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Modular Construction of Dendritic Carbosilanes. Organization of Dendrimer Connectivity around Bifunctional Precursors That Are Adapted for Sequential Convergent and Divergent Propagative Steps

Miguel Angel Casado and Stephen R. Stobart*

Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2

stobartz@uvvm.uvic.ca

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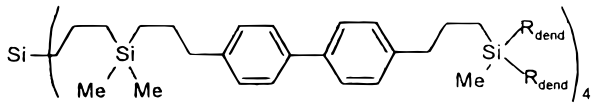
ABSTRACT



14

R_{dend} = $-CH_2(CH_2)_2Si(Me)[CH_2(CH_2)_2Si(Me)(CH_2CH{=}CH_2)_2]_2$

Regiospecific hydrosilylation of 1-bromo-4-(prop-2-enyl)benzene offers an efficient route to molecular building block precursors that can accommodate sequential divergent and convergent steps for dendritic extension, establishing a modular methodology for assembly and organization of connectivity used for synthesis of modified carbosilane dendrimers including 14.

Dendrimer chemistry has been elevated from curiosity to celebrity stature in little more than a decade of intense activity that has been led by Tomalia,[1] Frechet,[2] Newkome,[3] and their co-workers, who have drawn on ideas originally put into practice by Vögtle et al.[4] for "cascade" synthesis of noncyclic polyaza compounds. The archetypal topology, in which a regularly hyperbranched substructure radiates from a core atom to a dense homofunctional array of peripheral sites, is now the focus for a remarkable range of novel technological ideas that may be brought within reach by imaginative adaptation of a dendrimer periphery, through compartmentalization of unique chemistry at the dendrimer core, or developing core-periphery cooperative effects.[4b,5]

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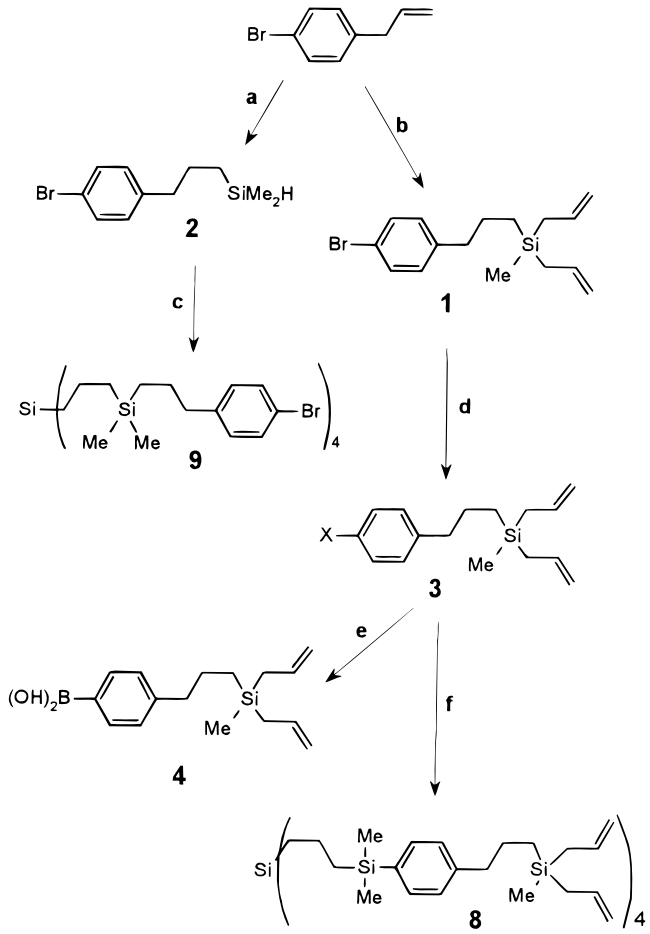
Dendrimer assembly relies on a reiterative procedure, usually using a divergent[6] routine that develops the characteristic shell heirarchy outward from a focal atom, or alternatively through convergent[7] strategy whereby the peripheral structure is preorganized by successive coupling of branched subunits into monodendron blocks that are brought together by attachment to a multifunctional core fragment. We have become interested in how these independent growth regimes might be managed together, to construct a dendritic framework from a building block that would become incorporated as an internal skeletal spacer rather than at the dendrimer periphery or its core, i.e., so that the aggregate product is built up from a nucleus that can act as a template to structure or compartmentalize its internal volume. We illustrate this idea by showing how a simple bifunctional substrate can be modified to permit consecutive divergent and convergent steps,[6,7] thereby establishing a modular program for linking up independent dendritic blocks.

Dendritic carbosilanes,[8] which are of special interest as a group because they are chemically inert and are fluid at high molecular weight, are assembled by Si−C bond formation that uses the silicon atoms as branch points to develop a paraffin-like network. These materials are currently accessible only by divergent synthesis (Grignard alkenyl group-transfer to Si alternating with platinum-catalyzed alkene hydrosilylation), although convergent coupling has recently been used to attach dendritic carbosilane fragments onto a core subunit through heteroatom (C_{Ph}−O−C) links as well as to construct carbosiloxane analogues.[9] The new approach to functionalized carbosilane monodendrons described below follows a logic that could be suited by adaptation to assembly of other dendrimer systems, and uses as its starting point two key reagents that are both obtained in high yields from a common source. Thus, the para-substituted bromobenzenes $BrC_6H_4(CH_2)_3SiMe_xCl_{3-x}$ (x = 1 or 2) may be converted either to the precursor $BrC_6H_4(CH_2)_3SiMe(CH_2CH{:}CH_2)_2$, **1** (97%), for initially bifurcate dendritic growth from Si followed by metalation (affording a dendritic aryl carbanion) to allow convergent C−C coupling onto the periphery of a dendritic carbosilane or to the silane $BrC_6H_4(CH_2)_3SiHMe_2$, **2** (78%), that can be incorporated as a peripheral group by

Scheme 1



Reagents: (a) $HSiMe_2Cl/H_2PtCl_6$, $LiAlH_4$; (b) $HSiMeCl_2/H_2PtCl_6$, $BrMgCH_2CH{=}CH_2$; (c) $Si(CH_2CH{=}CH_2)_4/H_2PtCl_6$; (d) Mg or n-BuLi; (e) $B(OMe)_3$, HCl; (f) $Si(CH_2CH_2CH_2SiMe_2Cl)_4$ (*i.e.* **7**)

hydrosilylation of a per(allyl-terminated) dendritic carbosilane then used for divergent aryl−aryl coupling, e.g., to the core bromophenyl fragment of a monodendron derived from **1**. Repetition of this routine (i.e., incorporating **2** then linking to the latter of a subunit derived from **1**) establishes a reiterative sequence to build complex hybrid assemblies.

We have observed that, while platinum-catalyzed hydrosilylation of commercially available *p*-bromostryrene is not completely[10] regioselective, 1-bromo-4-(prop-2-enyl)benzene may be obtained as the major product (80% purified yield) if the monometalation of *p*-dibromobenzene under Grignard conditions followed by nickel-catalyzed coupling[11] to 3-bromopropene is carefully controlled and that hydrosilylation

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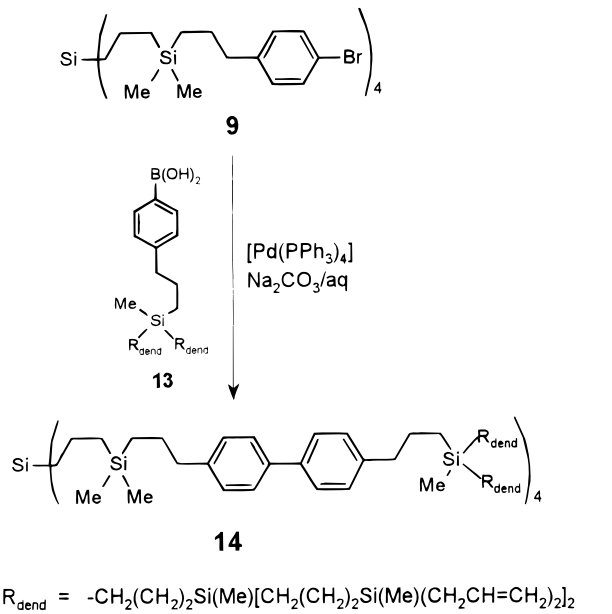
(10) (a) Under the same conditions that afford the chlorosilyl precursors of **1** and **2** as pure γ-silyl isomers, the hydrosilylated products obtained from *p*-bromostyrene were consistently found to be regioisomeric mixtures (^{1}H, ^{13}C, ^{29}Si NMR) containing at least 20% (depending on the silane) of the enantiomeric α-silyl isomer. (b) Lithiation of a carbosilane monodendron synthesized from *p*-bromostyrene has nevertheless recently been used as a means for attaching carbosilane units at the phosphorus(III) centers in ferrocenylphosphines: Oosterom, G. E.; van Haaren, R. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1119.

of this alkene using $HSiMe_xCl_{3-x}$ ($x = 1$ or 2) is regiospecific. The pure linear products so obtained react with $CH_2CH{:}CH_2$-MgBr or $LiAlH_4$ to afford[12] **1** or **2** directly. These new reagents satisfy two imperatives for use in further synthesis: (a) they do not contain $Si-C_{Ph}$ bonds, which can undergo facile solvolysis; (b) while metalation or boronation of the $Br-C_{Ph}$ bond is facile, this crucial functionality does not need to be protected during dendritic carbosilane expansion. Conversion of **1** to the aryl Grignard reagent $BrMgC_6H_4(CH_2)_3SiMe(CH_2CH{:}CH_2)_2$, **3**, followed by treatment with $B(OMe)_3$ then[13] HCl yields $(HO)_2BC_6H_4(CH_2)_3SiMe(CH_2CH{:}CH_2)_2$, **4**, which undergoes palladium-catalyzed (Suzuki) coupling with further **1** to afford the biphenyl $(CH_2{:}CHCH_2)_2MeSi(CH_2)_3C_6H_4-C_6H_4(CH_2)_3SiMe(CH_2CH{:}CH_2)_2$ (**5**), or with 4,4′-diiodobiphenyl to give the corresponding tetraphenyl $(CH_2{:}CHCH_2)_2MeSi(CH_2)_3C_6H_4-(C_6H_4)_2-C_6H_4(CH_2)_3SiMe(CH_2CH{:}CH_2)_2$ (**6**), isolated in 82 and 86% yield, respectively.

Application of reagents **1** and **2** to modular carbosilane dendrimer synthesis is illustrated as follows (Scheme 1). Conversion of **1** to **3** followed by addition of the latter to $Si(CH_2CH_2CH_2SiMe_2Cl)_4$ (**7**) affords $Si(CH_2CH_2CH_2SiMe_2C_6H_4CH_2CH_2CH_2SiMe(CH_2CH{:}CH_2)_2)_4$ (**8**), Pt-catalyzed addition of silane **2** to the simple substrate $Si(CH_2CH{:}CH_2)_4$ yields $Si(CH_2CH_2CH_2SiMe_2CH_2CH_2CH_2C_6H_4Br)_4$ (**9**), while treatment of the latter with **4**/$Pd(PPh_3)_4$ gives $Si(CH_2CH_2CH_2SiMe_2CH_2CH_2CH_2C_6H_4-C_6H_4CH_2CH_2CH_2SiMe(CH_2CH{:}CH_2)_2)_4$ (**10**), all prototypal transformations that use and generate dendrimer [G-1] analogues in 80% yield or better. However, **1** can be extended by two reiterative hydrosilylation cycles to a [G-2] monodendron (**11**) that can be cleanly metalated (Mg) and then added to **7**, so attaching 4 [G-2] units to a [G-1] core to yield a product of composition $C_{252}H_{476}Si_{33}$, (**12**), a colorless viscous oil (83%) with *M* 4433.2. Likewise, boronation of **11** to form its derivative **13** followed by coupling to **9** affords (see Scheme 2) analogue

Scheme 2



14 of **12**, $C_{288}H_{516}Si_{33}$ (*M* 4905.9; 57% after chromatographic purification) which remains fluid at ambient temperature. The rodlike biphenyl spacers introduced by the aryl−aryl coupling step into the skeletons of **10** and **14** may also be incorporated directly by using 4,4′-dibromobiphenyl as a precursor to analogues of reagents **1** and **2**, prototypes **8** and

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(12) All compounds have been characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{29}Si), elemental analysis, MALDI-TOF spectrometry and Gel Permeation Chromatography. Data for selected compounds are as follows. **1**: ^1H NMR ($CDCl_3$, δ) 7.38, 7.03 (d, 2H, C_6H_4), 5.74 (m, 2H, C*H*), 4.85 (m, 4H, $=CH_2$), 2.56 (t, 2H, CH_2), 1.59 (m, 2H, CH_2), 1.53 (d, 4H, CH_2), 0.60 (m, 2H, CH_2), 0.03 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 141.4 (C_6H_4), 134.6 (*C*H), 131.3, 130.2, 119.4 (C_6H_4), 113.2 ($=CH_2$), 39.2, 25.6, 21.3, 12.8 (CH_2), −5.8 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 1.02; MALDI-TOF (*m*/*z*, M + Ag^+) calcd 431, found 431. Anal. Calcd for $C_{16}H_{23}BrSi$: C, 59.47; H, 7.17. Found: C, 59.95; H, 7.16. **2**: ^1H NMR ($CDCl_3$, δ) 7.37, 7.03 (d, 2H, C_6H_4), 3.84 (m, 1H, Si*H*), 2.57 (t, 2H, CH_2), 1.63, 0.59 (m, 2H, CH_2), 0.05 (d, 6H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 141.5, 131.3, 130.3, 119.4 (C_6H_4), 38.8, 26.3, 13.8 (CH_2), −4.5 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) −13.05. Anal. Calcd for $C_{11}H_{17}BrSi$: C, 51.36; H, 6.66. Found: C, 51.82; H, 6.72. **8**: ^1H NMR ($CDCl_3$, δ) 7.46, 7.18 (d, 8H, C_6H_4), 5.80 (m, 8H, C*H*), 4.85 (m, 16H, $=CH_2$), 2.62 (t, 8H, CH_2), 1.64 (m, 8H, CH_2), 1.58 (d, 16H, CH_2), 1.36 (m, 8H, CH_2), 0.70 (m, 8H, CH_2), 0.56 (m, 8H, CH_2), 0.25 (s, 24H, CH_3), −0.05 (s, 12H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 143.2, 138.6 (C_6H_4), 134.8 (s, *C*H), 133.9, 128.3 (C_6H_4), 113.2 (s, $=CH_2$), 40.0, 25.9, 21.3, 21.2, 18.6, 17.5, 14.3 (CH_2), −2.8, −5.8 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 1.02 (4 Si), 0.78 (1 Si), −4.16 (4 Si); MALDI-TOF (*m*/*z*, M + Ag^+) calcd 1151, found 1151. Anal. Calcd for $C_{84}H_{140}Si_9$: C, 71.92; H, 10.06. Found: C, 72.27; H, 9.88. **9**: ^1H NMR ($CDCl_3$, δ) 7.40, 7.03 (d, 8H, C_6H_4), 2.60 (t, 8H, CH_2), 1.62 (m, 8H, CH_2), 1.40 (m, 8H, CH_2), 0.59 (m, 24H, CH_2), 0.02 (d, 24H, CH_3); ^{13}C NMR ($CDCl_3$, δ) 141.6, 131.3, 130.2, 119.3 (C_6H_4), 39.3, 26.0, 20.2, 18.6, 17.5, 15.2 (CH_2), −3.3 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 0.60 (1Si), 1.70 (4Si). Anal. Calcd for $C_{56}H_{88}Br_4Si_5$: C, 55.07; H, 7.26. Found: C, 56.30; H, 7.42. **10**: ^1H NMR ($CDCl_3$, δ) 7.47, 7.20 (d, 16H, C_6H_4), 5.80 (m, 8H, C*H*), 4.85 (m, 16H, $=CH_2$), 2.60 (t, 16H, CH_2), 1.65 (m, 16H, CH_2), 1.58 (d, 16H, CH_2), 1.40 (m, 8H, CH_2), 0.70 (m, 8H, CH_2), 0.60 (m, 24H, CH_2), 0.20 (s, 12H, CH_3), 0.00 (s, 24H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 141.6, 141.3, 138.6, 138.5 (C_6H_4), 134.7 (s, *C*H), 128.8, 126.8 (C_6H_4), 113.2 (s, $=CH_2$), 39.7, 39.5, 26.2, 25.8, 21.3, 20.3, 18.6, 17.6, 15.5, 13.0 (s, CH_2), −3.2, − 5.8 (s, CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 8.38 (4 Si), 12.09 (5 Si); MALDI-TOF (*m*/*z*, M + Ag^+) calcd 1983, found 1985. Anal. Calcd for $C_{120}H_{180}Si_9$: C, 76.85; H, 9.67. Found: C, 76.29; H, 9.59. **11**: ^1H NMR ($CDCl_3$, δ) 7.38, 7.02 (d, 2H, C_6H_4), 5.77 (m, 8H, C*H*), 4.84 (m, 16H, $=CH_2$), 2.55 (t, 2H, CH_2), 1.54 (m, 18H, CH_2), 1.40 (m, 12H, CH_2), 0.75 (m, 26H, CH_2), −0.02 (s, 15H, CH_3), −0.10 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 141.6 (C_6H_4), 134.8 (*C*H), 131.3, 130.2, 119.3 (C_6H_4), 113.1 (s, $=CH_2$), 39.4 (s, CH_2), 26.0, 21.8, 18.9, 18.8, 18.5, 18.3, 17.9, 17.6, 17.4, 13.8 (CH_2), −5.0, −5.3, −5.7 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 1.85 (1 Si), 1.199 (2 Si), 0.43 (4 Si); MALDI-TOF (*m*/*z*, M + Ag^+) calcd 1189, found 1188. Anal. Calcd for $C_{58}H_{107}Si_7$: C, 64.45; H, 9.98. Found: C, 64.06; H, 9.68. **12**: ^1H NMR ($CDCl_3$, δ) 7.42, 7.18 (d, 8H, C_6H_4), 5.80 (m, 32H, C*H*), 4.90 (m, 64H, $=CH_2$), 2.62 (t, 8H, CH_2), 1.60 (m, 72H, CH_2), 1.35 (d, 64H, CH_2), 1.05 (m, 8H, CH_2), 0.95 (m, 8H, CH_2), 0.62 (m, 96H, CH_2), 0.28 (s, 24H, CH_3), 0.10 (s, 24H, CH_3), −0.05 (s, 48H, CH_3), −0.10 (s, 12 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 143.2, 138.6 (C_6H_4), 134.8 (*C*H), 133.9, 128.3 (C_6H_4), 113.1 (s, $=CH_2$), 21.5, 18.8−17.5 (CH_2), 1.0, −2.8, −5.0, −5.7 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 1.71 (4 Si), 1.19 (8 Si), 0.88 (1 Si), 0.43 (16 Si), −4.11 (4 Si); MALDI-TOF (*m*/*z*, M + Ag^+) calcd 4541, found 4545. Anal. Calcd for $C_{252}H_{476}Si_{33}$: C, 68.27; H, 10.82. Found: C, 67.44; H, 10.32. **14**: ^1H NMR ($CDCl_3$, δ) 7.47, 7.20 (d, 16H, C_6H_4), 5.80 (m, 32H, C*H*), 4.85 (m, 48H, $=CH_2$), 2.60 (t, 16H, CH_2), 1.65 (m, 16H, CH_2), 1.58 (d, 64H, CH_2), 1.40 (m, 32H, CH_2), 0.60 (m, 134H, CH_2), 0.05 (s, 24H, CH_3), −0.03 (s, 48H, CH_3), −0.06 (s, 12H, CH_3), −0.10 (s, 24 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 141.6, 141.3, 138.6, 138.5 (C_6H_4), 134.7 (*C*H), 128.8, 126.8 (C_6H_4), 113.2 ($=CH_2$), 39.7, 39.5, 26.2, 25.8, 21.3, 20.3, 18.6, 17.6, 15.5, 13.0 (CH_2), −3.2, −5.8 (CH_3); $^{29}Si\{^1H\}$ ($CDCl_3$, δ) 1.69 (4 Si), 1. 03 (5 Si), 0.29 (24 Si); MALDI-TOF (*m*/*z*, M + Ag^+) calcd 5014, found 5019. Anal. Calcd for $C_{288}H_{516}Si_{33}$: C, 70.51; H, 10.60. Found: C, 70.70; H, 10.45.

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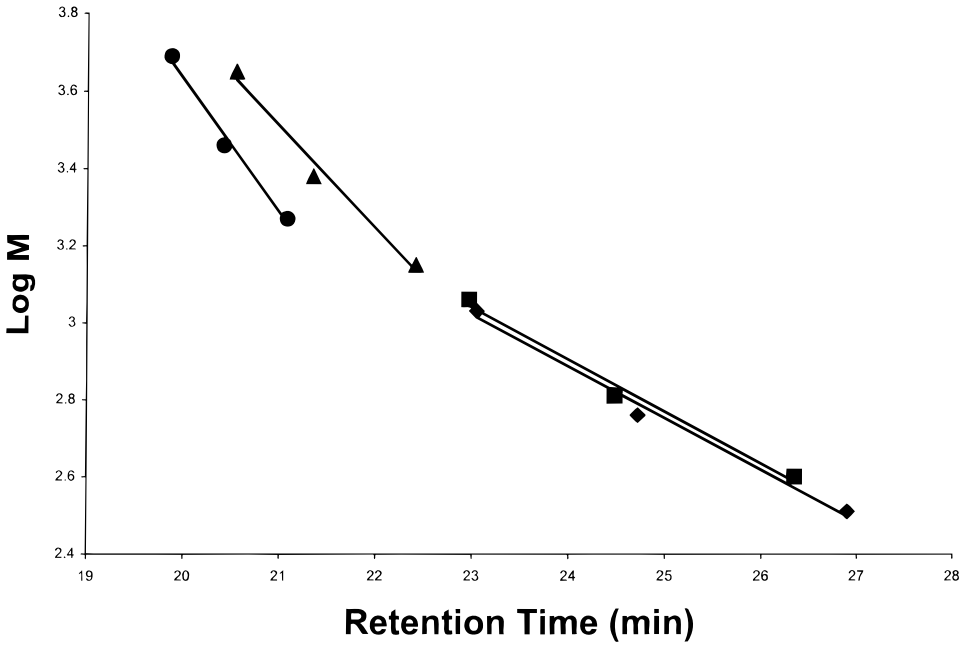

Figure 1. Plots of log M_n vs retention time for carbosilanes: ♦, compound **1** and its [G-1], [G-2] monodendron homologues; ▲, compound **8** and its [G-1], [G-2] dendrimer homologues; ● compound **10** and its [G-1], [G-2] dendrimer homologues; ■, bromobiphenyl analogue of bromophenyl monodendron **1** and its [G-1], [G-2] homologues.

9, and monodendron **11**, while metalation of the latter using BuLi (rather than Mg) may be used to join dendritic carbosilane blocks to other heteroatoms including O, Sn, Hg, and[10b] P.

Most significantly, the homologues to [G-2] for each family (including in particular modular components such as **9** and **11**) can be obtained as monodisperse, analytically pure materials: plots of GPC retention volume vs log M_n (Figure 1) are linear even for the core-functionalized [G-0] (i.e., **1**), [G-1], and [G-2] (i.e., **11**) series of bromophenyl monodendrons. Efficient convergent coupling of the latter, e.g., to give **12** or **14**, lays the foundation for a versatile, reiterative methodology that can be used to make defect-free assemblies with increased internal volume, expanded hydrodynamic radius, and larger peripheral surface area than those of carbosilane analogues obtained by divergent growth. Related accessible target structures include those based on compound **6** in which tetraphenyl, triphenyl, and biphenyl spacers are linked together through a dendritic skeleton.

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