DALTON
FULL PAPER

Syntheses of highly functionalized cube-octameric polyhedral oligosilsesquioxanes ($R_8Si_8O_{12}$)

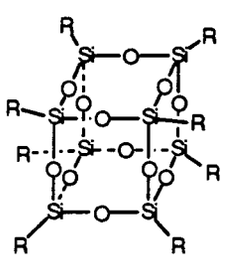
Frank J. Feher,* Kevin D. Wyndham, Daravong Soulivong and Frank Nguyen

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

Received 18th September 1998, Accepted 1st March 1999

Reactions of $[H_2N(CH_2)_3]_8Si_8O_{12}$ or its octahydrochloride salt with a variety of electrophiles, including anhydrides, lactones, acid chlorides, α,β-unsaturated esters and isocyanates, afforded functionalized $R_8Si_8O_{12}$ frameworks in good to excellent yields. Practical methods for the synthesis of $[HO(CH_2)_3]_8Si_8O_{12}$, $[OCN(CH_2)_3]_8Si_8O_{12}$ and $[(Ph_2PCH_2)_2N(CH_2)_3]_8Si_8O_{12}$ are also reported.

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of organosilicon oligomers that can be synthesized by the hydrolytic condensation of trifunctional organosilicon monomers.[1,2] This family of compounds has been known for more than 50 years,[3] but until recently the majority of known POSS lacked sufficient functionality for most chemical applications.[4] The pool of known POSS frameworks has expanded rapidly over the past several years. Some of this expansion is due to the discovery of new spontaneous self-assembly reactions that provide ready access to multigram quantities of several synthetically versatile POSS frameworks.[5,6] Another important reason is the development of general and highly efficient methodology for synthetically manipulating pendant groups on POSS frameworks.[6–9] One of the most useful precursors to highly functionalized cube-octameric POSS frameworks is $H_8Si_8O_{12}$ **1**, which is easily prepared from $HSiCl_3$.[10–12] This highly versatile framework can easily be chlorinated,[13] oxidized to spherosilicates[14,15] or treated with olefins to produce a variety of hydrosilylation products.[8,16–19] Unfortunately, hydrosilylation of **1** with α-olefins often produces a complex mixture of inseparable products because addition of Si–H to the double bond tends to form both α and β isomers unless the olefin is 3,3-disubstituted.[18,20]



1 R
2 $(CH_2)_3NH_2$
3 $(CH_2)_3OH$

As part of a general effort to develop practical routes to pure $R_8Si_8O_{12}$ frameworks with synthetically useful functional groups, we have been examining the chemistry of $(H_2NCH_2CH_2CH_2)_8Si_8O_{12}$ **2**,[20] which can easily be prepared in multigram quantities from an inexpensive organosilicon precursor.[6,20,21] Procedures for synthesizing amino acid and peptide derivatives of **2** have appeared recently.[22] In this paper we report the syntheses and characterization of many other potentially useful $R_8Si_8O_{12}$ frameworks derived from **2**. We also report a practical synthesis of $(HOCH_2CH_2CH_2)_8Si_8O_{12}$ **3**.

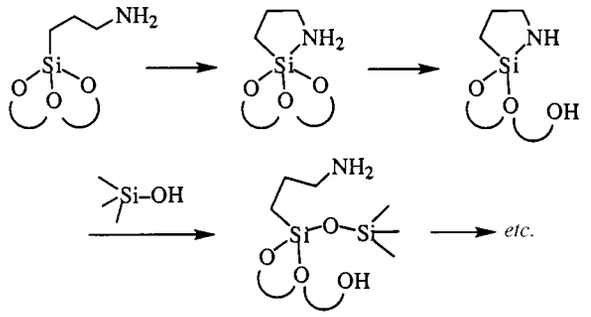
Results and discussion

The synthesis of compound **2** was first claimed in a 1991 US patent issued to Wacker-Chemie.[6] This amine, which is actually obtained as its octahydrochloride salt (*i.e.*, **2**·8HCl) under the conditions described in the patent, is a versatile precursor to many families of functionalized $R_8Si_8O_{12}$ frameworks. The hydrochloride salt of **2** is prepared in one step (35% yield) *via* the hydrolytic condensation of readily available γ-aminopropyltriethoxysilane (MeOH–concentrated HCl, 25 °C, 5 weeks).[20] It is highly soluble in water (>0.9 g mL^{-1}), slightly soluble in methanol (0.03 g mL^{-1}) and DMSO, sparingly soluble in DMF and triethylamine and poorly soluble or insoluble in most other organic solvents, including pyridine. It is also somewhat hygroscopic.

The neutralization of **2**·8HCl to the free amine is difficult to accomplish without compromising the Si/O framework. Some of the difficulties stem from the susceptibility of silsesquioxanes to base-catalysed polymerization and redistribution reactions,[23] but a far greater problem is the inherent instability of the free amine itself. Neutralization of **2**·8HCl to **2** is best accomplished by eluting methanol or 14:1 ethanol–water solutions of the hydrochloride salt across a column of Amberlite IRA-400 resin. Amine **2** is marginally stable in solution and appears to decompose rapidly when the solvent is removed. Small samples of **2** can be prepared by rapidly evaporating aliquots from the stock solution, but to avoid decomposition the amine should be prepared immediately before use or stored in MeOH solutions at −35 °C.

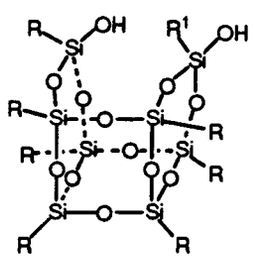
Amine **2** is stable in MeOH (without molecular sieves) at −35 °C and concentrations less than 30 mg mL^{-1} for several months. The shelf-life decreases to a few weeks at −10 °C and several hours at 25 °C. At concentrations greater than 30 mg mL^{-1} in 1:4 MeOH–DME a white resinous precipitate forms within a couple of hours. Analysis of this solid by ^{13}C and ^{29}Si NMR spectroscopy (CD_3CO_2D) indicates >50% decomposition of the Si_8O_{12} framework. Solutions of **2** in dry DMSO (over molecular sieves) can be prepared by neutralizing **2**·8HCl in DMSO or by evaporating MeOH from a solution of **2** in MeOH–DMSO (0 °C, 0.3 Torr, 2 h).

We suspect that there are at least two pathways for decomposition. The most rapid probably involves the formation of hydroxide *via* reaction of water with the free amine. Support for this pathway comes from the observation that other silsesquioxane frameworks are slowly decomposed by exposure to amine bases (*e.g.* Et_3N) in wet solvents and the fact that decomposition is much slower in anhydrous solvents (*e.g.* MeOH over 3 Å sieves). However, the fact that decomposition still occurs when solutions of compound **2** are prepared in DMSO and stored over molecular sieves is consistent with a second mechanism that does not require water. This mechanism might involve attack of the amine nitrogen on Si as illustrated in Scheme 1.



Scheme 1

Framework degradation is also a concern whenever **2**·8HCl is dissolved in water. Although **2**·8HCl is very stable in neutral or acid solutions, small amounts of base can produce free aminopropyl groups, which appear to catalyse framework cleavage when water is the solvent. In fact a ^{29}Si NMR sample of **2**·8HCl prepared in alkaline D_2O (pH 9) exhibits a prominent new set of resonances within 10 min of preparation. These resonances, which grow at the expense of the resonance for **2**·8HCl, eventually represent approximately 30% of the total integrated intensity after 45 min at 25 °C. Attempts to achieve higher conversion led to decomposition. We have not been able to isolate this compound in pure form because it appears to decompose or revert back to **2**·8HCl under many conditions. However, it is believed to be disilanol **4** because of its spectroscopic similarity to **5**.[24] Of particular spectroscopic relevance is the ^{29}Si NMR spectrum, which exhibits 6 resonances with relative integrated intensities of 1:1:1:1:2:2, two of which have chemical shifts characteristic of RSi(OH) groups in an Si_4O_4 ring (δ −56.0 and −56.9). Selective cleavage of a single Si–O–Si linkage in a $R_8Si_8O_{12}$ framework is now well established,[25–27] but to the best of our knowledge this transformation represents the first time selective cleavage has been observed in aqueous media.



4 R = R^1 = [$(CH_2)_3NH_3$]Cl
5 R = c-C_6H_{11}; R^1 = $CH_2CHC(C_6H_4OCH_2Ph)$

The simultaneous synthetic manipulation of many pendant groups requires remarkable efficiency if high yields of a single polyfunctional product are to be obtained. For a transformation of a pure octafunctional starting material (*e.g.* $X_8Si_8O_{12}$) into a pure octafunctional product (*e.g.* $Y_8Si_8O_{12}$), eight sequential chemical reactions must proceed with high conversion and without side reactions. The overall yield of $Y_8Si_8O_{12}$ is only 90% if the yield for each reaction is 98.7% or if as little as 1.3% of all X groups fail to react. The yield of $Y_8Si_8O_{12}$ quickly falls to 66% if conversion of X into Y is 95%. Since many $Y_8Si_8O_{12}$ compounds cocrystallize (or coprecipitate) with derivatives containing fewer Y groups (*e.g.* $Y_7XSi_8O_{12}$ or $Y_6X_2Si_8O_{12}$), the isolation of pure octafunctional products can be very difficult if the reactions are not clean or do not proceed to completion.

In spite of these obstacles, a wide variety of pure $R_8Si_8O_{12}$ frameworks can be prepared by treating **2** or its hydrochloride salt with electrophilic reagents. Provided that reactions are performed under conditions where framework degradation is avoided and competing side reactions do not occur, product yields are normally quantitative by ^{1}H and ^{13}C NMR spectroscopy, and all products can be confidently assigned as pure $R_8Si_8O_{12}$ compounds on the basis of their NMR and IR spectra, combustion analysis and/or mass spectrum. Table 1 summarizes many of our results.

The reactions of compound **2** with carboxylic acid derivatives provide access to a wide range of useful compounds, ranging from simple amides to $R_8Si_8O_{12}$ frameworks possessing eight peptide or carbohydrate residues. Simple amides can be prepared by treating **2**·8HCl with an acyl chloride in the presence of a tertiary amine [*e.g.* Et_3N, pyridine, $(i\text{-}Pr)_2NEt$]. For example, the reaction with benzoyl chloride (Table 1, entry 1) in DMF with $(i\text{-}Pr)_2NEt$ affords **6**.

Amides can also be prepared by treating **2** with anhydrides, such as succinic anhydride (entry 2) and maleic anhydride (entry 3). When performed in MeOH with a generous excess of the anhydride, excellent yields of pure octafunctional carboxylic acids are obtained. The reaction of **2** with maleic anhydride is particularly interesting because the product spontaneously precipitates from solution without coprecipitating partially functionalized derivatives.

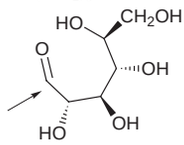
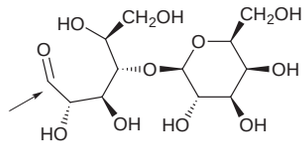
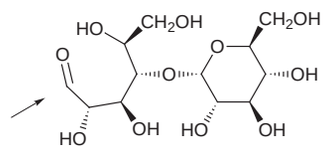
Octaamine **2** reacts with lactones to afford a variety of useful compounds. These reactions are relatively slow and generally require a generous excess of lactone to achieve the high conversions necessary for octafunctionalization. In the case of caprolactone (entry 4), acylation of **2** can be accomplished by heating **2** and an excess of lactone under vacuum at 70 °C for 3 to 4 h. In the case of carbohydrate lactones (entries 5–7), acylation should be performed at 25 °C for 1 to 3 d. For all of these reactions it is desirable to use **2** rather than its hydrochloride salt in combination with Na_2CO_3 or a tertiary amine. This limits the amount of base present in the reaction mixture and greatly reduces the formation of ill defined silsesquioxane resins derived from base-catalysed cleavage and polymerization of the Si_8O_{12} framework.

The NMR spectra of compounds **10**, **11** and **12** exhibit complex concentration-dependent behavior that is consistent with two distinct environments for the pendant groups. The reasons for this behavior are not known with certainty, but the two environments appear to be due to restricted rotation about the amide C–N bonds (*i.e. cis*/*trans* isomerization) and strong inter- and intra-molecular interactions between pendant carbohydrate groups (*i.e.* aggregation). This behavior, as well as a preliminary study of lectin binding by **11** and **12**, is discussed in ref. 28.

Octaamine **2** reacts readily with isocyanates to afford octafunctional ureas. For example, the reactions of **2** with allyl isocyanate (entry 8) and *n*-butyl isocyanate (entry 9) produce **13** and **14**, respectively. Freshly prepared solutions of **13** and **14** in DMSO (40 mg mL^{-1}) form gels that resist crystallization for more than a month, but crystalline samples can be obtained quickly by recrystallization from hot alcohol.

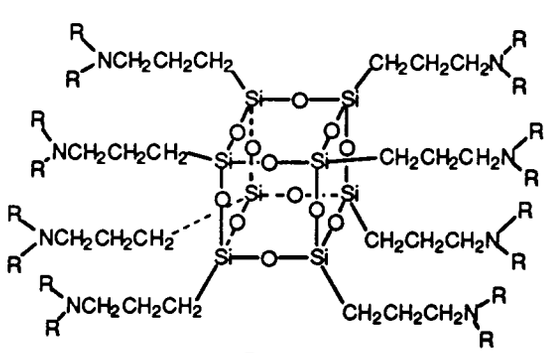
The reaction of compound **2** with phosgene Cl_2CO is particularly noteworthy because it provides access to an octaisocyanate (*i.e.* **15**) with many interesting possibilities as a precursor to both hybrid inorganic–organic materials[29,30] and more elaborate POSS frameworks. The synthesis of **15** can easily be accomplished on a small scale by adding saturated aqueous $NaHCO_3$ to a biphasic reaction mixture containing phosgene in CH_2Cl_2 and **2**·8HCl in water. Separation of the organic layer after 1 h, filtration through cotton (to dry) and evaporation of the solvent affords **15** as a colorless oil. On one occasion the yield of **15** was 80%, but all other times it was considerably lower (11 to 47%). The product obtained in this fashion is spectroscopically pure and can be used to prepare other frameworks, such as $[n\text{-}BuNHCONH(CH_2)_3]_8Si_8O_{12}$ **14** and $[t\text{-}BuNHCONH(CH_2)_3]_8Si_8O_{12}$ **18**. Isocyanate **15** appears to be indefinitely stable at low temperatures (−35 °C) and stable at elevated temperatures (25–80 °C) for short periods, but it quickly produces insoluble polyureas upon exposure to traces of water. It also appears to polymerize on standing at room temperature.

Table 1 Reactions of compound **2** with electrophilic reagents (E): $[H_2N(CH_2)_3]_8Si_8O_{12}$ + E ⟶ $[R^1R^2N(CH_2)_3]_8Si_8O_{12}$

Entry	E (equivalents)[a]	Reaction conditions	Product	R^1	R^2	Yield (%)[b]
1	$ClCOC_6H_5$ (12)[c]	$(i\text{-}Pr)_2NEt$, DMF, 0–25 °C, 10 h	**6**	H	COC_6H_5	49
2	Succinic anhydride (20)	CH_3OH, 25 °C, 10 h	**7**	H	$COCH_2CH_2CO_2H$	58
3	Maleic anhydride (28)	CH_3OH, 25 °C, 10 h	**8**	H	*cis*-$COCH{=}CHCO_2H$	64
4	ε-Caprolactone (80)	Neat, 70 °C, 3.4 h	**9**	H	$CO(CH_2)_5OH$	23
5	δ-Gluconolactone (32)	DMSO, 25 °C, 72 h	**10**	H		30
6	δ-Lactonolactone (14)	DMSO, 25 °C, 24 h	**11**	H		53
7	δ-Maltonolactone (15)	DMSO, 25 °C, 24 h	**12**	H		26
8	$H_2C{=}CHCH_2NCO$ (11)	DMSO, 25 °C, 10 h	**13**	H	$CONHCH_2C(H){=}CH_2$	90
9	$CH_3(CH_2)_3NCO$ (11)	DMSO, 25 °C, 3 h	**14**	H	$CONH(CH_2)_3CH_3$	65
10	Cl_2CO (27)	$NaHCO_3$ (aq), CH_2Cl_2, 0 °C, 1 h	**15**	CO	N.A.	11–47
11	$H_2C{=}CHCO_2CH_3$ (306)	CH_3OH, 25 °C, 24 h	**16**	R^2	$CH_2CH_2CO_2CH_3$	73
12	$CH_2O/(C_6H_5)_2PH$ (24)	CH_3OH, toluene, 65 °C, 14 h	**17**	R^2	$CH_2P(C_6H_5)_2$	37

[a] Equivalents of E per Si_8O_{12} framework. [b] Isolated yield for reaction that proceeded with complete conversion of $(CH_2)_3NH_2$ to $(CH_2)_3NR^1R^2$ as judged by ^1H and ^{13}C NMR spectroscopy. [c] Compound **2**·8HCl was used as the starting material.

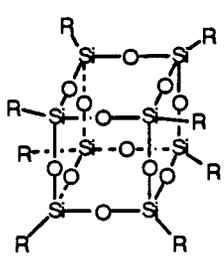
Frameworks with sixteen equivalent pendant groups can be prepared by replacing all amine protons of compound **2** with an appropriate electrophile. For example, the reaction of **2** with an excess of methyl acrylate produces **16**[20] under conditions typically used to prepare polyamidoamino (PAMAM) dendrimers from polyamine cores (entry 11).[31,32] Similarly, an interesting phosphine-substituted framework with sixteen Ph_2P groups can be prepared by adapting known methodology for attaching phosphine pendant groups to amine-terminated PAMAM dendrimers.[33] The reaction of **2** with an excess of CH_2O/Ph_2PH (Table 1, entry 12) affords **17**, while the same reaction performed using **2**·8HCl and excess of Et_3N appears to produce a hydrochloride salt of **17**.



R
16 $CH_2CH_2CO_2Me$
17 CH_2PPh_2

Synthesis of $[HO(CH_2)_3]_8Si_8O_{12}$ 3

Amine **2** and its hydrochloride salt are excellent precursors to a wide range of functionalized silsesquioxanes, but there are many applications where both the basicity of an amine or amide nitrogen atom and the ability of a primary amine to react with more than one equivalent of electrophile are undesirable. In these cases an $R_8Si_8O_{12}$ synthon with eight hydroxypropyl groups might be useful. We have therefore devised a method for preparing compound **3**.



R
3 $(CH_2)_3OH$
20 $(CH_2)_3Cl$
21 $(CH_2)_3I$
22 $(CH_2)_3ONO_2$

The immediate precursor to compound **3** is nitrate ester **22**, which is readily available in three steps from inexpensive $Cl(CH_2)_3SiCl_3$. Hydrolytic condensation of $Cl(CH_2)_3SiCl_3$ affords **20** in 25–40% yield,[6,8] which upon reaction with NaI affords **21**.[8] Hydrolysis of **21** is very difficult to achieve without destroying the Si_8O_{12} framework. However, first treating **21** with $AgNO_3$ in MeCN to produce **22**, then hydrogenolysis of **22** with 10% Pd/C in ethyl acetate–MeOH (800 psig H_2, 25 °C, 3 d) affords **3** as a waxy white solid in 85% overall yield. A related series of $[RSiO_{3/2}]_n$ frameworks possessing hydroxyalkyl substituents can also be prepared *via* hydrosilylation reactions of $[HSiO_{3/2}]_n$ with α,ω-trimethylsiloxyalkenes,[34] but product yields are typically lower (8–10%) and it is likely that addition of Si–H to the double bonds produces both α and β isomers.

Concluding remarks

We have identified practical routes to a wide variety of functionalized $R_8Si_8O_{12}$ frameworks, including $[HO(CH_2)_3]_8Si_8O_{12}$ **3**, $[OCN(CH_2)_3]_8Si_8O_{12}$ **15**, $[(Ph_2PCH_2)_2N(CH_2)_3]_8Si_8O_{12}$ **17** and many compounds derived from reactions of $[H_2N(CH_2)_3]_8Si_8O_{12}$ **2** with electrophilic reagents. Provided that reactions are performed under conditions where framework degradation is avoided and competing side reactions do not occur, good to excellent yields of many pure $R_8Si_8O_{12}$ compounds can be obtained.

Experimental

General experimental protocol and procedures have been

reported earlier.[24] Unless otherwise noted, all manipulations were performed under an atmosphere of dry nitrogen using either standard Schlenk techniques or a Vacuum Atmospheres Corp. Dri-Lab. Unless otherwise noted, reagent-grade chemicals were used without further purification for all work described here. Dimethyl sulfoxide (DMSO) was dried over activated 4 Å molecular sieves prior to use. Dimethylformamide (DMF) was distilled and stored under an atmosphere of dry nitrogen. Methanol was freshly distilled from magnesium turnings. 10% Pd/C (Aldrich) was activated under vacuum (200 °C, 0.001 Torr, 12 h), and used under an atmosphere of dry nitrogen. Phosgene was obtained as a 1.89 M solution in toluene (Fluka). Methyl acrylate (Aldrich) was distilled from CaH_2 under nitrogen immediately before use. γ-Aminopropyltriethoxysilane was obtained as a generous gift from Witco/OSi specialties.

The NMR spectra were recorded on General Electric GN-500 (^{1}H, 500.03; ^{13}C, 125.75; ^{31}P, 202.5; ^{29}Si, 99.37), Omega-500 (^{1}H, 500.22; ^{13}C, 125.79; ^{29}Si, 99.34) or Bruker DRX-500 (^{1}H, 500.03; ^{13}C, 125.74; ^{29}Si, 99.30 MHz) spectrometers, infrared spectra on a Perkin-Elmer 1600 Series FTIR spectrometer, mass spectra on a VG Analytical Autospec E double-focussing spectrometer or a Perceptive Biosystems matrix-assisted laser desorption ionization–time of flight (MALDI-TOF) Voyager DE STR spectrometer. Combustion analyses (C, H, N) were made with a Carlo Erba Instruments Fisons Elemental Analyzer. Melting points were measured with a Laboratory Devices Mel-Temp apparatus and are uncorrected.

Syntheses

Compound 2·8HCl. Concentrated HCl (200 mL) was added carefully with stirring to a solution of γ-aminopropyltriethoxysilane (150 mL, 0.641 mol) in MeOH (3.6 L) in a 4.0 L glass bottle. The bottle was capped and allowed to stand for 6 weeks at 25 °C. The product usually begins to crystallize from the reaction mixture after 3–4 weeks, but in the event that no crystals form spontaneously crystallization can be induced by agitating or adding seed crystals from a previous reaction. The product obtained in 30% yield (24.9 g) by filtering the reaction mixture, washing with cold MeOH, and drying (0.001 Torr, 25 °C) is spectroscopically pure and suitable for most purposes. An additional 4.2 g (5%) were collected by reducing the filtrate to 1/3 of its original volume. Analytically pure **2**·8HCl can be obtained as white microcrystalline powder by recrystallization from hot MeOH. ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 8.25 (s, NH_3, 24 H), 2.75 (t, CH_2N, 16 H), 1.71 (m, $SiCH_2CH_2$, 16 H) and 0.71 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 41.01 (s, CH_2N), 20.61 (s, $SiCH_2CH_2$) and 8.44 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.4 (s). Mass spectrum (MALDI-TOF, dihydroxybenzoic acid (DHB) matrix): calc. for $C_{24}H_{72}Cl_8N_8O_{12}Si_8$, $[M + H - 8\ HCl]^+$ *m*/*z* 881.29, found 881.4 (100%); $[M - NH_3 - 8\ HCl]^+$ *m*/*z* 863.25, found 863.4 (39%) [Found (Calc. for $C_6H_{18}Cl_2N_2O_3Si_2$): C, 24.69 (24.57); H, 6.40 (6.19); N, 9.40 (9.55)%]. mp 277 °C (decomp).

Compound 2 *via* neutralization of 2·8HCl. Amberlite IRA-400 ion-exchange resin (37 g) was prepared by successive washing with water (4 × 200 mL), 1 M NaOH (3 × 200 mL), water (6 × 200 mL) and the elution solvent, which was either MeOH, 4:1:1 EtOH–DME–2-propanol or 14:1 EtOH–water (6 × 200 mL); the resin was suspended in eluent and chilled (−10 °C, 2 h) before use. Half of the resin beads were loaded onto a column (3.5 cm outside diameter); the other half was used to dissolve a suspension of **2**·8HCl (6 g) in the minimum amount of eluent at 0 °C. Elution across the column produced a stock solution (15–20 mM, 250–300 mL, 0 °C) of **2** that tested negative for chloride. Small samples of **2** can be prepared by rapidly evaporating aliquots from the stock solution, but to avoid decomposition the amine should be prepared immediately before use or stored in MeOH solutions at −35 °C. ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 4.3 (s, NH_2 and H_2O), 2.50 (t, J = 7.4, CH_2N, 16 H), 1.42 (m, $SiCH_2CH_2$, 16 H) and 0.54 (t, J = 7.3 Hz, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, CD_3OD, 25 °C): δ 44.87 (s, CH_2N), 26.88 (s, $SiCH_2CH_2$) and 9.57 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, CD_3OD, 25 °C): δ −66.4 (s). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{24}H_{64}N_8O_{12}Si_8$, $[M + H]^+$ *m*/*z* 881.29, found 881.5 (100%); $[M - NH_3]^+$ 863.25, found 863.5 (49%).

Compound 4 in basic (pH 9) D_2O. The NMR spectrum of compound **2**·8HCl in basic (pH 9) D_2O exhibits prominent resonances assignable to **4** within 20 min of sample preparation. Attempts to isolate pure **4** were not successful, but a sample containing ≈30% of **4** was obtained by agitating a solution of **2**·8HCl (1.0 g, 0.853 mmol) in D_2O (pH 9, 0.5 mL) for 20 min at 25 °C. Addition of CH_3CO_2H (5 mL) and evaporation (25 °C, 10 Torr) produced a hard, colorless resin (1.147 g), which was triturated with EtOH (40 mL × 3). The remaining solid was collected by vacuum filtration, washed with EtOH and dried (25 °C, 0.001 Torr) to afford 775 mg of solid consisting of a 70:30 mixture of **2**·8HCl and **4** (by ^{13}C and ^{29}Si NMR). Samples containing approximately equimolar **2**·8HCl and **4** can be prepared by selective crystallization of **2**·8HCl from MeOH–EtOH (1:4 volume ratio) or by diffusion of MeCN into a methanol solution of **2**·8HCl and **4**, but disilanol **4** itself has resisted crystallization. ^{1}H NMR (125.8 MHz, D_2O, 25 °C): δ 2.95 (t, J = 8.0 Hz, CH_2N), 1.73 (m, $SiCH_2CH_2$, 16 H) and 0.74 (s, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, D_2O, 25 °C): δ 41.68–41.48 (m, CH_2N), 20.74–20.38 (m, $SiCH_2CH_2$), 9.75, 8.66, 8.56, 8.46 and 7.80 (s, 1:1:2:2:2 for $SiCH_2$ assuming 50% **2**·8HCl at δ 7.86). ^{29}Si-{^{1}H} NMR (99.4 MHz, D_2O, 25 °C): δ −56.0, −56.9, −65.1, −65.3, −66.3, −66.9 (s, 1:1:1:1:2:2 assuming 50% **2**·8HCl at δ −66.5).

Compound 6. Benzoyl chloride (0.11 mL, 1.02 mmol) was added dropwise to a suspension of compound **2**·8HCl (100 mg, 0.085 mmol) and $(i\text{-}Pr)_2NEt$ (0.30 mL, 1.7 mmol) in DMF (4 mL, 0 °C). After stirring overnight, the crude product was precipitated by dropwise addition to 1 M HCl (aqueous, 70 mL, 0 °C). Filtration, extraction with DMSO (4 mL), precipitation with cold saturated $NaHCO_3$ (70 mL), washing with water and drying *in vacuo* (25 °C, 0.01 Torr) afforded a white solid (133 mg). Analysis by ^{1}H and ^{13}C NMR spectroscopy indicated quantitative formation of **6**. Analytically pure material (71 mg, 49%) was prepared by slowly adding DMSO (10 mL) to a solution of **6** in MeCN (100 mL) at 0 °C. ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 8.45 (t, NH, 8 H), 7.78, (d, *o*-CH, 16 H), 7.40 (t, *p*-CH, 8 H), 7.37 (m, *m*-CH, 16 H), 3.18 (m, CH_2N, 16 H), 1.62 (m, $SiCH_2CH_2$, 16 H) and 0.64 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 166.27 (s, CO), 134.59, 130.95, 128.15, 127.10 (s, C_6H_5), 41.66 (s, CH_2N), 22.31 (s, $SiCH_2CH_2$) and 8.79 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.5. Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{80}H_{96}N_8O_{20}Si_8$, $[M + H]^+$ *m*/*z* 1713.50, found 1713.68 (47%); $[M + Na]^+$ 1735.48, found 1735.68 (50%).

Compound 7. A solution of compound **2** (88 mg, 0.100 mmol) in MeOH (4.0 mL) was added to succinic anhydride (200 mg, 2.0 mmol). Within 5 min of stirring at ambient temperature the anhydride completely dissolved to afford a clear solution, which was stirred overnight. Dropwise addition of the reaction mixture to water (30 mL, 25 °C) and evaporation of MeOH (25 °C, 0.01 Torr) afforded a white solid, which was collected by vacuum filtration, washed with water, dried, redissolved in MeOH and evaporated to dryness. The material prepared by this method (97 mg, 58%) is spectroscopically pure (by ^{1}H and ^{13}C NMR spectroscopy). An analytically pure sample (25 mg)

was prepared by slowly adding EtOH to a solution of **7** (30 mg) in MeOH (0.5 mL). ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 7.81 (br, NH, 8 H), 3.01 (br, CH_2N, 16 H), 2.40 (br, CH_2, 16 H), 2.30 (br, CH_2, 16 H), 1.43 (br, $SiCH_2CH_2$, 16 H) and 0.58 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 173.90 (s, CO), 170.94 (s, CO), 41.01 (s, CH_2N), 30.00 (s, CH_2), 29.17 (s, CH_2), 22.49 (s, $SiCH_2CH_2$) and 8.75 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.17 (s). IR (KBr): 1701, 1638 ($\nu_{NC=O}$), 1103vs cm^{-1} (ν_{SiOSi}). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{56}H_{96}N_8O_{36}Si_8$; $[M - H]^-$ *m/z* 1679.40, found 1679.2; $[M - 2H + Na]^-$ 1701.38, found 1701.2; $[M - C_4H_5O_3]^-$ 1579.38, found 1579.2 [Found (Calc. for $C_{14}H_{24}N_2O_9Si_8$): C, 40.40 (39.99); H, 5.79 (5.75); N, 6.70 (6.66)%].

Compound 8. A solution of compound **2** (440 mg, 0.499 mmol) and maleic anhydride (1.40 g, 0.014 mol) in MeOH (20 mL) was stirred overnight at 25 °C. The white precipitate that formed overnight was collected by filtration, washed with cold methanol, and dried (25 °C, 0.001 Torr) to afford **8** as a spectroscopically pure white solid (530 mg, 64%). An analytically pure sample (159 mg) was prepared by recrystallizing **8** (250 mg) from MeOH (40 mL, reflux to −30 °C). ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 9.04 (s, NH, 8 H), 6.37 (d, J = 12.5, CH, 8 H), 6.22 (d, J = 12.5 Hz, CH, 8 H), 3.15 (t, CH_2N 16 H), 1.54 (m, $SiCH_2CH_2$, 16 H) and 0.65 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (128.5 MHz, DMSO-d_6, 25 °C): δ 165.47, 165.40 (s, CO), 132.91, 131.64 (s, CH), 41.41 (s, CH_2N), 21.82 (s, $SiCH_2CH_2$) and 8.61 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.17 (s). IR (KBr): 1720, 1707, 1634vs, ($\nu_{NC=O}$), 1114vs cm^{-1} (ν_{SiOSi}). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{56}H_{80}N_8O_{36}Si_8$; $[M + Na]^+$ *m/z* 1687.27, found 1687.1; $[M - C_4H_2O_3 + H]^+$ 1567.29, found 1567.2; $[M - C_4H_2O_3 + Na]^+$ 1589.27, found 1589.1; $[M - H]^-$ 1663.28, found 1663.2; $[M - 2H + Na]^-$ 1685.26, found 1685.2; $[M - 2H + K]^-$ 1701.23, found 1701.1; $[M - C_4H_3O_3]^-$ 1565.27, found 1565.3 [Found (Calc. for $C_{14}H_{20}N_2O_9Si_2$): C, 40.54 (40.37); H, 4.90 (4. 84); N, 6.53 (6.73)%].

Compound 9. ε-Caprolactone (6.0 mL, 50.6 mmol) was added to a solution of compound **2** (540 mg, 0.630 mmol) in MeOH (20 mL). Methanol was promptly removed under vacuum (25 °C, 0.02 Torr), then the reaction mixture was heated under vacuum (70 °C, 0.02 Torr, 3–4 h). The hard, yellow, non-Si-containing solid produced was removed by filtration. Dropwise addition of the filtrate to CH_2Cl_2 (100 ml) over 0.5 h precipitated crude **9**, which was collected by filtration, washed with CH_2Cl_2, dissolved in MeOH, filtered and evaporated (25 °C, 0.001 Torr) to afford a tacky yellow solid (770 mg). Analysis of this solid by ^{1}H and ^{13}C NMR spectroscopy indicated the presence of only **9**. Purification was performed by adding a solution of **9** (770 mg) in EtOH (6 mL) dropwise to Et_2O (100 mL, 0 °C). Centrifugation of the resulting turbid suspension afforded a yellowish solid, which was dissolved in EtOH, decolorized with activated charcoal, and evaporated (25 °C, 0.001 Torr) to afford a pale yellow product (376 mg). This was dissolved in 20:1 CH_2Cl_2–MeOH (5 mL) and eluted across a thin pad of silica with 20:1 CH_2Cl_2–MeOH (80 mL). Evaporation of the solvent (25 °C, 0.001 Torr) afforded a pale yellow solid (262 mg). Samples obtained in this fashion are suitable for most purposes. Analytically pure product was prepared by dropwise addition of MeCN (20 mL, 0 °C) to a solution of **9** (83 mg) in MeOH (2 mL); vacuum filtration, washing with MeCN and drying (25 °C, 0.001 Torr) afforded **9** as a fine white powder (40 mg). ^{1}H NMR (500.2 MHz, MeOH-d_4, 25 °C): δ 8.1 (s, NH), 3.54 (t, J = 6.6, CH_2OH, 16 H), 3.15 (t, J = 7.0, CH_2N, 16 H), 2.20 (t, J = 7.6, $COCH_2$, 16 H), 1.64–1.53 (m, CH_2, 48 H), 1.38 [m, $CH_2(CH_2)_2OH$, 16 H] and 0.64 (t, J = 8.1 Hz, $SiCH_2$, 16H). ^{13}C-{^{1}H} NMR (125.8 MHz, MeOH-d_4, 25 °C): δ 174.02 (s, CO), 60.72 (s, CH_2OH), 40.74 (s, CH_2N), 34.94, 31.33, 24.91, 24.56 (s, CH_2), 21.94 (s, $SiCH_2CH_2$) and 7.93 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, MeOH-d_4, 25 °C): δ −66.4 [Found (Calc. for $C_{72}H_{144}N_8O_{28}Si_8 \cdot H_2O$): C, 47.78 (47.71); H, 8.21 (8.12); N, 5.86 (6.18)%].

Compound 10. A solution of compound **2** (500 mg, 0.57 mmol) in MeOH (20.0 mL) was added to a solution of δ-gluconolactone (3.20 g, 18.24 mmol) in dry DMSO (20 mL); the MeOH was immediately removed by stirring under vacuum (25 °C, 0.001 Torr). The solution was stirred under nitrogen (25 °C, 72 h), filtered, and then evaporated (30 °C, 0.01 Torr) to afford a colorless resin, which was dialysed against water (25 °C, 3 × 4 L) over a period of 24 h. Evaporation (30 °C, 0.01 Torr) of the resulting solution afforded **10** as a white powder. Analysis by ^{1}H and ^{13}C NMR spectroscopy indicated quantitative formation of **10**. Final purification was performed by slowly adding an excess of MeOH to an aqueous solution of **10** and cooling to −30 °C; vacuum filtration, washing with cold MeOH and drying (60 °C, 0.001 Torr, 3 d) afforded **10** as a white powder in 30% yield (400 mg). ^{1}H NMR (500.2 MHz, 31 mM in DMSO-d_6, 100 °C): δ 7.38 (br, NH, 8 H), 4.42–3.2 (m, carbohydrate, 88 H), 3.13, 2.80 (br, CH_2N, 16 H), 1.56, 1.53 (br, $SiCH_2CH_2$, 16 H) and 0.64 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, 31 mM in DMSO-d_6, 25 °C): δ 172.10 (s, CO), 79.87, 73.10, 72.04, 70.17, 63.10, 40.4 (br, CH_2N), 22.02 (br, $SiCH_2CH_2$) and 8.34 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, 63 mM in DMSO-d_6, 25 °C): δ −66.1 and −66.8. mp 160 °C (decomp.).

Compound 11. A solution of compound **2** (216 mg, 0.245 mmol) in MeOH (3.3 mL) was added to a solution of *O*-β-D-galactopyranosyl-(1→4)-D-glucono-1,5-lactone[35,36] (1.16 g, 3.41 mmol) in dry DMSO (*ca.* 3 mL); the MeOH was immediately removed by stirring under vacuum (25 °C, 0.007 Torr). The solution was stirred under nitrogen (25 °C, 24 h), filtered, and evaporated (30 °C, 0.01 Torr) to afford a colorless resin, which was dialysed against water (25 °C, 3 × 4 L) over a period of 24 h. Evaporation (30 °C, 0.01 Torr) of the resulting solution afforded **11** as a spectroscopically pure white powder (472 mg, 53%). Analytically pure product was obtained by slowly adding an excess of MeOH to an aqueous solution of **11** and cooling to −30 °C; vacuum filtration, washing with cold MeOH and drying (60 °C, 0.001 Torr) afforded **11** as a white powder (340 mg). ^{1}H NMR (500.0 MHz, 5 mM in DMSO-d_6, 25 °C): δ 7.66 (br, NH, 8 H), 5.17–3.38 (m, carbohydrate, 168 H), 3.10, 3.04 (br, CH_2N, 16 H), 1.47 (br, $SiCH_2CH_2$, 16 H) and 0.56 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.7 MHz, 5 mM in DMSO-d_6, 25 °C): δ 172.36 (s, CO), 104.66 (s, 1′-C), 83.16 (s, 4-C), 75.69, 73.22, 72.00, 71.70, 71.43, 71.17, 70.55, 68.23 (4′-C), 62.34 (s, 6-C), 60.72 (6′-C), 40.89 (br, CH_2N), 22.57 (br, $SiCH_2CH_2$) and 8.77 (br, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, 5 mM in D_2O, 25 °C): δ −65.9 and −66.9 (20%). Mass spectrum (MALDI-TOF, DHB-HIQ matrix): calc. for $C_{120}H_{224}N_8O_{100}Si_8$, $[M + Na]^+$ *m/z* 3624.1, found 3623.9; $[M - C_{12}H_{19}O_{11} + K]^+$ 3300.95, found 3302.0; $[M - C_{12}H_{19}O_{11} + Na]^+$ 3284.99, found 3284.0; $[M - C_{12}H_{19}O_{11} + H]^+$ 3261.99, found 3262.1 [Found (Calc. for $C_{120}H_{224}N_8O_{100}Si_8 \cdot 3H_2O$): C, 39.63 (39.40), H, 6.15 (6.34), N, 3.05 (3.06)%]. mp 148 °C (decomp.).

Compound 12. Amine **2** (65 mg, 0.075 mmol) was treated with *O*-α-D-glucopyranosyl-(1→4)-D-glucono-1,5-lactone[35,36] (370 mg, 1.088 mmol) as described above for the preparation of **11**. Isolation and purification as described above afforded **12** in 26% yield (70 mg) as an analytically pure white powder. ^{1}H NMR (500.0 MHz, 5 mM in D_2O, 25 °C): δ 7.98 (br, NH, 8 H), 4.95–3.30 (m, carbohydrate, 128 H), 3.13 (br, CH_2N, 16 H), 1.52 (br, $SiCH_2CH_2$, 16 H) and 0.59 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.7 MHz, 5 mM in D_2O, 25 °C): δ 174.66 (s, CO), 101.19 (s, 1′-C), 82.70 (s, 4-C), 73.58, 73.19, 73.06, 72.59, 72.50, 72.38, 62.81 (s, 6-C), 61.02 (6′-C), 42.1 (br, CH_2N), 22.65 (br,

$SiCH_2CH_2$) and 8.80 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, 5 mM in D_2O, 25 °C): δ −65.9, −66.9 (20%). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{30}H_{56}N_2O_{25}Si_2$; $[M + K]^+$ *m/z* 3641.1, found 3642.8; $[M + Na]^+$ 3624.1, found 3623.9; $[M - C_{12}H_{19}O_{11} + K]^+$ 3300.95, found 3299.8; $[M - C_{12}H_{19}O_{11} + Na]^+$ 3284.99, found 3283.9 [Found (Calc. for $C_{120}H_{224}N_8O_{100}Si_8 \cdot 4H_2O$): C, 39.29 (39.21); H, 6.28 (6.36); N, 2.66 (3.05)%].

Compounds 13 and 14. In a typical reaction the isocyanate (11 equivalents) was added to a solution of compound **2** (800 mg, 0.908 mmol) in $MeOCH_2CH_2OMe$–EtOH–2-propanol (4:1:1, 25 mL); the solution volume was reduced by a factor of two by evaporation (30 °C, 10 Torr). After 3–10 h the white solid formed by the reaction was collected, washed with cold CH_2Cl_2, then dried (25 °C, 0.001 Torr). Analysis of the crude product by NMR (^{1}H, ^{13}C, and ^{29}Si) spectroscopy indicated complete conversion of aminopropyl groups into urea functionalities and product purities greater than 95%. Pure **13** was prepared by recrystallizing the crude product from hot MeOH. Yield 1.27 g (90%). ^{1}H NMR (500.2 MHz, DMSO-d_6, 60 °C): δ 5.86–5.79 (m, $CH_2NHCONHCH_2CH$, 24 H), 5.10 (dd, J = 17.2, 1.6, CH, 8 H), 5.00 (d, J = 10.3 Hz, CH, 8 H), 3.62 (m, CH_2CH, 16 H), 2.98 (m, CH_2N, 16 H), 1.45 (m, $SiCH_2CH_2$, 16 H) and 0.59 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 60 °C): δ 157.81 (s, CO), 136.56 (s, CH), 113.99 (s, CH_2), 41.53 (s, CH_2N) 41.45 (s, CH_2N), 23.09 (s, $SiCH_2CH_2$) and 8.37 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 60 °C): δ −66.03 (s). IR (KBr): 1628, 1583vs, (ν_{NCO}), 1116vs cm^{-1} (ν_{SiOSi}) [Found (Calc. for $C_{56}H_{104}N_{16}O_{20}Si_8 \cdot EtOH$): C, 43.58 (43.75); H, 6.76 (6.96); N, 14.07 (14.07)%]. mp 220 °C (decomp.). Analytically pure **14** was obtained by recrystallization from $CHCl_3$–MeOH (1:1, −30 °C) followed by recrystallization from hot EtOH. Yield: 891 mg (65%). ^{1}H NMR (500.2 MHz, DMSO-d_6, 80 °C): δ 5.70 (t, NH, 8 H), 5.62 [t, $(CH_2)_3NH$, 8 H], 2.99 (m, CH_2N, 32 H), 1.46 (m, $SiCH_2CH_2$, 16 H), 1.36 (m, $CH_2CH_2CH_3$, 16 H), 1.26 (m, $CH_2CH_2CH_3$, 16 H), 0.87 (t, $CH_2CH_2CH_3$, 24 H) and 0.59 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 80 °C): δ 157.92 (s, CO), 41.32 (s, CH_2N), 38.68 (s, CH_2N), 31.74 (s, CH_2), 22.97 (s, $SiCH_2CH_2$), 19.04 (s, CH_2), 13.07 (s, CH_3) and 8.26 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 80 °C): δ −66.01 (s). IR (KBr): 1628, 1577vs ($\nu_{NC=O}$), 1124vs cm^{-1} (ν_{SiOSi}) [Found (Calc. for $C_{16}H_{34}N_4O_5Si_2$): C, 45.93 (45.90); H, 8.29 (8.19); N, 13.05 (13.38)%]. mp 161 °C (decomp.).

Compound 15. Following the general procedure described by Nowick *et al.*,[37] saturated $NaHCO_3$ (10 mL) was added dropwise at 0 °C with vigorous stirring to a biphasic mixture of phosgene (3 mL of 1.89 M toluene solution) in CH_2Cl_2 (10 mL) and compound **2**·8HCl (239 mg, 0.210 mmol) in water (4 mL). The pH was monitored and the reaction terminated when the aqueous layer became acidic (*ca.* 1 h at 0 °C). The organic layer was separated, dried by filtration through a wad of cotton, and then evaporated (25 °C, 0.001 Torr) to afford **15** as a colorless liquid, spectroscopically pure by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C): δ 3.33 (t, CH_2N, 16H), 1.73 (m, $SiCH_2CH_2$, 16H) and 0.77 (t, $SiCH_2$, 16H). ^{13}C-{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 122.05 (s, CO), 45.05 (s, CH_2N), 24.88 (s, $SiCH_2CH_2$) and 8.87 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −67.02 (s). IR (KBr): 2274vs ($\nu_{NC=O}$) and 1110vs cm^{-1} (ν_{SiOSi}) [Found (Calc. for polymerized product calculated for the formula $C_8H_{12}N_2O_5Si_2$): C, 35.13 (35.28); H, 4.90 (4.44); N, 10.17 (10.29)%].

Compound 16. Following the standard procedure for the synthesis of PAMAM dendrimers,[31,32] methyl acrylate (0.8 mL, 8.884 mmol) was added *via* syringe to a solution of freshly prepared compound **2** (65 mg, 0.029 mmol) in methanol (1 mL) under N_2(g). After 24 h at 25 °C analysis by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy indicated complete reaction of aminopropyl groups. Evaporation of the volatiles (25 °C, 0.001 Torr) produced a colorless, glassy solid, which was triturated with dry methanol and dried (25 °C, 0.001 Torr). All attempts to recrystallize or precipitate **16** as a powder were unsuccessful, but samples obtained in this fashion are spectroscopically pure and can be treated with ethylenediamine to produce amine-terminated PAMAM dendrimers.[20] Yield: 204 mg (73%). ^{1}H NMR (500.2 MHz, CD_3OD, 25 °C): δ 3.61 (s, CH_3, 48 H), 2.71 (t, CH_2CO, 32 H), 2.40 (m, CH_2NCH_2, 48 H), 1.51 (m, $SiCH_2CH_2$, 16 H) and 0.593 (t, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, CD_3OD, 25 °C): δ 174.53 (s, CO), 57.23 [s, $CH_2N(CH_2)_2$], 52.13 (s, CH_2CO_2), 50.34 (s, CH_3), 33.27 [s, $CH_2N(CH_2)_2$], 21.48 (s, $SiCH_2CH_2$) and 10.21 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, CD_3OD, 25 °C): δ −66.0 (s). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{88}H_{160}N_8O_{44}Si_8$, $[M + H]^+$ *m/z* 2257.88, found 2256.5 (47%); $[M + K]^+$ 2295.83, found 2295.9 (62%).

Compound 17. Following the general procedure described by Reetz *et al.*,[33] H_2CO (37%, 2 mL, 26.7 mmol) was added to a solution of $HP(C_6H_5)_2$ (497 mg, 2.67 mmol) in degassed MeOH (5 mL). This solution was stirred under nitrogen at 25 °C for 10 min, heated to 65 °C for 10 min, then evaporated to dryness (25 °C, 0.001 Torr). To the resulting residue was added a solution of compound **2** (97.5 mg, 0.111 mmol) in degassed 45% MeOH–toluene (7 mL). After heating at 65 °C for 14 h, the reaction mixture was evaporated (25 °C, 0.001 Torr) to afford a white solid. Purification was performed by thrice adding a solution of **17** in THF (1 mL) dropwise to MeOH (10 mL). A final washing with MeOH and drying *in vacuo* (25 °C, 0.001 Torr) afforded **17** as a fine white powder in 37% yield (165 mg). ^{1}H NMR (500.2 MHz, $CDCl_3$, 25 °C): δ 7.37–7.21 (br, C_6H_5, 160 H), 3.50 (br, CH_2, 32 H), 2.77 (br, CH_2N, 16 H), 1.51 (br, $SiCH_2CH_2$, 16 H) and 0.50 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 138.20 (d, J = 13.3, C_{quat}), 133.01 (d, J = 18.1, CH), 128.36 (s, CH), 128.26 (d, J = 6.5, CH), 58.93 (t, J = 9.5, CH_2N), 58.46 (d, J = 5.8 Hz, CH_2), 19.68 (s, $SiCH_2CH_2$) and 9.47 (s, $SiCH_2$). ^{31}P-{^{1}H} NMR (202.5 MHz, $CDCl_3$, 25 °C): δ −27.6 (s). ^{29}Si-{^{1}H} NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −66.3 (s) [Found (Calc. for $C_{58}H_{60}N_2O_3P_4Si_2$): C, 68.70 (69.76); H, 6.01 (5.97); N, 2.72 (2.76)%].

When the same reaction was performed using compound **2**·8HCl (78 mg, 0.066 mmol) in MeOH–C_6H_6–NEt_3 (2, 5, 8 mL, respectively) the product obtained in high yield appeared to be the octahydrochloride salt of **17**. ^{1}H NMR (500.2 MHz, pyridine-d_5, 25 °C): δ 7.61–7.34 (br, C_6H_5, 160 H), 3.75 (br, CH_2, 32 H), 3.07 (br, CH_2N, 16 H), 1.86 (br, $SiCH_2CH_2$, 16 H) and 0.85 (br, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, pyridine-d_5, 25 °C): δ 138.92 (d, J = 13.6, C_{quat}), 133.62 (d, J = 18.4, CH), 129.04 (s, CH), 128.94 (d, J = 6.5 Hz, CH), 59.04 (s, CH_2N), 58.98 (s, CH_2), 20.29 (s, $SiCH_2CH_2$) and 10.01 (s, $SiCH_2$). ^{31}P-{^{1}H} NMR (202.5 MHz, pyridine-d_5, 25 °C): δ −28.88 (s). ^{29}Si-{^{1}H} NMR (99.4 MHz, $CDCl_3$, 25 °C): δ −67.56 (s). The product tested positive for chloride (Ag^+ and Beilstein test).

Compounds 14 and 18 *via* reactions of 15 with *n*-BuNH$_2$ and *t*-BuNH$_2$. Isocyanate **15** was prepared as described above, but the organic layer obtained after filtration through cotton was reduced to 70 mL (25 °C, 10 Torr) then treated immediately with *n*-$BuNH_2$ or *t*-$BuNH_2$ (10 equivalents per NCO). A white suspension began to form within several minutes. After 1 h the reaction mixture was concentrated (25 °C, 0.001 Torr) and then filtered to collect the crude product, which was washed with cold MeOH and dried (25 °C, 0.001 Torr). Analysis by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy indicated complete conversion of aminopropyl groups into ureido groups. Analytically pure

samples were obtained by recrystallization from CH_2Cl_2–MeOH (−30 °C, 7 d). A sample of **14** prepared *via* reaction of **15** with *n*-$BuNH_2$ was indistinguishable from that prepared *via* reaction of **2** with *n*-BuNCO.

For **18**: yield 61 mg (18% from **2**·8HCl). ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 5.64 (t, CH_2NH, 8 H), 5.47 (br, CNH, 8H), 2.94 (m, CH_2N, 16 H), 1.41 (m, $SiCH_2CH_2$, 16 H), 1.21 (s, CH_3, 72 H) and 0.58 (t, $SiCH_2$, 16H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 157.65 (s, CO), 48.83 (s, C_{quat}), 41.15 (s, CH_2N), 29.23 (s, CH_3), 23.38 (s, $SiCH_2CH_2$) and 8.67 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.1 (s). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{16}H_{34}N_4O_5Si_2$; $[M + H]^+$ *m/z* 1673.83, found 1673.84 (80%); $[M + Na]^+$ 1695.82, found 1695.80 (100%); $[M - C_5H_9ON + H]^+$ 1574.77, found 1574.77 (26%).

Compound 22. A mixture of compound **21**[8] (1.00 g, 4.52 mmol) and $AgNO_3$ (3.00 g, 17.8 mmol) was refluxed in MeCN (50 mL) under an atmosphere of dry nitrogen for 48 h. The excess of silver salts was precipitated with saturated aqueous brine solution, then solvent was evaporated to a minimum volume (25 °C, 0.001 Torr). After addition of 1:1 chloroform–water and filtration through cotton, the organic layer was separated, dried over $MgSO_4$, and evaporated (25 °C, 0.001 Torr) to afford **22** as a light sensitive, microcrystalline, pale yellow solid (710 mg, 100%), which was used without further purification for the synthesis of **3**. ^{1}H NMR (500.2 MHz, DMSO-d_6, 25 °C): δ 4.47 (t, $J = 6.5$, CH_2O, 16 H), 1.74 (m, $SiCH_2CH_2$, 16 H) and 0.72 (t, $J = 7.7$ Hz, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 74.92 (s, CH_2O), 19.71 (s, $SiCH_2CH_2$) and 7.08 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −66.7 (s) [Found (Calc. for $C_6H_{12}N_2O_9Si_2$): C, 23.29 (23.07); H, 3.85 (3.87); N, 8.61 (8.97)%].

Compound 3. Hydrogenolysis was accomplished by adding compound **22** (554 mg, 0.443 mmol), 10% Pd/C (325 mg), ethyl acetate (10 mL) and dry MeOH (10 mL) to a small glass vessel in a Parr mini-reactor. The reactor was purged with H_2 (3 × 400 psig) then charged with H_2 (800 psig). After 3 d at 25 °C the reaction mixture was filtered and washed with dry MeOH (20 mL). Evaporation of the solvent (25 °C, 0.001 Torr) afforded **3** as a waxy white solid (335 mg, 85%). All attempts to prepare crystalline samples or powders were unsuccessful, but the product obtained in this fashion is spectroscopically pure (^{1}H, ^{13}C NMR). ^{1}H NMR (500.22 MHz, DMSO-d_6, 25 °C): δ 4.44 (br, OH, 8 H), 3.33 (t, $J = 6.8$, CH_2O, 16 H), 1.46 (m, $SiCH_2CH_2$, 16 H) and 0.56 (t, $J = 7.6$ Hz, $SiCH_2$, 16 H). ^{13}C-{^{1}H} NMR (125.8 MHz, DMSO-d_6, 25 °C): δ 62.90 (s, CH_2O), 25.82 (s, $SiCH_2CH_2$) and 7.59 (s, $SiCH_2$). ^{29}Si-{^{1}H} NMR (99.4 MHz, DMSO-d_6, 25 °C): δ −65.9 (s). Mass spectrum (MALDI-TOF, DHB matrix): calc. for $C_{24}H_{56}O_{20}Si_8$, $[M + Na]^+$ *m/z* 911.14, found 911.0 (100%); $[M + K]^+$ 927.11, found 928.1 (5%).

Acknowledgements

These studies were supported by the National Science Foundation and Phillips Laboratory (Edwards AFB). The NMR and mass spectra were determined at University of California using instruments acquired with funding from the National Science Foundation and National Institutes of Health.

References

1 M. G. Voronkov and V. Lavrent'ev, *Top. Curr. Chem.*, 1982, **102**, 199.
2 R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409.
3 D. W. Scott, *J. Am. Chem. Soc.*, 1946, **68**, 356.
4 M. G. Voronkov, T. N. Martynova, R. G. Mirskov and V. I. Belyi, *Zh. Obshch. Khim.*, 1979, **49**, 1522; T. N. Martynova, V. P. Korchkov and P. P. Semyannikov, *J. Organomet. Chem.*, 1983, **258**, 277.
5 F. J. Feher and T. A. Budzichowski, *J. Organomet. Chem.*, 1989, **379**, 33.
6 R. Weidner, N. Zeller, B. Deubzer and V. Frey, *U. S. Pat.*, 5 047 492, 1991.
7 F. J. Feher, D. Soulivong, A. G. Eklund and K. D. Wyndham, *Chem. Commun.*, 1997, 1185.
8 U. Dittmar, B. J. Hendan, U. Flörke and H. C. Marsmann, *J. Organomet. Chem.*, 1995, **489**, 185.
9 C. Zhang and R. M. Laine, *J. Organomet. Chem.*, 1996, **521**, 199.
10 C. L. Frye and W. T. Collins, *J. Am. Chem. Soc.*, 1970, **92**, 5586.
11 P. A. Agaskar, *Inorg. Chem.*, 1991, **30**, 2707.
12 P. G. Harrison, C. Hall and R. Kannengiesser, *Main Group Met. Chem.*, 1997, **20**, 515.
13 V. W. Day, W. G. Klemperer, V. V. Mainz and D. M. Millar, *J. Am. Chem. Soc.*, 1985, **107**, 8262.
14 P. A. Agaskar, V. W. Day and W. G. Klemperer, *J. Am. Chem. Soc.*, 1987, **109**, 5554.
15 A. R. Bassindale and T. Gentle, *J. Organomet. Chem.*, 1996, **521**, 391.
16 D. Herren, H. Bürgy and G. Calzaferri, *Helv. Chim. Acta*, 1991, **74**, 24.
17 A. R. Bassindale and T. E. Gentle, *J. Mater. Chem.*, 1993, **3**, 1319.
18 T. E. Gentle and A. R. Bassindale, *J. Inorg. Organomet. Polym.*, 1995, **5**, 281.
19 J. V. Crivello and R. Malik, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 1997, **35**, 407.
20 F. J. Feher and K. D. Wyndham, *Chem. Commun.*, 1998, 323.
21 M.-C. Gravel and R. M. Laine, *ACS Polym. Prepr.*, 1997, **38**, 155.
22 F. J. Feher, K. D. Wyndham, M. A. Scialdone and Y. Hamuro, *Chem. Commun.*, 1998, 1469.
23 E. Rikowski and H. C. Marsmann, *Polyhedron*, 1997, **16**, 3357.
24 F. J. Feher, J. J. Schwab, D. M. Tellers and A. Burstein, *Main Group Chem.*, 1998, **2**, 169.
25 F. J. Feher, D. Soulivong and F. Nguyen, *Chem. Commun.*, 1998, 1279.
26 F. J. Feher, D. Soulivong and A. E. Eklund, *Chem. Commun.*, 1998, 399.
27 F. J. Feher, D. Soulivong and G. T. Lewis, *J. Am. Chem. Soc.*, 1997, **119**, 11323.
28 F. J. Feher, K. D. Wyndham and D. J. Knauer, *Chem. Commun.*, 1998, 2393.
29 J. D. Lichtenhan, *Comments Inorg. Chem.*, 1995, **17**, 115.
30 J. D. Lichtenhan, in *Silsesquioxane-based Polymers*, ed. J. C. Salamone, *Polymeric Material Encyclopedia*, CRC Press, New York, 1996, vol. 10, pp. 7768–7778.
31 D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, 1985, **17**, 117.
32 A. D. Meltzer, D. A. Tirrell, A. A. Jones, P. T. Inglefield, D. M. Hedstrand and D. A. Tomalia, *Macromolecules*, 1992, **25**, 4541.
33 M. T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1526.
34 F. Dietsche and R. Mülhaupt, 215th National Meeting of the American Chemical Society Meeting, Dallas, TX, March 1998, poster presentation.
35 K. Kobayashi, H. Sumitomo and Y. Ina, *Polym. J.*, 1985, **17**, 567.
36 T. J. Williams, N. R. Plessas and I. J. Goldstein, *Carbohydr. Res.*, 1978, **67**, C1.
37 J. S. Nowick, D. L. Holmes, G. Noronha, E. M. Smith, T. M. Nguyen and S. L. Huang, *J. Org. Chem.*, 1996, **61**, 3929.

Paper 8/07302C