2.2 g, 12.1 mmol) in hexane at 0 °C. After *ca.* 12 h at room temperature volatiles were removed *in vacuo* yielding a yellow oil. Addition of pentane (8 cm^3) gave a white precipitate of the *title compound*. This was filtered, washed with cold pentane (3 × 5 cm^3) and dried *in vacuo* (0.9 g, 40%), m.p. 50—55 °C (decomp.). ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.20 (9 H, s, $SiMe_3$), (3 H, s, CCH_3), 6.0—7.1 (3 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 1.7 ($SiMe_3$), 23.51 (CCH_3), 109.6, 113.5, 138.5, 155.9, 171.0 (aromatic); ^{7}Li n.m.r. (116.64 MHz, C_6D_6), δ 1.74 (s); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −6.05 (s). Molecular weight (cryoscopy in benzene), 387(4); calc. 372.5.

Synthesis of $[Li_7(mtmsap)_5(amp)_2]$ **(4)**.—n-Butyl-lithium (2.8 cm^3, 1.7 mol dm^{-3}, 4.90 mmol) was added slowly to a stirred solution of Hamp (0.15 g, 1.40 mmol) and Hmtmsap (0.63 g, 3.50 mmol) in hexane (3 cm^3) at 0 °C. A white precipitate formed after addition of most of the $LiBu^n$ which dissolved on stirring at room temperature for *ca.* 5 min. After 10 min a fine white precipitate of the product deposited. This was washed with ice-cold pentane (2 × 5 cm^3) and dried *in vacuo* (yield 1.89 g, 68%), m.p. 98—100 °C. ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.15 (9 H, s, $SiMe_3$), 1.98 (3 H, s, CCH_3), 2.06 (3 H, s, CCH_3), 5.8—7.0 (6 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 1.6 ($SiMe_3$), 23.9, (CCH_3) 107.7, 109.3, 110.8, 112.7, 137.4, 138.2, 154.8, 155.6, 170.1, 171.9 (aromatic); ^{7}Li n.m.r. (116.64 MHz, C_6H_5Me), δ 1.99 (s), (35 °C); δ 2.77, 2.65, 2.45, 2.09, 1.84, 1.68, 1.53, 1.29, 0.98, 0.87, 0.43, −0.42, −0.93, −1.23 (relative ratio *ca.* 6:9:10:6:6:5:5:6:4:4:3:3:1:1) (−80 °C); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −4.89 (s).

Synthesis of $[\{Li(OEt_2)(tmsaq)\}_2]$ **(5)**.—n-Butyl-lithium (1.5 cm^3, 1.6 mol dm^{-3}, 2.4 mmol) in hexane was added to Htmsaq (0.5 g, 2.31 mmol) in OEt_2 at 0 °C, yielding a red then orange solution from which orange crystals of the product deposited at −30 °C overnight. These were collected, washed with ice-cold pentane (3 × 5 cm^3) then dried *in vacuo* (0.52 g, 77%), m.p. 135—140 °C. ^{1}H N.m.r. (90 MHz, C_6D_6), δ 0.15 (9 H, s, $SiMe_3$), 0.83 (6 H, t, CCH_3), 3.10 (4 H, q, CH_2), 6.40—8.05 (6 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 2.2 ($SiMe_3$), 14.7 (CCH_3), 65.4 (CH_2), 111.8, 117.9, 120.1, 128.8, 137.1, 145.1 (aromatic CH), 135.1, 143.8, 161.1 (aromatic quaternary); ^{7}Li n.m.r. (116.64 MHz, C_6D_6), δ 2.80 (s); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −10.01 (s).

Synthesis of [Li(tmen)(tmsaq)] **(6)**.—A solution of $LiBu^n$ (2.6 cm^3, 1.6 mol dm^{-3}, 4.2 mmol) and tmen (0.63 cm^3, 0.48 g, 4.2 mmol) was cooled to 0 °C and Htmsaq (0.90 g, 4.2 mmol) slowly added yielding a red solution. At −30 °C overnight, crystals of the product deposited. These were collected, washed with ice-cold pentane (3 × 5 cm^3) then dried *in vacuo* (0.88 g, 68%), m.p. 106 °C. ^{1}H N.m.r. (80 MHz, C_6D_6), δ 0.48 (9 H, s, $SiMe_3$), 1.78 (16 H, s, tmen), 6.5—7.9 (6 H, m, aromatic); ^{13}C n.m.r. (20.1 MHz, C_6D_6), δ 2.5 ($SiMe_3$), 45.8 (NCH_3), 57.0 (NCH_2), 115.1, 119.5, 130.2, 132.4, 137.0, 141.9, 166.5 (aromatic); ^{7}Li n.m.r. (116.64 MHz, C_6D_6), δ 2.47 (s); ^{29}Si n.m.r. (59.63 MHz, C_6D_6), δ −11.76 (s); *m/e* (M^+) 338 (1), 216 (21), 201 (97), 116 (49), 58 (100%).

Synthesis of $[\{Li(tmsaq)\}_2]$ **(7)**.—To a solution of $LiBu^n$ in hexane (3.0 cm^3, 1.7 mol dm^{-3}, 4.8 mmol) at room temperature, Htmsaq (1.0 g, 4.63 mmol) was slowly added yielding a red solution then a fine pale yellow precipitate of the product. This was collected, washed with ice-cold pentane (3 × 5 cm^3), and dried *in vacuo* (0.79 g, 77%), m.p. 100 °C. ^{7}Li N.m.r. (116.64 MHz, C_6D_6), δ 2.48 (s).

Structure Determination.—Unique data sets were measured within the specified $2\theta_{max.}$ limits at *ca.* 295 K on specimens

Table 6. Non-hydrogen atom co-ordinates for **(4)**

	Ligand 1			Ligand 2			Ligand 3			Ligand 4		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.153 7(5)	0.185 0(7)	−0.068 1(7)	0.314 5(5)	0.076 3(6)	0.035 3(7)	0.190 7(5)	0.493 0(7)	−0.326 2(8)	0.067 3(5)	0.309 4(7)	−0.251 9(8)
C(1)	0.126 9(6)	0.230 5(8)	0.002 3(9)	0.277 1(6)	0.058 5(9)	0.103 4(7)	0.173 4(7)	0.557 9(9)	−0.261 5(10)	0.058 6(8)	0.245 4(10)	−0.338 3(11)
N(2)	0.167 4(5)	0.318 4(7)	0.053 5(7)	0.257 4(5)	0.130 7(7)	0.153 2(7)	0.207 3(5)	0.579 2(7)	−0.164 9(8)	0.117 5(6)	0.227 3(8)	−0.359 0(9)
C(3)	0.143 9(8)	0.369 1(9)	0.124 0(11)	0.210 2(7)	0.116 4(10)	0.213 3(10)	0.191 8(8)	0.643 5(10)	−0.092 2(11)	0.118 4(11)	0.161 9(13)	−0.443 7(15)
C(31)	0.193 6(8)	0.465 2(11)	0.177 1(12)	0.190 7(8)	0.198 4(11)	0.260 6(12)	0.232 5(9)	0.656 9(12)	0.009 4(14)	0.188 6(11)	0.149 0(13)	−0.454 3(14)
C(4)	0.080 4(8)	0.338 1(11)	0.150 5(12)	0.182 7(8)	0.030 7(11)	0.224 7(11)	0.141 4(9)	0.687 5(11)	−0.120 3(13)	0.055 0(12)	0.117 2(14)	−0.511 0(16)
C(5)	0.039 8(8)	0.249 3(11)	0.098 1(12)	0.206 9(8)	−0.039 5(11)	0.183 4(12)	0.109 3(8)	0.670 2(11)	−0.216 8(13)	−0.005 3(11)	0.135 6(13)	−0.495 2(15)
C(6)	0.059 8(7)	0.195 5(10)	0.025 3(11)	0.252 8(8)	−0.028 8(10)	0.121 1(11)	0.123 6(8)	0.607 3(11)	−0.289 9(12)	−0.010 4(10)	0.197 7(13)	−0.411 4(14)
Si	0.110 3(2)	0.073 9(3)	−0.138 7(3)	0.345 0(2)	−0.002 8(3)	−0.036 6(4)	0.174 6(4)	0.473 2(3)	−0.453 0(4)	0.003 6(2)	0.353 1(3)	−0.209 4(4)
C(100)	0.098 7(8)	−0.010 8(10)	−0.063 7(11)	0.273 5(9)	−0.103 8(11)	−0.120 0(12)	0.209 4(11)	0.576 9(14)	−0.492 1(16)	0.052 0(9)	0.440 4(11)	−0.089 2(12)
C(101)	0.019 2(8)	0.059 0(10)	−0.219 0(12)	0.411 5(9)	−0.043 4(12)	0.040 8(13)	0.079 0(10)	0.419 4(13)	0.519 2(14)	−0.067 8(9)	0.265 8(12)	−0.181 6(13)
C(102)	0.166 5(8)	0.044 5(10)	−0.226 1(11)	0.391 5(8)	0.059 1(10)	−0.115 6(11)	0.222 6(10)	0.386 9(13)	−0.493 1(15)	−0.042 0(10)	0.408 3(12)	−0.299 0(14)
Li	0.286(1)	0.533(1)	−0.222(2)	0.242(1)	0.326(2)	−0.021(2)	0.254(1)	0.176(1)	0.025(2)	0.392(1)	0.196(2)	0.066(2)
Solvent *	0.277(4)	0.838(6)	0.440(6)	0.326(3)	0.787(4)	0.309(4)	0.225(5)	0.884(6)	0.496(7)	0.386(1)	0.798(4)	0.270(4)

	Ligand 5			Ligand 6			Ligand 7		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.447 5(6)	0.215 5(7)	0.260 2(8)	0.336 7(5)	0.291 7(6)	0.039 7(7)	0.240 1(5)	0.370 6(6)	−0.141 7(7)
C(1)	0.503 9(7)	0.238 2(9)	0.221 7(11)	0.360 9(7)	0.371 5(9)	0.113 1(10)	0.294 7(6)	0.361 5(8)	−0.186 9(9)
N(2)	0.493 7(5)	0.254 4(6)	0.131 3(8)	0.758 8(5)	0.369 1(7)	0.206 7(8)	0.333 3(5)	0.434 3(6)	−0.211 6(7)
C(3)	0.549 3(8)	0.283 7(9)	0.093 8(11)	0.379 3(7)	0.448 6(10)	0.281 5(11)	0.385 7(7)	0.424 0(9)	−0.260 4(10)
C(31)	0.531 6(9)	0.305 5(12)	−0.004 8(13)	0.378 1(9)	0.436 2(12)	0.383 7(14)	0.425 7(8)	0.506 6(10)	−0.287 6(11)
C(4)	0.620 0(8)	0.292 6(9)	0.139 4(11)	0.398 1(8)	0.532 0(10)	0.265 0(12)	0.403 1(7)	0.340 6(10)	−0.282 6(10)
C(5)	0.632 1(8)	0.273 9(10)	0.228 7(12)	0.402 2(8)	0.536 2(11)	0.169 1(12)	0.364 9(7)	0.267 9(10)	−0.257 2(10)
C(6)	0.576 9(8)	0.244 3(10)	0.270 7(11)	0.384 7(7)	0.457 9(10)	0.090 4(11)	0.310 8(7)	0.277 2(9)	−0.208 3(9)
Si	0.453 3(3)	0.184 7(4)	0.371 0(4)						
C(100)	0.361 8(11)	0.167 2(14)	0.399 5(16)						
C(101)	0.477 2(11)	0.076 9(15)	0.363 7(16)						
C(102)	0.514 9(10)	0.279 1(13)	0.482 9(15)						
Li	0.161(1)	0.377(2)	−0.279(2)	0.146(1)	0.265(2)	−0.178(2)	0.353(1)	0.242(2)	0.225(2)
Solvent *	0.698(4)	0.046(5)	0.434(6)	0.232(4)	0.869(5)	0.565(6)	0.283(5)	0.761(6)	0.347(8)

* For fragment 8, $x = 0.321(4)$, $y = 0.861(5)$, $z = 0.403(6)$; fragments are modelled as carbon atoms, populations 1.0(1—3), 0.5(4—8).

Table 7. Non-hydrogen atom co-ordinates for (**5**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
N(1)	0.374 4(8)	0.011 7(9)	0.178 1(9)	Si	0.209 7(4)	0.161 8(4)	0.273 1(4)
C(1)	0.392(1)	−0.118(1)	0.239(1)	C(100)	0.048(1)	0.170(1)	0.246(1)
C(2)	0.541(1)	−0.218(1)	0.220(1)	C(101)	0.242(1)	0.329(1)	0.207(1)
N(3)	0.652(1)	−0.170(1)	0.149(1)	C(102)	0.152(1)	0.172(1)	0.481(1)
C(4)	0.786(2)	−0.251(2)	0.138(1)	O	0.655 8(10)	0.145 2(9)	0.106 8(10)
C(5)	0.822(1)	−0.388(2)	0.189(2)	C(11)	0.663(2)	0.272(2)	0.035(2)
C(6)	0.714(2)	−0.437(1)	0.258(1)	C(12)	0.813(2)	0.267(2)	−0.050(2)
C(7)	0.565(1)	−0.357(1)	0.277(1)	C(13)	0.679(2)	0.136(2)	0.240(2)
C(8)	0.444(2)	−0.397(1)	0.352(1)	C(14)	0.565(2)	0.141(2)	0.371(2)
C(9)	0.306(1)	−0.302(2)	0.369(1)	Li	0.583(2)	0.019(2)	0.059(2)
C(10)	0.280(1)	−0.166(1)	0.317(1)				

Table 8. Non-hydrogen atom co-ordinates for (**6**)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.897 4(4)	−0.079 3(5)	0.157 0(2)	0.408 9(4)	0.346 5(6)	0.097 3(2)
C(1)	0.833 1(5)	−0.080 3(7)	0.187 9(3)	0.324 2(5)	0.371 6(7)	0.076 5(2)
C(2)	0.851 2(5)	−0.154 9(7)	0.231 4(2)	0.297 8(5)	0.500 3(8)	0.063 3(2)
N(3)	0.931 8(4)	−0.219 3(6)	0.238 0(2)	0.362 5(4)	0.592 2(6)	0.074 4(2)
C(4)	0.952 1(6)	−0.287 3(8)	0.276 5(3)	0.345 0(7)	0.709 7(9)	0.062 4(3)
C(5)	0.894 3(7)	−0.297 2(9)	0.313 2(3)	0.259 3(8)	0.749 1(11)	0.036 4(4)
C(6)	0.814 8(6)	−0.236 1(9)	0.306 1(3)	0.193 0(7)	0.659 4(12)	0.026 5(3)
C(7)	0.785 8(5)	−0.163 6(8)	0.266 4(2)	0.209 4(6)	0.534 1(10)	0.038 7(3)
C(8)	0.704 7(6)	−0.096 7(10)	0.257 9(3)	0.144 7(9)	0.435 4(12)	0.027 4(3)
C(9)	0.683 5(5)	−0.027 1(10)	0.217 9(3)	0.166 4(6)	0.315 4(11)	0.040 8(3)
C(10)	0.747 0(5)	−0.018 9(9)	0.183 4(3)	0.251 4(6)	0.282 1(9)	0.064 7(3)
Si	0.882 7(2)	0.001 3(3)	0.105 0(1)	0.452 9(2)	0.198 0(3)	0.106 5(1)
C(100)*	0.865 7(7)	0.176 9(8)	0.110 3(3)	0.412 2(13)	0.109 7(16)	0.153 8(6)
C(101)*	0.991 5(7)	−0.020 8(9)	0.076 0(3)	0.494 3(16)	0.113 7(22)	0.061 2(7)
C(102)*	0.785 3(7)	−0.058 6(9)	0.061 9(3)	0.570 0(14)	0.238 4(23)	0.157 6(7)
Li	0.995 6(9)	−0.199 8(12)	0.177 7(5)	0.480 7(10)	0.505 2(16)	0.106 2(5)
C(a1)	1.200 2(6)	−0.129 7(11)	0.165 1(5)	0.586 6(7)	0.650 4(12)	0.039 0(3)
C(a2)	1.179 2(8)	−0.199 7(18)	0.239 7(4)	0.672 3(7)	0.473 8(12)	0.069 4(4)
N(a)	1.145 5(4)	−0.216 5(6)	0.189 9(2)	0.607 4(4)	0.570 8(7)	0.080 6(2)
C(a)	1.157 9(7)	−0.339 3(10)	0.174 6(6)	0.648 7(7)	0.647 2(13)	0.120 5(3)
C(b)	1.097 5(7)	−0.413 3(9)	0.151 6(4)	0.624 1(9)	0.644 2(17)	0.160 8(4)
N(b)	0.997 9(4)	−0.384 3(6)	0.147 1(2)	0.539 1(5)	0.591 2(8)	0.172 6(2)
C(b1)	0.961 0(6)	−0.386 1(9)	0.098 7(3)	0.477 5(8)	0.682 0(14)	0.187 4(4)
C(b2)	0.946 9(8)	−0.475 9(9)	0.172 8(4)	0.563 7(8)	0.502 1(18)	0.212 2(4)

* The $SiMe_3$ group of molecule 2 is disordered: alternative sites (occupancy 0.5) are 0.574 9(12), 0.192 5(22), 0.106 9(9), for C(100); 0.416 8(18), 0.081 3(21), 0.045 6(8), for C(101); 0.393 9(18), 0.083 6(20), 0.142 2(9), for C(102).

Table 9. Non-hydrogen atom co-ordinates for (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
N(1)	0.493 4(2)	0.039 9(4)	0.642 7(4)	C(8)	0.301 9(3)	0.022 5(6)	0.761 0(6)
C(1)	0.430 7(3)	0.034 9(5)	0.684 8(5)	C(9)	0.347 8(3)	−0.028 7(6)	0.829 5(6)
C(2)	0.380 9(3)	0.091 8(5)	0.614 9(5)	C(10)	0.411 0(3)	−0.022 7(6)	0.792 5(5)
N(3)	0.398 8(2)	0.153 0(5)	0.509 8(4)	Si	0.554 65(8)	0.073 5(2)	0.741 2(2)
C(4)	0.354 6(3)	0.211 1(6)	0.448 0(6)	C(100)	0.622 3(3)	0.133 4(6)	0.646 2(6)
C(5)	0.289 8(3)	0.212 5(7)	0.481 0(6)	C(101)	0.530 8(3)	0.197 1(6)	0.852 0(6)
C(6)	0.272 8(3)	0.149 5(7)	0.582 6(7)	C(102)	0.586 0(3)	−0.055 1(6)	0.838 0(6)
C(7)	0.317 0(3)	0.086 7(6)	0.653 6(6)	Li	0.489 4(5)	0.110 3(9)	0.470 0(9)

mounted in capillaries using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with Mo-K_α radiation sources (λ = 0.710 6_9 Å) and operating in conventional $2\theta/\theta$ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' [$I > 2\sigma(I)$ for (**6**)] and used in the large block least-squares refinements, without absorption correction, after solution of the structures by direct methods. As usual for compounds of this type, the accessible data were generally limited by high thermal motion and high light-atom content, adversely affecting precision of the determinations. Where possible, and meaningful to do so, anisotropic thermal parameters were refined for all non-hydrogen atoms [except for (**4**), where non-hydrogen atoms were refined isotropically]; (x, y, z) and $(U_{iso.})_H$ were included constrained at estimated values. Residuals quoted on $|F|$ at convergence are conventional R, R'; statistical weights, derived from $\sigma^2(I) = \sigma^2(I_{diff.}) +$

$n[10^{-4}\sigma^4(I_{\text{diff.}})]$ were used. Neutral complex scattering factors were used;[33] computation used the XTAL program system[34] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond parameters.

Crystal data for (**1**). $C_{13}H_{25}LiN_2OSi$, M = 260.3, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 10.75(1), b = 10.09(1), c = 9.782(7) Å, α = 95.83(7), β = 110.10(7), γ = 116.96(7)°, U = 845(1) Å^3, D_c = 1.02 g cm^{-3} (Z = 1 dimer), $F(000)$ = 284, μ_{Mo} = 1.3 cm^{-1}. Specimen length *ca.* 0.3 mm; $2\theta_{\text{max.}}$ = 40°, N = 1 580, N_o = 1 072; R = 0.061, R' (n = 5) = 0.037.

Crystal data for (**2**). $C_{15}H_{31}LiN_4Si$, M = 302.4, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 12.010(5), b = 20.585(9), c = 17.405(8) Å, β = 109.73(3)°, U = 4 050(3) Å^3, D_c = 0.99 g cm^{-3} (Z = 8), $F(000)$ = 1 328, μ_{Mo} = 1.2 cm^{-1}. Specimen length *ca.* 0.3 mm (twin, necessitating deletion of some data); $2\theta_{\text{max.}}$ = 45°, N = 4 510, N_o = 1 665; R = 0.14, R' (n = 5) = 0.14.

Crystal data for (**4**). $C_{57}H_{89}Li_7N_{14}Si_5 \cdot 0.5C_6H_{14}$ (?), triclinic, space group $P\bar{1}$, a = 19.79(1), b = 15.57(1), c = 14.06(1) Å, α = 102.41(5), β = 100.53(5), γ = 103.57(5)°, U = 3 986(4) Å^3, $D_c \approx$ 1.00 g cm^{-3} (Z = 2), $F(000)$ = 1 290, μ_{Mo} = 1.3 cm^{-1}. Specimen length *ca.* 0.4 mm; $2\theta_{\text{max.}}$ = 40°, N = 7 046, N_o = 3 638; R = 0.097, R' (n = 5) = 0.099.

Crystal data for (**5**). $C_{16}H_{25}LiN_2OSi$, M = 289.4, triclinic, space group $P\bar{1}$, a = 10.85(1), b = 10.176(9), c = 9.901(7) Å, α = 84.13(6), β = 63.86(6), γ = 66.06(6)°, U = 893(1) Å^3, D_c = 1.08 g cm^{-3} (Z = 1 dimer), $F(000)$ = 320, μ_{Mo} = 1.3 cm^{-1}. Specimen length *ca.* 0.3 mm; $2\theta_{\text{max.}}$ = 45°, N = 2 144, N_o = 931; R = 0.075, R' (n = 5) = 0.066.

Crystal data for (**6**). $C_{18}H_{31}LiN_4Si$, M = 338.5, monoclinic, space group $P2_1/c$, a = 14.44(1), b = 10.498(9), c = 28.41(2) Å, β = 96.68(5)°, U = 4 277(5) Å^3, D_c = 1.05 g cm^{-3} (Z = 8), $F(000)$ = 1 472, μ_{Mo} = 1.2 cm^{-1}. Specimen length *ca.* 0.5 mm; $2\theta_{\text{max.}}$ = 45°, N = 5 572, N_o = 2 076; R = 0.080, R' (n = 4) = 0.063.

Crystal data for (**7**). $C_{24}H_{30}Li_2N_4Si_2$, M = 444.6, orthorhombic, space group *Pbca* (D_{2h}^{15}, no. 61), a = 21.039(7), b = 10.995(3), c = 10.871(5) Å, U = 2 515(1) Å^3, D_c = 1.17 g cm^{-3} (Z = 4), $F(000)$ = 944, μ_{Mo} = 1.55 cm^{-1}. Specimen length *ca.* 0.4 mm; $2\theta_{\text{max.}}$ = 50°, N = 2 179, N_o = 1 154; R = 0.071, R' (n = 1) = 0.064.

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