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Synthesis and Characterization of Lithiated Dendrimers

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The synthesis of the precursor phenylthiomethyl-functionalized carbosilane dendrimers $Si[(CH_2)_3SiMe_2CH_2SPh]_4$ (**1**) and $Si\{(CH_2)_3Si[(CH_2)_3SiMe_2CH_2SPh]_3\}_4$ (**2**) is described. Reacting **1** and **2** with lithium naphthalenide gives the first lithiomethyl-functionalized dendrimers $Si[(CH_2)_3SiMe_2CH_2Li]_4$ (**7**) and $Si\{(CH_2)_3Si[(CH_2)_3SiMe_2CH_2Li]_3\}_4$ (**11**). Deutero, trimethylsilyl, trimethylstannyl, and tri-*n*-butylstannyl derivatives of these dendrimers, as well as a method to enable isolation of the lithiated dendrimers as solids, are described.

Introduction

The rising demand for materials with improved and novel properties has shifted the emphasis in polymer research from traditional linear polymers, via cross-linked and branched polymers, to the hyperbranched or dendritic polymers. This new class of highly branched three-dimensional molecules has intrigued researchers, and numerous review articles have been published in recent years.[1,2] Many applications for dendrimers have been found, one of the most exciting applications being the use of dendrimers as an immobilization phase for homogeneous catalysts.[3] From our ongoing research into dendrimers and their applications in organometallic chemistry,[2,4] it has become clear that the number of synthetic routes available to attach an organometallic moiety to the branches of a dendrimer is limited. This limitation is mainly due to the requirement to employ reactions that have a quantitative yield in order to prevent imperfections in the dendrimer buildup.[5,6] It was envisaged that a greater range of dendrimers could be synthesized by using a polylithiated dendrimer.[7] Despite the fact that alkyllithium reagents are useful and versatile reagents for both organic and organometallic synthesis, they (i) are air and moisture sensitive, (ii) are prone to decomposition by β-hydride elimination,[8] and (iii) have limited stability in some solvents such as THF. Since dendrimer synthesis requires quantitative reactions, the synthesis of such lithiated dendrimers constitutes a considerable challenge.

For the synthesis of known bis(lithiomethyl)silanes, a limited number of reports are available in the literature. Recently a report by Strohmann et al. described the high-yield synthesis of a series of bis(lithiomethyl)silanes[9] and tetrakis(lithiomethyl)silanes[10] by reductive cleavage of C−S bonds with lithium naphthalenide. Our strategy was to apply the method of Strohmann et al.[9,10] to the synthesis of dendrimers. An important consideration in our strategy was to prevent possible decomposition through β-hydrogen elimination, as well as stabilizing the carbanion, by using a lithiomethyldimethylsilyl group.

Results and Discussion

We synthesized the first generation carbosilane dendrimer $Si[(CH_2)_3SiMe_2CH_2SPh]_4$ (**1**) and the corresponding second generation dendrimer $Si\{(CH_2)_3Si[(CH_2)_3SiMe_2CH_2SPh]_3\}_4$ (**2**). These compounds are accessible via catalytic hydrosilylation of tetraallylsilane (**3**) and $Si[(CH_2)_3Si(CH_2CH{=}CH_2)_3]_4$ (**4**) with the known[11] $HSiMe_2CH_2SPh$ (**5**) (see Scheme 1). Compounds **1** and **2** were isolated as colorless, air-stable oils in nearly quantitative yields.

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(5) The composition of dendrimers formed in reaction of the arms with less than 100% yield can be calculated from the yield of the specific reaction using the following formula: $P = (N!/n!m!)Y^n(1 - Y)^m$; where P = mole fraction of product; $N = n + m$ = total number of reactive groups; n = number of reacted groups; m = number of unreacted groups; and Y = reaction yield. For example a reaction with a yield of 95% on a dendrimer with 4 arms gives a mole fraction of $P = (4!/4!0!)(0.95)^4(0.05)^0 = 0.815$ of pure product. The other 18.5% are impure dendrimers with one or more branches unreacted.

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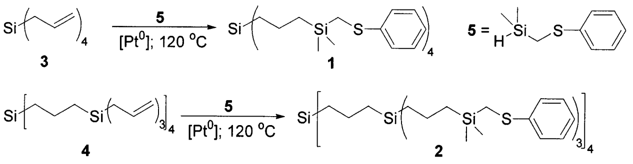
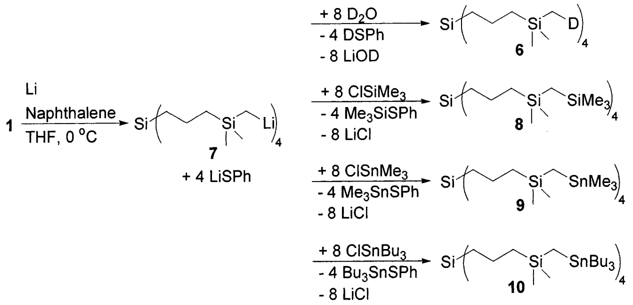
Scheme 1. Synthesis of 1 and 2



Scheme 2. Synthesis of 7 and Its Reactions

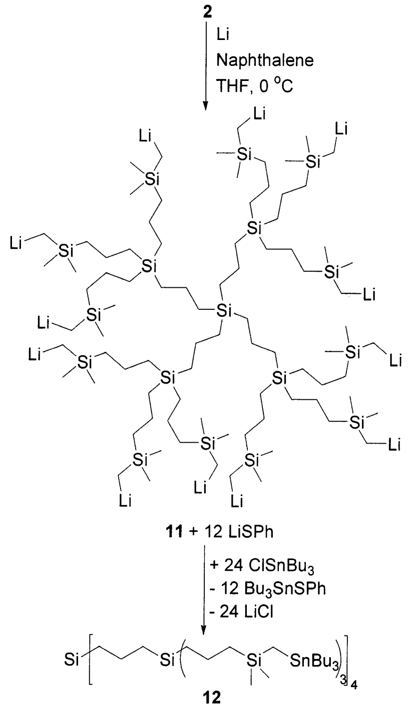


Generation of Lithiated Dendrimers in Situ. Following the method of Strohmann et al.,[9,10] we reacted **1** with a slight excess of lithium naphthalenide ($LiC_{10}H_8$) at −41 °C, followed by quenching with excess D_2O. The reaction proceeded rapidly and completely to give the desired deuterated dendrimer $Si[(CH_2)_3SiMe_2CH_2D]_4$ (**6**), as was concluded from the ^1H and ^{13}C NMR spectra of the product after isolation. In addition to the deuterated dendrimer, however, 4 equiv of DSPh was formed, as well as 8 equiv of naphthalene. The product was isolated by repeated column chromatography, which reduced the yield of final product to 9%. The NMR signals attributable to the four branches appeared at the same chemical shift due the high symmetry of the molecule, confirming that complete conversion had taken place.

After several attempts, we formulated a system that successfully avoided the problems in separation of the product from the side products.[12] In this procedure, ca. 25 mol % naphthalene is used, with an excess of lithium, at 0 °C. The phenylthiomethyl dendrimers **1** and **2** are added slowly, making sure the green/blue color of the lithium naphthalenide is always present during reaction. These reactions are complete in about 1 h. Fortunately, the generated lithium reagent is stable enough in THF to “survive” for this time.

The tetralithiated reagent $Si[(CH_2)_3SiMe_2CH_2Li]_4$ (**7**) was analyzed by quenching the generated reagent in situ with D_2O, $ClSiMe_3$, $ClSnMe_3$, or $ClSnBu_3$ at 0 °C (Scheme 2). The products were separated from the salts by extraction into hexane. Separation from the thiol HSPh (formed by hydrolysis of LiSPh) was achieved by washing the hexane solutions with dilute aqueous base. Heating under vacuum at ±100 °C removed the bulk of the naphthalene through sublimation. The resulting mixtures contained ca. 90% of the desired dendrimers, which were then purified by column chromatography over silica gel, eluting with hexane to yield $Si[(CH_2)_3SiMe_2CH_2D]_4$ (**6**), $Si[(CH_2)_3SiMe_2CH_2SiMe_3]_4$ (**8**), $Si[(CH_2)_3SiMe_2CH_2SnMe_3]_4$ (**9**), and $Si[(CH_2)_3SiMe_2CH_2SnBu_3]_4$ (**10**) as colorless, air-stable oils. Full and unambiguous characterizations were performed by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section).

Scheme 3. Synthesis of Lithiated Dendrimer with 12 Functionalities and Its Reaction



A similar procedure was successfully performed for the second generation phenylthiomethyl dendrimer **2**, resulting in the formation of the second generation lithiated dendrimer **11**. Quenching **11** with $ClSnBu_3$ in situ gave the second generation tributyltin-terminated derivative **12** (see Scheme 3). Satisfactory characterization data for **12** were obtained (see Experimental Section). To the best of our knowledge, **7** and **11** are the first examples of methyllithium-functionalized dendrimers, and the second generation dendrimer **11** is, with 12 carbanionic functionalities, the largest alkyllithium reagent reported to date.

Isolation of Lithiated Dendrimers. Due to the difficulty of isolation of a lithiated dendrimer from the side products formed, and with a view to obtaining pure materials, we investigated a slightly different route. Alkyltributyltin compounds are known to be convenient precursors for the generation of alkyllithium reagents via metathetical metal−metal exchange.[13] In 1980, Seitz and Zapata[14] reported the high-yield synthesis of (trimethylsilylmethyl)lithium from (trimethylsilylmethyl)tributyltin and BuLi in THF. The side product of the

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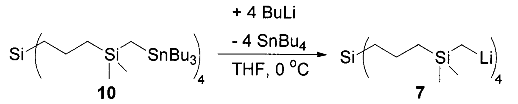
Scheme 4. Synthesis of 7 via Tin–Lithium Exchange Reaction



reaction, tetrabutyltin, can easily be removed by extraction into pentane.

Following this method,[14] we attempted the synthesis of the tetralithiated compound **7**. A solution of **10** in THF was treated with 4.0 equiv of BuLi at 0 °C (Scheme 4). The yellow mixture slowly decolorized. After 30 min the solvent was evaporated and the mixture of a white solid and a clear liquid was extracted with pentane. ^{1}H NMR spectroscopy on the isolated solid product in benzene-d_6/THF-d_8 indicated that **7** had formed. The resonances due to the tributyltin moiety had disappeared and a singlet at ca. −1.8 ppm, integrating for eight protons, was evident. This signal was attributed to the four CH_2Li moieties in the dendrimer. The value of −1.8 ppm is similar to literature values for (trimethylsilylmethyl)lithium.[15,16] The rest of the spectrum showed the expected resonances consistent with the product.

Compound **7** is not soluble in any common organic solvents other than THF; it is an extremely air-sensitive solid, and it reacts slowly with THF. We tried several strategies to obtain suitable crystals for X-ray crystallography, but only amorphous solids were obtained.

Further evidence for the formation and isolation of the lithiated dendrimer was provided by quenching NMR samples with D_2O and $ClSiMe_3$. After quenching, ^{1}H NMR spectra identical to those obtained from the previously isolated **6** and **8** were observed.

It is important in these reactions that *exactly* 4 equiv of butyllithium is used, as any excess of butyllithium co-aggregates with the dendrimer upon workup. We found that it was subsequently not possible to separate the aggregated butyllithium from the lithiated dendrimer. The polylithiated compounds **7** and **11** may be versatile reagents with useful applications in the field of organometallic dendrimers.

Isolation of **11** via the tin/lithium exchange reaction was hampered by the increased sensitivity of the compound. In our hands we always found observable traces of decomposition in the NMR spectra of **11**, presumably due to reaction with traces of moisture and/or oxygen during workup.

Conclusions

Dendrimers containing four and 12 phenylthiomethyl functionalities have been prepared. These dendrimers react with lithium naphthalenide in a C−S bond-cleavage reaction to give lithiomethyl-functionalized dendrimers. The dendrimer with four functionalities was derivatized by reaction with various trialkylsilyl and -stannyl chlorides. The dendrimer with 12 functionalities was derivatized by reaction with tributyltin chloride. The tetrakis(tributyltin) dendrimer was subsequently reacted with butyllithium to give the lithiomethyl-functionalized dendrimer. This dendrimer was isolated as a solid and characterized by NMR spectroscopy.

Experimental Section

General Remarks. Lithiated dendrimers are extremely air-sensitive compounds. Manipulations were carried out under purified nitrogen using glovebox (MBraun Unilab) or standard Schlenk line techniques under purified argon.[17] Solvents were dried by passage through a column containing alumina (neutral, Brockmann grade I) and distilled from sodium/benzophenone ketyl prior to use.[18] All reagents were stored under argon. Butyllithium (1.6 M in hexanes), chlorodimethylsilane, chlorotrimethylsilane, thioanisol, and trichlorosilane were purchased from Sigma Aldrich. $HSiMe_2CH_2SPh$[11] and $Si[(CH_2)_3Si(CH_2CH{=}CH_2)_3]_4$[19] were prepared by literature methods. Karstedt catalyst[20] was prepared according to literature methods and stored under argon as a 1% Pt solution in toluene.

NMR spectra were recorded on either a Varian Unity-400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz) spectrometer or a Varian Mercury-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) spectrometer at ambient temperature. Chemical shifts were referenced to TMS using either the residual protio impurities in the solvent (^{1}H NMR), the solvent resonances (^{13}C NMR), or external TMS (^{29}Si NMR). Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the range 450−4400 cm^{-1}. Spectra were recorded on neat samples between NaCl plates. Mass spectra were determined by Dr. P. Boshoff of the mass spectrometry unit at the Cape Technikon. The selected m/z values given refer to the isotopes ^{1}H, ^{12}C, ^{28}Si, ^{32}S, and ^{120}Sn. In all cases, the isotopic distribution pattern was checked against the theoretical distribution. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyzer in the microanalytical laboratory of the University of Cape Town.

Synthesis of 1. A mixture of **5** (4.92 g, 27 mmol), **3** (1.5 mL, 6.48 mmol), and Karstedt catalyst solution (200 μL) was heated to 120 °C for 18 h.[21] The volatiles were removed in vacuo at 140 °C, leaving a colorless oil and a black precipitate. The oil was filtered over a pad of silica gel, eluting with hexane. Removal of the volatiles in vacuo gave **1** as a colorless oil. Yield: 5.79 g (97%). IR (cm^{-1}): 3072 (w, $\nu(\mathrm{CH_{ar}})$), 3057 (w, $\nu(\mathrm{CH_{ar}})$), 3016, 2952 (s, $\nu_{as}(\mathrm{CH_3})$), 2911 (s, $\nu_{as}(\mathrm{CH_2})$), 1934 (w), 1851 (w), 1784 (w), 1717 (w) (monosubstituted benzene), 1581 (m, $\nu(\mathrm{C{=}C})$), 1479 (m, $\nu(\mathrm{C{=}C})$), 1438 (s, $\delta_{as}(\mathrm{CH_2})$), 1390, 1333, 1249 (s, $\delta_s(\mathrm{CH_3})$), 1138, 1085, 1067, 1025, 982, 943, 909, 844 (s, $\nu(\mathrm{SiMe_2})$), 736 (s, $\gamma(\mathrm{CH})$), 697, 689 (s, $\gamma(\mathrm{CH})$), 668 (S−C), 472. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.06 (24 H, s, 8 Me), 0.55 (8 H, m, ^3J(H,H) = 8 Hz, 4 CH_2Si), 0.70 (8 H, m, ^3J(H,H) = 8 Hz, 4 $SiCH_2$), 1.30 (8 H, m, 4 $CH_2\mathit{CH_2}CH_2$), 2.09 (8 H, s, 4 CH_2S), 7.3−6.9 (20 H, m, 4 Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ −3.2 (8 C, 8 Me), 17.2 (4 C, 4 $\mathit{C}H_2S$), 17.4 (4 C, 4 $\mathit{C}H_2Si$), 18.5 (4 C, 4 $Si\mathit{C}H_2$), 19.9 (4 C, 4 $CH_2\mathit{C}H_2CH_2$), 124.6 (4 C, C-4 of SPh), 126.1 (8 C), 128.6 (8 C) (C-2, -6 and C-3, -5 of SPh), 140.4 (4 C, C-1 of SPh). ^{29}Si{^{1}H} NMR ($CDCl_3$, 79.45 MHz): δ 0.95 (1 Si, $\mathit{Si}CH_2$), 2.04 (4 Si, $\mathit{Si}Me_2$). MS (FAB): m/z 919 (0.5, M$^+$ − H), 905 (2, M$^+$ − CH$_3$), 811 (3, M$^+$ − SPh), 797 (100, M$^+$ − CH$_2$SPh), 697 (30, M$^+$ − C$_3$H$_6$Si(Me$_2$CH$_2$SPh), 589

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[21] The reaction was followed by monitoring the disappearance of the peak at 1610 cm^{-1} in the IR spectrum of the mixture (associated with $\nu(\mathrm{C{=}C})$).

(2, $\mathrm{M^+ - CH_2SPh - C_2H_4SiMe_2CH_2SPh}$), 575 (2, $\mathrm{M^+ - CH_2SPh - C_3H_6SiMe_2CH_2SPh}$), 475 (4, $\mathrm{M^+ - 2\ C_3H_6SiMe_2CH_2SPh}$), 181 (80, $\mathrm{SiMe_2CH_2SPh^+}$). Anal. Calcd for $\mathrm{C_{48}H_{76}S_4Si_5}$: C, 62.54; H, 8.31; S, 13.91. Found: C, 62.1; H, 8.4; S, 13.5.

Synthesis of 2. Karstedt catalyst solution (100 μL) was added to a mixture of **4** (0.50 g, 0.62 mmol) and **5** (1.5 g, 8.24 mmol), and the mixture was heated to 130 °C for 16 h. The excess silane was distilled off in vacuo at 130 °C, and the catalyst was removed by filtration over a pad of silica, eluting with dichloromethane. The solvent was removed in vacuo to give **2** as a colorless oil. Yield: 1.79 g (96%). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): δ 0.11 (72 H, s, 24 Me), 0.59 (40 H, m, 20 $\mathrm{CH_2Si}$), 0.75 (24 H, m, 12 $\mathrm{C\mathit{H}_2SiMe_2}$), 1.45−1.20 (32 H, m, 16 $\mathrm{CH_2C\mathit{H}_2CH_2}$), 2.13 (24 H, s, 12 $\mathrm{SCH_2}$), 7.3−7.0 (60 H, m, 12 SPh). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 75.5 MHz): δ −3.1 (24 C, 8 Me), 17.2 (12 C, 4 $\mathrm{CH_2S}$), 17.4 (12 C, 4 $\mathrm{CH_2Si}$), 18.5 (12 C, 4 $\mathrm{SiCH_2}$), 19.9 (12 C, 4 $\mathrm{CH_2\mathit{C}H_2CH_2}$), 124.6 (12 C, C-4 of SPh), 126.1 (24 C), 128.6 (24 C)(C-2, -6 and C-3, -5 of SPh), 140.4 (12 C, C-1 of SPh), The "core" propyl chain was not visible due to low intensity of the signal. ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$, 79.45 MHz): δ 0.50 (1 Si, $\mathrm{Si(CH_2)_4}$), 0.76 (4 Si, $\mathrm{SiCH_2}$), 1.99 (12 Si, $\mathrm{SiMe_2}$). Anal. Calcd for $\mathrm{C_{156}H_{252}S_{12}Si_{17}}$: C, 62.67; H, 8.50. Found: C, 63.0; H, 8.6.

Synthesis of 6, 8, 9, and 10. The preparation of **6**, **8**, **9** and **10** all followed the same general method; a representative preparation is given for **6**.

Synthesis of 6. Lithium metal pieces (0.090 g, 13 mmol) were added to a solution of naphthalene (0.090 g, 0.70 mmol) in THF (5 mL) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **1** (0.600 g, 0.65 mmol) in THF (4 mL) was added at such a rate that the green color of lithium naphthalenide did *not* disappear (±1 h). The mixture was cooled to −40 °C, and $\mathrm{D_2O}$ (2.0 mL) in THF (2.0 mL) was added. The color of the lithium naphthalenide disappeared completely within seconds to leave a colorless/gray solution. The volatiles were removed in vacuo, and the products were partitioned between hexane (10 mL) and water (10 mL). The aqueous layer was extracted with hexane (3 × 10 mL), and the organic phases were combined. The organic phase was washed successively with water (3 × 10 mL), dilute aqueous NaOH (3 × 10 mL), water (3 × 10 mL), and brine (3 × 10 mL), dried over $\mathrm{MgSO_4}$, and filtered, and the volatiles were evaporated in vacuo. The bulk of the naphthalene was sublimed out of the product at 150 °C, 10^{-3} mmHg. Chromatography over silica gel, eluting with hexane, gave **6** as a colorless oil. Yield: 0.265 g (83%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz): δ −0.12 (8 H, t, ^2J(D,H) = 2 Hz, 4 $\mathrm{C\mathit{H}_2D}$), −0.10 (24 H, s, 8 Me), 0.49 (16 H, m, ^3J(H,H) 8 Hz, 4 $\mathrm{C\mathit{H}_2Si}$), 1.27 (8 H, m, 4 $\mathrm{CH_2C\mathit{H}_2CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.6 MHz): δ −1.9 (4 C, t, ^1J(C,D) = 18 Hz, 4 $\mathrm{\mathit{C}H_2D}$), −1.6 (8 C, 8 Me), 17.5 (4 C, 4 $\mathrm{\mathit{C}H_2Si}$), 18.6 (4 C, 4 $\mathrm{\mathit{C}H_2Si}$), 21.6 (4 C, 4 $\mathrm{CH_2\mathit{C}H_2CH_2}$). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$, 79.45 MHz): δ 0.50 (1 Si, $\mathrm{\mathit{Si}CH_2}$), 0.74 (4 Si, $\mathrm{\mathit{Si}Me_2}$). MS (FAB): *m/z* 492.37854 ($\mathrm{M^+}$) ($\mathrm{C_{24}H_{56}D_4Si_5}$ requires 492.37925), 462 ($\mathrm{M^+ - 2Me}$), 376 ($\mathrm{M^+ - C_3H_6SiMe_2CH_2D}$), 361 ($\mathrm{M^+ - C_3H_6SiMe_2CH_2D - CH_3}$), 260 ($\mathrm{M^+ - 2C_3H_6SiMe_2CH_2D}$), 186 ($\mathrm{C_3H_6SiC_3H_6SiMe_2CH_2D^+}$), 144 ($\mathrm{SiC_3H_6SiMe_2CH_2D^+}$), 100 ($\mathrm{SiC_3H_6SiMe_2{}^+}$), 74 ($\mathrm{SiMe_2CH_2D^+}$). Anal. Calcd for $\mathrm{C_{24}H_{56}D_4Si_5}$: C, 58.45; H, 11.44. Found: C, 59.1; H, 11.7.

8: colorless oil. Yield: 0.461 g (87%). IR: (cm^{-1}) 2952 (s, ν_{as}(Me)), 2911 (s, ν_{as}($\mathrm{CH_2}$)), 1448 (m, δ_{as}($\mathrm{CH_2}$)), 1412 (m), 1353 (m), 1333 (m), 1250 (s, δ_{s}(Me)), 1141 (m), 1051 (s), 983 (w), 943 (w), 909 (s), 837 (vs br, ν($\mathrm{SiMe_3}$)), 789 (s), 762 (s, ν($\mathrm{SiMe_3}$)), 687 (s), 614 (w), 589 (w), 553 (w). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz): δ −0.29 (8 H, s, 4 $\mathrm{SiC\mathit{H}_2Si}$), 0.00 (24 H, s, 4 $\mathrm{SiMe_2}$), 0.03 (36 H, s, 4 $\mathrm{SiMe_3}$), 0.57 (16 H, m, ^3J(H,H) = 8 Hz, 8 $\mathrm{C\mathit{H}_2Si}$), 1.35 (8 H, m, 4 $\mathrm{CH_2C\mathit{H}_2CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.6 MHz): δ −0.5 (8 C, 4 $\mathrm{SiMe_2}$), 1.4 (12 C, 4 $\mathrm{SiMe_3}$), 2.8 (4 C, 4 $\mathrm{Si\mathit{C}H_2Si}$), 17.7 (4 C, 4 $\mathrm{\mathit{C}H_2Si}$), 18.7 (4 C, 4 $\mathrm{\mathit{C}H_2Si}$), 23.0 (4 C, 4 $\mathrm{CH_2\mathit{C}H_2CH_2}$). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$, 79.45 MHz): δ 0.5 (1 Si, $\mathrm{\mathit{Si}(CH_2)_4}$), 0.82 (4 Si, 4 $\mathrm{\mathit{Si}Me_3}$), 1.0 (4 Si, 4 $\mathrm{\mathit{Si}Me_2}$). MS (EI): *m/z* 776 ($\mathrm{M^+}$, 0.8), 705 (7), 643 (13), 566 ($\mathrm{C_{28}H_{62}Si_6}$, 60), 493 ($\mathrm{C_{25}H_{53}Si_5}$, 100), 442 ($\mathrm{C_{21}H_{50}Si_5}$, 59), 331 ($\mathrm{C_{18}H_{31}Si_3}$, 93%). Anal. Calcd for $\mathrm{C_{36}H_{92}Si_9}$: C, 55.58; H, 11.92. Found: C, 55.8; H, 12.2.

9: colorless oil. Yield: 0.74 g (80%). IR (cm^{-1}): 2951 (s, ν_{as}(Me)), 2911 (s, ν_{as}($\mathrm{CH_2}$)), 2875 (s, ν_{s}(Me)), 1448 (m, δ_{s}(Me)), 1412, 1357, 1333, 1246 (s, δ_{s}(SiMe)), 1215, 1188 (m, δ_{s}(SnMe)), 1141, 1079, 998, 941, 906, 833 (s, ν_{as}(SiC)), 772, 720, 581, 524 (s, ν_{as}(SnC)). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz): δ −0.26 (8 H, s, ^2J(H,Sn) = 56 Hz, 4 $\mathrm{SiC\mathit{H}_2Sn}$); −0.02 (24 H, s, 4 $\mathrm{SiMe_2}$), 0.10 (36 H, s, 4 $\mathrm{SnMe_3}$), 0.58 (16 H, t, ^3J(H,H) = 8 Hz, 8 $\mathrm{SiC\mathit{H}_2}$), 1.34 (8 H, m, 4 $\mathrm{CH_2C\mathit{H}_2CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.6 MHz): δ −8.00 (4 C, ^1J(C, $^{119/117}$Sn) = 202/193 Hz, $\mathrm{Si\mathit{C}H_2Sn}$), −5.65 (12 C, 4 $\mathrm{SnMe_3}$), −0.22 (8 C, 4 $\mathrm{SiMe_2}$), 17.65 (4C, $\mathrm{Si\mathit{C}H_2C}$), 18.75 (4 C, $\mathrm{Si\mathit{C}H_2C}$), 22.24 (4 C, $\mathrm{CH_2\mathit{C}H_2CH_2}$). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$, 79.45 MHz): δ 0.82 (1 Si, $\mathrm{Si(CH_2)_4}$), 4.07 (4 Si, 4 $\mathrm{\mathit{Si}Me_2}$). Anal. Calcd for $\mathrm{C_{36}H_{92}Si_5Sn_4}$: C, 37.95; H, 8.13. Found: C, 38.1; H, 8.4.

10: colorless oil. Yield: 0.992 g, (92%), R_f(silica/hexane) 0.95. IR (cm^{-1}): 2954 (s, ν_{as}(Me)), 2921 (s, ν_{as}($\mathrm{CH_2}$)), 2871 (s, ν_{s}(Me)), 2853 (s, ν_{s}($\mathrm{CH_2}$)), 1464 (s, δ_{as}($\mathrm{CH_2}$)), 1416, 1376 (s, δ_{s}(Me)), 1356, 1339, 1291, 1246 (s, δ_{s}($\mathrm{SiMe_3}$)), 1214, 1180, 1142, 1070, 1043, 992. 960, 906, 861, 831 (s, ν($\mathrm{SiMe_2}$)), 770, 723 (s, δ(($\mathrm{CH_2})_x$)), 689, 668, 592 (s, ν(SnC)), 506 (s, ν_{as}(SnC)). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz): δ −0.40 (8 H, s, ^2J(H,Sn) = 56 Hz, 4 $\mathrm{SiC\mathit{H}_2Sn}$), −0.09 (24 H, s, 4 $\mathrm{SiMe_2}$), 0.50 (16 H, m, 8 $\mathrm{SiC\mathit{H}_2C}$), 0.95−0.68, 1.5−1.2 (116 H, m, $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CCH_2Me}$, CMe, $\mathrm{SiCCH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100 MHz): δ −8.8 (4 C, ^1J(C,$^{119/117}$Sn) = 202/193 Hz, 4 $\mathrm{Si\mathit{C}H_2Sn}$), −0.1 (8 C, ^3J(C,$^{119/117}$Sn) = 12.0/10.6 Hz, 4 $\mathrm{SiMe_2}$), 10.4 (12 C, ^1J(C,$^{119/117}$Sn) = 323.6/309.8 Hz, 4 $\mathrm{Sn(\mathit{C}H_2C)_3}$), 13.7 (12 C, 12 $\mathrm{C\mathit{Me}}$), 17.7 (4 C, 4 $\mathrm{Si\mathit{C}H_2C}$), 18.8 (4 C, 4 $\mathrm{Si\mathit{C}H_2C}$), 23.5 (4 C, 4 $\mathrm{SiCH_2\mathit{C}H_2CH_2}$), 27.5 (12 C, ^2J(C,$^{119/117}$Sn) = 58.2/55.0 Hz, 12 $\mathrm{\mathit{C}H_2Me}$), 29.2 (12 C, ^3J(C,$^{119/117}$Sn) = 20.0/18.4 Hz, 4 $\mathrm{Sn(CH_2\mathit{C}H_2)_3}$). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$, 79.45 MHz) δ 0.59 (1 Si, $\mathrm{\mathit{Si}CH_2}$), 3.10 (4 Si, ^2J(Si,Sn) = 22.9 Hz, 4 $\mathrm{\mathit{Si}CH_2Sn}$). MS (FAB): *m/z* fragments only. Anal. Calcd for $\mathrm{C_{72}H_{164}Si_5Sn_4}$: C, 52.56; H, 10.04. Found: C, 53.0; H, 9.4.

Synthesis of 12. Lithium metal pieces (0.100 g, 14.5 mmol) were added to a solution of naphthalene (0.100 g, 0.78 mmol) in THF (5 mL) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **2** (0.600 g, 0.201 mmol) in THF (3 mL) was added at such a rate that the green color of lithium naphthalenide did *not* disappear (±1 h). The resulting solution was cooled to −40 °C, and tributyltin chloride (1.0 mL, 3.7 mmol) was added quickly. The color disappeared completely within seconds to leave a colorless/gray solution. The volatiles were removed in vacuo, and the products were suspended in hexane (5 cm^3). The solution was filtered over a pad of alumina, eluting with hexane. The volatiles were evaporated in vacuo, and the residual tributyltin chloride was distilled off at 230 °C/0.01 mmHg. Chromatography over silica gel, eluting with hexane, gave **12** as a colorless oil. Yield: 0.992 g (92%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz): δ −0.34 (24 H, s, ^2J(H,Sn) = 56 Hz, 12 $\mathrm{SiCH_2Sn}$), −0.02 (72 H, s, 24 Me), 0.55 (64 H, m, 32 $\mathrm{SiC\mathit{H}_2C}$), 0.95−0.68, 1.5−1.2 (116 H, m, $\mathrm{SnCH_2C}$, $\mathrm{CCH_2C}$, $\mathrm{CCH_2Me}$, CMe, $\mathrm{SiCCH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.6 MHz): δ −8.7 (4 C, ^1J(C,$^{119/117}$Sn) = 202/193 Hz, 4 $\mathrm{Si\mathit{C}H_2Sn}$); −0.1 (8 C, ^3J(C,$^{119/117}$Sn) = 12.0/10.6 Hz, 4 $\mathrm{SiMe_2}$), 10.4 (12 C, ^1J(C,$^{119/117}$Sn) = 323.6/309.8 Hz, 4 $\mathrm{Sn(\mathit{C}H_2C)_3}$), 13.7 (12 C, 12 $\mathrm{C\mathit{Me}}$), 17.7 (4 C, 4 $\mathrm{Si\mathit{C}H_2C}$), 18.8 (4 C, 4 $\mathrm{Si\mathit{C}H_2C}$), 23.5 (4 C, 4 $\mathrm{SiCH_2\mathit{C}H_2CH_2}$), 27.5 (12 C, ^2J(C,$^{119/117}$Sn) = 58.2/55.0 Hz, 12 $\mathrm{\mathit{C}H_2Me}$), 29.2 (12 C, ^3J(C,$^{119/117}$Sn) = 20.0/18.4 Hz, 4 $\mathrm{Sn(CH_2\mathit{C}H_2)_3}$). Anal. Calcd for $\mathrm{C_{228}H_{516}Si_{17}Sn_{12}}$: C, 53.07; H, 10.08. Found: C, 53.3; H, 9.9.

Synthesis of 7. A solution of BuLi in hexane (450 μL, 2.2 M, 0.99 mmol) was added to a solution of **10** (0.360 g, 0.224

mmol) in THF (1.0 mL) at 0 °C in one leg of an H-type Schlenk tube.[22] The mixture was stirred for 30 min at 0 °C, during which time the initially yellow solution faded to colorless. Several drops of BuLi in hexane were added to the other leg of the H-type Schlenk tube for solvent drying during purification. The volatiles were evaporated in vacuo to leave a white solid and a colorless oil. Pentane (2.0 mL) was introduced into the leg containing the BuLi and was distilled onto the solid (through this extra drying procedure, pure solvents were guaranteed). The mixture was stripped with pentane to remove residual THF. Pentane (10 mL) was added, and the mixture was washed a further three times with pentane by filtering to the "butyllithium" leg and distilling the solvent onto the lithiated dendrimer. The volatiles were removed in vacuo to leave a white solid, **7**, in one leg and a yellow oil ($SnBu_4$ + BuLi) in the other. Quantitative conversion was confirmed by the NMR spectra. ^{1}H NMR (C_6D_6/THF-d_8, 300 MHz): δ −2.2 (8 H, s, 4 CH_2Li); 0.02 (24 H, s, 8 Me), 0.60 (8 H, t, ^3J(H,H) = 8 Hz, 4 CH_2Si), 0.75 (8 H, t, ^3J(H,H) = 8 Hz, 4 CH_2Si), 1.60 (8 H, m, 4 $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6/THF-d_8, 75 MHz): δ −7.9 (4 C, 4 CH_2Li), 4.7 (8 C, 8 Me), 20.3 (4 C, 4 CH_2Si), 21.4 (4 C, 4 CH_2Si), 28.1 (4 C, 4 $CH_2CH_2CH_2$). One drop of D_2O was added to an NMR sample of **7**, and the ^{1}H NMR spectrum of the resulting product was identical to the spectrum of **6** prepared from **1**. To another sample, an excess of chlorotrimethylsilane was added, resulting in a ^{1}H NMR spectrum identical to that of **8** prepared from **1**.

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[22] A simplified design of the H-type Schlenk tube described in: Wayda, A. L.; Dye, J. L. *J. Chem. Educ.* **1985**, *62*, 356.