

## METALLATION OF AMINOSILANES: PREPARATION, INFRARED AND $^1\text{H}$ AND $^7\text{Li}$ NMR SPECTRA OF MONO- AND POLY-LITHIATED DERIVATIVES OF (*Si*-*n*-BUTYLAMINO)METHYLSILANES ("SILAZATES") \*

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### Summary

The reaction of aminosilanes  $\text{Me}_{4-x}\text{Si}(\text{NHBu}^n)_x$  ( $x = 1-4$ ) with appropriate amounts of *n*-butyllithium gave the *N*-lithio derivatives  $\text{Me}_{4-x}\text{Si}(\text{NHBu}^n)_y(\text{NLiBu}^n)_{x-y}$  ( $x = 1, y = 0$  (I);  $x = 2, y = 0$  (II), 1 (III);  $x = 3, y = 0$  (IV), 1 (V), 2 (VI);  $x = 4, y = 0$  (VII), 1 (VIII), 2 (IX), 3 (X)). Their infrared and  $^1\text{H}$  NMR spectra are reported, along with the  $^7\text{Li}$  NMR spectra of solutions of compounds I–IV and their complexes with PMDETA or TMEDA in *n*-pentane, diethyl ether, and THF. Inferences are drawn about the nature of solution species, and the analogy between tetra-imido anionic species  $\text{Si}(\text{NR})_4^{4-}$  ("silazates") and the ortho-silicate anion is explored.

### Introduction

Many recent studies have involved compounds containing Si–N–alkali metal bonds [1], with especial emphasis on lithium examples and in particular the compound  $(\text{Me}_3\text{Si})_2\text{NLi}$ . Thus, besides reports of its use to synthesise disilylamido derivatives of many elements (often with unusual coordination numbers and reactivity), its structure has been determined in the solid [2] and gas [3] phases and also as a solid 1:1 complex with diethyl ether [4] and with 12-crown-4 [5]. Of particular relevance to this work are studies of its  $^1\text{H}$  and  $^7\text{Li}$  NMR spectra in various solvents: in hydrocarbons, a dimer  $\rightleftharpoons$  tetramer equilibrium was postulated, while diethyl ether and THF caused progressively greater solvation and reduced oligomerization, so that in the last solvent the predominant species was inferred to be the solvated monomer [6]. Related derivatives  $\text{R}_3\text{SiNLiR}'$  have been reported as reaction intermediates, but have not been isolated [7].

\* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

A compound of the type  $R_2Si(NLiR')_2$  was first characterised by Fink [8,9]. He found that  $Me_2Si(NLiSiMe_3)_2$  was dimeric in non-polar solvents, and proposed a structure with intermolecular  $N \rightarrow Li$  interactions. By contrast, the partially-lithiated compound  $Me_2Si(NHSiMe_3)(NLiSiMe_3)$  was monomeric in  $CCl_4$  solutions, and intramolecular  $N \rightarrow Li$  interactions were suggested. Much more recently, Bürger and his co-workers have re-examined these two compounds [10] and used the former to prepare cyclic  $\overline{MN(SiMe_3)SiMe_2NSiMe_3}$  derivatives of a range of transition metals [11,12]. They have also determined the structure of solid  $Me_2Si(NLiBu^t)_2$ , showing it to be dimeric, and centred on an electron-deficient, flattened bisphenoidal  $Li_4N_4$  cluster [13].

The same group have also prepared examples of the previously unknown type  $RSi(NLiR')_3$ . The compounds in which  $R = Me, Ph$  or  $Bu^t$ ;  $R' = SiMe_3$  [14] or  $R = Ph, R' = Bu^t$  [13] all possess a central clustered  $Li_6N_6$  core (again electron deficient) in which the Li atoms occupy the vertices of a trigonal antiprism and are 3-coordinate by N. These compounds react as bidentate ligands with Ti halides [12].

No examples of  $Si(NLiR)_4$  derivatives have been previously reported.

In our own studies, dating from 1982, we wished to investigate systems which, while not so sterically hindered as the previously reported  $N-SiMe_3$  derivatives, still retained adequate solubility in hydrocarbons. Compounds with  $N-Bu^n$  groups were chosen in order to fulfil this condition and also to provide additional information from  $^1H$  NMR spectra. Apart from the structural interest of such Si-N-Li systems, an important aim was to assess their potential as intermediates for the synthesis of new polysilazane chains and clusters, and of Si-N-metal derivatives.

## Results and discussion

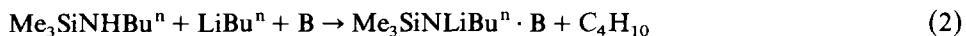
### Preparations

In the simplest case, equimolar amounts of  $Me_3SiNHBu^n$  and  $n$ -butyllithium reacted together in  $n$ -hexane for 2 h at room temperature; butane was evolved (IR). After removal of solvent, the resulting oil was distilled at  $108-110^\circ C/5 \times 10^{-3}$  Torr to give  $Me_3SiNLiBu^n$  (I) as a colourless glassy-looking solid (eq. 1) which softened at about  $57^\circ C$  [15].



It is very soluble in organic solvents such as hydrocarbons and ethers; attempted recrystallisation from THF gave crystals which were separated only with difficulty from the viscous mother-liquor. On pumping in vacuo, these crystals lost THF to give an oil, suggesting that they are a weakly-bound complex.

With stronger Lewis bases such as tetramethylethylenediamine (TMEDA) \* and pentamethyldiethylenetriamine (PMDETA) \*\*, 1 : 1 complexes quickly precipitated from concentrated hexane solution (eq. 2):



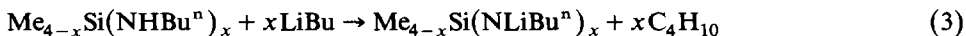
(B = TMEDA, PMDETA)

\* TMEDA =  $Me_2NCH_2CH_2NMe_2$ .

\*\* PMDETA =  $(Me_2NCH_2CH_2)_2NMe$ .

These crystalline products, initially colourless, quickly became yellow when stored at room temperature, either in vacuo or under nitrogen.

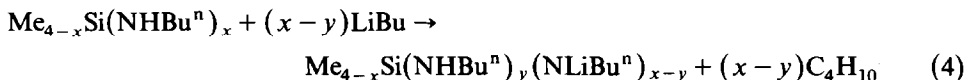
Analogous reactions with corresponding polyaminosilanes and stoichiometric amounts of *n*-butyllithium gave the series of poly-lithiated derivatives  $\text{Me}_{4-x}\text{Si}(\text{NLiBu})_x$  ( $x = 2-4$ ; eq. 3):



( $x = 2$  (II), 3 (IV), 4 (VII))

The products II (m.p. 104–105°C, involatile up to 170°C/ $1 \times 10^{-3}$  Torr), (IV) (m.p. 250–255°C (dec.)) and VII (dec. > 150°C) are all colourless solids, progressively less soluble in organic solvents. Thus  $\text{Si}(\text{NLiBu}^n)_4$  (VII) was rapidly precipitated during its preparation: it is essentially insoluble in hydrocarbons and only sparingly soluble in THF. This is consistent with a polymeric structure in the solid state, possibly derived from the  $\text{Li}_4\text{N}_4$  cluster-linked structure of  $[\text{Me}_2\text{Si}(\text{NLiBu}^n)]_2$  [13], but extended into two or three dimensions. The tetra-lithio species is less stable thermally than II and IV, and decomposed appreciably in a sealed tube under vacuum after 24 h, even in the dark.

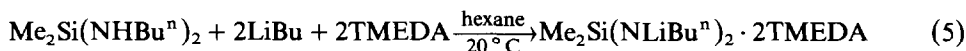
When smaller quantities of *n*-butyllithium were used, it was possible to isolate partially lithiated species, formulated as III, V, VI, VIII IX and X in eq. 4:



( $x = 2, y = 1$  (III);  $x = 3, y = 1$  (V), 2 (VI);  $x = 4, y = 1$  (VIII), 2 (IX), 3 (X))

Thus the colourless solid III is considered, from its infrared and NMR spectra, to be  $\text{Me}_2\text{Si}(\text{NHBu}^n)(\text{NLiBu}^n)$  rather than a 1:1 mixture or complex of  $\text{Me}_2\text{Si}(\text{NHBu}^n)_2$  and  $\text{Me}_2\text{Si}(\text{NLiBu}^n)_2$ . This compound is only slightly soluble in *n*-hexane, but readily dissolves in diethyl ether and THF; it decomposes at 85–87°C. Similarly VIII (m.p. 170°C (dec.)) and IX were produced as white crystalline solids by recrystallisation from a small amount of ether, but V, VI, and X were formed only as oils.

It was further shown that compounds II, III, and IV could form adducts with *N*-donors, of general composition  $\text{II} \cdot 2\text{B}$ ,  $\text{III} \cdot \text{B}$  and  $\text{IV} \cdot 3\text{B}$  ( $\text{B} = \text{TMEDA}$  or  $\text{PMDETA}$ ), as exemplified by eqs. 5 and 6.



They were all formed as microcrystalline white solids, rather sparingly soluble in hydrocarbons.

All the lithiated derivatives I–X together with the *N*-donor complexes of compounds I–IV were extremely susceptible to hydrolysis, and were shown to react readily with  $\text{SiCl}$  compounds (e.g.  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_2\text{SiCl}_2$ ) to give a range of  $\text{SiNSi}$  derivatives [16].

#### *Infrared spectra*

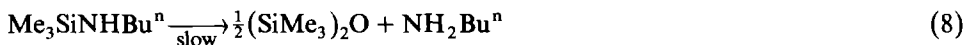
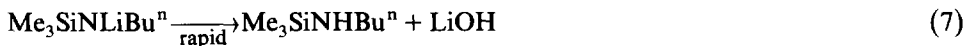
The most prominent infrared bands of compound I in the region 4000–650  $\text{cm}^{-1}$  are shown in Table 1, together with those of  $\text{Me}_3\text{SiNHBu}^n$  [16] for comparison.

TABLE I  
SELECTED IR BANDS FOR THE LITHIATED DERIVATIVES <sup>a</sup>

I	Me <sub>3</sub> SiNHBu <sup>a, b</sup>	II	III	IV	V	VI	VII	VIII	IX	X	Suggested assignment
	3418w		3300w		3340w	3320w			3380w	3418m } 3389w }	$\nu(\text{N-H})$
1258s } 1244vs }	1260s } 1250vs }	1245vs } 1230sh }	1248s	1240s	1244s	1245s	1258w	1295w } 1246w }	1258w } 1244w }	1285m } 1247w }	$\nu(\text{SiMe}_3)$ +?
1147m } 1108mw } 1072vs } 1050sh }	1130m } 1118s } 1100m } 1060m }	1145vs } 1112s } 1050vs }	1214w } 1150m } 1108s } 1079s }	1144m } 1100sh } 1068vs }	1210w } 1148s } 1104s } 1070vs } 1050sh }	1212w } 1150s } 1106s } 1080vs } 1057sh }	1220w } 1140s } 1110s } 1055vs }	1220w } 1142s } 1105s } 1065vs }	1210w } 1148s } 1144s } 1110vs } 1082vs }	1212m } 1148sh } 1108vs }	$\nu(\text{NC})$
991m	1038m } 972m }	988vs } 912m }	995m } 972m }	988s } 962m }	991m } 965m }	997m } 968m }	976s } 950sh }	984s } 965sh }	1050sh } 990m }	994m } 967s } 950sh }	
904m } 868vs }	894s } 875s }	902s } 830vs } 800s }	904m } 855vs } 828vs }	903m } 869m } 812vs }	902m } 850sh } 814vs }	903m } 850sh } 817vs }	908s } 884m } 828vs }	904s } 880m } 814vs }	910m } 880m } 838s } 820s }	900s } 880s } 825vs }	$\nu(\text{Si-N})$
768m } 740s }	748m } 680m }	758vs } 727s }	779s } 740m }	762vs } 724s }	789s } 764s }	789s } 766s }	780vs } 720s }	780s } 760s } 728s }	785m } 760m }	780vs } 730vs }	

<sup>a</sup> Recorded as Nujol mulls for compounds II-X. Compound I gave identical values as a Nujol mull or a thin smear. <sup>b</sup> Recorded as a thin film.

When the sample of I was exposed to air for 2 s, the spectrum became essentially that of  $\text{Me}_3\text{SiNHBu}^n$ , together with a strong band at  $3770\text{ cm}^{-1}$  assigned to  $\text{LiOH}$ . After further exposure to air for 2 min, absorptions due to  $\text{Me}_3\text{SiNHBu}^n$  were much reduced in intensity, and new bands appeared, assigned to  $\text{NH}_2\text{Bu}^n$  (e.g.  $3360$ ,  $1670$  and  $1580\text{ cm}^{-1}$ ) and  $(\text{Me}_3\text{Si})_2\text{O}$  (e.g.  $1070\text{ cm}^{-1}$ ). This indicates that hydrolysis occurs in two stages (eqs. 7 and 8):



Similar experiments were carried out for the other lithiated derivatives II–X. In all cases, considerable hydrolysis was observed after 2 s exposure to air, as shown by the appearance of new peaks attributed to  $\text{LiOH}$  and the corresponding amine  $\text{Me}_{4-x}\text{Si}(\text{NHBu}^n)_x$  ( $x = 2-4$ ). The absence of such peaks in the original sample was a useful check in establishing that no adventitious hydrolysis had occurred. Table 1 lists the most prominent peaks, together with suggested assignments based on comparisons with spectra of the parent amines [16] and related compounds [17].

All the parent amines  $\text{Me}_{4-x}\text{Si}(\text{NHBu}^n)_x$  show  $\nu(\text{NH})$  bands in the region  $3415-3420\text{ cm}^{-1}$ : while this band is of course absent for compounds I, II, IV and VII, it appears for the partially lithiated species at lower frequencies ranging from  $3300-3390\text{ cm}^{-1}$ , and increasing in the order: III < VI < V < IX < X (it was not observed in the case of compound VIII). This suggests that H-bonding effects are significant, especially in the case of  $\text{Me}_2\text{Si}(\text{NHBu})(\text{NLiBu})$  (III). While significant  $\text{HBu}_n \cdots \text{HNBu}$  interactions are not expected, because of the generally low basicity of aminosilanes [18], interactions of the type  $\text{LiBu}_n \cdots \text{HNBu}$  are likely, as a result of the enhanced electron density on N attached to Li; in solution, the latter will doubtless compete with  $\text{LiBu}_n \cdots \text{LiNBu}$  interactions, known to occur in the solid state [13,14]. The resulting formation of oligomeric species in solution is consistent with the observed low solubility of compound III in hydrocarbons; good donor solvents will tend to break down these oligomers.

On passing from the amine  $\text{Me}_3\text{SiNHBu}^n$  to compound I, there is an increase in the frequency assigned to  $\nu(\text{Si}-\text{N})$ , from  $894$  to  $904\text{ cm}^{-1}$ , but a decrease in the main  $\nu(\text{N}-\text{C})$  frequency from  $1118$  to  $1072\text{ cm}^{-1}$ , consistent with an increasing negative charge on nitrogen and some ionic character in the Li–N bond. Compounds II, IV and VII behave similarly. Corresponding effects have been noted for the pairs  $(\text{Me}_3\text{Si})_2\text{NH}/(\text{Me}_3\text{Si})_2\text{NLi}$  [19] and  $\text{Me}_3\text{SiOH}/\text{Me}_3\text{SiOLi}$  [20].

Bands in the regions  $1285-1290$  and  $1035-1040\text{ cm}^{-1}$ , considered to involve  $\delta(\text{SiNHC})$  modes, are seen in the spectra of all the parent amines, but not in those of any of the lithiated derivatives I–VIII. However, weak bands in the range  $1210-1215\text{ cm}^{-1}$  observed for compounds III, V, VI, IX and X (but not for the fully-lithiated species) are possibly related to this vibration, perturbed by H-bonding effects.

### *NMR spectra*

#### *<sup>1</sup>H spectra*

Observed peaks for compounds I–X are shown in Table 2, together with some corresponding values for the parent amines. Several points may be noted:

TABLE 2

<sup>1</sup>H NMR DATA ( $\delta$  in ppm) (m, multiplet; b, broad)

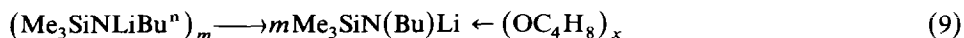
	$\alpha$ -CH <sub>2</sub>	$\beta$ -, $\gamma$ -CH <sub>2</sub>	$\omega$ -CH <sub>3</sub>	Me <sub>n</sub> Si	Solvent
I	3.00t(2)	1.43m(4)	0.98t(3)	0.20s(9)	C <sub>6</sub> D <sub>6</sub>
I	3.38t(2)	1.78m(4)	1.35t(3)	0.32s(9)	C <sub>4</sub> D <sub>8</sub> O
Me <sub>3</sub> SiNHBU <sup>n</sup>	2.70q(2)	1.35m(4)	0.93m(3)	0.05s(9)	CDCl <sub>3</sub>
II	3.15t(4)	1.51m(8)	1.10m(6)	0.40s(6)	C <sub>6</sub> D <sub>6</sub>
III <sup>a</sup>	3.28b(2); 2.75b(2)	1.47b(8)	1.04m(6)	0.38s(6)	C <sub>6</sub> D <sub>6</sub>
IV	3.15m(6)	1.50m(12)	1.05t(9)	0.55s(3)	C <sub>6</sub> D <sub>6</sub>
V <sup>b</sup>	3.30b(4); 2.98b(2)	1.53m(12)	1.11m(9)	0.58s(3)	C <sub>6</sub> D <sub>6</sub>
VI <sup>b</sup>	3.28b(2); 2.98b(4)	1.48m(12)	1.10m(9)	0.55s(3)	C <sub>6</sub> D <sub>6</sub>
VII	2.65b(8)	1.21m(16)	0.75m(12)	—	C <sub>4</sub> D <sub>8</sub> O
VIII <sup>c</sup>	3.23b(?); 3.05b(?)	1.60b(16)	1.07b(12)	—	C <sub>6</sub> D <sub>6</sub>
IX <sup>c,d</sup>	3.19b(?); 2.96m(?)	1.53b(16)	1.10t(12)	—	C <sub>6</sub> D <sub>6</sub>
X <sup>c,e</sup>	3.15b(?); 2.83m(?)	1.41m(16)	0.93m(12)	—	C <sub>6</sub> D <sub>6</sub>

<sup>a</sup>  $\alpha$ -CH<sub>2</sub> for Me<sub>2</sub>Si(NHBU<sup>n</sup>)<sub>2</sub>: 2.72q(4). <sup>b</sup>  $\alpha$ -CH<sub>2</sub> for MeSi(NHBU<sup>n</sup>)<sub>3</sub>: 2.80t(6). <sup>c</sup>  $\alpha$ -CH<sub>2</sub> for Si(NHBU<sup>n</sup>)<sub>4</sub>: 2.80t(8). <sup>d</sup> N-H, 0.68b (cf. Si(NHBU<sup>n</sup>)<sub>4</sub>, 0.63s). <sup>e</sup> N-H, 0.45 b.

(i) Lithiation produces a marked deshielding of the  $\alpha$ -CH<sub>2</sub> protons of the n-butyl group, but this effect scarcely extends further along the C<sub>4</sub> chain. For example the  $\delta$  values for  $\alpha$ -CH<sub>2</sub> in I and Me<sub>3</sub>SiNHBU<sup>n</sup> are 3.00 and 2.70, while those for IV and MeSi(NHBU<sup>n</sup>)<sub>3</sub> are 3.15 and 2.80 respectively.

(ii) Methyl protons in SiMe<sub>n</sub> groups are also deshielded on lithiation: values of  $\delta$  for the parent amines lie in the range 0.02–0.05, while those for fully-lithiated species increase steadily from 0.20 (I) to 0.55 (IV). Similar values have been found for related compounds, viz. Me<sub>2</sub>Si(NLiSiMe<sub>3</sub>)<sub>2</sub>,  $\delta$  0.25 [10]; Me<sub>2</sub>Si(NLiBu<sup>t</sup>)<sub>2</sub>,  $\delta$  0.32 [13]; MeSi(NLiSiMe<sub>3</sub>)<sub>3</sub>,  $\delta$  0.55 [14].

(iii) Solvent substitution of benzene-*d*<sub>6</sub> by THF-*d*<sub>8</sub> results in a general downfield shift, shown for compound I in Table 1. This is interpreted in terms of deoligomerization (eqs. 9), discussed further in the next section.



The resulting monomer complex will have increased ionic character in the N–Li bond, while the coordination number of Li is expected to increase (see below).

(iv) Partially-lithiated derivatives show two distinct resonances associated with  $\alpha$ -CH<sub>2</sub> protons of the butyl group. Thus compound III showed a broad multiplet at  $\delta$  2.75 (cf. Me<sub>2</sub>Si(NHBU<sup>n</sup>)<sub>2</sub>,  $\delta$  2.72), assigned to NHCH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>, together with a downfield peak of the same integrated intensity at  $\delta$  3.28, assigned to NLiCH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>. Further confirmation came from the spectra of V and VI; both showed groups of resonances centred at  $\delta$  2.98 and near  $\delta$  3.3, and the ratios (higher-field peak/lower-field peak) of their integrated intensities were 2/4 and 4/2 respectively, as required by the suggested assignment above. Two distinct sets of  $\alpha$ -CH<sub>2</sub> resonances were also observed for compounds VIII, IX and X, but accurate integrations could not be made because of the compounds' rather low solubility. In all cases, no evidence for non-rigidity was found over the temperature range 253–300 K. This is consistent with observations on the partially-metallated compound Me<sub>2</sub>Si(NHSiMe<sub>3</sub>)(NNaSiMe<sub>3</sub>), which gave distinct <sup>1</sup>H (and <sup>13</sup>C) resonances for the two SiMe<sub>3</sub> groups, and was described as rigid on the NMR timescale [10].

(v) Surprisingly, the  $\text{SiMe}_n$  resonances of the partially-lithiated compounds were hardly shifted from those of their fully-lithiated counterparts. Thus II and III gave similar values, as did IV, V and VI.

(vi) Resonances due to N-H protons were not observed in the case of the partially-lithiated species III, V and VI (no doubt being obscured by  $\text{SiMe}_n$  signals). However, compounds IX and X gave a peak close to that of  $\text{Si}(\text{NHBu}^n)_4$  at  $\delta$  0.63.

### <sup>7</sup>Li spectra

Values of <sup>7</sup>Li chemical shifts for the compounds I-IV and their adducts with PMDETA or TMEDA are shown in Table 3. Three solvents of differing donor strength were employed, n-pentane, diethyl ether, and THF, and in most cases measurements were made at two temperatures, 300 and 253 K.

*Me<sub>3</sub>SiNLiBu<sup>n</sup> and its complexes.* These results are the easiest to interpret. The single sharp resonance of I in n-pentane solution moves slightly up-field on cooling, but there is no other change. The ether and THF solutions behave similarly, but resonance occurs at progressively higher fields; essentially no concentration dependence is seen in THF solutions.

The 1 : 1 complex I · PMEDTA shows two resonances in all three solvents: values of  $\delta$  lie in the range 1.58-1.85, close to those for I alone in THF and for complex I · TMEDA in THF.

TABLE 3

<sup>7</sup>Li NMR DATA (relative to 1 M LiBr in methanol-*d*<sub>4</sub>)

Compound	Conc. (M)	Solvent					
		n-pentane		Et <sub>2</sub> O		THF	
		300 K	253 K	300 K	253 K	300 K	253 K
I	1.3	2.67	2.54	1.94	1.86	-	-
	0.6	-	-	-	-	1.69	1.57
	2.6	-	-	-	-	1.68	1.57
I · PMDETA	0.4	{ 1.85(31)	-	1.70(60)	-	1.77(100)	-
		{ 1.77(100)	-	1.58(100)	-	1.63(32)	-
I · TMEDA	0.6	-	-	-	-	1.67	1.63
II <sup>a</sup>	0.65	{ 2.86(84)	2.88(85)	2.19(100)	2.14(100)	1.86(100)	1.88(100)
		{ 1.82(100)	1.75(100)	1.91(12) <sup>b</sup>	1.85(15) <sup>b</sup>	1.44(21)	1.70(24)
II · 2TMEDA	0.3	-	-	-	-	{ 1.99(100)	1.94(100)
						{ 1.45(25)	1.34(40)
III	0.5	{ 2.03(100)	2.01(100)	1.94	{ 1.90(30)	1.44	1.35
		{ 1.75(12)	1.70(24)				
III · PMDETA	0.5	{ 2.10(48)	1.65	-	-	-	-
		{ 1.71(100)					
IV <sup>c</sup>	0.5	2.56	2.44	{ 2.32(100)	2.19(42)	2.21(100)	2.01(100)
				{ 1.82(35)	1.69(100)	1.65(6)	1.44(10)
IV · 3PMDETA	0.2	1.75	1.68	-	-	-	-

<sup>a</sup> Compare  $\text{Me}_2\text{Si}(\text{NLiBu}^t)_2/\text{n-hexane}$ ,  $\delta$  1.9 vs. aq. LiI [13]. <sup>b</sup> Probable III impurity. <sup>c</sup> Compare  $\text{MeSi}(\text{NLSiMe}_3)_3$ ,  $\delta$  2.0 [14] and  $\text{PhSi}(\text{NLiBu}^t)_3$ ,  $\delta$  2.4 [13] (both in n-hexane vs. aq. LiI).

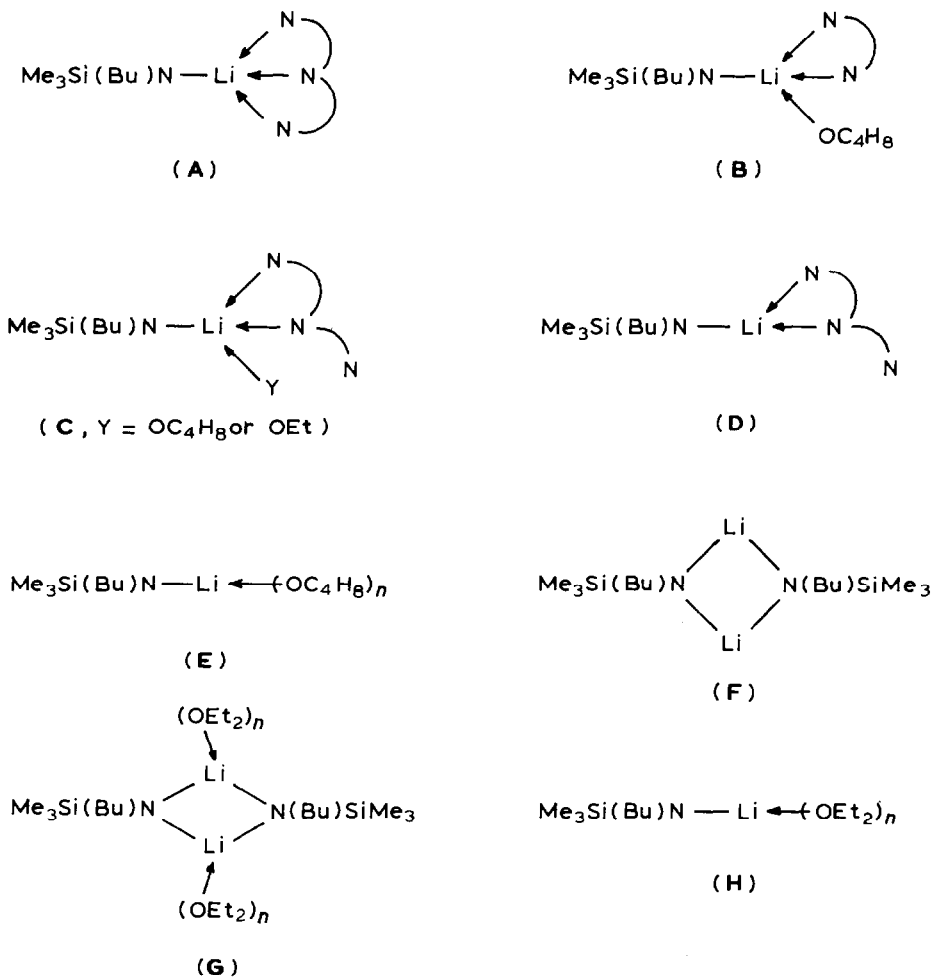


Fig. 1. Possible solution structures for  $\text{Me}_3\text{SiNLiBu}^n$  (I).

It seems reasonable that (i) change of solvent will produce relatively minor changes in  $\delta$  if the solute remains structurally the same; (ii) changes in the degree of oligomerization of the solute will produce relatively major changes in  $\delta$ ; and (iii) changes in the extent of solvation of a particular oligomer will produce intermediate changes in  $\delta$ . Furthermore (and related to (ii) and (iii) above), increases in the effective coordination number of lithium are expected to lead to upfield shifts: for instance, 2-coordinate Li will be less shielded than 4-coordinate Li, other things being equal.

Some possible solution structures for compound I are shown in Fig. 1. In general, the strong chelating donor PMDETA will favour the formation of monomeric species [21], and resonances around  $\delta$  1.6–1.7 are attributed to 4-coordinate complexes such as **A**. Similarly the complex  $\text{I} \cdot \text{TMEDA}$  in THF is expected to give a 4-coordinate mixed species **B**, with a similar value of  $\delta$ . A complication arises, however, in the case of PMDETA complexes in donor solvents because equilibrium



10 is likely: the stronger base THF will push this equilibrium further to the right than Et<sub>2</sub>O, forming relatively more C. Consequently the more intense (higher-field) peak in the I · PMEDTA/Et<sub>2</sub>O system ( $\delta$  1.58) is assigned to A; the correspond-



ing peak for the THF solution ( $\delta$  1.63) is less intense, consistent with the argument above. Conversely, the peak at  $\delta$  1.70 for the Et<sub>2</sub>O system (which is less intense) is assigned to C, and corresponds to the more intense peak ( $\delta$  1.77) for the THF solution. It is a little worrying that the <sup>7</sup>Li shift for I · TMEDA in THF (B,  $\delta$  1.67) is nearer to that assigned to species A, whereas B appears more similar to C (Y = THF). However, the shift difference is not large, and the steric requirements of TMEDA and of PMDETA acting as a bidentate ligand are clearly not identical. Finally, the minor lower-field resonance ( $\delta$  1.85) observed for I · PMEDTA in n-pentane may be due to a 3-coordinate species D in equilibrium with the more abundant 4-coordinate species A.

Compound I alone in THF apparently consists of a single species, logically E, formed as in eq. 9 and expected to have a shift value similar to those of B and C (Y = THF); this is observed to be the case. Compound I in n-pentane produces a signal at much lower field, attributed (by analogy with (Me<sub>3</sub>Si)<sub>2</sub>NLi [2,3,6]) to a 2-coordinate oligomer such as the dimer F or a corresponding higher cyclic oligomer. The intermediate single peak observed for I in Et<sub>2</sub>O suggests that a 3-coordinate solution species is present. But it is not possible to distinguish between an oligomer complex (e.g. G,  $n = 1$ ), a monomer complex (e.g. H,  $n = 2$ ), or a mixture of the two, interconverting rapidly on the NMR time-table (eq. 11). This is consistent with the moderate donor ability of Et<sub>2</sub>O, while the stronger donor THF



apparently gives only monomer complexes.

*Me<sub>2</sub>Si(NLiBu<sup>n</sup>)<sub>2</sub> (II), Me<sub>2</sub>Si(NHBU<sup>n</sup>)(NLiBu<sup>n</sup>) (III), and MeSi(NLiBu<sup>n</sup>)<sub>3</sub> (IV) and their complexes.* The <sup>7</sup>Li spectra of solutions of these compounds show some of the same general features as those of Me<sub>3</sub>SiNLiBu<sup>n</sup>; thus (i) when each of them is dissolved in various solvents, the values of  $\delta$  decrease in the order: n-pentane > Et<sub>2</sub>O > THF; (ii) values of  $\delta$  decrease, usually by about 0.1, when the temperature is lowered from 300 to 253 K; (iii) the complex IV · 3PMDETA shows a single signal about  $\delta$  0.8 upfield from that of IV in n-pentane.

Other features differ, however. For example, II in n-pentane shows two peaks of nearly equal height at  $\delta$  2.86 and  $\delta$  1.82, suggesting that at least two species are present, with coordination numbers of 2 and 3 respectively. The closely-related compound Me<sub>2</sub>Si(NLiBu<sup>1</sup>)<sub>2</sub> is known to be dimeric in the solid state, with a central Li<sub>4</sub>N<sub>4</sub> core in which Li is 3-coordinate by N (ref. 13). It therefore seems reasonable that the II/n-pentane system contains similar dimer units with 3-coordinate Li, in equilibrium with a more open oligomeric structure in which Li is 2-coordinate. By contrast, n-pentane solutions of IV appear to contain only one species, which is 2-coordinate; the tris-lithio compounds MeSi(NLiSiMe<sub>3</sub>)<sub>3</sub> and PhSi(NLiBu<sup>1</sup>)<sub>3</sub> are dimeric in the solid state, with Li 3-coordinate by N (ref. 14), and it therefore appears that if this structure is also adopted by solid IV, it does not persist in solution.

Several other systems provide evidence for at least two species in equilibrium in

solution, namely II/Et<sub>2</sub>O, II/THF, II·2TMEDA/THF, III/n-pentane, III·PMEDTA/n-pentane, IV/Et<sub>2</sub>O, and IV/THF. The system IV/Et<sub>2</sub>O is particularly interesting, since the relative intensity ratio (low-field signal/high-field signal) changes from 100/35 to 42/100 as the temperature falls from 300 to 253 K, showing that lower temperatures favour a species (or several rapidly-exchanging species) in which the coordination number of Li is higher.

#### Mass spectra

While dimeric ions  $M_2^+$  have been reported in the mass spectra of  $(\text{Me}_3\text{Si})_2\text{NLi}$  [22] and  $\text{Me}_2\text{Si}(\text{NLiSiMe}_3)_2$  [10], no corresponding ions have been found in this study for compounds I, II or IV. Thus I shows  $m/z$  281 as its heaviest ion  $(M_2 - 21)^+$ , corresponding to loss of LiN from the dimer. A series of complex eliminations, chiefly of hydrocarbon fragments and  $\text{Me}_3\text{Si}$ , leads to abundant iminium species such as  $(\text{Me}_3\text{SiN}=\text{CH}_2)^+$  (base peak),  $(\text{BuN}=\text{CH}_2)^+$  and  $(\text{Me}_2\text{SiHN}=\text{CH}_2)^+$ .

More drastic rearrangement seems to occur with II, where  $m/z$  355 is the heaviest ion, corresponding to  $(M_2 - \text{SiMe}_2 - \text{Me})^+$ , and providing some evidence for dimers in the solid phase. By contrast, IV gave only ions corresponding to fragmented monomers.

#### Conclusions

Besides the fully-lithiated species  $\text{Me}_{4-x}\text{Si}(\text{NLiBu}^n)_x$  ( $x = 1-4$ ), it has been possible also to prepare partially lithiated derivatives  $\text{Me}_{4-x}\text{Si}(\text{NHBu}^n)_y(\text{NLiBu}^n)_{x-y}$  ( $x = 2, y = 1; x = 3, y = 1, 2; x = 4, y = 1-3$ ). In particular, no indication of the presence of fully-lithiated species was found in the IR or <sup>1</sup>H and <sup>7</sup>Li NMR spectra of the partially-lithiated compounds III, V, VI or VIII-X. This observation should be compared with recent reports by Bürger et al. on related systems derived from  $\text{RSi}(\text{NHSiMe}_3)_3$ ,  $\text{Me}_2\text{Si}(\text{NHBu}^1)_2$ , and  $\text{PhSi}(\text{NHBu}^1)_3$ , where <sup>7</sup>Li NMR monitoring suggested that fully-lithiated species were preferentially formed, even with low LiR/amine starting ratios [13,14]. On the other hand, lithiation of  $\text{Me}_2\text{Si}(\text{NHSiMe}_3)_2$  first gave the mono-lithio derivative, and more vigorous conditions were needed to introduce the second metal atom [10]. It has been shown in this study that H-bonding of the type  $\text{RLiN} \rightarrow \text{HNR}$  occurs when  $\text{R} = n\text{-Bu}$ , and this will tend to stabilise partially-lithiated derivatives. Such H-bonding seems less likely to be significant when  $\text{R} = t\text{-Bu}$  (for steric reasons) or  $\text{SiMe}_3$  (for steric and electronic reasons).

Analysis of the <sup>7</sup>Li NMR results has permitted a reasonably self-consistent interpretation in terms of differing Li coordination numbers in various solvents and when complex-forming ligands are present. Figure 2 shows provisional correlations between different species: oligomers with low Li coordination are favoured in n-pentane solution, while monomers with higher Li coordination are probably formed with THF and with chelating di- and tri-amines. No certain distinction can be drawn between situations G and H in Fig. 1 (or their THF analogues), and Et<sub>2</sub>O occupies a particularly ambiguous position. Only structures in which Li has a coordination number from 2 up to 4 have been considered as candidates, because although Li is 5- and 6-coordinate in the corresponding oxo-system  $\text{Li}_4\text{SiO}_4$  (see below), the imido compounds in the present study are far more hindered sterically.

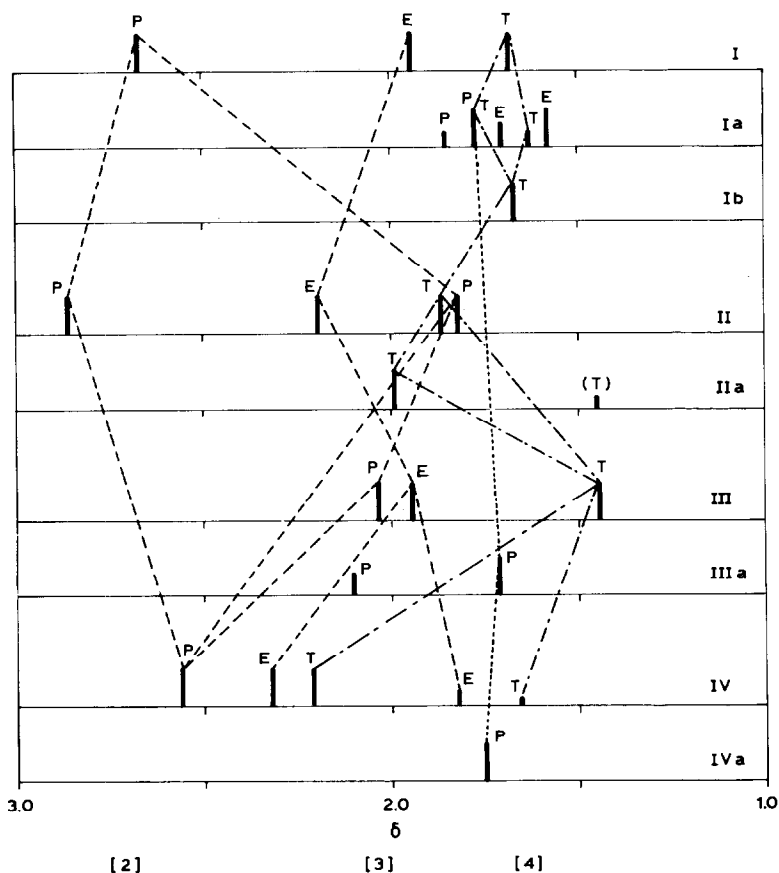


Fig. 2.  ${}^7\text{Li}$  NMR shifts for compounds I-IV and their complexes. [P, n-pentane; E, diethyl ether; T, tetrahydrofuran solvents]. Ia = I · PMDETA; Ib = I · TMEDA; IIa = II · 2TMEDA; IIIa = III · PMDETA; IVa = IV · 3PMDETA.

In this connection, it may be noted that the reported solid complexes between Si-N-alkali metal compounds and ethers, e.g.  $\text{Me}_2\text{Si}(\text{NLiSiMe}_3)_2 \cdot \text{B}$  (B = THF, dioxane), labile  $\text{Me}_2\text{Si}(\text{NNaSiMe}_3) \cdot \text{OEt}_2$  [10], and  $[(\text{Me}_3\text{Si})_2\text{NLi} \cdot \text{OEt}_2]_2$  [4], have only one ether molecule per Li, with corresponding low Li coordination numbers.

It is interesting to compare compound VII with its pseudo-isoelectronic analogue in the oxygen system,  $\text{Li}_4\text{SiO}_4$ . The structure of the latter consists of discrete  $\text{SiO}_4$  tetrahedra, linked by  $\text{LiO}_n$  polyhedra ( $n = 4, 5, 6$ ), such that the possible Li positions are only partially filled [23] \*. Both compounds are doubtless intermediate in type between the covalent forms J and L ( $M = \text{Li}$ ), with additional  $\text{O}-\text{Li} \cdots \text{O}$  or  $\text{N}-\text{Li} \cdots \text{N}$  interactions, and the completely ionic forms K and M ( $M = \text{Li}$ ) shown in Fig. 3.

When Li is replaced by a more electropositive metal, the ionic forms K and M will become more important [10]. This leads us to propose the generic name

\* In comparison,  $\text{Li}_4\text{GeO}_4$  also contains  $\text{GeO}_4$  tetrahedra held together by Li, but its coordination number is not greater than 4 [23].

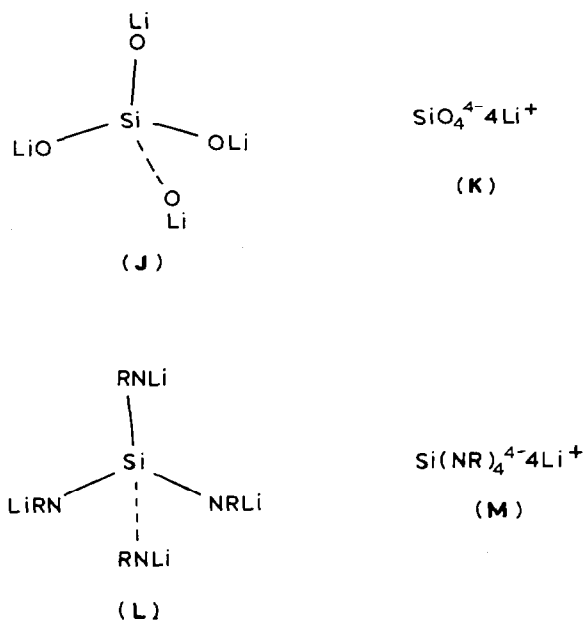


Fig. 3. Covalent and ionic representations of silicates and silazates (see text).

“silazates” for species such as  $\text{Si}(\text{NMR})_4/\text{Si}(\text{NR})_4^{4-} \cdot 4\text{M}^+$ , by analogy with silicates. It is tempting to suppose that the great variety of silicate structures might be matched by similar (but probably not identical) silazate structures – for example, the pyroxene anion analogue  $[\text{Si}(\text{NR})_2(\mu\text{-NR})]_n^{2n-}$ . Similarly, the fully-lithiated alkylsilicon compounds I, II and IV are formally analogues of silanolates  $\text{R}_{4-n}\text{Si}(\text{OM})_n$  ( $n = 1-3$ ) [24].

## Experimental

### Techniques

Compounds were handled in conjunction with a high-vacuum system (for volatiles) and a high-integrity  $\text{N}_2$ -filled dry box (for solids); preparations were carried out in demountable vessels fitted either with all-glass capillary breakers or with Teflon taps [16a]. Spectroscopic samples were similarly made up with complete exclusion of water and oxygen.

IR spectra were obtained with Perkin–Elmer 457 and 557 instruments, while for  $^1\text{H}$  NMR measurements a Bruker WP80DS spectrometer was used. The  $^7\text{Li}$  spectra were measured at 155.460 MHz on a Bruker WH400 machine, using a 1 M solution of  $\text{LiBr}$  in methanol- $d_4$  as external reference. EI (70 eV) mass spectra were observed with an AEI MS702 spectrometer, using an all-glass direct insertion device.

### Chemicals

All solvents and amines were rigorously dried and fractionated before use. The series of *N*-*n*-butylaminosilanes were prepared by long refluxing of an excess of *n*-butylamine with the appropriate methylchlorosilane [25] in light petroleum (60–80 °C). The products were separated by filtration and vacuum fractionation,

and characterised by elemental analysis, mass, IR and NMR spectra [16]. Solutions of *n*-butyllithium were standardised before use.

#### *Acid equivalent weights*

A sample of known weight was digested in an excess of standard hydrochloric acid solution for 2 h, then back-titrated with standard alkali. For a compound  $\text{Me}_{4-x}\text{Si}(\text{NHBu})_y(\text{NLiBu})_{x-y}$ , the acid equivalent weight = (formula weight)/( $2x - y$ ).

#### *[Si-(N-*n*-butyl-N-lithioamino)]trimethylsilane (I)*

$\text{LiBu}^n$  (0.595 g, 9.29 mmol) in *n*-hexene (5 ml) was added slowly to stirred  $\text{Me}_3\text{SiNHBU}^n$  (1.350 g, 9.29 mmol) at 0 °C. After degassing, the mixture was stirred at 20 °C for 2 h. Solvent was removed and distillation of the residue at 108–110 °C/ $5 \times 10^{-3}$  Torr gave I (1.234 g, 8.17 mmol, 88%) as a colourless solid. Acid equivalent, 77.3 (calc 75.6). Found: C, 54.0; H, 11.5; N, 9.0.  $\text{C}_7\text{H}_{18}\text{LiNSi}$  calc.: C, 55.6; H, 12.0; N, 9.3%).

Other compounds II–X were made in analogous fashion, using stoichiometric amounts of  $\text{LiBu}^n$ . Exceptionally, compound VII was prepared in a 10/1 v/v hexane/THF mixture, as it was essentially insoluble in hydrocarbons. Analyses, etc. are shown in Table 4: it appears from the acid equivalent values that VIII may be contaminated by IX (which is less soluble in  $\text{Et}_2\text{O}$  than VIII).

#### *Tris(N-*n*-butyl-N-lithioamino)methylsilane · 3PMDETA adduct*

$\text{MeSi}(\text{NLiBu}^n)_3$  (IV) (0.59 g, 2.1 mmol), *n*-pentane (2 ml) and an excess of PMDETA (1.30 g, 7.5 mmol) were mixed at 0 °C in a vessel fitted with a sintered

TABLE 4  
ANALYTICAL DATA AND MELTING POINTS FOR COMPOUNDS II–X

Composition	Analyses (Found (calc) (%))			Acid equiv. (Found (calc))	M.p. (°C)
	C	H	N		
II $\text{C}_{10}\text{H}_{24}\text{Li}_2\text{N}_2\text{Si}$	55.2 (56.1)	10.5 (11.3)	12.6 (13.1)	54.0 (53.6)	104 <sup>a</sup>
III $\text{C}_{10}\text{H}_{25}\text{LiN}_2\text{Si}$	55.9 (57.7)	11.4 (12.1)	12.7 (13.4)	67.1 (69.4)	85 (dec.) <sup>b</sup>
IV $\text{C}_{13}\text{H}_{30}\text{Li}_3\text{N}_3\text{Si}$	55.6 (56.3)	10.9 (10.9)	14.9 (15.1)	46.0 (46.6)	250–255 (dec.) <sup>a</sup>
V $\text{C}_{13}\text{H}_{31}\text{Li}_2\text{N}_3\text{Si}$	58.1 (57.5)	11.9 (11.5)	14.6 (15.5)	54.7 (54.3)	– <sup>c</sup>
VI $\text{C}_{13}\text{H}_{32}\text{LiN}_3\text{Si}$	58.3 (58.8)	12.2 (12.2)	15.0 (15.8)	63.6 (66.4)	– <sup>c</sup>
VII $\text{C}_{16}\text{H}_{36}\text{Li}_4\text{N}_4\text{Si}$	57.2 (56.4)	11.4 (10.7)	16.5 (16.5)	41.6 (42.5)	130 (dec.) <sup>d</sup>
VIII $\text{C}_{16}\text{H}_{37}\text{Li}_3\text{N}_4\text{Si}$	56.6 (57.5)	11.1 (11.2)	16.1 (16.8)	51.5 (47.8)	170 <sup>e</sup>
IX $\text{C}_{16}\text{H}_{38}\text{Li}_2\text{N}_4\text{Si}$	57.1 (58.5)	11.5 (11.7)	16.8 (17.1)	55.2 (54.7)	186–188 <sup>e</sup>
X $\text{C}_{16}\text{H}_{39}\text{LiN}_4\text{Si}$	58.4 (59.6)	12.1 (12.2)	17.1 (17.4)	63.3 (64.5)	– <sup>c</sup>

<sup>a</sup> Recrystallised from *n*-hexane/–25 °C. <sup>b</sup> Precipitated from solution during reaction. <sup>c</sup> Oil, could not be recrystallised. <sup>d</sup> Isolated from *n*-hexane/THF solution as 1:1 THF adduct; analysis figures relate to unsolvated compound. <sup>e</sup> Recrystallised from  $\text{Et}_2\text{O}/20$  °C.

glass filter. A white precipitate formed immediately; the mixture was stirred for 10 min at room temperature, then the precipitate was filtered off and washed repeatedly with n-pentane (yield 1.59 g, 2.0 mmol, 95%).

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