Dendrimeric silatrane wedges

Tim Kemmitt *,[a] and William Henderson [b]

[a] *The New Zealand Institute for Industrial Research and Development, PO Box 31-310, Lower Hutt, New Zealand*
[b] *Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand*

The first three generations of a silatrane-containing† dendrimeric wedge have been synthesised and isolated. This organosilicon dendrimeric wedge is the first example containing pentacoordinate silicon. The branching multiplicity, *M*, has been directed in the synthesis method, to form molecule 1 where *M* = 2 at each silatrane branching point. A second route was used where *M* = 3, 2 and 1 at successive branching points to form a second generation wedge 2. Electrospray mass spectrometry has been successfully used in the characterisation of the various silatranes. At low cone voltages, the compounds containing a residual trialkanolamine group predominantly show strong multiply charged ions of the type $[M + H + xNH_4]^{(x+1)+}$ (*x* = 0–3), while those compounds containing epoxy groups, show strong $[M + xNH_4]^{x+}$ ions, where *x* = 1–4. At high cone voltages the silatranyl cation fragment can be detected.

Introduction

Synthesis of dendrimeric molecules has caught the imagination of many research groups during the last few years.[1–8] These highly branched, tree-like polymers first gained attention due to their well defined three-dimensional morphology and monodisperse molecular masses. The inclusion of functional components as part of the building blocks in each generation, or as a surface coating of the molecule has produced new materials with specific properties. This multiplication of functionality is the quintessential feature of dendrimer synthesis, and can result in materials exhibiting amplified functionality, or new bulk properties not seen in the unassembled building blocks or in traditional polymers. Thus, for example dendrimers containing terminal carboxylic acid moieties,[9] multiple redox centres,[10–17] chiral surfaces [18,19] and frameworks,[20–24] guest-selective pores,[25,26] and homogenous catalysts [27] and other functionalities [28–32] have been produced which have potential applications in many diverse areas. A number of dendrimers incorporating silanes, carbosilanes and polysiloxanes have also been reported.[33–37]

Dendrimers can be prepared by divergent [1–5] or convergent [38,39] stepwise growth. A protection–deprotection strategy allows a single generation to be added in each step and each generation introduces a multiplicity allowing branching to occur in the next generation. We report here the synthesis of two silatrane dendrimeric wedges. The first example, **1**, contains a branching multiplicity of two throughout. Each successive generation of the second example, **2**, exhibits a reduced branching multiplicity, falling from *M* = 3 to 2 to 1. Thus the synthetic strategies employed conveniently lead to wedges of contrasting topologies. Each generation of pendant glycidoxy groups is available for reaction with added amine, and each generation of trialkanolamine thus produced, can react with added trimethoxysilyl functionalities to form the silatrane moieties, building up the dendrimer in a convergent manner. Silatranes have stimulated much research activity over the years,[40–44] not least because of their biological activities. A detailed review of the widespread range of activities has been published.[45] Applications in rodenticides, insecticides and crop yield enhancement have shown significant potential.[46–48] The availability of an entirely new class of silatrane-containing material may provide novel biological properties.

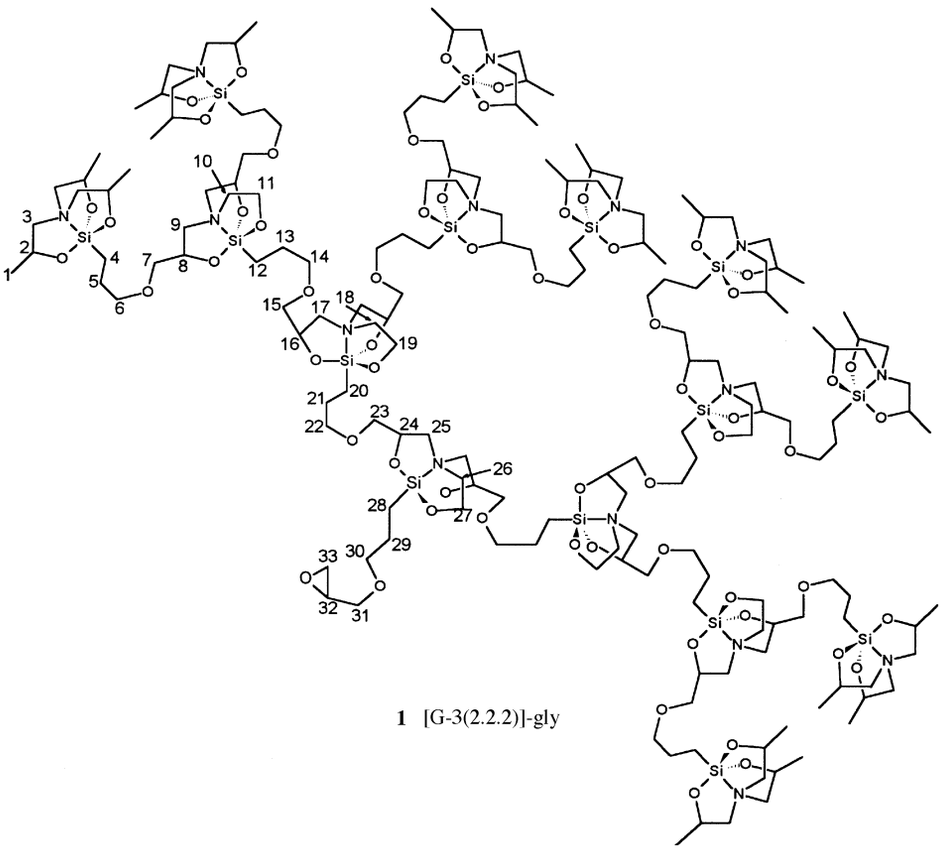
Dendrimers used to date have commonly had fixed branching multiplicities, *M*, of 2 or 3. The multiplicity of branching is determined by the linking functionality employed, and for a given dendrimer, this is often inflexible. The branching multiplicity in the current example can conveniently be controlled by the synthesis route (Schemes 1 and 2) to form a linear connection (no branching), (*M* = 1), a two-branched fork, (*M* = 2) or a three-branched fork, (*M* = 3). Regulating the growth in this way results in the ability to influence the morphology of the polymer as well as the size and shape of the interbranch pores. Another important structural factor is the chirality imposed by the glycidoxy groups. Synthesis of enantiopure trialkanolamines has been demonstrated to be generally straightforward with high regioselectivity,[49] thus production of chirality-controlled dendrimers should be possible using this route. However, this study merely establishes the feasibility of the approach and diastereomers have been used throughout.

The concept of controlled molecular architecture [50] and the formation of 'dendritic *layer*- and *segment-block* copolymers,' [39] in conjunction with control of the structural chirality, leads to the possibility of controlling the pore shapes and sizes between and within the wedges, thereby designing a host for a specific guest. Sterically specific groups of this type could have applications in selective or chiral catalysis, or even artificial enzymes, where the dendrimers can influence the size and shape of reactants approaching or leaving a reactive centre.[51] A recent investigation involved the construction of a dendrimer around an electrophore to modify its electrochemical behaviour,[52] suggesting a potential method for the selective synthesis of redox catalysts.

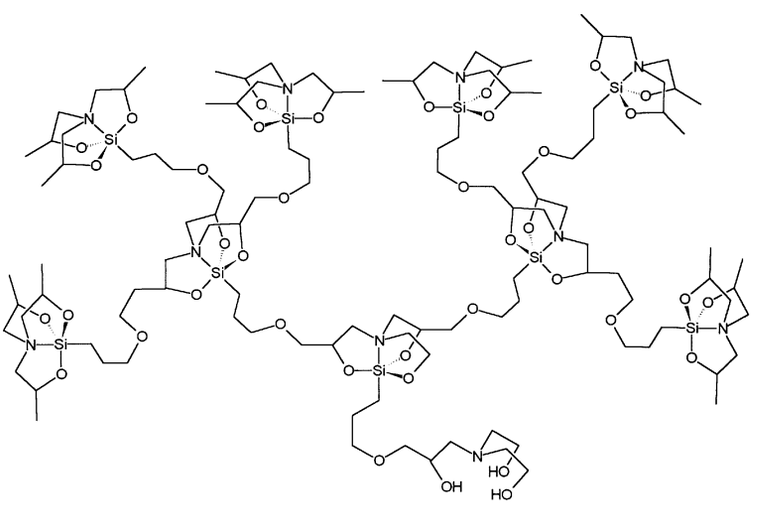
Results and discussion

The reaction of trimethoxy(glycidoxypropyl)silane with diethanolamine results in the formation of a crystalline polymer.[53] Two distinct rections characterise the polymerisation process. Reaction of the glycidoxy group with diethanolamine forms a trialkanolamine (Scheme 1), which can go on to react with a trimethoxysilyl group to form a silatrane (Scheme 2). Thus once the glycidoxy groups have begun to react, polymerisation can occur at both ends of the molecules. Controlling this reaction by initially protecting one end of the silane reagent (in this case by capping the silane with a trialkanolamine to form a silat-

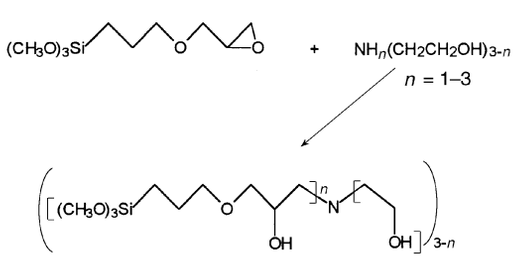
† Silatrane refers to 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane. However, silatranes are generally accepted to contain an N ⟶ Si coordinate bond.



1 [G-3(2.2.2)]-gly



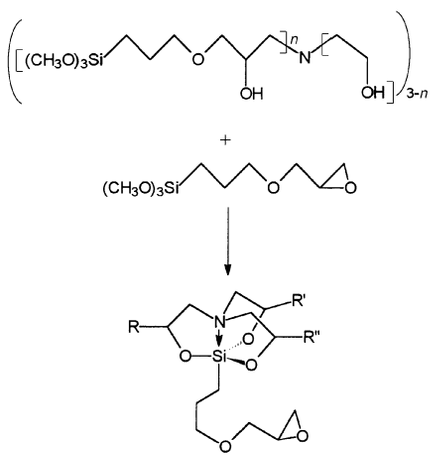
2



Scheme 1

rane) prevents the polymerisation process from occurring. Thus **3a–b** (generation $G = 0$) were isolated and purified using flash column chromatography from the reactions between trimethoxy(glycidoxypropyl)silane and the trialkanolamines triethanolamine and triisopropanolamine respectively. Reactions of the pendant glycidoxy group with suitable amines or ammonia, form trialkanolamines, as typified by the reactions of **3a** with diethanolamine or **3b** with ethanolamine to form **4** and **5** respectively. Further reaction can only take place on addition of more of the silane reagent which contains a trimethoxysilyl group. Thus sequential addition of each reagent allows the polymer to be built up in a controlled way. The reaction stops after each step as each functionality is alternately protected. The branching multiplicity is determined by *n*, the number of silane substituents attached to the trialkanolamine as shown in Scheme 2. The generation number, *G*, is defined as 0 for compounds **3**, and undergoes an integer increase for each successive (glycidoxypropyl)silatrane generation addition. The intermediate trialkanolamines do not represent an increase in the generation number, but convert the wedges into mono-, di- or tridendrons[2] depending on the alkanolamine used. Thus for **5**, $G = 0$, for **8**, $G = 1$, *etc*.

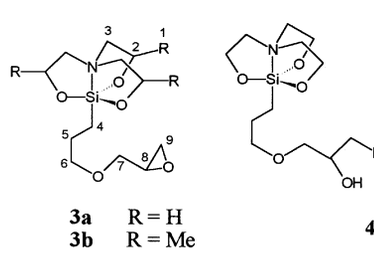
On reacting **3a** with diethanolamine, the formation of a significant amount of **6** occurred, which probably ensued *via* an exchange reaction: the trialkanolamine formed during the reaction displaced the triethanolamine from some of the silatrane **3a** molecules. This liability is much reduced for substituted trialkanolamines, as is evidenced in the reactions of **3b**, where no such exchange was seen to occur. Compound **6** was formed independently from the reaction of **4** with a further equivalent of trimethoxy(glycidoxypropyl)silane, however, some transesterification during this reaction led to the production of some **3a**. The lability of the triethanolamine of the $G = 0$ silatranes, led us to concentrate on the triisopropanolamine derivatives, which proved to be much more stable.



Scheme 2 R–R″ = H, $CH_2O(CH_2)_3Si(OCH_3)_3$, *etc*.

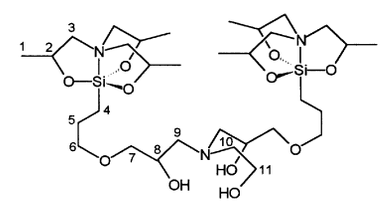
Adding the next generation to **5** involved the reaction with a further mole equivalent of trimethoxy(glycidoxypropyl)silane to form **7**. Further reaction with ethanolamine resulted in the trialkanolamine **8**. Repeating these steps added a further generation, forming the glycidyl compound **9**, and amine **10** respectively. Finally, reaction with a further aliquot of trimethoxy(glycidoxypropyl)silane resulted in the third generation compound **1**, which contained a constant branching multiplicity of $M = 2$ in each shell. The purification of each compound was achieved by flash column chromatography using hexane–ethyl acetate or ethyl acetate–methanol solvent systems. The polarities of the alternate products containing glycidoxy or trialkanolamine functionalities differed significantly, allowing the reaction progress to be easily monitored and enabling the straightforward separation of the product. No significant by-product formation was detected.

Dendrimer **2** was started by reacting three equivalents of **3b** with ammonia in methanol. The reaction was carried out in a

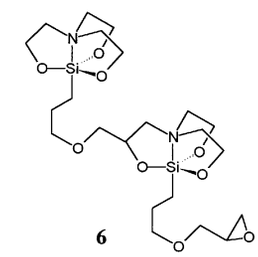


3a R = H
3b R = Me

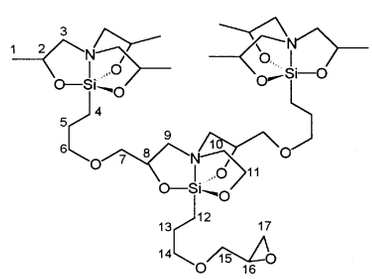
4



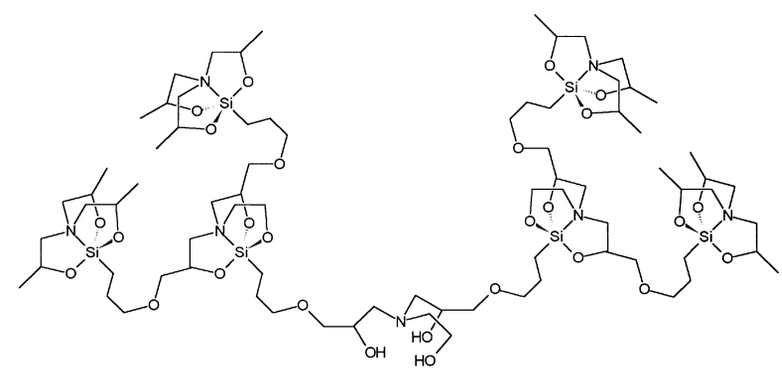
5



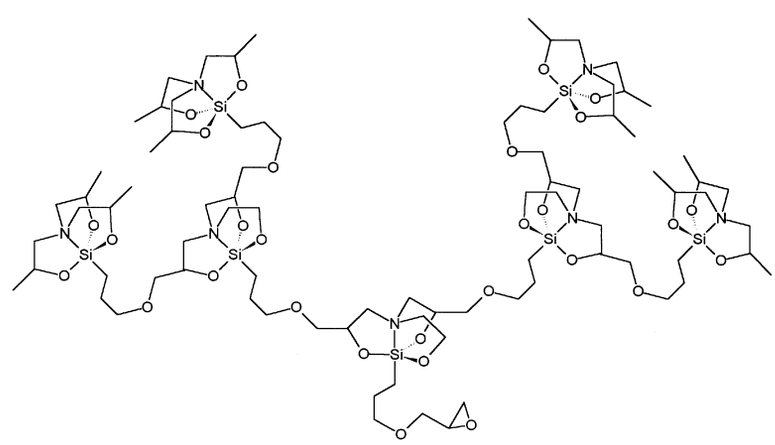
6



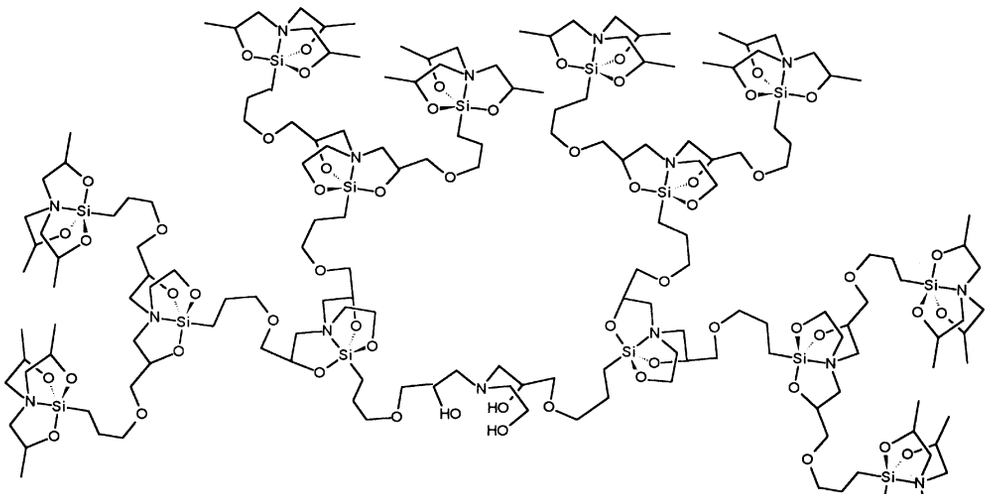
7



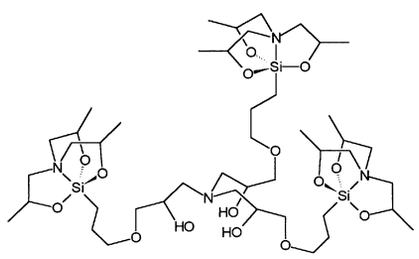
8



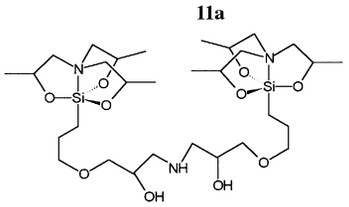
9



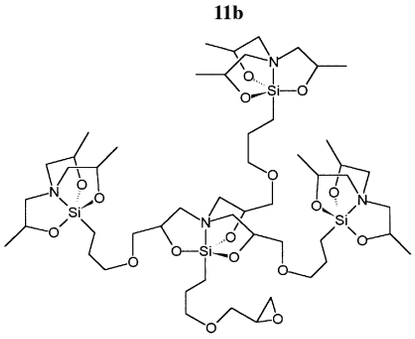
10



11a



11b



12

screw top vial at 60 °C for 3 days. The triply branched compound **11a** was formed, together with a similar amount of the disubstituted secondary amine **11b** intermediate. These were chromatographically separated, and no attempt was made to optimise the conditions. The next step involved the reaction of **11a** with a further mole of trimethoxy(glycidoxypropyl)silane to form **12**. Subsequent generations were formed by reaction of **12** with ethanolamine, trimethoxy(glycidoxypropyl)silane, and diethanolamine consecutively, to form respectively, **13**, **14** and **2**. The resulting wedge exhibits multiplicities of 3, 2 and 1 in successive generations.

Characterisation

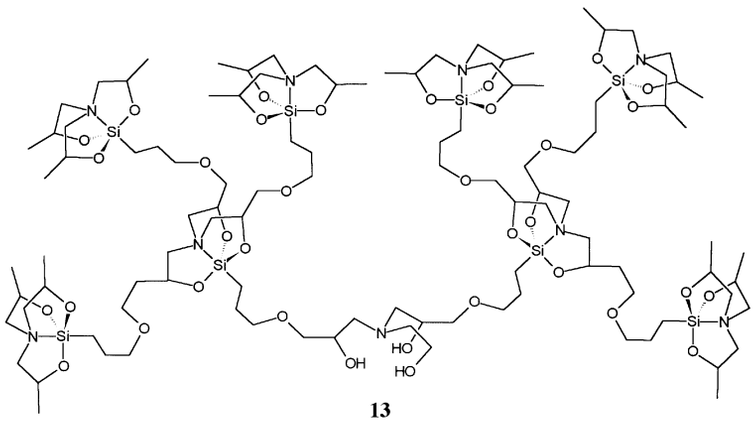
The compounds **1**–**14** isolated as viscous oils or low melting, amorphous solids. The large numbers of diastereomers present prevented crystallisation from occurring and resulted in rather large melting ranges. All products were isolated by chromatography on flash silica, and identified as single spots of TLC. As noted previously for the larger molecules, inclusion of water and/or solvent molecules often resulted in unacceptable microanalytical data,[31] although addition of various multiples of H_2O to the calculated figures generally correlated well with the experimental data. By taking small samples of the compounds and heating to 70–80 °C *in vacuo* over extended periods (*ca.* 24 h) it was found that acceptable data could be obtained. The multinuclear ^{1}H, ^{13}C and ^{29}Si NMR spectra were consistent with the products indicated. Electrospray mass spectrometry was an essential aid in the confirmation of the products. The lack of extraneous peaks in the mass spectra attested to the purity of the products.

Nuclear magnetic resonance spectra

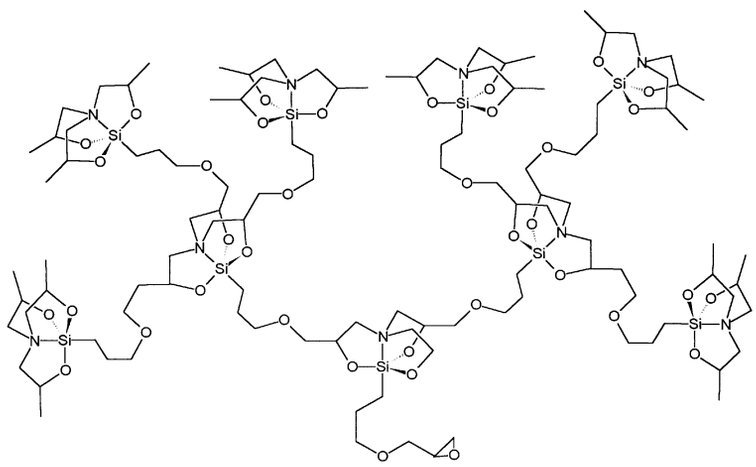
Each dendrimeric wedge contains $Mc + M$ chiral centres, where c = the total number of chiral centres in the previous generation and M is the multiplicity of branching at the focal point. The large number of epimers resulted in broad and complex overlapping multiplets across the proton NMR spectra. The ^{13}C data were also very complex in the later generations, however, DEPT experiments helped to determine the number of signals for each carbon type. Of great significance were the CH_2O and CHO signals of the glycidyl ring which were immediately recognisable, appearing clear of the other signals, *ca.* 44.5 ppm and 50.8 ppm respectively. Thus, the presence or absence of these signals assisted in distinguishing between the alternate (glycidoxy or amine) products.

Carbon-13 spectra. The ^{13}C NMR data are collected in Table 1. The trialkanolamine signals appeared in characteristic positions for silatrane derivatives.[54] The triisopropanolamino derivative contained *RRR/SSS* and *RRS/SSR* diastereomers (stereoisomers A and B, Fig. 1), the former having single ^{13}C peaks for each carbon type, while the latter, being less symmetrical, exhibited separate signals for each of the CH_2, CH and CH_3 carbons of the triisopropanolamine cage. The addition of further generations did not significantly influence the triisopropanolamine resonances of the generation $G = 0$.

The alkanolamine compound **5**, exhibited two peaks for each of the carbons C8–C11 due to the DL and two *meso* forms of the disubstituted trialkanolamine functionality, while C4–C7 showed only a single signal for each carbon type. Formation of the next generation silatrane, **7**, resulted in different *meso* and DL isomers (Fig. 1). The DL form is unsymmetrical, so two signals are seen for each of C6–C9. The two *meso* forms are sym-



13



14

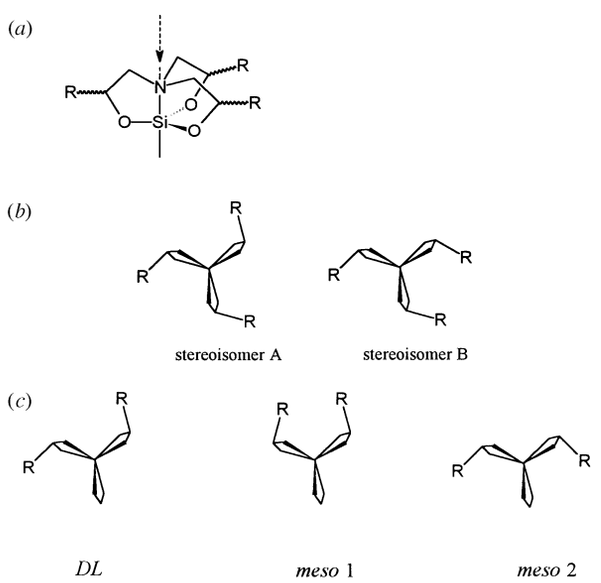


Fig. 1 Viewing along the N–Si axis shown by the dotted arrow in (*a*) demonstrates the unique isomers possible for the tri- and di-substituted silatranes containing identical R-groups in (*b*) and (*c*)

metrical but inequivalent and each form results in a separate signal for each of C6–C9. Both C10 and C11 of the unsubstituted arm of the silatrane, and C12, exhibit one peak for the DL and one each for the two *meso* forms. Subsequent disubstituted compounds showed the same trends in their ^{13}C NMR spectra for each of the glycidyl and trialkanolamine functionality types. However, the rapid increase in signal numbers with each generation made it difficult to fully assign all the signals beyond this generation. In particular, the multitude of CH_2N carbon signals, due to the presence of very similar carbons in the many stereoisomers meant that many of the signals were very close or coincident. In addition, the relative intensities of these signals became very small as further shells were added.

Silicon-29 spectra. ^{29}Si NMR spectra showed broad signals ($w_{\frac{1}{2}}$ *ca.* 25 Hz) in the region −66.2 to −69.8 ppm, being in the characteristic range of alkyl silatranes.[54] The data are collected in Table 2 and demonstrate the sensitivity of the silicon resonance to the configurations of the chiral bridges of the triisopropanolamine cage. Thus for compound **1** and its intermediate building blocks, **3b**, **5**, **7**, **8**, **9** and **10**, the peripheral shell exhibited signals in two positions, *ca.* −66.5 and −69 ppm, in the ratio 3:1 which can be assigned to the stereoisomers B and A respectively. These are split into two or three signals each as the steric influence of subsequent generations become manifest. The preceding shell exhibited peaks at around −67.5 and −69.2 ppm, corresponding to the *meso* and DL forms of the silatranes containing two chiral centres. Again, these were split due to the chiralities of previous and subsquent generations. The resonances for the next shell inwards appeared around −68 and −69.4 ppm. Poor signal-to-noise made it difficult to determine the resonance positions for the focal silatrane of the third generation wedge, a problem compounded by the expected low intensities (see Table 3) and high probability that all the shells containing disubstituted silatranes have common or overlapping resonance positions. Fig. 2 shows the ^{29}Si NMR spectrum of **1** showing the peaks assigned to various shells.

Dendrimer **2** includes triply and doubly substituted silatrane types and was expected to exhibit a relatively complex ^{29}Si NMR spectrum. Signals corresponding to the different generations were identified by comparing spectra of the sequential

Table 1 ^{13}C NMR data for the compounds **1**–**14**

C[a]	1 CH_3	2 CHO	3 CH_2N	4/12/20/28 $SiCH_2$	5/13/21/29 $-CH_2-$	6/14/22/30 CH_2O	7/15/23/31 OCH_2	8/16/24/32 CHO	9/17/25/33 CH_2	10/18/26 NCH_2	11/19/27 CH_2O
1	20.4, 20.5 20.8, 23.2	63.3, 64.9, 65.1, 66.8	58.9, 61.7, 61.8, 65.2	12.0, 12.3	25.2	75.2	73.0, 73.2 73.4/71.0 /72.8	66.4, 67.9, 68.1, 68.9 69.4/50.9	[b]52.1, 54.5, 55.4, 55.7, 56.7, 58.3, 58.5, 59.4, 57.5, 60.3 //44.6		
2	20.3, 20.4 20.7, 23.1	63.3, 64.9, 65.0, 66.8	58.9, 61.7, 61.9, 65.2	11.8–12.4	25.0–25.1	74.9, 75.2	72.8, 73.0 73.3	65.8, 66.2 66.8, 67.0 67.5, 68.3 69.0	[b]50.2, 50.8, 51.7, 52.9, 54.9, 55.0, 57.9, 59.7, 60.1, 60.4, 61.1, 64.1		
3a		57.6	51.0	11.6	24.8	74.7	70.9	50.8	44.4		
3b	20.3, 20.4, 20.7, 23.2	63.3, 64.9, 65.0, 66.8	58.9, 61.7, 61.9, 65.2	11.9, 11.95	25.1	75.1	71.2	50.9	44.6		
4		57.8	51.1	11.8	25.0	74.7	72.7	68.3	57.0	57.6	59.7
5	20.2, 20.3, 20.7, 23.1	63.3, 64.9, 65.0, 66.8	58.9, 61.6, 61.8, 65.1	11.9	25.0	74.9	72.9	69.0, 67.9	58.5, 59.3	57.6, 58.3	59.7, 60.2
6		57.5	50.8	11.75/11.8	24.9	74.9/74.7	72.8/70.8	66.4/50.7	54.0/44.3	51.2, 51.7	57.35, 57.4
7	20.3, 20.4, 20.7, 23.2	63.3, 64.9, 65.0, 66.7	58.8, 61.6, 61.8, 65.1	11.9, 11.95 /12.0, 12.1, 12.7	25.1	75.1, 75.15 75.2, 75.3 /75.0	73.0, 73.1 73.3, 73.2 /71.0	66.3, 66.33 67.8, 68.0 /50.9	52.0, 54.4 55.3, 56.7 /44.6	54.5, 55.68 55.7	57.4, 58.3 58.5
8	20.4, 20.5 20.8, 23.2	63.4, 65.0 65.1, 66.9	59.0, 61.8 62.0, 65.3	12.0/12.2	25.15/25.2	75.15, 75.3 75.4/75.0	73.2, 73.3 73.4/72.8	66.4, 67.9 68.2/69.1, 68.2	[b]52.1, 54.5, 54.6, 55.5, 55.8, 56.9, 57.5, 58.4, 59.4, 59.9, 60.3, 60.4		
9	20.3, 20.4, 20.7, 23.2	63.3, 64.9, 65.0, 66.8	58.9, 61.7, 61.9, 65.2	11.9, 12.0 12.1, 12.2	25.1	75.1, 75.2 75.3	73.0, 73.1 73.4// 71.0	66.3, 67.8 68.0// 50.9	[b]52.1, 54.5, 55.5, 55.8, 56.9, 57.5, 58.6, 60.4 //44.7		
10	20.4, 20.5 20.9, 23.3	63.4, 65.0 65.1, 66.9	59.0, 61.8 62.0, 65.3	12.0, 12.3	25.2, 25.3	75.2	72.8, 73.1 73.2, 73.5	66.4, 67.9 68.1//69.0	[b]52.1, 54.6, 55.5, 55.8, 56.9, 57.5, 58.6, 60.4		
11a	20.3, 20.4 20.8, 23.2	63.4, 64.9 65.0, 66.8	58.7, 61.7, 61.9, 65.1	11.9	25.0	75.0	72.9	67.6, 68.6 69.4	59.9, 59.95 60.2		
11b	20.2, 20.3 20.6, 23.1	63.2, 64.8 64.9, 66.7	58.8, 61.6, 61.7, 65.1	11.9	25.0	74.85, 74.9	72.95, 73.0	68.5	52.1, 52.2		
12	20.3, 20.4 20.8, 23.1	63.3, 64.9, 65.1, 66.8	59.0, 61.7 61.9, 65.2	11.8/ 11.9, 12.3	25.1/25.0	75.1, 75.2 75.3/74.9	73.0, 73.4 /71.0	67.0, 67.6 68.4/50.9	54.9, 58.0 59.9, 60.3 /44.8		
13	20.3, 20.4 20.8, 23.2	63.3, 64.9, 65.0, 66.8	58.9, 61.7, 61.9, 65.2	11.8	25.1	75.1–75.3	72.7, 73.3	67.0, 67.5 68.3/ 66.2, 68.1, 69.0	54.9, 58.0 59.8, 60.3 /55.5, 58.3	57.4, 58.3	59.3, 60.2
14	20.3, 20.4 20.8, 23.2	63.3, 64.9, 65.1, 66.8	58.9, 61.7, 61.9, 65.2	11.8–12.4	25.0–25.1	74.9/75.3/	73.0, 73.4 //71.0	66.2, 67.0 67.5, 67.7/ 68.3/ 50.8, 50.9	[b]54.9, 55.5, 58.1, 59.9 //44.7		

[a] Carbon atom number and type. Numbering scheme as indicated in graphics **1**, **3**, **5** and **7**. Dendrimer shells delineated by solidus (/). Double solidus (//) indicates incomplete data or assignment. [b] Carbon types 9–11 and subsequent shells not distinguished from each other.

Table 2 ^{29}Si NMR data for the compounds **1**–**14**

	Shell 0/ppm	Shell 1/ppm	Shell 2/ppm	Shell 3/ppm
1		−67.9, −69.4	−67.5, −69.1	−66.3, −66.4, −68.6, −68.7
2		−68.8	−66.4, −69.7	
3a[a]	−66.6			
3b	−66.5, −68.9			
4[a]	−66.4			
5	−66.2, −68.6			
6[a]	−66.4, −67.9			
7	−67.7, −67.8, −69.4	−66.7, −66.8, −69.0, −69.1, −69.2		
8	−67.7, −67.8, −69.4	−66.6, −66.65, −66.7, −69.0, −69.05, −69.1		
9	−68.0, −69.5	−67.6, −69.2	−66.4, −66.5, −68.8	
10	−68.0, −69.4	−67.5, −69.2	−66.3, −66.4, −68.7, −68.8	
11a	−66.4, −68.8			
11b	−66.5, −68.9			
12	−68.8	−66.4, −69.8		
13	−68.8	−66.4, −69.8		
14		−68.8	−66.3, −69.8	

All samples run in $CDCl_3$ except [a], CD_3OD solution.

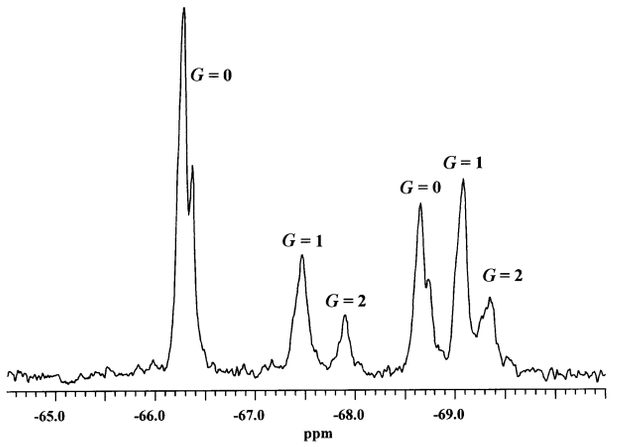


Fig. 2 ^{29}Si NMR spectrum of compound **1** with peaks assigned to silatranes in various shells of the dendrimeric wedge

Table 3 Calculated ^{29}Si NMR peak intensity ratios for dendrimeric wedges **1** and **2**, assuming full relaxation of the ^{29}Si nuclei and statistical distribution of chiral centres

Dendrimer	Shell 0	Shell 1	Shell 2	Shell 3
1	[b] 2:1:1	[b] 4:2:2:	[b] 8:4:4:	[a] 24:8:
2	[b] 2:1:1	[a] 6:2:	[a] 18:6:	

[a] *RSS*/*SSR*:*RRR*/*SSS*. [b] DL: *meso* 1:*meso* 2.

dendrimeric wedges prepared in the stepwise formation of **2**. The peripheral shell had signals due to stereoisomers A and B as for compound **1**. The preceding shell also contained triply substituted species, thus the signals for these partly coincided. The next shell inwards contains a disubstituted silatrane and was expected to add three further signals (1 DL and 2 *meso*) to the spectrum. These would be expected to fall around −67.5 and −69.2 ppm by comparison with the disubstituted silatrane signals in compound **1**. Assignment of peaks was assisted by considering their relative intensities. Assuming statistical distribution between *R* and *S* configurations, and equivalent relaxation of the silicon nuclei, the peak intensity ratios would be expected to be: *G* = 0 *RRS*/*SSR*:*RRR*/*SSS*: *G* = 1 *RRS*/*SSR*:*RRR*/*SSS* ≡ 9:3:3:1 (see Table 3). In reality, many of the minor signals for the later generations are not observed (Table 2) due to their low intensities, coincident positions and/or unfavourable signal-to-noise ratios. The alkanolamine functionalised compounds have ^{29}Si NMR spectra virtually identical to the previous glycidoxy compound.

Electrospray mass spectrometry (ESMS)

ESMS is a relatively new mass spectrometric ionisation technique,[55] which has been extensively applied to the analysis of biological molecules.[56–58] Applications to the characterisation of inorganic species are fewer, though there is rapidly increasing interest in this field. To the best of our knowledge there are no reports on the study of silatranes by ESMS, and few describing the analysis of dendrimeric materials in general,[59,60] though one describing the characterisation of polyether-derived dendrimers has appeared recently.[61] An alternative technique, matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was recently demonstrated to be a useful tool in the analysis of dendrimers.[32,62] The various silatrane dendrimeric wedges described herein have been characterised by ESMS. Data for those compounds containing secondary or tertiary amino groups are summarised in Table 4, while data for the glycidoxy derivatives are summarised in Table 5.

All of the silatrane compounds contain ether moieties which provide a facile mechanism for ion formation either as the protonated species $[M + H]^+$, or by complex formation with NH_4^+ or alkali metal cations. Ethers, and particularly polyethers, typically show strong principal ions in ESMS spectra, and a number of studies of polyethers and polyether-derived materials have been reported in the literature.[63–66] For the silatranes containing free secondary or tertiary amines the high basicity of these groups is also expected to contribute to strong $[M + H]^+$ ions in their positive-ion spectra. The silatrane Si–O groups might also participate in the ionisation process *via* protonation of the oxygen atoms.

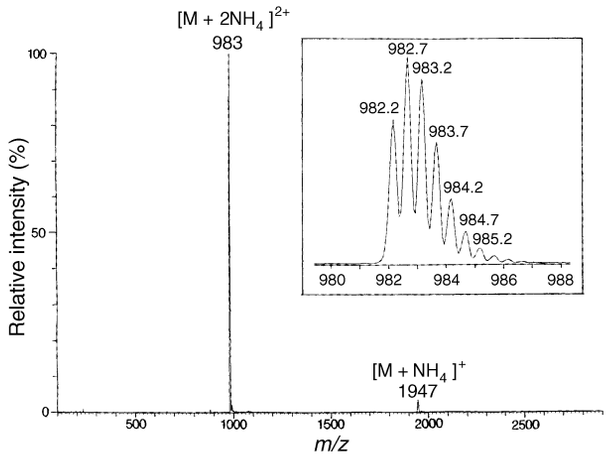


Fig. 3 ESMS spectrum (cone voltage 20 V) of compound **9**. Isotope pattern showing half dalton line spacings (inset) indicating the 2+ ionic charge.

An additional advantage in the use of ESMS is the ability to obtain mass spectra of large molecules, by multiple charging. This has the effect of reducing the *m*/*z* ratio into the observable range of the (*e.g.* quadrupole) mass spectrometer. Such behaviour has been widely utilised for the analysis of peptides and proteins,[56–58] but is less well documented for other classes of compounds.[67,68] Polyethers are capable of binding more than one cation simultaneously[69,70] suggesting that analysis of the higher dendrimeric silatranes should indeed be readily achievable by ESMS.

For the glycidoxy compounds (*i.e.* **1**, **3**, **6**, **7**, **9**, **12** and **14**) ions of the type $[M + xNH_4]^{x+}$ were commonly observed at low cone voltages, with the value of *x* increasing with the size of the molecle. This can be illustrated by compound **9** as an example; the positive-ion ES spectrum at a cone voltage of 20 V is illustrated in Fig. 3. The principal ion at a low cone voltage is the dication $[M + 2NH_4]^{2+}$ (*m*/*z* 982), readily identified by its characteristic isotope pattern. A smaller peak due to $[M + NH_4]^+$ (*m*/*z* 1947) is also observed. These general principles can be extended to the analysis of the larger compound **14**, where $[M + 3NH_4]^{3+}$ ions are also observed, showing the characteristic 0.333 mass unit separation between adjacent peaks in the isotope distribution pattern. However, for **3** the major ion in the positive-ion spectrum was the ammonium aggregate ion $[2M + NH_4]^+$, though at higher cone voltages (40 V or greater) the $[M + H]^+$ and $[M + NH_4]^+$ ions were predominant. Acetonitrile solutions invariably contain traces of residual ammonia, this being the source of the NH_4^+ ions. No addition of water to the epoxide moiety was found to occur during the analysis.

For the silatrane wedges containing a basic tertiary amine group (*i.e.* **2**, **4**, **8**, **10**, **11** and **13**) there is a subtle difference in the nature of the observed ions. For such compounds a series of ions of the type $[M + H + xNH_4]^{(x+1)+}$ ($x = 0$–3) are readily observed at a low cone voltage (20 V). As expected, there is an increased tendency to form more highly charged ions with an increase in the wedge size. This is illustrated in Fig. 4 for compound **10**. It seems reasonable that the tertiary amine group

Table 4 ESMS data[a] for silatranes containing epoxide groups

Compound (M)[b]	Cone voltage/V	Ions (*m*/*z*, %)
1 (4057)	+20	$[M + 4NH_4]^{4+}$ (1033, 100%), $[M + 3NH_4]^{3+}$ (1371, 53), $[M + 2NH_4]^{2+}$ (2047, 5), plus unidentified peaks at *m*/*z* 725 and 904
3 (331)	+20	$[M + H]^+$ (332,. 10%), $[M + NH_4]^+$ (349, 20), unidentified (523, 17), $[2M + NH_4]^+$ (680, 100)
	+40	$[C_9H_{18}NO_3Si]^+$ (216, 12%), $[M + H]^+$ (332, 100), $[M + NH_4]^+$ (349, 63), $[2M + NH_4]^+$ (680, 8)
	+60	$[C_9H_{18}NO_3Si]^+$ (216, 100%), $[M + H]^+$ (332, 68)
6 (534)	+20	$[M + NH_4]^+$ (552, 100%), $[2M + NH_4]^+$ (1086, 20)
7 (863)	+20	$[M + NH_4]^+$ (881, 100%), $[2M + NH_4]^+$ (1747, 6)
	+50	$[M + H]^+$ (864, 7%), $[M + NH_4]^+$ (881, 100), $[2M + NH_4]^+$ (1745, 4)
9 (1928)	+20	$[M + 2NH_4]^{2+}$ (983, 100%), $[M + NH_4]^+$ (1947, 3)
	+50	$[M + NH_4 + H]^{2+}$ (973.5, 30%), $[M + 2NH_4]^{2+}$ (983, 100), $[M + NH_4]^+$ (1947, 8)
	+70	$[C_9H_{18}NO_3Si]^+$ (216, 58%), $[C_9H_{18}NO_3Si(NCMe)]^+$ (257, 27), $[M + 2H]^{2+}$ (965, 51), $[M + NH_4 + H]^{2+}$ (773.5, 100), $[M + 2NH_4]^{2+}$ (983, 50), $[M + NH_4]^+$ (1947, 53)
12 (1151)	+20	$[M + 2NH_4]^{2+}$ (593, 100%), $[M + NH_4]^+$ (1168, 72), $[2M + NH_4]^+$ (2320, 3)
	+60	$[M + NH_4]^+$ (1168, 100%)
14 (2502)	+20	$[M + 3NH_4]^{3+}$ (852, 100%), $[M + 2NH_4]^{2+}$ (1269.5, 75), $[M + NH_4]^+$ (2521, 2)
	+60	$[M + 2NH_4]^{2+}$ (1269.5, 100%), $[M + NH_4]^+$ (2521, 20)

[a] Species are identified by the largest peak in the isotope distribution pattern. [b] Calculated mass corrected for relative isotope abundances.

Table 5 ESMS data[a] for silatranes containing free amino groups

Compound (M)[b]	Cone voltage/V	Ions (*m*/*z*, %)
2 (2607)	+20	$[M + 2NH_4 + H]^{3+}$ (882, 100%), $[M + NH_4 + H]^{2+}$ (1314, 12), plus a number of other unidentified peaks
5 (723)	+20	$[M + H]^+$ (724, 100%), $[M + NH_4]^+$ (741, 7), $[2M + H]^+$ (1447, 28), $[2M + NH_4]^+$ (1466, 6), $[3M + H]^+$ (2172, 2)
	+100	$[M + H]^+$ (724, 100%), $[M + NH_4]^+$ (741, 3), $[2M + H]^+$ (1447, 3)
8 (1788)	+20	$[M + NH_4 + H]^{2+}$ (903, 100%), $[M + H]^+$ (1789, 1)
	+50	$[M + 2H]^{2+}$ (895, 32%), $[M + NH_4 + H]^{2+}$ (903, 100), $[M + H]^+$ (1788, 2)
	−100	$[M - H]^-$ (1787, 100%)
10 (3917)	+20	$[M + 3NH_4 + H]^{4+}$ (994, 100%), $[M + 4NH_4]^{4+}$ (998, 17), $[M + 2NH_4 + H]^{3+}$ (1318, 71), $[M + 3NH_4]^{3+}$ (1324, 14), $[M + NH_4 + H]^{2+}$ (1969, 7), $[M + 2NH_4]^{2+}$ (1977, 2)
11a (1010)	+20	$[M + H]^+$ (1011, 100%), $[3M + 2H]^{2+}$ (1517, 5), $[2M + H]^+$ (2022, 3)
	+100	$[M + H]^+$ (1011, 100), $[2M + H]^+$ (2022, 3)
	+160	$[C_9H_{18}NO_3Si]^+$ (216, 25%), $[C_9H_{18}NO_3Si(NCMe)]^+$ (257, 8), $[M + H]^+$ (1011, 100)
11b (679)	+20	$[M + H]^+$ (680, 100%), $[2M + H]^+$ (1359, 5)
	+100	$[M + H]^+$ (680, 100%) plus a number of minor peaks
13 (2362)	+20	$[M + 3H]^{3+}$ (789, 2%), $[M + NH_4 + 2H]^{3+}$ (794, 11), $[M + 2NH_4 + H]^{3+}$ (800, 22), $[M + 3NH_4]^{3+}$ (806, 1), $[M + 2H]^{2+}$ (1182, 12), $[M + NH_4 + H]^{2+}$ (1191, 100), $[M + 2NH_4]^{2+}$ (1199, 3), unidentified (1583, 6), $[M + H]^+$ (2364, 12), $[M + NH_4]^+$ (2380, 1)

[a] Species are identified by the largest peak in the isotope distribution pattern. [b] Calculated mass corrected for relative isotope abundances.

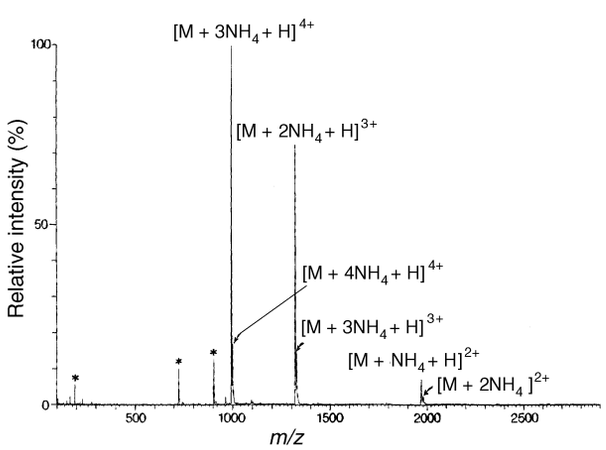
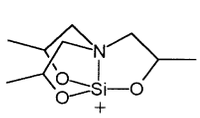


Fig. 4 ESMS spectrum (cone voltage 20 V) of compound **10** showing a range of $[M + H + xNH_4]^{x+}$ ions

readily protonates, with a variable number of ammonium ions acting as additional hydrogen-bond donors to ether and/or silatrane oxygen atoms, thus accounting for the preferred stoichiometry of ion formation. The species $[M + xNH_4]^{x+}$, though observed, were much smaller for the aminosilatranes (Table 4) than for the glycidoxy-silatranes (Table 5) as illustrated in Fig. 3.

The silatranes reported herein appear to possess considerable stability, as indicated by the continued observation of a strong $[M + H]^+$ ion up to very high cone voltages (*e.g.* 160 V for **11b**). However, at such high voltages some fragmentation does occur, and small peaks due to the silatranyl cation $[C_9H_{18}NO_3Si]^+$ (**15**) (*m*/*z* 216) and its acetonitrile solvate (*m*/*z* 257) are often also observed. Formation of **15** appeared to be particularly pronounced for **3b**.



15

Silatranes containing hydroxy groups are also expected to yield ions of the type $[M - H]^-$ in their negative-ion spectra, *via* deprotonation of the OH group. This behaviour is commonly observed for other hydroxylic molecules, including carbohydrates which are often used as negative-ion mass standards for electrospray instruments. As a representative example, compound **8** showed such a negative ion at a high cone voltage (−100 V).

Conclusion

The investigations reported here demonstrate the utility of the glycidoxypropyl(trimethoxy)silane entity as a convenient building block for dendrimeric wedge synthesis. The convenient control of branching multiplicity is aptly demonstrated. ESMS has been shown to be an excellent tool to identify the products, and the presence of silatrane units provides a useful ^{29}Si NMR probe to assist in their characterisation.

Experimental

The alkanolamines triethanolamine [tris(2-hydroxyethyl)amine], diethanolamine [bis(2-hydroxyethyl)amine] and ethanolamine (2-hydroxyethylamine) were dried and distilled prior to use. Trispropanolamine [tris(2-hydroxypropyl)amine] (Aldrich) and trimethoxy(glycidoxypropyl)silane (Dow Corning) were used as supplied. Methanol was dried using magnesium turnings, distilled and stored on 3 Å molecular sieves. ^{29}Si NMR spectra were run at 99.6 MHz on a Varian 500 spectrometer at ambient temperature. Inverse gated decoupling was used to minimise the effects of negative NOE. Long relaxation times necessitated using a 90 s relaxation delay or addition of $Cr(acac)_3$ to shorten T_1. Samples (150 mg) were made up in 5 mm tubes using $CDCl_3$ for a lock signal. Tetramethylsilane (TMS) (5%) was added as an internal reference (0 ppm).

Electrospray mass spectra were obtained in both positive- and negative-ion modes as indicated, using a VG Platform II mass spectrometer. The mobile phase was a 1:1 v/v acetonitrile–water mixture. The silatranes were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mM, and spectra were recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 μl sample loop. A Thermo Separation Products Spectra System P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 ml min^{-1}, and nitrogen was employed both as a drying and nebulising gas. Cone voltages were typically varied from 5 to 160 V, in order to investigate the effect of higher voltages on fragmentation of parent ions. Confirmation of species is aided by comparison of the observed and calculated isotope distribution patterns, the latter being calculated using the ISOTOPE computer program.[71]

The nomenclature developed for dendrimers[72,73] has been adapted here to allow for the variation in multiplicity within the dendrimeric wedge. Thus the shorthand notation used here follows the form [G-n($M_1M_2M_3$ . . .)]-f, where [G-n] refers to the generation number (n = 0, 1, 2, . . .), M_1 refers to the multiplicity at the first shell, M_2 at the second shell *etc.* and f refers to the functional group at the focal point. Although the synthesis route is convergent, the first shell is always that one immediately adjacent to the focal point of the wedge. The alkanolamines carry the multiplicity information for the next generation. The functional groups trialkanolamines or dialkanolamines and glycidyl are represented by TAA and gly respectively.

1-Glycidoxypropylsilatrane 3a‡

Trimethoxy(glycidoxypropyl)silane (9.44 g, 0.04 mol) and triethanolamine (9.56 g, 0.04 mol) were dissolved in dry methanol (10 ml). Toluene (30 ml) was added and the mixture refluxed for 16 h. The methanol was removed by slow azeotropic distillation, until the reaction was complete. Solvent removal followed by flash column chromatography isolated the product as a viscous colourless oil (9.035 g, 78%), TLC 80:20 EtOAc–MeOH, R_f = 0.3 (Calc. for $C_{12}H_{23}NO_5Si$: C, 49.8; H, 8.0; N, 4.8. Found: C, 49.8; H, 7.9; N, 4.8%).

‡ The numbering system used in the Experimental section for the silatranes refers to the numbering of the bicyclo system.

1-Glycidoxypropyl-3,7,10-trimethyl-silatrane 3b [G-0]-gly

Trimethoxy(glycidoxypropyl)silane (11.8 g, 0.05 mol) and triisopropanolamine (9.54 g, 0.05 mol) were stirred together in methanol (5 ml) and toluene (40 ml). A few drops of $Ti(OPr^i)_4$ catalyst was added and the mixture refluxed for 18 h. The solvent was removed and the product isolated by flash column chromatography as a viscous, colourless oil (14.07 g, 85%), TLC, EtOAc, R_f = 0.5 (Calc. for $C_{15}H_{29}NO_5Si$: C, 54.4; H, 8.8; N, 4.2. Found: C, 54.2; H, 9.0; N, 4.1%).

***N*-{3-[3-(Silatran-1-yl)propyloxy]-2-hydroxypropyl}bis(2-hydroxyethyl)amine 4**

Diethanolamine (1.05 g, 0.01 mol) and glycidoxypropylsilatrane **3a** (2.89 g, 0.01 mol) were combined in dry methanol and refluxed for 16 h. Two products were evident from TLC, 50:50 EtOAc–MeOH, R_f = 0.1, 0.3, which were separated using flash column chromatography and identified by ^{1}H, ^{13}C and ^{29}Si NMR as **4** (1.14 g, 29%) and **6** (1.4 g, 52%).

Bis{3-[3-(3,7,10-trimethylsilatran-1-yl)propyloxy]-2-hydroxypropyl}-2-hydroxyethylamine 5 [G-0(2)]-TAA

Ethanolamine (2.1 g, 0.035 mol) was added to a dry methanol (10 ml) solution of **3b** (22.8 g, 0.07 mol). The reaction was refluxed for 16 h. Removal of the solvent followed by flash column chromatography gave the product as a colourless, viscous oil (21.7 g, 85.8%), TLC, 50:50 EtOAc–MeOH, R_f = 0.5 (Calc. for $C_{32}H_{65}N_3O_{11}Si_2$: C, 53.1; H, 9.1; N, 5.8. Found: C, 53.O; H, 9.1; N, 5.9%).

[G-1(2)]-gly 7

Following a similar reaction technique to **3b** above, trimethoxy(glycidoxypropyl)silane (7.05 g, 0.03 mol) and **5** (21.56 g, 0.03 mol) combined to produce **7** (19.25 g, 75%), TLC, 80:20 EtOAc–MeOH, R_f = 0.55 (Calc. for $C_{38}H_{73}N_3O_{13}Si_3$: C, 52.8; H, 8.5; N, 4.9. Found: C, 52.6; H, 8.2; N, 5.0%).

[G-1(2.2)]-TAA 8

Reaction between **7** (18.73 g, 0.022 mol) and ethanolamine (0.663 g, 0.011 mol) according to the method described for **5** above gave **8**, isolated as a crispy, colourless, amorphous solid (15.66 g, 80.7%), mp 42–46 °C, TLC, 50:50 EtOAc–MeOH, R_f = 0.3 (Calc. for $C_{78}H_{153}N_7O_{27}Si_6$: C, 52.4; H, 8.6; N, 5.5. Found: C, 52.6; H, 8.5; N, 5.8%).

[G-2(2.2)]-gly 9

Following a similar reaction technique to **3b** above, trimethoxy(glycidoxypropyl)silane (1.44 g, 6.1 mmol) and **8** (10.89 g, 6.1 mmol) combined to produce **9**, isolated as a crispy, colourless, amorphous solid (9.52 g, 80.9%), mp 60–62 °C, TLC, 50:50 EtOAc–MeOH, R_f = 0.6 (Calc. for $C_{84}H_{161}N_7O_{29}Si_7$: C, 52.3; H, 8.4; N, 5.1. Found: C, 52.6; H, 8.4; N, 5.2).

[G-2(2.2.2)]-TAA 10

Reaction between **9** (8.83 g, 4.58 mmol) and ethanolamine (0.14 g, 2.3 mmol) according to the method described for **5** above gave **10**, isolated as a crispy, colourless, amorphous solid (4.70 g, 52%), mp 75–79 °C, TLC, 50:50 EtOAc–MeOH, R_f = 0.18 (Calc. for $C_{170}H_{329}N_{15}O_{59}Si_{14}$: C, 52.1; H, 8.5; N, 5.4. Found: C, 52.1; H, 8.4; N, 5.3%).

[G-3(2.2.2)]-gly 1

A mixture of trimethoxy(glycidoxypropyl)silane (0.15 g, 0.64 mmol) and **10** (2.44 g, 0.62 mmol) was heated under argon to 200 °C for 20 min in the absence of a solvent. The reaction mixture darkened slightly, but the product was isolated using flash column chromatography and identified as **1** (0.9 g, 35%), TLC, 50:50 EtOAc–MeOH, R_f = 0.5 (Calc. for $C_{176}H_{337}N_{15}O_{61}Si_{15}$: C, 52.1; H, 8.4; N, 5.2. Found: C, 52.4; H, 8.5; N, 5.2%).

Tris{3-[3-(3,7,10-trimethylsilatran-1-yl)propyloxy]-2-hydroxypropyl}amine 11a [G-0(3)]-TAA

Ammonia (15 ml of a 2 M solution in methanol) was added to a solution of **3b** (29.79 g, 0.09 mol) in methanol (60 ml). The mixture was divided into several aliquots and dispensed into air-tight screw-top vials. These were held at 60–65 °C for four days. After cooling and removal of solvent, the two major products were separated and purified using flash column chromatography. These were **11a** and **11b**, tris- and bis-{3-[3-(3,7,10-trimethylsilatran-1-yl)propyloxy]-2-hydroxypropyl}-amines, yields 11.0 g (36%) and 10.5 g (51.5% based on ammonia), TLC, 50:50 EtOAc–MeOH, $R_f = 0.6$, 0.2, respectively. There was no attempt to optimise the yield of **11a** (Calc. for $C_{45}H_{90}N_4O_{15}Si_3$: C, 53.4; H, 9.0; N, 5.5. Found: C, 53.3; H, 9.1; N, 5.4%).

[G-1(3)]-gly 12

Following a similar reaction technique to **1** above, trimethoxy-(glycidoxypropyl)silane (1.23 g, 5.2 mmol) and **11a** (5.26 g, 5.2 mmol) combined to produce **12** (3.24 g, 54%), TLC, 50:50 EtOAc–MeOH, $R_f = 0.66$ (Calc. for $C_{51}H_{98}N_4O_{17}Si_4$: C, 53.2; H, 8.6; N, 4.9. Found: C, 53.1; H, 8.6; N, 4.8%).

[G-1(2.3)]-TAA 13

Reaction between **12** (3.05 g, 2.65 mmol) and ethanolamine (0.08 g, 1.32 mmol) according to the method described for **5** above gave **13** (1.82 g, 58.3%), TLC, 50:50 EtOAc–MeOH, $R_f = 0.45$ (Calc. for $C_{104}H_{203}N_9O_{35}Si_8$: C, 52.8; H, 8.7; N, 5.3. Found: C, 52.9; H, 8.8; N, 5.2%).

[G-2(2.3)]-gly 14

Following a similar reaction technique to **1** above, trimethoxy-(glycidoxypropyl)silane (0.154 g, 0.66 mmol) and **13** (1.55 g, 0.66 mmol) combined to produce **14** (1.60 g, 97%), mp 57–63 °C, TLC, 50:50 EtOAc–MeOH, $R_f = 0.57$ (Calc. for $C_{110}H_{211}N_9O_{37}Si_9$: C, 52.8; H, 8.5; N, 5.0. Found: C, 52.5; H, 8.6; N, 5.0%).

[G-2(1.2.3)]-TAA 2

Reaction between **14** (1.60 g, 0.61 mmol) and diethanolamine (0.064 g, 0.61 mmol) according to the method described for **5** above gave **2** (0.5 g, 31%), TLC, 50:50 EtOAc–MeOH, $R_f = 0.35$ (Calc. for $C_{114}H_{222}N_{10}O_{38}Si_9$: C, 52.5; H, 8.6; N, 5.4. Found: C, 52.5; H, 8.6; N, 5.3%). A further product (0.7 g) was not identified.

Acknowledgements

W. H. thanks the University of Waikato for financial support, the New Zealand Lottery Grants Board for a grant towards the mass spectrometer and Wendy Jackson for technical assistance. Thanks also to C. Lensink, K. R. Morgan and H. Wong.

References

1 J. Issberner, R. Moors and F. Vogtle, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2413.
2 D. A. Tomalia, A. M. Naylor and W. A. Goddard, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138.
3 H.-B. Mekelburger, E. Jaworek and F. Vogtle, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1571.
4 J. F. G. A. Jansen, H. W. I. Peerlings, E. M. M. De Brabander-Van den Berg and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1206.
5 W. T. S. Huck, F. C. J. M. Van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 8293.
6 G. R. Newkome, *Advances in Dendritic Macromolecules, 1*, JAI, Greenwich, CT, 1994.
7 G. R. Newkome, *Advances in Dendritic Macromolecules, 2*, JAI, Greenwich, CT, 1995.
8 D. A. Tomalia and H. D. Hurst, *Top. Curr. Chem.*, 1993, **165**, 193.
9 S. A. Kuzdzal, C. A. Monnig, G. R. Newkome and C. M. Moorefield, *J. Chem. Soc., Chem. Commun.*, 1994, 2139.
10 S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto and V. Balzani, *Chem. Eur. J.*, 1995, **1**, 211.
11 S. Roffia, M. Marcaccio, C. Paradisi, F. Paulucci, V. Balzani, G. Denti, S. Serroni and S. Campagna, *Inorg. Chem.*, 1993, **32**, 3003.
12 S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1493.
13 B. Alonso, M. Moran, C. M. Casado, F. Lobete, J. Losada and I. Cuadrado, *Chem. Mater.*, 1995, **7**, 1440.
14 S. Achar and R. J. Puddephatt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 847.
15 S. Achar and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1994, 1895.
16 M. R. Bryce, W. Devonport and A. J. Moore, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1761.
17 S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace and N. Micali, *J. Am. Chem. Soc.*, 1995, **117**, 1754.
18 G. R. Newkome, X. Lin and C. D. Weis, *Tetrahedron: Asymmetry*, 1991, **2**, 957.
19 J. A. Kremers and E. W. Meijer, *J. Org. Chem.*, 1994, **59**, 4262.
20 D. Seebach, J.-M. Lapierre, K. Skobridis and G. Greiveldinger, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 440.
21 H.-F. Chow, L. F. Fok and C. C. Mak, *Tetrahedron Lett.*, 1994, **35**, 3547.
22 L. J. Twyman, A. E. Beezer and J. C. Mitchell, *Tetrahedron Lett.*, 1994, **35**, 4423.
23 H. Brunner and S. Altmann, *Chem. Ber.*, 1994, **127**, 2285.
24 P. Murer and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2116.
25 H. Ritter, *GIT Fachz. Lab.*, 1994, **38**, 615.
26 E. M. M. De Brabander-Van den Berg and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1308.
27 J. W. J. Knapen, A. W. Van der Made, J. C. De Wilde, P. W. N. M. Van Leeuwen, P. Wijkens, D. M. Grove and G. Van Koten, *Nature* (*London*), 1994, **372**, 659.
28 D. Seyferth, T. Kugita, A. L. Rheingold and G. P. A. Yap, *Organometallics*, 1995, **14**, 5362.
29 S. Achar, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1996, **15**, 43.
30 P. Lange, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1996, **35**, 637.
31 G. Chessa and A. Scrivanti, *J. Chem. Soc., Perkin Trans. 1*, 1996, 307.
32 F. Dandliker, F. Diederich, J.-P. Gisselbrecht, A. Louati and M. Gross, *Angew. Chem., Int. Ed. Engl.*, 1996, **34**, 2725.
33 A. Sekiguchi, M. Nanjo, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1995, **117**, 4195.
34 J. B. Lambert, J. L. Pflug and C. L. Stern, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 98.
35 F. Lobete, I. Cuadrado, C. M. Casado, B. Alonso, M. Moran and J. Losada, *J. Organomet. Chem.*, 1996, **509**, 109.
36 J. B. Lambert, J. L. Pflug and J. M. Denari, *Organometallics*, 1996, **15**, 615.
37 D. Seyferth, D. Y. Son, A. L. Rheingold and R. L. Ostrander, *Organometallics*, 1994, **13**, 2682.
38 E. W. Kwock, T. X. Neenan and T. M. Miller, *Macromolecules*, 1992, **25**, 3143.
39 C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1992, **114**, 8405.
40 M. G. Voronkov, V. M. Dyakov and S. V. Kirpichenko, *J. Organomet. Chem.*, 1982, **233**, 1.
41 S. N. Tandura, M. G. Voronkov and N. V. Alekseev, *Top. Curr. Chem.*, 1986, **131**, 99.
42 E. Lukevits, O. Pudova and R. Sturkovich, *Molecular Structure of Organosilicon Components*, Ellis Horwood, Chichester, 1989.
43 R. J. P. Corriu, *J. Organomet. Chem.*, 1990, **400**, 81.
44 C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371.
45 M. G. Voronkov, *Top. Curr. Chem.*, 1979, **84**, 77.
46 C. B. Beiter, M. Schwarcz and G. Crabtree, *Soap Chem. Spec.*, 1970, **46**, 38.
47 M. A. Horsham, C. J. Palmer, L. M. Cole and J. E. Casida, *J. Agric. Food Chem.*, 1990, **38**, 1734.
48 L. Bihatsi, G. Ripka, P. Hencsei and L. Kotai, *Hung. J. Ind. Chem.*, 1991, **20**, 59.
49 W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1994, **116**, 6142.
50 K. L. Wooley, C. J. Hawker and J. M. J. Frechet, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1059.
51 H. Brunner, *J. Organomet. Chem.*, 1995, **500**, 39.
52 F. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and E. M. Sanford, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1739.

53 C. L. Frye, G. A. Vincent and W. A. Finzel, *J. Am. Chem. Soc.*, 1971, **93**, 6805.
54 R. K. Harris, J. Jones and S. Ng, *J. Magn. Reson.*, 1978, **30**, 521.
55 J. B. Fenn, M. Mann, C. K. Meng, S. F. Wu and C. M. Whitehouse, *Mass Spectrom. Rev.*, 1990, **9**, 37.
56 M. Mann and M. Wilm, *Trends Biochem. Sci.*, 1995, 219.
57 M. Mann, *Org. Mass Spectrom.*, 1990, **25**, 575.
58 C. M. Whitehouse, R. N. Dreyer, M. Yamashita and J. B. Fenn, *Anal. Chem.*, 1985, **57**, 675.
59 B. L. Schwartz, A. L. Rockwood, R. D. Smith, D. A. Tomalia and R. Spindler, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 1552.
60 G. J. Kallos, D. A. Tomalia, D. M. Hedstrand, S. Lewis and J. Zhou, *Rapid Commun. Mass Spectrom.*, 1991, **5**, 383.
61 H.-F. Chow, I. Y.-K. Chan and C. C. Mak, *Tetrahedron Lett.*, 1995, **36**, 8633.
62 H. S. Sahota, P. P. Lloyd, S. G. Yeates, P. J. Derrick, P. C. Taylor and D. M. Haddleton, *J. Chem. Soc., Chem. Commun.*, 1994, 2445.
63 C. Crescenzi, A. Di Corcia, R. Samperi and A. Marcomini, *Anal. Chem.*, 1995, **67**, 1797.
64 K. B. Sherrard, P. J. Marriott, M. J. McCormick, R. Colton and G. Smith, *Anal. Chem.*, 1994, **66**, 3394.
65 R. Saf, C. Mirtl and K. Hummel, *Tetrahedron Lett.*, 1994, **35**, 6653.
66 T. Nohmi and J. B. Fenn, *J. Am. Chem. Soc.*, 1992, **114**, 3241.
67 U. N. Anderson, C. J. McKenzie and G. Bojesen, *Inorg. Chem.*, 1995, **34**, 1435.
68 J. S. Klassen, A. T. Blades and P. Kebarle, *J. Am. Chem. Soc.*, 1994, **116**, 12 075.
69 K. Wang, X. Han, R. W. Gross and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, 1995, 641.
70 G. W. Gokel, D. M. Goli and R. A. Schultz, *J. Org. Chem.*, 1983, **48**, 2837.
71 L. J. Arnold, *J. Chem. Educ.*, 1992, **69**, 811.
72 C. J. Hawker and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010.
73 C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

Paper 6/05135I
Received 23*rd July* 1996
Accepted 14*th October* 1996