Dendrimeric Organochalcogen Catalysts for the Activation of Hydrogen Peroxide: Improved Catalytic Activity through Statistical Effects and Cooperativity in Successive Generations

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Received July 18, 2000

Abstract: Dendrimeric polyphenylsulfides, -selenides, and -tellurides are prepared in high yield using propyloxy spacers to connect the phenylchalcogeno groups to the dendrimeric core. The selenides and tellurides catalyze the oxidation of bromide with hydrogen peroxide to give positive bromine species that can be captured by cyclohexene in two-phase systems. The corresponding sulfides show no catalytic activity. The increase in the rate of catalysis followed statistical effects for 1, 6, and 12 phenyltelluro groups. However, the increase in the rate of catalysis exceeds statistical contributions for the first few generations with 1, 3, 6, and 12 phenylseleno groups and suggested cooperativity among phenylseleno groups. The increase in catalytic rate was lost upon replacing all but one phenylseleno group with phenoxy groups. On the basis of H_2O_2 consumed, the dendrimer with 12 phenylseleno groups has a turnover number of >60 000 mol of H_2O_2 consumed per mole of catalyst.

Hydrogen peroxide is a powerful oxidant thermodynamically yet is environmentally friendly, yielding water and oxygen upon decomposition. Many reactions with H_2O_2 are limited by the kinetics of reaction, even though the reactions may be favored by thermodynamics. Examples of such reactions are the oxidation of halides to the corresponding halogen/hypohalous acid,[1] which are slow at neutral pH and ambient temperature and the oxidation of thiols to disulfides.[2,3] Nature has solved the problems associated with the kinetics of H_2O_2 oxidation in these examples through the evolution of enzymes such as the haloperoxidases (chloroperoxidases[4] and bromoperoxidases[5]) and the thiolperoxidases (glutathione peroxidase and other seleno enzymes).[3,6,7] To use H_2O_2 in a broader range of synthetic transformations, chemists strive to achieve similar reactivity and selectivity with catalysts designed in the laboratory.[8]

Organotellurides and selenides are catalysts for the activation of H_2O_2 that undergo two-electron redox processes at the chalcogen atom during the catalytic cycle.[2,3,6,9] Peroxide oxidation of the organochalcogenide gives the corresponding oxide (or its hydrate), which then acts as an oxidant (kinetically superior to H_2O_2) for a variety of substrates. The organochalcogenide is regenerated in the process to resume the catalytic cycle.

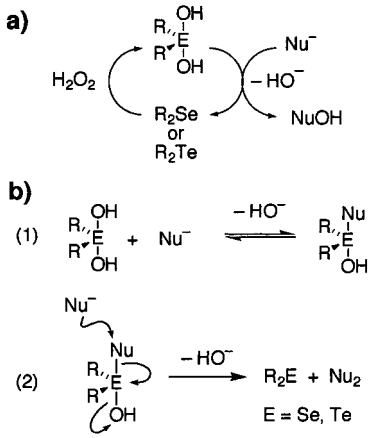

Figure 1. The catalytic cycle of diorganochalcogenides with hydrogen peroxide. (a) Direct nucleophilic attack at a hydroxy ligand of the dihydroxy selenane or tellurane intermediate. (b) Ligand exchange followed by nucleophilic attack at the new ligand.

For the selenide and telluride catalysts that have been described, the rate-limiting step in the catalytic process is the rate of oxidation of the chalcogenide.[9] Following oxidation, selenoxides and telluroxides reversibly add H_2O to form stable hydrates—the trigonal-bipyramidal dihydroxy selenanes and telluranes of Figure 1.[6,9,10] It has been proposed that the oxidation of substrates such as the halides or thiols by dihydroxy

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10.1021/ja002649+ CCC: $20.00
Published on Web 12/12/2000

chalcogenanes involves either direct attack of the nucleophile at a hydroxy ligand (Figure 1a)[9] or ligand substitution at the chalcogen followed by nucleophilic attack or reductive elimination (Figure 1b).[6]

Traditionally, the molar activity of catalysts has been optimized through structure−activity relationships derived from substituent changes. While the catalytic properties of selenides and tellurides can be improved through proper choices of substituents, stereoelectronic effects can only go so far with respect to increasing rates of oxidation of the chalcogen atom.[3,9]

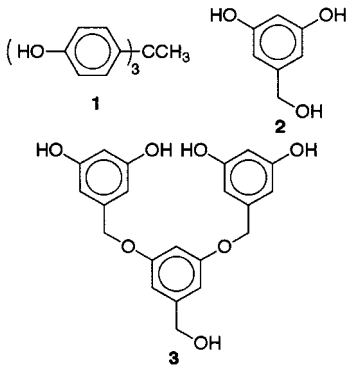
Recent developments in the synthesis of dendrimeric molecules[11] suggest that molecules with improved catalytic properties can be designed through statistical means in addition to conventional structure−activity relationships. In dendrimeric molecules, catalytic functionality can be placed at the terminus of the individual arms of the dendrimer[12] or within the dendrimer architecture.[13] The reactivity of the molecule on a molar basis then becomes a function of the total number of individual reactive groups as well as a function of the reactivity of the individual groups. Dendrimers also impose order within the molecules since, on average, reactive groups will be the same distance from the central core. In certain catalytic systems, a "dendrimer effect"[11] is observed in which the catalytic activity of individual groups increases[14,15] or decreases[16] with each successive dendrimer generation.

We have prepared catalysts for peroxide activation that are based on dendrimeric molecules terminating in phenylseleno[15] or phenyltelluro groups. These molecules are efficient catalysts in two-phase systems and illustrate not only statistical effects for the phenyltelluro-containing systems with respect to the number of catalytic groups but also the "dendrimer effect" with greater than statistical increases in catalytic activity per reactive group in each successive generation for the phenylseleno-containing systems. The corresponding dendrimeric molecules terminating in phenylthio groups show no catalytic activity with H_2O_2, which suggests that the dendrimer architecture alone is not responsible for the observed catalytic activity.

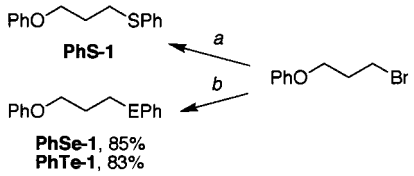
Results and Discussion

Part A. Synthesis of Catalysts. Dendrimer catalysts for the activation of H_2O_2 must survive an oxidizing environment, which limits the types of functional groups that can be employed in their synthesis. The use of 1,1,1-tris(4-hydroxyphenyl)ethane (**1**, Chart 1) as a core molecule to which dendritic wedges can be attached has been elegantly developed by Fréchet.[17] Dendrimeric ethers derived from compound **1** should be relatively unreactive toward either H_2O_2 or the hypohalous acids produced under the conditions described herein.

Chart 1



Scheme 1[a]



[a] Key: (a) PhSH, NaOEt/EtOH/THF, 83%. (b) NaEPh (E = Se, Te) from $(PhE)_2/NaBH_4$ in 1 M NaOEt in EtOH/THF.

3,5-Dihydroxybenzyl alcohol (**2**) can be used to construct dendritic wedges that are also stable to H_2O_2. Attachment of arms containing single arylchalcogenide functionality directly to **2** would provide the first-generation dendritic wedge, which, when joined with **1**, would produce molecules with six reactive groups. Higher generations can be derived by the linking of compound **2** to itself in an iterative process to produce dendritic wedges such as **3** that can then be joined to the central core to produce molecules with 12 reactive groups (Chart 1).[18]

The introduction of the chalcogenide groups can be done early in the construction of the dendrimer or in a final step for construction of either a dendritic wedge or the final dendrimer. Phenylchalcogenide groups were successfully linked to phenols via propyloxy spacers as shown in Scheme 1. We have demonstrated that replacing aryl groups with alkyl groups gives chalcogenides that are more readily oxidized than diaryl chalcogenides.[19] Similarly, the propyloxy spacers should provide more electron-rich organochalcogenides for catalysis relative to the diaryl tellurides previously examined. In addition to demonstrating the feasibility of the chemistry, the 3-phenoxypropyl phenylchalcogenides (**PhE−1**, E = S, Se, Te) represent control, unit-functionality chalcogenides to which the catalytic activity of the dendrimeric molecules described below can be compared.

Catalysts derived from dendritic wedges **2** or **3** terminating in 3-hydroxypropyl ethers require a synthetic sequence to differentiate the phenolic, benzyl, and alkyl hydroxyls. Two

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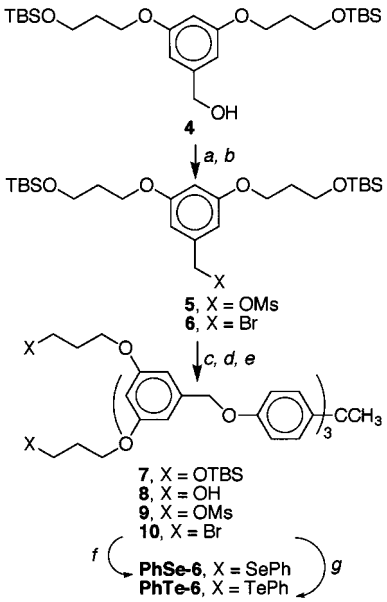
Scheme 2[a]



[a] Key: (a) MsCl, Et_3N, CH_2Cl_2. (b) LiBr, THF, 94% of **6** from **4**. (c) **1**, 18-crown-6, K_2CO_3, acetone, 91% of **7**. (d) Bu_4NF, THF/DMF, 91% of **8**. (e) *i*. MsCl, Et_3N, THF/CH_2Cl_2; *ii*. LiBr, 94% of **10**. (f) NaSePh from $(PhSe)_2/NaBH_4$ in 1 M NaOEt in EtOH/THF, 85%. (g) NaTePh from $(PhTe)_2/NaBH_4$ in 1 M NaOEt in EtOH/THF, 82%.

equivalents of 1-bromo-3-(*tert*-butyldimethylsilyloxy)propane[20] were attached to benzyl alcohol **2** with potassium carbonate and catalytic 18-crown-6 to give **4** in 73% yield (Scheme 2). Benzyl alcohol **4** was converted to the corresponding benzyl bromide in two steps. The mesylate **5** was first prepared, but not isolated, and was then treated in situ with lithium bromide to give benzyl bromide **6** in 94% isolated yield overall.[21] Three equivalents of dendritic wedge **6** were attached to core molecule **1** with potassium carbonate in acetone to give dendrimer **7** with six arms terminating in *tert*-butyldimethylsilyl ethers in 91% isolated yield. The silyl-protecting groups were removed with Bu_4NF in THF[22] to give alcohol **8** in 91% yield and **8** was then converted to bromide **10** in 94% yield via the mesylate **9**. The addition of arylchalcogenide anions to **10** gave dendrimers **PhE**−**6** bearing six functional groups.

The proof of structure for the dendrimers in this series was the 3-fold symmetry apparent in the ^{13}C NMR spectra. Dendrimer **7** terminating in six *tert*-butyldimethylsilyl ethers displayed the expected 17 signals in its ^{13}C NMR spectrum for a 3-fold symmetric molecule. Dendrimer **8** terminating in six 3-hydroxypropyl groups and dendrimer **10** terminating in six 3-bromopropyl groups each displayed 14 signals in their ^{13}C NMR spectra. Dendrimers **8** and **10** also gave the expected parent ions by positive FAB mass spectrometry. The ^{13}C NMR spectra of both **PhSe**−**6** and **PhTe**−**6** displayed the expected 18 signals for 3-fold symmetric molecules. The MALDI-TOF mass spectrum of **PhSe**−**6** gave the expected parent ion cluster following protonation, which was superimposed on a weak M + 18 cluster corresponding to the addition of water to the parent ion. The telluride analogue **PhTe**−**6** was easily fragmented and did not give a parent ion by either MALDI-TOF or electrospray mass spectrometry. However, the elemental analysis for **PhTe**−**6** was within 0.1% of theoretical for C and H.

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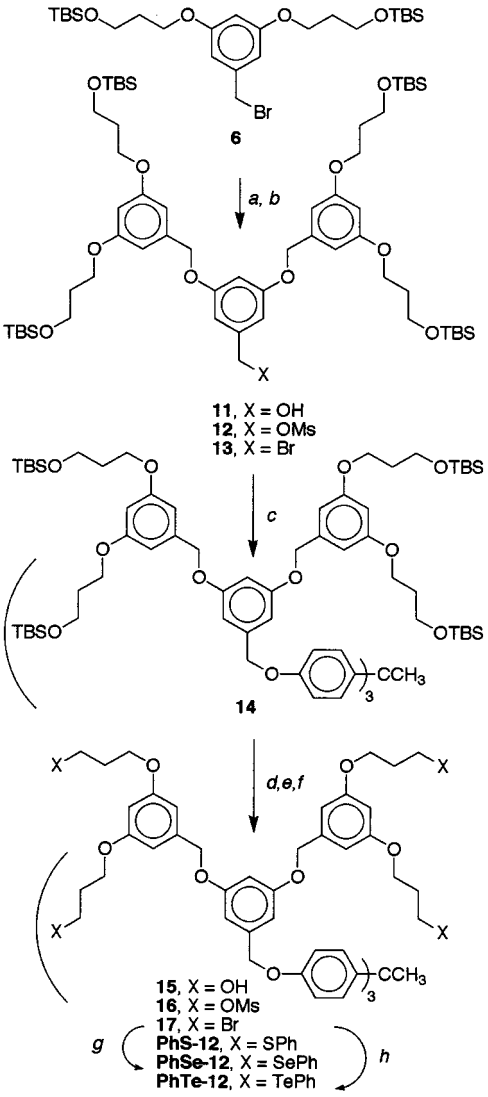
Scheme 3[a]



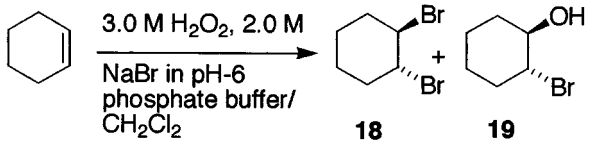
[a] Key: (a) **2**, 18-crown-6, K_2CO_3, acetone, 24 h, 91% of **11**. (b) *i*. MsCl, Et_3N, THF/CH_2Cl_2; *ii*. LiBr, THF, 81% of **13** from **11**. (c) **1**, 18-crown-6, K_2CO_3, acetone, 91% of **14**. (d) Bu_4NF, THF/DMF, 91% of **15**. (e) *i*. MsCl, Et_3N, THF/CH_2Cl_2; *ii*. LiBr, THF, 81% of **17** from **15**. (f) NaSPh, THF/EtOH, 90% of **PhS**−**12**. (g) NaSePh from $(PhSe)_2/NaBH_4$ in 1 M NaOEt in EtOH/THF, 68% of **PhSe**−**12**. (h) NaTePh from $(PhTe)_2/NaBH_4$ in 1 M NaOEt in EtOH/THF, 84%.

Two equivalents of bromide **6** were attached to the phenolic hydroxyls of 3,5-dihydroxybenzyl alcohol (**2**) with potassium carbonate and acetone as shown in Scheme 3 to give alcohol **11** in 87% isolated yield. The alcohol **11** was converted to the corresponding bromide in two steps via initial formation of the mesylate **12**, which was then treated in situ with LiBr in THF to give the dendritic wedge **13** in 81% overall yield. Dendritic wedges **11** and **13** gave satisfactory elemental analyses, appropriate parent ions by positive FAB mass spectrometry, and the expected 16 signals in their ^{13}C NMR spectra to confirm their structural assignments.

Compound **13** was attached to the core molecule **1** with potassium carbonate in acetone to give dendrimer **14** with 12 silyloxypropyl arms in 91% yield (>99% per arm). The silyl-protecting groups were removed with Bu_4NF to give alcohol **15** in 88% yield. Dendrimer **15** was converted to mesylate **16** and then to bromide **17** in 75% overall yield.

The addition of phenylchalcogenide anions to **17** gave dendrimers **PhE**−**12** in 68−90% isolated yield (Scheme 3).

Scheme 4



Even though the isolated yields are far from quantitative, they correspond to 97−99% yields for reaction of each individual arm of the dendrimer.

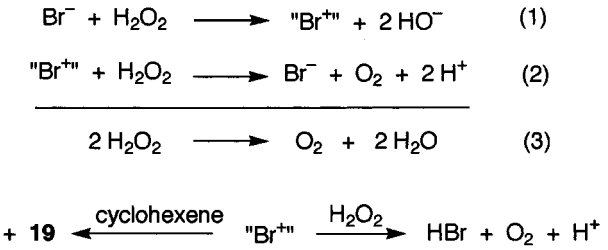
As before, the 3-fold symmetry of the dendrimeric molecules simplified their structural assignments. Dendrimer **14** terminating in 12 *tert*-butyldimethylsilyl ethers displayed the expected 22 signals in its ^{13}C NMR spectrum for a 3-fold symmetric molecule. Dendrimer **15** terminating in twelve 3-hydroxypropyloxy groups and dendrimer **17** terminating in six 3-bromopropyloxy groups displayed 19 signals each in their ^{13}C NMR spectra. Dendrimer **15** gave the expected parent ion at *m*/*z* 2101 ($C_{119}H_{144}O_{33} + H^+$) by MALDI-TOF mass spectrometry, and dendrimer **17**, the immediate precursor to the **PhE**−**12** dendrimers, gave a weak, poorly resolved isotope cluster for the parent ion of the dodecabromide at *m*/*z* 2845 ($C_{119}H_{132}{}^{79}Br_{12}O_{21} + H^+$). The ^{13}C NMR spectra of **PhS**−**12**, **PhSe**−**12**, and **PhTe**−**12** displayed the 23 signals expected for 3-fold symmetric molecules. Although **PhSe**−**12** and **PhTe**−**12** were easily fragmented, **PhS**−**12** gave a weak parent ion cluster at the expected *m*/*z* 3205 ($C_{191}H_{192}O_{21}S_{12} + H^+$) and a stronger ion at *m*/*z* 3259 corresponding to the sodium adduct of a bisoxide of **PhS**−**12** ($C_{191}H_{192}O_{23}S_{12} + {}^{23}Na^+$). The ^1H NMR spectra of the molecules in this series were also consistent with the expected functionality and the 3-fold symmetry.

Part B. Oxidation of Bromide with Hydrogen Peroxide in the Presence of Dendrimeric Organochalcogenide Catalysts.

The "Model" Reaction for Catalysis. Control Studies for the Uncatalyzed Bromination of Cyclohexene. In our earlier studies, we examined the rate of bromination of cyclohexene in two-phase systems with H_2O_2 (3.0 M) and NaBr (2.0 M) in the presence of various telluride catalysts as well as the ratio of *trans*-1,2-dibromocyclohexane (**18**) and *trans*-2-bromocyclohexanol (**19**) products (Scheme 4).[9] For comparison purposes, we used the same conditions to evaluate the **PhE**−**1**, **PhE**−**6**, and **PhE**−**12** molecules for catalytic activity with H_2O_2. The two-phase conditions were necessitated by the lack of aqueous solubility of **PhE**−**1**, **PhE**−**6**, and **PhE**−**12**.

The oxidation of bromide with H_2O_2 in control experiments was followed by the rate of formation of **18** and **19** in a two-phase system of 0.5 M cyclohexene in CH_2Cl_2 for the organic phase and an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer (0.1 M) at 296.0 ± 0.1 K. The control experiments were compared to the catalyzed reactions described below at 296.0 ± 0.1 K in which catalysts **PhE**−**1**, **PhE**−**6**, and **PhE**−**12** were present in 0.4−2.5 mM concentrations in the organic phase and the aqueous phase consisted of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer (0.1 M). We do not know the exact nature of the brominating species (Br_2, HOBr, Br_3^-) and refer to them collectively as "Br^+" in the text. Under these standard conditions, the uncatalyzed reaction gave the appearance of products with $k_{obs} = (5.521 \pm 0.004) \times 10^{-5}$ s^{-1} with a 45:55 (± 2%) ratio of **18** to **19** (average of five runs ± standard error from the mean). The value of k_{obs} for the uncatalyzed reaction was subtracted from values of k_{obs} for the catalyzed reactions described below to correct for the background reaction not catalyzed by the chalcogenide.

Scheme 5



Preparative reactions were run to examine the efficiency of the two-phase reactions for scavenging "Br^+" with cyclohexene. Bromine was dissolved in pH-6 phosphate buffer, and excess cyclohexene in dichloromethane was added to the aqueous solution. The organic phase was concentrated to give a 46:54 mixture of **18** to **19** in >95% isolated yield based on added bromine in the absence of H_2O_2.

Since we had demonstrated that cyclohexene under our standard conditions would scavenge positive bromine sources efficiently, we next examined the percentage of NaBr oxidized by H_2O_2 that is actually trapped by the cyclohexene. Under our standard conditions, 100 mmol of H_2O_2 are present. The number of mmoles of **18** and **19** produced during reaction would give a direct indication of the efficiency of bromide oxidation. A control reaction of 20 mL of 0.5 M cyclohexene in CH_2Cl_2 and an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer was stirred at 296 ±1 K for 48 h. Evolution of gas was noted upon mixing that persisted during the time course of reaction. After 48 h, the reaction was complete. The quantities of brominated products were determined (1) by gas chromatography relative to an internal standard of known concentration and (2) by concentrating the organic layer and determining yield and composition by ^1H NMR. The control reaction produced (2.25 ± 0.06) mmol of brominated **18** and **19** per 100 mmol of H_2O_2 as a 45:55 (± 2%) mixture of **18** to **19**.

While bromide is oxidized to "Br^+" by H_2O_2 as shown in eq 1 of Scheme 5, "Br^+" reacts with H_2O_2 to produce HBr, O_2, and a proton as shown in eq 2 of Scheme 5.[23] The net reaction is the disproportionation of H_2O_2 with either bromide or "Br^+" as a catalyst (eq 3, Scheme 5). Thus, in competition with the addition of a "Br^+" source to cyclohexene is the disproportionation of H_2O_2 from reaction with some form of "Br^+".

The rate of oxygen formation in H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer at 296 ± 1 K was monitored with an oxygen electrode. The reaction was initiated by the addition of NaBr to a degassed solution of H_2O_2 in pH-6 phosphate buffer. Following a short induction period (<200 s),[23a] the initial rate of $(2.3 \pm 0.2) \times 10^{-4}$ M s^{-1} observed for the formation of dioxygen can be compared to the initial rate of $(5.85 \pm 0.05) \times 10^{-6}$ M s^{-1} observed for the formation of brominated products in the two-phase reactions with cyclohexene. The roughly 40:1 ratio of initial rates is consistent with the 2.25% conversion of H_2O_2 to brominated products observed in the preparative studies above. The evolution of oxygen accounts for the gas evolved during the process as well as the remainder of the H_2O_2 in the preparative studies.

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Table 1. Observed Pseudo-First-Order Reate Constants for the Bromination of Cyclohexene with NaBr, H_2O_2, and Catalyst in a Two-Phase System of Dichloromethane and pH-6 Phosphate Buffer

catalyst	mM	k_{obs}, s^{-1}	k_{cat}, M^{-2} s^{-1}	k_{rel}	k_{rel}/PhE	ratio **18**/**19**	mmol (**18** + **19**)/100 mmol H_2O_2
none		$(5.521 \pm 0.004) \times 10^{-5}$				45:55 (± 1)	2.25 ± 0.06
PhTe−1	2.5	$(2.96 \pm 0.02) \times 10^{-4}$	$(4.82 \pm 0.04) \times 10^{-2}$	1.0	1.0	37:63 (± 1)	1.96 ± 0.02
PhTe−6	0.5	$(3.16 \pm 0.04) \times 10^{-4}$	$(2.61 \pm 0.04) \times 10^{-1}$	5.5	0.9	30:70 (± 1)	2.03 ± 0.05
PhTe−12	0.45	$(6.69 \pm 0.04) \times 10^{-4}$	$(6.82 \pm 0.04) \times 10^{-1}$	14.1	1.2	27:73 (± 1)	2.10 ± 0.05
PhSe−1	2.5	$(6.12 \pm 0.05) \times 10^{-5}$	$(1.2 \pm 0.1) \times 10^{-3}$	0.025	0.025	42:58 (± 1)	2.26 ± 0.03
PhSe−3	2.5	$(1.94 \pm 0.02) \times 10^{-4}$	$(2.78 \pm 0.04) \times 10^{-2}$	0.58	0.19	37:63 (± 1)	2.28 ± 0.03
PhSe−6	2.5	$(1.08 \pm 0.02) \times 10^{-3}$	$(2.05 \pm 0.04) \times 10^{-1}$	4.3	0.71	44:56 (± 1)	2.35 ± 0.02
PhSe−12	0.40	$(9.17 \pm 0.02) \times 10^{-4}$	1.08 ± 0.02	22.4	1.9	38:62 (± 1)	2.37 ± 0.02
PhSe−1−PhO−5	0.63	$(6.00 \pm 0.03) \times 10^{-5}$	$(3.8 \pm 0.2) \times 10^{-3}$	0.079	0.079	42:58 (± 1)	2.26 ± 0.02
PhS−1	2.5	$(5.2 \pm 0.1) \times 10^{-5}$				45:55 (± 1)	2.12 ± 0.02
PhS−12	1.0	$(4.95 \pm 0.09) \times 10^{-5}$				45:55 (± 1)	2.06 ± 0.02

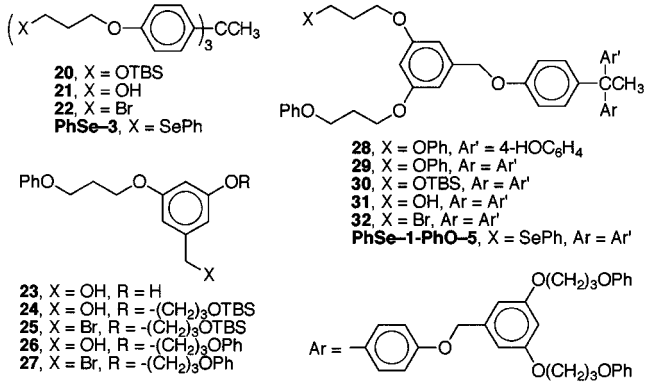
Telluride-Catalyzed Reactions. In our earlier studies, tellurides were far superior catalysts for H_2O_2 activation relative to the corresponding selenides.[9] An organic phase of 0.5 M cyclohexene in CH_2Cl_2 and a catalyst **PhTe−1**, **PhTe−6**, or **PhTe−12** present at 0.45−2.5 × 10^{-3} M were added to an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer (0.1 M) at 296 ± 1 K. A more rapid initial evolution of oxygen was noted upon mixing that persisted during the time course of reaction. After reaction was complete, the quantities of brominated products were again determined (1) by gas chromatography relative to an internal standard of known concentration and (2) by concentrating the organic layer and determining the composition by ^{1}H NMR. These values were also used as infinity points in the calculation of rate constants for catalysis (k_{cat}). The **PhTe−1**, **PhTe−6**, or **PhTe−12** catalysts gave 1.96−2.10 mmol of brominated products per 100 mmol of H_2O_2 consumed (Table 1). The initial pH of 6 remained constant throughout the course of reaction.

The rapid decomposition of H_2O_2 with "Br^+" consumes H_2O_2 while reducing "Br^+" to Br^-. The net reaction is primarily the disproportionation of H_2O_2, and the original 2.0 M concentration of NaBr remains relatively unchanged during the course of reaction (loss of 2 mmol from the initial 65 mmol at the start of the reaction). Thus, the kinetics for formation of brominated cyclohexene products follow pseudo-first-order behavior in which the concentration of bromide remains nearly constant at 2.0 M. In the reactions described, roughly half of the H_2O_2 consumed produces "Br^+" via oxidation of the catalyst. The "Br^+" then partitions between reaction with cyclohexene (roughly 2% of the "Br^+") and reaction with a second molecule of H_2O_2 (roughly 98% of the "Br^+").

The observed pseudo-first-order rate constants (k_{obs}) for the formation of *trans*-1,2-dibromocyclohexane (**18**) and *trans*-2-bromocyclohexanol (**19**) in a two-phase system of 0.5 M cyclohexene in CH_2Cl_2 for the organic phase and an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer at 296.0 ± 0.1 K are compiled in Table 1. Values for the catalyzed reactions are the average of duplicate runs. It should be noted that in our initial communication of this work,[15] we reported values of the initial rates out of concern that concentrations of both H_2O_2 and bromide might be changing with time. Since only the concentration of H_2O_2 is changing significantly with time, pseudo-first-order rate constants are reported here and were measured over two or more half-lives. The pseudo-first-order rate constants are intrinsically more accurate for determination of values of k_{cat} than the initial rates.

The rate constants for catalysis (k_{cat}) are also compiled in Table 1. These values were calculated by subtracting the rate for uncatalyzed bromination of cyclohexene from values of k_{obs} and then dividing by the concentration of NaBr (2.0 M) and the concentration of catalyst (assumed to be in the organic phase). Dividing k_{cat} by the number of dendrimer arms gives the rate constant for catalysis per PhTe group. These values are compiled in Table 1 as values of k_{rel}/PhE group where k_{cat} for **PhTe−1** is assigned a k_{rel} value of 1. The **PhTe−1**, **PhTe−6**, and **PhTe−12** catalysts have nearly identical reactivity on a per functional group basis (k_{rel}/PhTe of 1.0, 0.9, and 1.2, respectively) as one would expect if statistical effects were dominant with an increasing number of dendrimer arms.

Chart 2



Selenide-Catalyzed Reactions. We had originally prepared the selenide molecules for comparison to what we thought we would be the much better telluride molecules. We were particularly surprised by the catalytic activity of the **PhSe−6** and **PhSe−12** molecules as described below. The phenylselenide catalysts **PhSe−1**, **PhSe−6**, and **PhSe−12** gave 2.26−2.37 mmol of brominated products per 100 mmol of hydrogen peroxide consumed (Table 1). These values were independent of the concentration of catalyst over a range of 0.4−2.5 × 10^{-3} M.

Values of k_{obs} for the formation of **18** and **19** with the selenide catalysts are compiled in Table 1 as well as values of k_{cat}, k_{rel} (in comparison to **PhTe−1**), and k_{rel}/PhE group. The selenide catalysts show increasing values of k_{rel}/PhSe in successive generations with values of 0.025, 0.71, and 1.9 for **PhSe−1**, **PhSe−6**, and **PhSe−12**, respectively. In fact, the **PhSe−12** catalyst surpasses the **PhTe−12** catalyst in catalytic activity. The increase was sufficiently dramatic that we prepared two additional catalysts: selenide catalyst **PhSe−3** with three arms to have an intermediate data point between the **PhSe−1** and **PhSe−6** molecules and **PhSe−1−PhO−5** with six dendrimer arms but only one phenylseleno group and five phenoxy groups (Chart 2).

Attachment of three 1-bromo-3-(*tert*-butyldimethylsilyloxy)-propane molecules to **1** gave trisilyl ether **20** in 46% isolated yield. The trisilyl ether **20** was desilylated with Bu_4NF to give the triol **21** in 91% yield followed by conversion of **21** to

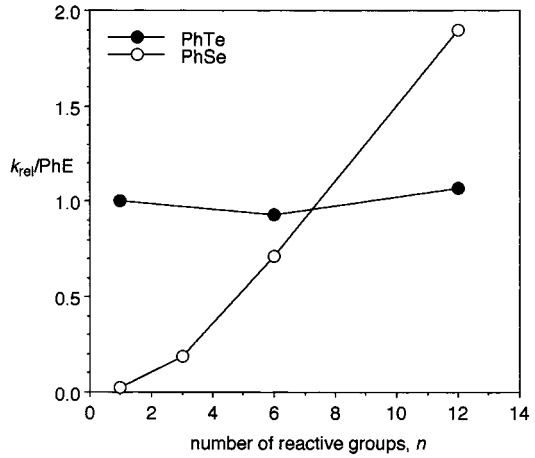


Figure 2. The relative rate constants for catalysis of each phenylchalcogeno group (k_{rel}/PhE) in molecules with *n* arms terminating in phenylchalcogeno groups. The rate constant for catalysis for **PhTe−1** was arbitrarily assigned a k_{rel}/PhE value of 1.

tribromide **22** in 95% isolated yield with CBr_4 and PPh_3.[24] The addition of sodium phenylselenide to **22** gave the **PhSe−3** molecule in 83% isolated yield. Values of k_{cat}, k_{rel}, and k_{rel}/PhSe group for **PhSe−3** are compiled in Table 1, and k_{rel}/PhSe group for **PhSe−3** is roughly 8 times that for **PhSe−1** and is roughly one-fourth that of **PhSe−6**. Experimental details for the formation of **20−22** are compiled in the Supporting Information.

One equivalents of 1-bromo-3-(*tert*-butyldimethylsilyloxy)-propane[20] was attached to benzyl alcohol **2** with potassium carbonate and catalytic 18-crown-6 to give **23** in 27% isolated yield and **4** in 49% isolated. Compound **23** was converted to **24** with 1-bromo-3-phenoxypropane, potassium carbonate, and 18-crown-6 in 80% isolated yield. The benzyl alcohol **24** was converted to benzyl bromide **25** in 92% overall yield through initial formation of the mesylate followed by displacement with LiBr. The addition of 2 equiv of 1-bromo-3-phenoxypropane to benzyl alcohol **2** gave benzyl alcohol **26** in 99% isolated yield, which was then converted to benzyl bromide **27** in 97% overall yield via formation of the mesylate and displacement with LiBr.

The addition of 2.2 equiv of dendritic wedge **27** to core molecule **1** gave a nearly 1:1 mixture of **28** with two arms and dendrimer **29** with three dendritic wedges attached. While these two compounds were not readily separated, the mixture was separated from unreacted **1** and the product with one dendritic wedge attached via chromatography on SiO_2. Compound **28** was combined with bromide **24** to give a mixture of dendrimers **29** and **30**. Desilylation of **30** gave alcohol **31**, which was readily separated from **29**. The overall yield of **31** was 15% from **1**. Alcohol **31** was converted to bromide **32** via the mesylate. The addition of sodium phenylselenide to bromide **32** gave **PhSe−1−PhO−5** in 78% isolated yield. Experimental details for the formation of **23−32** are compiled in the Supporting Information. The value of k_{cat} for **PhSe−1−PhO−5** compiled in Table 1 is comparable to **PhSe−1** and k_{rel}/PhSe is roughly 6 to 7% of the value of **PhSe−6**.

Comparison of k_{cat}/PhE values for the selenide and telluride catalysts is shown graphically in Figure 2. The telluride catalysts **PhTe−1**, **PhTe−6**, and **PhTe−12** illustrate the statistical effects one might associate with increasing the number of reactive groups per molecule. As shown in Table 1, k_{cat} for **PhTe−6** ($2.64 \times 10\ M^{-1}\ s^{-1}$) is roughly 6 times the k_{cat} value of $4.8 \times 10^{-2}\ M^{-2}\ s^{-1}$ observed for **PhTe−1** with one arm and k_{cat} for **PhTe−12** ($6.82 \times 10^{-1}\ M^{-2}\ s^{-1}$) is roughly 12 times this value with comparable reactivity per PhTe group (Figure 2). The statistical nature of the increase in reactivity suggests that each phenyltelluro group acts independently of the others and that there is no cooperativity among the phenyltelluro groups from proximity within the dendrimer architecture. In contrast, the increase in catalytic activity observed in the selenide series is much greater than that expected from statistical effects, which suggests cooperativity among the PhSe groups and a higher-order dependence of k_{rel}/PhSe on the number of dendrimer arms, *n*.

The value of k_{cat} for **PhSe−1−PhO−5** ($3.8 \times 10^{-3}\ M^{-2}\ s^{-1}$) is comparable to k_{cat} for **PhSe−1** ($1.2 \times 10^{-3}\ M^{-2}\ s^{-1}$) and k_{rel}/PhSe for **PhSe−1−PhO−5** (0.079) is approximately 10% of the value of k_{rel}/PhSe for **PhSe−6** (0.71). These data suggest that cooperativity among PhSe-groups is responsible for the nonstatistical increase in catalytic activity observed with **PhSe−6** and **PhSe−12** and not a quirk of these particular dendrimer architectures.

Sulfide-Catalyzed Reactions. Monosulfides have yet to show catalytic activity with H_2O_2 in these kinds of reactions, and a comparison of the catalytic effects of the **PhS−1** and **PhS−12** molecules might indicate contributions from the dendrimer architecture to catalysis. Values of k_{obs} for the formation of **18** and **19** with **PhS−1** and **PhS−12** are compiled in Table 1. Phenylthio groups do not catalyze the reaction of H_2O_2 with halide salts in either the unit-functional species **PhS−1** or in the dendrimer species **PhS−12** with twelve arms. In point of fact, both molecules appeared to inhibit the bromination of cyclohexene slightly under our standard conditions, which suggests that one of the heavier chalcogen atoms selenium or tellurium must be present for catalysis to occur.

Control Reactions to Determine Reaction Order with Respect to Bromide and Catalyst. While we had assumed that the catalytic process was first order with respect to both bromide and catalyst, we ran control reactions with various concentrations of **PhSe−3** and bromide to confirm this assumption as shown in Figure 3. (**PhSe−3** has a convenient rate range from 0.0015 to 0.015 M in catalyst and from 0.5 to 4.0 M in bromide at 0.0025 M catalyst for our studies.) Figure 3a shows the effects of increasing bromide concentration from 0.5 to 4.0 M on the rate of catalysis in the two-phase system with **PhSe−3** at 0.0025 M and H_2O_2 at 3.0 M. The linear relationship is consistent with a first-order dependence in bromide concentration. Similarly, the rate of catalysis increases linearly with increasing concentration of **PhSe−3** as shown in Figure 3b, which is consistent with a first-order dependence in catalyst. The *y*-intercept of $8.73 \times 10^{-5}\ s^{-1}$ is close to the rate constant of $5.52 \times 10^{-5}\ s^{-1}$ measured for the uncatalyzed oxidation of bromide by H_2O_2 under these conditions.

Turnover Numbers with the PhE−12 Dendrimers. A preparative run with the **PhSe−12** catalyst at 4×10^{-4} M in an organic phase of 2.5 M cyclohexene in CH_2Cl_2 and an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH-6 phosphate buffer (0.5 M) at 296 K was complete within 1 h. Four additional aliquots of H_2O_2 (100 mmol each) were added sequentially following the initial reaction at 30-min intervals, and the reaction mixture was allowed to stir an additional hour following the final addition. A total of 16.1 mmol of brominated products was isolated (4.8 mmol of **18** and 11.3 mmol of **19**), which corresponds to 3.2% oxidation of bromide from 500 mmol total of H_2O_2.

(24) Axelrod, E. H.; Milne, G. M.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139−2141.

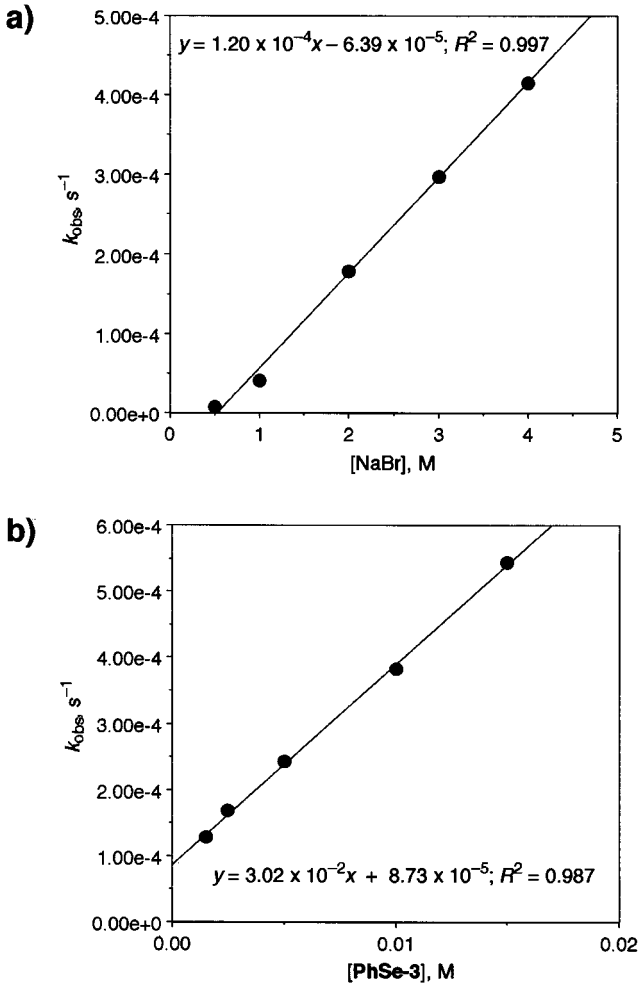


Figure 3. Effects of (a) increasing bromide concentration with 3.0 M H_2O_2 and 0.0025 M **PhSe−3** and (b) increasing **PhSe−3** concentration with 2.0 M NaBr and 3.0 M H_2O_2 on the rate constants for the bromination of cyclohexene in two-phase systems of dichloromethane and pH-6 phosphate buffer.

A second reaction without catalyst was run, duplicating the intervals between additions of H_2O_2 and products were isolated after 3.5 h. A total of 0.47 mmol of brominated products was isolated (0.22 mmol of **18** and 0.25 mmol of **19**) from the uncatalyzed process.

The 16.1 mmol of product were produced from 0.008 mmol of **PhSe−12** catalyst. This corresponds to a turnover number of >2000 mol of brominated product/mol of **PhSe−12** and to a turnover number of >60 000 mol of H_2O_2/mol of **PhSe−12** for the decomposition of H_2O_2. Half of the H_2O_2 consumed during the reaction is most likely from the reaction of "Br^+" with H_2O_2 as shown in Scheme 5. Thus, >30 000 mol of "Br^+"/mole of **PhSe−12** is produced under these conditions. These turnover numbers are based on when we stopped reactions for convenience of scale, not on degradation of the catalyst. Recovered **PhSe−12** showed no loss of catalytic activity when resubmitted to the conditions of reaction.

The reaction sequence was repeated with 0.010 mmol of the **PhTe−12** catalyst to produce 14.4 mmol of brominated products (4.3 mmol of **18** and 10.1 mmol of **19**). This corresponds to turnover numbers of >1400 mol of brominated product/mol of **PhTe−12**, >50 000 mol of H_2O_2/mol of **PhTe−12** for the decomposition of H_2O_2, and >25 000 mol of "Br^+"/mole of **PhTe−12**.

Summary and Conclusions

Our original hypothesis was that attaching multiple reactive groups to dendrimer architectures would enhance catalytic activity through statistical effects based on the number of reactive groups. The validity of this hypothesis was demonstrated with the **PhTe−1**, **PhTe−6**, and **PhTe−12** molecules where values of the k_{rel}/PhTe group are fairly constant for 1, 6, and 12 arms (Table 1). However, the "dendrimer effect" or cooperativity observed in the phenylseleno series was unexpected with the k_{rel}/PhSe group increasing by a factor of 80 from monoselenide **PhSe−1** to dendrimer **PhSe−12**.

Dendrimeric molecules can be treated as spherical molecules within a few generations.[11] The surface area of a sphere increases more slowly than the volume. Consequently, functionality on the surface of a dendrimer is packed more tightly in each successive generation. If adjacent functionality were to interact, then each generation of dendrimer should bring the functional groups closer together and increase cooperativity. In the telluride series, the nearly constant catalytic activity for each individual phenyltelluro group suggests that there is little if any cooperativity between the phenyltelluro groups. In contrast, the catalytic activity of each individual phenylseleno group increases with each generation, which argues for interaction between adjacent phenylseleno groups.

The catalytic activity of the **PhSe−1−PhO−5** dendrimer with a single catalytic functionality is nearly identical to that of **PhSe−1** with a single arm. Furthermore, the phenylthio groups in neither the monomeric species **PhS−1** nor the dendrimer species **PhS−12** with 12 arms catalyze reactions with H_2O_2. These observations affirm that the dendrimer architecture alone does not contribute to the catalysis observed with the selenides and tellurides and that the nonstatistical increase in catalytic activity observed in the phenylseleno series is due to cooperativity among selenium atoms.

If one assumes that oxidation of the organoselenium groups is rate-limiting, several scenarios are plausible to explain the cooperativity observed in the selenide dendrimers. The intramolecular interaction of dihydroxy selenanes in molecules with more than one oxidized phenylseleno group might create new functionality (perhaps with Se−O−Se linkages) that is readily oxidized by H_2O_2 and undergoes a similar catalytic cycle with halide salts. Both organoselenides and organotellurides are known to form intermolecular contacts that are less than van der Waals' radii apart.[25] As the local concentration of phenylseleno groups on the dendrimer surface increases, intramolecular selenium(II)−selenium(II) interactions might accelerate oxidation and, consequently, the rate of catalysis. Similarly, the interaction of a selenium(II) center with an adjoining selenium(IV) center might also lead to enhanced rates of oxidation. Early generation dendrimers are capable of folding back on the core to provide "buried" reactive groups, which may be more reactive than groups on the dendrimer surface.[26] Finally, dendrimers may form aggregates that have increased reactivity relative to single molecules.[27] In ongoing work, we are exploring several of these issues to explain the unexpected reactivity of the organoselenide dendrimers.

Experimental Section

General. All reactions were performed under dry argon. All glassware was previously dried in an oven at 150 °C prior to use.

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(26) Naidoo, K. J.; Hughes, S. J.; Moss, J. R. *Macromoloecules* **1999**, *32*, 331−341.

(27) Huang, B.; Parquette, J. R. *Org. Lett.* **2000**, *2*, 239−242.

Chemicals were purchased from Aldrich Chemical Co. and used as received. Melting points were uncorrected. Flash chromatography was performed using silica gel (40 μm 60 Å) from Mallinckrodt Baker, Inc. Concentration of solvents was performed on a Büchi rotoevaporator.

Preparation of 1-Bromo-3-(*tert*-butyldimethylsilyloxy)propane. 4-(Dimethylamino)pyridine (1.89 g, 0.015 mol), 3-bromo-propanol (28.0 mL, 0.310 mol), Et_3N (56.0 mL, 0.402 mol), TBSCl (56.00 g, 0.372 mol), and anhydrous THF (450 mL) were stirred at ambient temperature for 18 h. The reaction was quenched with aqueous, saturated NH_4Cl, and extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (1:4 CH_2Cl_2−hexanes) followed by distillation (50−100 °C, 5 Torr) to give 78.0 g (99.5%) of 1-bromo-3-(*tert*-butyldimethylsilyloxy)propane[19] as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (t, 2 H, J = 6 Hz), 3.50 (t, 2 H, J = 6 Hz), 2.05 (quint, 2 H, J = 6 Hz), 0.87 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 60.36, 35.49, 30.61, 25.85, 18.24, −5.44.

Preparation of 3,5-Bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]-benzyl Alcohol (Dendritic Wedge 4). 3,5-Dihydroxybenzyl alcohol (**2**, 17.5 g, 0.125 mol), 18-crown-6 (6.61 g, 0.025 mol), K_2CO_3 (51.9 g, 0.375 mol), acetone (800 mL), and 1-bromo-3-(*tert*-butyldimethylsilyloxy)propane (64.9 g, 0.256 mol) were stirred at reflux for 48 h. The solution was concentrated, and the white paste was partitioned between equal volumes of CH_2Cl_2 and water. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude oil was purified by flash chromatography on silica gel, eluting with CH_2Cl_2 to give 44.1 g (73%) of alcohol **4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.48 (s, 2 H), 6.37 (s, 1 H), 4.60 (d, 2 H, J = 6 Hz), 4.02 (t, 4 H, J = 6 Hz), 3.77 (t, 4 H, J = 6 Hz), 1.95 (quint, 4 H, J = 6 Hz), 1.69 (t, 1 H, J = 6 Hz), 0.87 (s, 18 H), 0.02 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.38, 143.16, 105.06, 100.49, 65.42, 64.49, 59.51, 32.37, 25.92, 18.31, −5.38; IR (film, NaCl) 3500−3200, 2960, 1590, 1465, 1255, 1160, 1100, 840 cm^{-1}; FAB(+)MS, m/z 485 ($C_{25}H_{48}O_5Si_2$ + H^+). Anal. Calcd for $C_{25}H_{48}O_5Si_2$: C, 61.93; H, 9.98. Found: C, 61.64; H, 10.03.

Preparation of 3,5-Bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]-benzyl Bromide (Dendritic Wedge 6). The dendritic alcohol wedge **4** (43.8 g, 0.0903 mol), Et_3N (12.5 g, 0.126 mol), MsCl (15.5 g, 0.135 mol), and anhydrous THF (150 mL) were stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 2 h to give mesylate **5**. Lithium bromide (41.6 g, 0.479 mol) was added, and the resulting mixture was allowed to stir 16 h. The reaction mixture was concentrated, and the residual oil was partitioned between equal volumes of water and CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel eluted with CH_2Cl_2 to give 46.5 g (94%) of bromide **6** as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50 (d, 2 H, J = 2 Hz), 6.37 (t, 1 H, J = 2 Hz), 4.39 (s, 2 H), 4.02 (t, 4 H, J = 6 Hz), 3.77 (t, 4 H, J = 6 Hz), 1.95 (quint, 4 H, J = 6 Hz), 0.87 (s, 18 H), 0.03 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.33, 139.55, 107.47, 101.43, 64.58, 59.46, 32.32, 25.90, 18.29, −5.41; IR (film, NaCl) 2930, 1600, 1460, 1255, 1100, 835 cm^{-1}; FAB(+)MS, m/z 549 ($C_{25}H_{47}{}^{81}BrO_4Si_2$ + H^+). Anal. Calcd for $C_{25}H_{47}BrO_4Si_2$: C, 54.82; H, 8.65. Found: C, 54.54; H, 8.58.

Attachment of 6 to the Core Molecule 1. Preparation of 1,1,1-Tris[4-(3,5-bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]benzyloxy)-phenyl]ethane (Dendrimer 7). 1,1,1-Tris-(4-hydroxyphenyl)ethane (**1**, 0.21 g, 0.69 mmol), 18-crown-6 (50 mg, 0.19 mmol), K_2CO_3 (0.14 g, 1.0 mmol), acetone (5.0 mL), and dendritic wedge **6** (1.50 g, 2.7 mmol) were stirred at reflux for 48 h. The solution was concentrated, and the white paste was partitioned between equal volumes of CH_2Cl_2 and water. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (CH_2Cl_2 and then 10% EtOAc in CH_2Cl_2) to give 1.06 g (91%) of **7** as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, 6 H, J = 9 Hz), 6.83 (d, 6 H, J = 9 Hz), 6.55 (d, 6 H, J = 2 Hz), 6.30 (t, 3 H, J = 2 Hz), 4.92 (s, 6 H), 4.02 (t, 12 H, J = 6 Hz), 3.77 (t, 12 H, J = 6 Hz), 2.08 (s, 3 H), 1.95 (quint, 6 H, J = 6 Hz), 0.86 (s, 54 H), 0.02 (s, 36 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.32, 156.76, 141.93, 139.28, 129.55, 113.90, 105.66, 100.66, 69.92, 64.40, 59.43, 50.56, 32.33, 30.74, 25.90, 18.26, −5.40; IR (film, NaCl) 2955, 1740, 1600, 1510, 1460, 1250, 1170, 1100, and 840 cm^{-1}. Anal. Calcd for $C_{95}H_{156}O_{15}Si_6$: C, 66.85; H, 9.21. Found: C, 66.95; H, 9.26.

Desilylation of the 3-(*tert*-Butyldimethylsilyloxy)propyl Groups of 7. Preparation of 1,1,1-Tris[4-(3,5-bis[3-hydroxypropyloxy]benzyloxy)phenyl]ethane (Dendrimer 8). A solution of **7** (18.5 g, 10.8 mmol) in 1.0 M Bu_4NF in THF (130 mL, 130 mmol, 2 equiv/TBS group) was allowed to stir at ambient temperature for 16 h. The solution was poured into water (250 mL), and the pH was adjusted to 6 with 0.05 N HCl. The products were extracted into EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified via by flash chromatography on silica gel (1:2:9 MeOH−THF−Et_2O) to yield 10.1 g (91%) of **8** as a colorless oil: ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.89 (s, 12 H), 6.56 (s, 6 H), 6.41 (s, 3 H), 4.97 (s, 6 H), 3.98 (t, 12 H, J = 6 Hz), 3.54 (t, 12 H, J = 6 Hz), 2.01 (s, 3 H), 1.82 (quint, 12 H, J = 6 Hz); ^{13}C NMR (75 MHz, THF-d_8) δ 161.58, 158.09, 142.89, 140.70, 130.40, 114.66, 106.29, 101.11, 70.57, 65.63, 59.08, 51.71, 33.62, 30.94; IR (film, NaCl) 3500−3200, 2930, 1665, 1600, 1455, 1385, 1165, 1065, and 835 cm^{-1}; FAB(+)MS, m/z 1021 ($C_{59}H_{72}O_{15}$ + H^+). Anal. Calcd for $C_{59}H_{72}O_{15}$: C, 69.39; H, 7.11. Found: C, 69.58; H, 7.22.

Preparation of 1,1,1-Tris[4-(3,5-bis[3-bromopropyloxy]benzyloxy)phenyl]ethane (Dendrimer 10). The alcoholic dendrimer **8** (3.85 g, 3.77 mmol), Et_3N (4.60 g, 45.5 mmol), MsCl (5.18 g, 45.2 mmol), CH_2Cl_2 (70 mL), and anhydrous THF (70 mL) were stirred at 0 °C for 2 h to give mesylate **9**, which was not isolated. Anhydrous, granular LiBr (15.0 g, 173 mmol) was then added, and the resulting mixture was allowed to stir for 16 h at ambient temperature. The reaction mixture was concentrated, and the oil was partitioned between equal volumes of water and CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted twice more with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (CH_2Cl_2, then 50% EtOAc in CH_2Cl_2) to give 3.91 g (74%) of **10** as a glass: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, 6 H, J = 9 Hz), 6.85 (d, 6 H, J = 9 Hz), 6.58 (s, 6 H), 6.41 (s, 3 H), 4.95 (s, 6 H), 4.08 (t, 12 H, J = 6 Hz), 3.58 (t, 12 H, J = 6 Hz), 2.29 (quint, 12 H, J = 6 Hz), 2.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.99, 156.68, 142.01, 139.59, 129.59, 113.93, 105.96, 100.81, 69.83, 65.31, 50.60, 32.24, 30.72, 29.98; IR (film, NaCl) 3035, 2975, 1605, 1515, 1250, 1180, 1030, and 830 cm^{-1}; FAB(+)MS, m/z 1405 ($C_{59}H_{66}{}^{81}Br_6O_9$ + H^+) Anal. Calcd for $C_{59}H_{66}Br_6O_9$: C, 50.67; H, 4.76. Found: C, 50.71; H, 4.81.

Preparation of 3,5-Bis(3,5-bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]benzyloxy)benzyl Alcohol (Dendritic Wedge 11). 3,5-Dihydroxybenzyl alcohol (**2**, 4.63 g, 33.0 mmol), 18-crown-6 (1.75 g, 6.62 mmol), K_2CO_3 (13.7 g, 99.1 mmol), acetone (500 mL), and dendritic wedge **6** (38.0 g, 69.4 mmol) were stirred at reflux for 48 h. The solution was concentrated, and the white paste was partitioned between equal volumes of CH_2Cl_2 and water. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude oil was purified by flash chromatography (1:1 Et_2O−petroleum ether) to give 31.0 g (87%) of **11** as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (d, 2 H, J = 2 Hz), 6.52 (t, 1 H, J = 2 Hz), 6.39 (t, 2 H, J = 2 Hz), 4.94 (s, 4 H), 4.61 (d, 2 H, J = 7 Hz), 4.02 (t, 8 H, J = 6 Hz), 3.77 (t, 8 H, J = 6 Hz), 1.95 (quint, 8 H, J = 6 Hz), 1.62 (t, 1 H, J = 7 Hz, exchanges with D_2O), 0.86 (s, 36 H), 0.02 (s, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.41, 160.17, 143.36, 138.99, 105.74, 105.67, 101.28, 100.75, 70.03, 65.32, 64.52, 59.53, 32.35, 25.90, 18.28, −5.41; IR (film, NaCl) 3500−3200, 2955, 1600, 1460, 1255, 1165, 1100, 840 cm^{-1}; FAB(+)MS m/z 1073 ($C_{57}H_{100}O_{11}Si_4$ + H^+). Anal. Calcd for $C_{57}H_{100}O_{11}Si_4$: C, 63.76; H, 9.39. Found: C, 63.82; H, 9.52.

Preparation of 3,5-Bis(3,5-bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]benzyloxy)benzyl Bromide (Dendritic Wedge 13). The dendritic alcohol wedge **11** (5.79 g, 5.39 mmol), Et_3N (0.80 g, 7.9 mmol), MsCl (0.92 g, 8.0 mmol), CH_2Cl_2 (100 mL), and anhydrous THF (100 mL) were stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 2 h to give mesylate **12**. Lithium bromide (2.34 g, 26.9 mmol) was added, and the resulting mixture was allowed to stir 16 h. The reaction mixture was concentrated, and the residual oil was partitioned between equal volumes of water and CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (1:1

Et_2O−petroleum ether) to give 4.92 g (81%) of **13** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (d, 2 H, J = 2 Hz), 6.54 (d, 4 H, J = 2 Hz), 6.52 (t, 1 H, J = 2 Hz), 6.40 (t, 2 H, J = 2 Hz), 4.93 (s, 4 H), 4.39 (s, 2 H), 4.02 (t, 8 H, J = 6 Hz), 3.77 (t, 8 H, J = 6 Hz), 1.95 (quint, 8 H, J = 6 Hz), 0.87 (s, 36 H), 0.002 (s, 24 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.27, 159.86, 139.56, 138.67, 107.93, 105.58, 101.98, 100.66, 69.91, 64.32, 59.34, 33.38, 32.27, 25.85, 18.19, −5.45; IR (film, NaCl) 2930, 1600, 1460, 1255, 1100, and 835 cm^{-1}; FAB-(+)MS, m/z 1137 ($C_{57}H_{99}{}^{81}BrO_{10}Si_4$ + H^+) Anal. Calcd for $C_{57}H_{99}BrO_{10}Si_4$: C, 60.23; H, 8.78. Found: C, 60.33; H, 8.83.

Attachment of 13 to 1. Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-(*tert*-butyldimethylsilyloxy)propyloxy]benzyloxy)benzyloxy]-phenyl)ethane (Dendrimer 14). 1,1,1-Tris-(4-hydroxyphenyl)ethane (**1**, 0.860 g, 2.81 mmol), 18-crown-6 (0.22 g, 0.83 mmol), K_2CO_3 (1.55 g, 11.2 mmol), acetone (500 mL), and dendritic wedge **13** (10.2 g, 8.98 mmol) were stirred at reflux for 48 h. The solution was concentrated, and the white paste was partitioned between equal volumes of CH_2Cl_2 and water. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, filtered, and concentrated. The crude oil was purified by flash chromatography on silica gel (CH_2Cl_2) to give 8.92 g (91%) of **14** as a colorless glass: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, 6 H, J = 9 Hz), 6.85 (d, 6 H, J = 9 Hz), 6.66 (s, 6 H), 6.54 (s, 15 H), 6.39 (s, 6 H), 4.93 (s, 18 H), 4.01 (t, 24 H, J = 6 Hz), 3.76 (t, 24 H, J = 6 Hz), 2.09 (s, 3 H), 1.94 (quint, 24 H, J = 6 Hz), 0.85 (108 H), 0.01 (s, 72 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.41, 160.14, 156.76, 142.16, 139.37, 138.91, 129.67, 113.91, 106.45, 105.81, 102.70, 100.78, 70.08, 64.51, 59.50, 50.70, 32.35, 31.80, 25.90, −5.42; IR (film, NaCl) 2955, 1740, 1595, 1460, 1165, 1100, and 835 cm^{-1}. Anal. Calcd for $C_{191}H_{312}O_{33}Si_{12}$: C, 66.04; H, 9.05. Found: C, 65.66; H, 9.31.

Desilylation of the 3-(*tert*-Butyldimethylsilyloxy)propyl Groups of 14. Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-hydroxypropyloxy]benzyloxy)benzyloxy]phenyl)ethane (Dendrimer 15). A solution of **14** (8.72 g, 2.51 mmol) in 60 mL of 1.0 M Bu_4NF in THF (60 mmol, 2 equiv/TBS group) was allowed to stir at ambient temperature for 16 h. The solution was poured into water (250 mL), and the pH was adjusted to 6 with 0.05 N HCl. The products were extracted into EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The crude oil was purified by repeated digestion with CH_2Cl_2 to give 4.65 g (88%) of **15** as a colorless glass: ^{1}H NMR (300 MHz, THF-d_8) δ 6.96 (d, 6 H, J = 9 Hz), 6.82 (d, 6 H, J = 9 Hz), 6.66 (s, 6 H), 6.56 (s, 15 H), 6.40 (s, 6 H), 4.95 (s, 18 H), 4.03 (t, 24 H, J = 6 Hz), 3.65 (t, 24 H, J = 6 Hz), 3.59 (s, 12 H, exchanges with D_2O), 2.06 (s, 3 H), 1.90 (quint, 24 H, J = 6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.50, 161.20, 158.00, 142.92, 140.83, 140.36, 130.41, 114.71, 106.96, 106.35, 101.95, 101.25, 70.63, 65.63, 59.14, 51.46, 33.53, 30.59; IR (film, NaCl) 3500−3200, 2950, 1595, 1460, 1165, 1060, and 830 cm^{-1}; MALDI-TOF MS, m/z 2101 ($C_{119}H_{144}O_{33}$ + H^+). Anal. Calcd for $C_{119}H_{144}O_{33}$: C, 67.98; H, 6.90. Found: C, 67.90; H, 6.91.

Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-bromopropyloxy]-benzyloxy)benzyloxy] phenyl)ethane (Dendrimer 17). The alcoholic dendrimer **15** (2.79 g, 1.32 mmol) and Et_3N (4.75 g, 47 mmol), MsCl (5.52 g, 48.0 mmol), CH_2Cl_2 (100 mL), and anhydrous THF (100 mL) were stirred at 0 °C for 2 h to give the mesylate **16**, which was not isolated. Anhydrous, granular LiBr (23.0 g, 265 mmol) was then added, and the resulting mixture was allowed to stir for 16 h at ambient temperature. The reaction mixture was concentrated, and the oil was partitioned between equal volumes of water and CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted twice more with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was purified via flash chromatography on silica gel (CH_2Cl_2, then 50% EtOAc in CH_2Cl_2) to give 2.79 g (75%) of **17** as a colorless glass: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, 6 H, J = 9 Hz), 6.83 (d, 6 H, J = 9 Hz), 6.65 (s, 6 H), 6.53−6.56 (m, 15 H), 6.40 (s, 6 H), 4.94 (s, 18 H), 4.06 (t, 24 H, J = 6 Hz), 3.56 (t, 24 H, J = 6 Hz), 2.27 (quint, 24 H, J = 6 Hz), 2.09 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.03, 156.74, 142.04, 139.56, 139.22, 129.60, 113.96, 106.44, 106.05, 101.53, 100.93, 69.95, 69.88, 65.38, 50.62, 32.25, 30.85, 29.91; IR (film, NaCl) 3035, 2975, 1605, 1510, 1250, 1180, 1030, and 830 cm^{-1}; MALDI-TOF MS, m/z 2869 ($C_{119}H_{132}{}^{81}Br_{12}O_{21}$ + H^+). Anal. Calcd for $C_{119}H_{132}Br_{12}O_{21}$: C, 50.02; H, 4.66. Found: C, 50.12; H, 4.69.

Preparation of Phenylchalcogenide Anions. A. Sodium Phenylsulfide. Benzenethiol was dissolved in 1.0 M NaOEt in EtOH [0.055 g (0.5 mmol)/mL] to generate an ethanol solution of 1.0 M NaSPh.

B. Sodium Phenylselenide. Sodium borohydride was added slowly in 0.2 equivalent aliquots to a solution of diphenyl diselenide in 1.0 M NaOEt in EtOH [0.078 g (0.25 mmol) of PhSeSePh/mL] heated at reflux under an argon atmosphere until the solution became colorless and transparent.

C. Sodium Phenyltelluride. Sodium borohydride was added slowly in 0.2 equivalent aliquots to a solution of diphenyl ditelluride in 1.0 M NaOEt in EtOH [0.102 g (0.25 mmol) of PhTeTePh/mL] heated at reflux until the solution became colorless and transparent.

Preparation of 1-Phenoxy-3-(phenylthio)propane (PhS−1). 1-Phenoxy-3-(phenylthio)propane was prepared via the addition of 1-bromo-3-phenoxypropane (5.38 g, 25.0 mmol) in 50 mL of THF to 29 mL (29 mmol) of 1 M NaSPh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with ether. The combined ether extracts were washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated. The product was purified via flash chromatography on silica gel eluted with 20% CH_2Cl_2 in hexanes to give 5.35 g (83%) of **PhS−1** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dxd, 2 H, J = 1.5, 8 Hz), 7.28 (m, 4 H), 7.16 (t, 1 H, J = 7.5 Hz), 6.93 (t, 1 H, J = 7.5 Hz), 6.87 (d, 2 H, J = 8 Hz), 4.06 (t, 2 H, J = 6 Hz), 3.11 (t, 2 H, J = 7 Hz), 2.10 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.69, 136.15, 129.35, 129.00, 128.82, 125.82, 120.64, 114.40, 65.77, 30.00, 28.80; EIMS, m/z 244.094 (Calcd for $C_{15}H_{16}OS$: 244.092) Anal. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; Found: C, 74.00; H, 6.74.

Preparation of 1-Phenoxy-3-(phenylseleno)propane (PhSe−1). 1-Phenoxy-3-(phenylseleno)propane was prepared via the addition of 1-bromo-3-phenoxypropane (2.30 g, 10.7 mmol) in 50 mL of THF to 30 mL (15 mmol) of 0.5 M NaSePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with CH_2Cl_2. The combined ether extracts were washed with saturated Na_2CO_3 solution (3 × 20 mL), dried over $MgSO_4$, and concentrated. The product was purified via flash chromatography on silica gel eluted with 20% CH_2Cl_2 in hexanes to give 2.66 g (85%) of **PhSe−1** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, 2 H, J = 8 Hz), 7.24−7.30 (m, 5 H), 6.95 (t, 1 H, J = 7 Hz), 6.89 (d, 2 H, J = 8 Hz), 4.06 (t, 2 H, J = 6 Hz), 3.11 (t, 2 H, J = 6 Hz), 2.18 (quint, 2 H, J = 7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.68, 132.37, 129.99, 129.33, 128.97, 126.70, 120.59, 114.36, 66.55, 29.64, 23.63; IR (film, NaCl) 3055, 2940, 1600, 1585, 1495, 1475, 1245, 1170, 1030, 755, 690 cm^{-1}; EIMS, m/z 292 ($C_{15}H_{16}O^{80}Se$). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.76; H, 5.49.

Preparation of 1-Phenoxy-3-(phenyltelluro)propane (PhTe−1). 1-Phenoxy-3-(phenyltelluro)propane was prepared via the addition of 1-bromo-3-phenoxypropane (1.75 g, 8.14 mmol) in 60 mL of THF to 24 mL (12 mmol) of 0.5 M NaTePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with CH_2Cl_2. The combined ether extracts were washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated. The product was purified via flash chromatography on silica gel eluted with 20% CH_2Cl_2 in hexanes to give 2.30 g (83%) of **PhTe−1** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, 2 H, J = 7 Hz), 7.28−7.32 (m, 3 H), 7.22 (t, 2 H, J = 8 Hz), 6.98 (t, 1 H, J = 7 Hz), 6.91 (d, 2 H, J = 8 Hz), 4.03 (t, 2 H, J = 6 Hz), 3.08 (t, 2 H, J = 6 Hz), 2.30 (quint, 2 H, J = 7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.65, 138.17, 129.32, 129.10, 127.50, 120.60, 114.38, 111.64, 68.39, 31.18, 4.29; IR (film, NaCl) 3065, 2935, 1600, 1585, 1495, 1475, 1245, 1170, 1030, 755, 690 cm^{-1}; EIMS, m/z 342 ($C_{15}H_{16}O^{130}Te$). Anal. Calcd for $C_{15}H_{16}OTe$: C, 53.01; H, 4.71. Found: C, 52.92; H, 4.71.

Preparation of 1,1,1-Tris[4-(3,5-bis[3-(phenylseleno)propyloxy]-benzyloxy)phenyl]ethane (PhSe−6). Hexabromide **10** (0.54 g, 0.39 mmol) in 20 mL of THF was added to 7 mL (3.5 mmol) of 0.5 M NaSePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products

were extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified via flash chromatography on silica gel (2:1 hexanes−CH_2Cl_2 and then 10% EtOAc in CH_2Cl_2) to give 0.61 g (85%) of **PhSe−6** as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, 12 H, J = 7 Hz), 7.29−7.33 (m, 18 H), 7.10 (d, 6 H, J = 9 Hz), 6.95 (d, 6 H, J = 9 Hz), 6.65 (s, 6 H), 6.46 (s, 3 H), 5.03 (s, 6 H), 4.10 (t, 12 H, J = 6 Hz), 3.16 (t, 12 H, J = 7 Hz), 2.21−2.24 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.98, 156.63, 141.88, 139.33, 132.38, 129.86, 129.50, 128.96, 126.72, 113.85, 105.74, 100.62, 69.76, 66.76, 50.50, 30.66, 29.59, 23.95; IR (film, NaCl) 3050, 2940, 1600, 1505, 1455, 1265, 1165, 1020, 830, 735; MALDI-TOF MS, *m*/*z* 1861 ($C_{95}H_{96}O_9{}^{80}Se_6$ + H^+) and *m*/*z* 1878, corresponding to the addition of water ($C_{95}H_{96}O_9{}^{80}Se_6$ + H_2O). Anal. Calcd for $C_{95}H_{96}O_9Se_6$: C, 61.49; H, 5.15. Found: C, 61.41; H, 5.25.

Preparation of 1,1,1-Tris[4-(3,5-bis[3-(phenyltelluro)propyloxy]-benzyloxy)phenyl]ethane (PhTe−6). Hexabromide **10** (0.47 g, 0.34 mmol) in 20 mL of THF was added to 6.0 mL (3.0 mmol) of 0.5 M NaTePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified via flash chromatography on silica gel (2:1 hexanes−CH_2Cl_2 and then 10% EtOAc in CH_2Cl_2) to give 0.59 g (82%) of **PhTe−6** as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 12 H, J = 7 Hz), 7.31 (t, 6 H, J = 7 Hz), 7.24 (t, 12 H, J = 7 Hz), 7.08 (d, 6 H, J = 9 Hz), 6.93 (d, 6 H, J = 9 Hz), 6.60 (s, 6 H), 6.40 (s, 3 H), 5.00 (s, 6 H), 4.04 (t, 12 H, J = 6 Hz), 3.10 (t, 12 H, J = 7 Hz), 2.32 (quint, 12 H, J = 7 Hz), 2.18 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.95, 156.64, 141.89, 139.29, 138.17, 129.52, 129.10, 127.51, 113.86, 111.58, 105.75, 100.64, 69.80, 68.56, 50.52, 31.15, 31.05, 4.28; IR (film, NaCl) 3050, 2935, 1595, 1505, 1455, 1245, 1160, 1015, 830, 735. Anal. Calcd for $C_{95}H_{96}O_9Te_6$: C, 51.84; H, 4.54. Found: C, 51.89; H, 4.46.

Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-(phenylthio)propyl-oxy]benzyloxy)-benzyloxy]phenyl)ethane (PhS−12). The **PhS-12** dendrimer was prepared via the addition of **17** (0.12 g, 0.042 mmol) in 15 mL of THF to 1.0 mL (1.0 mmol) of 1 M NaSPh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with EtOAc. The combined organic extracts were washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated. The crude product was purified by digesting the residual oil in ether for 5 h. The solvent was decanted away periodically and replaced prior to a final decanting and drying under high vacuum to give 0.121 g (90%) of **PhS−12** as a colorless glass: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, 24 H, J = 8 Hz), 7.23 (t, 24 H, J = 8 Hz), 7.12 (t, 12 H, J = 8 Hz), 6.97 (d, 6 H, J = 9 Hz), 6.82 (d, 6 H, J = 9 Hz), 6.65 (s, 6 H), 6.52 (s, 15 H), 6.35 (s, 6 H), 4.90−4.93 (m, 18 H), 4.01 (t, 24 H, J = 6 Hz), 3.07 (t, 24 H, J = 7 Hz), 2.03−2.08 (m, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.66, 160.17, 160.08, 156.79, 142.08, 139.55, 139.12, 136.15, 129.64, 129.23, 128.91, 125.99, 114.00, 106.48, 106.00, 101.59, 100.94, 70.04, 66.13, 50.67, 31.76, 30.18, 28.84; IR (film, NaCl) 3055, 2930, 1595, 1165, 1060, and 735 cm^{-1}; MALDI-TOF MS, *m*/*z* 3205 ($C_{191}H_{192}O_{21}S_{12}$ + H^+), *m*/*z* 3259 ($C_{191}H_{192}O_{23}S_{12}$ + $^{23}Na^+$). Anal. Calcd for $C_{191}H_{192}O_{21}S_{12}$: C, 71.50; H, 6.03. Found: C, 71.38; H, 6.35.

Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-(phenylseleno)propyloxy]benzyloxy)-benzyloxy]phenyl)ethane (PhSe−12). The **PhSe−12** dendrimer was prepared via the addition of **17** (0.16 g, 0.054 mmol) in 15 mL of THF to 3 mL (1.5 mmol) of 0.5 M NaSePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with EtOAc. The combined organic extracts were washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated. Digesting the residual oil in ether for 5 h purified the crude product. The solvent was decanted away periodically and replaced prior to a final decanting and drying under high vacuum to give 0.14 g (68%) of **PhSe−12** as a colorless glass: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.48 (m, 24 H), 7.19−7.24 (m, 36 H), 6.98 (d, 6 H, J = 9 Hz), 6.84 (d, 6 H, J = 9 Hz), 6.66 (s, 6 H), 6.51−6.54 (m, 15 H), 6.33 (s, 6 H), 4.91−4.93 (m, 18 H), 4.00 (t, 24 H, J = 6 Hz), 3.04 (t, 24 H, J = 7 Hz), 2.09−2.13 (m, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.16, 160.09, 156.78, 142.08, 139.52, 139.05, 132.56, 129.97, 129.66, 129.09, 126.86, 113.97, 106.43, 105.93, 101.53, 100.85, 70.01, 69.89, 66.90, 50.62, 30.20, 29.67, 24.05; IR (film, NaCl) 3050, 2940, 1595, 1165, 1060, and 735 cm^{-1}. Anal. Calcd for $C_{191}H_{192}O_{21}Se_{12}$: C, 60.83; H, 5.13. Found: C, 60.71; H, 5.12.

Preparation of 1,1,1-Tris(4-[3,5-bis(3,5-bis[3-(phenyltelluro)propyloxy]benzyloxy)-benzyloxy] phenyl)ethane (PhTe−12). The **PhTe−12** dendrimer was prepared via the addition of **21** (0.20 g, 0.070 mmol) in 25 mL of THF to 3.4 mL (1.7 mmol) of 0.5 M NaTePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with EtOAc. The combined organic extracts were washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and concentrated. Digesting the residual oil in ether for 5 h purified the crude product. The solvent was decanted away periodically and replaced prior to a final decanting and drying under high vacuum to give 0.26 g (84%) of **PhTe−12** as a colorless glass: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 24 H, J = 7 Hz), 7.21 (t, 12 H, J = 7 Hz), 7.13 (t, 24 H, J = 7 Hz), 6.98 (d, 6 H, J = 9 Hz), 6.83 (d, 6 H, J = 9 Hz), 6.65 (s, 6 H), 6.53 (s, 3 H), 6.48 (s, 15 H), 6.30 (s, 6 H), 4.88−4.94 (m, 18 H), 3.94 (t, 24 H, J = 6 Hz), 3.00 (t, 24 H, J = 7 Hz), 2.21 (quint, 24 H, J = 6 Hz), 2.08 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.11, 156.79, 142.08, 139.56, 139.02, 138.31, 129.65, 129.19, 127.61, 114.01, 111.65, 106.46, 105.95, 101.59, 100.92, 70.05, 69.95, 68.56, 50.67, 31.25, 31.21, 29.66, 4.28; IR (film, NaCl) 3050, 2935, 1595, 1160, 1060, and 735 cm^{-1}. Anal. Calcd for $C_{191}H_{192}O_{21}Te_{12}$: C, 52.68; H, 4.44. Found: C, 52.33; H, 4.39.

Preparation of 1,1,1-Tris[4-(3-[phenylseleno]propyloxy)phenyl]-ethane (PhSe−3). Tribromide **22** (2.50 g, 3.74 mmol) in 50 mL of THF was added to 30 mL (15 mmol) of 0.5 M NaSePh in EtOH. The reaction mixture was stirred at ambient temperature for 16 h and was then poured into water. The products were extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, and concentrated. The crude product was purified via flash chromatography on silica gel (2:1 hexanes−CH_2Cl_2 and then CH_2Cl_2) to give 3.13 g (93%) of **PhSe−3** as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, 6 H, J = 7 Hz), 7.23−7.28 (m, 9 H), 7.01 (d, 6 H, J = 9 Hz), 6.80 (d, 6 H, J = 9 Hz), 4.05 (t, 6 H, J = 6 Hz), 3.12 (t, 6 H, J = 7 Hz), 2.18 (quint, 6 H, J = 7 Hz), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.76, 141.83, 132.50, 130.01, 129.57, 129.06, 126.81, 113.57, 66.67, 50.53, 20.73, 29.75, 24.10; IR (film, NaCl) 3055, 2940, 1605, 1580, 1510, 1475, 1245, 1180, 1022, 830, 735, 690; FAB(+)MS, *m*/*z* 901 ($C_{47}H_{48}O_3{}^{80}Se_3$ + H^+). Anal. Calcd for $C_{47}H_{48}O_3Se_3$: C, 62.88; H, 5.39. Found: C, 63.02; H, 5.49.

Preparation of 1,1,-Bis[4-(3,5-bis[3-(phenyoxy)propyloxy]benzyl-oxy)phenyl]-1-[4-[3-(3-phenoxy)propyloxy]-5-[3-(phenylseleno)pro-pyloxy]benzyloxy)phenyl]ethane (PhSe−1−PhO−5). Sodium boro-hydride (0.0045 g, 0.19 mmol, 1.5 equiv) was added to a solution of diphenyl diselenide (0.0185 g, 0.059 mmol, 0.75 equiv) in 40 mL of THF and 40 mL of 1.5 M NaOEt in EtOH. The resulting solution was heated at reflux until the solution was clear. A THF solution of bromide **32** (0.116 g, 0.079 mmol, 1.0 equiv, Supporting Information) was then added dropwise. The reaction was allowed to stir at reflux for 24 h. The reaction mixture was concentrated, and 100 mL of water was added. The products were extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The crude product mixture was purified via chromatography on SiO_2 (hexane/CH_2Cl_2, 1/9) to give 0.0954 g (78%) of **PhSe−1−PhO−5** as a thick yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 2.0, 7.2 Hz, 2 H), 7.21−7.30 (m, 10 H), 7.01 (d, J = 8.8, 7 H), 6.90−6.96 (m, 16 H), 6.84 (d, J = 8.4 Hz, 7 H), 6.59 (s, 5 H), 6.55 (s, 1 H), 6.44 (s, 2 H), 6.40 (s, 1 H), 4.93 (s, 6 H), 4.14 (t, J = 6.0 Hz, 20 H), 4.02 (t, J = 6.0 Hz, 2 H), 3.07 (t, J = 7.2, 2 H), 2.24 (quint, J = 6.0 10 H), 2.14 (quint, J = 6.0, 2 H), 2.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.18, 160.16, 160.11, 158.747, 156.73, 142.00, 141.98, 139.47, 139.44, 132.51, 129.92, 129.57, 129.41, 129.04, 126.81, 120.67, 114.42, 113.93, 105.86, 100.76, 100.74, 69.86, 66.85, 64.49, 64.17, 53.40, 50.58, 30.73, 29.68, 29.22, 24.05; MALDI-TOF MS, *m*/*z* 1558.6 (Calcd for $C_{95}H_{96}O_{14}{}^{80}Se$ + H_2O: 1558.6).

Uncatalyzed Reactions of H_2O_2 and Bromide in pH-6 Phosphate Buffer. A. Preparative Runs. Sodium bromide (6.63 g, 0.064 mol) was added to a stirred (constant-rate, overhead stirrer at 50 rpm with a 1.0" stirblade), two-phase mixture of 4.10 g (0.050 mol) of cyclohexene in 20 mL of CH_2Cl_2 and an aqueous phase of 20 mL of

pH-6 phosphate buffer (0.1 M) and 12 mL of 30% H_2O_2 (100 mmol) in a constant-temperature bath held to 296.0 ± 0.1 K. After 24 h (7 half-lives), the ratio of products was determined by gas chromatography and, following concentration, by ^{1}H NMR. The molar quantity of brominated products was determined to be (2.25 ± 0.06) mmol of **18** and **19** in a 45:55 ratio for duplicate runs.

B. Kinetic Runs. Sodium bromide (6.63 g, 0.064 mol) was added to a stirred (constant-rate stirrer as described above), two-phase mixture of 4.10 g (0.050 mol) of cyclohexene and diphenyl ether (20 mg, 1 mg/mL, inert to reaction conditions) in 20 mL of CH_2Cl_2 and an aqueous phase of 20 mL of pH-6 phosphate buffer (0.1 M) and 12 mL of 30% H_2O_2 (100 mmol) in a constant-temperature bath held to 296.0 ± 0.1 K. The organic layer was sampled periodically by gas chromatography, and the rate of appearance of the brominated products **18** and **19** was compared to that of the internal standard. The infinity point for the pseudo-first-order kinetics (constant bromide concentration of 2.0 M) was 2.25 mmol from the preparative runs.

Initial Rates of Dioxygen Formation. Rates of dioxygen formation were monitored using an OM-1 biological oxygen meter connected to a microprobe (Microelectrodes, Inc., Londonderry, NH). A solution of 20 mL of pH-6 phosphate buffer (0.1 M) and 12 mL of 30% H_2O_2 (100 mmol) was sparged with nitrogen to reduce the amount of dissolved O_2. Reaction was initiated by the addition of 6.63 g (64 mmol) of NaBr. The rate of dioxygen formation was calculated directly from a plot of the percent dioxygen in the buffer solution versus time using an oxygen concentration of 2.47×10^{-4} M in air-saturated water as the standard. An initial reaction velocity of $(2.3 \pm 0.1) \times 10^{-4}$ M s^{-1} was determined from triplicate runs.

Catalyzed Reactions of H_2O_2 and Bromide in pH-6 Phosphate Buffer. A. Preparative Runs. Sodium bromide (6.63 g, 0.064 mol) was added to a stirred (constant-rate stirrer as described above), two-phase mixture of 4.10 g (0.050 mol) of cyclohexene and catalyst (0.008 to 0.05 mmol) in 20 mL of CH_2Cl_2 and an aqueous phase of 20 mL of pH-6 phosphate buffer (0.1 M) and 12 mL of 30% H_2O_2 (100 mmol) in a constant-temperature bath held to 296.0 ± 0.1 K. After 3−24 h (≥7 half-lives), the ratio of products was determined by gas chromatography and, following concentration, by ^{1}H NMR. These values, as well as ratios of **18** to **19**, are compiled in Table 1. The pH of the aqueous phase remained constant throughout the course of the reaction.

B. Kinetic Runs. Sodium bromide (6.63 g, 0.064 mol) was added to a stirred (constant-rate stirrer as described above), two-phase mixture of 4.10 g (0.050 mol) of cyclohexene, diphenyl ether (20 mg, 1 mg/mL), and catalyst (0.008 to 0.05 mmol) in 20 mL of CH_2Cl_2 and an aqueous phase of 20 mL of pH-6 phosphate buffer (0.1 M) and 12 mL of 30% H_2O_2 (100 mmol) in a constant-temperature bath held to 296.0 ± 0.1 K. The organic layer was sampled periodically by gas chromatography, and the rate of appearance of the brominated products **18** and **19** was compared to that of the internal standard. Infinity points were determined from the preparative runs.

Turnover Numbers with PhSe−12. Sodium bromide (6.63 g, 0.064 mol) was added to a stirred (constant-rate stirrer as described above), two-phase mixture of 4.10 g (0.050 mol) of cyclohexene and catalyst (30.2 mg, 8.00 mmol) in 20 mL of CH_2Cl_2 and an aqueous phase of 20 mL of pH-6 phosphate buffer (0.5 M) and 12 mL of 30% H_2O_2 (100 mmol) in a constant-temperature bath held to 296.0 ± 0.1 K. Every 0.5 h, additional 12-mL (100 mmol) aliquots of 30% H_2O_2 were added to a total of 500 mmol of H_2O_2. The organic phase was concentrated, and the products were separated by chromatography on silica gel eluted with 3% EtOAc in hexanes to give 1.64 g (4.8 mmol) of **18** and 2.02 g (11.3 mmol) of **19**.

A second reaction without catalyst was similarly charged with H_2O_2 and the products were isolated 3.5 h following the initial addition of NaBr. The organic phase was washed with cold sodium bisulfite to reduce any H_2O_2 present, dried, and concentrated. The products were separated by chromatography on silica gel eluted with 3% EtOAc in hexanes to give 0.052 g (0.22 mmol) of **18** and 0.045 g (0.25 mmol) of **19**.

Acknowledgment. We thank the Augmentation Awards for Science and Engineering Research Training (AASERT) Program, Office of Naval Research, and the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work.

Supporting Information Available: Experimental details for the preparation of intermediates **20** through **32** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002649+