A Novel Phenol for Use in Convergent and Divergent Dendrimer Synthesis: Access to Core Functionalisable Trifurcate Carbosilane Dendrimers—The X-ray Crystal Structure of [1,3,5-Tris{4-(triallylsilyl)phenylester}benzene]

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Abstract: The organosilane 4-(triallylsilyl)phenol (**1**) was synthesised in high yield by two different routes starting from two different silyl-protected phenols. One of these routes involves the first example of a retro-[1,4]-Brook rearrangement of the triallylsilyl fragment. Compound **1** can be used as a readily functionalisable dendrimer core unit and was applied in the divergent and convergent synthesis of carbosilane dendrimers. An improved synthesis of chlorotriallylsilane, which is essential to the synthesis of **1**, is also presented. Novel trifurcate carbosilane dendrimers, up to the second generation, have been synthesised by the divergent route starting from **1**. These new materials have been fully characterised by a combination of NMR, IR and mass spectroscopy (EI or MALDI-TOF), GPC and elemental analysis. Additionally, the use of **1** for the convergent synthesis of a carbosilane dendrimer is demonstrated by the formation of the dendron [1,3,5-tris{4-(triallylsilyl)phenylester}benzene] (**7**). Compound **7** has been further characterised by single-crystal X-ray diffraction and represents not only the first structurally elucidated aryl triester, but also the first structurally characterised triallylorganosilane. The idealised (gas phase) structures of several of these new materials have been determined by means of MM2 molecular structure calculations. The largest carbosilane dendrimer (**[G-2]**) has a distorted spherical structure. This is in contrast to dendron **7**, which is shown to have an almost planar structure with respect to the central aromatic ring and the three ester groups.

Keywords: dendrimers • molecular modeling • organosilanes • structure elucidation • synthesis design

Introduction

Dendrimer chemistry is rapidly becoming an important area within polymer science.[1, 2] Dendrimers are highly branched mono-dispersed macromolecules that emanate from a central core. They are usually produced in a step-wise manner by a repetitive reaction sequence. Hence, these materials have a well-defined size, molecular weight, internal connectivity and specific number of end-groups.[1] We have been interested in the use of dendrimers as inert frameworks for the attachment of catalytically active transition metal complexes[3–5] and in the investigation of molecular sensor technology (i.e., nanoprobe devices).[6] The synthesis of dendrimer molecules that contain an Si atom as the branch point, with strong Si–C bonds as the connecting structure, has enabled the investigation of a number of robust dendritic carbosilanes.[2a, 3–5, 7] However, the widespread application of these new materials is limited by the repetitive multi-step procedures (i.e., divergent syntheses) that are usually used in dendrimer production.[1, 2, 7] This problem has been partially overcome by the convergent approach presented by Fréchet,[2d, 8] in which small repeat units (*dendrons*) are coupled to a multi-functional core and

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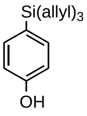
Supporting information for this article (a full list of the NMR (^{1}H and ^{13}C, with selected assignments), IR, MS (or MALDI-TOF) and GPC data for compounds **1**, **2**, **4**–**7**, **[G-1]** and **[G-2]** (2 pages)) is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the authors.

can thus allow the facile assembly of large dendrimers.[1, 2, 8] All of the previously characterised carbosilane dendrimers have been made solely by the divergent method.[7a–v] This approach invariably leads to the formation of dendrimers containing branch defects as a result of a small percentage of incomplete reactions in one or more of the synthetic steps.[1, 2g,h] The work presented herein includes a study of the synthesis of carbosilane dendrimers by either the divergent or convergent approach and includes the characterisation (NMR, GPC, MALDI-TOF) of core functionalisable trifurcate carbosilanes.[7l,m]

There were several key requirements that had to be met by our dendrimer core unit. These considerations are based on the foreknowledge that dendrimer synthesis is inherently labour intensive and thus the compounds should be useful for a variety of diverse applications. Our pre-requisites therefore call for a polyfunctional molecule that meets the following criteria: i) ease of attachment of transition metal complexes or molecular probes[6, 10] and ii) tolerance to the conditions necessary for carbosilane dendritic growth (hydrosilation conditions and inertness to Grignard reagents). With this in mind, the target core unit was chosen to be the novel organosilane: 4-(triallylsilyl)phenol (**1**).[9] This simple molecule features two key components that meet the requirements detailed above. Firstly, the triallylsilyl fragment serves as the initiation point for further (divergent) dendrimer growth. Secondly, the phenolic OH group can be readily functionalised with either a transition metal fragment,[10a] a molecular probe (e.g., a pyrene group[7h]) or it can serve as the point of attachment in convergent synthesis. This group can also be readily protected by, for example, the (tBu)Me$_2$Si group.[11]



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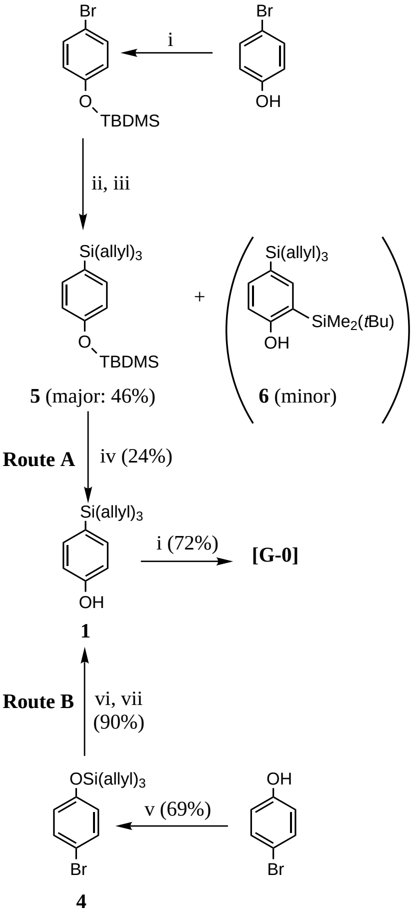
Abstract in Dutch: *De organosilaanverbinding, 4-trialkylsilylphenol (**1**), werd in hoge opbrengst gesynthetiseerd via twee verschillende routes uitgaande van silyl-beschermde phenolen. Eén van deze routes is het eerste voorbeeld van een Retro-[1,4]-Brook omlegging van een trialkylfragment. Verbinding **1** kan als een geschikte gefunctionaliseerde, dendritische kerneenheid gebruikt worden en kan in zowel de divergente als de convergente synthese van carbosilaan-dendrimeren toegepast worden. De synthese van **1** werd mogelijk gemaakt doordat de bereiding van zuiver triallylchloorsilaan op essentiële punten kon worden verbeterd. Nieuwe trifurcate carbosilanen tot en met de tweede generatie werden via een divergente syntheseroute uitgaande van **1** gesynthetiseerd. Het gebruik van **1** in een convergente syntheseroute leidde tot de synthese van het dendron [1,3,5-tris{4-(triallylsilyl)phenylester}benzeen] (**7**). Verbinding **7** is niet alleen de eerste aryltriester maar ook het eerste triallylsilaan waarvoor de structuur (m. b. v. X-ray) in de vaste stof kon worden opgehelderd. De geïdealiseerde (gasfase) structuren van de verschillende nieuwe verbindingen werden berekend met behulp van MM2 moleculaire structuurberekeningen. In tegenstelling tot dendron **7** dat een haast vlakke structuur heeft met de centrale aromaatring en de drie estergroepen in een vlak, heeft het grootste carbosilaandendrimeer (**[G-2]**) een verstoorde sferische structuur.*

In this report, we expand on our earlier preliminary communication[9] that described the synthesis of **1**. This compound can be used as a versatile component in both the convergent *or* divergent syntheses of carbosilane dendrimers and has potential for the attachment of molecular probes or transition metal complexes onto the dendrimer core.[1, 10]

Results and Discussion

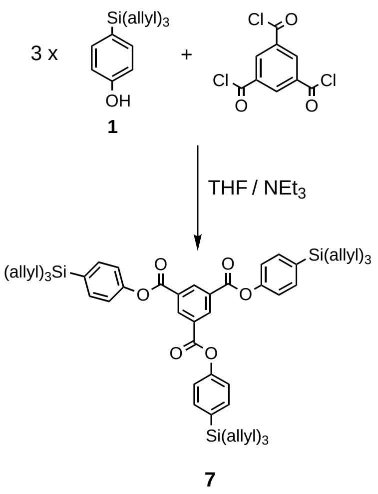
Synthesis of 4-(triallylsilyl)phenol (1): Two synthetic pathways can be used in the production of this novel organosilane (Scheme 1); however, both require relatively large quantities of chlorotriallylsilane [ClSi(CH$_2$CH=CH$_2$)$_3$, (**2**)]. This halosilane was first produced over forty years ago by Scott and Frisch;[12] however, their procedure involves a nonselective reaction of allylmagnesium bromide (3 equiv) with SiCl$_4$, followed by fractional distillation (yield ≈25%). Therefore, we used triallylsilane [HSi(CH$_2$CH=CH$_2$)$_3$, (**3**)], readily accessible from allylmagnesium bromide and trichlorosilane



Scheme 1. i) tBuMe$_2$SiCl, NEt$_3$, C$_6$H$_6$; ii) 2 × nBuLi, Et$_2$O; iii) ClSi(allyl)$_3$ (**2**, 1.2 equiv), Et$_2$O; iv) nBu$_4$NF, THF; v) ClSi(allyl)$_3$ (**2**, 1.2 equiv), NEt$_3$, C$_6$H$_6$; vi) 2 × tBuLi, Et$_2$O; vii) aq. NH$_4$Cl.

in diethyl ether,[13] in order to avoid this tedious purification procedure. Compound **3** was then converted to **2** (72 % yield) by treatment with cupric chloride (2 equiv) in boiling acetonitrile in the presence of an organic base, followed by extraction with pentane (see Experimental Section).

Having obtained this essential component, the two synthetic pathways depicted in Scheme 1 were followed to obtain the desired phenol **1**. Route A has the advantage that a silyl-protected analogue of **1** (i.e., **5**) is produced first and can thus be used for divergent dendrimer synthesis without further modification.[9, 14] Route B produces **1** directly by means of a low temperature (O→C) [1,4]-silyl migration from the lithio derivative of **4** (i.e., 4-(triallylsiloxy)phenyllithium).[9, 15] Compound **4** is readily synthesised by the treatment of 4-bromophenol with **2** (see Experimental Section). Route B represents, to our knowledge, the first example of an anionically induced migration (homo-Brook rearrangement) of the triallylsilyl fragment.[15]



Scheme 2. Synthesis of [1,3,5-tris{4-(triallylsilyl)phenylester}benzene] (**7**).

Convergent carbosilane dendrimer synthesis: 4-(Triallylsilyl)phenol (**1**) was used to produce a simple dendrimer in order to investigate whether this phenol would be useful in other convergent dendrimer syntheses.[8, 9] Thus, the treatment of a THF solution of freshly recrystallised 1,3,5-benzenetricarbonyl trichloride (1 equiv) with **1** (3.1 equiv), in the presence of NEt_3, and subsequent chromatographic separation produced dendron **7** in 69 % isolated yield (Scheme 2).

Compound **7**, which contains nine terminal allyl groups, is a colourless oil that solidifies to a glass upon standing for several months. It has been fully characterised by NMR spectroscopy, TLC and elemental analysis (see Experimental Section). A notable feature of **7** is the diagnostic downfield singlet in the ^1H NMR spectrum that is assigned to the three protons of the central aromatic triester ring ($\delta = 9.23$). The straightforward synthesis of **7** clearly demonstrates the utility of **1** in convergent dendrimer synthesis.[9]

Compound **7** presents a rare opportunity to examine the solid-state structure of the triallylsilyl fragment. To date, there are no reported examples of a compound which contains this unit that has been characterised by single-crystal X-ray diffraction methods. A suitable crystal was grown with some difficulty from a dodecane solution of **7** by slow evaporation of the solvent in a stream of air over a period of approximately two weeks. A molecular plot of **7** is shown in Figure 1 along with some pertinent bond lengths and bond and torsion angles.[16]

The Si–C bond lengths are similar to those found in other tetraorganosilanes, as is the length of the allylic C=C bond. Of particular note is the almost perpendicular arrangement of all three terminal aromatic groups with respect to the central phenyl ring. This feature is in contrast to that previously found in related organometallic pincer-type[20] dendrons that contain three metal-bound (formal) aryl carbanions (i.e., [1,3,5-$\{ClPt(NCN')C(=O)\}_3C_6H_3$]; $NCN' = \{2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}OC_6H_3\}$) and related systems.[6, 10b] It can be seen in Figure 1, that the relative spacing between the three organosilyl groups is large and hence there is considerable room for further expansion (i.e., dendritic growth).[1, 2]

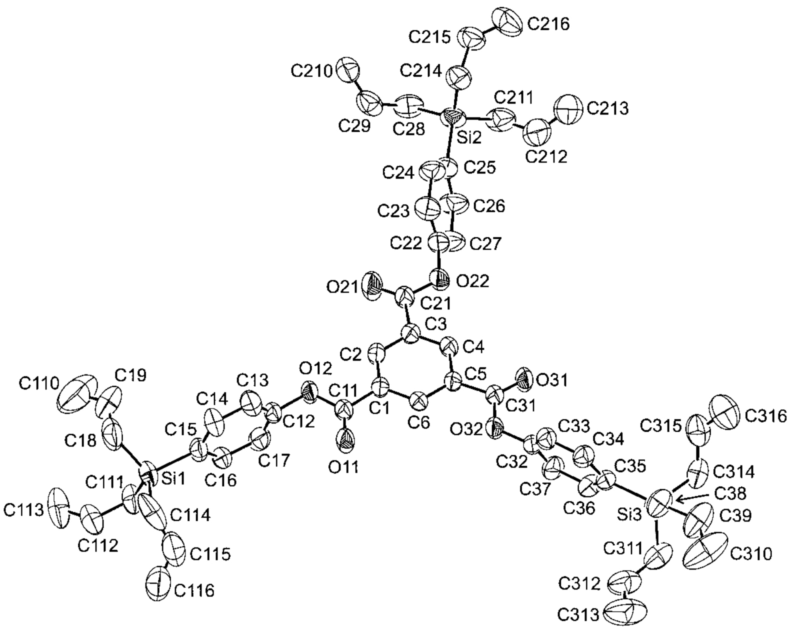
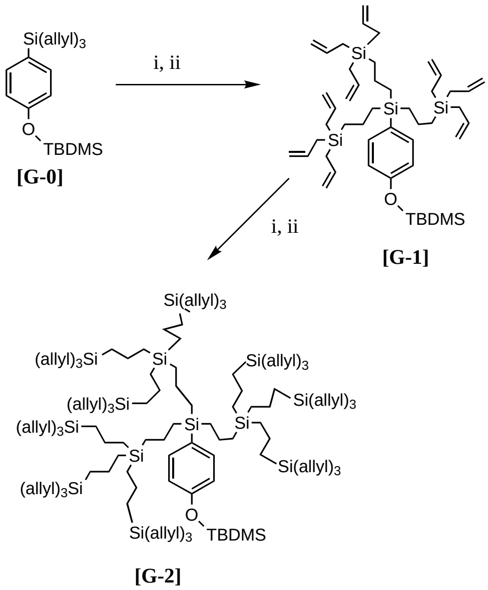


Figure 1. Displacement ellipsoid (50 % probability) plot of **7** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: Si1–C18 1.857(7), Si1–C111 1.848(6), Si1–C114 1.883(8), Si2–C28 1.877(6), Si2–C211 1.900(6), Si2–C214 1.879(6), Si3–C38 1.875(5), Si3–C311 1.866(6), Si3–C314 1.891(6), C18–C19 1.450(14), C111–C112 1.496(7), C114–C115 1.483(13), C28–C29 1.489(8), C211–C212 1.494(11), C214–C215 1.457(7), C38–C39 1.485(8), C311–C312 1.495(10), C314–C315 1.482(10), C19–C110 1.217(14), C112–C213 1.340(11), C215–C316 1.292(10). Interplanar angles [°] between the least-squares planes of the central benzene ring and of C12–C17: 87.62(18), of C22–C27: 74.53(19) and of C32–C37: 78.80(19).

Divergent carbosilane dendrimer synthesis: As noted in the introduction, our goal is to create new materials for applications in nanoprobe devices and catalysis. In this regard, we have tested a number of dendrimer catalysts of generation numbers 1 and 2 in a membrane reactor system.[5] The design of this equipment allows for the recovery of the product or the catalyst by ultrafiltration technology.[21] This work has revealed that even small dendrimers (of generation **[G-1]** or larger) can be easily retained (or recovered) by modern synthetic membranes. Calculations (MM2) have indicated that these materials have diameters that are less than ≈25 Å.[5] Therefore, the growth dimensions of the materials synthesised here have been restricted to generation 2 (**[G-2]**).

The synthetic strategy has been developed previously and involves classical hydrosilation[22] of **5** (i.e., **[G-0]**) with excess $HSiCl_3$ and Speier's Catalyst ($[H_2PtCl_6] \cdot H_2O$). This readily gave the intermediate anti-Markovnikov hydrosilylated product (**[G-0.5]**).[22, 23] Completion of this reaction is easily monitored by in-situ ^1H NMR spectroscopy (disappearance of olefinic resonances; see the Experimental Section) of **[G-0]** or by the absence of the characteristic C=C stretching frequency in the IR spectrum ($\tilde{\nu} = 1639\ \mathrm{cm^{-1}}$).[3–5, 7a–n, 9] Treatment of **[G-0.5]** with a slight excess (relative to the number of terminal Cl groups) of allylmagnesium bromide and isolation by flash chromatography yielded the pure **[G-1]** dendrimer, as a colourless and malodorous oil, in 72% yield (Scheme 3).



Scheme 3. i) $HSiCl_3$, cat.: $[H_2PtCl_6]$, hexane; ii) excess $H_2C{=}CHCH_2MgBr$, Et_2O.

Compound **[G-1]** was fully characterised by NMR (^1H and $^{13}C\{^1H\}$) and IR spectroscopy, TLC, GPC, MALDI-TOF and elemental analysis. The general physical properties, such as colour, etc., are very similar to the spherical carbosilane dendrimers reported previously.[2a, 7b,e] The idealised gas-phase structure (MM2 level of calculation) of **[G-1]** and the parent complex **5** (**[G-0]**) are shown in Figure 2.

A repetition of the reaction conditions that were used to produce **[G-1]** from **[G-0]** was employed to produce dendrimer **[G-2]** (Scheme 3). The **[G-2]** dendrimer was isolated in 66% yield following chromatographic separation. This dendrimer is also a colourless oil and exhibits similar spectroscopic properties to the **[G-1]** compound (see the Experimental Section and the Supplementary Material). Characterisation of **[G-2]** was carried out by IR and NMR spectroscopy, elemental analysis and GPC techniques (see Supplementary Material).[7a–p] All of this information is fully consistent with the formation of **[G-2]** as given in Scheme 3. Molecular mechanics (MM2) calculations suggest that the overall geometry of this dendrimer is best described as a distorted spherical structure (Figure 3). The close proximity of the terminal allyl groups to the protected OH functionality is clearly shown and this suggests that a cagelike encapsulation of the dendrimer interior may be occurring. This aspect will be the subject of later study.

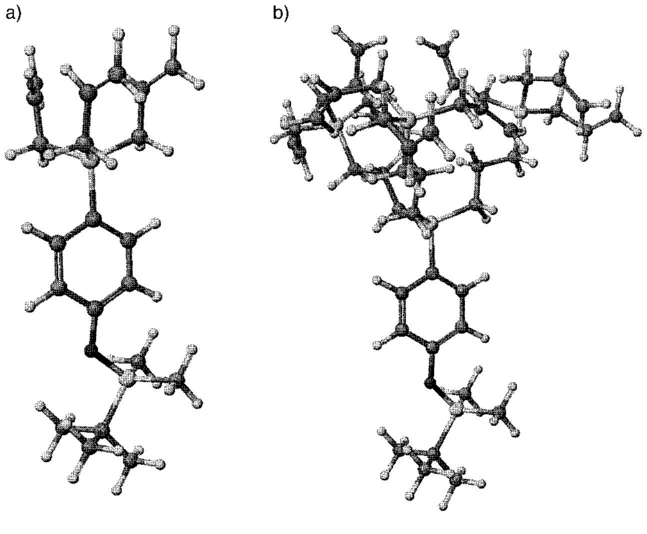


Figure 2. The calculated (MM2) gas-phase molecular structures for a) **[G-0]** and b) **[G-1]**.

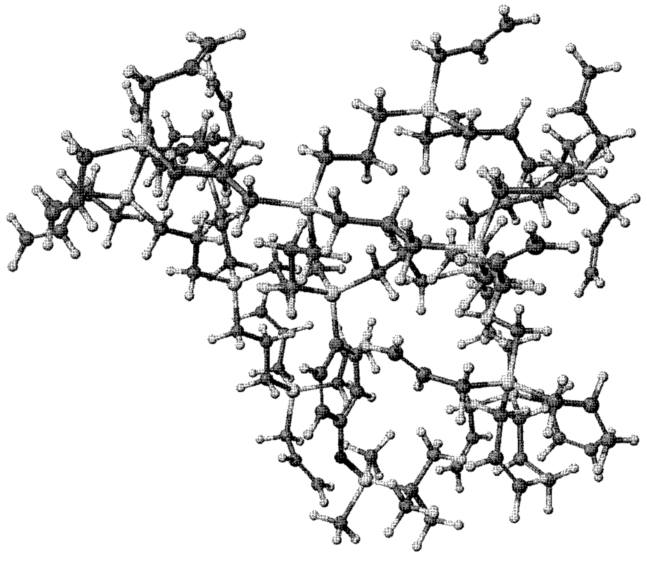


Figure 3. The calculated (MM2) gas-phase molecular structure of **[G-2]**.

Conclusions

The results presented here are intended to serve as the starting point for a variety of new applications for carbosilane dendrimers (e.g., the trifurcate compounds **[G-1]** or **[G-2]** in the present study). This can only be possible if a functional group is present that can be readily manipulated without disturbing the carbosilane framework. In this case, the phenolic group of 4-(triallylsilyl)phenol (**1**) represents this segment of the dendrimer. Protection of this functionality by the (tBu)Me_2Si fragment is facile (to give **5**) and the silyl group can be readily removed by an F^- source (vide supra). As discussed by Corey[24a,b] and others,[24c] the bulky silyl group attached to the phenolic oxygen atom is not affected by organometallic reagents and is, therefore, ideal for our purposes.[24] Phenols can be readily coordinated to transition metal fragments by direct reaction or via prior conversion to alkali metal phenoxides. This has been previously demonstrated in, for example, the formation of H-bonded transition metal α-networks.[10a] Moreover, the reactive O–H bond can be used for the attachment of molecular probe fragments (e.g., pyrene, a fluorescent indicator[25]). Thus, the results described above have laid the groundwork for further investigations into the properties and uses of carbosilane macromolecules.

The synthesis of the novel carbosilane dendrimer core unit, 4-(triallylsilyl)phenol (**1**) involves a novel retro-[1,4]-Brook rearrangement of the triallylsilyl fragment. In addition, compound **1** has been shown to be useful for *both* convergent and divergent dendrimer syntheses. The first triallylorganosilane to be characterised by single crystal X-ray diffraction has also been reported.

These results emphasise that common synthetic methods can be used to produce dendrimers that allow for facile core functionalisation. The use of trifurcate (carbosilane) dendrimers remains an area of supramolecular chemistry that is relatively unexplored[7l,m] and this work has helped to open a potential gateway to a variety of investigations. We shall report further results with these materials in due course.

Experimental Section

General: All solvents were dried over sodium biphenyl ketyl (Et_2O, THF, hydrocarbons) or CaH_2 (CH_2Cl_2, CH_3CN) and distilled under a nitrogen atmosphere prior to use. Unless otherwise stated, the reactions were carried out under an atmosphere of dry nitrogen at room temperature (RT). All reagents were obtained from commercial sources and were used without further purification, except iPr$_2$NEt (redistilled from CaH_2) and $HSiCl_3$ (degassed by repetitive freeze-pump-thaw techniques to remove HCl and O_2). Infrared spectra were recorded in solution with a Unicam FT-IR 5000 spectrophotometer. The ^{1}H (200 and 300 MHz) and ^{13}C{^{1}H} (50 and 75 MHz) NMR spectra were recorded at RT (298 K) with a Bruker AC 200, WH 200 or AC 300 instrument with $SiMe_4$ as the external standard with the samples in $CDCl_3$ solution, unless otherwise stated. Flash chromatography was performed on silica (230–400 mesh, Merck). All MALDI-TOF measurements were performed as previously described.[26] Microanalyses were obtained from H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany). Molecular mechanics calculations (MM 2 level) were performed with the CAChe program package (Oxford Molecular Group).

Synthesis of chlorotriallylsilane ([4-chloro-4-(2-propenyl)-4-sila-1,6-heptadiene], 2):[12] Cupric chloride (8.40 g, 84.8 mmol) was suspended in MeCN (20 mL) at 0 °C and the mixture stirred for 20 min. Diisopropylethylamine (Hünig's base, 12 mL, 67 mmol) was then added slowly (**Caution, exothermic!**) to yield a dark brown, oily solution. Triallylsilane **3**[13] (5.96 g, 39.2 mmol) was added to this mixture at RT and the contents of the reaction flask were subsequently heated to 80 °C overnight. The resulting dark brown suspension was extracted with pentane (3 × 75 mL) under nitrogen and was filtered, and the pentane extracts were combined. The pentane was boiled off and the residue flash-distilled under vacuum, whereby the volatile components were trapped in a flask cooled with liquid nitrogen. A colourless, air- and moisture-sensitive liquid was isolated upon warming to RT. The properties of this material were identical to those of an authentic sample of chlorotriallylsilane.[12] Yield: 5.05 g (72 %); ^{1}H NMR: $\delta = 5.80$ (m, 3 H), 5.00 (d, 6 H, ^3J(H,H) = 12.4 Hz), 1.88 (d, 6 H, ^3J(H,H) = 7.9 Hz); ^{13}C{^{1}H} NMR: $\delta = 131.5$, 116.0, 22.6; MS (70 eV, EI): m/z (%): 186 (0.5) [M]$^+$.

Synthesis of [4-(*tert*-butyldimethylsiloxy)triallylsilylbenzene] (5 or [G-0])

Method A: The silyl ether [4-(*tert*-butyldimethylsiloxy)bromobenzene] (6.14 g, 21.4 mmol) was dissolved in pentane (25 mL) and cooled to −78 °C. A solution of tBuLi (1.5 M, 30 mL, 45 mmol) in pentane was added dropwise and the mixture was then allowed to warm slowly to RT. A thick white precipitate formed that dissolved upon the addition of Et_2O (30 mL) at −78 °C. The mixture was then quenched with **2** (4.5 mL, 24 mmol) added with a syringe. The resulting mixture was warmed to ambient temperature and the precipitate that had formed was filtered through a plug of layered Celite and silica gel. The solids that were filtered off were washed with C_6H_6 (2 × 50 mL). The combined organic fractions were distilled to remove the solvent and the resulting crude golden brown oil was subjected to separation by flash chromatography on silica gel (230–400 mesh silica, EtOAc/hexanes 3:100, v/v). The product was obtained as a colourless liquid after solvent removal as the fastest eluting column fraction. Yield: 3.53 g (46 %); $R_f = 0.60$ (EtOAc/hexanes 3:100); ^{1}H NMR: $\delta = 7.38$ (d, 2 H, AB pattern: ^3J(H,H) = 8.2), 6.85 (d, 2 H), 5.82 (m, 3 H), 4.91 (m, 6 H), 1.84 (d, 6 H, d, ^3J(H,H) = 8.0 Hz), 1.00 (s, 9 H), 0.22 (s, 6 H); ^{13}C{^{1}H} NMR: $\delta =$ 156.7, 135.6, 134.1, 128.1, 119.7, 114.1, 25.7, 19.8, 18.2, −4.3; $C_{21}H_{34}OSi_2$ (358.7): calcd C 70.32, H 9.55; found C 70.21, H 9.55; MS (70 eV, EI): m/z (%): 358 (0.5) [M]$^+$. A second product, an isomer of the above compound, was also obtained in this reaction and purified chromatographically as above. This was identified as [2-(*tert*-butyldimethylsilyl)-4-(triallylsilyl)phenol] (**6**). Yield: 0.49 g (6 %); $R_f = 0.35$ (EtOAc/hexanes 3:100); ^{1}H NMR: $\delta = 7.50$ (d, 1 H, ^3J(H,H) = 1.6 Hz), 7.38 (dd, 1 H, ^3J(H,H) = 8.0 Hz, 1.7), 6.69 (d, 1 H, ^3J(H,H) = 8.0 Hz), 5.78 (m, 3 H), 4.91 (m, 6 H), 4.63 (s, 1 H), 1.83 (d, 6 H, ^3J(H,H) = 7.9 Hz), 0.91 (s, 9 H), 0.33 (s, 6 H); ^{13}C{^{1}H} NMR: $\delta = 161.7$, 143.3, 136.8, 134.1, 125.1, 121.9, 114.5, 114.2, 26.8, 19.9, 17.7, −4.7; $C_{21}H_{34}OSi_2$ (358.7): calcd C 70.32, H 9.55; found C 70.42, H 9.46; MS (70 eV, EI): m/z (%): 317 (20) [M − allyl]$^+$.

Method B: NEt_3 (5 mL) was added to a solution of **1** (1.0 g, 4.1 mmol) in C_6H_6 (30 mL) at RT. tBuMe$_2$SiCl (0.63 g, 4.2 mmol) was added to this stirred mixture and the resulting solution was heated to 70 °C for 48 h. Isolation of the product was performed as above. Yield: 62 % (0.91 g). When imidazole in DMF[21a] was used instead of C_6H_6/NEt_3, the yield was found to be lower, with the formation of other side-products.

Synthesis of [4-(triallylsilyl)phenol] (1):

Method A: Water (2 drops) and a THF solution of [nBu$_4$NF] (1 M, 0.9 mL, 0.9 mmol) were added to a solution of **5** (0.31 g, 0.87 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 15 min during which time the colour changed from colourless to light yellow. A solution of aq. NaCl (10 %) was added and the organic layer separated. The aqueous layer was extracted with Et_2O (3 × 20 mL) and the combined organic layers dried over $MgSO_4$. The solution was filtered and the ethers distilled off to yield a yellow oil. This mixture was separated by flash chromatography (EtOAc/hexanes 50:50) to yield the product as a colourless oil. Yield: 0.05 g (24 %); $R_f = 0.70$ (EtOAc/hexane 50:50); ^{1}H NMR: $\delta = 7.37$ (d, 2 H, ^3J(H,H) = 6.6 Hz), 6.91 (d, 2 H), 5.81 (m, 3 H), 4.90 (m, 6 H), 3.19 (br, 1 H), 1.82 (d, 6 H, ^3J(H,H) = 8.0 Hz); ^{13}C{^{1}H} NMR: $\delta = 156.6$, 136.3, 136.0, 134.0, 115.0, 114.2, 19.8; $C_{15}H_{20}OSi$ (244.4): calcd C 73.71, H 8.25; found C 73.84, H 8.19.

Method B: A sample of **4** (1.46 g, 4.5 mmol) was dissolved in Et_2O (20 mL) and the solution cooled to −78 °C. A pentane solution of tBuLi (1.5 M, 6.0 mL, 9.0 mmol) was added dropwise by syringe to the stirring mixture, which was then allowed to warm slowly to RT (2 h) and stirred overnight. This yielded a light yellow solution. Saturated aq. NH_4Cl (20 mL) was added and the organic layer separated. The aqueous portion was extracted with Et_2O (3×20 mL), the organic layers were combined and all volatile components of the mixture were removed by a rotary evaporator. This procedure yielded a yellow oil. The pure product was isolated as above. Yield: 0.99 g (90 %).

Synthesis of [4-(triallylsiloxy)bromobenzene] (4): NEt_3 (20 mL) was added to a solution of 4-bromophenol (5.0 g, 29 mmol) in benzene (100 mL). The mixture was stirred at RT for 10 min, followed by the dropwise addition of **2** (≈5 mL) over a period of 5 min. The mixture was then stirred overnight. The fluffy white precipitate that had formed was filtered off by passing the solution through a glass frit preceeded by a plug of Celite and silica gel. Volatile components of the filtrate were removed with a rotary evaporator to yield a light brown oil. Separation of the components of this oil by flash chromatography (EtOAc/hexanes 1:100) gave the product as a colourless oil. Yield: 6.44 g (69 %); $R_f = 0.35$ (EtOAc/hexanes 1:100); ^1H NMR: $\delta = 7.34$ (d, 2H, $^3J(H,H) = 8.0$ Hz), 6.76 (d, 2H), 5.78 (m, 3H), 4.95 (m, 6H), 1.81 (d, 6H, $^3J(H,H) = 8.0$ Hz); $^{13}C\{^1H\}$ NMR: $\delta = 153.7$, 132.4, 132.2, 121.9, 114.2, 115.4, 20.9; MS (70 eV, EI): m/z (%): 322 (2) $[M(^{79}Br)]^+$; $C_{15}H_{19}OSiBr$ (323.3): calcd C 55.73, H 5.92; found C 55.62, H 5.86.

Synthesis of [1,3,5-tris{4-(triallylsilyl)phenylester}benzene] (7): NEt_3 (12 mL) was added to a solution of **1** (0.64 g, 2.6 mmol) in THF (50 mL) and the mixture was stirred at RT for 10 min. Freshly recrystallised 1,3,5-benzenetricarbonyl trichloride (0.22 g, 0.83 mmol) was added to this rapidly stirred solution and a white precipitate formed immediately. Stirring was continued for 18 h and then the mixture was filtered through Celite and evaporated to dryness to yield an off-white oil. The product was isolated as a colourless and very viscous liquid by flash chromatography (hexanes/Et_2O 2:1). This oil gave a glassy solid upon standing at RT for several months. Yield: 0.51 g (69 %) [a quantity of unreacted **1** ($R_f = 0.47$) was also recovered (0.15 g (98 %))]; $R_f = 0.84$ (hexanes/Et_2O 2:1); ^1H NMR (300 K): $\delta = 9.23$ (s, 3H), 7.63 (d, 6H, $^3J(H,H) = 8.4$ Hz), 7.28 (d, 6H), 5.80 (m, 9H), 4.93 (m, 18H), 1.89 (m, 18H); $^{13}C\{^1H\}$ NMR: $\delta = 163.1$, 151.6, 136.0, 135.6, 133.5, 131.2, 120.8, 114.5, 19.5; $C_{54}H_{60}O_6Si_3$ (889.3): calcd C 72.93, H 6.80, Si 9.47; found C 72.81, H 6.78, Si 9.59.

Synthesis of [4-{(*tert*-butyldimethylsiloxy)-tris-(3-{triallylsilyl}propyl)silyl}-benzene] [G-1]: $HSiCl_3$ (2.0 mL, 20 mmol) and $[H_2PtCl_6] \cdot H_2O$ (0.020 g, 0.045 mmol) were added to a hexane (20 mL) solution of **[G-0]** (2.05 g, 5.8 mmol). The mixture was placed in a Carius tube equipped with a Teflon stopcock and then sealed. The apparatus was placed in an oil bath and heated to 50 °C for 18 h. A ^1H NMR spectrum of this crude material indicated the complete absence of any alkenyl protons [$\delta = 7.34$ (d, 2H, $^3J(H,H) = 8.4$ Hz), 6.88 (d, 2H), 1.68 (m, 12H), 1.48 (m, 6H), 1.02 (s, 9H), 0.24 (s, 6H)]. This brown solution was placed briefly under vacuum (to remove residual $HSiCl_3$) and then added dropwise to a solution of allylmagnesium bromide (70 mmol) in Et_2O (100 mL) at 0 °C. The contents of the mixture were stirred at RT overnight. The resulting milky white suspension was then quenched with aq. NH_4Cl (200 mL, 10 %). The organic layer was isolated and the aqueous layer extracted with Et_2O (3×50 mL). Organic fractions were then combined and all the volatile components were removed with a rotary evaporator. The resulting oil was then purified by flash chromatography (hexanes/EtOAc 100:3). The solvent was removed in vacuo to give a colourless oil. Yield: 3.40 g (72 %); $R_f = 0.84$ (hexane/EtOAc 100:3); ^1H NMR (300 K): $\delta = 7.30$ (d, 2H, $^3J(H,H) = 7.4$ Hz), 6.83 (d, 2H), 5.75 (m, 9H), 4.86 (m, 18H), 1.58 (d, 18H, $^2J(H,H) = 8.1$ Hz), 1.36 (m, 6H), 0.99 (s, 9H), 0.82 (m, 6H), 0.63 (m, 6H), 0.20 (s, 6H); $^{13}C\{^1H\}$ NMR: $\delta = 156.4$, 135.3, 134.4, 129.8, 121.3, 120.1, 119.6, 113.4, 22.6, 25.6, 19.6, 18.1, 17.6, 16.5, -4.4; GPC (RI detector): $M_w/M_n < 1.07$ ($M_W < 1000$ vs. polystyrene); MALDI-TOF: m/z (%): 923 (100) $[M+Ag]^+$: correct isotope pattern), 771 (<3) $[M - C_3H_6]^+$, 616 (<1); $C_{48}H_{82}OSi_5$ (815.6): calcd C 70.68, H, 10.13, Si 17.22; found C 70.64, H 10.18, Si 17.34.

Synthesis of [G-2]: $HSiCl_3$ (1.0 mL, 10 mmol) and $[H_2PtCl_6] \cdot H_2O$ (0.020 g, 0.045 mmol) were added to a hexane (20 mL) solution of **[G-1]** (0.35 g, 0.43 mmol). The mixture was placed in a Carius tube equipped with a Teflon stopcock and sealed. The apparatus was placed in an oil bath and heated to 60 °C for 48 h. A ^1H NMR spectrum of this crude material indicated the complete consumption of all alkenyl protons [$\delta = 7.29$ (d, $^3J(H,H) = 7.9$ Hz), 6.83 (d), 1.71 – 1.29 (m), 1.00 (s), 0.93 (m), 0.67 (m), 0.21 (s)]. This solution was placed under vacuum (to remove excess $HSiCl_3$) and then added dropwise to a solution of allylmagnesium bromide (≈30 mmol) in Et_2O (70 mL) at 0 °C. The mixture was stirred and slowly warmed to RT overnight. The resulting milky white suspension was then quenched with aq. NH_4Cl (100 mL, 10 %). The organic layer was isolated and the aqueous layer extracted twice with Et_2O (60 mL). Organic fractions were combined and dried ($MgSO_4$), and all volatile components were removed by means of rotary evaporation. The resulting crude opaque oil was purified by flash chromatography (hexanes/EtOAc 100:3). The product was isolated after removal of all volatile components in vacuo as a malodorous and slightly opaque, colourless oil. Yield: 0.62 g (66 %); $R_f = 0.51$ (hexanes/EtOAc 100:3); ^1H NMR (300 K): $\delta = 7.31$ (d, 2H, $^3J(H,H) = 7.8$ Hz), 6.82 (d, 2H), 5.77 (m, 27H), 4.86 (m, 54H), 1.59 (d, 54H, $^2J(H,H) = 8.1$ Hz), 1.33 (brm, 24H), 0.98 (s, 9H), 0.82 (m, 12H), 0.60 (m, 36H), 0.21 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz): $\delta = 156.3$, 135.2, 134.3, 129.8, 121.3, 120.1, 119.6, 113.5, 22.8, 25.6, 19.4, 18.5, 18.4, 18.2, 17.4, 17.1, 16.5, -4.5; $C_{129}H_{226}OSi_{14}$ (2186.5): calcd C 70.86, H 10.42, Si, 17.99; found C 70.94, H 10.48, Si 17.93; GPC (EMP detector): $M_w/M_n < 1.02$ ($M_W = 1300$ vs. polystyrene).

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