Dendrimers Derived from 1 → 3 Branching Motifs

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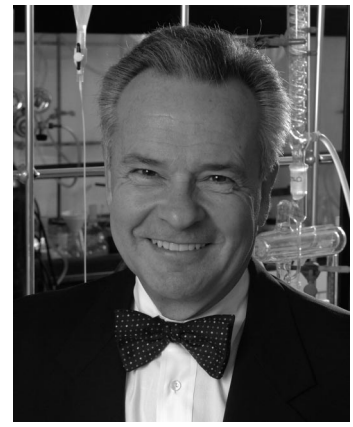
1. Introduction

In 2008, we overviewed[1] poly(amido amine)s, polypropylenimines, and related dendrimers and dendrons possessing diverse 1 → 2 branching patterns that were predominately made via divergent procedures. The historic aspects of dendrimer chemistry and an overview of the conventional modes of construction have been reported in detail.[2−5] Since 2001, topical reviews over extensive specialized and interesting subsets of dendrimers have also appeared.[4,6−21] These include dendrimers designed for diverse applications (sensing, catalysis, molecular recognition, photonics, and nanomedicine),[22] dendrimer-based nanomedicine,[23−46] drug delivery[12,47− 50] gene delivery,[28,51] light-harvesting,[52] metallodendrimers,[53−59] organoiron-mediated dendrimer syntheses,[60] metallocene dendrimers as electrochrome molecular batteries,[61] functionalized dendrimers,[62] dendritic effect,[63] dynamers,[64] catalysis,[57,65−80] porphyrin dendrimers,[81− 84] nanocomposites,[85] redox aspects,[26,86−90] olefin metathesis,[91,92] dendrimers in solution,[93,94] photoactive dendrimers,[82,95−99] P dendrimers,[100−119] Si-containing dendrimers,[120] new modes of construction,[121−133] glycodendrimers and multivalent neoglycocongates,[134−141] biohybrid polymer capsules,[142] dendritic polyglycerols[143] for biomedical applications.[144] dendritic liquid crystals,[145,146] dendronized polymers,[147−149] chiral dendrimers,[150,151] cleavable dendrimers,[152−154] dendritic nanomaterials,[155] electrode design,[156] solubility enhancers,[157] fullerene-rich dendrimers,[158−167] unimolecular micelles,[168,169] gelators,[170,171] light-emitting diodes,[172−174] environmental remediation,[175] MRI agents,[176−179] biomimetics,[180] folded dendrimers,[181] dendritic gold nanoparticles,[182,183] nonlinear optics,[184,185] quantum dots,[186] molecular recognition,[187] peptide dendrimers,[188] toxicity of nanocarriers,[189,190] triazine dendrimers,[191] polyamino dendrimers,[192] water-soluble fluorescent dendrimers,[193] energy dissipation in multichromophoric dendrimers,[194] hyperbranched polymers,[195] dendritic and dendronized polymers via click chemistry,[196−198] self-assembly, disassembly, and self-organization of dendronized polymers,[199] hierarchical structures of dendritic polymers,[200] monomers for tailored dendrimers,[201] branched oligogermanes,[202] and dendrigraft polymers,[203] and tailored materials for ophthalmic, orthopedic, and biotech applications.[204]

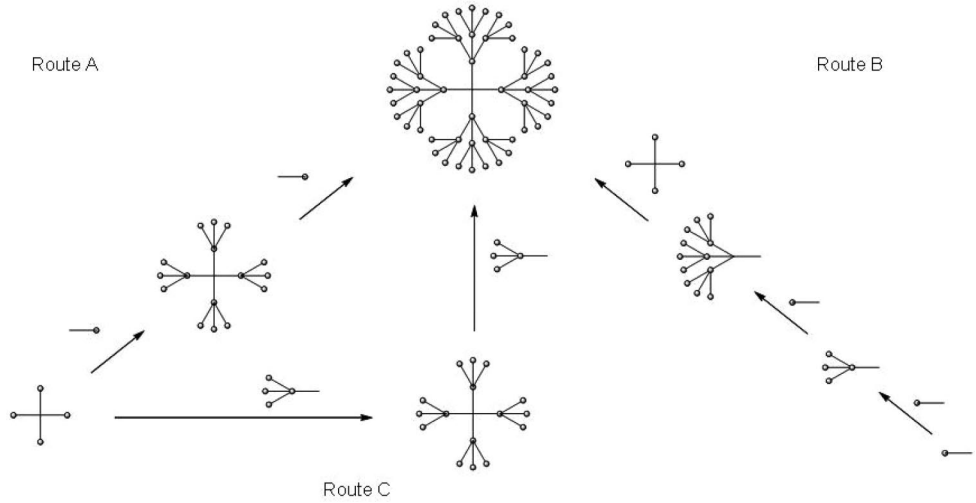
Herein, a comprehensive review for the 1 → 3 and 1 → (2 + 1) branching motifs has been compiled. In general, most divergently generated 1 → 2 branched dendrimers were assembled by addition of simple nonbranched monomers by means of a Michael reaction, whereas most of the 1 → 3 branched dendrimers have been prepared using preformed 1 → 3 branching (mini)dendrons or monomers, which were constructed via a predendron. Utilizing these precursors or monomers in the convergent synthesis with a central core gives the synthetic advantage of having fewer reactions occurring within a single molecule. This greatly reduces the number of branching and focal defects within the macromolecule, compared with those constructed using the purely divergent method of synthesis, yielding near uniformity and monodispersity in many cases. Upon construction of the layers or generations as they are commonly called, the number of surface groups on a tetravalent core for a 1 → 3 branched dendrimer increases (4, 12, 36, 108, ...) faster than that of a 1 → 2 branched dendrimer (4, 8, 16, 32, 64, ...). Using branched monomers offers unique opportunities to instill controlled polyfunctionalization and localized steric hindrance or protection. Scheme 1 shows the different modes of construction with a tetravalent core moiety. Route A



George R. Newkome received his B.S. and Ph.D. in chemistry from Kent State University. He joined Louisiana State University in 1968, becoming a full professor in 1978 and Distinguished Research Master in 1982. In 1986, he moved to the University of South Florida as Vice President for Research and Professor of Chemistry, becoming a Distinguished Research Professor in 1992. In 2001, he was appointed as Oelschlager Professor of Science and Technology at the University of Akron, where he is also Professor of Polymer Science and Chemistry, Vice President for Research, Dean of the Graduate School, and President of the University's Research Foundation. He has edited and authored 20 books, over 420 journal publications, and numerous patents resulting from research in supra-(macro)molecular chemistry, molecular dendritic and fractal assemblies, nanochemistry, inorganic−organic interfaces, molecular inclusion chemistry, molecular electronics, and photonics.

Carol Shreiner received her B.S. in chemistry in 1999 from the University of Pittsburgh. She received her Ph.D. in chemistry in 2004 from The University of Akron working in the laboratory of Professor David A. Modarelli focusing on electron acceptor-containing ruthenium and osmium bisterpyridine complexes as photosynthetic reaction center mimics. She then joined Professor George R. Newkome's research group as a postdoctoral fellow focusing on sterically hindered, shape-persistent terpyridine complexes. In 2007, she joined the faculty at Hiram College where she is currently an Assistant Professor in the chemistry department.

Scheme 1. The Convergent and Divergent Routes to Dendrimer Construction



illustrates the divergent method of construction, building outward from a tetravalent core. Transformation of the new termini at each generation allows for further substitution and dendritic growth. As the molecule grows, the steric crowding on the periphery gives rise to unreacted loci, leading to an imperfect structure, which is amplified with increasing generations. Attaching preformed dendrons of specific generation size via a convergent method (route B) has distinct advantages over the traditional divergent procedure using the Michael reaction and allows for a more uniform macromolecule, especially at higher generations. Route C utilizes branched monomers or minidendrons via a divergent process. The divergent construction, using 1 → 2 or 1 → 3 branched monomers, permits either divergent or convergent assembly giving access to different dendritic families. Few theoretical studies have been conducted with these 1 → 3 branching homopolymers[205] and comparative studies with their 1 → 2 branching counterparts have been very limited, but a few do exist and will be considered.

2. 1 → 3 C-Branched

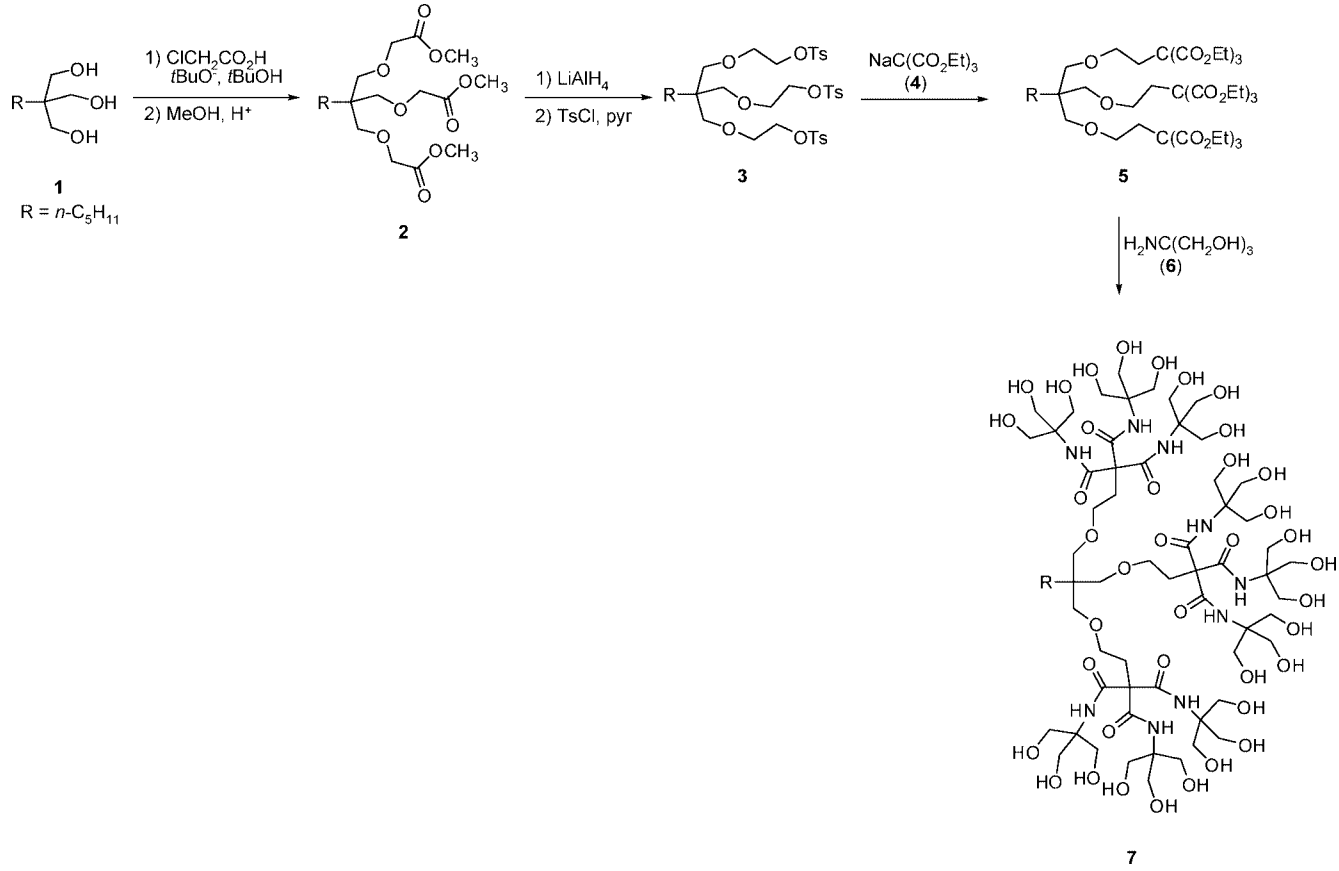
2.1. 1 → 3 C-Branched, Amide Connectivity

2.1.1. 1 → 3 C-Branched, Amide (TRIS) Connectivity

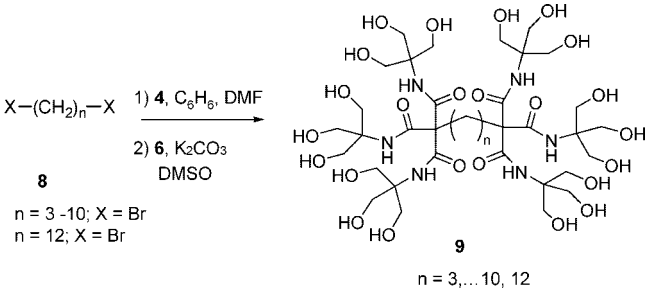
In 1985, Newkome et al. reported[206] the first example of divergently constructed cascade tree-like macromolecules utilizing sp^3-carbon atoms as 1 → 3 branching centers for the monomeric dendrons. Although these initial syntheses were not strictly iterative, notable dendritic preparative features were explored and exploited. The incorporated building blocks possessed tetrahedral, tetrasubstituted C-branching centers that maximized branching for a C-based system and differential monomer layering (analogous to block copolymer construction). The molecular architecture was modeled from the Leeuwenberg model[207,208] for trees, as described by Tomlinson;[209] since this original series was terminated by hydroxyl moieties, the simple descriptive term "arborols" was coined. The initial core consisted of a one-directional 1,1,1-tris(hydroxymethyl)alkane (**1**) and used two readily available building blocks: trialkyl methanetricarboxylates[210−212] or their sodium salts (the "triester", **4**) and tris(hydroxymethyl)-aminomethane ("TRIS", **6**; Scheme 2). The use of an appropriate spacer between branching centers was found to be necessary due to steric hindrance associated with the quaternary carbon center, as subsequent studies have shown.[213] To circumvent retardation of these chemical transformations, a three-atom distance was needed between the branch point and the reactive chemical center. Thus, triol **1** was treated with the chloroacetic acid, esterified (MeOH, H^+) to produce polyester **2**, reduced (LAH), and transformed (TsCl) to the corresponding tris(tosylate) **3**, which upon treatment with the sodio anion of triester **4** generated the nonaester **5**. Subsequent amidation of this ester **5** with TRIS (**6**) afforded the desired one-directional 27-arborol (**7**), which was fully characterized and shown to be water-soluble, thus affording entrance to the supramolecular concept of "unimolecular micelles"[206] and the first 1 → 3 branching dendrimer. Interestingly, each of the branching centers was different, but this early example also attained the third generation. The overall amidation using TRIS under anhydrous basic (K_2CO_3) conditions in DMSO actually undergoes an initial facile transesterification, followed by a rapid intramolecular rearrangement to give the amide product(s).[214] One of the simplest members of this one-directional family is derived from the treatment of TRIS with glutaric anhydride to give $HO_2C(CH_2)_3COHNC(CH_2OH)_3$, which upon heating generated a series of hyperbranched poly(amidoester)s.[215] The length of the alkyl chain determined the product's surfactant character; thus, the cmc of [9]-6, where [9] = the number of terminal hydroxyl groups and 6 = the number of carbon atoms in the alkyl chain, was ascertained and the pressure−area isotherms were determined for the less soluble [9]-8 and [9]-10.[216]

In the early applications of this procedure,[217] methyl 1-adamantanecarboxylate was treated with TRIS in dry DMSO to generate (90%) the desired amide-triol product; similarly, 1,3,5,7-tetrakis(methoxycarbonyl)adamantane was transformed to the dodecaol.[218] The use of 1-[(mesyloxy)methyl]adamantane with triethyl methanetricarboxylate[210−212] in DMF with anhydrous K_2CO_3 failed to undergo the expected nucleophilic substitution; whereas, the related 1-[(mesyloxy)ethyl]adamantane under identical conditions gave (>90%) the triester, as a colorless solid, which was transformed (70%) to the nonaol upon treatment with TRIS.[217] The 1-adamantanecarboxylic acid was converted ($SOCl_2$) to the corresponding acyl halide, which upon addition of $H_2NC(CH_2CH_2CH_2OAc)_3$, derived from the commercially available $O_2NC(CH_2CH_2CH_2OH)_3$ in two-steps

Scheme 2. Utilization of Triester and Aminotriol Monomers to Construct a 27-Arborol[206]



Scheme 3. Cascade Construction of Dumbbell-Shaped Molecules (9)[206] That Form Stacked Aggregates in Aqueous Environments



(acylation[219] and catalytic reduction) in nearly quantitative yields, gave the amide triacetate, which was saponified to the triol and oxidized to the triacid; the next generation was synthesized in a similar manner. The related 1,3,5,7-tetrakis(chlorocarbonyl)adamantane with $H_2NC(CH_2CH_2CH_2OAc)_3$ gave (68%) the dodecaacetate.[218] The reaction of 1-(methoxycarbonyl)adamantane with $H_2NC(CH_2CH_2CH_2OH)_3$ failed to give the desired amide; these difficulties lead to the two-step preparation of $H_2NC(CH_2CH_2CO_2CMe_3)_3$ (di-*tert*-butyl 4-amino-4-[2-(*tert*-butoxycarbonyl)ethyl]heptanedioate; "Behera's amine"),[217] which will be considered in more detail in section 2.1.4.

Application of this two-step procedure (Scheme 3), nucleophilic substitution of a substrate possessing an appropriate leaving group with the anion of triester **4** to generate a polyester, followed by amidation with TRIS (**6**), was extended to the preparation of dumbbell-shaped, two-directional arborols **9**.[220] Treatment of 1,ω-dibromo- or di(mesyloxy)alkanes (**8**) with anion **4**, followed by reaction with TRIS (**6**), afforded the bisnonaols (**9**), which possess unique structural features when $n = 8-12$, permitting them to stack in an orthogonal array [Figure 1a], resulting in the formation of nanofibers via a supramolecular self-assembly process. These resultant aggregates form aqueous, thermally reversible gels,[214] based on the maximization of lipophilic−lipophilic and hydrophilic−hydrophilic interactions at <2 wt %. Fluorescence and electron microscopy, as well as light scattering experiments, provided evidence for supramolecular stacking and a rodlike micellar topology of these aggregates at low concentrations ($n = 10$ at <1 wt %).

Since these two-directional arborols self-assemble in an organized manner so that the lipophilic alkyl chain moieties are orthogonally juxtaposed, any functionality incorporated on this linkage would, by necessity, be preorganized for subsequent interactions. The introduction of a central alkyne bond (e.g., **10**) was accomplished by the transformations shown in Scheme 4. Following the conversion of diol **10** to the corresponding mesylate **11**, application of the simple two-step procedure gave rise to polyols **12** or **13** depending on the ester reagents used (i.e., a malonate or triester). Upon dissolution in water, the resultant alkyne **12** formed a gel in a manner analogous to that of the alkane-bridged bolaamphiphile **9**. Figure 1b shows the postulated stacking motif in the electron micrograph of **12** supporting the helical morphology and the deviation from idealized orthogonal chain orientation by the presence of the rigid, linear central alkyne moiety.[221] The large diameters of the twisted aggregates [Figure 1b] probably result from the packing of individual rods into the grooves of adjacent helical rods, or aggregates, thus producing a "super-coil" or "molecular rope". Such predetermined self-assembly has been denoted as "automorphogenesis" by Lehn.[222]

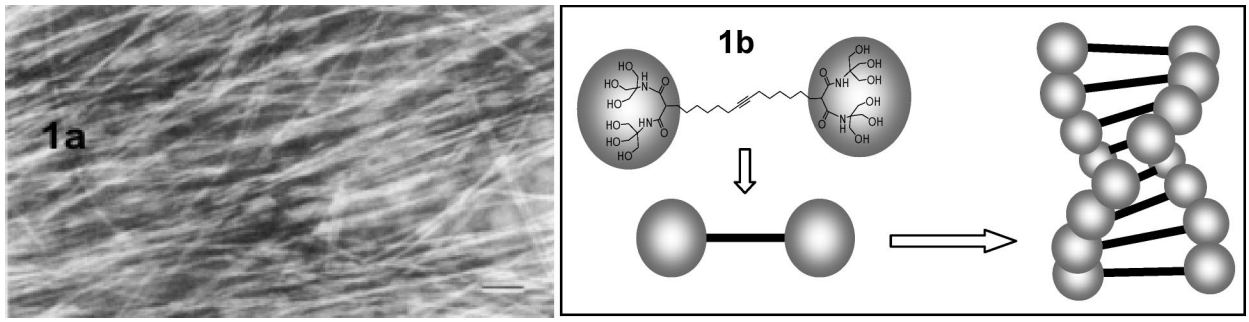
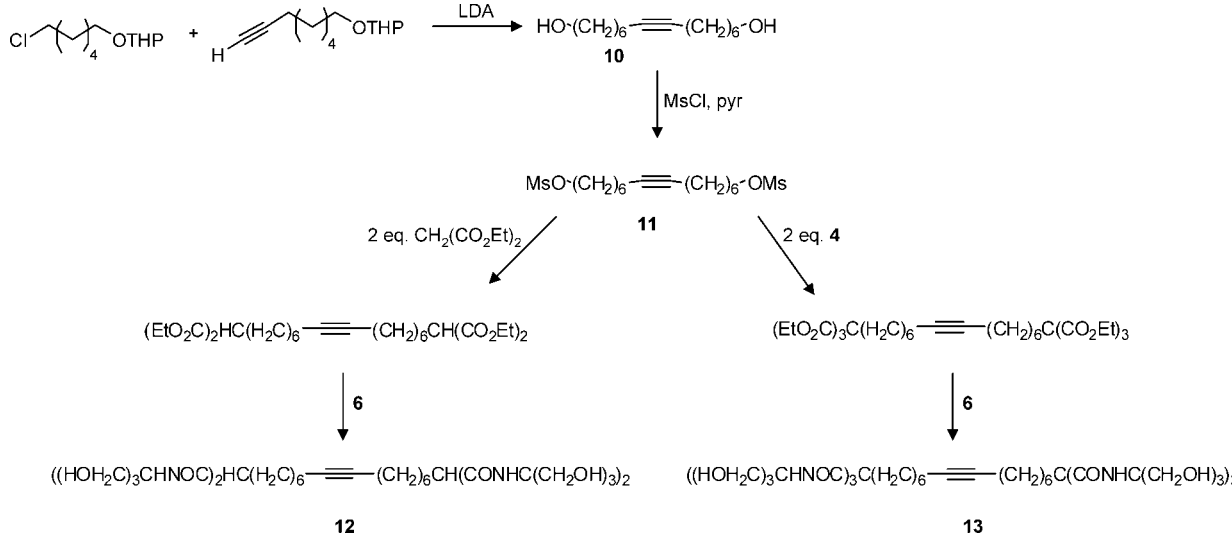


Figure 1. Electron micrograph of the two-dimensional self-assembled product.[220] Linear aggregates are formed with flexible alkyl bridges (a)[220] [Reprinted with permission from ref 220. Copyright 1986 The Royal Society of Chemistry], whereas curved ropelike structures result from the incorporation of bridge structural rigidity such as an alkyne moiety demonstrated by the nonorthogonal, dumbbell-like stacking[221] of the arborol (b).

Scheme 4. Synthetic Methodology[221] for the Incorporation of an Alkyne Unit within a Two-Dimensional Cascade



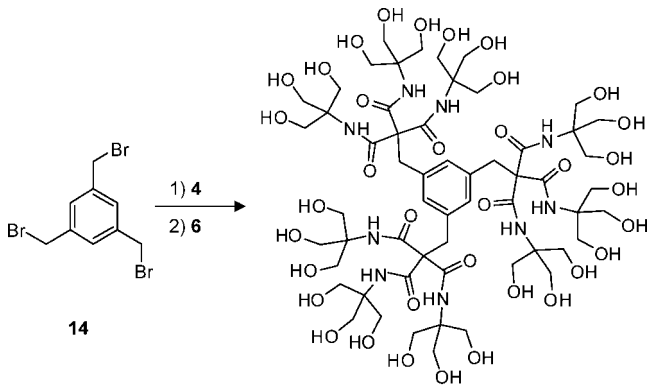
Newkome et al.[223] probed the inner lipophilic region of these two-directional bolaamphiphiles by the incorporation of bulkier and rigid 4,4′- and 3,3′,5,5′-biphenyls, as well as an elongated series of spirane cores, which introduced varying degrees of intermolecular interactions causing disruption to the aggregation process. Based on computational images, a better understanding of the molecular interactions during the initial stages of preorganization prior to gelation was proposed. Encapsulation or guest inclusion during the gelation process was examined as well as modeled.

Russo et al.[224] examined the two-directional arborol **9** ($n = 10$) in MeOH−water mixtures via light and SAXS, DSC, and freeze−fracture transmission electron microscopy. The self-assembly of these bolaamphiphiles was shown to "interact" in a side-by-side alignment resulting in the formation of bundles. Participation of individual self-assembled "fibers" in multiple bundles forms an extended three-dimensional, reversible gel network.[225] Above certain concentrations depending on the hydrophilic/hydrophobic balance, these thermally reversible gels were formed, and by means of wide-angle X-ray scattering studies, details concerning the fibrous gel structure were ascertained; solvent character appeared to affect the average domain length and fluorescently labeled two-directional arborols were prepared and shown not to retard fibrillar construction.[226]

Since this arborol **9** is comprised of two hydrophilic groups connected by a hydrophobic linkage, they fit the simple definition of a bolaamphiphile; a term derived from bolaform amphiphile originally introduced in 1951 by Fuoss and Edleson.[227] In 1984, when Fuhrhop and Mathieu[228] reported the synthesis and self-assembly of several bolaamphiphiles, these two-directional surfactant-like macromolecules represented a simple entrance to the bolaamphiphile arena; this subject as well as the related hydrogels have been highlighted[229,230] and reviewed.[131,132,170,170,231−238]

Numerous other related bolaamphiphilic examples have appeared based on the following: α,ω-terminal alkane polyols;[239−246] 4,4′-bis[[*N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]-7,7-diamidoheptyl]thio]-5,5′-dimethyltetrathiafulvalene (a self-assembled molecular wire);[247] $Me_3N^+(CH_2)_n-$(thiophenyl)$_n-(CH_2)_nN^+Me_3$ $2Br^-$;[248,249] 5,7-dodecadiynedioic acid bis-capped with 1-glucosamide;[250] *N*,*N*′-bis(2-deoxy-D-glucopyranosid-2-yl)-[251] or bis(*O*-galactopyranosyl)- and bis(*O*-lactosyl)alkane-α,ω-dicarboxamides;[252] *N*,*N*-eicosanedioyl-di-L-glutamic acid;[253,254] bolaamphiphilic phosphocholines;[255−258] α,ω-bis[2-(trimethylammonio)ethylphosphate]alkanes;[258−260] bis-galactoamido- (as well as 1- or 2-glucosamido-) alkane-α,ω-dicarboxamides;[261−263] carbohydrate-terminated bolaamphiphiles;[264−266] unsymmetrical peptide bolaamphiphiles;[267] ω-hydroxy quaternary ammonium bolaform surfactants;[268] α,ω-dinucleobase bolaamphiphiles;[269−271] two-component dendritic gels;[272−275] poly(glycerol−succinic acid)−PEG hybrid dendritic−linear polymers;[276,276−279] poly(L-lysine) dendrimer-*block*-poly(ethylene glycol)-*block*-poly(L-lysine) dendrimer;[280,281] diacetylenes with terminal *s*-triazines;[282] L-glutamic acid modified diacetylenic lipid;[283] $Me_3N^+(CH_2)_n-O-(aryl)_n-O(CH_2)_nN^+Me_3$ $2X^-$;[284−289] $Me_3N^+(CH_2)_nO-$

Scheme 5. Construction[312] of a Cascade Triad 15



aryl−N═N−aryl−$O(CH_2)_nN^+Me_3$ $2Br^-$;[290] 1,10-bis[3′-hydroxy-4′-(2″-pyridinylazo)phenoxy]decane;[291] triblock copolymers;[292] azobenzene-4,4′-dicarboxylic acid bis(pyridinohexyl [or undecyl] ester) dibromide;[293,294] oligo(*p*-phenylene-based molecular dumbbells;[295] L-phenylalanine-derivatized alkanes;[296] hemifluorinated bifunctional bolaamphiphiles for gene delivery;[297] chiral water-soluble perylenedimides;[298,299] dithiophene-based X-shaped bolaamphiphiles;[300] boronic acid-appended bolaamphiphile;[261] shamrock surfactants (triple-headed amphiphiles);[301] multiarmed gemini;[302,303] sugar-based gemini surfactants;[304] peptide-based cationic gemini surfactants.[305]

Menger and Keiper[233] presented an interesting review of "gemini surfactants" or bis-surfactants, which self-assemble at low concentrations. Alami and Holmberg also overviewed the related topic of heterogemini surfactants.[306] Fernandes et al. treated $(HOCH_2)_3CNHCO(CH_2)_nCONHC(CH_2OH)_3$, where $n = 0-2$, with [bis(2-pyridylmethyl)amine]trichloroiron(III); a crystal structure for (μ-oxo)bis[(oxalate)⟨[bis(pyridylmethyl)amine]iron(III)⟩ and $[(HOCH_2)_3CNHCOCH_2]_2$ was reported.[307] A series of Janus-like amphiphilic dendrimers were prepared of which the hydrophobic function was based on Fréchet dendrons possessing lipophilic aliphatic fragments and the hydrophilic portion was constructed from TRIS-termini.[308,309] An interesting mini-overview by Fred Menger entitled "Amphiphiles I Have Known" has appeared in which he describes the 25 amphiphilic systems that were prepared in his laboratories.[310]

Two simple dendrimers terminated with four TRIS groups were reacted with 4 equiv of $[H_4P_2V_3W_{15}O_{62}]^{-5}$ in dry polar aprotic organic solvent to generate the corresponding tetra(polyoxometalate)s (POM), which were shown to catalyze the oxidation of tetrahydrothiophene by both *tert*-BuO_2H and H_2O_2; the catalysts were recovered, thus opening the door to making POM-bound polymeric materials.[311]

A related three-directional member of this series[312] was based on a benzene [9]^3-arborol [**15**; 27-cascade:benzene-[3−1,3,5]:(ethylidene):(3-oxo-2-azapropylidene):methanol],[313,314] which was prepared by a two-step (alkylation−amidation or triester−TRIS) reaction sequence using 1,3,5-tris(bromomethyl)benzene as the core (**14**; Scheme 5). Electron microscopy and subsequent light scattering data suggested that **15** aggregated by the packing of ca. 40 molecules of this hydrophilic triad possessing three small spheres into an overall spherical array of ca. 20 nm (diameter), which is very reminiscent of globular micelles.

Dynamic light scattering experiments of **15** in aqueous solutions have been reported.[315] This benzene[9]^3-arborol in water forms aggregates, which have dynamic properties very similar to that of single polymer chains in solvents in the crossover region (qr_h) ≈ 1, where q is the absolute value of the scattering vector and r_h is the hydrodynamic radius of the scattering particles. The size of these particles appeared to be concentration independent within the concentration range ($3.5 \times 10^{-3}c^+ \leq c \leq 13.37 \times 10^{-3}c^+$, where $c^+ = 1$ mol dm^{-3}) studied. From the ratio of the scattered light intensity to the square of the absolute value of the scattering vector $(\Gamma_{max}/q^2)_o$ at the limit $q \Rightarrow o$, a hydrodynamic radius of r_h = O(100 nm) was calculated.

The synthesis of water-soluble calixarenes (**19** and **20**; Scheme 6), termed "silvanols" (molecular forests), possessing dendritic polyhydroxy spheres on the upper rims of [1$_n$]metacyclophanes was demonstrated.[316] The initial polytrimethylammonium calixarene (i.e., **16**)[317−319] was converted by established procedures to the crystalline dodecaester [1$_4$]metacyclophane, **18**, whose X-ray structure confirmed the assigned structure. Treatment of polyester **18** with TRIS generated the [36]-silvanol **19**. Electron micrographs of **19** showed it to possess a diameter of 5.7 nm relating to six aggregating macromolecules, as predicted by molecular modeling. The use of [1$_8$]metacyclophane **17**, as the starting material, gave rise to the corresponding [72]-silvanol **20** via the same series of steps.

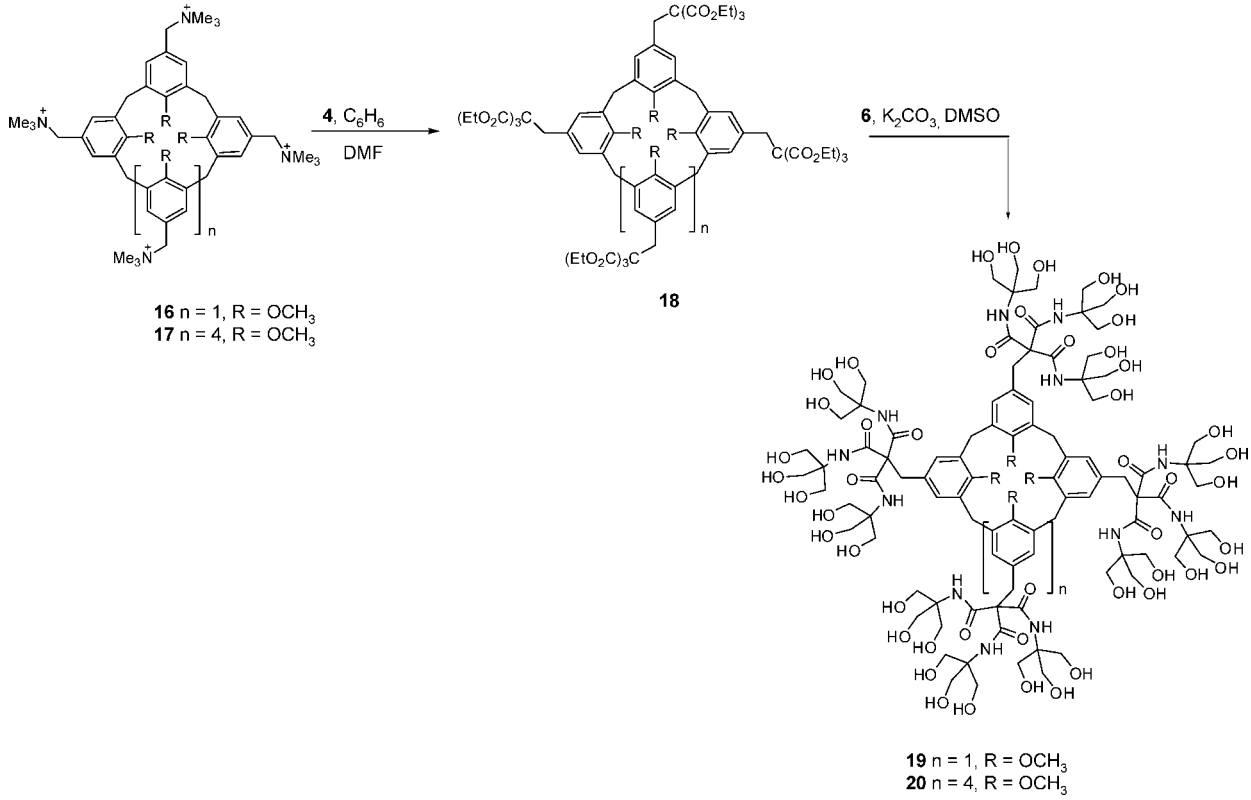
The simplest 1 → 3 branched monomer TRIS has been used for simple amidation in which it readily transforms esters to the corresponding amide by a facile two-step procedure, transesterification followed by rearrangement.[214] This ester triol transformation (K_2CO_3, DMSO, TRIS) has been demonstrated in the conversion of numerous initially nondendritic hydrophobic materials into more hydrophilic compounds: e.g., a neutral, cyclophanedodecaalcohol,[320] diverse (cyclo)alkyl[321] and benzene cores,[321,322] and lower rim polyhydroxylated calix[4]arenes.[323] Other nonionic TRIS-based polyols, useful as sugar macronutrient substrates in low-calorie food formulations, have been reported by Yalpani et al.[324]

Alvarez and Strumia[325] studied two protocols for obtaining hydrophilic acrylic acid−ethylene glycol dimethylacrylate matrices. One of the methods included CDI-based coupling with TRIS and copolymerization of hydrophilic monomers. The use of tris(hydroxymethyl) acrylamidomethane [THAM, CH_2═$CHCONHC(CH_2OH)_3$][326−328] or its protected acetonide ⟨CH_2═$CHCONHC[(CH_2O)_2CMe_2](CH_2OH)$⟩[329] has been shown[330] to lead to not only interesting surfactants but also to potential mini-dendronized polymers by protecting two of the three arms.

In 1985, application of this simple two-step dendritic construction to a polymer core, specifically chloromethyl-functionalized polystyrene, was reported.[331] Another example of the identical procedure was reported[332] except that they utilized another polymeric core backbone, derived from a functionalized vinyl ether monomer. These are very early examples of dendritic "comb" macromolecules.

Sugawara and Matsuda[333] developed TRIS-based cascades that were modified to include photoactive azide groups for attachment to polyethylene surfaces creating new hydrophilic surfaces; interestingly, these were early examples of one-component of today's "click" chemistry.[334−339] Prior to cascade amide formation, azide introduction was effected by reaction of *p*-azidobenzoyl chloride with the appropriate monoalcohol di- or triester extended ω-hydroxyalkyl derivatives of **6**, which with TRIS generated the desired polyol

Scheme 6. Silvanol Construction[316] on a Calixarene Plateau



dendron; subsequent reaction with the polyethylene (PE) surfaces was accomplished by UV radiation. PE surfaces that were so modified were found to be wettable with water. Biomolecular surface assemblies using branched as well as nonbranched alcohols for coating were shown to have "well-structured" molecular organization and high packing densities. This simple conversion of an ester to amide-triol has been utilized[340] to transform polyesters, for example, PAMAMs, to the arborol surface; such materials possess high water-solubility and unimolecular micellar properties.[206]

TRIS has been easily transformed into other interesting reagents. TRIS was N-protected (Boc_2O) to give (97%) $BocHNC(CH_2OH)_3$, then O-benzylation or O-allylation afforded (63−65%) $BocHNC(CH_2OBn)_3$ or $BocHNC(CH_2OCH_2CH{=}CH_2)_3$; last, deprotection (TFA) removed the Boc protecting group to quantitatively generate $H_2NC(CH_2OBn)_3$ and $H_2NC(CH_2OCH_2CH{=}CH_2)_3$, respectively.[323] The $H_2NC(CH_2O\text{-galactosyl})_3$ was developed by Lee[341] in his early studies of multivalency, and then this methodology was utilized by Stoddart et al. to generate different small three-directional dendrimers[342] as well as the larger 1 → 2 N-branched dendrimers coated with the related $H_2NC(CH_2O\text{-glycoside})_3$[343−349] or $H_2NC(CH_2O\text{-}\alpha\text{-D-mannopyranoside})_3$[350−352] dendrons; also see refs 138, 353−355 The TRIS (Boc-protected 5-aminolevulinic acid) has been similarly prepared and attached to three-directional cores.[356] The related $O{=}C{=}NC(CH_2O\text{-}\alpha\text{-D-mannopyranoside})_3$ has been prepared from the corresponding amino-dendron[350] and utilized in the attachment of these dendrons to other cores, for example, β-cyclodextrin.[357,358]

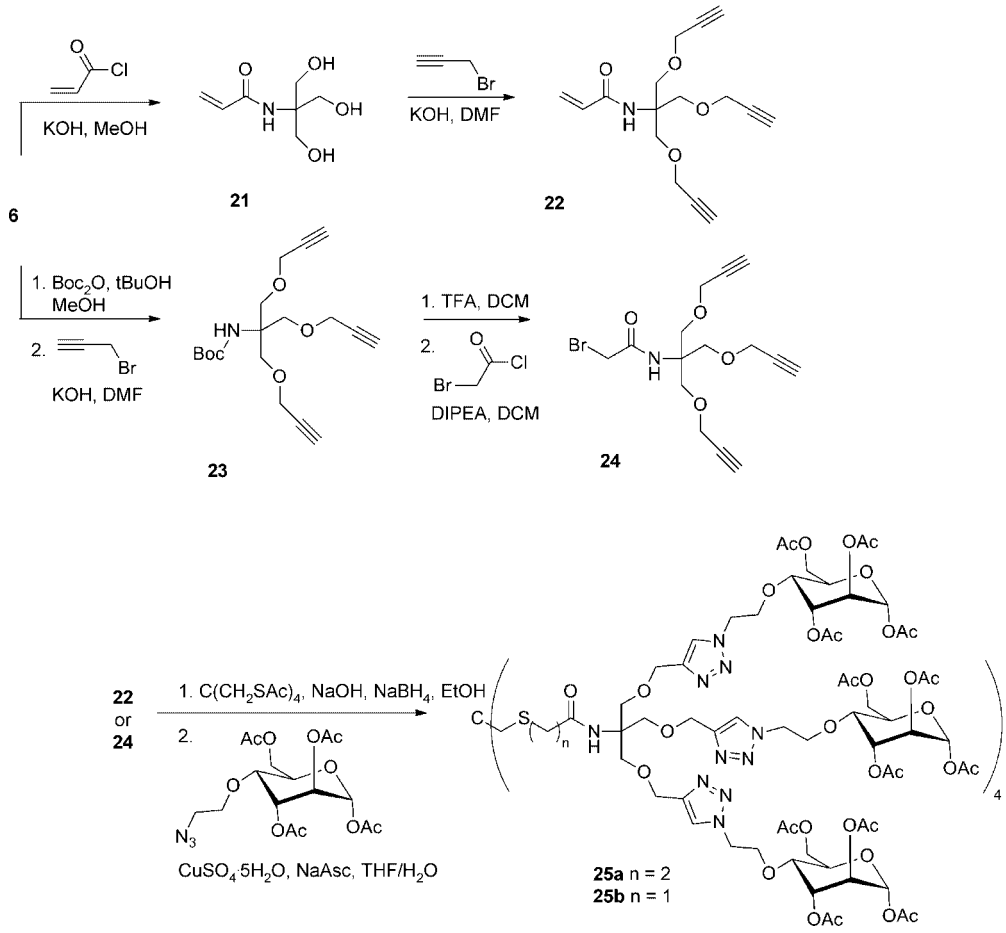
Recently, Roy et al.[359] constructed, via click couplings, a family of glycodendrimers using peripheral α-D-mannopyranoside moieties and TRIS derivatives bearing alkyne units (Scheme 7). TRIS (**6**) was treated with acroyl chloride in KOH and MeOH affording (89%) the triol **21**, which with 3-bromopropyne gave (75%) **22**. Similarly, after initially Boc-protecting (90%) the amino group on TRIS, triether formation (65%), deprotection, and acylation gave the α-bromoacetamide **24**. Reaction with the suitable polythiol core with azidoethyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside, using click conditions, gave the protected glycan, for example, **25**.

2.1.2. 1 → 3 (1 → 2) C-Branched, Amide (TRIS) Connectivity

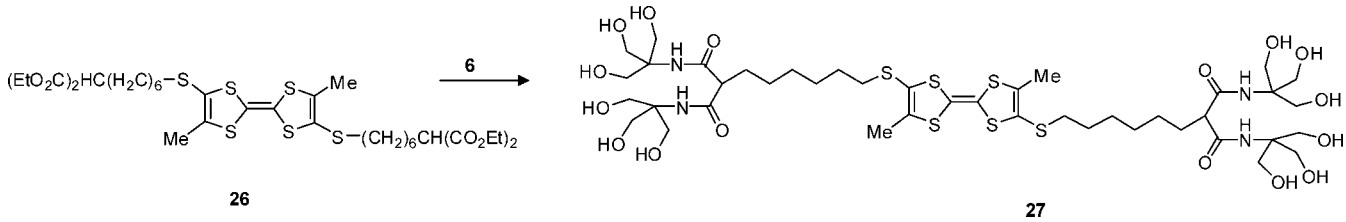
Although Newkome et al.[214] reported a series of two-directional arborols, this original process utilized a 1 → 3 C-branching motif; under more drastic amidation conditions, the triester, especially the methyl ester, readily decomposed to the 1 → 2 C-branched products identical to that derived from the monoalkylation of malonates. Subsequent treatment of the malonate esters with TRIS gave rise to the [6]-$(X)_n$-[6] arborol series (e.g., **12**; see Scheme 4).

Jørgensen et al.[247] utilized this molecular organization (dumbbell-like stacking) to incorporate TTF (a substrate currently of interest[360] in such areas as molecular electronics and organomagnetism) within the central lipophilic region (Scheme 8) of the self-assembled, supramolecular structures. A multistage synthesis was undertaken in which the derivatized TTF core **26** was assembled. Treatment of tetraester **26** with TRIS generated the desired TTF-bis-arborol (**27**). Calculations based on an orthogonal stacking with the TTF core possessing the *trans* conformation indicated that the diameter of the stack of molecules should be ca. 3.5 nm. Aggregates derived from dodecaol **27** clearly reveal (microscopy) thin string-like assemblages with lengths on the order of tens of micrometers and diameters on the order of ca. 100 nm. These structures are therefore superstructures derived from single strands, an observation analogous to that previously reported.[214,361]

Scheme 7. Glycodendrimer Scaffolds[359] Derived from Polyfunctionalized TRIS and Mannoside Derivatives



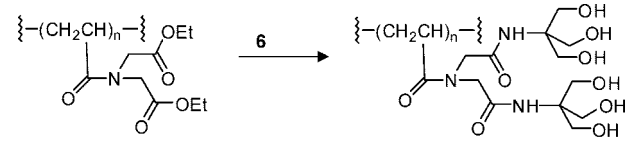
Scheme 8. Introduction of TTF into the Lipophilic Backbone of Two-Directional Arborols (27)[247] for the Construction of "Molecular Wires"



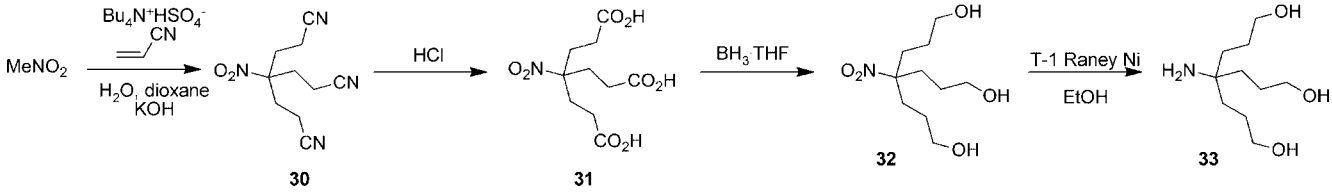
Relying on this procedure[214,361] to create a series of polyarborols, Saito et al.[362] prepared a series of hydroxylated poly(acrylamide)s. Initially, acryloyl chloride was treated with $HN(CH_2CO_2Et)_2$, then polymerized (AIBN) to yield the polyester **28** possessing a 1 → 2 N-branching exterior. Its subsequent treatment with TRIS then gave the desired 1 → 3 C-branched polyol **29** (Scheme 9). Based on surface tension data, the hydrophilicity of related series of polymers possessing mono-, tri-, and hexa-(CH_2OH) termini unexpectedly decreased as the number of hydroxyl groups per repeat unit increased. This was attributed to increased intramolecular H-bonding effectively reducing the number of OH moieties available for interaction at the aqueous interface. Matsuda and Sugawara[363] later applied a similar strategy (i.e., reaction of TRIS with either a di- or triester to afford the corresponding hexa- or nona-alcohol units) for the modification of a nonionic poly(vinyl ether). Li et al. used either *N*-tris(hydroxymethyl)methylacrylamide or 2-methacryloylamino-2-hydroxymethylpropan-1,3-diol, derived from the respective acyl chloride and TRIS;[364] these monomers were transformed into hyperbranched poly(ether amide)s and partially capped with *N*-isopropylacrylamide.

The interesting monomer $\langle BocHN(CH_2)_nCONHC[(CH_2)_3NHR]_2CO_2H\rangle$ ("bis-ornithine" scaffold) has been transformed into either linear or dendritic motifs, and these constructs were shown to be capable of transporting several cargoes at the same time permitting an increase of intracellular transport.[365]

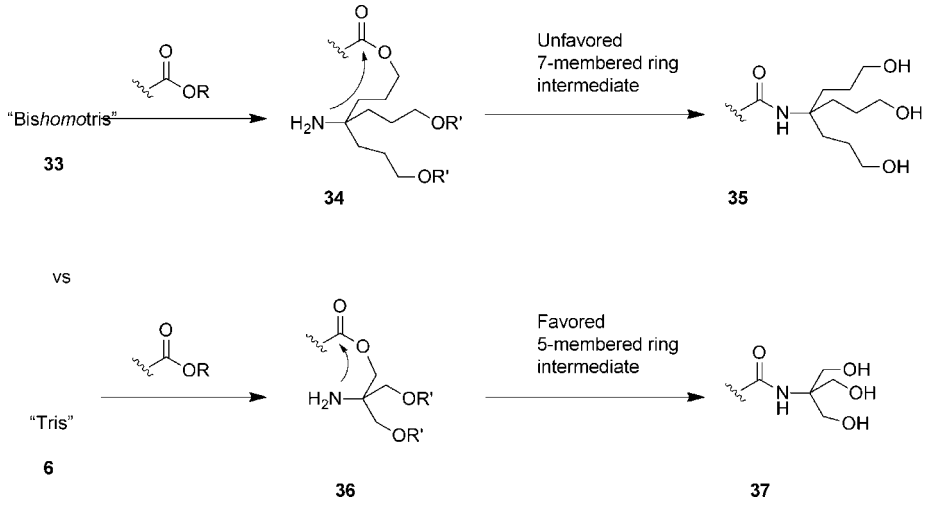
Scheme 9. Polyhydroxylation[362] of Polyacrylamide



Scheme 10. Synthesis of BishomoTRIS,[214] the Bishomologated Analog of TRIS



Scheme 11. Rationale for the Difficulties Encountered with the Amino Acylation of BishomoTRIS[214]



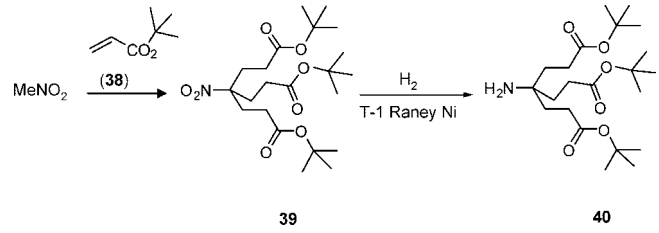
2.1.3. 1 → 3 C-Branched, Amide (BishomoTRIS) Connectivity

In order to circumvent the unfavorable S_N2-type substitution[366] adjacent to neopentyl positions that can prevent continued iteration using "triester−tris" methodology, a new monomer "bishomoTRIS" **33** was prepared (Scheme 10).[367−370] Reaction of nitromethane with acrylonitrile gave the trinitrile **30**, which was then hydrolyzed to the triacid **31** and reduced to the corresponding predendron **32**. Lastly, its heterogeneous reduction afforded the desired colorless crystalline amine **33**, whose single-crystal X-ray structure was determined.[371] The use of bishomoTRIS (**33**) to replace TRIS (**6**) in the original alkylation−amidation sequence gave rise to transesterification products. The absence of the desired amide product suggested that the facile intramolecular rearrangement, when using TRIS, proceeded via a five-membered intermediate ester **36** to give amide **37** (Scheme 11). It was therefore postulated[214] that an unfavorable seven-membered transition state (**34**) precluded amide formation when bishomoTRIS was employed. Treatment of this intermediate ester **34** with base (KOH) in DMSO forced amidation, however, in extremely poor (<10%) yields.

Whitesell and Chang[372] reported the preparation of $H_2NC(CH_2CH_2CH_2SH)_3$ from bishomoTRIS in a four-step procedure. This aminotrithiol was used to directionally align helical peptide polymerization on gold and ITO glass surfaces. Unidirectional alignment of macromolecules and their polarizability are of interest in the area of supramolecular chemistry and molecular electronic devices.[373] Hence, dendritic branching combined with "anchoring" units (e.g., sulfur affinity for gold) are logical choices to assist in noncovalent as well as covalent molecular organization.

von Kiedrowski et al.[374] described the synthesis of trigonal "trisoligonucleotidyls" based on a solid-phase phosphoramidite protocol in which the desired branching was incorporated using the bishomoTRIS monomer. Bimolecular complexes of these tripodal DNA constructs were described as forming nanoscale acetylene and cyclobutadiene architectures by self-assembly.

Scheme 12. Two-Step Construction[377] of an Aminotriester Monomer 40

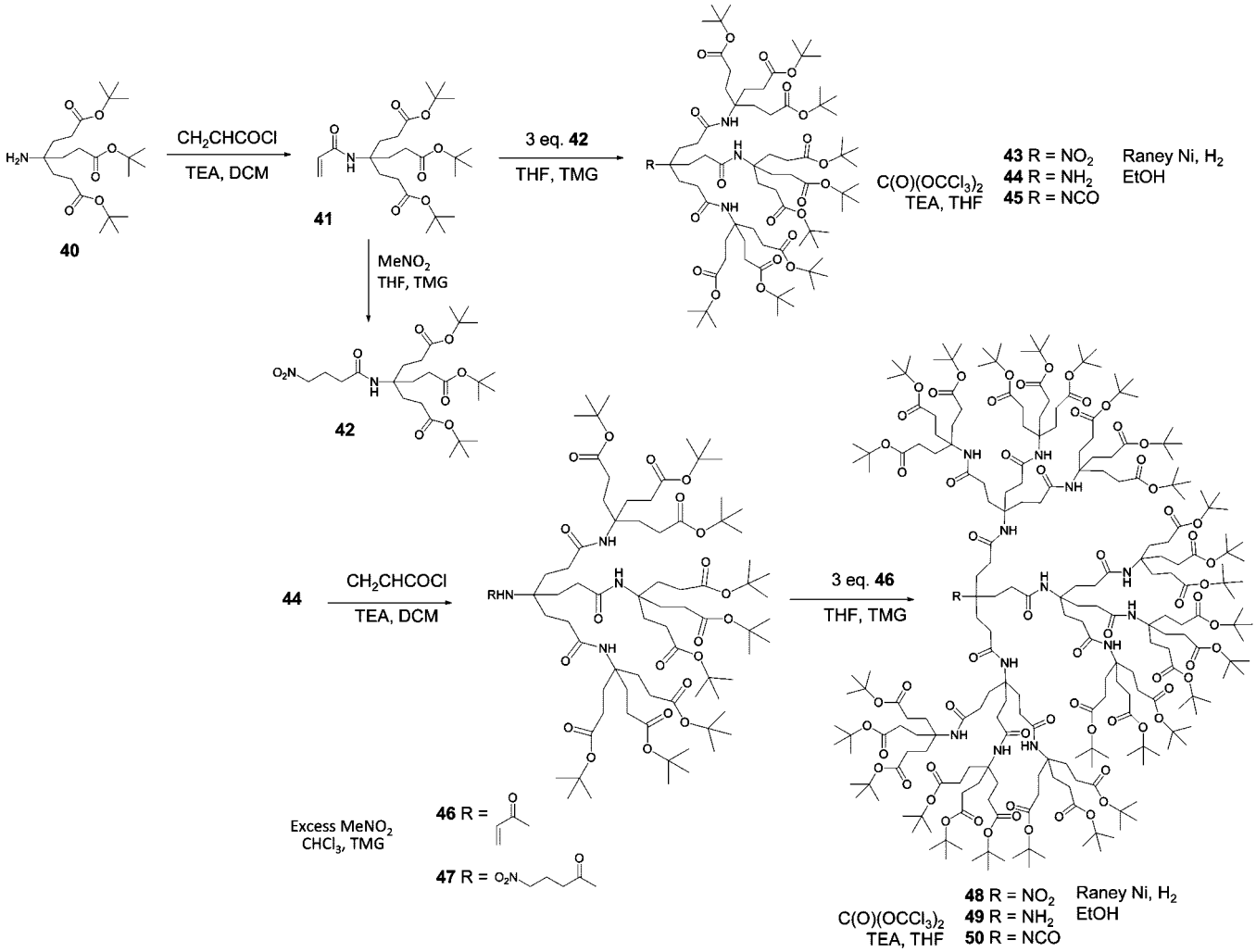


Nishimura et al.[179,375,376] utilized the predendron $O_2NC[(CH_2)_3OH]_3$ to react with the oxazoline of *N*-acetyllactosamine octaacetate giving (75%) the nitro[tris[propyl-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside]]methane, which was reduced to the corresponding amine dendron and last amidated with acryloyl chloride. The olefinic dendron underwent radical copolymerization with acrylamide affording a water-soluble clustered glycopolymers.[375]

2.1.4. 1 → 3 C-Branched, Amide Connectivity (via Behera's Amine)

Addition of the anion of $MeNO_2$ to α,β-unsaturated carbonyls and nitriles, followed by reduction of the nitro group to an amine (Scheme 12), provided the basis for the synthesis[377] of amine **40**. Thus, treatment of $MeNO_2$ with *tert*-butyl acrylate (**38**) in the presence of base (Michael reaction;[378] Triton-B) gave (ca. 80−95%) di-*tert*-butyl 4-[2-(*tert*-butoxycarbonyl)ethyl]-4-nitroheptanedioate (**39**) via modification of a literature procedure.[217] Catalytic reduction[379] of this predendron **39** quantitatively afforded the desired amine **40**[380] (named "Behera's amine", after a colleague who successfully prepared it for the first time). Uniquely, during

Scheme 13. A Simple Convergent Synthesis[389] of the Family of Amine and Isocyanate Dendrons



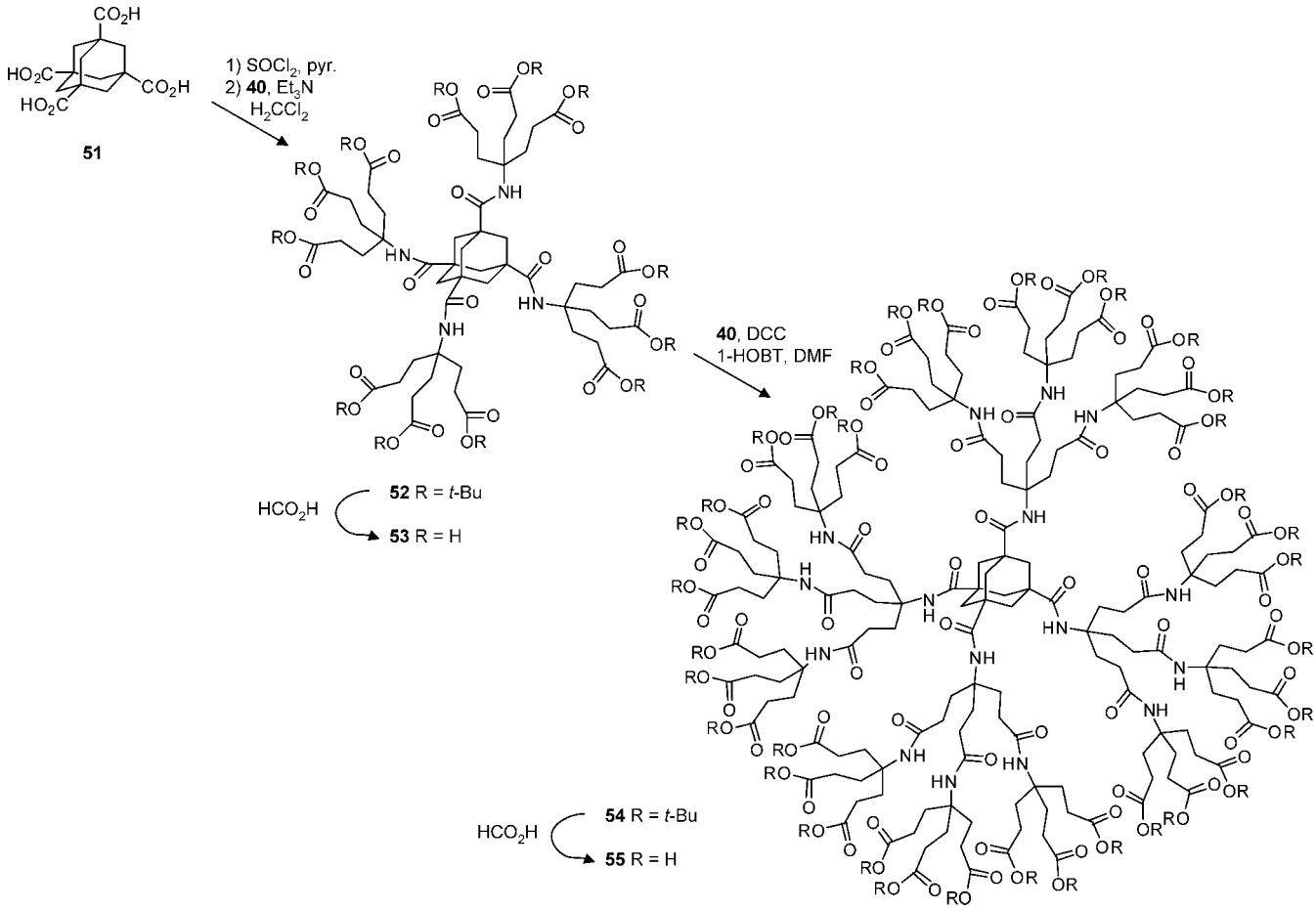
the hydrogenation step, this monomer does not undergo the normal facile formation of the intramolecular lactam that is the predominant course in the other related but lesser branched esters;[381] however, this cyclization does slowly occur at elevated temperatures (>60 °C). Although the original catalytic reduction with Raney nickel was conducted in EtOH,[217] when *n*-heptane was used, the yields improved to 98% and the melting point increased.[382] The X-ray structure of the intermediate predendron **39** confirms the extended conformation with 15 of the 16 torsion angles in the antiorientation (mean value of 176.6°).[383]

A divergent approach to the larger G2 and G3 amine dendrons (**44** and **49**, respectively) was also accomplished.[384] Treatment of **40** with triphosgene generated the related isocyanate,[385,386] and the related G2 and G3 dendrons (**45** and **50**, respectively) were similarly formed from the corresponding dendrons (Scheme 13).[387] Brettreich and Hirsch developed a convergent procedure,[388] which utilized $O_2NC(CH_2CH_2CO_2H)_3$ from the hydrolysis of **39** followed by standard amidation (HOBT and DCC) and reduction using Raney nickel to generate the related G2 and G3 dendrons.

An alternate route[389] to this family of amino as well as isocyanate dendrons has been accomplished in which amine **40** was treated with acryloyl chloride to give (96%) the activated monomer **41**, which with $MeNO_2$ formed (93%) **42**. When 3 equiv of **41** was treated with **42**, the G2 predendron **43** was obtained (91%); it was then reduced (>95%) to the G2 amine **44**, which with triphosgene generated (70%) the corresponding isocyanate **45**. This simple procedure was repeated starting with the G2 amine affording (93%) initially **46**, then **47** (88%), which was treated with its precursor **46** to afford (70%) the G3 predendron **48**, followed by reduction (73%) to the G3 amine **49** and last its conversion (57%) to the G3 isocyanate **50**. The advantage of this family of isocyanates is their stability, selective reaction with primary substituents, and ease of formation.

The G1 amine monomer **40** and its larger G2 and G3 dendrons have been successfully attached to diverse core molecules, for example, from $C_{60}[C(CO_2(CH_2)_3CO_2H)_2]_n$,[156,390−402] $C_{60}[CR(CO_2(CH_2)_3CO_2H)_1]_n$,[156,393,397,399,400,403−410] C_{60} *e*,*e*,*e*-trisadducts[411] and hexakisadducts,[412] dendronized metalloporphyrin−C_{60} conjugates,[413] (carboxymethyl)cellulose,[414−417] glucuronic acid,[418] ferrocenecarboxylic acid,[419−422] metallophthalocyanines,[423] ferrocene di(carboxylic acid),[419] cobaltocenium carboxylic acid,[424] 6-methylcytosine,[425] 3,5-dibromobenzoic acid,[426] 5-⟨1,3[bis(2,2′:6′,2″-terpyridin-4′-ylethynyl)]benzene⟩,[426] 5,5′-di(alkoxymethyl)-2,2′:6′,2″-terpyridine,[427] 4,4′-dicarboxamido-2,2′-biquinoline,[428] 2,4,6-trichlorotriazine with C1-ferrocene, C3-Fréchet dendron, and C5-dendron,[429] long-chain fatty acids affording topical microbicides with anti-HIV, anti-STD pathogens, antibacterial, and antifungal activity,[430−435] synthetic phage mimics for high-affinity peptide-based collagen targeting,[436] 4,4′-bipyridine[*N*-$(CH_2)_5CO_2H$; *N*′-R],[437−440] 4,4′-bipyridine[*N*-$(CH_2)_5CO_2H$; *N*′-Fréchet G1 or G2 dendron],[441] PEG(dicar-

Scheme 14. Construction of Dendrimers Using the Tetravalent Adamantane-Core Tetracarboxylic Acid[217,218]



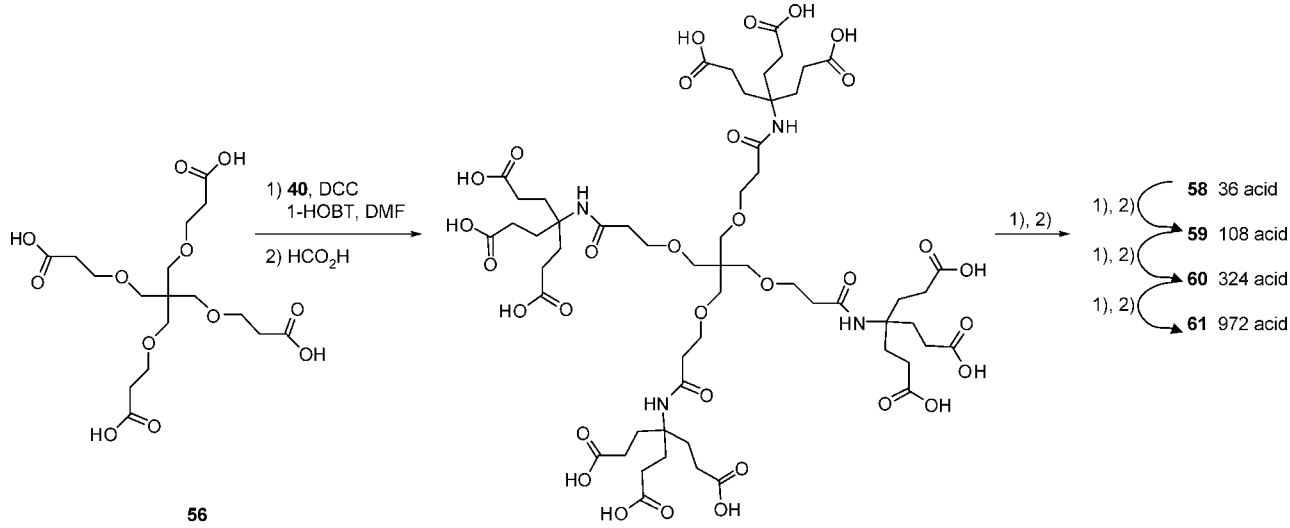
boxylic acids),[156,442,443] terephthalates affording two-directional amphiphilic materials,[382] 5-nitroisophthalic acid chloride,[444−446] oxidized single wall carbon nanotubes [(ClCO)$_n$SWNT],[447] *N*-*Z*-glycine,[448] calixarene[NHCOCH$_2$CO$_2$H]$_2$,[396,449,450] perylenetetracarboxdiimide ("perylene bisimide") [*N*- and *N*,*N*′-(CH$_2$)$_5$CO-],[298,299,451,452] 4-(1-pyrenyl)butyric acid,[453−456] dansyl chloride,[457] 6-(4-methoxyphenoxy)hexanoic acid,[440] 5α-cholestan-3-amines and 5α-cholestan-3-yl aminoethanoates,[458] metalloporphyrin,[401] and trimesic acid core and coated with 3-hydroxypyridin-4-one for iron chelation.[459] Meijer et al. have utilized the series of AB$_2$, AB$_3$, AB$_4$, and AB$_5$, based on a combination of **40** and H$_2$NCMe(CH$_2$CH$_2$CO$_2$CMe$_3$)$_2$[460] monomers, to prepare asymmetric polyamide dendrons possessing N-terminal cysteine residues at the periphery that were functionalized with C-terminal thioester peptides.[461] A novel series of sterically hindered *cis*-platinum complexes have been prepared[462] from *cis*-PtL$_2$ and H$_2$NC(CH$_2$CH$_2$CO$_2$CMe$_3$)$_3$ affording *cis*-Pt[H$_2$NC(CH$_2$CH$_2$CO$_2$CMe$_3$)$_3$]$_2$, which can be deprotected (HCO$_2$H) to give the corresponding water-soluble complex that does not bind to DNA!

To add diversity to the attachment of this dendron family, the related G1 isocyanate monomer as well as the related larger dendrons G2 **45** and G3 **50** have been successfully reacted with amines creating urea connectivity, for example, 3-(triethoxysilyl)propylamine[463,464] and 3-[3,5-di(terpyridinyl)phenoxy]propylamine, and with alcohols affording carbamate connectivity, for example, cellulose[465,466] and MeO−PEG−OH.[467]

The use of amine **40** with different cores has demonstrated its utility (Scheme 14) in divergent dendritic construction. Thus, when 1,3,5,7-tetrakis(chlorocarbonyl)adamantane,[468] prepared (SOCl$_2$, 100%) from the corresponding tetraacid **51**[218] or in one step (20−30%) from 1-adamantanecarboxylic acid with oxalyl chloride under photolysis conditions,[469] was treated with aminotriester **40**,[217] the pure solid dodecaester **52** was isolated (61%). The hydrolysis (HCO$_2$H) of the ester groups yielded (94%) the corresponding acid **53**. Amidation using peptide coupling conditions[470,471] of dodecaacid **53** with a slight excess of amine **40** in purified DMF[472,473] afforded (58%) the microcrystalline G2 36-ester **54**, which when treated with formic acid gave (96%) 36-cascade: tricyclo[3.3.1.1^{3,7}]decane[4−1,3,5,7]:(3-oxo-2-azapropylidyne):(3-oxo-2-azapentylidyne):propanoic acid (**55**).

Newkome et al.[474,475] reported the use of Behera's amine **40** in the synthesis of the G1-(**57**) to G5-(**61**) polyamido dendritic series by an iterative, divergent procedure (Scheme 15), based on the ethereal tetraacid[476] **56**, constructed via Bruson's method,[477] by an exhaustive 1,4-addition of acrylonitrile to pentaerythritol, followed by hydrolysis. The crystalline Michael addition intermediate, 5,5-bis(4-cyano-2-oxabutyl)-1,9-dicyano-3,7-dioxanonane, was supported by its X-ray crystal structure.[478] Repetition of the amidation (DCC coupling)[470]−deprotection (HCO$_2$H) sequence generated the G5 dendrimers with purported molecular weights of 165 909 amu for the 972-ester and 111 373 amu for the 972-cascade:methane[4]:(3-oxo-6-oxa-2-azaheptylidene):(3-oxo-2-azapentylidyne):^{4}propanoic acid (**61**). Structural support for these amide-based dendrimers included typical spectroscopy procedures as well as DOSY NMR,[479] whereby diffusion coefficients were ascertained via pulse field gradient NMR for each generation of the water-soluble polycarboxylic

Scheme 15. Iterative Procedure[474] for the Preparation of Dendrimers with Flexible Pentaerythritol-Based Cores



56

57

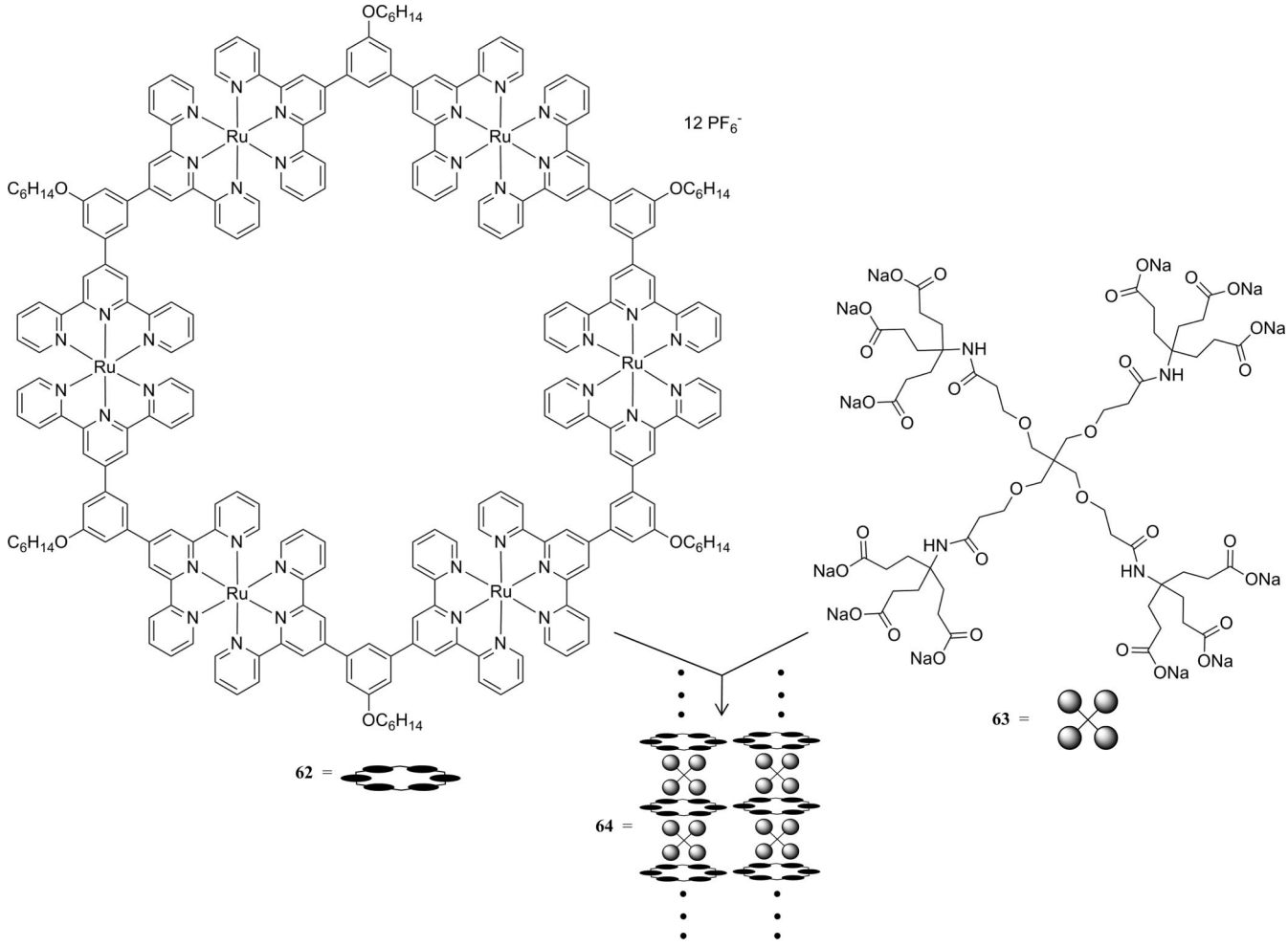
acid dendrimers. Both the G2 (**58**) and G3 (**59**) polyesters have been made by a convergent approach using the G2 and G3 dendrons[387] with core **56**; the larger dendrimers in this series are not monomolecular in character, as has been noted for other divergently generated dendrimers.

Application of the Stokes−Einstein equation gave dendritic hydrodynamic radii (tabulated at acid, neutral, and basic pHs) that correlated well with those obtained via SEC measurements and computer generated molecular modeling.[474] At different solution pH values, the hydrodynamic radii change in this acid-terminated series, which is noteworthy; in general, the size of the G3 acid **59** increased 35% from pH 3.64 to pH 7.04 corresponding to a 264% increase in overall dendritic volume. Similar results have been obtained by others[480] in the 1 → 2 N-branched PAMAM series. Monnig et al.[481] extended these experiments to estimate analyte−dendrimer/solvent distribution coefficients (*K*) and capacity factors. Thermodynamic parameters (i.e., *H*, *S*, *G*) pertaining to analyte solubilization within this dendritic series were obtained via examination of *K* with respect to temperature. Capacity factors were shown to increase linearly as a function of increasing dendrimer concentration. It was also determined that as the dendritic polyacid's size increased, entropy became the dominant force in analyte solubilization. This dendritic macromolecule series (**57**−**60**) was examined[482] as potential micellar substitutes in electrokinetic capillary chromatography[483] employing aqueous mobile phase conditions; separation of a series of alkyl parabens using these dendrimers yielded significantly enhanced efficiency and resolution compared with traditional methods using surfactants, such as SDS. Also, molecular relaxation studies have demonstrated that the G1 *tert*-butyl ester-terminated dendrimer possessed rheological properties similar to those of large polymers.[484]

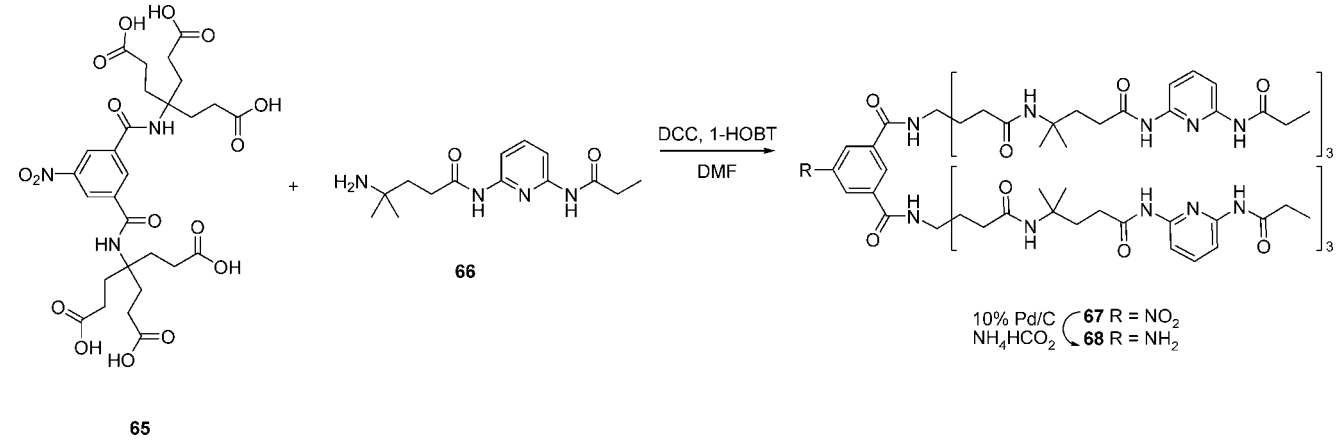
Dubin et al.[485] studied the dissociation of Newkome's carboxylic acid terminated dendrimers[474] via potentiometric titration. Theoretical surface potentials, obtained via the nonlinearized Poisson−Boltzmann equation, were found to be larger than those determined by experiment for the G2−4 levels in NaCl. This was rationalized by a counterion binding effect. The observation of even larger surface potentials upon changing the counterion to Me_4N^+, supported the explanation. Dubin et al.[486] further used capillary electrophoresis to examine counterion-binding effects on the mobility of these carboxylate-terminated polyamides. Titration studies showed that the effective surface charge density of the G5 dendrimer was lower than the geometric surface charge density; counterion binding was attributed to this effect. The applied electric field on the mobility of these carboxyl-terminated dendrimers was measured by capillary electrophoresis at applied voltages varying from 5 to 30 kV; at high velocities *V*, these dendrimers were outstripped of their ion atmospheres at high *V*, whereas at low ionic strength, the increase in the size of the ion atmosphere led to increased frictional drag with increasing field strength.[487] Small-angle neutron scattering was used to evaluate the solution behavior of these G3 and G5 carboxylic acid-terminated dendrimers as a function of dendrimer concentration, pH, and ionic strength;[488] these results of contrast matching measurements indicated an accumulation of an excess concentration of surface [Me_4N^+] counterions and that the thickness of these counterions was between 4 and 6 Å, which is consistent with related studies.[485,486] The linear unnatural amines and carboxylic acids, based on amide connectivity and possessing identical repeat units to that of the four-directional dendrimers, were prepared and compared;[489] unexpected insoluble behavior of the linear series even at low molecular weight was observed, which is in stark contrast to the related dendrimers, suggesting a high degree of intra- and intermolecular H-bonding for the linear series.

The facile hydrolysis (HCO_2H) of the terminal *tert*-butyl groups generated the corresponding poly(carboxylic acid), which with KOH or NaOH gave the related polycarboxylate. These polyanions have very interesting properties in that they can displace mono- and dianionic counterions, in essence a dense packed polyanion.[490] Thus, to demonstrate this property, a rigid hexameric metallomacrocycle [$(\mathbf{62})^{+12}(PF_6^-)_{12}$] was prepared;[491,492] treatment of this dodecacationic complex with the dodecaanionic G1 dendrimer[474] [$(\mathbf{63})^{-12}(Na^+)_{12}$] generated initially the neutral, sphere-like motif [$(\mathbf{62})^{+12}(\mathbf{63})^{-12}$] (**64**) (Scheme 16), which rapidly self-assembled to generate nanofibers. The use of the related larger G3 dendrimer[474] afforded a series of megamers, since there is insufficient surface space to accommodate nine of these hexametallic macrocycles. These polyanionic dense-packed counterions

Scheme 16. The Formation of Dendrimer−Metallomacrocycle Composites[490]



Scheme 17. The Use of Behera's Amine in the Synthesis of a Hexafunctionalized Dendron[493]

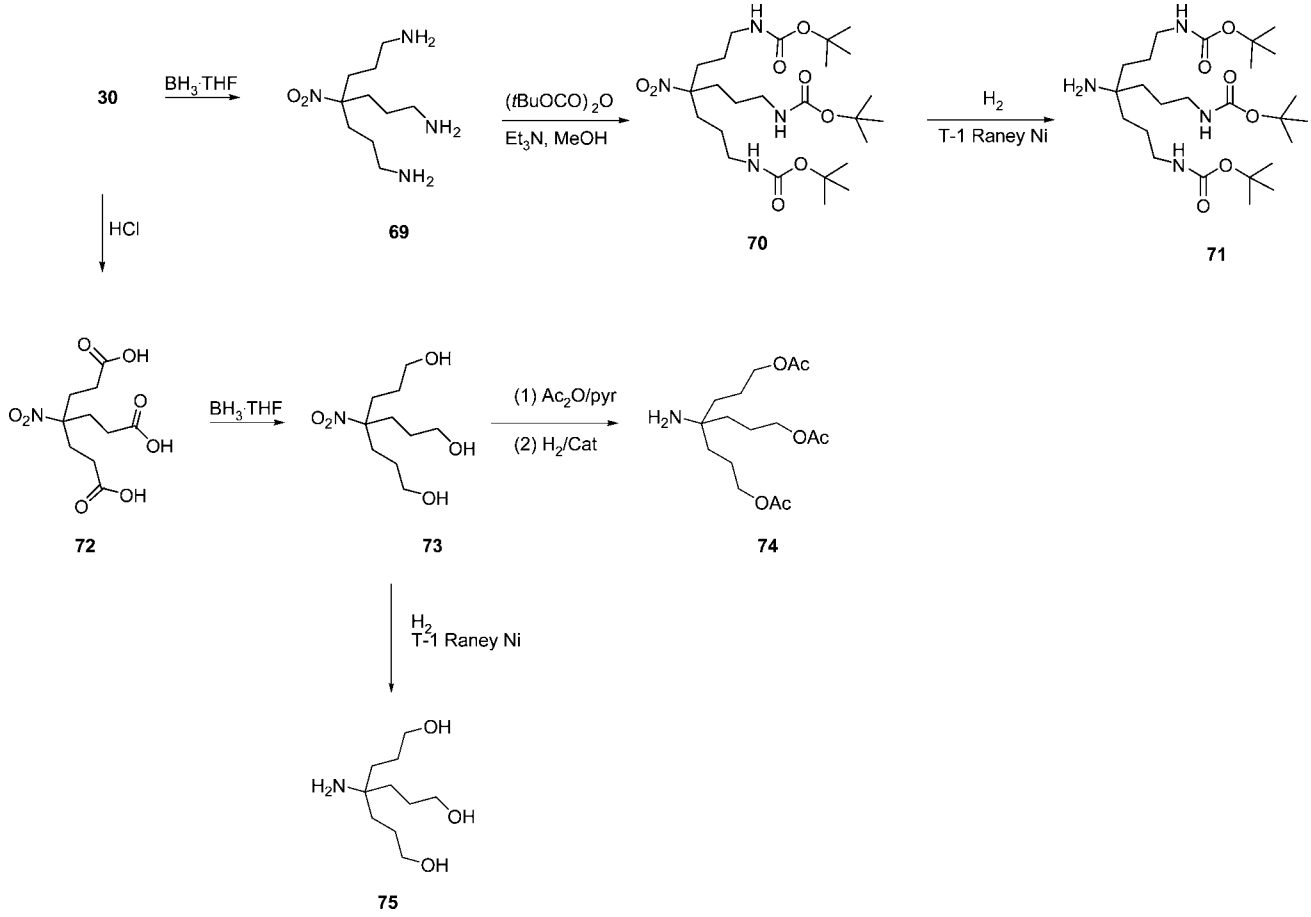


can lead to ion pair superstructures in which the randomness of singly charged counterions is eliminated.

Strumia et al.[493] have used Behera's amine for the surface modification of activated polymeric matrices with 2,6-bis(acylamino)pyridine units that are capable of molecular recognition. The treatment of 5-nitroisophthalic acid with **40**, followed by hydrolysis, gave **65**, which with **66** generated the hexafunctionalized predendron **67**, which can be reduced with ammonium formate in the presence of a Pd catalyst to the desired **68** (Scheme 17). The use of these modified beads in affinity chromatography was described.

The related neutral (alcohol, acetate, carbamate) and basic (primary amine) termini for this G1−3 series were constructed so that comparisons of the surface moieties on a totally comparable inner core could be made;[475] in conclusion, the use of dendrimers as size standards must be carefully controlled due to the pronounced pH dependence of their hydrodynamic radii. These polyamide cascades were prepared by coupling the appropriate polyacid with either the aminotris(*tert*-butyl carbamate) **70** or aminotris(acetate) **74** monomers (Scheme 18). Trinitrile **30**, prepared from $MeNO_2$ and a slight excess of CH_2═CHCN under basic

Scheme 18. Preparation of Monomers[475] for the Modular Introduction of Terminal Amines and Alcohols



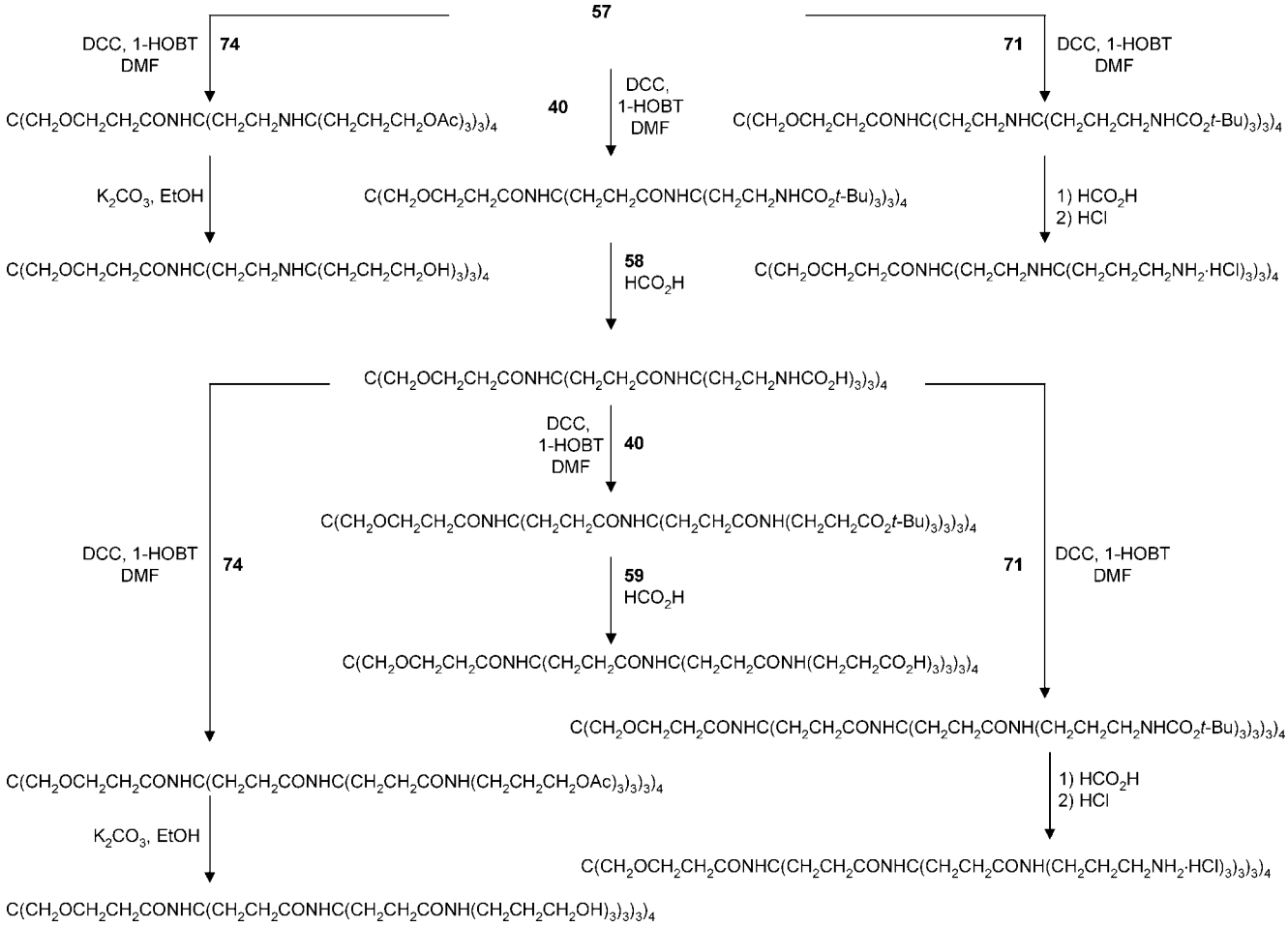
conditions, was reduced with borane to give (~100%) the triamine **69**, which upon treatment with di-*tert*-butyl dicarbonate[494,495] gave the tricarbamate **70**, followed by catalytic reduction with T-1 Raney nickel,[496] afforded the desired amino dendron **71** in excellent overall yield. The precursor to bishomoTRIS (**75**, Scheme 18) was prepared via hydrolysis of trinitrile **30** to give the triacid **72**, which was subsequently reduced (BH_3-THF) to generate (95%) the triol **73**, which was either acylated (Ac_2O) affording triacetate **74** or benzylated ($C_6H_5CH_2Cl$) to create the trisether in overall high yield. The treatment of triol **75** with $SOCl_2$ gave (84%) the corresponding trichloride ammonium salt, which with base readily cyclized to give (74%) 1-azoniatricyclo-[3.3.3.0]undecane chloride.

Miller et al.[497] terminally modified the polyacid (G2; 36 acid groups) with oligothiophenes and examined their "vapoconductivity. Unlike the PAMAM counterparts,[498,499] which possess internal tertiary amines capable of undergoing facile oxidations, these materials, based on Behera's amine, are stable to oxidation conditions. Cast films of the polyoligothiophenes were oxidized with I_2 vapor to give electron conductivities of $\sigma = 10^{-3}$ s/cm. Exposure to organic vapors dramatically enhanced the conductivity of the films. For example, acetone vapor showed an 800-fold conductivity increase over unsaturated materials.

The modular syntheses[475] of the three related cascade families from the corresponding polyacids and the appropriately designed monomer are shown in Scheme 19. In each case, building block coupling utilized standard DCC[500]/DMF/1-HOBT[501] peptide coupling conditions. Removal (HCO_2H) of the protecting *tert*-butyl groups afforded the corresponding polyacids or polyamines; transesterification (K_2CO_3, EtOH) of the acetate-coated cascades liberated the hydroxy-terminated dendrimers.

Newkome et al.[502] employed their 1 → 3 modular monomers for the construction of tailored infrastructures possessing internal site(s) for molecular recognition. Formation of the desired three-component monomer, prepared by a high-dilution procedure (Scheme 20), was accomplished by reaction of (1 equiv) Behera's amine **40** with glutaryl dichloride (**76**), followed by reaction with excess 2,6-diaminopyridine (**77**) in a single-pot reaction to afford the extended aminotriester **78**. Treatment of the free 6-aminopyridino focal group with the ethereal tetraacyl chloride **79**, derived from **56**,[476] gave the G1 dendrimer **80**, which was divergently expanded by the above amidation−hydrolysis sequence using excess **78**. This series of dendrimers exhibited excellent internal H-bonding-based molecular recognition of guests possessing imide functionality (e.g., **81**).[503] The ^{1}H NMR titration experiments revealed consistent, albeit small (0.5 to 0.7 ppm), downfield shifts of the pertinent amide protons using glutarimide, as the molecular guest. Hyperfine-shifted ^{1}H NMR signals of the Co(II) complexes of these dendrimers possessing internal 2,6-diamidopyridine moieties have been fully assigned by means of 1D and 2D NMR techniques, including NoE differences, EXSY, COSY, and TOCSY.[504] The cancer therapeutic drug AZT was also used as a molecular guest to demonstrate the utility of site-specific incorporation of H-bonding receptors. The construction of related linear and convergent wedges possessing 2,6-di(acylamino)pyridine subunits, capable of molecular recognition, has also been reported;[493] these moieties were attached to an activated agarose matrix by surface modification, then evaluated for the formation of H-bonded complexes. Halabi

Scheme 19. Synthesis of a Complementary Series of Hydroxy-, Amino-, and Carboxy-Terminated Dendrimers[475]

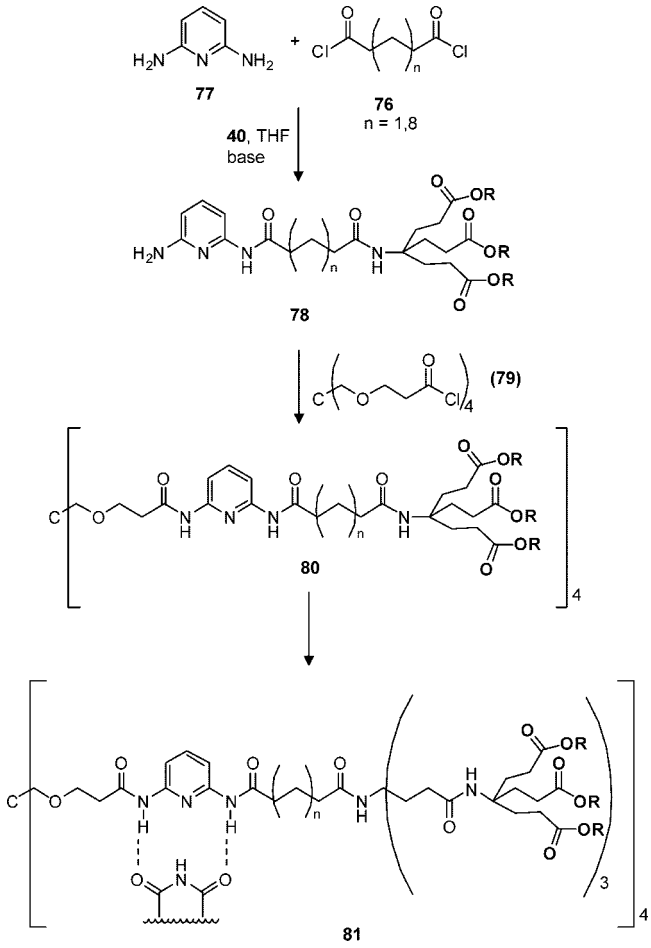


and Strumia also reported the use of $C(CH_2OCH_2CH_2CO_2H)_4$ with $H_2NC[(CH_2O)_2CMe_2]CH_2OH$ to give a mixture having both ester and amide connectivity; the product mixture was treated with acryloyl chloride to give the final desired product mixture.[505,506] In order to detect any residual acid termini, the treatment of the product with 9-anthryldiazomethane afforded insight into the number of residual carboxylic acid termini after incomplete tier growth;[507] this also gave entrée into combinatorial products. Thus, the construction of **78** was conducted with insufficient quantities of Behera's amine giving rise to imperfect dendritic products with residual internal acid moieties. Qualitative analysis of structural integrity could be easily accessed, and the potential to internally functionalize the slightly imperfect dendrimer was envisioned.

By using application-oriented monomers, Newkome et al.[508−510] created anthraquinone-based,[508] redox-active dendrimers (Scheme 21). Synthesis of the functionalized monomers was achieved via a three-component, single-pot reaction using glutaryl dichloride (**76**), amine **40**, and 1,4-diaminoanthraquinone (**82**) to give the homologated aminotriester **83**. Connection of amine **83** to the flexible core **79** generated the G1 ester **84** that was subsequently transformed (HCO_2H) to the corresponding acid and reacted with excess amine **40** affording the G2 36-ester **85**; divergent growth generated the higher generations. Progressive steric congestion of the redox centers was shown, via cyclic voltammetry, to retard electron transfer kinetics as well as to result in irreversible electrochemistry. Similar incorporation of 1,4- or 1,5-dianthraquinone-based constructs as well as the use of a rigid adamantane core was intended to separate the redox centers.[511] The use of more rigid spacer units between branching centers and the redox sites via the use of aryl diacyl chlorides has also been examined, along with the attendant electrochemistry.[512] The electrochemical comparison of these anthraquinoid architectures has been reported.[510] The incorporation of *N*,*N*′-bis(3-aminopropyl)piperazine (**86**) was accomplished by its treatment with **76** and Behera's amine to generate the 1:1:1 (20%; **87**) and the two-directional 1:2:2 (**88**) dendrimers (Scheme 22). Reaction of the functionalized dendron **87** with the tetraacid chloride **79** gave the appropriate four-directional dendrimer **89**, which was transformed to the G2 product by hydrolysis, and subsequent treatment with excess Behera's amine.[513] These dendrimers upon treatment with Cu(II) afforded a simple route to metallodendrimers via the metal complexation at the donor centers. Numerous other recognition sites have been incorporated via this simple two-step procedure, such as 3,3′- and 5,5′-(2,2′-dipyridino) subunits.[514,515]

Diederich et al.[516] assembled a series of homo- and heteroleptic Ru(II) complexes based on 2,2′:6′,2″-terpyridine (**90**) possessing either hydrophilic or hydrophobic 4′-functionalized dendrons **91**. Scheme 23 shows the generalized assembly process utilizing a dendronized alkyne with the 3,5-dihalo starting ligand via a Sonogashira cross-coupling procedure.[517−519] Interestingly, the complexes failed to form when the G2 dendrons were employed; in view of the distant locations of these dendrons relative to the site of complexation, this seems unusual; however, the solubility of the R-tpyRuCl$_3$ is critical to the assembly process.

Scheme 20. Site-Specific Molecular Recognition[502] within the Dendritic Superstructure



Dendrimers with PEG-extended interiors have been produced (Scheme 24) by the use of $N_3CH_2CH_2O(CH_2CH_2O)_2CH_2CO_2H$ (**94**) as the connector moiety, which was prepared in four steps from tri(ethylene glycol). The amidation of amine **40** with **94** extended the focal substituent **95**; then either reduction of the N_3 to the terminal amine **96** or hydrolysis to the corresponding triacid **97** afforded access to the desired building blocks. Combination of these components gave the larger dendritic wedges (**100**, **102**) that were ultimately connected to the four-directional core **79** affording the PEG-extended dendrimers (**103**, **104**, **105**); after construction and extensive *in vacuo* drying to remove that encapsulated water, addition of lithium triflate to a $CHCl_3$ solution of these dendrimer resulted in dissolution of the triflate, which is notably insoluble in dry $CHCl_3$. Pulsed gradient NMR techniques have been used to study the self-diffusion of these PEG-extended dendrimers possessing carboxylic acid termini in aqueous solutions of neutral PVA and of cationic PAAm; the ionic binding of the diffusants with PAAm is stronger than their H-bonding with PVA.[520,521]

Rockendorf and Lindhorst[418] reported the treatment of tetraacetylglucuronic acid (**106**) and glycosyl azide (**107**) with amine **40** to give the dendronized azide **108** (**a**, 53%; **b**, 79%), which was reacted with *N*-Fmoc-β-alanine affording (68%) the amide-extended protected amine **109** (Scheme 25). Selective deprotection (79%) of the *tert*-butyl groups gave the triacid **110**, which was treated with 2-aminoethylmannoside[523] to generate the anticipated glycopeptides **111**.

The synthesis of dendrons based on amine **40** possessing a PEG-extended glycol surface has been reported,[448] in which **40** is N-protected with *N*-*Z*-glycine in 86% yield, de-esterified (92%), and subsequently extended (ca. 70%) with either 2-aminoethoxy- or 2-aminoethoxyethoxy-*O*-α-peracetyl-D-mannose.[524−526] The *N*-$C_6H_5CH_2OCO-$ group was removed (80−90%) to give the expected dendrons, which were subsequently attached to 5-(4′-carboxyphenyl)-10,15,20-triphenylporphyrin (**115**), and last O-deacetylation[527] afforded a good overall yield of the glycodendritic porphyrins (**116**, **117**; Scheme 26).

A trisuccin hydrazide derivative was synthesized in three-steps from $HO_2CCH_2CH_2(O=)CNHC(CH_2CH_2CONHOBn)_3$ by sequential treatment with $BocNHNH_2$ (1-HOBT, DCC), reduction (H_2, Pd/C), and last deprotection (TFA, thioanisole, $HSCH_2CH_2SH$, anisole) to give $H_2NHN(O=)CCH_2CH_2(O=)CNHC(CH_2CH_2CONHOH)_3 \cdot TFA$.[528]

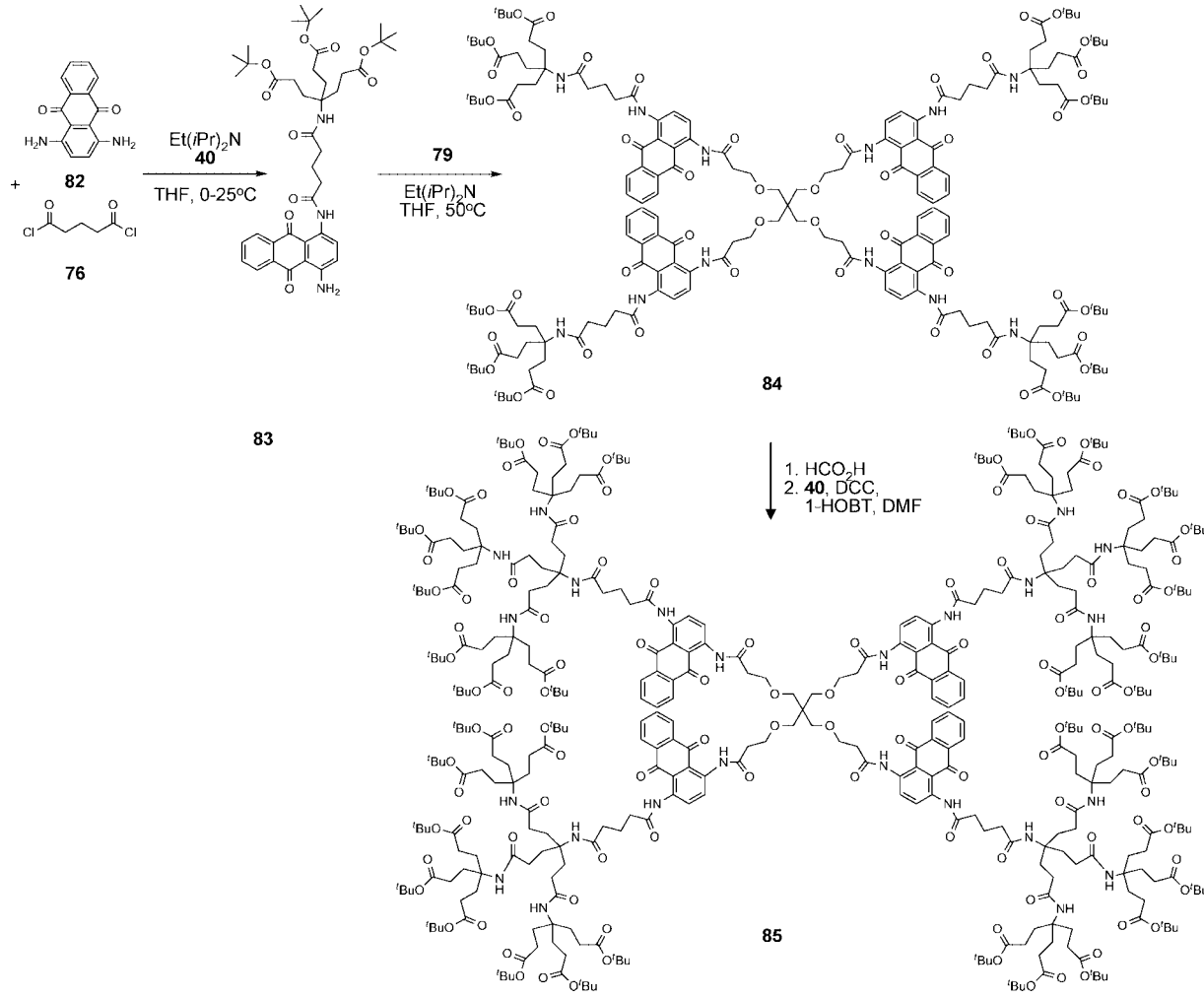
A series of complementary isocyanate-based 1 → 3 branched monomers, predicated on Behera's amine triester construction, have been produced.[384,386,529−531] The applications of these isocyanates are noted below under urea (section 2.13) or carbamate (section 2.14) connectivity.

The surface of the G2 predendron **118**, derived from $O_2NC(CH_2CH_2CO_2H)_3$ and amine **40**, was treated with a monoprotected α,ω-diaminoalkane, followed by deprotection; attachment of diBoc-trifylguanidine and reduction of focal moiety gave the free amine **120** (Scheme 27); fluorescein isothiocyanate was then focally attached followed by subsequent deprotection of the surface groups, giving the preplanned product **122**.[532] Utilizing this methodology for the intracellular transport of bioactive entities into specific subcellular locations might overcome some of the limitations in drug delivery and give insight into drug transport. Substitution of fluorescein with other linkages created a dendritic molecular transporter conjugate IgGMT enabling intracellular uptake of biologically active IgG antibodies that inhibit syncytia formation in respiratory syncytial virus green fluorescent protein infected human epithelial cells (HEp-2).[533] The assembly of a nanoscopic dendritic delivery system facilitated the rapid cellular uptake of a nanoparticle−peptide conjugate with up to 25 copies of the peptide cargo thus establishing a new route for the implementation of protein and oligonucleotide drugs.[534]

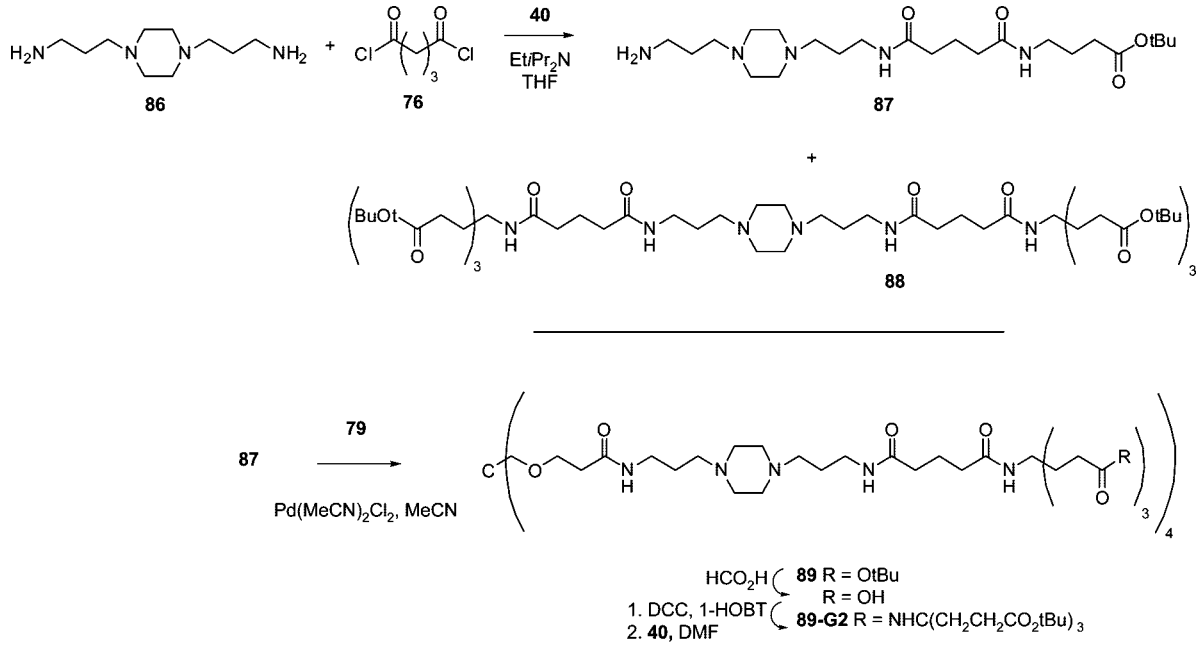
Comparative studies have been conducted by Diederich et al. in which their two-directional dendritic structures possess rigid cores, for example, diphenylacetylene and two G1 1 → 3 C-branched dendrons: one is lipophilic and the other is hydrophilic.[33,535,536] A library of amphiphilic, self-assembling dendrimers was created to evaluate the effects of structural modifications on transfection efficiencies.[537]

Brütting et al.[392] modified C_{60} to incorporate the G2 Behera's amine dendrons (ester-terminated) affording good solubility in linear PPV for the purpose of enhancing photovoltaic properties of this conjugated polymer. Essentially, the C_{60} dendrimer was added to suppress recombination of photogenerated charge carriers. Investigation of these blends as films layered between ITO and Al was reported.[392] Hirsch et al.[391] attached two G2 Behera's amine dendrons to a C_{60} possessing ten lipophilic chains and then hydrolyzed the ester moieties to generate a novel globular amphiphile; the aggregation of this amphiphile was studied with cyro-TEM. Guldi, Hirsch et al.[161,393,401,405,407,485] studied by fluorescence spectroscopy and transient absorption spectroscopy the association of different fullerene monoadducts possessing one or two G2 Behera's amine dendrons with carboxylate termini with the zinc analogue of cytochrome

Scheme 21. Redox-Active, Anthraquinone-Based Dendrimers (85) of Newkome et al.[509]

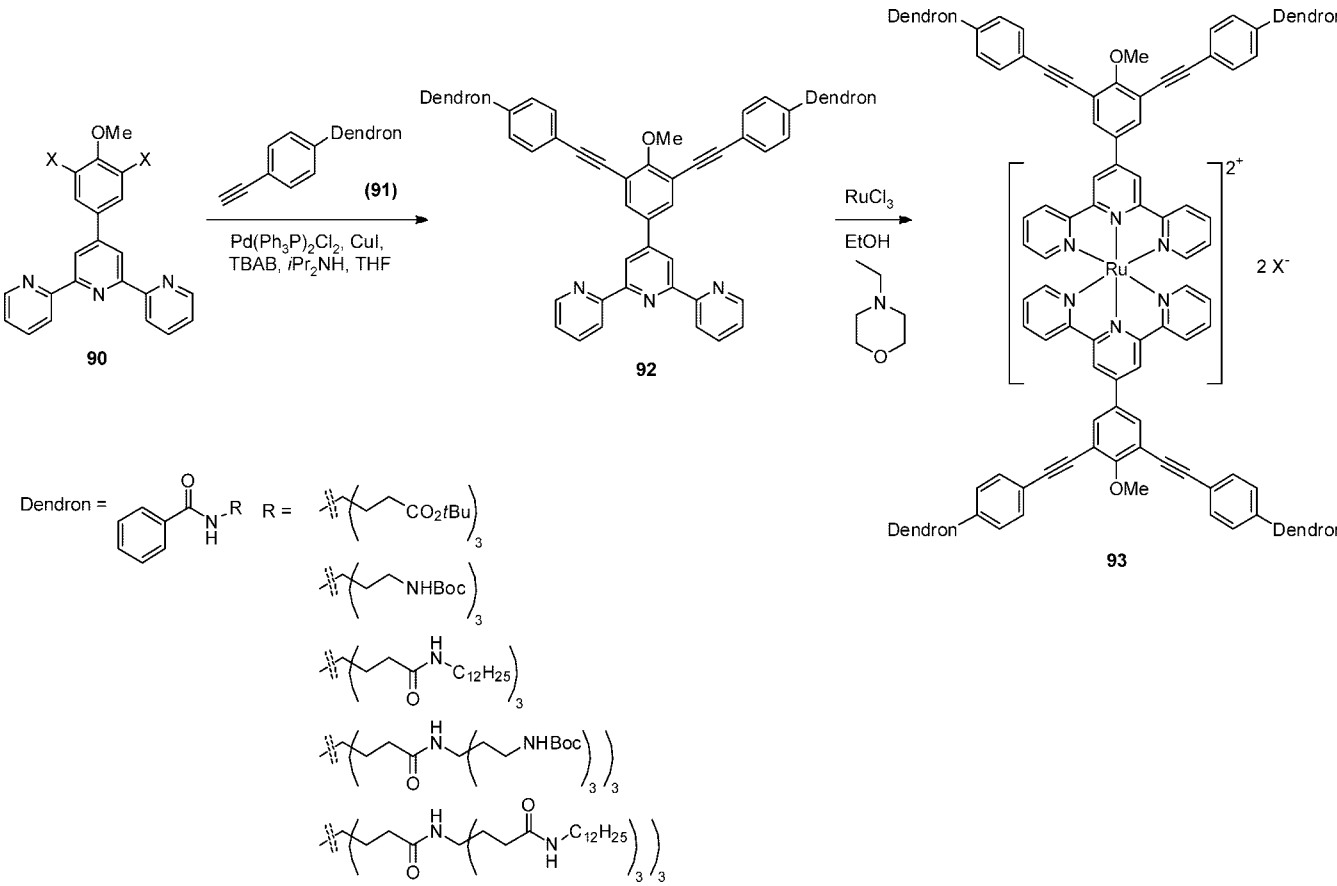


Scheme 22. Incorporation of Donor Centers for Metal Encapsulation[513]



c; the photoinduced electron transfer within the electrostatic complex was proven, and these findings were also supported by CD as well as MD simulations. The attachment to fullerene of a [6:0]-hexaadduct carrying six pyropheophoride *a* moieties has been reported.[538,539] The intracellular uptake and phototoxicity of a fullerene [5:1]-hexaadduct with six 31,32-didehydrophytochlorin groups were compared with the fullerene-free analogues from which the extent of intracellular uptake was influenced by both the nanomolecular size and amphiphilicity of the fullerene structure.[540] Fullerene sugars

Scheme 23. Assembly[516] of Amphiphilic Metallodendrimers with Bisterpyridine Ruthenium(II) Cores



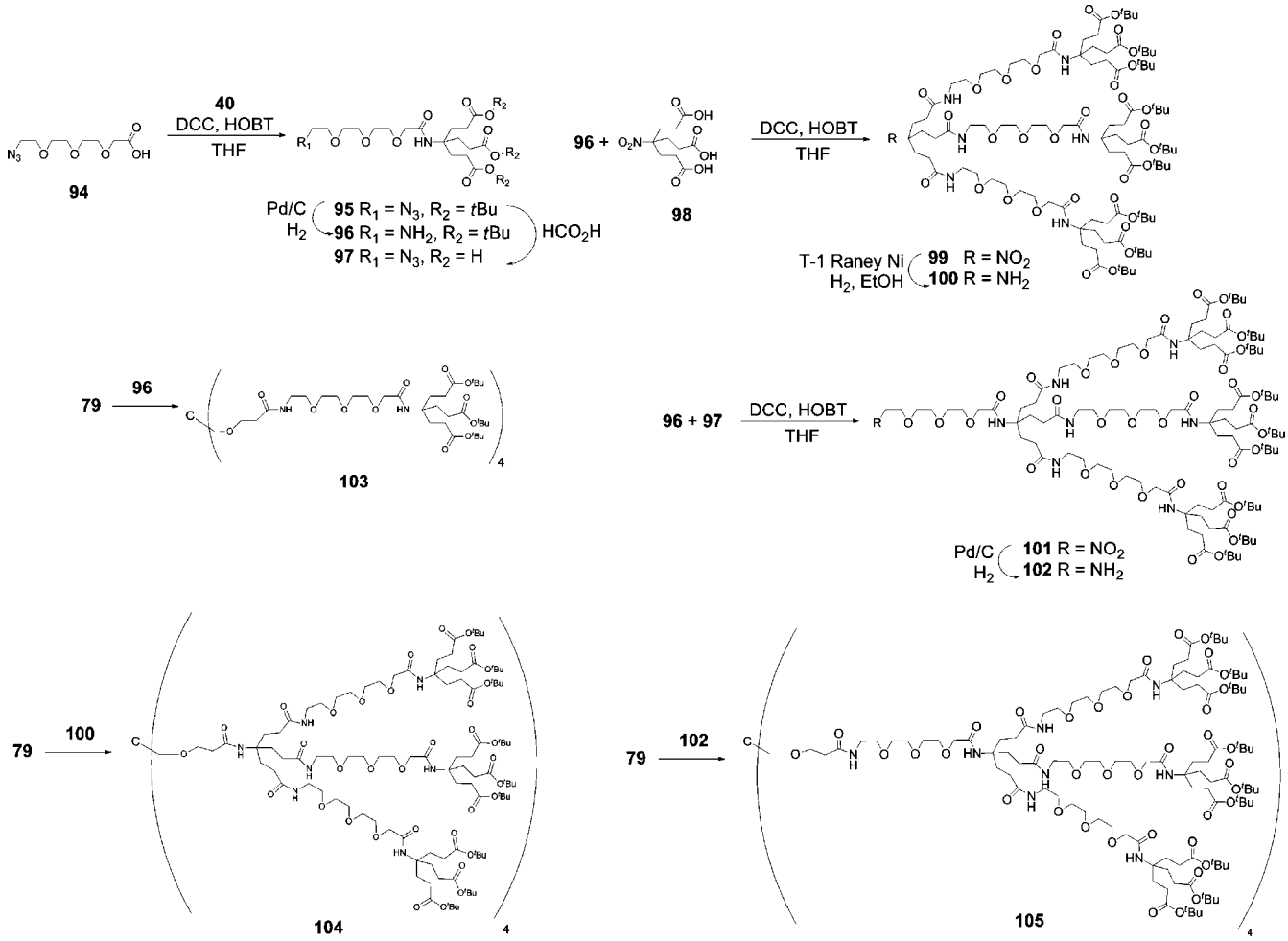
containing two dendritic α-D-mannopyranosides attached via a 1,9-dihydro-1*a*-aza-1(2)*a*-homo(C_{60}-I_h)[5,6]fullerene surface connectivity have been reported.[541] More recently, Hirsch et al.[542] created a water-soluble dendrocalixarene **124** from 5,11,17,23-tetraamino-25,26,27,28-tetrakis(dodecyloxy)calix[4]arene (**123**) via a known procedure,[543] which was treated with methyl 4-(chlorocarbonyl)benzoate then sequentially saponified, amidated with amine **40** in DMF, and last hydrolyzed; they demonstrated that 12 of the amphicalixarene **124** formed spherical and structurally persistent micelles at pH 7, which coexist with rod-like micelles (Scheme 28).

Narayanan and Wiener[544] created a two-directional dendron, based on a protected ethylenediamine core, which, after divergent construction using established procedures, was deprotected and subsequently self-assembled around a Co(III) center in a convergent manner. Other cores have been dendronized with these Behera's amine dendrons.[457]

Kaifer et al. have utilized the Behera's amine dendrons to probe the effects of dendron mass on the resultant structure's properties as well as their degree of encapsulation and site isolation. Their work elegantly probes the subtle or not-so-subtle differences of different dendrons; a short review of their work has recently appeared;[56] also see ref 545 After minor modification[419,421] of the original synthesis of Behera's amine[217] as well as that of the G2 and G3 members, the covalent attachment of electroactive and fluorescent moieties at the focal center of these G1−3 dendrons (Figure 2) was initiated by utilizing traditional amidation with the desired acyl halide. Reaction of these dendrons with chlorocarbonylferrocene gave reasonable yields (31−49%) of the products possessing the *tert*-butyl ester surface.[419−421] Ferrocene derivatives have shown fast reversible electrochemical kinetics via a one-electron oxidation; comparative studies showed that the G1 dendron had little effect on the electrochemical behavior as indicated by the rate constant (k^o = (80 ± 20) × 10^3 cm/s), whereas the G2 and G3 members (k^o = (17 ± 3) × 10^3 cm/s and (5 ± 1) × 10^3 cm/s, respectively) demonstrated increasing protection from the electrode surface caused by the additional dendritic bulk. In dichloromethane, the half-wave potentials for ferrocene oxidation suggested that increased dendron size helps to stabilize the positively charged oxidized ferrocenium unit. Kaifer et al. then incorporated a single 4,4′-bipyridinium group at the focal location of this family[437,439] and demonstrated that as the dendron's size increases, its inner sheltered region, which is more polar than the dichloromethane bulk solution, affected the microenvironment of the redox center housed therein. Cobaltocenium has been similarly introduced onto these dendrons using the corresponding acid or acyl chloride in dry DMF with HATU.[424] The half-wave potential for the one-electron reduction for cobaltocenium shifted to more negative values with increasing dendron bulk, but these were minor changes with increasing size. Five new 4,4′-bipyridinium-cored two-directional dendrimers with a G1−3 Fréchet dendron at one end and a G1−3 Newkome dendron at the other have been prepared and characterized.[441]

Kaifer et al.[56,89,187,546,547] have had long ongoing interests in host−guest chemistry, and thus the supramolecular interactions of β-cyclodextrin (β-CD) and cucurbituril hosts with the metallocene guests were a natural area of investigation. The addition of β-CD to the ferrocene acid surface series in an aqueous environment showed two major effects on the voltammetric response: first, the apparent half-wave potential for one-electron oxidation of ferrocene was shifted to more positive values, and second, the overall current levels of the

Scheme 24. Formation of 1 → 3 Branched PEG-Extended Dendrons[522]



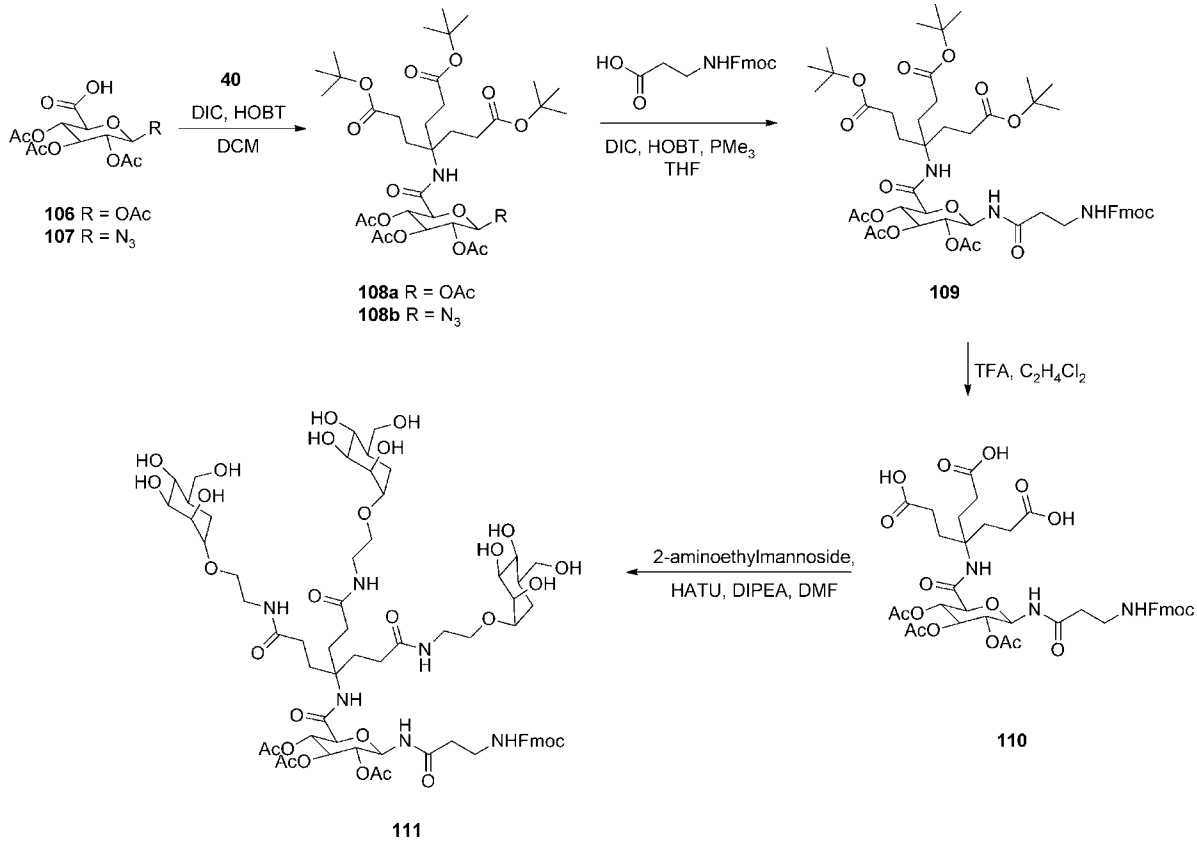
voltammetric peaks decreased.[421] Optimizing the fit of the digitally simulated voltammograms to the experimental data showed the K values for the β-CD association to be 950, 250, and 50 M^{-1} for the G1−G3 series, respectively; the larger dendron prevents or retards the appropriate host−guest interaction. When cucurit[7]uril was used as the host,[438,548,549] increasing dendron size decreased the intensity of electrostatic repulsions opposing host−guest association; however, the trends observed with cucurit[7]uril are quite different from those of β-CD, since dendron growth did not decrease the binding affinity in any obvious way.[422] The cobaltocenium-attached dendrons were very similar to the related ferrocenium dendrons.

Kaifer et al.[429] further started to compare the steric bulk of different dendrons; this is a critical start to better understanding of dendrons since all are certainly not created equal. A better understanding of the size, shape, and physical properties of related dendrons is an essential starting point to choose the appropriate dendron for the particular property desired. Their initial studies compared the 1→ 3 C-branched (Newkome-type)[217] with the 1 → 2 aryl-branched (Fréchet-type)[550] dendrons in which they focused on the electrochemical parameters of the ferrocene moiety and the diffusion coefficients of the particular dendron(s) (Figure 3).[429] Their conclusions are as follows:[56] "the Fréchet dendrons expand as wedges away from the core, while the Newkome dendrons are more effective at changing the polarity of the microenvironment around the ferrocene residue. This is probably a reflection of the more highly branched AB_3 architecture of the Newkome dendrons and their greater flexibility."

Dubin et al.[551] examined the size-exclusion chromatography of G1−5 Behera's amine-based, carboxylic acid-terminated dendrimers **40** as a permeation model for charged particles into like-charged cavities. Chromatography was performed using a porous glass stationary phase and the partition coefficients, K_{sec}, were determined for solute diameters from 2−8 nm at neutral pH in ionic strengths ranging from 0.01 to 0.09 M. Observed degree-of-particle permeation was generally 20% to 100% greater than the calculated values based on the theory of Smith and Deen[552] for like-charged-spheres permeating cylindrical pores, which were determined to overestimate the repulsive forces arising from the employment of a linearized form of the Poisson−Boltzmann equation.

Dubin et al.[553] also examined complex formation between these carboxyl-terminated dendrimers and charged poly(dimethyldiallylammonium chloride) using turbidimetry, dynamic light scattering, viscometry, and potentiometric titration. All of these techniques demonstrated a discontinuity, observed in all methods at a well-defined pH, corresponding to incipient complex formation. A model was described for polyelectrolyte backbone distortion in which the elastic resistance to bending around the shape of the macro-ion acted in opposition to the attractive Coulombic forces. Studies using the complex formation of the G3 dendritic polycarboxylic acid and copolymers of [(methacrylamido)propyl]-trimethylammonium chloride and acrylamide have been reported as a function of ionic strength, turbidimetry titration, and dynamic light scattering.[554]

Scheme 25. The Surface Functionalization of Dendronized Saccharides[418]



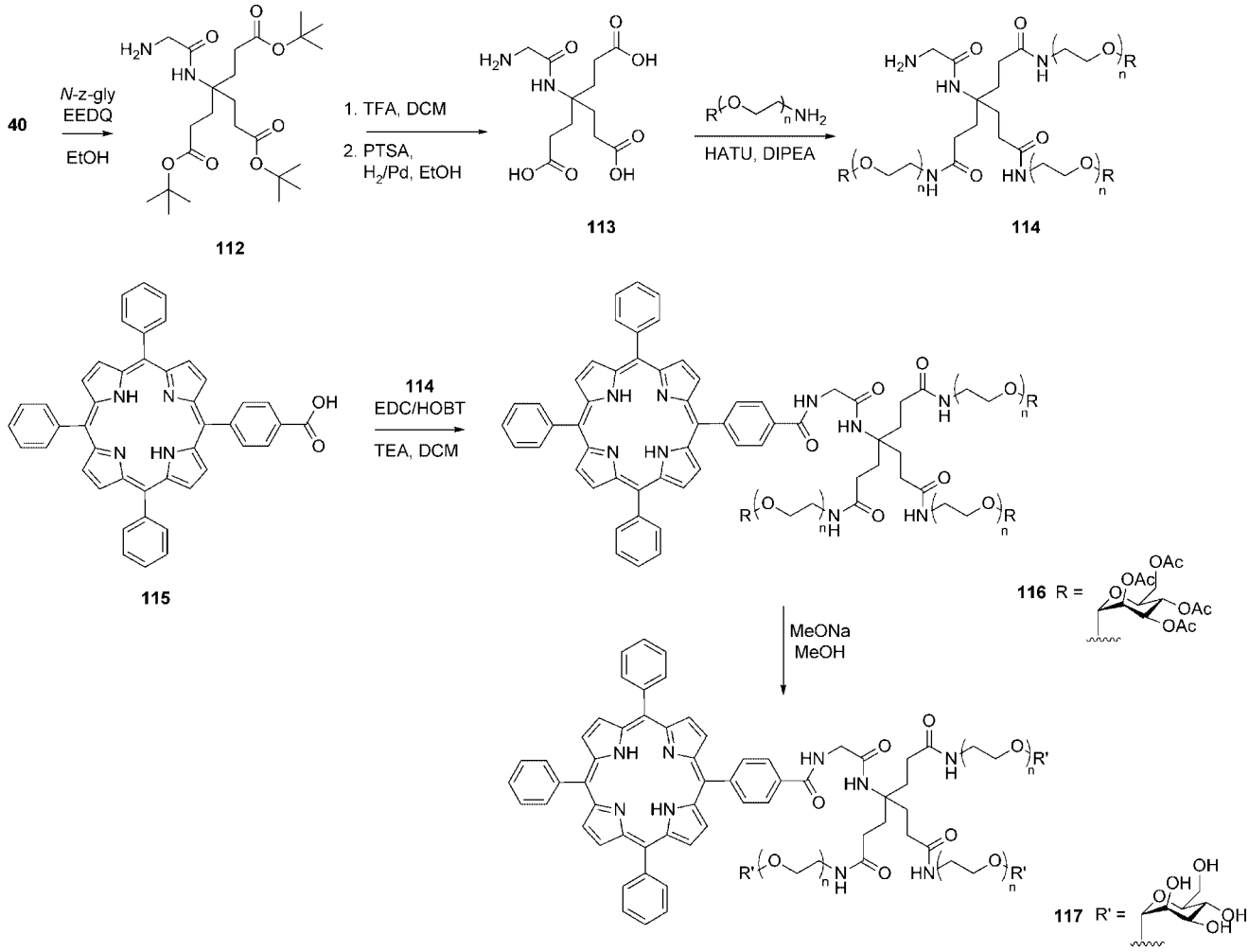
Harmon et al.[555] examined molecular relaxations of the *tert*-butyl and methyl ester-terminated derivatives of these polyamides; their study included MS, TGA, DSC, X-ray diffraction, and dielectric analysis. Glass transition temperatures and apparent activation energies were both observed to increase with increasing generation as well as size of the termini. Secondary transitions also increased in temperature with increasing generation. Ionic conductivity was found to dominate electrical properties at high temperatures. The miscibility of the G1 dendrimer (*tert*-butyl ester of **57**) and PMMA was attributed to hydrogen bonding of the PMMA side chain with the internal amido functionality; an electric modulus treatment of the dielectric data in the α_D region of a 20% blend resulted in T_g, ΔH, and ΔM values comparable to the G1 dendrimer confirming the presence of an isolated dendrimer phase, which coexisted with a partially miscible dendrimer−PMMA phase.[556]

2.2. 1 → 3 C-Branched and Alkyl Connectivity

Although initial efforts utilizing bishomoTRIS as a dendron were less than ideal due to its inability to affect complete amine acylation, the nitro intermediates proved to be excellent precursors to a diverse series of C-based, alkyl monomeric reagents. The construction of an all-saturated, symmetrical, 1 → 3 C-branched hydrocarbon infrastructure was designed based on the bishomoTRIS predendron **32**. The preparation of the unimolecular micelle designated Micellanol **140** was subsequently accomplished by Newkome et al.[557−559] Scheme 9 shows the synthesis of core **136** and the key monomer **138** for their preparation. The nitrotriol **32** was protected with benzyl chloride to give triether **132**, which underwent an interesting denitration−cyanoethylation[560] upon treatment with *n*-Bu_3SnH and AIBN in the presence of acrylonitrile generating intermediate **133**. Nitrile **133** plays a key role, since it was easily converted to either the core **136** [previously prepared from tetrakis(2-bromoethyl)methane from citric acid[561] in 17 steps (ca. 1% overall yield), tetrakis(β-carbethoxyethyl)methane[562] (ca. 70%), or γ-pyrone[563] in 8 steps (24% overall yield)] or the desired alkyne monomer **138** (Scheme 29). Hydrolysis of nitrile **133** gave acid **134**, which was quantitatively reduced (BH_3·THF) to the alcohol **135**. This was transformed via concomitant deprotection (HBr) and dehydroxylation−bromination to give the core **136** in excellent overall yield.[564] Treatment of alcohol **135** with $SOCl_2$ gave the desired monochloride **137**, which when reacted with lithium acetylide gave the functionally differentiated alkyne **138**. Ober et al.[565] deprotected (Pd/C, H_2, EtOH) the above triol **134** to generate (90%) $HO_2CCH_2CH_2C[(CH_2)_3OH]_3$, which was transformed into $ClOCCH_2CH_2C[(CH_2)_3O_2C(CH_2)_p(CF_2)_qF]_3$ and then appended to a hydroxylated polystyrene-*b*-1,2/3,4-isoprene). This same triol **134** was transformed into $HO_2CCH_2CH_2C[(CH_2)_3O(CH_2CH_2O)_nMe]_3$,[566,567] which was used by Diederich et al. in their models for hemoglobin and myoglobin.[568−582] The second generation was similarly prepared using acid **134**, which was transformed to the *tert*-butyl ester and deprotected to the triol; then addition of $HO_2CCH_2CH_2C[(CH_2)_3O(CH_2CH_2O)_nMe]_3$ and deprotection gave the desired product.[567]

Tetrakis(2-bromoethyl)methane,[563] $C(CH_2CH_2Br)_4$, reacted poorly with hindered nucleophiles; however with either azide or cyanide ions, the respective azide and nitrile were easily generated both of which were reduced to corresponding $C(CH_2CH_2NH_2)_4$[583] (91%) and $C(CH_2CH_2CH_2NH_2)_4$ (65%). The related larger homologue **136** was unaffected upon association with the bulky nucleophiles. Treatment of tetrabromide **136** with 4 equiv of the lithium salt of alkyne **138** afforded the desired tetraalkyne **139**, which was reduced

Scheme 26. Preparation of Glycodendrons[448]



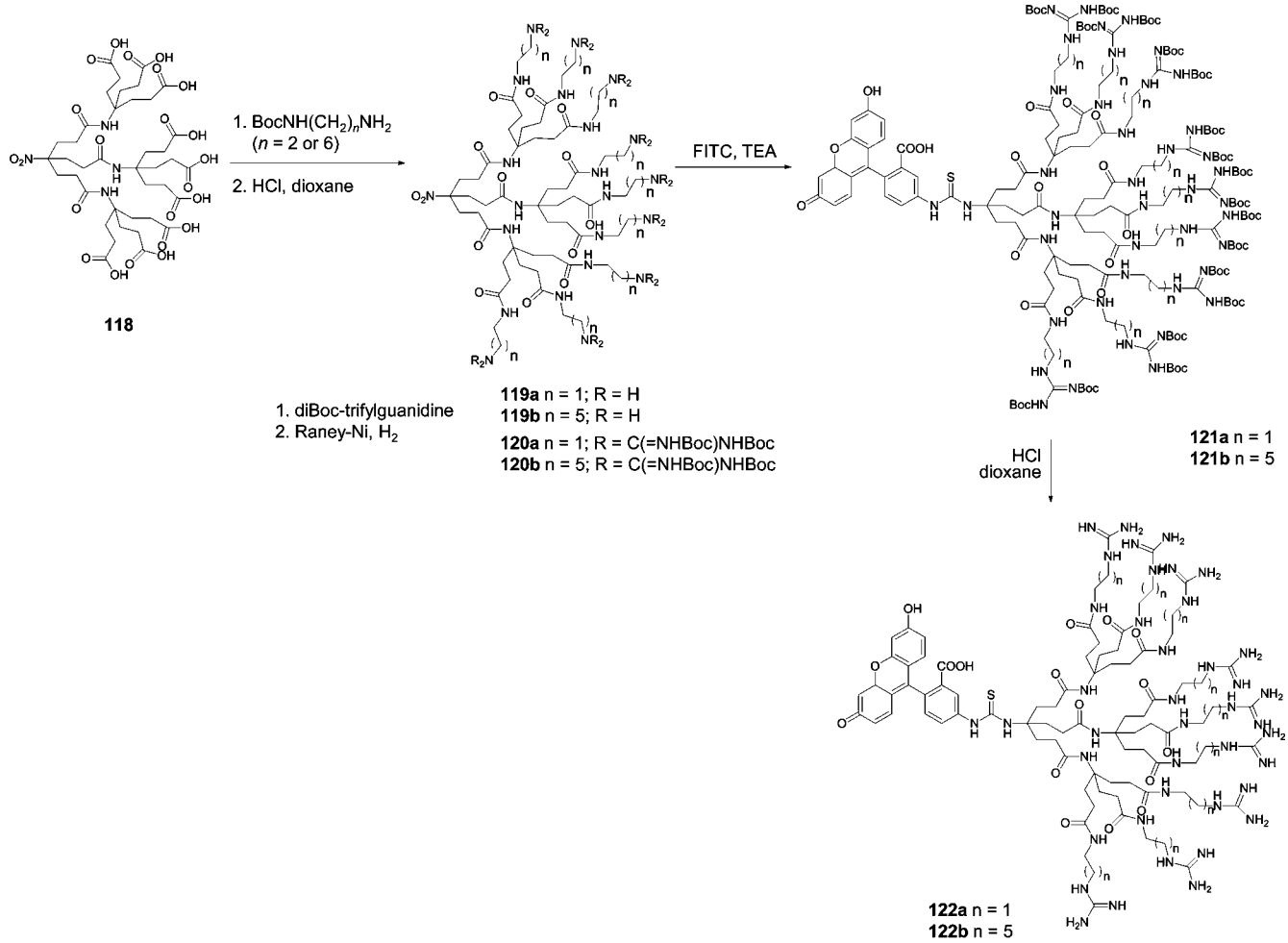
and deprotected to afford the saturated dodecaalcohol **140**. Polyol **140** was then converted to the corresponding polychloride (Scheme 30), which was treated with slightly over 12 equiv of alkyne dendron **138** to yield the 36-benzyl ether **141**. Reduction and hydrogenolysis of tetraalkyne **141** gave rise to the 36-Micellanol [**142**; 36-cascade:methane[4]:(nonylidyne)^2:propanol].[368−370] Its water-solubility was further enhanced by oxidation (RuO_4) and conversion (Me_4NOH) to the corresponding polytetramethylammonium 36-Micellanoate **143**.

The "unimolecular" micellar characteristics[206] were established for poly(ammonium carboxylate) **143**[368,559,584] via UV analysis of guest molecules, such as pinacyanol chloride, phenol blue, and naphthalene, combined with fluorescence lifetime decay experiments employing diphenylhexatriene as a molecular probe. The monodispersity or absence of intermolecular aggregation and molecular size were determined by electron microscopy.

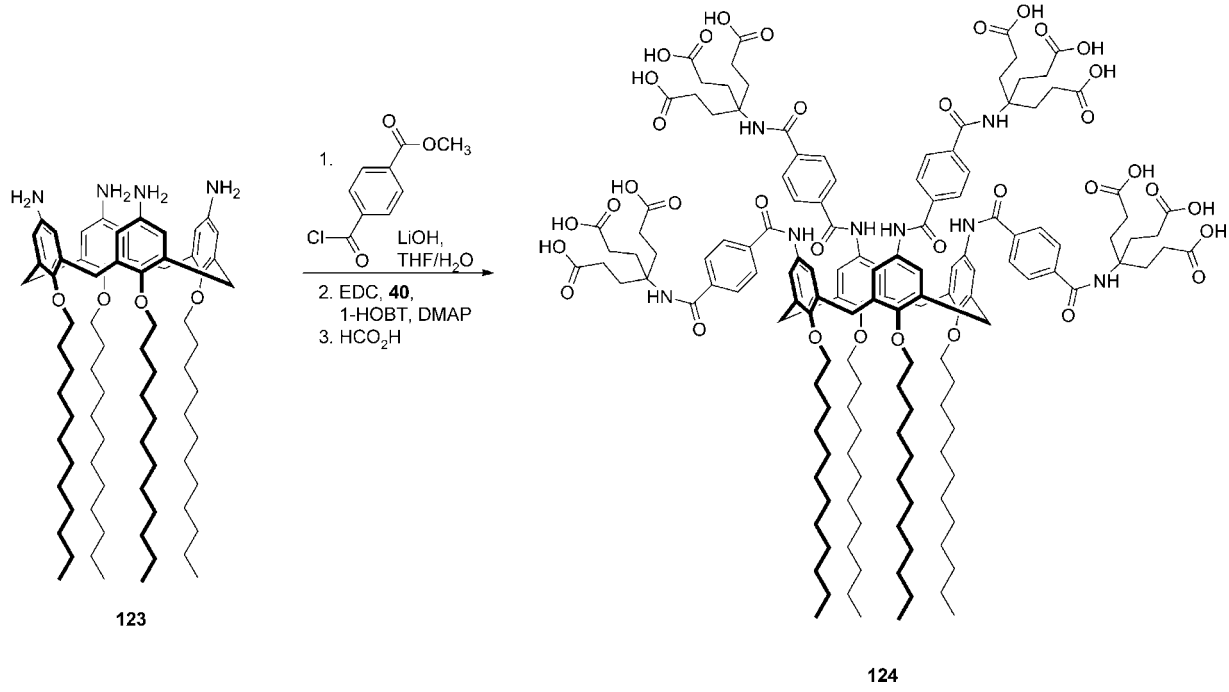
The polyalkyne precursors to the hydrocarbon-based unimolecular micelles[584] allowed the testing of chemical modification at specific sites within the interior of a cascade infrastructure.[585] Treatment of the alkynes **139** or **141** with decaborane afforded excellent yields of the 1,2-dicarba-*closo*-dodecaboranes[586] (*o*-carboranes) or with $Co_2(CO)_8$ gave the desired poly(dicobalt carbonyl) clusters.[587]

Astruc et al. demonstrated the $CpFe^+$-induced nonaallylation of mesitylene,[588] which was followed by a regiospecific hydroboration and oxidation to generate the desired nonaol,[589] a key starting point for their synthesis of giant (macro)molecules. This mesitylene-cored nonaol was also transformed to the nonaiodo[590,591] and then nonaammonium iodide salt, which with $AgBF_4$ was converted (98%) to the corresponding fluoroborate salt.[592,593] Treatment of the ammonium iodide salts with $AgBF_4$ in EtOH gave the corresponding BF_4^- ammonium salt, which with commercial $H_3PW_{12}O_{40}$ and H_2O_2 gave the desired ammonium salts of $\langle[PO_4[WO(O_2)_2]_4]_3^-\rangle$ (POM).[592,594] These POM dendrimers with a peroxophosphotungstate core, constructed by ionic bonding, were air-stable, recoverable catalysts for the oxidation reactions using hydrogen peroxide.[595] The $CpFe^+$-induced allylation of 3,3′,5,5′-tetramethylbiphenyl was accomplished to generate the dodecaallyl product,[596] which was transformed to the dodecaol, dodecaiodide, and dodecaammonium salts.[592,593] When $CpFe^+$-induced allylation of *p*-xylene was accomplished, the resultant hexaallyl product $\langle FeCp[(\eta^6\text{-}p\text{-}C_6H_4[C(CH_2CH{=}CH_2)_3]_2\rangle$ could be transformed either to the metal-free product by photolysis in the presence of PPh_3 in MeCN giving $p\text{-}C_6H_4[C(CH_2CH{=}CH_2)_3]_2$ or with $[Ru(PCy_3)_2Cl_2(=CHPh)]$ forming $\langle FeCp[(\eta^6\text{-}p\text{-}C_6H_4[C(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)]_2\rangle$ and cyclic/linear oligomers,[91,92,597] whereas $p\text{-}C_6H_4[C(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)]_2$ with the second generation Grubbs catalyst $\langle Ru(=CHPh)(PCy_3)_2[C(NMesitylCH_2)_2Cl_2]\rangle$ resulted in cyclic and linear polymers; also see ref 596. Astruc et al. demonstrated the facile transformation of the nonaol with acrylonitrile in the presence of base followed by reduction

Scheme 27. The Surface Coating of G2 Dendron with Guanidine and Inclusion of a Fluorescein Focal Group[532]



Scheme 28. Generation of a Novel Dendrocalixarene[542]



(69%) to the extended nonaamine (**144**; Scheme 31; see below).[598,599] Acylation of **144** with cobalticinecarbonyl chloride gave the desired G1 dendrimer **145** possessing terminal cobalticinium groups. Different variations of this procedure have led to larger members of the cobalticinium and ferrocenium-coated family; the exoreceptor sensing of biologically important anions has been reported.[55,600]

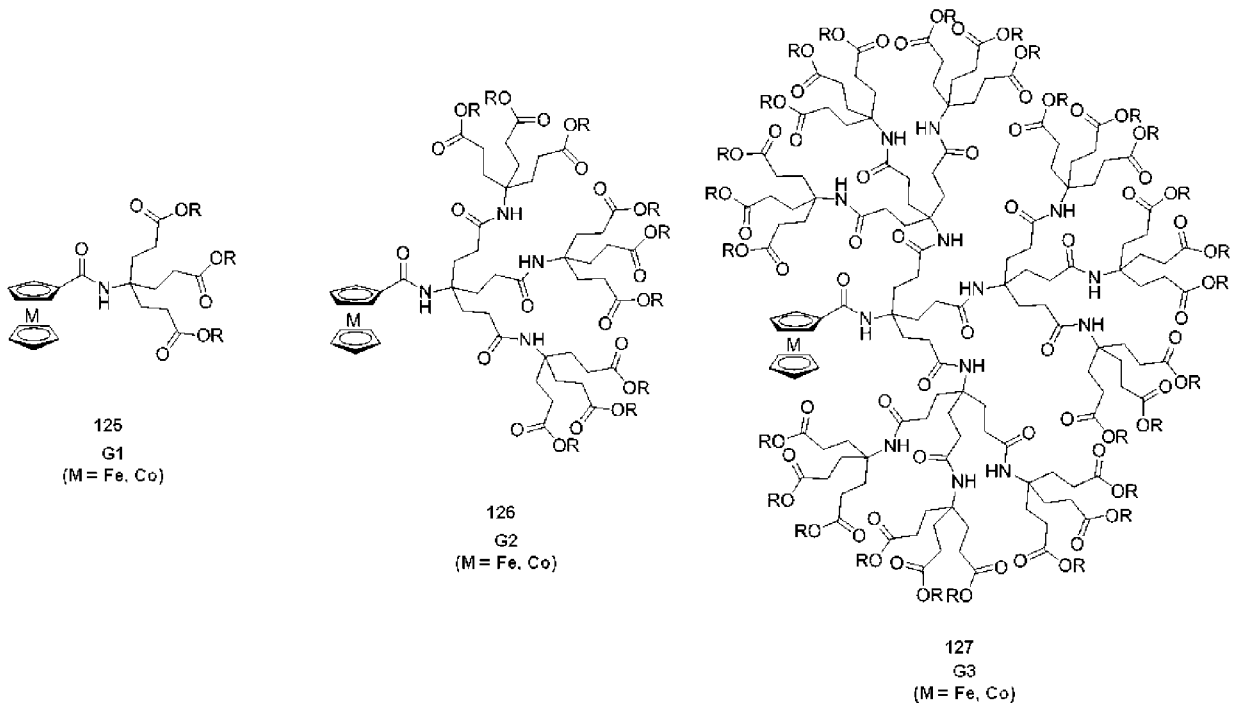


Figure 2. General ferrocenium and cobaltocenium G1−3 dendrons.[437]

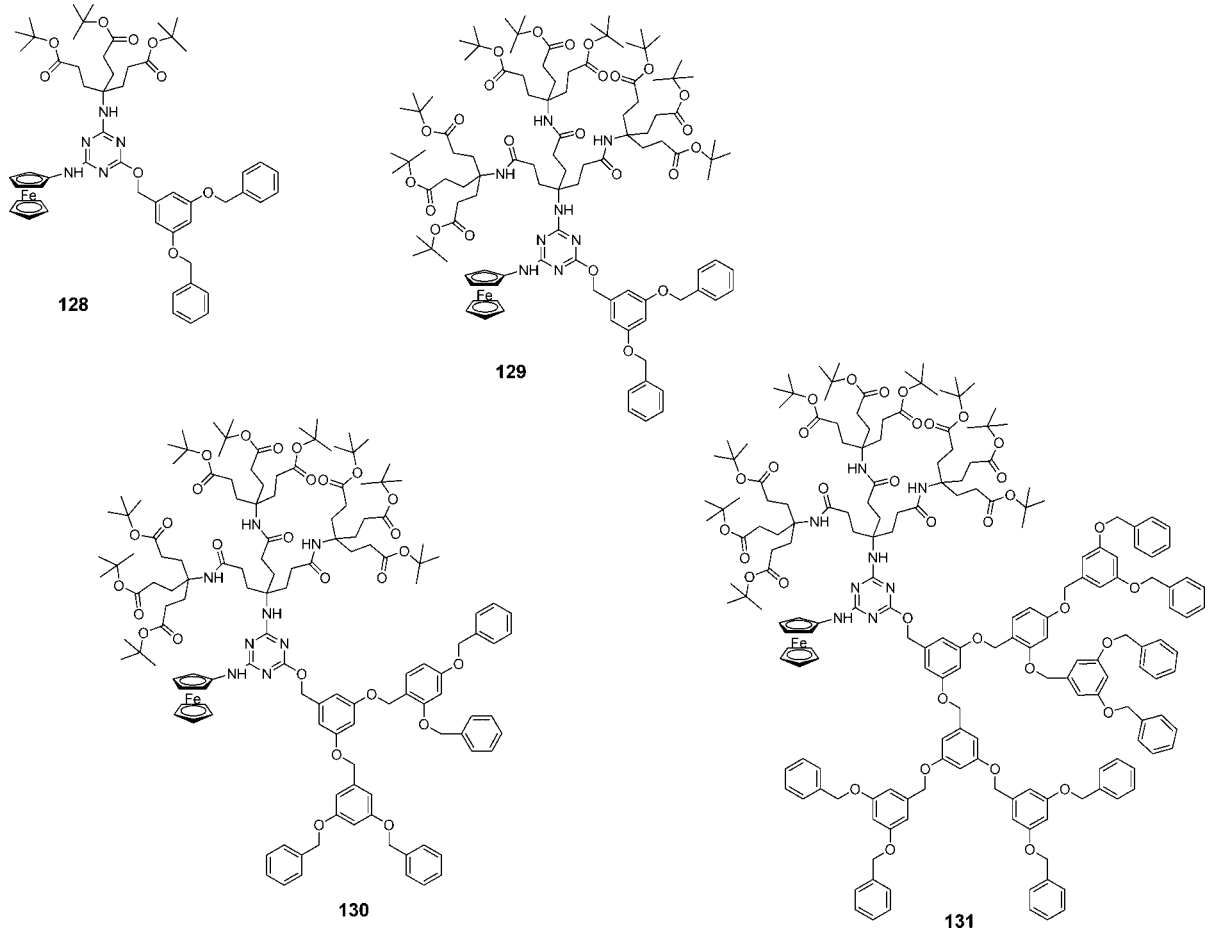
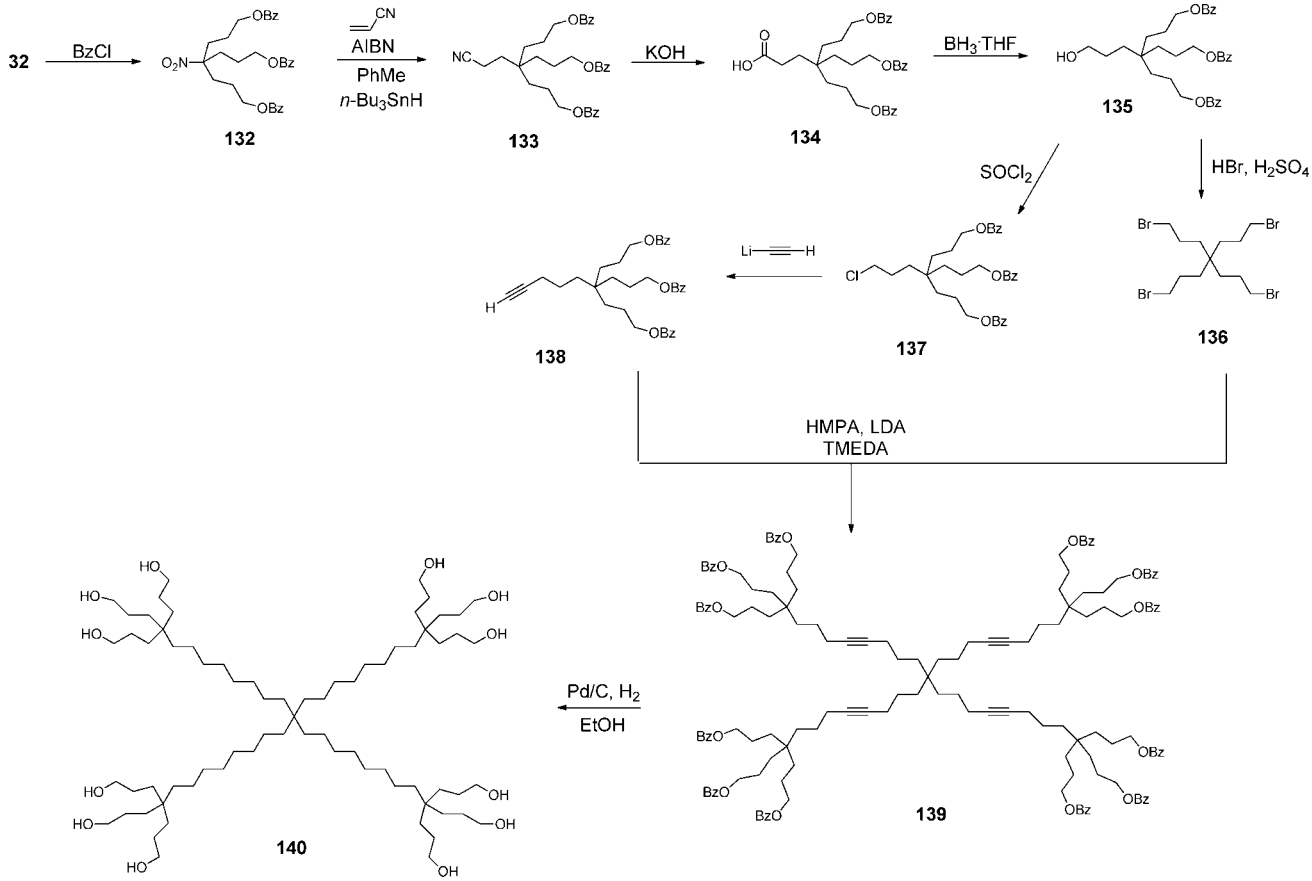


Figure 3. Hybrid dendrimers.[429]

Madder et al.[601,602] built a simple 1 → 3 scaffold on their way to tripodal receptors in which MeCHO was treated with RNH_2 in CH_2═CHCN to generate $OHCC(CH_2CH_2CN)_3$; carbonyl reduction and protection gave $TBSOH_2CC(CH_2CH_2CN)_3$, which was reduced (RaNi, N_2H_4) to give $TBSOH_2CC[(CH_2)_3NH_2]_3$. Subsequent amidation, hydrolysis, and Jones oxidation gave their desired scaffold $HO_2CC[(CH_2)_3NHR]_3$.

Scheme 29. Sequence for the Preparation of Alkyl Monomers (136 and 138) Used in the Construction of Unimolecular Micelles[557−559]



2.3. 1 → 3 C-Branched, Ester Connectivity

The use of citric acid as a 1 → 3 branched monomer offers easy access to a potentially utilitarian route to dendritic constructs from Mother Nature. Technically, citric acid is a 1 → (2 + 1) monomer, since the central carboxylic acid is on a quaternary carbon and will possess a different rate of reaction than the other two. The treatment of diacid **146** with thionyl chloride generated the bisacyl chloride, which was reacted with citric acid in the presence of pyridine at room temperature to give the G1 two-directional **148**, which can be converted to the corresponding hexaacyl chloride and then citric acid with pyridine or **148** with citric acid in the presence of DCC gave the G2 bis-nonaacid **150** (Scheme 32).[603] The G2 product was subsequently transformed to the G3 level. Although published, a thorough proof-of-products is necessary, since there are many side reactions that can occur with such a mode of construction.

Another interesting related 1 → (2 + 1) C-branched monomer can be created from glycerol (propane-1,2,3-triol) (**151**) by initial treatment with benzoyl chloride, followed by a Jones oxidation affording the 1,3-disubstituted acetone **153**, which with di(isopropyl)amine generated the azahemiacetal **154**, as shown in Scheme 33. Removal of the protecting benzoyl moieties gave the free hydroxy groups (**155**), which are esterified and last deprotected to afford the 1 → (2 + 1) building block **157**, which led to peptide pharmaceuticals that can penetrate the blood−brain barrier.[604] The zero-generation synthetic triglycerides have been investigated[604] as vehicles for peptide delivery across the blood−brain barrier.

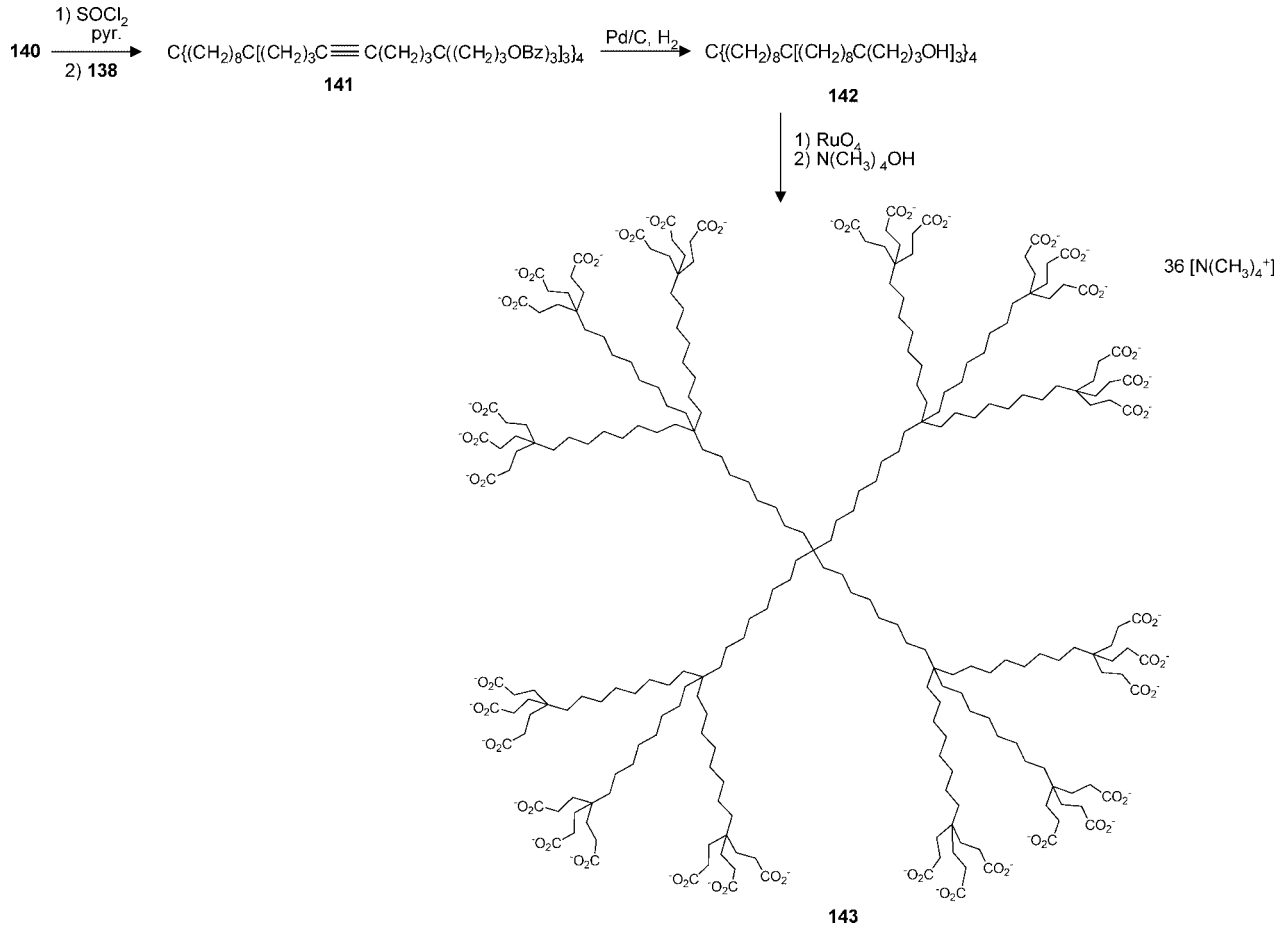
The 18-electron complex $\langle[(\eta^6\text{-}C_6Me_6]Fe^{II}[\eta^5\text{-}C_5H_4CO(OC_6H_4C(CH_2CH{=}CH_2)_3)PF_6]\rangle$ was readily reduced in THF at ambient temperature to give the stable 19-electron complex $\langle[\eta^6\text{-}C_6Me_6]Fe^{I}[\eta^5\text{-}C_5H_4CO(OC_6H_4C(CH_2CH{=}CH_2)_3)]\rangle$;[605] the appended dendron is a pivotal component to Astruc's quest of giant dendrimers.

2.4. 1 → 3 C-Branched, Ether Connectivity

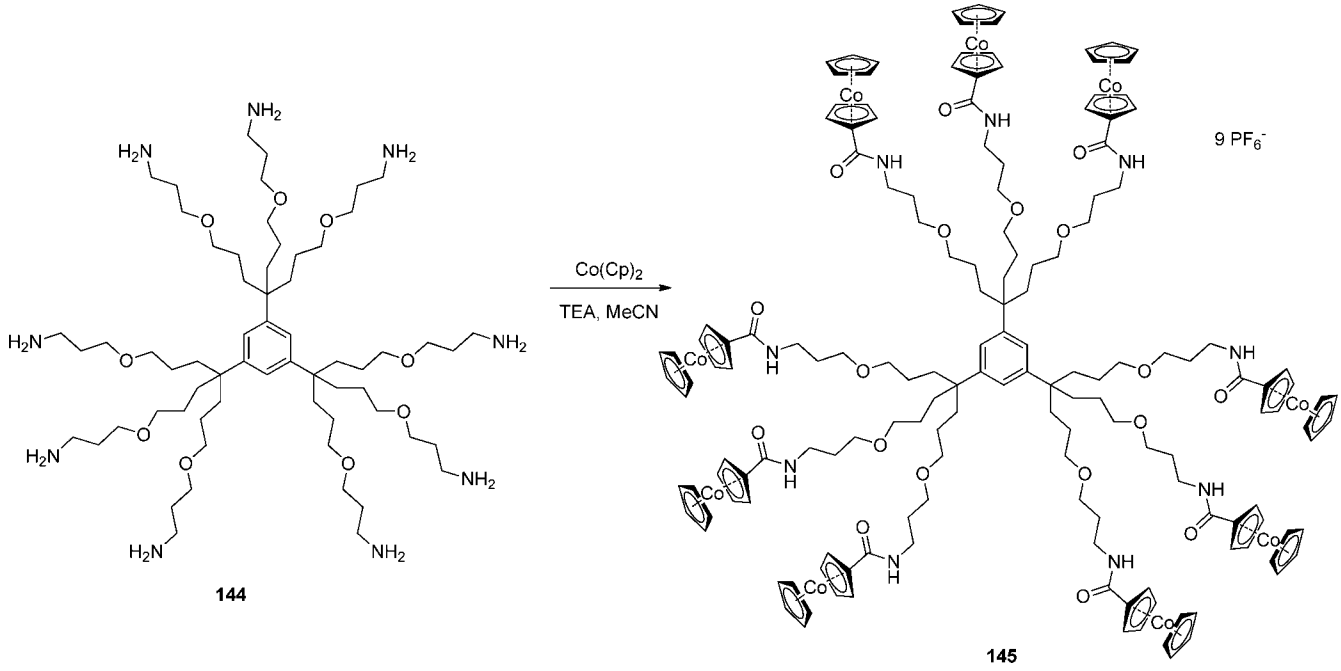
The useful $HOC_6H_4C(CH_2CH{=}CH_2)_3$ monomer has also played a pivotal role in Astruc's construction of gigantic dendrimers via either a divergent or convergent procedure:[130,590,606−608] ferrocene-coated metallodendrimers;[591,609−612] azobenzene-connected ferrocene-coated metallodendrimers;[613] glycodendrimers containing xylopyranoside termini;[614] giant cobalticinium dendrimers;[615] 18 allyl hexaruthenium dendrimer;[616] polyanionic dendrimers capable of binding to acetylcholine;[611,617] octahedral cluster-cored polyolefin dendrimers;[611,618−621] air-stable polyoxometalate-cored dendrimers;[593,622] poly(ethylene glycol) (PEGed) dendrimers;[623,623] and different click dendrimers.[623−626] Vincent et al. recently reported the use of air-stable, highly reactive, and recyclable [Cu($C18_6$tren)]Br, where $C18_6$tren = tris(2-dioctadecylaminoethyl)amine, as an effective recyclable catalyst for "click" reactions.[627]

Similar chemistry was conducted with the G2 dendron $\langle HOC_6H_4C[(CH_2)_3OC_6H_4C(CH_2CH{=}CH_2)_3]_3\rangle$ possessing nonaferrocenyl moieties.[609,628] These authors also fabricated electrodes with dendronized nanoparticles containing either the tri- or nonaferrocenyl dendrons; the modified electrodes

Scheme 30. Preparation of the Poly(tetramethylammonium salt) of Micellanoic Acid (143)[557,584]

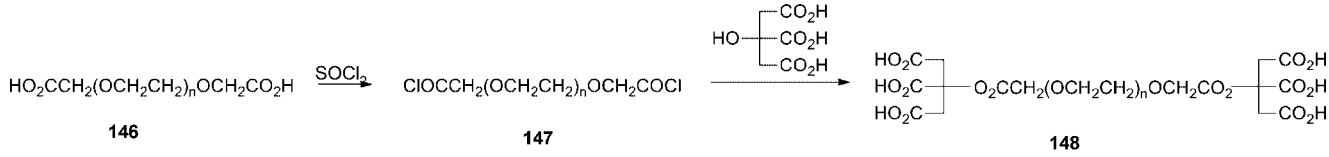


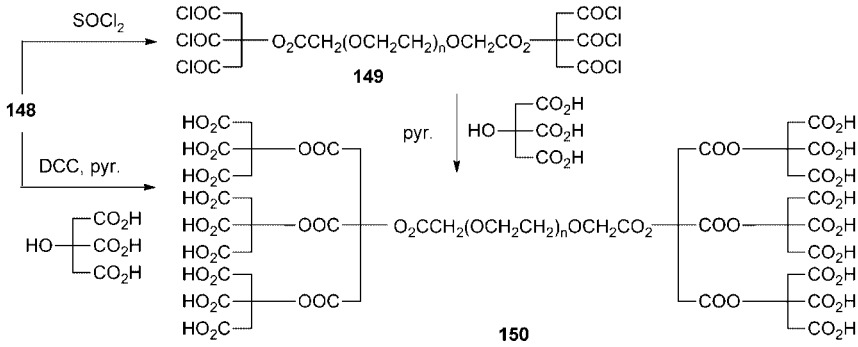
Scheme 31. Simple Methodology to the Cobalticinium-Terminated Dendrimers



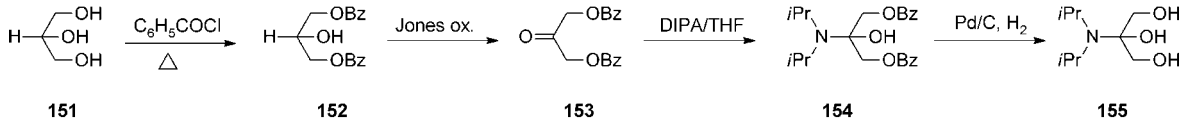
recognized the $H_2PO_4^-$ and ATP^{2-} anions even in the presence of other anions.[628,629] Extension of the focal site of **158** with 1,4-di(bromomethyl)benzene gave (91%) **159** that was smoothly reacted with ⟨[FeCp(η^6-C_6Me_6][PF_6]⟩ to generate (60%) the hexafunctionalized product **160**;[630] similarly, the ferrocenyl analogue of **159** created the ferrocenyl product (Scheme 34). The H-bond connectivity of a simple poly(propylene amine)-terminated dendrimer with these triallyl or triferrocenylalkyl monomers generated redox-active metallodendrimers that were used for the electrochemical recognition of the $H_2PO_4^-$ and adenosine triphosphate (ATP^{2-}) anions.[631,632] Interestingly, the treatment of this G2 dendron with $EtCO_2C_6H_4C[(CH_2)_3I]_3$ did not give the expected G3 dendron, but rather, $HOC_6H_4C(CH_2CH{=}CH_2)[(CH_2)_3$-

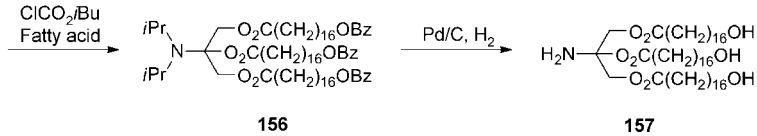
Scheme 32. The Use of Citric Acid as a Monomer in Dendrimer Formation[603]





Scheme 33. Peptide Targeting and Delivery Systems Based on the 1 → (2 + 1) Building Block Derived from Glycerol[604]





$OC_6H_4C[(CH_2)_3OC_6H_4C(CH_2CH{=}CH_2)_3]_3]_2$ was isolated in quantitative yield after saponification.[633]

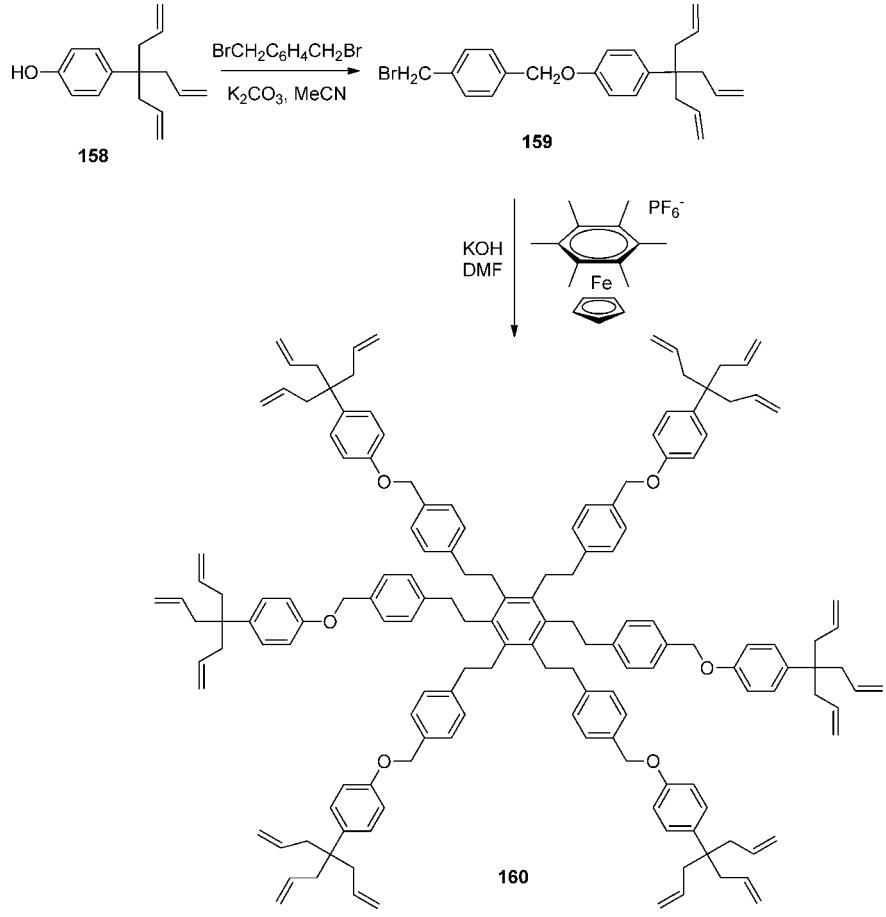
Scheme 35 illustrates the treatment of the G2 dendron **161** with 1,4-di(bromomethyl)benzene giving the extended **162**, which was converted to the ammonium salt, which gave the tetrakis(diperoxotungsto)phosphate-cored dendrimer **163**.[622] These polyoxometalates were air-stable, efficient, recoverable, and reusable catalysts for the selective oxidation of alkenes to epoxides, sulfides to sulfones, and alcohols to ketones in an aqueous $CDCl_3$ biphasic medium with hydrogen peroxide as the oxidant. Structurally related aryl sulfide- and *n*-propyl-terminated metallodendrimers were also prepared. The attachment of this G2 dendron to 4,4′-di(bromomethyl)-2,2′-bipyridine has been demonstrated and opens the door to the introduction of diverse metal cores.[612]

2.5. 1 → 3 C-(Pentaerythritol-Based) Branched, Ether Connectivity

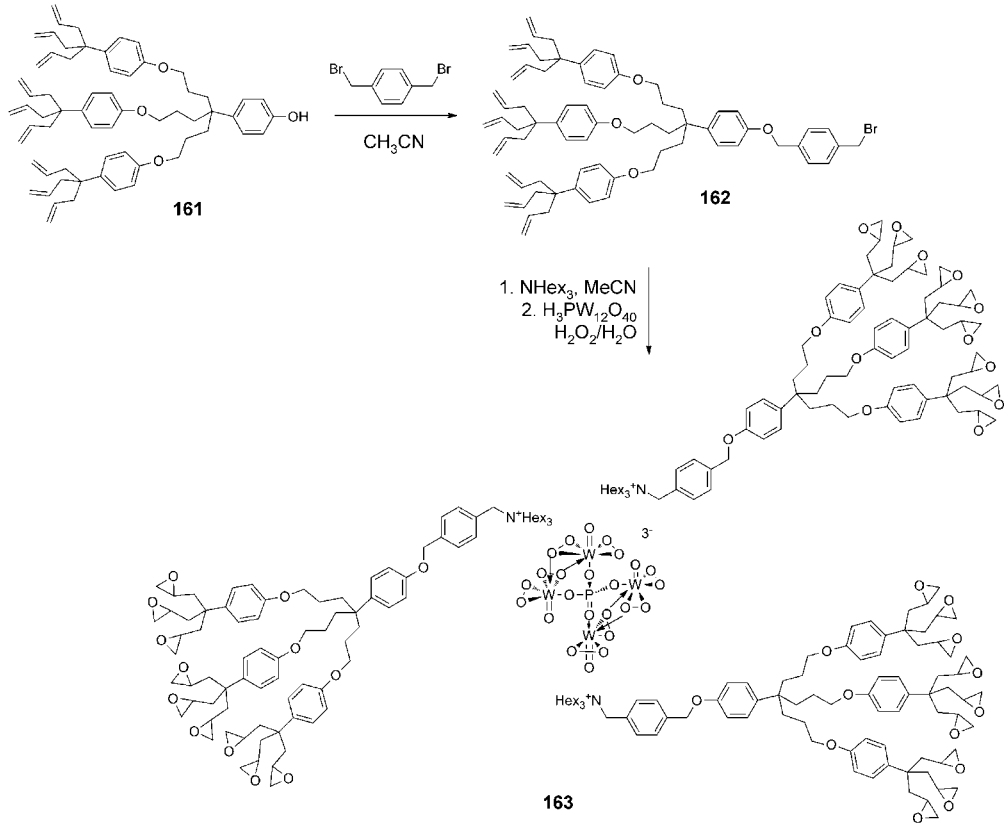
Hall et al.[634,635] reported the initial synthesis of polyethereal and polythioethereal dendrimers possessing the shortest distance between branching centers (Scheme 36). The use of pentaerythrityl tetrabromide (**164**),[636] as the core, with the potassium oxyanion of the corresponding orthoester of pentaerythritol **165**, as the 1 → 3 monomer, afforded the protected dodecaol **166**. Deprotection and subsequent two-step conversion of the hydroxy groups to the dodecabromide, via the dodecatosylate, provided the precursor for the construction of the next tier. The G2 36-polyol **167** was subsequently transformed by this simple procedure to the G3 108-polyol **168**, which is the most densely packed dendrimer in the 1 → 3 branching series yet reported, as evidenced by the branching defects encountered after the formation of the G2 level[3,637] presumably resulting from an increasing number of neopentyl displacements required for tier construction. Due to the structural constraints, "One of the major problems with the synthesis for [these] dendrimers is that it is extremely difficult to verify the purity of the isolated products."[634]

Ford et al.[638] reported the use of these ethereal dendrimers, in which the terminal polyols were converted to the corresponding homologated polyamines; subsequent alkylation (excess MeI) generated the polyammonium salts, for example, the G2 36-tetraalkyl ammonium salt **169** (Scheme 37). The rate constants for the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate in water showed that reaction in the G2 polyammonium dendrimer is 10 times faster than that in the related G1, 20 times faster than that in water alone, but 10 times slower than that with the hydrophilic polystyrene latex TMAQ60x1. Cramer et al. also noted that the use of the orthoacetate of pentaerythritol **165c**, instead of the orthoformate **165a**, adds to the stability of this building block thus enhancing its versatility.[639] Use of such "tied-back" building blocks facilitates nucleophilic substitutions, even at hindered neopentyl centers. The polyionic constructs $C(CH_2OCH_2CH_2N^+Me_3)_4$ ($4I^-$), $C[CH_2OCH_2C(CH_2OCH_2CCH_2N^+Me_3)_3]_4$ ($12I^-$), and $C[CH_2OCH_2C[CH_2OCH_2C(CH_2OCH_2CH_2N^+Me_3)_3]_4]_4$ ($36I^-$) have been employed in "ion-exchange displacement chromatography".[640] The use of **165c** with 1,4-di(bromomethyl)benzene gave a bis-orthoester, which was transformed into $[Me_3N^+(CH_2)_2$-

Scheme 34. The Hexasubstitution of Hexamethylbenzene[630]

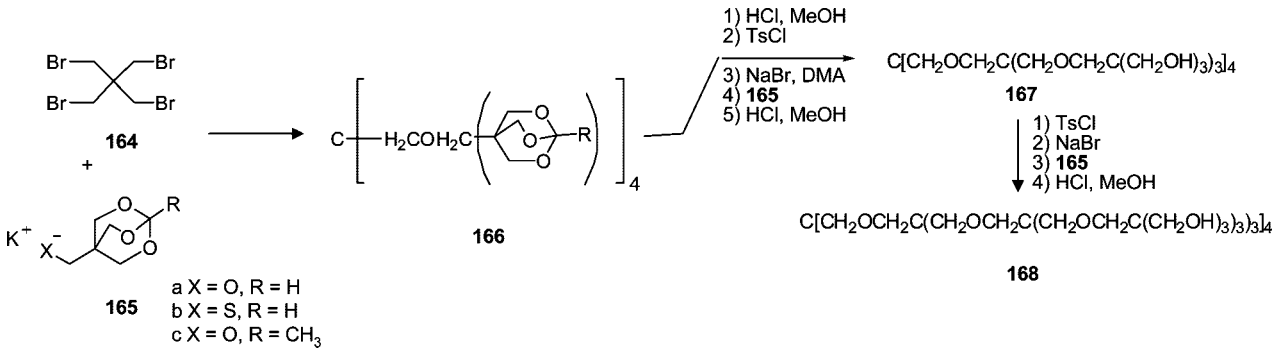


Scheme 35. Construction[622] of Air-Stable Polyoxometalate-Cored Dendrimers

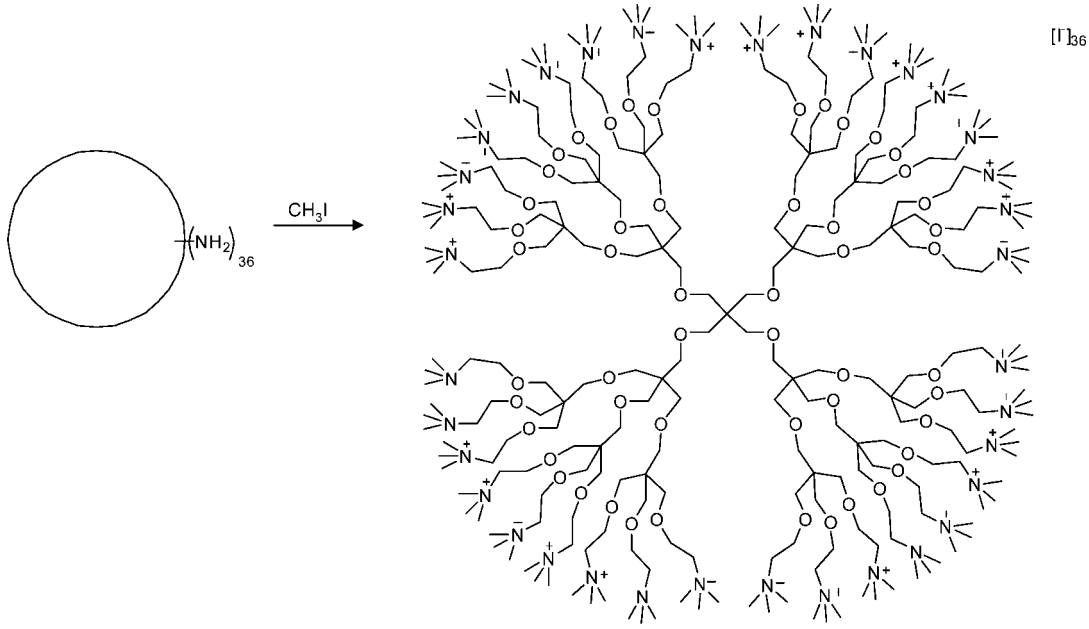


$OCH_2]_3CCH_2OCH_2(C_6H_4)CH_2OCH_2C[CH_2O(CH_2)_2N^+Me_3]_3$ in a five-step sequence.[639] Similarly, $O[CH_2C(CH_2OH)_3]_2$ was converted into $O[CH_2C(CH_2OCH_2CH_2N^+Me_3)_3]_2$.[639] The treatment of pentaerythritol with chloroacetyl chloride gener-

Scheme 36. Construction[634,635] of Highly Compact Pentaerythrityl-Based Dendrimers (166−168)



Scheme 37. Poly(ammonium iodide) Dendrimers[638] Prepared for Catalytic Ester Hydrolysis

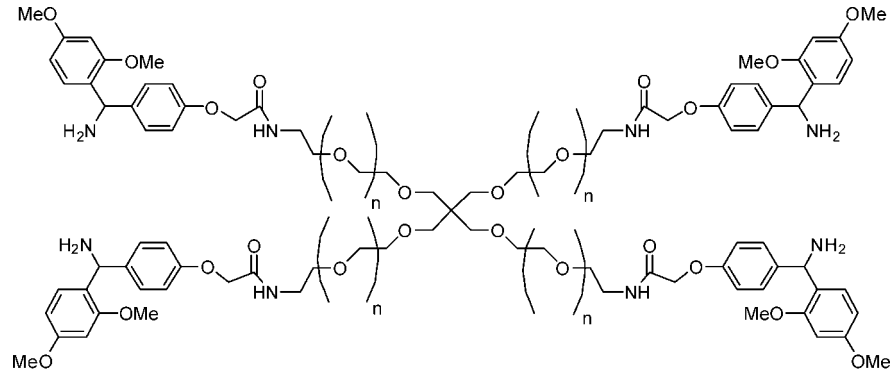


169

ated $C[CH_2O(C{=}O)CH_2Cl]_4$, which with sodium dithiobenzoate gave (95%) the desired $C[CH_2O(C{=}O)CH_2S_2CC_6H_5]_4$, as viscous red oil.[641] As an interesting core, $C(CH_2OCH_2C{\equiv}CH)_4$ was easily formed and utilized in a click coupling.[642] The use of pentaerythritol tetraacrylate (PETA) has also been described as a multifunctional Michael acceptor.[643]

The treatment of pentaerythritol with acrylonitrile in the presence of base gave the expected $C(CH_2OCH_2CH_2CN)_4$, which was hydrolyzed to the tetraacid, then to the corresponding acyl chloride, and last with pentachlorophenol to afford $C(CH_2OCH_2CH_2CO_2C_6Cl_5)_4$. Subjecting this activated tetraester with initially 3 equiv of $H_2NCH_2CON(OH)Me$, followed by 1 equiv of 9-(aminomethyl)anthracene generated the desired branched product via the 1 → 3 intermediate, $C_6Cl_5O_2CCH_2CH_2OCH_2C[CH_2OCH_2CH_2CONHCH_2CON(OH)Me]_3$,[644] demonstrating this to be a convenient route to diverse 1 → 3 branched monomers. Also mentioned was the use of $HSCH_2C(CH_2OH)_3$[645] to get to similar products via $RSCH_2C(CH_2OCH_2CH_2CN)_3$ and $RSCH_2C(CH_2OCH_2CH_2CO_2R')_3$, where $R' = Me$ or $-C_6Cl_5$.

Treatment of pentaerythritol with 3.1 equiv of acrylonitrile in base and then use of Fischer esterification conditions generated $HOCH_2C(CH_2OCH_2CH_2CO_2Me)_3$, which can be O-protected and then reduced to $ROCH_2C(CH_2OCH_2CH_2CH_2OH)_3$.[646,647] A series of oligonucleotide dendrimers possessing three-, nine-, or 27-arms have been reported and studied by Shchepinov et al.;[646−648] they proposed applications for oligonucleotide array/DNA chip technology.[649] A simple but interesting pentaerythritol-based dendron, $HOH_2CC[CH_2O(CH_2)_3CH{=}CH_2]_3$ (**170**), has been utilized in the construction of the first "Janus-like" supramolecular liquid crystals via the intermediate $[H_2C{=}CH(CH_2)_3OCH_2]_3CCH_2O_2C(CH_2)_3CONHC[CH_2O(CH_2)_2CO_2CMe_3]_3$, in which the olefin side is transformed by means of silylation chemistry and the ester side by tradition carbon conversions.[650] Treatment of pentaerythritol with 5-bromopentene in aqueous NaOH, catalyzed by (n-Bu_4NBr), gave an easily separable mixture of $C[CH_2O(CH_2)_3CH{=}CH_2]_4$ and $HOH_2CC[CH_2O(CH_2)_3CH{=}CH_2]_3$, whose focal position was extended with 5-bromopentanoic acid affording $Br(CH_2)_4CO_2H_2CC[CH_2O(CH_2)_3CH{=}CH_2]_3$; subsequent treatment with 4-hydroxy-4′-cyanobiphenyl created the desired mesogenic system.[651] Oxidation ($NaIO_4$, $RuCl_3 \cdot 3H_2O$)[652] of $Ph_2(t\text{Bu})SiOCH_2C(CH_2OCH_2CH{=}CH_2)_3$ gave (52%) $Ph_2(t\text{Bu})SiOCH_2C(CH_2OCH_2CO_2H)_3$, which was transformed into a cryptand.[653] The above dendron **170** was readily converted (PPh_3, I_2, imidazole; 90%) to $IH_2CC[CH_2O(CH_2)_3CH{=}CH_2]_3$,[654,655] which with PEG gave (80%) the two-directional bis-triolefin[656] that was successfully terminated with either a 1-thiolactose[657] or 2-acetamido-2-deoxy-1-thio-β-D-glucopyranoside.[658]



171

Figure 4. Kim's[663] multivalent soluble supports.

The attachment of pentaerythritol onto carbon nanotubes was demonstrated in which oxidized nanotubes were converted ($SOCl_2$) to the acyl chloride, then pentaerythritol was added at 70 °C to give the desired ester-connected triol; treatment with 5-norborene-2-carboxylic acid and then benzylidene-bis(tricyclohexylphosphine)rutheniumdichloride (1st generation Grubbs catalyst) created the catalyst-functionalized nanotubes.[659]

Early on, a series of related "cascadols", prepared from pentaerythritol, was reported[660] by the coupling of $C[(CH_2OCH_2)_2CH_2OH]_4$ as the core with 4 equiv of $[Ph_3COCH_2(CH_2OCH_2)_2]_3C(CH_2OCH_2)_2CH_2OMs$ as the branched monomer; limited supportive data are available. Tang et al.[661] successfully constructed a series of pentaerythritol-derived oligoglycols. Thus, the monoprotection of ethylene glycol with dihydropyran gave (84%) $HOCH_2CH_2$-OTHP, which with $C(CH_2Br)_4$ in the presence of NaH/diglyme afforded (53%) $BrH_2CC(CH_2OCH_2CH_2OTHP)_3$; subsequent addition of $PMBO(CH_2CH_2O)_2H$ gave (68%) $PMBO(CH_2CH_2O)_2H_2CC(CH_2OCH_2CH_2OTHP)_3$, which can be easily selectively deprotected by treatment with DDQ generating (68%) dendron $HO(CH_2CH_2O)_2H_2CC$-$(CH_2OCH_2CH_2OTHP)_3$. This 1 → 3 dendron was subsequently coupled with $C(CH_2Br)_4$ affording (37%) $C[CH_2O(CH_2CH_2O)_2H_2CC(CH_2OCH_2CH_2OTHP)_3]_4$, which was quantitatively terminally deprotected (cat. HCl/MeOH) giving $C[CH_2O(CH_2CH_2O)_2H_2CC(CH_2OCH_2CH_2OH)_3]_4$. Werner et al. created enzymatically degradable heparin−poly(ethylene glycol) gels from the commercially available hydroxyl-terminated available sPEG.[662]

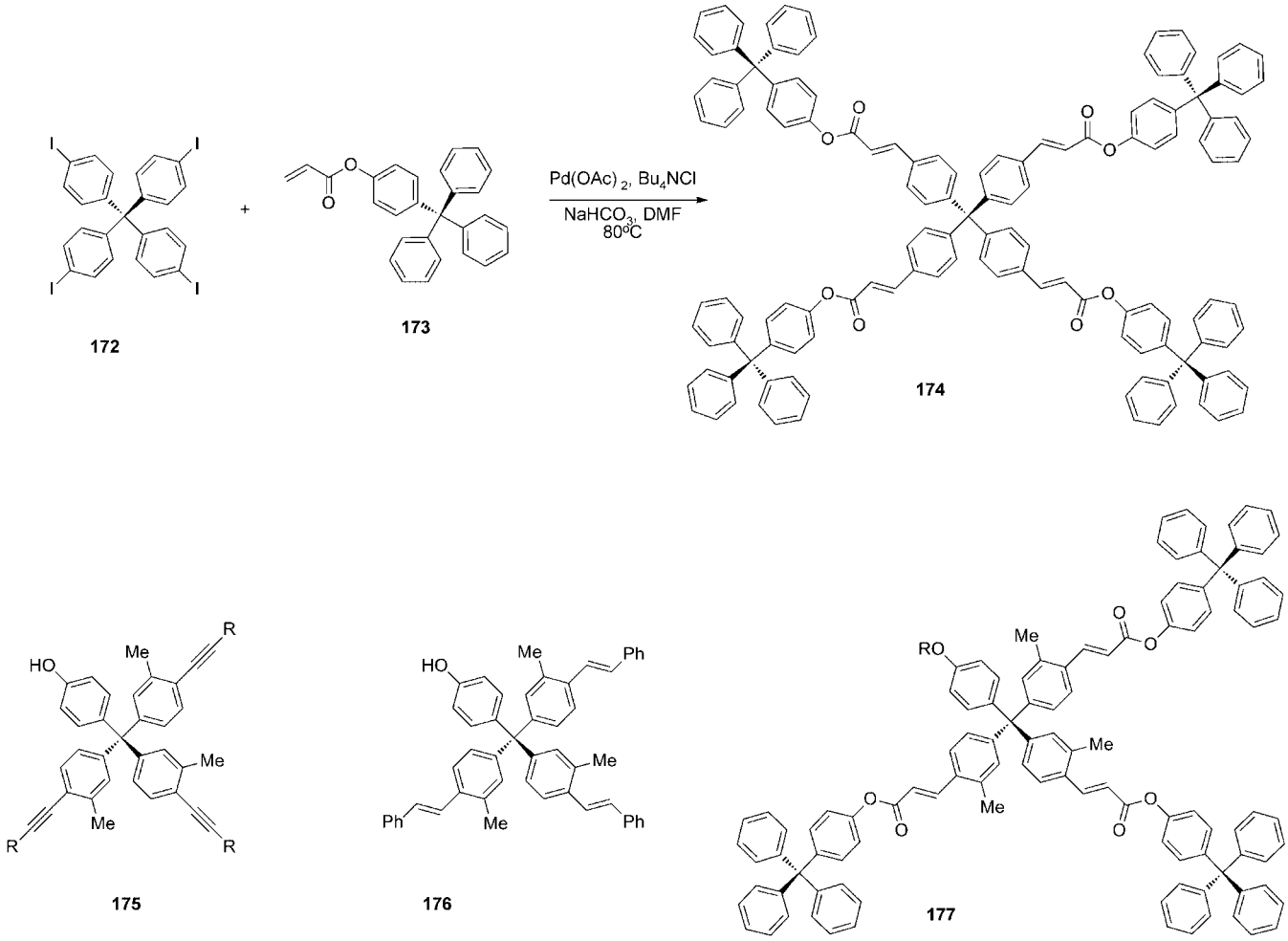
Kim et al.[663] employed a branched architecture in a process, termed "combinatorial synthesis on multivalent oligomeric supports", whereby multiple compound copies are constructed on soluble scaffolds via solution-phase synthesis, followed by size-based isolation. Although not strictly a dendrimer, tetraamine (**171**; Figure 4) was prepared from the commercially available tetravalent PEG oligomer, possessing an average molecular weight of 2000 amu. The hydroxyl termini were transformed to amines and coupled (diisopropyl carbodiimide) to an acid-functionalized, aminobenzylidine unit. These newly introduced amines were then used to prepare a library of di- and trisubstituted guanidines.

The commercially available dipentaerythrityl, $O[CH_2C$-$(CH_2OH)_3]_2$, is an interesting crowded bis(1 → 3)-core that has been transformed to $O[CH_2C(CH_2OCH_2CH_2N^+$-$Me_3)_3]_2$,[639] $O[CH_2C(CH_2N_3)_3]_2$,[664] $O[(CH_2CH_2O)_n$-$C(CH_2N_3)_3]_2$,[664] $O[CH_2C(O_2CCH_2N^+Me_2R)_3]_2$ (R = C_6, C_8, or C_{12}),[302] $O[CH_2C(CH_2O_2CPhHCSC(=S)SMe)_3]_2$,[665] $O[CH_2C(CH_2OC_6H_4R)_3]_2$ [where R = NO_2, NH_2, CHO, Br, I, CN, CH_2OH, $B(OH)_2$, 4,6-diamino-1,3,5-diaminotriazinyl-2-yl],[666,667] $O[CH_2C(CH_2O_2C$-3-pyridinyl$)_3]_2$,[668] $O[CH_2C(CH_2O_2CCH{=}CH_2)_3]_2$, and $\langle H_2C{=}HC(O{=}C)$-$OCH_2]_2(HOH_2C)CCH_2OCH_2C[CH_2O(C{=}O)CCH{=}CH_2]_3$,[669] as well as an amphiphilic hyperbranched polyetherealpolyol capable of conversion to stable nanocomposites via decomposition of the organometallic precursors.[670]

Hanessian et al.[671,672] have transformed pentaerythritol into a family of very useful 1 → 3 branched monomers, for example, $HOCH_2C(CH_2N_3)_3$, $HOCH_2C(CH_2OCH_2CH_2N_3)_3$, and $CH{=}CHCH_2OCH_2C(CH_2OCH_2CH_2NH_2)_3$. *Note: care must be exercised handling polyazides, since there are reported examples of detonation*. The triprotection of pentaerythritol easily gives $HOCH_2C[(CH_2O)_3CMe]_3$,[673] which permits selective functionalization at one arm, then deprotection of the ortho ester and simple conversion to a series of useful reagents: $HOCH_2C(CH_2NH_2)_3$,[673] $ROCH_2C$-$(CH_2OSCN)_3$, $C_6H_5CH_2OCH_2C(CH_2SH)_3$, and $CH_2{=}CHCH_2$-$OCH_2C(CH_2SH)_3$.[674] The related 1 → 3 monomer, $TBSOCH_2C(CH_2OCH_2C{\equiv}CH)_3$, has been synthesized and utilized in click-related construction;[642,675] the pentaerythritol allyl ether $[HOH_2CC(CH_2OCH_2CH{=}CH_2)_3$, TAE][676] and $IH_2CC(CH_2CH{=}CH_2)_3$[656] are also available and can be transformed to the corresponding saccharide. Another simplified monomer is $HOH_2CC(CH_2Br)_3$, which is commercially available and used as a flame retardant.[677] The first synthesis of a "Majoral-type" glycodendrimer possessing covalently bound α-D-mannopyranoside residues via the $-OC(CH_2N_3)_3$ termini and utilizing a click procedure has been reported.[678] A useful 1 → 3 branched monomer, $(i\text{-}Pr)_2NP$-$(OCH_2CH_2CN)OCH_2C[CH_2O(CH_2)_3OR]_3$, has been utilized in the solid-phase synthesis of multivalent glycoconjugates on a DNA synthesizer.[679] Pentaerythritol has been easily converted[680] to series of useful 1 → 3 C-branched monomers for dendrimer construction: $HOH_2CC(CH_2Cl)_3$, $CH_2{=}CHCH_2COCH_2C(CH_2Cl)_3$, $CH_2{=}CHCH_2COCH_2C$-$(CH_2OH)_3$, $Me_3SiC{\equiv}CCH_2OCH_2C(CH_2Cl)_3$, and $HC{\equiv}CCH_2OCH_2C(CH_2Cl)_3$, as well as some diphosphino counterparts.

Constable et al.[681] created several interesting pentaerythritol-based metallodendrimers, in which initially 4′-chloroterpyridine[682] was treated with pentaerythritol in different ratios to give either $C(CH_2O$-tpy$)_4$, the core, or tpy-$OCH_2C(CH_2OH)_3$, the 1 → 3 C-branched monomer, which was transformed to the desired metallomonomer, $[(Cl_3Ru)$-

Scheme 38. Heck-Type Reaction Afforded Access to Tetraphenylmethane-Based Structures[684]



$tpyOCH_2C(CH_2OH)_3$]. Reaction of the core with four of these metallomonomers in the presence of a reducing environment gave $\langle C[CH_2O\text{-}tpyRu(II)tpy\text{-}OCH_2C(CH_2OH)_3]_4\rangle^{8+}$, which with $[tpyRu(II)tpy\text{-}Cl]^{2+}$ generated (25%) the desired $\langle C[CH_2\text{-}O\text{-}tpyRu(II)tpy\text{-}OCH_2C(CH_2O\text{-}tpyRu(II)tpy)_3]_4\rangle^{32+}$, which is soluble in MeCN and polar organic solvents.

Kim, Aida, et al.[683] reported the synthesis of dendritic scaffolds that demonstrated "remarkable dendritic effects on photoinduced charge separation"; their "Py2F3" ligand was derived from a 1 → 3 C-branched TRIS monomer possessing one Fréchet dendron with two directed pyridine moieties and three fullerene units.

2.6. 1 → 3 C-(Tetraphenylmethane) Branched, Alkene and Ester Connectivity

Sengupta and Sadhukhan[684] described the assembly of tetraphenylmethane-based architectures (Scheme 38) employing a 4-fold Heck reaction (Jeffery's conditions)[685] to give the best results; tetrakis(4-iodophenyl)methane[684,686,687] (**172**) was coupled to the activated alkene **173** to afford the G1 dendrimer **174**. The reaction was also conducted using the corresponding tetradiazonium salt in place of the iodo monomer. Several 1 → 3 tetraphenylmethane dendrons (e.g., **175**−**177**) possessing diverse functionality were reported. The attachment of a *tert*-butyl derivative of **177** to 9,10-di(chloromethyl)anthracene has been accomplished, and the resultant dendrimer underwent energy transfer from the peripheral stilbene units to the internal core.[688] The dendron, 4-[tris[3′-methyl-4′-(ethynylphenyl)phenyl]C]phenol, was also reacted with 9,10-bis(chloromethyl)anthracene to generate (54%) the related, rigid 9,10-bis[4-[tris[3′-methyl-4′-(ethynylphenyl)phenyl]C]phenoxymethyl]anthracene.[689] To further expand the connectivity, the three-directional core, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, was used to generate the desired rigid G1 dendrimer in 33% yield.[690] Hatano and Kato[691] created a novel compressed series of rigid family; treatment of 1,4-di(methoxycarbonyl)benzene with $MeOC_6H_4MgBr$ gave (78%) the desired intermediate diol, which was reacted with phenol in the presence of acid, followed by BBr_3 to deprotect and generate $[HO\text{-}(C_6H_4)]_3C(C_6H_4)_nC[(C_6H_4)OH]_3$ in 63% yield; these were last capped with Percec's dendron (3,4,5-tridodecyloxybenzyl; section 9.1). The related polyphenyls (n = 2,3) and 5,5′-(2,2′-dipyridino) core were also prepared in good overall yields.[691]

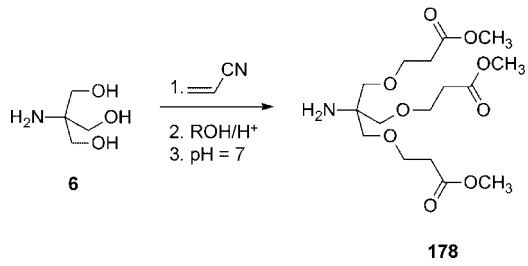
Related material tetrakis(4-iodophenyl)methane[692] has been subjected to either the Pd-catalyzed Heck couplings with styrene, pentafluorostyrene, and 4,4′-*tert*-butylvinylstilbene to yield the corresponding polyalkenes[693] or the Jeffery's phase transfer conditions[685] with excess allyl alcohol to produce the sensitive tetrakis(2-formylethyl) derivative.[686] The synthesis and use of the related 4-tris(4′-iodo-3′-methylphenyl)methylphenol have been described.[694,695] The use of the related and easily prepared tetrakis(4′-aminophenyl)methane in porous organic polymers has been reported;[696,697] this tetraamine makes an ideal core for related materials. Treatment of tetraphenylmethane with bromine in the presence of iron fillings gave tetrakis(4-bromophenyl)-

methane, which was treated with TMS-protected acetylene via a Sonogashira reaction, followed by deprotection affording tetrakis(4-ethynylphenyl)methane in 65% overall yield.[698,699] When tetrakis(4-cyanophenyl)methane[700] is treated with anhydrous $ZnCl_2$ at 400 °C for 48 h, a 3D porous black rock-like network was created and shown to be a novel hyperbranched construct comprised of tetraphenylmethane moieties connected by triazine rings.[701] The use of the starting material, tetrakis(4-iodophenyl)methane, has been shown to give either 4-[2-(4-formylphenyl)ethynyl]phenyltris[4-(2-(pyridinyl)ethynyl)phenyl]methane or 4-ethynylphenyl-tris[4-(2-(4-pyridinyl)ethynyl]phenyl]methane in two or three steps, respectively; the introduction of a porphyrin moiety and a fulleropyrrolidine was accomplished, and the construct was used as a model for light harvesting.[702]

2.7. 1 → 3 C-Branched, Ether and Amide Connectivity

Using a series of simple 1 → 3 C-branched monomers,[213] a diverse collection of dendritic macromolecules has been devised and easily prepared. The ethereal amine building block **178** (i.e., tris[(carbethoxy)ethoxymethyl]aminomethane; "Lin's amine") was easily prepared[703] in two steps from initially TRIS (**6**) and acrylonitrile via a Michael-type addition, followed by ethanolysis (Scheme 39). Although there is a small amount of N-addition, the major product resulted from O-addition. The corresponding *tert*-butyl ester derivative and related nitrile have also been prepared[704,705] from TRIS and *tert*-butyl acrylate and acrylonitrile in 38% and 71% yields, respectively. Cardona and Gawley utilized this monomer to convergently[704] generate a G2 dendron with the *tert*-butyl triester.

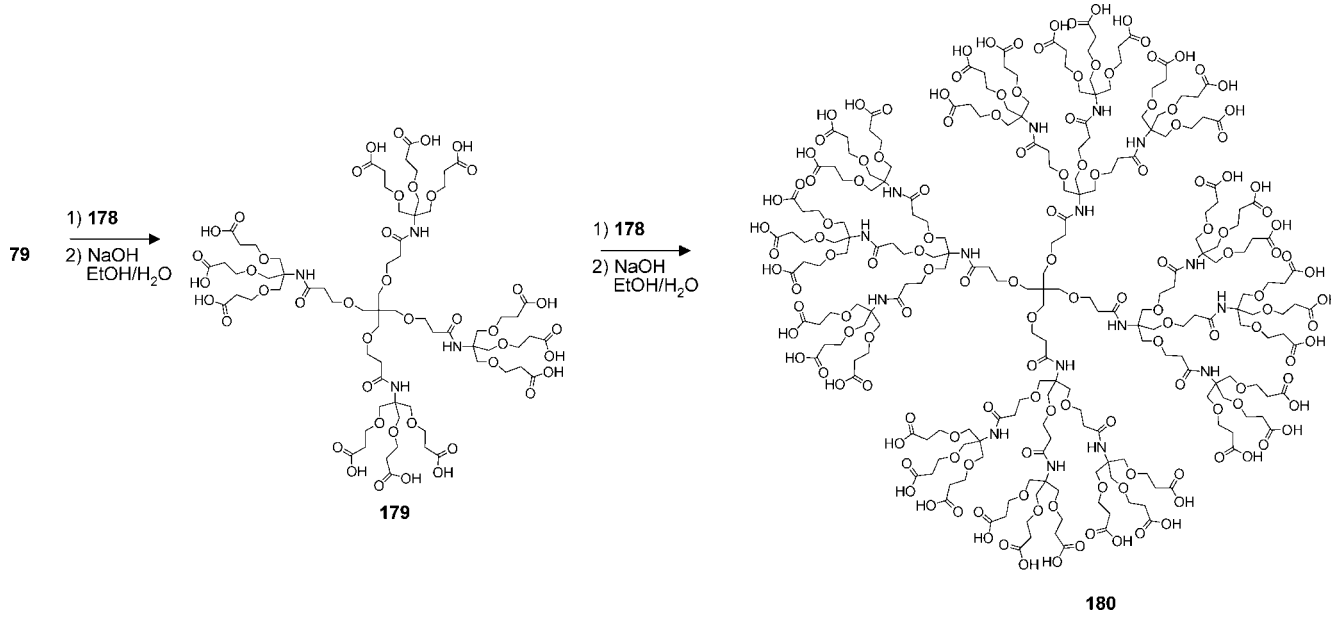
Scheme 39. Preparation of the Core and Lin's Amine (178)[703]



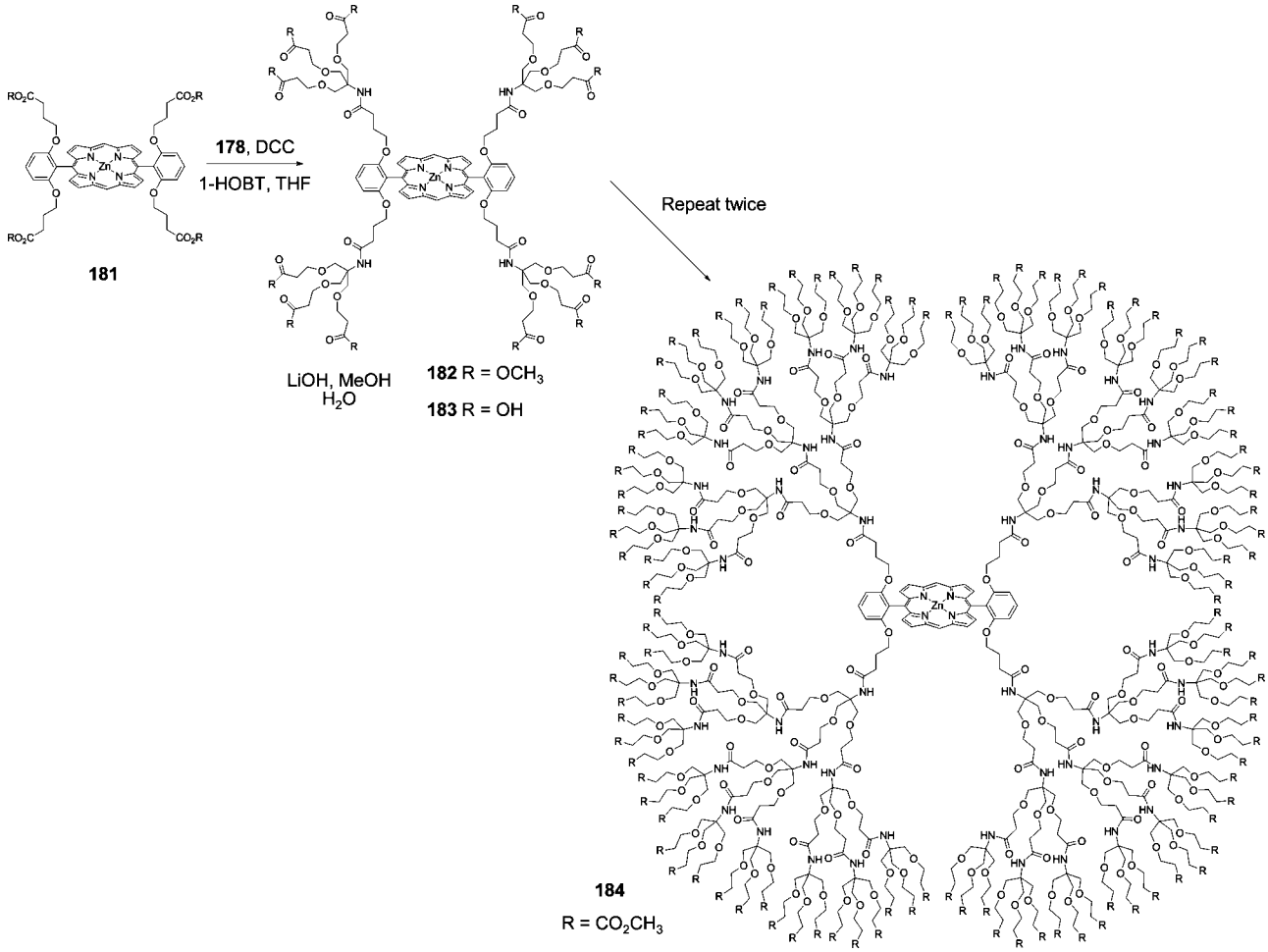
The core was similarly synthesized[703] by the treatment of pentaerythritol with a slight excess of acrylonitrile to afford (76%) the $C(CH_2OCH_2CH_2CN)_4$,[478] which was refluxed in anhydrous MeOH saturated with dry HCl to give (85%) $C(CH_2OCH_2CH_2CO_2Me)_4$; sequential hydrolysis gave the corresponding tetraacid, and then with $SOCl_2$ the desired $C(CH_2OCH_2CH_2COCl)_4$ was generated in high overall yield. Treatment of this tetraacyl chloride **79** with the ethereal amine **178** gives the dodecaester; subsequent saponification afforded (84%) the corresponding dodecaacid **179** (Scheme 40). Additional tiers, such as the G2 36-cascade:methane[4]:(3-oxo-6-oxa-2-azaheptylidyne)^2:4-oxapentanoic acid (**180**), were prepared by the use of standard peptide coupling conditions (DCC/1-HOBT/DMF) giving rise to the poly(ethereal-amido) cascade series.[703] The $C(CH_2OCH_2CH_2CN)_4$ was readily reduced to the readily accessible and useful ethereal $C[CH_2O(CH_2)_3NH_2]_4$ core;[706,707] an improved procedure to this pivotal core was reported but via the corresponding tetraacid, tetraol, tetramesylate, and tetraazide, followed by reduction to the desired tetraamine in excellent overall yield.[708] In 1991 for the first time, the G1 and G2 members of this achiral dendrimer family were coated with chiral moieties, for example, tryptophan, demonstrating the relationship between molecular ellipicity and the number of surface chiral sites.[709]

The initial acrylonitrile and TRIS product $H_2NC(CH_2OCH_2CH_2CN)_3$[213] has been utilized as a simple 1 → 3 C branching monomer, which with succinic anhydride quantitatively gave $HO_2CCH_2CH_2CONHC(CH_2OCH_2CH_2CN)_3$.[710] Lastly, esterification followed by reduction ($NaBH_4$, $NiCl_2$, MeOH), Boc-protection, and saponification gave the desired $HO_2CCH_2CH_2CONHC[CH_2O(CH_2)_3NHBoc]_3$ in excellent overall conversion. The repetitive coupling of this dendron to a CutiCore resin greatly enhanced loading capacity and was thus shown to be useful in solid-phase peptide syntheses.[710] The initial $H_2NC(CH_2OCH_2CH_2CN)_3$ has been transformed in high yield to the protected $ZHNC(CH_2OCH_2CH_2CH_2NH_2)_3$ or $BocHNC(CH_2OCH_2CH_2CO_2H)_3$;[711] similar chemistry gave rise to the G2 dendrons, which were capped with chlorambucil residues for the preparation of antibody−multidrug

Scheme 40. Preparation of Poly(ethereal amido) Cascades Employing a TRIS-Based Aminotriester Monomer[703]



Scheme 41. Zn-Porphyrins Provide Unique Cores[742] for the Study of Electron Transport through Dendritic Superstructures



immunoconjugates. The related $BocHNCH_2CH_2CONHC(CH_2OCH_2CH_2CONHCH_2C{\equiv}CH)_3$ has been a useful monomer in the study of interactions of oligomannose dendrons with human monoclonal antibodies 2G12 and DC-SIGN.[712]

The use of the Lin-based TRIS scaffolds in diverse applications has appeared: using the G1 dendron for collagen-like triple helices,[713] promoting water-solubility for a synthetic lectin analog for biomimetic disaccharide recognition,[714] making a bridge between a Gd complex and surface glucose or galactose termini,[715] permitting a rapid generation of trivalent antigens for the degranulation of mast cells,[716] enhancing solubility of Pt porphyrin in phosphorescence quantum yield experiments,[717] studying the electrochemical behavior of redox-active cores,[718] using Gly-Pro-Nleu and Gly-Nleu-Pro sequences to create collagen mimetics,[719] allowing H-bonding within a dendritic environment and studying the optical behavior of focally placed tryptophan in biological systems,[720] carbohydrate recognition in water by a tricyclic polyamide receptors possessing four G1 dendrons,[721] using glycolipids containing a cluster galactoside moiety for the hepatic asialoglycoprotein receptor and bile acid ester moiety for liposome incorporation,[722] enabling dPEGylation reagent for commercial applications,[723] detecting microenvironmental H-bonding effects on tryptophan fluorescence (G1 and G2),[724] synthesizing dendron (G1 and G2) metalloglycodendrimers terminated with mannose, glucose, or galactose,[725−727] allowing binding of DNA with G1 and G2 dendrons terminated with spermine[728,729] and their *in vitro* delivery of DNA when administered with chloroquine,[729] conjugating G1 and G2 dendronized oligoguanidines with fluorescein or green fluorescent protein mutant as molecular cargoes,[730] modifying beads to be effective in binding proteins, such as glutathione-*S*-transferase and fused proteins, as well as suppress the nonspecific binding of proteins,[731] effective G1 and G2 dendron protection of encapsulated gold nanoparticles,[732] creating a series of neutral dendritic metallomacromolecules using −[tpyRu(II)tpy] connectivity,[733,734] analyzing the water-soluble diethylenetriaminepentaacetic acid Gd^{3+} complex core G1 and G2 dendrons,[735] metallophthalocyanines with G1 and G2 dendrons,[736] forming G1−G3 dendronized bipyridine, which was subsequently transformed to a Ru(II)-cored metallodendrimer,[737,738] detecting bathochromic shift of the fluorescence emission using the dansyl moiety with increasing generation (G1−3),[739] synthesizing fluorescent sensors with dendronized pyrene,[740] and stabilizing gold−silica nanoshells in cell culture media and tracking nanoparticles in mammalian cell cultures.[741]

Diederich et al.[742] reported the divergent synthesis of dendrimers possessing porphyrin cores with the aim of modeling redox potentials of electroactive chromophores via environmental polarity modification. These dendrimers can be considered as electron-transfer protein mimics, for example, proteins such as cytochrome *c*; oxidation potentials for cytochrome *c* in aqueous solution are known to be 300−400 mV more positive than those reported for similarly ligated heme mimics lacking hydrophobic peptide encapsulation.

The iterative route to these porphyrin-core dendrimers employed the readily available ethereal building block **178**.[703]

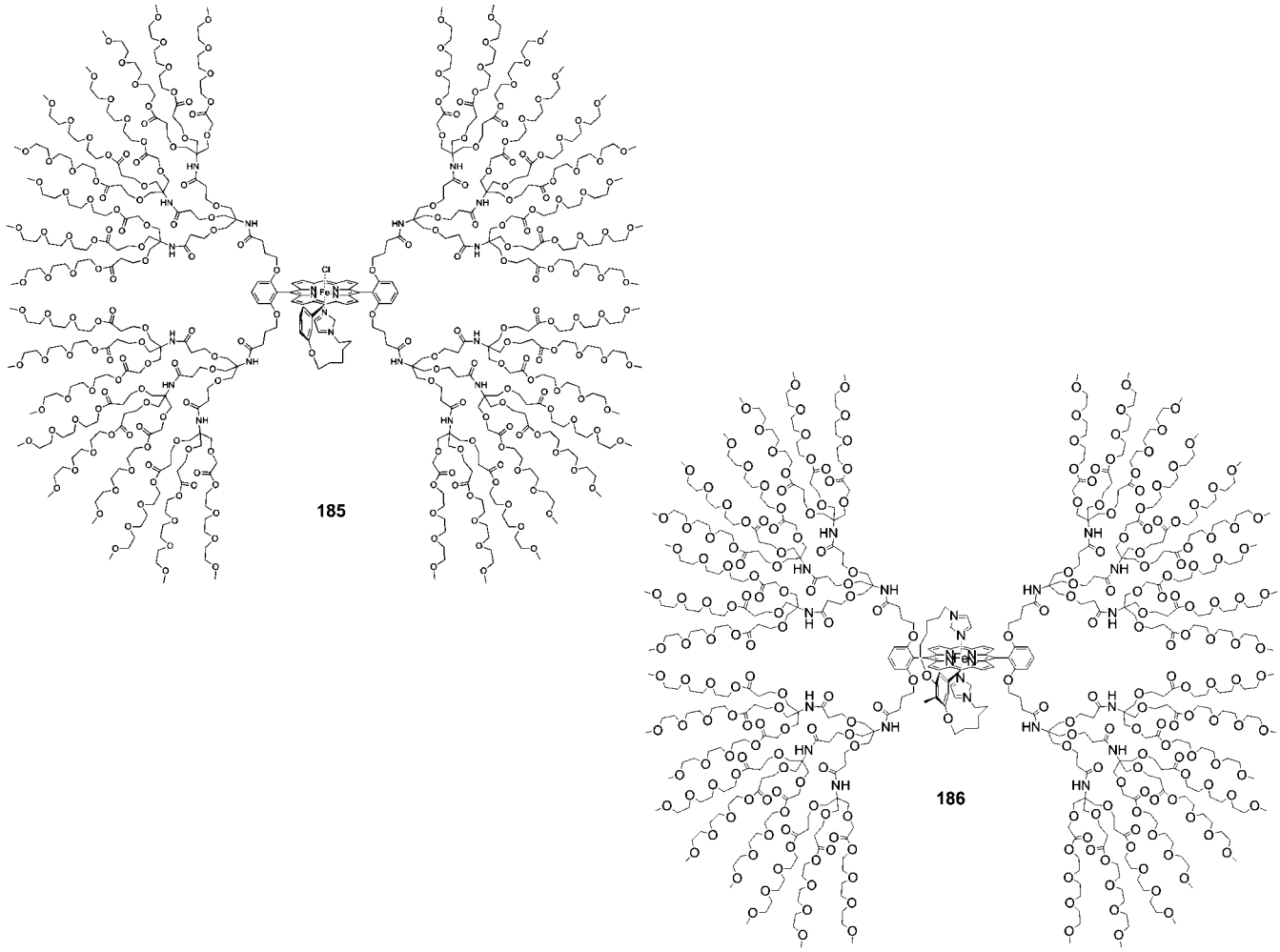


Figure 5. Novel dendronized porphyrins that were models for heme monooxygenases[577] and cytochromes.[578]

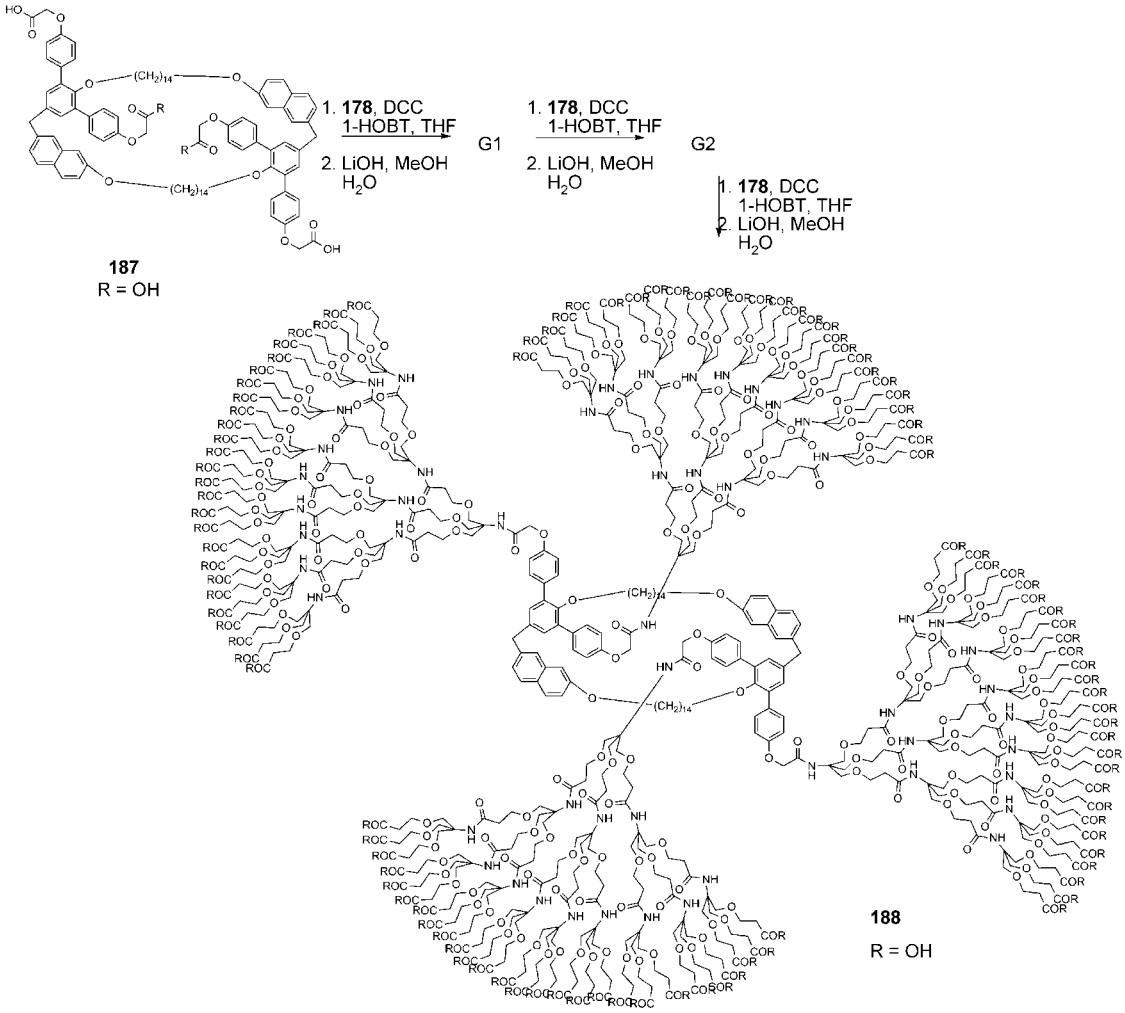
Thus, amine acylation (DCC, 1-HBT, THF) of monomer **178** (Scheme 41) with tetraacid **181** afforded the G1 dodecaester **182**, which upon termini saponification (LiOH, MeOH/H_2O) gave the polyacid **183**. Repetition of this sequence allowed the construction of two additional tiers, for example, ester **184**. Dendrimer characterization was accomplished by ^{13}C, ^{1}H NMR, and FT-IR spectroscopy, as well as mass spectrometry using FAB and MALDI-TOF MS techniques. Molecular ion base peaks were observed in the MALDI-TOF for polyester **184** [18 900 amu (calcd. 19 044 amu)] along with minor peaks at ~37 000 amu and ~54 000 amu corresponding to ionic gas-phase dimer and trimer complexes.

The CV of the Zn-porphyrin dendrimers in THF and CH_2Cl_2 with [$Bu_4N^+PF_6^-$] (0.1 M) electrolyte revealed first oxidation potentials up to 300 mV (THF) less positive than the corresponding values obtained for the "unshielded" tetraester Zn-porphyrin core. These preliminary electrochemical experiments suggested dendritic encapsulation of redox-active chromophores could effectively influence the electrophoric environment; controlled and well-conceived cascade architectures can lead to new avenues of selective redox catalyst design. The structure−property relationships in dendritic encapsulation have been reviewed by Gorman and Smith.[743]

A series of dendronized iron(II) porphyrins with an axial imidazole attached to the porphyrin core were synthesized; the exterior termini were derived from Lin's amine with a tri(ethylene glycol) monomethyl ester component to instill water solubility. These porphyrins with controlled axial ligation at the iron center possess a vacant coordination site available for ligand binding; thus, they were shown with one tethered imidazole (**185**) to form NO complexes[575] and were models for (1) heme monooxygenases[577] with two tethered imidazoles, (2) cytochromes,[578] and (3) *T*-state hemoglobin and myoglobin in the presence of 1,2-dimethylimidazole (**186**) (Figure 5).[576] Two types of polyPEGed cobalt(II) porphyrins[568,570,744] were prepared and investigated (CW, ENDOR, EPR, and HYSCORE) in the presence of 1,2-dimethylimidazole, pyridine, and 1-methylimidazole;[579] their resultant data showed that there was an increased ionicity in the cobalt−dioxygen bond in the [porphyrin−Co(II)−dimethylimidazole]−O_2 complex.

Modarelli et al. synthesized a series of porphyrin dendrimers possessing G1−G3 dendrons derived from Lin's amine possessing 2-methylanthroquinone termini;[745] these dendrimers underwent rapid through-space photoinduced electron transfer. The zinc porphyrin containing these ethereal dendrons exhibited almost complete quenching of the porphyrin fluorescence; an intramolecular electron-transfer was proposed.[746] There have been few studies in which the effects of different dendrons were evaluated. Vinogradov et al. reported the oxygen quenching constants of selected phosphorescent palladium porphyrin cores possessing different dendrons;[747] the composition of the dendrons and solvent effects were major influences on the molecular encapsulation. The comparison of G4 polyglutamic porphyrin dendrimer

Scheme 42. Dendrophane Construction[754,756]



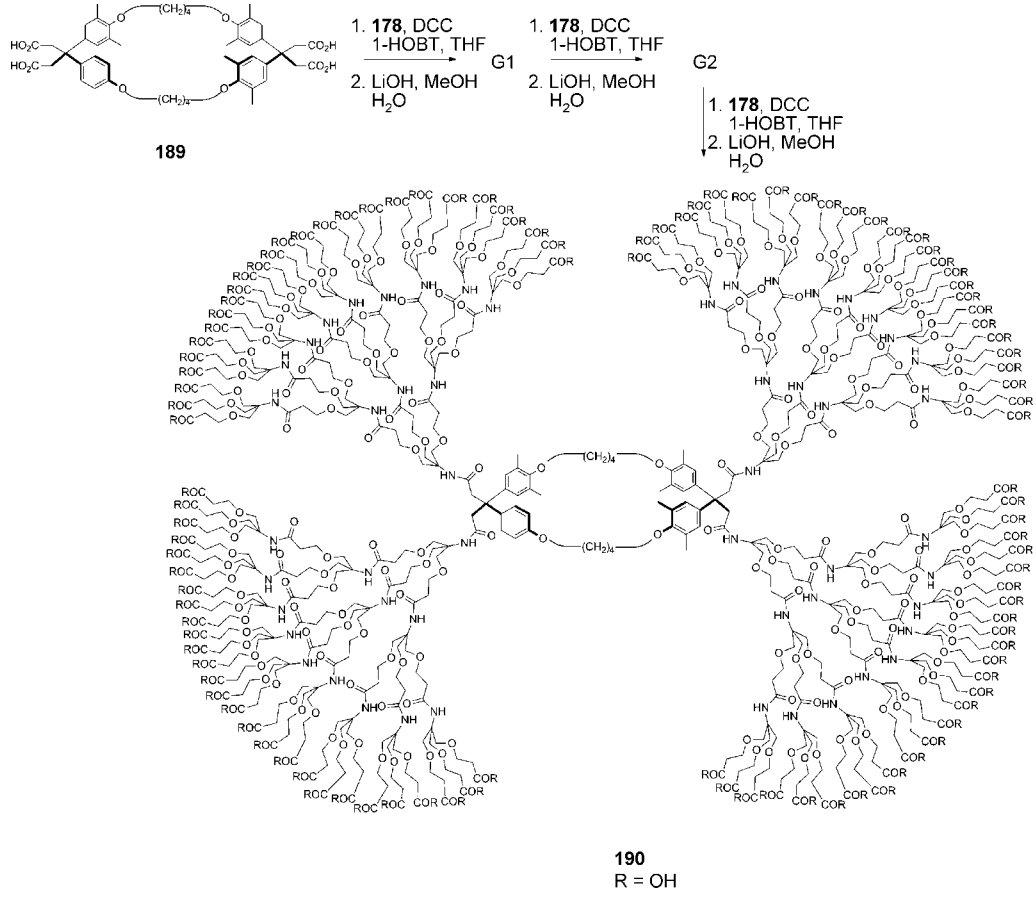
with 64 terminal carboxylates to the G1 poly(ester amide) tetrabenzoporphyrin dendrimer with 36 peripheral carboxylates was reported in which both had very similar p*K*'s (ca. 6.2 and 6.3, respectively) suggesting a significant electrostatic shielding of the core by the termini. Since these dendrimers cannot penetrate through phospholipid membranes, when the polyglutamic dendrimer was captured inside phospholipid liposomes (which were subsequently suspended in solution possessing the G1 dendrimer), upon pH changes in the bulk solution, the only response was from the external dendrimer.[748,749] These results suggested that porphyrin dendrimers can be utilized as fluorescent pH indicators for gradient measurements. Also see their interesting work of dendronized porphyrins and tetrabenzoporphyrins for related synthetic details.[750,751]

Small C_{60} adducts have been terminated with Lin's monomer, then transesterified with 11-[(4′-cyano-4-biphenyl)yl]-1-undecanol[752] affording initial insight into the thermotropic behavior of fullerene derivatives.[753]

Similar dendron monomers have been used to prepare "dendrophanes",[754] which possess an internal cyclophane core. A short perspective by Diederich and Felber has appeared[755] concerning the dendritic microenvironments, such as with these dendrophanes, dendroclefts, and dendronized porphyrins. Key reactions for core construction[756−758] included a Cs_2CO_3-promoted dimerization of hydroxynaphthalene benzyl ether to form the cyclic cavity. A 4-fold Suzuki cross-coupling introduced four phenolic moieties that were subsequently treated with $BrCH_2CO_2Me$ and saponified to yield the desired tetravalent core (**187**; Scheme 42), which was treated (DCC, *n*-BuOH) with monomer **178** to give the G1 dodecaester that was saponified (LiOH, THF/MeOH/H_2O) to afford (100%) the dodecaacid; subsequent repetition of these two steps gave the larger G2 and G3 family members (i.e., **188**) in reasonable yields. Inclusion complexes (1:1) with steroids were examined, and notably the dendritic shell remained open for molecular encapsulation. Iron(II) porphyrins were also prepared with four G1 and then G2 Lin's dendrons terminated with small PEG groups;[569] the equilibrium behavior of O_2 and CO binding was evaluated, in which their O_2 affinities were shown to be about 1500 times that of hemoglobin and "picket-fence" porphyrin.

Synthesis, binding properties, and crystallographic data of the core (Scheme 43), as well as that of other cyclophanes, for example, tetraacid **189**, have been reported.[759] Their use in the synthesis of the G3 dendrimers (e.g., **190**) that can act as water-soluble receptor models for globular protein recognition sites has been described.[756] Dendrons using the TRIS-based monomer **178**[703] were prepared[760] by amine protection (BzOCOCl) then saponification (NaOH, H_2O, MeOH) to give the corresponding triacid, and then coupling (DCC, HOBT, THF) with 3 equiv of amine **178** afforded the Boc-protected nonaester, which was hydrogenation (HCO_2NH_4, 10% Pd/C, EtOH) to give the G2 dendron **192**. Transformation to the nonaacid followed by treatment with more amine **178** gave the G3 wedge that was subsequently converted

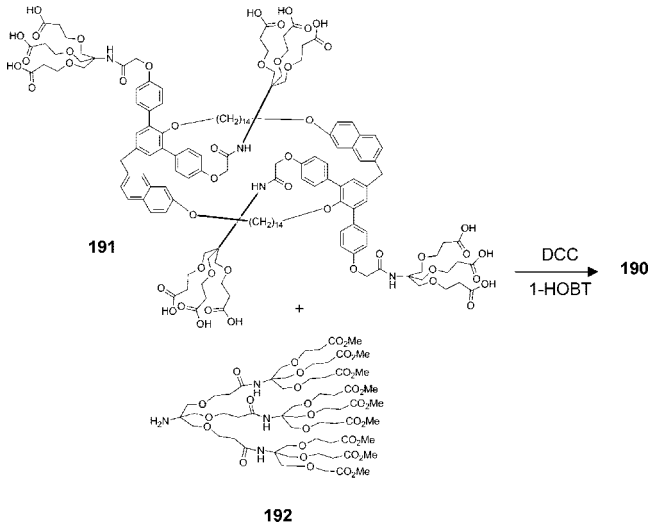
Scheme 43. Dendrophanes[756] That Are Capable of Complexing Flat Aromatic-Type Guests



to the free amino-27 dendron. The G3 dendrimer **190** was also prepared via a "semiconvergent" route (Scheme 44) where the G2 dendron[760] **191** was reacted with the G1 dendrophane **191**; spectra of this material proved to be identical to that produced by the divergent route. Attempted divergent preparation of the G4 dendrophanes was unsuccessful.

By use of the 6-(*p*-toluidino)naphthalene-2-sulfonate as a fluorescent probe for a series of dendrophanes possessing cyclophane core **189**, it was found that core micropolarity decreased as dendrimer size increased, that is, from H_2O to MeOH to EtOH from G1 to G3, respectively. A G1 water-soluble, nonionic dendrimer, based on core **189**[756] and possessing terminal tri(ethylene glycol) monomethyl ether moieties, was constructed for complex formation comparison to its carboxylic acid analogue; stability of the naphthalenediol complexes in buffered D_2O was markedly reduced presumably due to cavity occupation by the less polar PEG units. Dendrophanes, prepared using core **187**, were examined for their capacity to complex testosterone; for all cases, binding constants were determined.

Scheme 44. Semiconvergent Protocol for Construction of the Third Tier Dendrophanes[756]

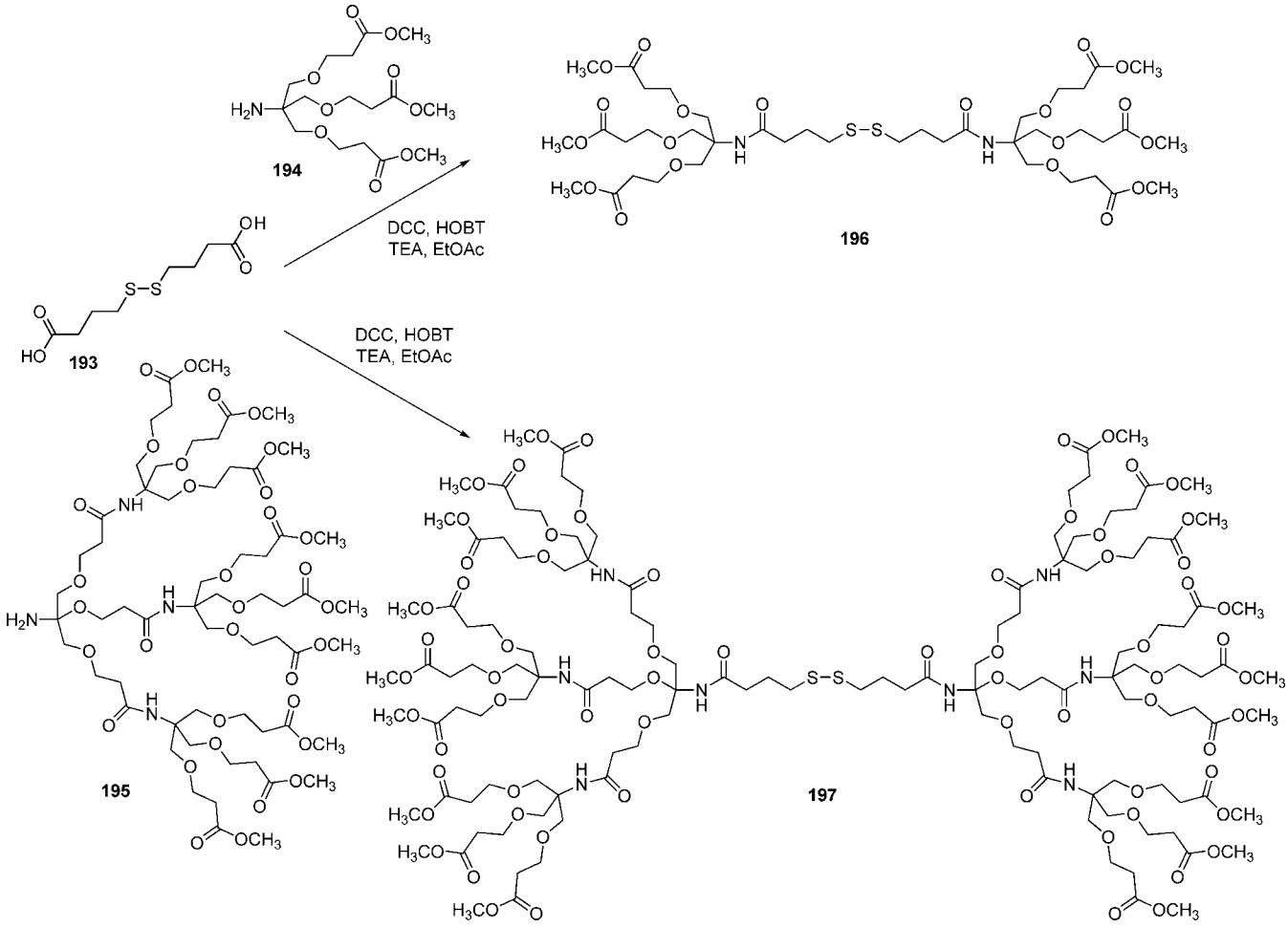


The G2 dendron **192**[760] was converted to the nonaacid, which was allowed to form a molecular layer on an aminosilylated surface via multipoint ionic interactions;[761] tapping mode AFM showed individual dendrons self-assembled on the aminosilylated surface.

Kayser, Altman, and Beck[762] constructed a hexaalkynyl α-amino acid, accessed via Pd-mediated coupling of *p*-ethynylphenylalanine to hexabromobenzene, and then the exterior was modified with ethereal aminotriester **178**,[703] as well as lysine monomers analogous to that of Denkewalter[763] and Shao and Tam.[764]

A pyrene-tethered tripodal triether-acid chelator, utilizing the Lin's amine (**178**), has been reported;[765] the complexation with Eu^{3+} generated an "antenna effect" between the pyrene chromophore and Eu^{3+} ion core. The G2 dendron possessing a pyrene focal substituent, derived from 1-pyrenylbutyric acid, has also been prepared.[766] Other materials, for example, N-protected tryptophan and *N*-methyltryptophan,[724] have been dendronized with these ethereal dendrons and the fluorescence studies permitted the probing of the tryptophan's microenvironment. The complexation of Gd(III) has been realized using monomer **178** as part of the molecular

Scheme 45. Synthesis of Dendrons[732] Possessing a Thiol Focal Moiety



construct resulting in the formation of ZHNC[CH_2-$OCH_2CH_2CON(CH_2CH_2NCOsugar)_2]_3$.[767]

Perylenediimide dendrons, possessing *N*-[$CH_2(CH_2)_n$-$NHCOC(CH_2OCH_2CH{=}CH_2)_3$], where $n = 1$ or 2, have been described[768] and shown to form liquid crystalline phases;[769] the needed dendron, $H_2NCH_2CH_2NHCOC$-$(CH_2OCH_2CH{=}CH_2)_3$, for treatment with perylene-3,4,9,10-tetracarboxylic dianhydride was prepared by a Jones oxidation of $HOCH_2C(CH_2OCH_2CH{=}CH_2)_3$ to give the desired focal acid group, which was treated with $SOCl_2$, followed by ethylenediamine.

Treatment of dithiodibutyric acid **193** with either the G1 (**194**) or G2 (**195**) dendrons generated (27% or 65%) the two-directional ligands **196** and **197**, respectively (Scheme 45), which were each subjected to a solution of $HAuCl_4$ in EtOH while maintaining the S to Au ratio of 1:1; then a freshly prepared ethanolic $NaBH_4$ solution was rapidly added affording the gold nanoparticles.[732] These dendrons **194** and **195** were reported to be significantly more effective at protecting the encapsulated gold nanoparticles than the L-lysine-based dendrons.

The small G1 dendrimers, C[$CH_2OCH_2CH_2CONH$-$(CH_2OCH_2CHOR'CH_2OR)_3]_4$, where R = COC(Me)=$CH_2$, R′ = H, COCH=$CH_2$, COMe, or $CO(CH_2)_{14}Me$, possessing secondary and primary terminal hydroxy moieties have been reported and studied by photo-DSC.[770] The related C[CH_2-$OCH_2CH_2COCH_2CONH(CH_2OCH_2CH_2CONHCH_2CON$-$HC_6H_4SO_2R^*)_3]_4$, where R* = *R*,*R*-(NHCHPhCHPhNH_2), has been *in situ* transformed to the related Ru complex, which was demonstrated to possess high catalytic enantioselectivity in the asymmetric transfer hydrogenation of ketones and imines.[771]

The use of ferrocene as a core, utilizing 1,1′-bis(chlorocarbonyl)-[772] or 1,1′-bis(fluorocarbonyl)-ferrocene,[773] with monomer **178** or its G2 analogue gave rise to the desired ferrocene dendrimer **198** (Figure 6), whereas with $H_2NC[CH_2OCH_2CH_2CO_2(CH_2CH_2O)_3Me]_3$, the related G1 PEG counterpart was generated.[774]

The focal connection of the G2 and G3 dendrons derived from **178** to either coumarin or dansyl as fluorescent probes was accomplished and then attached to ArgoGel solid-phase synthesis beads.[775] Treatment of these functionalized beads with rhodamine demonstrated that rhodamine can penetrate throughout the beads to acylate the remaining sites.

Strumia et al. have treated C[$CH_2OCH_2CH_2$-$CONH(CH_2OCH_2CH_2CO_2H)_3]_4$ with 5-amino-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane in the presence of CDI in THF to generate a mixture of ester and amide connection thus leaving either amino or alcohol free functional groups at the termini, which subsequently were reacted with acryloyl chloride to generate the polyfunctionalized surface.[506] The preparation of $H_2NC(CH_2OCH_2CH_2CN)_3$,[213] H_2NC-$(CH_2OCH_2CH_2CO_2Me)_3$, and $H_2NC(CH_2OCH_2CH_2CO_2$-*t*-$Bu)_3$ and their treatment with 5-nitroisophthalic acid chloride afforded the corresponding 1 → (2 + 3) predendrons, which were catalytically reduced to the related amines or hydrolyzed/saponified to their carboxylic acids.[446] These monomers were next treated with either methyl biphenyl diisocyanate or

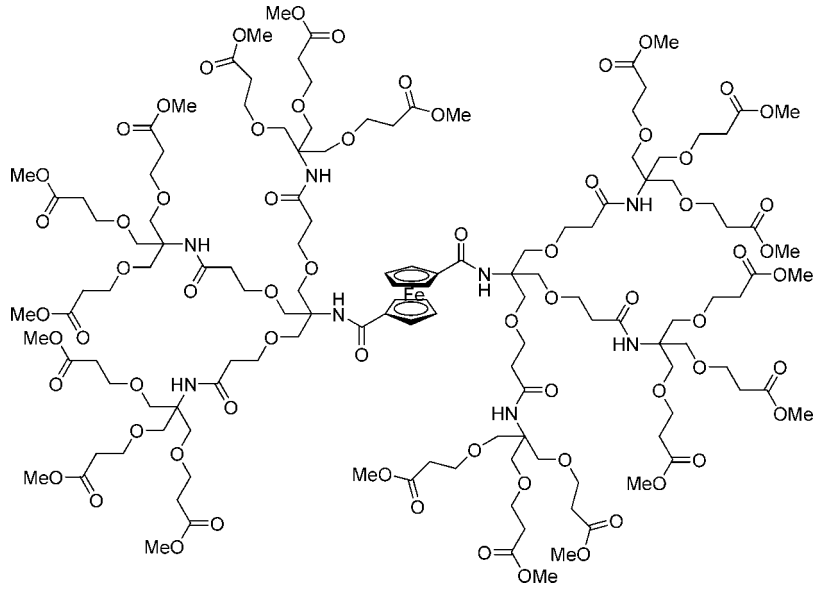


Figure 6. The dendronized ferrocene **198**.[774]

poly(monomethyl)itaconate to generate the corresponding MDI[444] and PMMI oligomers, also for functionalized supports with sugar dendritic ligands.[445]

Treatment of $C[CH_2OCH_2CH_2CONHC(CH_2OH)_3]_4$ with mixtures of aromatic urethane acrylates and octadecyl isocyanates gave a series of modifiers whose ratio of appendages can be adjusted to fulfill the requirements of UV-curable powder coatings.[776]

The polymer derived from 4,4′-di(hexafluoroisopropylidene)diphthalic anhydride and 3,5-diaminobenzoic acid was treated with either $H_2NC(CH_2OCH_2CH_2CN)_3$ or $H_2NC(CH_2OCH_2CH_2CO_2CMe_3)_3$; the dendron-modified polyimide forms robust multilayers with controlled porosity and refractive index.[777]

Ornelas and Weck reported[778] the use of the G2 dendron based on Behera's amine **40** to initially extend the focal site with $Fmoc(CH_2)_2O(CH_2)_2OCH_2CO$; then hydrolysis of the *tert*-butyl moieties and amidation with $H_2N(CH_2)_3N_3$ and deprotection of the Fmoc afforded $H_2N(CH_2)_2O(CH_2)_2$-$OCH_2CONHC[(CH_2)_2CONHC[(CH_2)_2CONH(CH_2)_3N_3]_3]_3$, which was subsequently used in the creation of a novel multifunctional dendrimer. Recently, the functionalization of these dendrons with PEG moieties using click chemistry afforded dendrons with a PEGylated surface without any metal contamination; their procedure is an excellent example of a "strain-promoted alkyne azide cycloaddition" affording macromolecules derived from mild and metal-free conditions, with no side-products, tolerance to functional groups, and in high yields.[779]

2.8. 1 → 3 C-Branched, Ether, Amide, and Urea Connectivity

Fromont and Bradley[780] transformed TRIS to the Lin's monomer [**178**; $H_2N(CH_2OCH_2CH_2CO_2Me)_3$], which was converted by treatment with $(Boc)_2O$ to the corresponding isocyanate [$O{=}C{=}NC(CH_2OCH_2CH_2CO_2Me)_3$]. This monomer was reacted with the aminomethylpolystyrene resin to generate a novel dendronized resin, which was subsequently capped with 1,3-diaminopropane in order to enhance the loading capability of the resin.[780] The construction of related dendronized resins has also been reported.[781]

2.9. 1 → 3 C-Branched, Ether, Amide, and Carbamate Connectivity

Smith et al. generated G1 and G2 spermine-terminated dendrons,[782] for example, G1 $BnO(O{=})CNC[CH_2$-$OCH_2CH_2CONH(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2]_3$, from Lin's amine and used the trifluoroacetyl protecting groups[783] to react with the cholesterol reagents[784] or a class II hydrophobin, a mesoscale surfactant protein from *Trichoderma reesei*,[782] as well as the extremely high, salt-independent binding affinities for DNA,[728] and protein−polymer conjugates.[785]

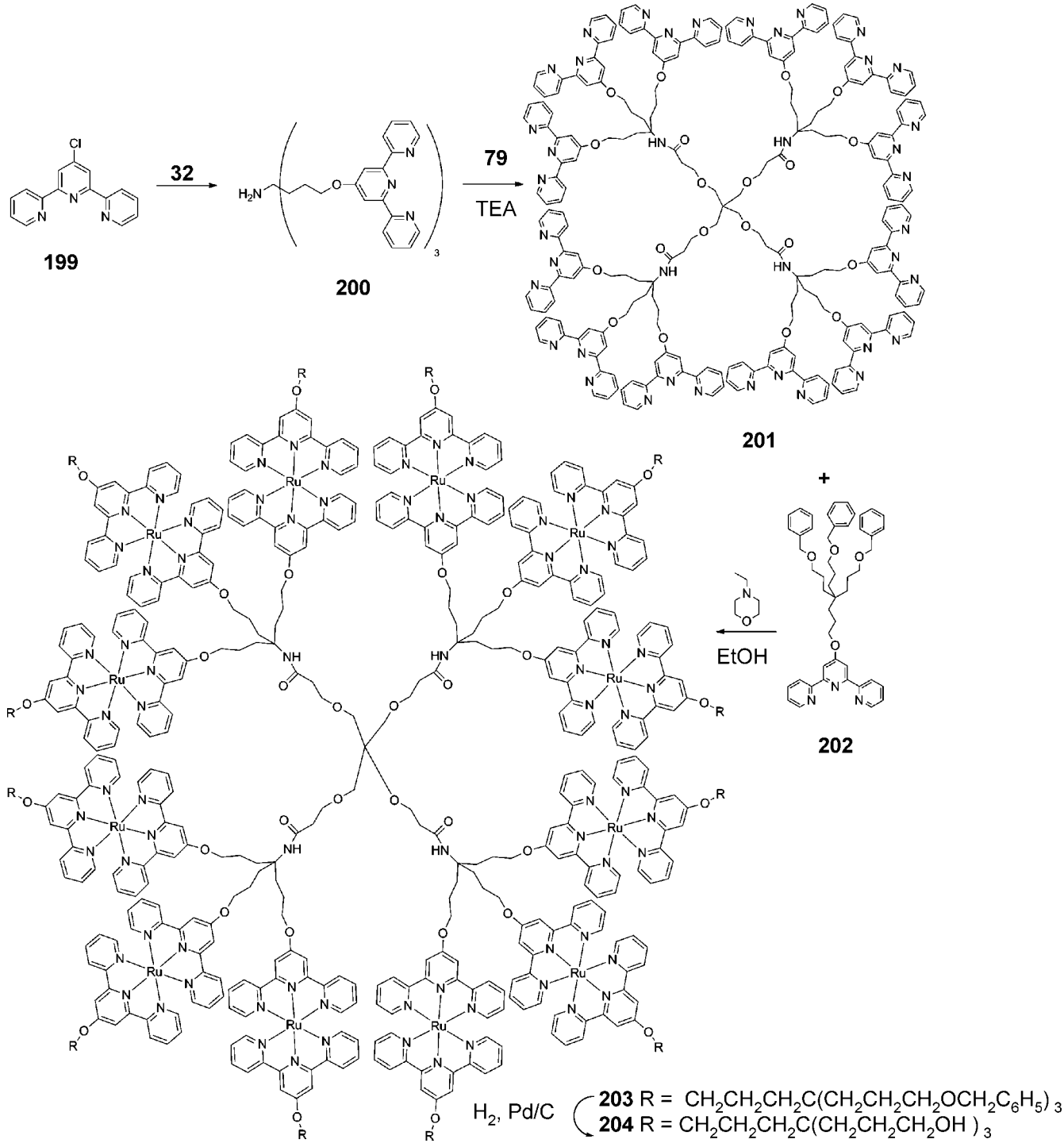
2.10. 1 → 3 C-Branched, Ether, Amide, Urea, and Carbamate Connectivity

Park et al.[786] prepared $FmocNH(CH_2)_6NHCONHC$-$[CH_2OCH_2CH_2CONHC(CH_2OCH_2CH_2CO_2H)_3]_3$, which was placed on a gold surface coated with 11-mercaptoundecylamine, then the residual surface amines were acetylated, and the Fmoc-protecting group was removed. Fluorescence data showed that amine/dendrimer density was 0.083 units per 100 Å^2. The dendrimer layer was treated with succinimidyl D-biotin to attach it to the free amino group; the streptavidin−biotin interactions were evaluated by means of surface plasmon resonance spectroscopy.

2.11. 1 → 3 C-Branched, Ether, Amide, and [Bisterpyridine Ru(II)] Connectivity

In 1993, the introduction of terpyridine−Ru(II)−terpyridine [tpy-Ru-tpy] connectivity in dendritic constructs was demonstrated[787] to be a very effective method to assemble dendrimers and linear macromolecules. Additionally, the metal center permitted the proof-of-structural purity, since the chemical shift data of the unsymmetrical, diamagnetic product along with the absence of uncomplexed starting ligands and paramagnetic reagent are structurally defining. Thus, the treatment of 4′-chloroterpyridine[682] (**199**) with amine **33**[682] predominately gave the O-substitution product **200**, and the core was assembled by subsequent treatment with $C(CH_2OCH_2CH_2COCl)_4$ (**79**), derived from the corresponding tetraacid,[502] affording **201**.[476,703] The second com-

Scheme 46. Assembly of Components to Generate the First Metallodendrimer[787] with [tpy-Ru-tpy] Connectivity

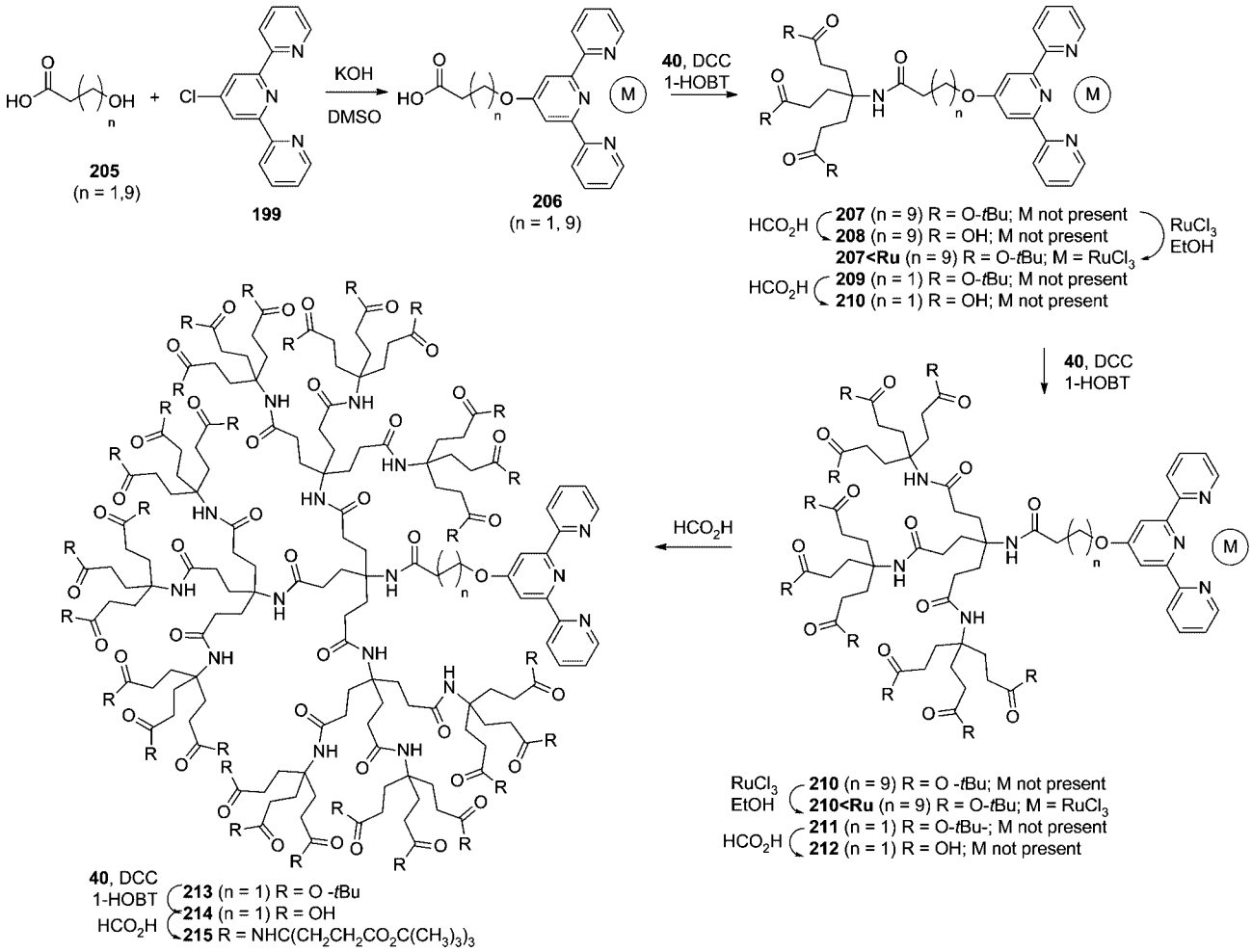


ponent was prepared by the reaction of $HO(CH_2)_3C[(CH_2)_3OCH_2C_6H_5)]_3$[557] with the same 4′-chloroterpyridine affording the desired 1 → 3-C branching ligand **202**, which was treated with $RuCl_3 \cdot 3H_2O$ generating the desired complex dendron; mixing a 1:4 ratio of core **201** to this $RuCl_3$ complex under reducing conditions generated (76%) the red crystalline, dodecaruthenium heteroleptic complex **203**.[787] Debenzylation under reductive conditions generated the polyol surface (**204**; Scheme 46).

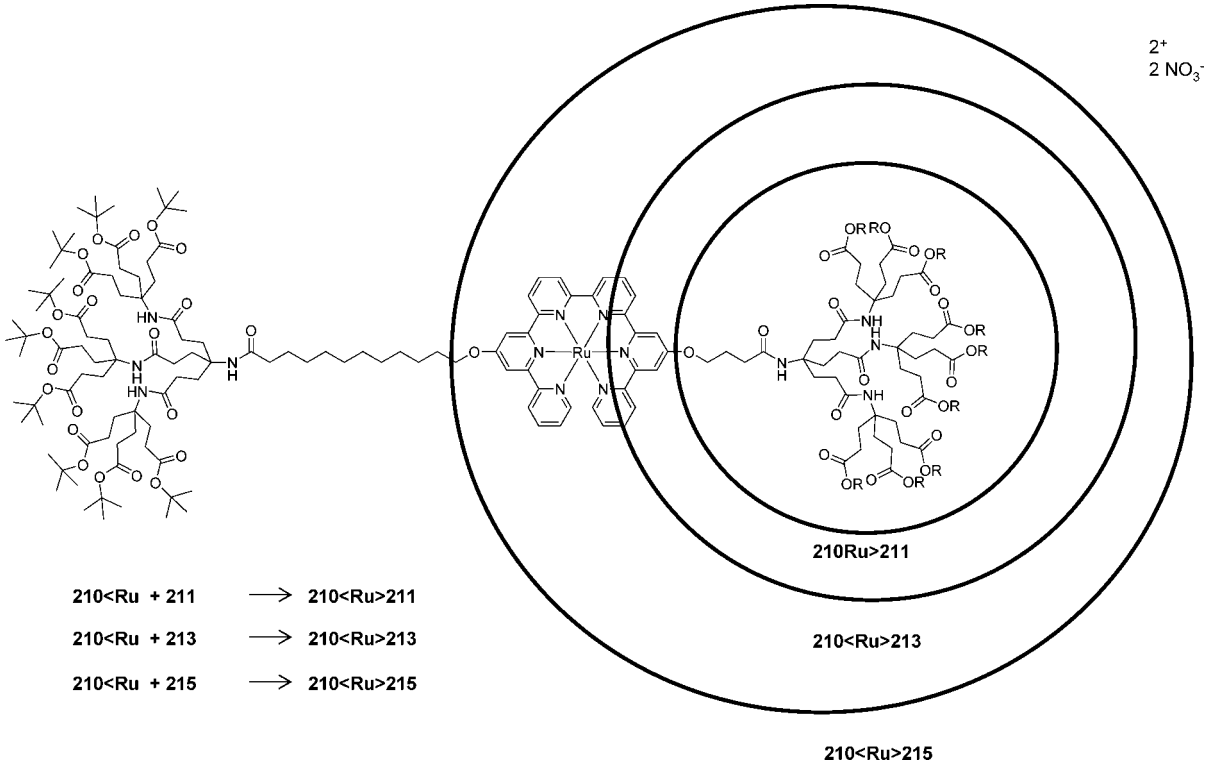
A series of "locks" and "keys" were prepared[788,789] using two different ω-hydroxycarboxylic acids as an entrée to each component. After the etherification with 4′-chloroterpyridine, the terminal carboxyl moiety was treated sequentially with Behera's amine[377] to generate the G1,2 keys (**207**, **210**) via the longer hydroxyacid, whereas the G1−4 locks (**209**, **211**, **213**, **215**) were created in a similar manner but from the shorter hydroxyacid causing the terpyridine to be encapsulated within the G4 periphery (Scheme 47). The keys were transformed to the corresponding Ru(II) complexes, then treated (1:1) with the different locks (Scheme 48). In all cases, the [tpy-Ru-tpy] coupling was demonstrated but with the G1,2 keys with the G4 lock, the resultant [tpy-Ru-tpy] connectivity was *inside* the lock portion as shown by CV data.

This simple connectivity was expanded to incorporate two [tpy-Ru-tpy] connections per arm in order to expand the

Scheme 47. Assembly[788] of Macromolecular Key and Lock Components



Scheme 48. Assembly[788] of Macromolecular Keys and Locks



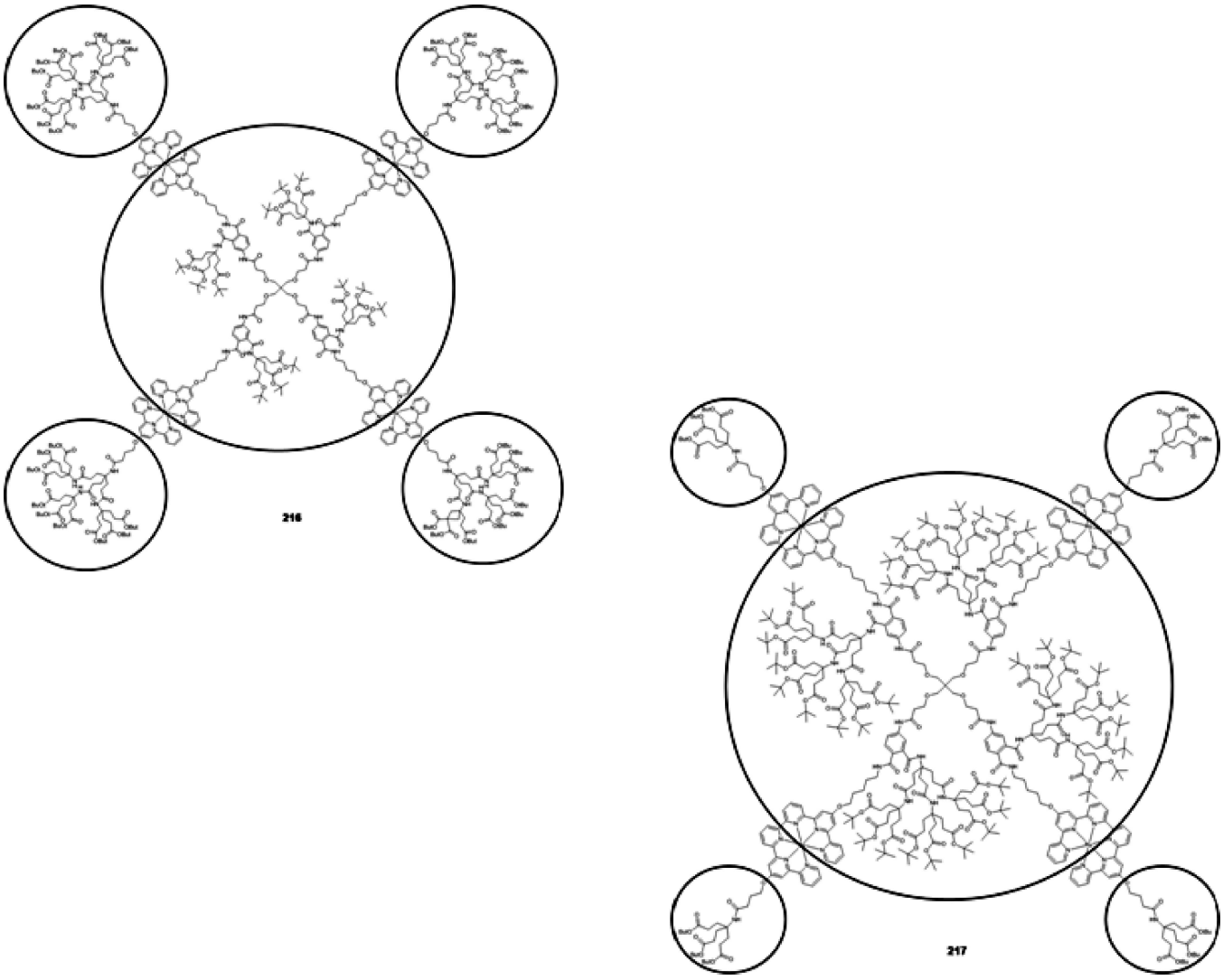


Figure 7. Isomeric metallodendrimers.[791]

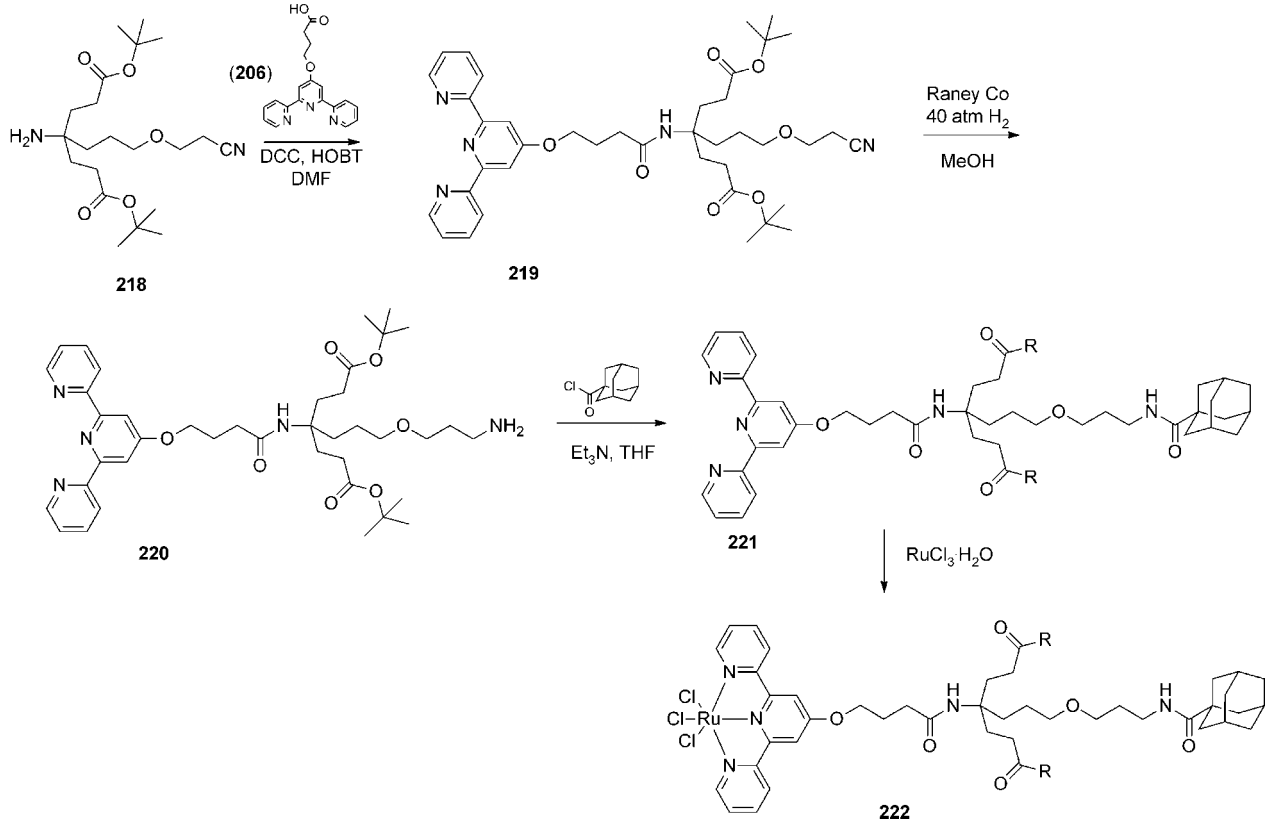
distance between the core and branching points, using similar components.[790] By addition of a 1,2 aryl branching point with this mode of construction, a pair of isomeric dendrimers (**216**, **217**) (Figure 7) were prepared by treating the metal-free core with the desired Ru(III) dendrons, which became the external component.[791] These are structural isomers possessing the same molecular formula. Details and the introduction to isomeric dendrimers as well as neutral species without external counterions offer entrée to structurally designed metallodendrimers with internally charge-balanced composition.[792]

The use of a 1 → (2 + 1) monomer, $\langle H_2NC(CH_2CH_2CO_2CMe_3)_2[(CH_2)_3OCH_2CH_2CN]\rangle$ **218** (Scheme 49), permitted the construction of **224**,[793] which can be selectively hydrolyzed to give the eight internal free acid sites (**225**) or with base eight internal carboxylate moieties (**226**) (Scheme 50) so that after complexation, the overall molecule is electronically neutral or possesses no external counterions. This zwitterionic structure offers initial insight to novel supramolecular properties of such assemblies. The terminal adamantanes were subsequently capped with β-cyclodextrin demonstrating the structural openness of these surface adamantane moieties as demonstrated by the easy molecular encapsulation.

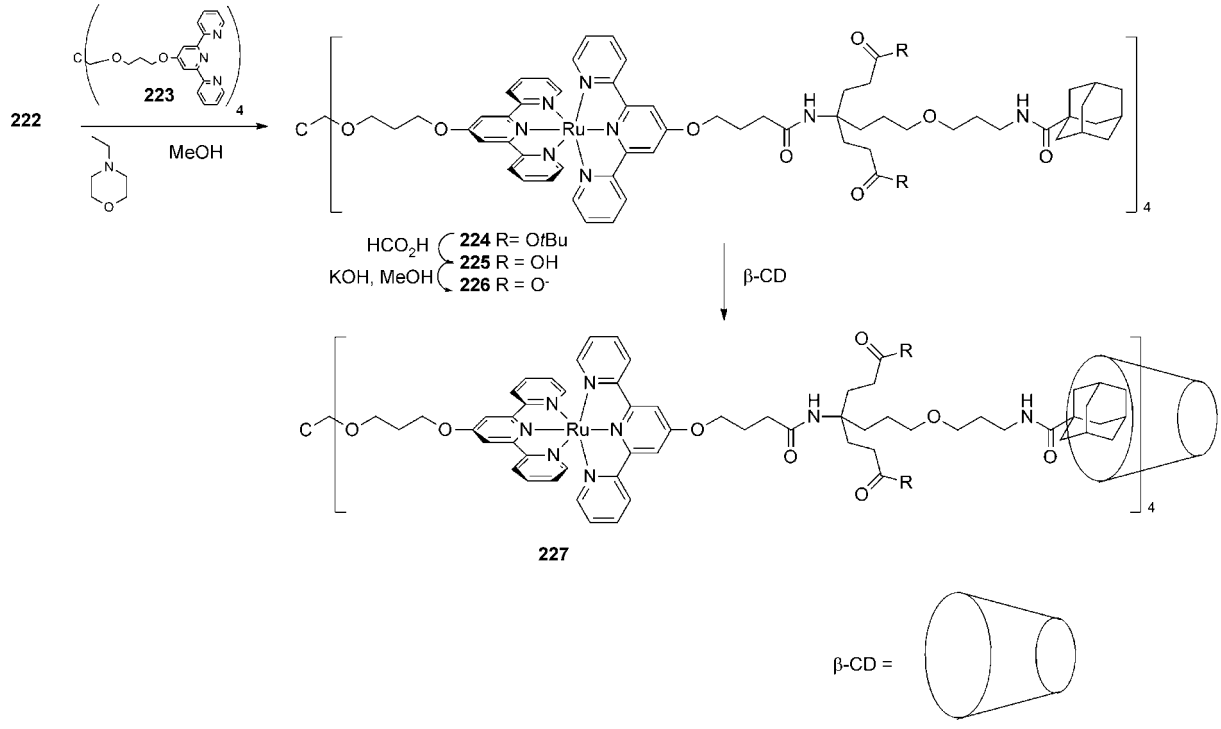
A reconfiguration of this type of 1 → (2 + 1) branching motif was initiated from $H_2N(CH_2)_5O$-tpy with CH_2═CHCOCl to generate (91%) the corresponding amide, followed by addition of $MeNO_2$ with base to give (75%) $O_2N(CH_2)_3CONH(CH_2)_5O$tpy, which was transformed to the desired 1 → (2 + 1) predendron by the Michael addition of two equivalents of *tert*-butyl acrylate. Catalytic reduction of this predendron gave the desired dendron $H_2NC[(CH_2)_2CO_2CMe_3]_2[CH_2CH_2CONH(CH_2)_5O$tpy], which with $C(CH_2OCH_2CH_2CO_2H)_4$ generated the expanded core possessing two internal carboxylate counterions for each metal(II) connection. The reaction of the Ru(III) termini under reducing conditions permitted access to bis-terpyridine Ru(II)-based macromolecules capable of being transformed to isomeric and zwitterionic forms.[792]

A series of metallodendrimers created by means of this terpyridine−Ru(II)−terpyridine connectivity but utilizing a PPI scaffold has given access to either homogeneous or heterogeneous surfaces.[794] The combinatorial assembly afforded avenues to interesting recoverable catalysts. DSC, TGA, and decomposition kinetics and temperatures of the constructs possessing the heterogeneous surface were measured.

Scheme 49. Formation of the Key Monomer to the Charge Neutral Metallodendrimers[793]



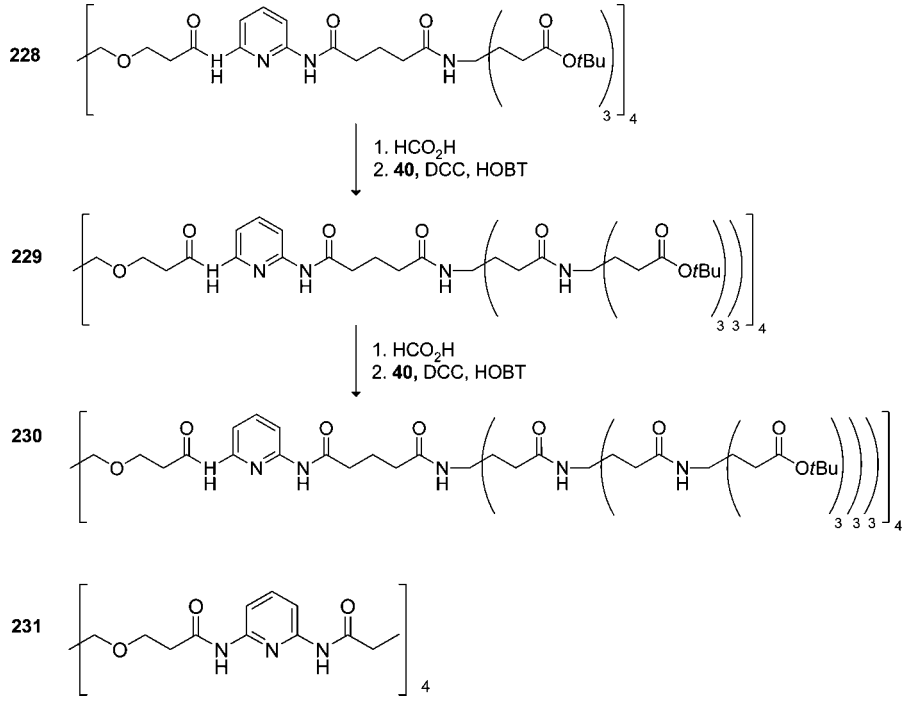
Scheme 50. Formation of Overall Charge-Neutral Metallodendrimers[793]



2.12. 1 → 3 C-Branched, Ether, Amide, and 5,5′-Bipyridinyl, 2,6-Pyridinyl, 5,5′-Bipyrimidinyl, or 1,4-Piperidinyl Connectivity

Following a simple procedure in which 1 equiv of $H_2NC(CH_2CH_2CO_2CMe_3)_3$[377] was treated with glutaryl dichloride (**76**), followed by monoacylation of the appropriate diamine, for example, 5,5′-diamino-2,2′-bipyridine, 5,5′-diamino-2,2′-bipyrimidine, 2,6-diaminopyridine, or *N*,*N*′-bis(3-aminopropyl)piperidine, these polyfunctional dendrons were attached to the simple tetrakisacyl chloride core **79** generating the desired internally functionalized dendrimers (**228**−**231**; Scheme 51).[514,789] To demonstrate the unimolecular micelle properties of these internally tetrafunctional interiors, **228** was treated with barbituric acid; NMR studies

Scheme 51. A Route to Internal Functionalization[789]



indicate the internal host−guest formation of a H-bonded complex. Another NMR study using **228** with the paramagnetic Co(II) as a molecular probe showed their usefulness in the detailed investigation of the dynamics and structures of such synthetic macromolecules.[504,795] The incorporation of the 5,5′-bipyridino moieties was synthetically detailed, and the internally tetrafunctionalized dendrimer was treated with $[Ru(bpy)_2Cl_2]$; the resultant tetracomplex demonstrated that the internally incorporated ligands were open to facile internal complexation.[796]

2.13. 1 → 3 C-Branched, Urea Connectivity

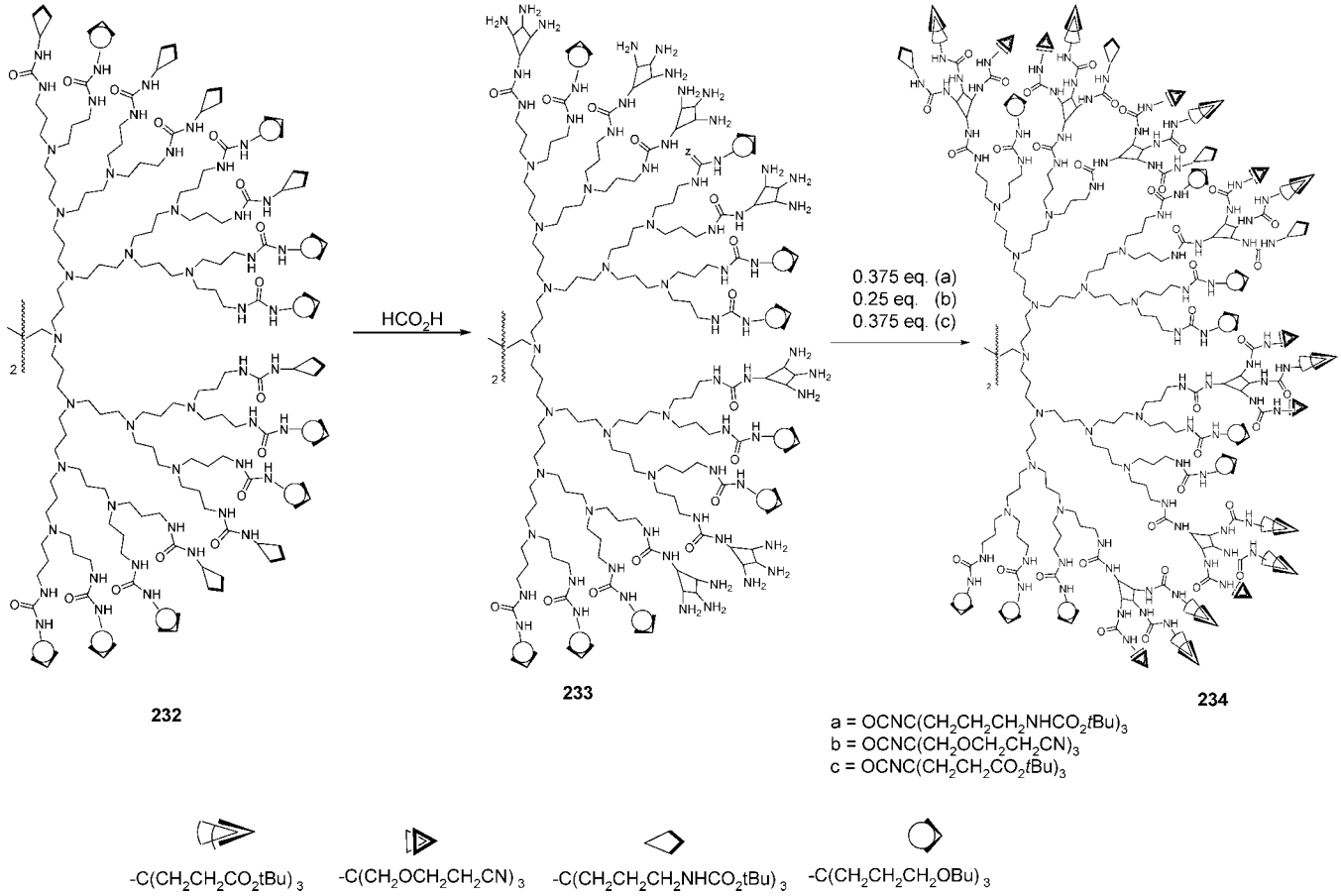
A family of isocyanate monomers, that is, $OCNC(CH_2CH_2R)_3$, where R = CO_2CMe_3, CN, CH_2NHZ, or CH_2OZ,[529−531,797] noted above, have also been reacted with polypropylenimine dendrimers to generate a series of urea-connected products possessing protected alcohol, amine, ester, and nitrile termini.[798] As an extension to this work, these isocyanates, which all possess similar reactivity, have been combinatorially used for the construction of multifunctional dendrimers.[384,530,531,797,798] Essentially, stoichiometric mixtures of monomers were reacted at the same time to produce a multifunctional material, such as **232**, which can be further elaborated via the selective deprotection of a specific set of functional group(s) as in polyamine **233** and subsequent reaction with another set of logically chosen monomers to give novel tailored, polyfunctional materials (i.e., **234**; Scheme 52). These architectures can be considered to be a species between hyperbranched polymers and dendrimers. Ramifications of this protocol include the rapid macromolecular property modification and the construction of dynamic heterogeneous surfaces.[530,531]

A series of these isocyanates[797] and their use in combinatorial chemistry[386,799] were reported in which $O_2NC[(CH_2)_3CN]_3$[367] was reduced (BH_3·THF) to $O_2NC[(CH_2)_3NH_2]_3$, which was Boc-protected giving $O_2NC[(CH_2)_3NHBoc]_3$, followed by reduction [Ni(R), H_2] to the amine $H_2NC[(CH_2)_3NHBoc)]_3$ and last conversion to the isocyanate $O{=}C{=}NC[(CH_2)_3NHBoc]_3$;[800] this isocyanate was treated with $C[CH_2O(CH_2)_3NH_2]_4$[708] affording the G1 dendrimer, which was deprotected and converted into the related G2 dendrimer. Similarly, Bradley et al.[801] transformed $H_2NC[(CH_2)_3NHBoc]_3$[475] into the corresponding isocyanate $O{=}C{=}N{-}C[(CH_2)_3NHBoc]_3$ in 93% yield upon treatment with DMAP and $(Boc)_2O$.[802] Polystyrene aminomethyl and TentaGel resins were treated with this isocyanate, followed by terminal hydrolysis (TFA) to give the free surface amines; then the reaction sequence was repeated to create the G2 and G3 dendronized resins.[803]

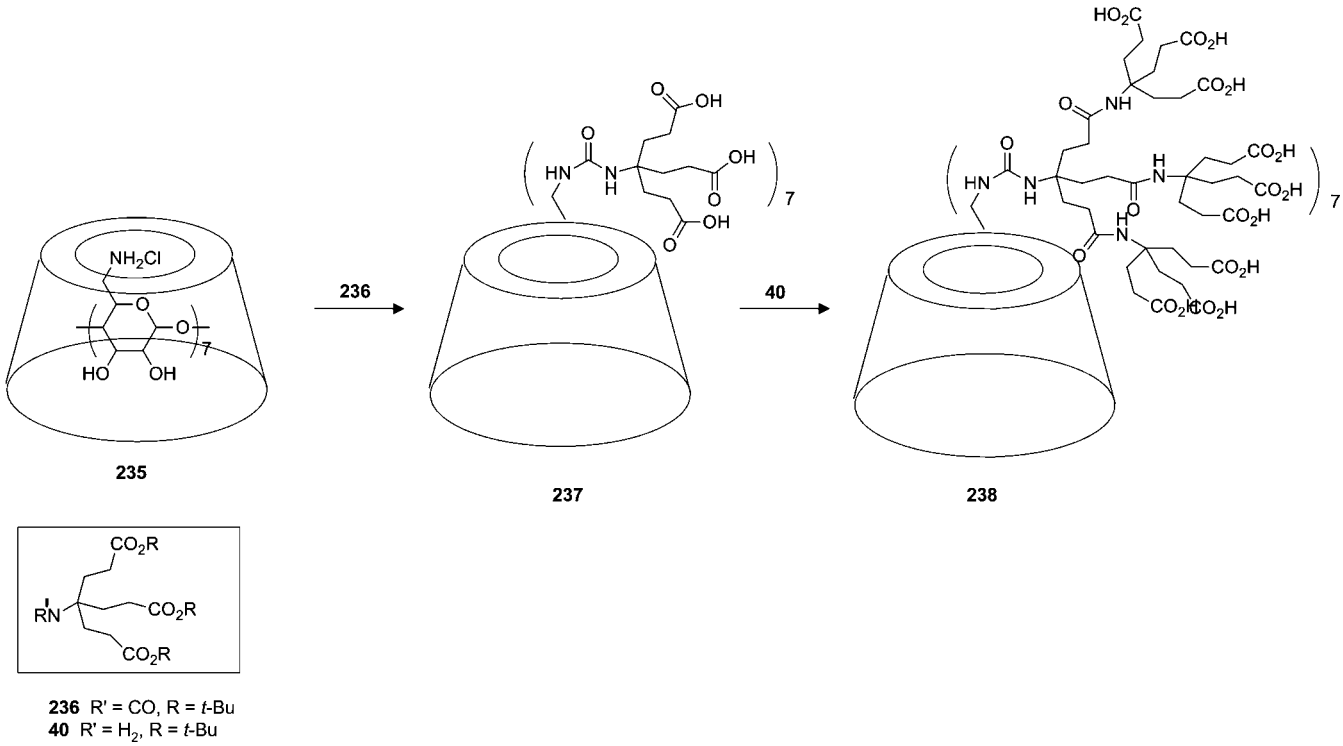
The isocyanate monomer possessing *tert*-butyl esters was treated with the free amino groups on an activated glass surface in order to instill the tree-like surface properties in which the amount of branched reagent bound to the silica was determined to be between 0.68 (G1) and 0.07 (G3) mmol/g depending on generation size (based on the quantification of the thermal decomposition of the *tert*-butyl esters and measuring the release of isobutylene).[387] The synthesis of the G3 benzyl-terminated dendrons possessing a $(EtO)_3SiCH_2CH_2CH_2NHCON[C(R)_3]$ focal group, where R = $-CH_2CH_2CONC[(CH_2)_2CONHC[(CH_2)_2CONC[C(CH_2)_3OCH_2C_6H_5]_3]_3]_3$, afforded a simple one-step route for the *in situ* creation of a surface-bound, sol−gel dendritic stationary phase on the inner walls of fused silica columns;[463] such phases showed unique selectivity in high-resolution capillary gas chromatograph reaching detection limits of parts per trillion and possessing excellent thermal and solvent stability properties.[804] A TRIS-related carbamate dendron has also been incorporated into a resin.[805]

Stable isocyanates, generated from Behera's amine and related focal amines, have been reacted with many isolated functional groups, such as being grafted onto the narrowring side of β-cyclodextrin to create a new macromolecular building block for use in convergent self-assembly of dendrimer-based networks.[806] Construction began by selective conversion of the upper rim, primary hydroxyl moieties to amine groups (**235**),[807] followed by treatment with the

Scheme 52. Combinatorial Layering (232 → 233 → 234) of Monomers Resulting in Asymmetric Dendrimer Construction[797,798]



Scheme 53. Dendrimerized Cyclodextrin and Molecular Assembly[806]



isocyanate triester (**236**) yielding the 21-acid **237** after treatment with formic acid (Scheme 53). Subsequent coupling with the corresponding aminotriester (**40**), followed by deesterification produced the G2 polyacid **238**. Molecular recognition properties of the cyclodextrin moiety were conserved and demonstrated by the molecular inclusion of phenolphthalein and its subsequent forced displacement by adamantane. The self-assembly potential was demonstrated via the coordination of two dendritic cyclodextrins to the adamantane-terminated ends of a tetra(ethylene glycol) chain

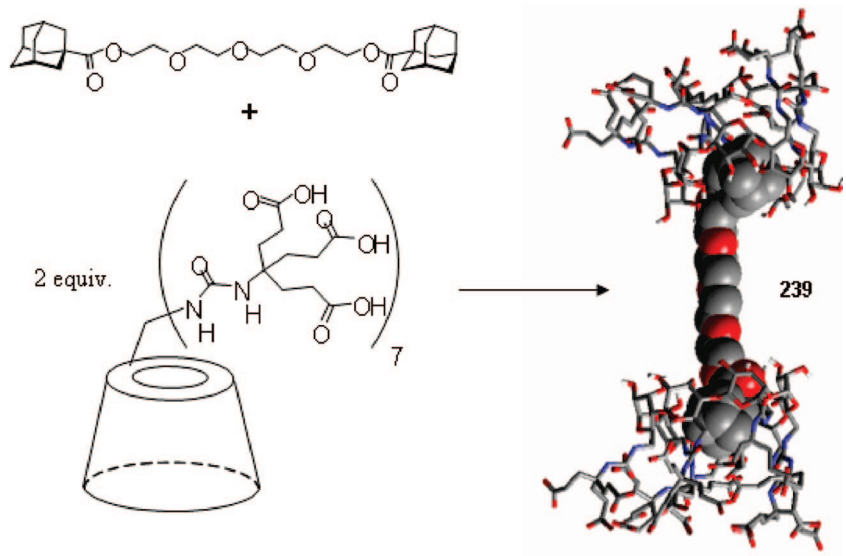
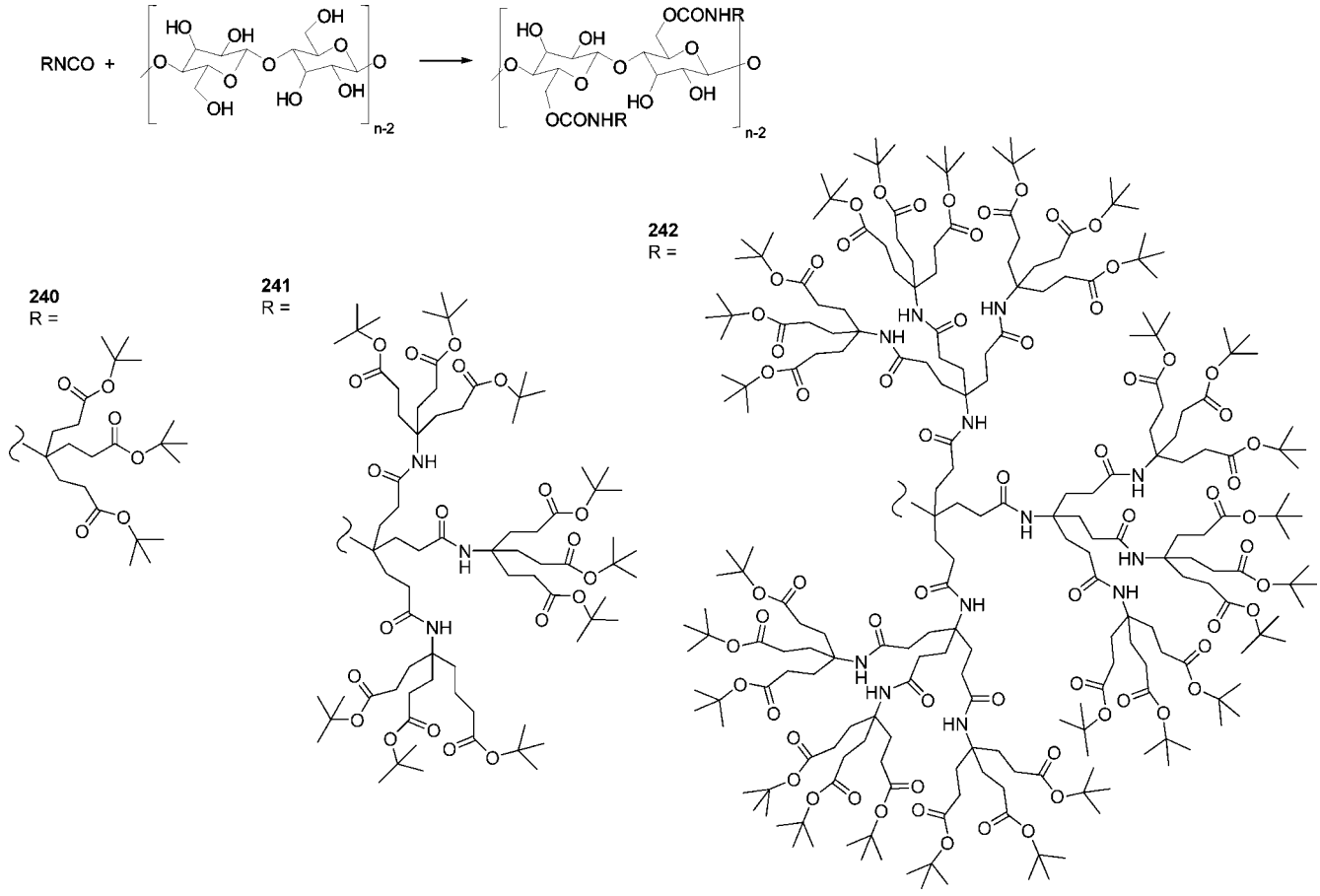


Figure 8. Demonstrated self-assembly properties of the dendritic cyclodextrin. Reprinted with permission from ref 806. Copyright 1998 The Royal Society of Chemistry.

Scheme 54. The Regioselective Dendronization of Cellulose[465]



(e.g., **239**; Figure 8); dendritic self-assembly has recently appeared.[808]

2.14. 1 → 3 C-Branched, Carbamate Connectivity

A series of regioselectively dendronized cellulose derivatives have been reported in which cellulose in a DMA/LiCl solvent system was treated with G1−G3 (**240**−**242**; Scheme 54) isocyanate dendrons; the resultant dendronized cellulose derivatives were characterized.[465] These structurally congested isocyanates were shown to selectively react with cellulose[385] at the primary hydroxyl moiety with little or no reaction at the secondary hydroxyl groups. The synthesis of regioselective combinatorial-type dendronized cellulose was accomplished by the treatment of cellulose with related isocyanates, for example, $OCNCR_3$, where R = $-CH_2CH_2CO_2CMe_3$, $-CH_2OCH_2CH_2CN$, and $-(CH_2)_3OSiMe_2(CMe_3)$;[466] these materials were characterized and shown to possess a wide range of solubility in organic solvents. The

novel regiospecific dendronization of cellulose permitted the uniform preparation of CdS quantum dot nanoparticles; the photooptical properties, morphology, and biocompatibility studies have been reported.[809]

2.15. 1 → 3 C-Branched, Ether and Urea Connectivity

Bradley et al.[805] transformed $H_2NC(CH_2OCH_2CH_2CN)_3$[703] into the focal-protected $C_6H_5CH_2O_2CNHC(CH_2OCH_2CH_2CN)_3$, which was sequentially reduced (BH_3·THF), Boc-protected (37%, two-steps) at the free terminal amino groups, debenzylated (10% Pt/C, H_2; 92%), and treated with [$(Boc)_2O$/DMAP][802] to generate (91%) the corresponding isocyanate $OCNC(CH_2OCH_2CH_2CH_2NHBoc)_3$ in 93% yield. Polystyrene aminomethyl resins and TentaGel resin were treated with this isocyanate, followed by deprotection (TFA) to give the free terminal amines; the reaction sequence was repeated to create the G2 and G3 dendronized resins.[803] The tridensyl labeled monomer, for example, $OCNC(CH_2OCH_2CH_2CH_2NHdansyl)_3$, was prepared and subsequently attached to a peptide generating the fluorogenic peptide.[810] A tris-fluorescein probe that can undergo self-quenching was utilized in a combinatorial library synthesis in order to map the substrate specificity of proteases.[811]

2.16. 1 → 3 C-Branched, Ester and Amide Connectivity

Although not strictly a dendrimer, the reaction of glutaric anhydride or succinic anhydride with TRIS at ambient temperatures gave $HO_2C(CH_2)_nCONHC(CH_2OH)_3$ ($n = 3$ or 2, respectively), which led to a hyperbranched poly(ester amide) possessing the desired 1 → 3 C-branching motif.[215] When polylactide was melted with this biodegradable hyperbranched material ($n = 2$) to enhance its flexibility and toughness, there was no loss in comprehensive performance.[812]

2.17. 1 → 3 C-Branched, Aryl and AlkylSiMe$_2$ Connectivity

Astruc and his co-workers have devised a simple and elegant methodology to produce large dendritic systems; they have produced many interesting reviews that need to be read for synthetic details, analysis, description of properties, and a true appreciation of their beautiful work in macromolecular assemblies.[26,26,55,69,76,88,182,600,813−818] Their procedures have led to "dendrimer construction extending beyond the dense-packing limit that is supported *inter alia* by ^1H, ^{13}C, and ^{29}Si NMR spectra recorded after each reaction, indicating that these reactions are clean within the NMR accuracy".[606] Their methodology utilized very mild reaction conditions with high-yield [$CpFe^+$]-induced[819] perallylation in simple methyl or polymethyl aromatics to give triallylphenol building blocks, section 2.4; this was reported to give a simple divergent route to dendrimers via hydroboration of the polyallyl group conversion to the mesylates and nucleophilic substitution with the triallylphenoxide monomer (**158**).[590,591] The initial yields were lower than desired; however, lengthening the tether circumvented this problem. The hydrosilylation of the polyolefin cores with dimethylchlorosilane using the Karstedt catalyst [Pt(divinyltetramethyldisiloxane) complex][820,821] in ethereal solvent, previously demonstrated by Seyferth,[822,823] was used as the initial step. Then, nucleophilic displacement of chloride from the terminal R-$SiMe_2Cl$ with the triallylphenoxide was catalyzed with NaI in DMF. The hydrosilylation is virtually quantitative without isomerizationm and subsequent nucleophilic substitution is also a high yield conversion;[606] the divergent construction (G2, **244**; Scheme 55) was repeated to G9, which possesses ideally 177 147 allyl moieties!

2.18. 1 → 3 C-Branched, Aryl, Ether, and AlkylSiMe$_2$ Connectivity

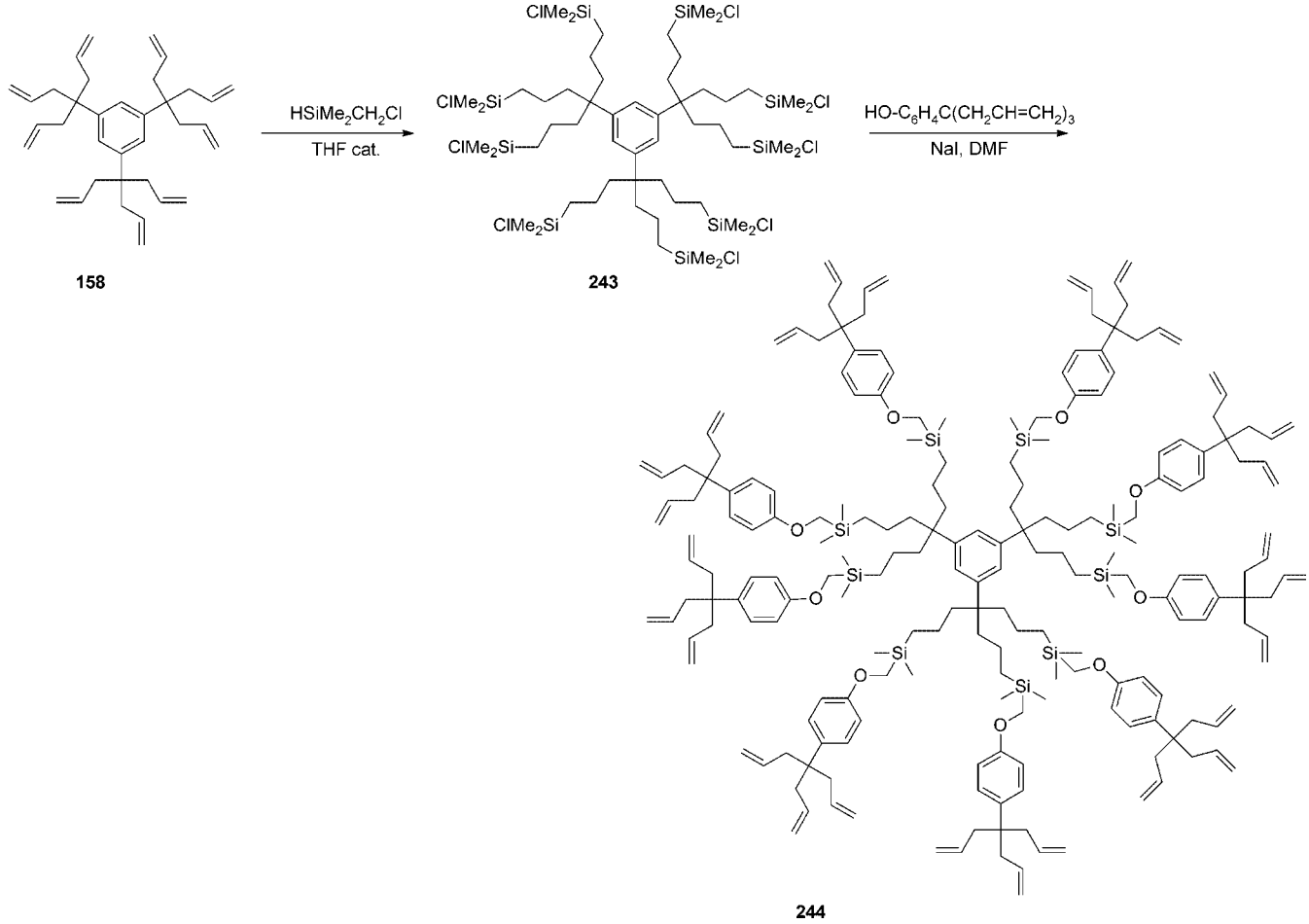
The basic (one-pot) synthesis of large dendrimers possessing polyallyl termini was demonstrated by hydrosilylation using $HSiMe_2Cl$ with the Karstedt catalysis, followed by the $HOC_6H_4C(CH_2CH{=}CH_2)_3$ (**246**) monomer (Scheme 56).[130,824] Numerous modifications of this simple procedure have led to different utilitarian products. From the 1 → 3 monomer **246** with similar chemistry, the convenient 1 → 9 dendron, $HOC_6H_4C[(CH_2)_3SiMe_2CH_2OC_6H_4C(CH_2CH{=}CH_2)_3]_3$, was created and its growth to the 1 → 27 dendron was accomplished by treatment with $EtCO_2C_6H_4C[(CH_2)_3SiMe_2CH_2I]_3$, followed by saponification freeing the phenolic focal moiety.[633] The initial nona-allylation of mesitylene was followed by Pt-catalyzed hydrosilylation using (chloromethyl)disilane extending the tether, and NaI-catalyzed Williamson coupling with *p*-hydroxybenzonitrile afforded a nonanitrile core that was coordinated to [$RuCp(PPh_3)_2Cl$] using $TlPF_6$ to give (45%) ultimately the nonacationic nonaruthenium complex.[825] The attachment of a benzoate moiety at each terminus upon saponification gave rise to a family of water-soluble dendrimers.[826]

Large cobaltinium dendrimers have been constructed[615] by the conversion of **158** with $HSiMe_2CH_2Cl$ and Karstedt catalyst, followed by a Finkelstein reaction with NaI in acetone generating **245**; then, a Williamson etherification with **246** generated the G2 dendrimer **247**. The simple process is repeated up to the G7 level; each generation possessing the polyiodo surface was capped utilizing a pentamethylcobalticinium salt containing long chain and phenol termini. Similarly, the iodo-coated dendrimers were transformed to pentamethylferrocene termini, which were demonstrated to act as molecular electrochrome batteries.[61,827−829] These types of dendrimers coated with alkylferrocenyl termini were shown to be useful in the redox recognition of the oxo anions $H_2PO_4^-$ and ATP^{2-} by CV.[830]

This convenient dendron **158** possessing triferrocenyl surface termini[831] was readily elongated and altered to generate a thiol focal group $\langle HSCH_2C_6H_4CH_2OC_6H_4C[(CH_2)_3SiMe_2R]_3\rangle$ (R = ferrocene or CH_2NHCOferrocene), which can be oxidized to give two-directional dendrimers possessing a central disulfide connector or reacted with gold particles to create a protected gold surface with a ferrocenyl outer covering.[26] An extended G2 dendron, $\langle HSC_6H_4CH_2OC_6H_4C[(CH_2)_3OC_6H_4C(CH_2CH{=}CH_2)_3]_3\rangle$, capped with ferrocenyl moieties along with long-chain thiols has been used (**251**; Scheme 57)[26] to create stabilized gold nanoparticles by a direct Brust-type procedure.[832−835]

Olefin cross-metathesis using Astruc dendrimers possessing terminal polyolefin surfaces with the second generation Grubbs catalyst has been reported.[621] The tethers between the olefin moieties and internal points-of-contact have been lengthened to minimize normal facile intramolecular metatheses. Treatment of the terminal olefin (e.g., **252**) with the normal conversion sequence ($HSiMe_2CH_2Cl$, Cl → I, etherification) gave a new expanded terminal olefin **253**, which

Scheme 55. The Use of Dendron 158 in the Divergent Synthesis of Giant Dendrimers[606]



with $CH_2{=}CHCO_2R$ in the presence of the Grubbs catalysis formed dendrimers with an acrylate surface (**254**; Scheme 58). This procedure can be similarly applied to polymers and coated gold nanoparticles.[611] The intermediary expanded polyolefin **253** can also be activated by the same $HSiMe_2CH_2Cl$, Cl → I, etherification sequence to give **255**, which was transformed to a new series of piano-stool iron complexes **256**.[836] When instead of nitrile **255** the related $HOC_6H_4CO_2Me$ was used, followed by saponification, the water-soluble dendrimer possessing a sodium benzoate surface was generated;[617] it was demonstrated to interact with acetylcholine in water-soluble assemblies.

The monomer $HOC_6H_4C(CH_2CH{=}CH_2)_3$ (**246**) has been transformed[628,629] into $HOC_6H_4C[(CH_2)_3SiMe_2Fc]_3$ (**257**); the reaction of the tris-olefin **246** or the ferrocenyl ligand **257** with 3,5-di(bromomethyl)pyridine generated ligands **258** or **259**, respectively (Scheme 59).[620] Treatment of the N-ligand **259** with $\langle[(n\text{-}Bu)_4N]_2Mo_6Br_{14}(CF_3SO_3)\rangle$ gave the hexa- (**260**) or monosubstituted clusters, respectively.[620] The related nonferrocene analogues[618,619] were also created, as well as those with larger Fréchet-type dendrons possessing the ferrocene coat.[620]

The reaction of $HOC_6H_4C(CH_2CH{=}CH_2)_3$ with ferrocenyldimethylsilane gave the desired $HOC_6H_4C[(CH_2)_3SiMe_2Fc]_3$, which was extended with *p*-iodomethylstyrene, then subjected to AIBN-induced radical polymerization.[837]

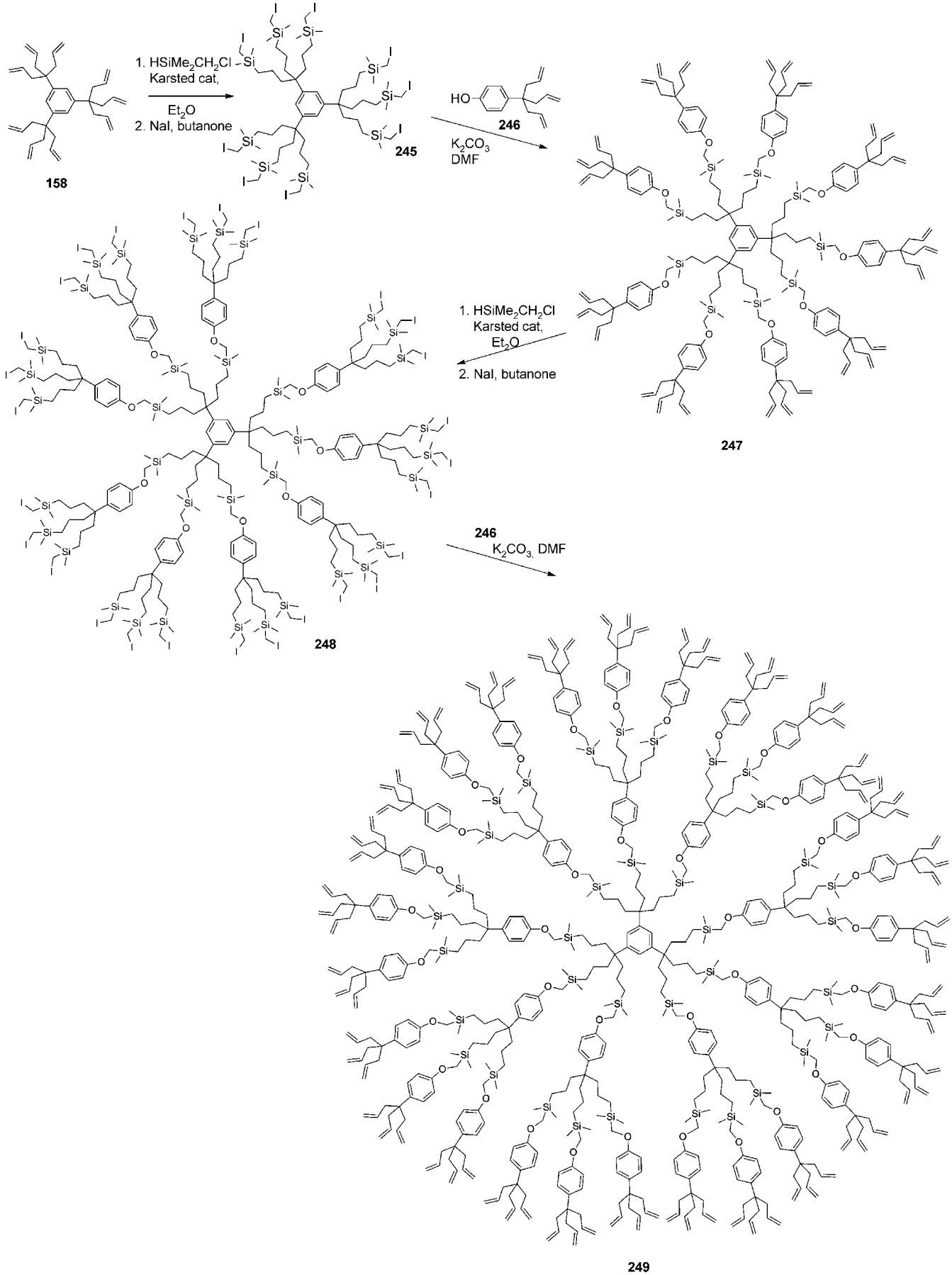
The synthesis of $[Fe_4Cp_3(\eta^5\text{-}C_5H_4COCl)]$ has been accomplished in two steps from the known $[FeCp(CO)]_4$[838] and its attachment to the surface of different 1 → 3 C-branched dendrimers has been reported;[839] their applications to oxo anion and adenosine-5′-triphosphate sensing have been shown.

2.19. 1 → 3 C-Branched, Aryl, Ether, AlkylSiMe$_2$, and Triazole Connectivity

The introduction of triazole connectivity utilizing these iodo dendrimers, for example, **245**, was devised by their treatment with $HOC_6H_4OCH_2C_6H_2(OCH_2C{\equiv}CH)_3$ to generate the next tier with a polyalkyne **261**, which can be "clicked" with diverse azides to give easy conversion to macromolecules coated with xylopyranoside termini[614] or ferrocene termini, **262**[840] (Scheme 60).

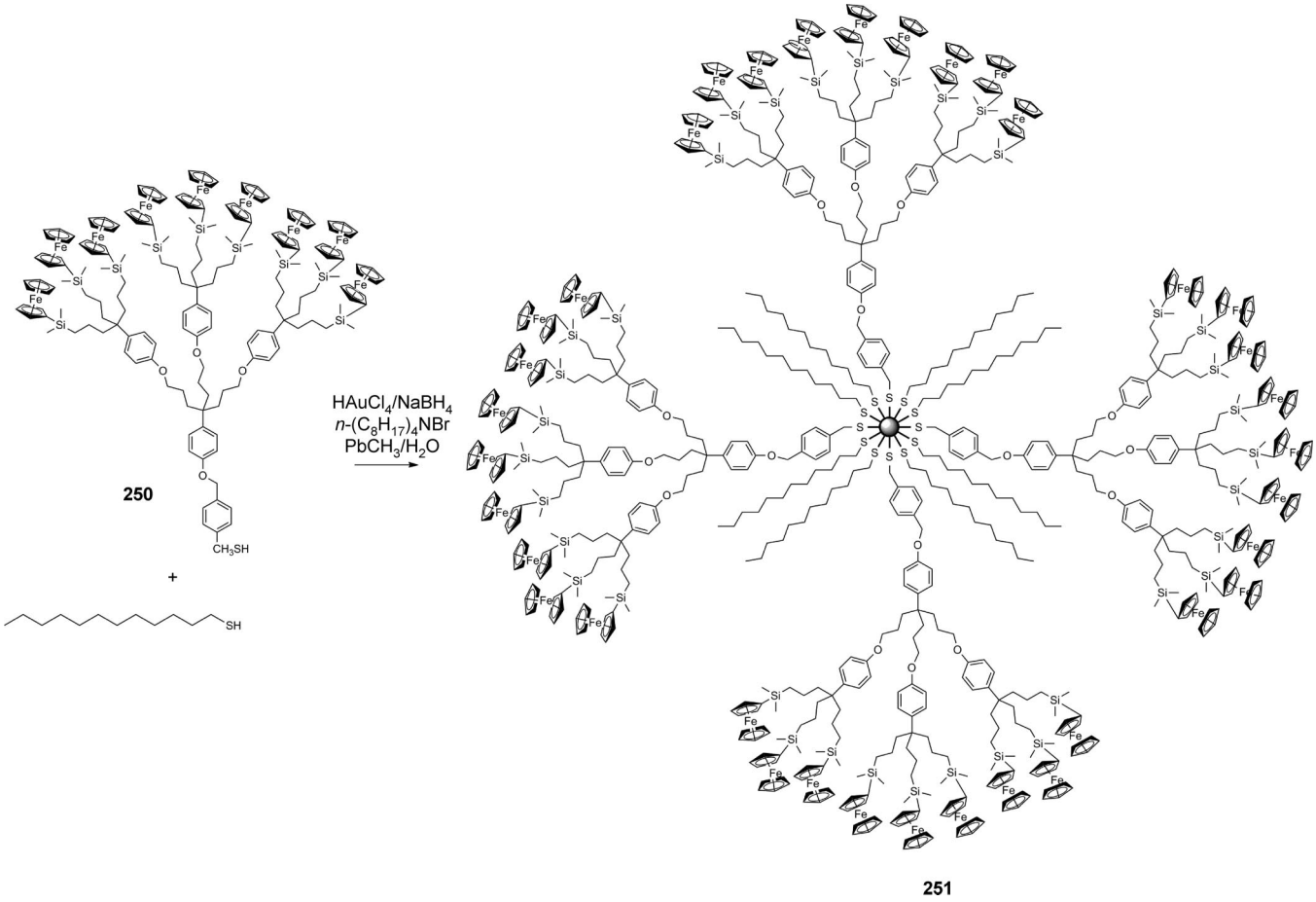
Conversely, the dendrimer surface can be coated with azide moieties by treatment of the polyolefin with $HSiMe_2CH_2Cl$ and Karstedt catalyst, followed by NaN_3,[624] then $HC{\equiv}CCH_2\text{-}OC_6H_4C(CH_2CH{=}CH_2)_3$,[626,814] generated from the above monomer $HOC_6H_4C(CH_2CH{=}CH_2)_3$ with $HC{\equiv}CCH_2Br$ in the presence of base. This procedure permitted multiple click combinations at different tiers (Scheme 61) and afforded a family of ferrocene-coated products;[625,626,840−843] the number of Pd(II) moieties that were introduced into the dendrimers was monitored using CV,[843] and their potential for novel electrochemical sensors and devices has been approached.[844] The reduction of the Pd(II)-triazole dendrimers using $NaBH_4$ gave rise to Pd nanoparticles, which were stabilized either by several dendrimers or encapsulation within the dendrimer.[841] The use of $HC{\equiv}CCH_2SO_3Na$ with the dendrimers possessing polyazido units and Cu(I) catalysis gave rise to

Scheme 56. The Use of a Convenient Dendrimer to Build Giant Macromolecules[615]



a family of water-soluble, sulfonated dendrimers (**270**) capable of stabilizing palladium nanoparticles, which were shown to be highly efficient catalysts for olefin hydrogenations and Suzuki couplings (Scheme 62)[845] in an aqueous

Scheme 57. Polyferrocenyl Gold Nanoparticle-Cored Dendrimers[26]



media and at room temperature.[624,846] These azido-terminated dendrimers (**269**) were capped with $HC{\equiv}CCH_2O(CH_2CH_2O)_4$-$CH_2C_6H_2[O(CH_2CH_2O)_3Me]_3$ to generate a G0 dendrimer (27 arms), G1 dendrimer (81 arms), and G2 dendrimer possessing 243 tri(ethylene glycol) termini; gold nanoparticles were readily stabilized by either several G0 (amu 8820, diameter 9 ± 1 nm) dendrimers or encapsulation within the larger G1 (diameter 18 ± 2 nm) species.[623] Water-soluble "clicked" and "non-clicked" dendrimers of the Astruc-type have been demonstrated to form dendrimer-encapsulated, as well as dendrimer-stabilized, gold nanoparticles.[847]

The reaction of $HOC_6H_4C(CH_2CH{=}CH_2)_3$ with $HSiMe_2$-CH_2Cl gave the desired $HOC_6H_4C[(CH_2)_3SiMe_2Cl]_3$ that was extended (K_2CO_3, DMF) with *p*-iodomethylstyrene, then subjected to AIBN-induced radical polymerization, followed by conversion to the corresponding azide, which was last treated with ethynylferrocene affording the dendronized polymer.[837]

2.20. 1 → 3 C Branched, $SiMe_2$ Connectivity

A simple dendron derived from $HOC_6H_4C(CH_2CH{=}CH_2)_3$ has been transformed[628,629] into $HOC_6H_4C[(CH_2)_3SiMe_2Fc]_3$, which was reacted with the octahedral molybdenum cluster $\langle[n\text{-}Bu_4N][Mo_6Br_8(CF_3SO_3)_6]\rangle$ by the substitution of all six terminal triflate ligands generating the Mo_6-cluster-cored octadecylferrocenyl dendrimer (Figure 9).[57,619,848] Modifications of a key monomer, $HOC_6H_4C[(CH_2)_3SiMe_2CH_2X]_3$, derived from $HOC_6H_4C(CH_2CH{=}CH_2)_3$ by treatment with $HSiMe_2(CH_2Cl)$, at both the focal site and three terminal positions offer numerous interesting possibilities, especially in the fabrication of catalysts and sensors.

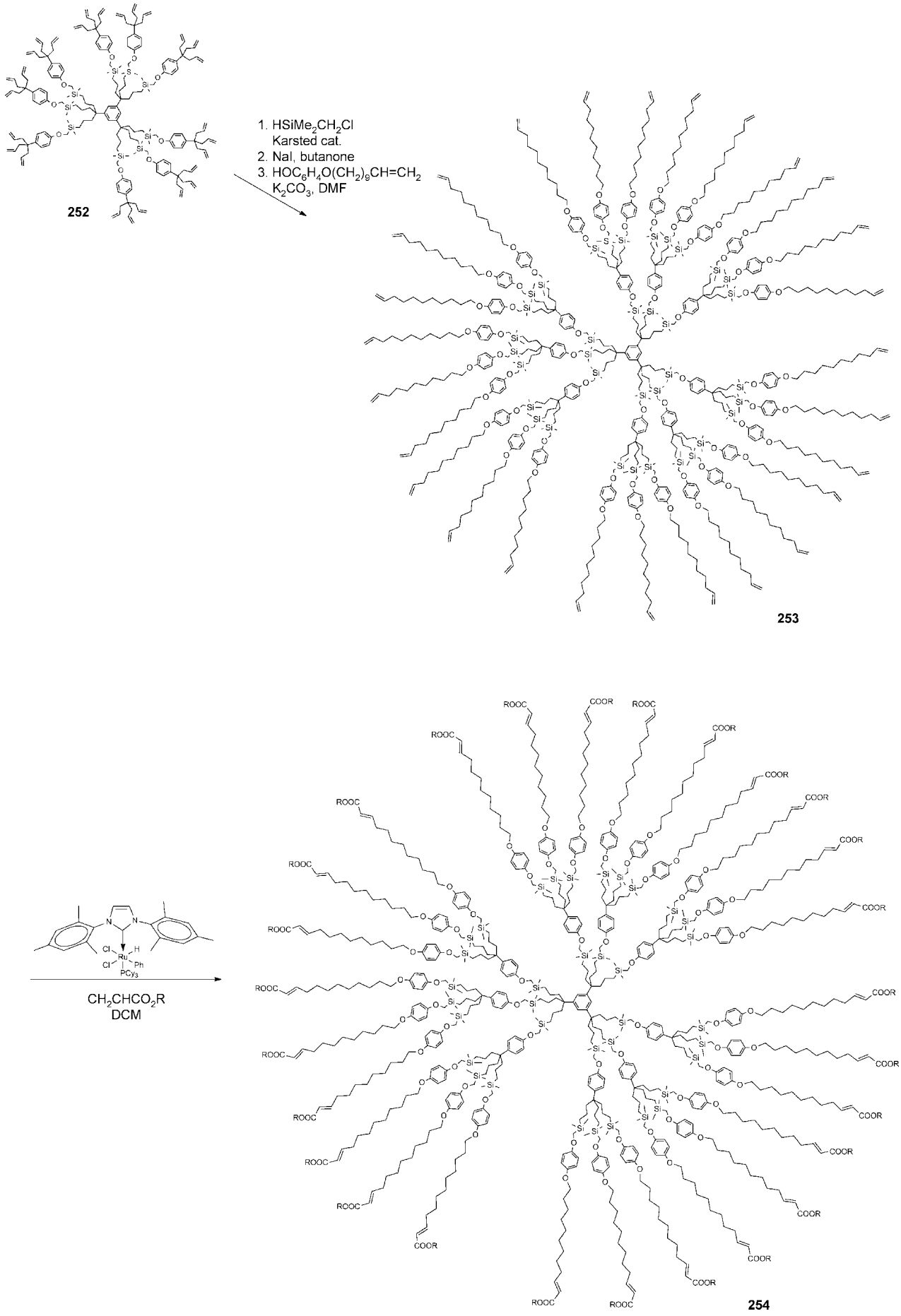
2.21. 1 → 3 C Branched, $SiMe_2$, Ammonium, and Amide Connectivity

Hydrogen bonding has been utilized by Astruc et al. to assemble redox-active metallodendrimers using HOC_6H_4C-$[(CH_2)_3SiMe_2CH_2NHCOFc]_3$ with polypropylenimine dendrimers (Figure 10); these materials were shown to recognize $H_2PO_4^-$.[631,831]

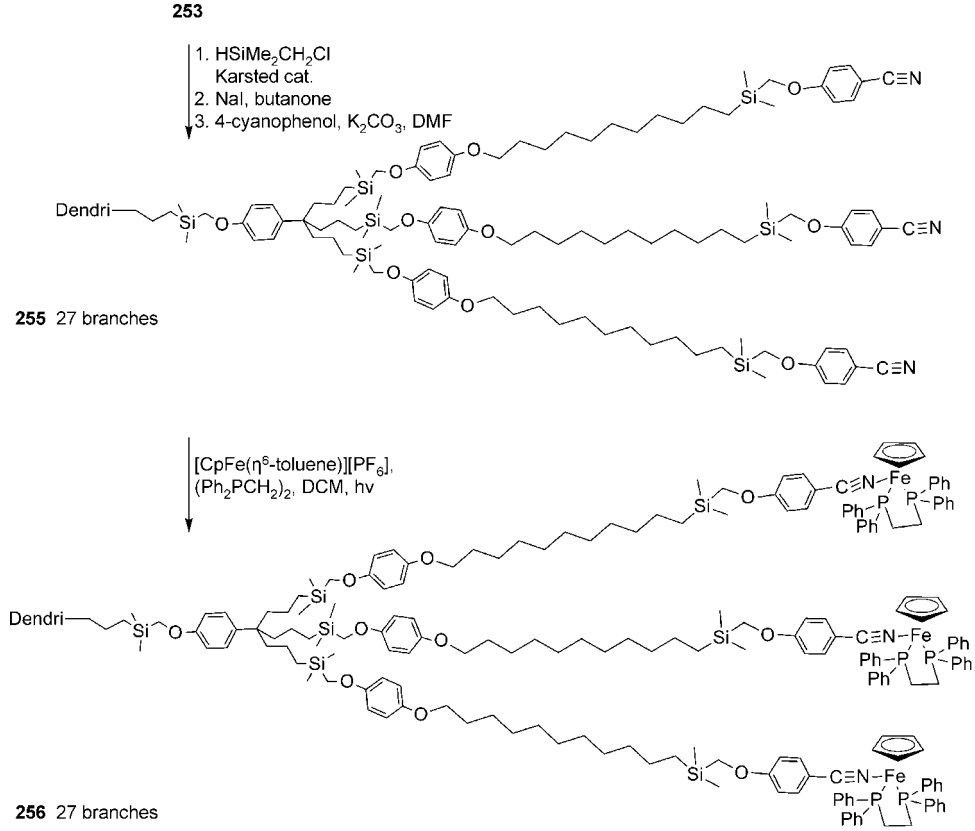
2.22. 1 → 3 C and 1 → 2 N-Branched, Amide Connectivity

Enhanced water dissolution of the PAMAM dendrimers was easily accomplished[849] by application of the initial arborol procedure (TRIS, base/solvent);[206] the PAMAM dendrimers with TRIS in the presence of K_2CO_3 gave moderate yields of the products possessing the polyol surface. These dendrimers are highly water-soluble and were shown to act as "unimolecular micelles"; benzoic acid, 2-hydroxybenzoic acid, and 4-nitro-2,6-dibromophenol were used to demonstrate their supramolecular properties.[849] The TRIS-terminated PAMAM series (PAMAM−OH) possesses novel solubilization properties in view of the internal amino branching centers coupled with the neutral, water-soluble outersurface;thus,$[CH_2N(CH_2CH_2CONHCH_2CH_2N(CH_2CH_2$-$CONC(CH_2OH)_3)_2)_2]_2$ was an early example of receptor properties for aromatic carboxylic acids as found in common drugs, such as ibuprofen[850] and benzoic acid.[340] The sol−gel entrapment of this dendrimer possessing the 24 hydroxy termini has been reported, and the dendrimer could not be leached from the sol−gel, since it was covalently immobilized by condensation.[851] Because of the enhanced water

Scheme 58. Surface Modification[611,621] via a Metathesis Procedure



Scheme 58. Continued



solubility and the noncomplexing exterior hydroxy groups toward metal ions of these PAMAM−OH, Crook et al.[852,853] and many others have used these materials for the encapsulation of nanoparticles; their use in conjugation with microbial S-layer proteins showing topochemical properties afforded avenues to patterned arrays of Pt nanoparticles.[854]

2.23. 1 → 3 C and 1 → 2 N-Branched, Amide and Ether Connectivity

Kuroda and Swager[855,856] functionalized polymer conjugates via treatment of 2,5-diiodo-1,4-hydroquinone with $BrCH_2CO_2Et$ in the presence of K_2CO_3, 2-butanone, followed by sequential saponification (NaOH, MeOH) and treatment with oxalyl chloride, $HN(CH_2CO_2Et)_2$, and last TRIS (DMSO, K_2CO_3) to generate the desired dendron $[Aryl]-O-CH_2CON[CH_2CONHC(CH_2OH)_3]_2$.

Astruc et al.[857] prepared an early example of a simple metallodendrimer coated with ferrocene termini; comparisons showed that the dendritic effect is maximal for the $1,3,5\text{-}C_6H_3[C[(CH_2)_3O(CH_2)_3N(CH_2)_3NHCOFc)_2]_3]_3$ and steric surface saturation occurred for the related metallodendrimer possessing 36 ferrocene termini. The simpler metallodendrimer, $1,3,5\text{-}C_6H_3[C[(CH_2)_3O(CH_2)_3NHClCo^+]_3]_3$, where Co^+ = cobalticinium, was prepared and shown using CV and ^1H NMR to be effective in sensing small inorganic anions, for example, $H_2PO_4^-$, HSO_4^-, and Cl^-.[858]

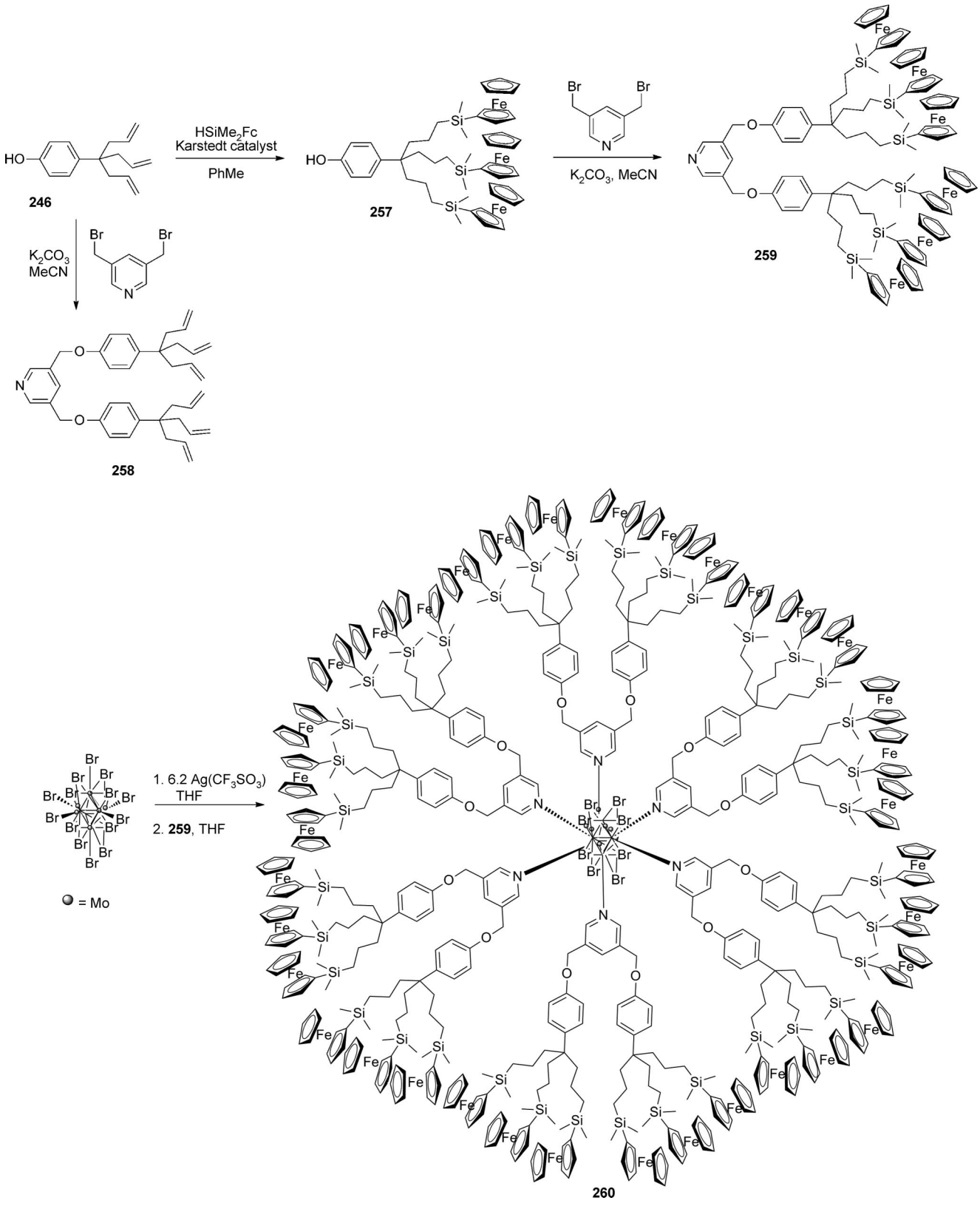
2.24. 1 → 3 C-Branched and (2 + 1) C-Branching Motif

It has been known but little practiced that depending on the strength of the base, reaction times, ratio of reagent, and related factors, $MeNO_2$ as well as other CH_n possessing electron-withdrawing substituents can be selectively substituted depending on these and other conditions. Thus, $MeNO_2$ can be transformed to initially XCH_2NO_2, then $XYCHNO_2$, and last, $XYZCNO_2$. These processes are reversible depending on reaction conditions and reagent stoichiometry; most importantly, the reduction of the focal nitro to an amino group prevents subsequent substituent scrambling generally associated with the unwanted retro-Michael reactions; the product distribution is thus locked upon reduction of the nitro group. This opens a door to interesting combinations of 1 → 3 branched monomers, for example, the 1 → (2 + 1) and 1 → (1 + 1 + 1) variety, thus permitting the introduction of selective substitution within the dendritic infrastructure after assembly.

In 2003, Newkome et al.[859] reported a family of related 1 → (2 + 1) monomers (Scheme 63) from 4-nitrobutanol, derived from the controlled Michael reaction of $MeNO_2$ with $CH_2{=}CHCO_2Me$, followed by ester reduction. The use of the known core $C(CH_2OCH_2CH_2COCl)_4$ (**79**) permitted the assembly of various G1 dendrimers. Although initial studies were directed to internal specific substitution per dendron, it was apparent by the selection of the appropriate dendron that either internal or external selections or both were possible, as shown in Scheme 64, in which acetoxy moieties were generated at each level. Scheme 65 demonstrates the single unique site on the periphery of each dendron, which when attached to the same tetraacyl chloride core gave **290** possessing four terpyridinyl moieties on the surface, and upon addition of Ru(II), intramolecular cycloaddition occurred in nearly quantitative yield generating a dendritic spirane **291**[860] (Scheme 66).

In 2006, the application of these reagents was used to assemble molecular conifer trees (**292** and **293**), as shown in Figure 11.[460] This demonstrated that judicious selection of designer branched monomers can lead to the assembly of precisely created dendritic structures.

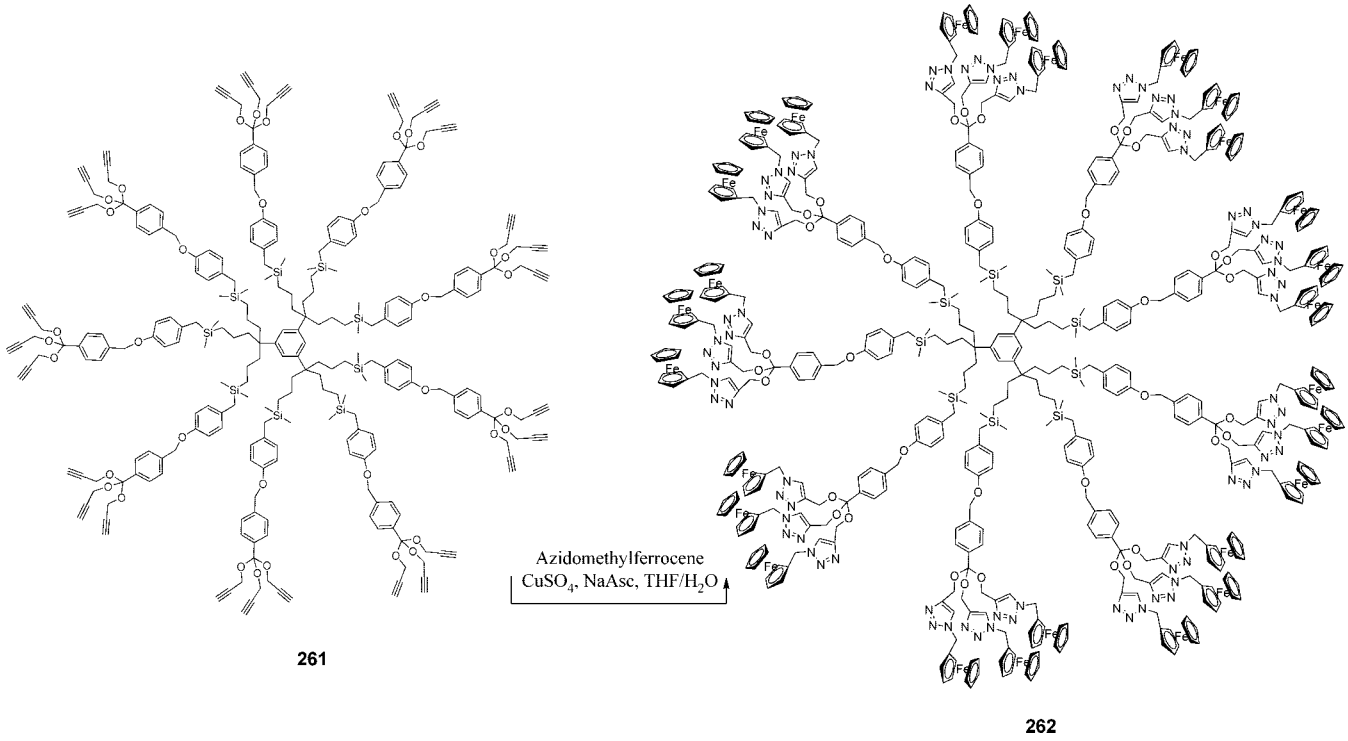
Scheme 59. Metallodendrimers[620] Possessing Mo-Cluster Core



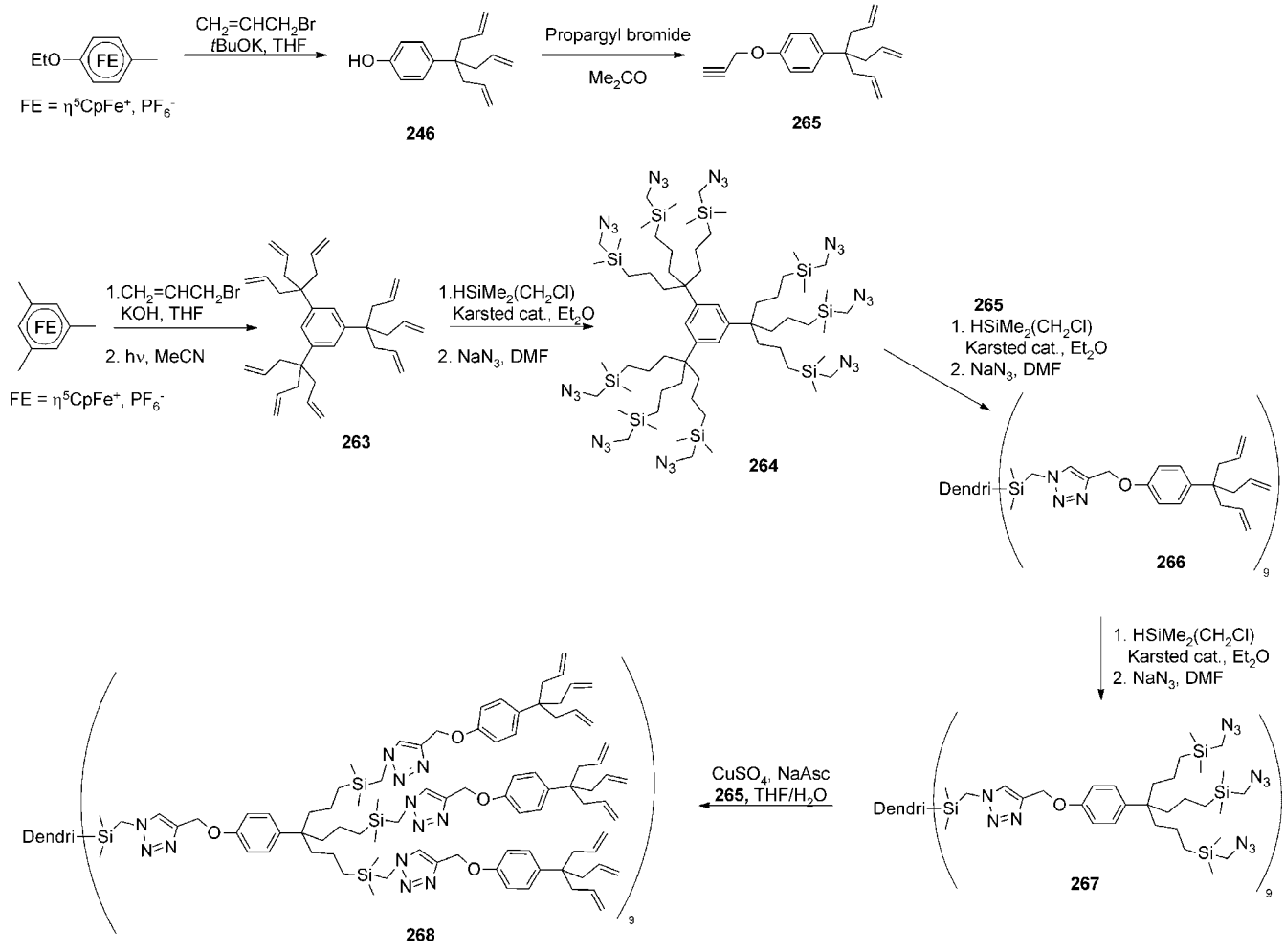
Weck et al.[861−864] utilized similar methodology to create a series of multifunctional dendrimers, as shown in Scheme 67. The incorporation of the specific reactive site at a single locus on each attached dendron permitted the creation of two unique sites at different ends of a two-direction dendrimer. This opens many novel pathways to intramolecular and intermolecular oligomeric materials.

Recently, pseudopeptide carriers were prepared by modular assembly from an α,α-disubstituted amino acid termed "bis-ornithine". The initial monomer possesses the $1 \rightarrow (2 + 1)$ structure, for example, $HO_2CC[(CH_2)_3NHZ)]_2[NHCO(CH_2)_nNHBoc]$.[365,865−867] Due to its insolubility, they were structurally modified in different ways.

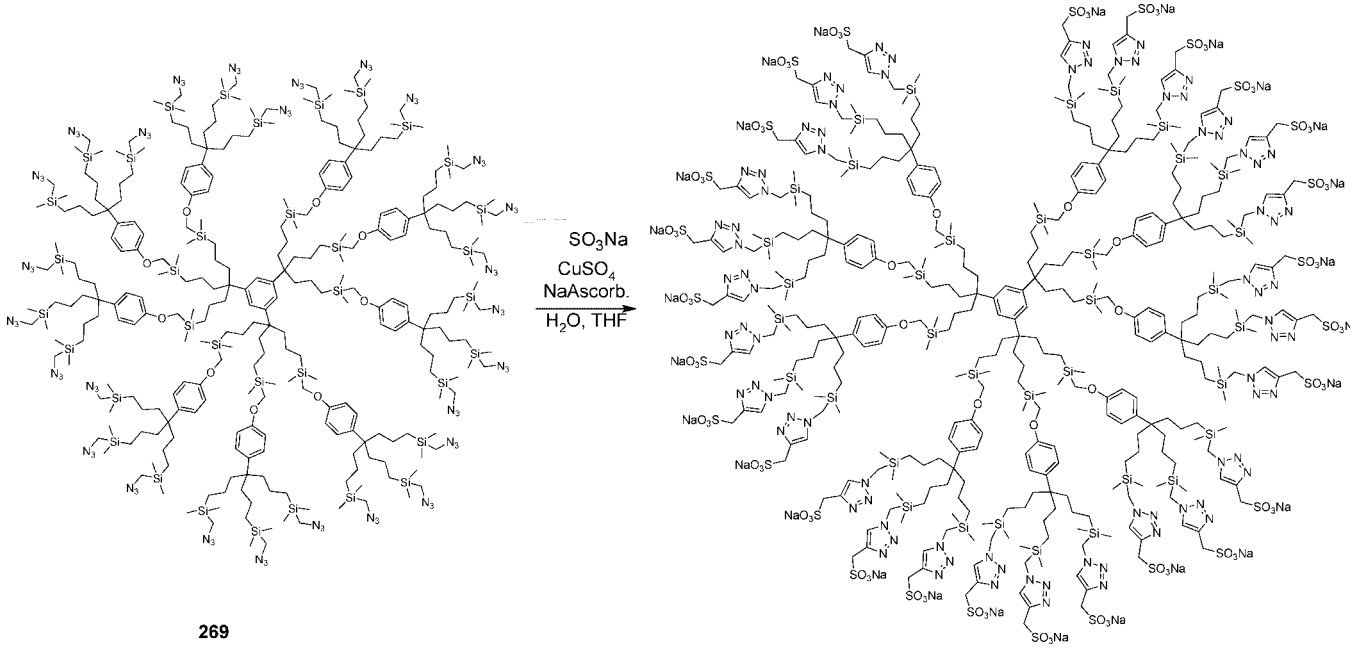
Scheme 60. Reaction of Dendrimers Possessing Terminal Alkynes with Azide Reagents[840]



Scheme 61. Multitiered Click Assembly[843] of Internal Polyfunctional Dendrimers



Scheme 62. Water-Soluble Dendrimers[624] Capable of Stabilizing Palladium Nanoparticles



269 270

2.25. 1 → 3 and 1 → 2 C-Branched, Amide, Ether, and Amine Connectivity

Astruc et al.[868] treated the octabenzyl core **305** with $H_2NC(CH_2OCH_2CH_2CN)_3$[869] to generate the G2 level (**306**); reduction and treatment with either [FeCp(C_5H_4COCl] or [FeCp*(η_6-C_6H_5F)][PF_6] gave **307** and **308**, respectively (Scheme 68).

3. 1 → 3 N-Branched

3.1. 1 → 3 N-Branched, Alkyl Connectivity

Rengan and Engel[870] reported and reviewed[871] the synthesis of polyammonium cascade polymers (Scheme 69), which were prepared by initial quaternization of triethanolamine (**309**) with either an alkyl (e.g., methyl or benzyl) halide or 2-chloroethanol to give excellent yields (>95%) of the three-

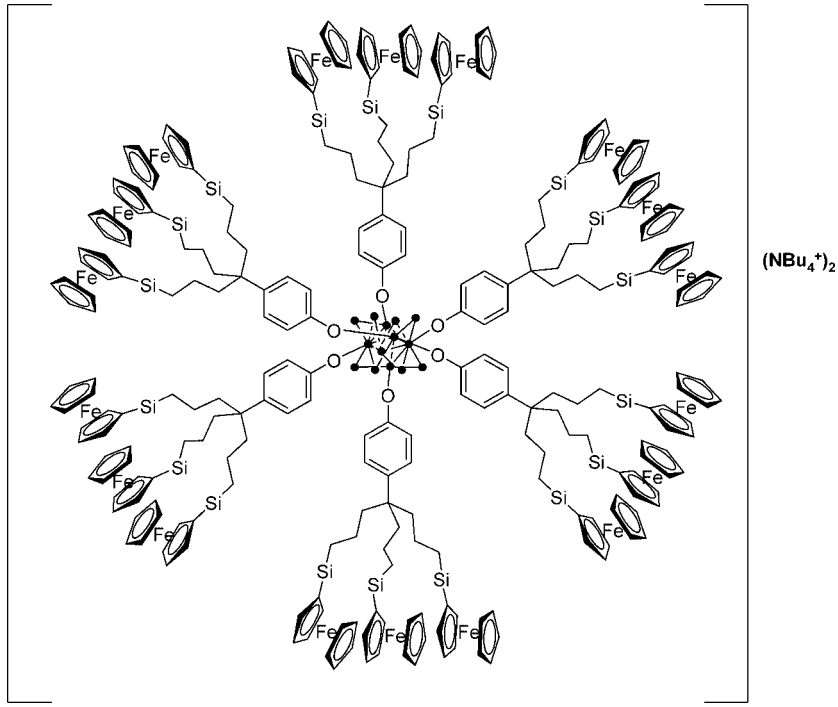


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Figure 9. A Mo-cluster-cored octadecylferrocenyl dendrimer.[848]

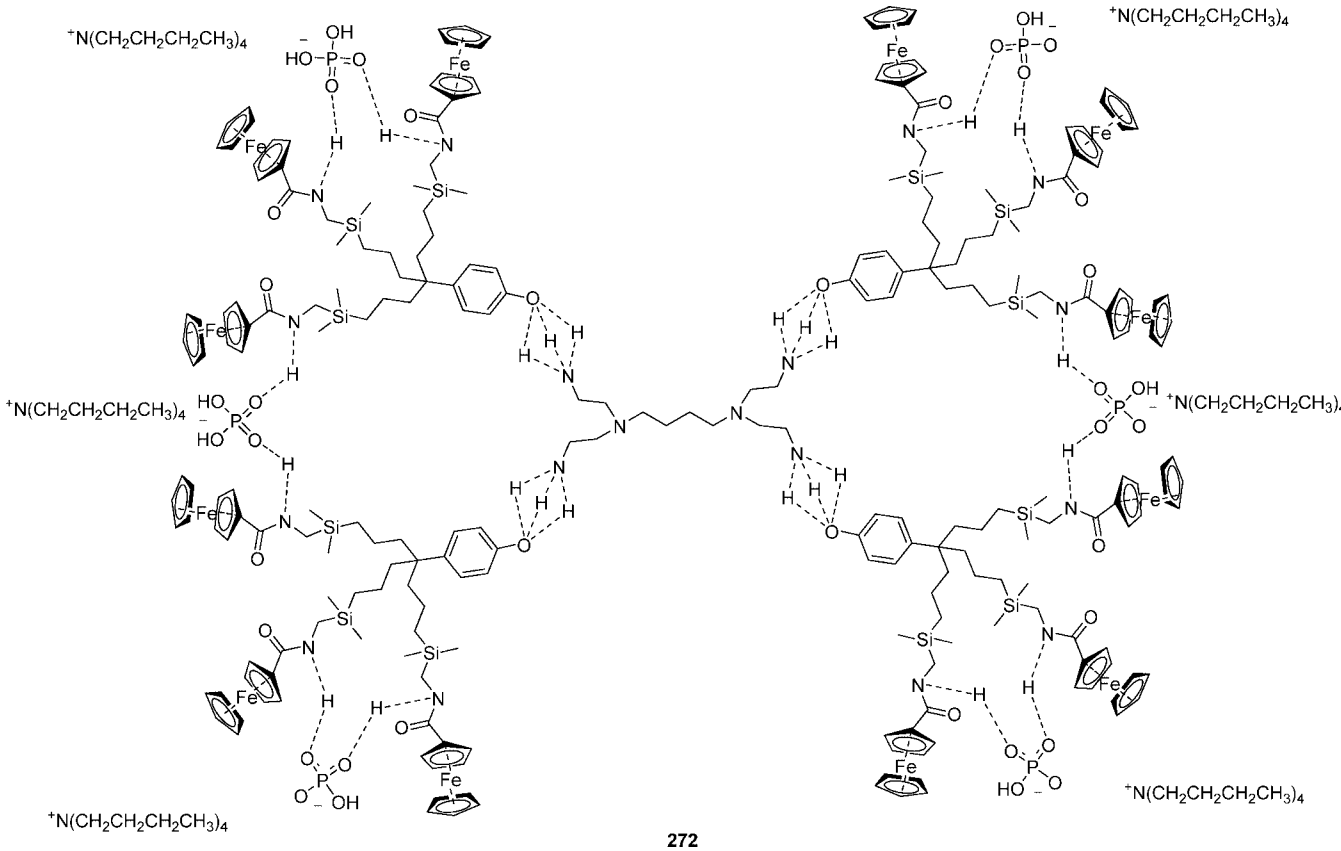

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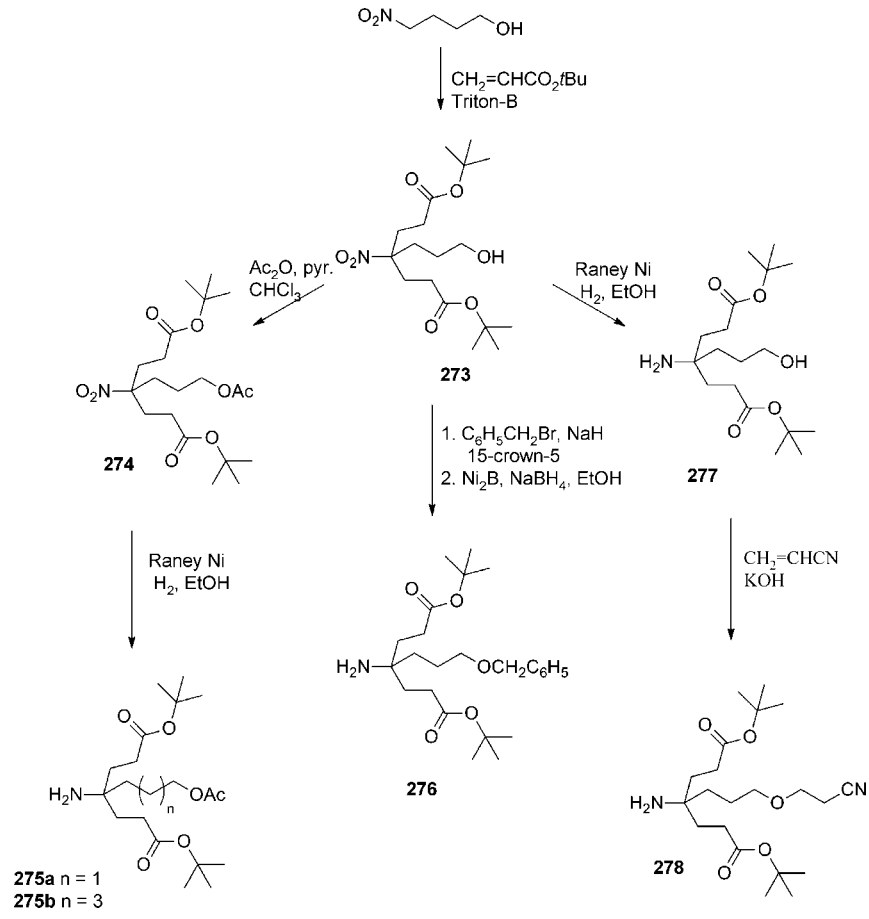
Figure 10. Astruc's dendrimers[631] that are capable of recognizing $H_2PO_4^-$.

Scheme 63. Synthesis of 1 → (2 + 1) Dendrons[859]



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277

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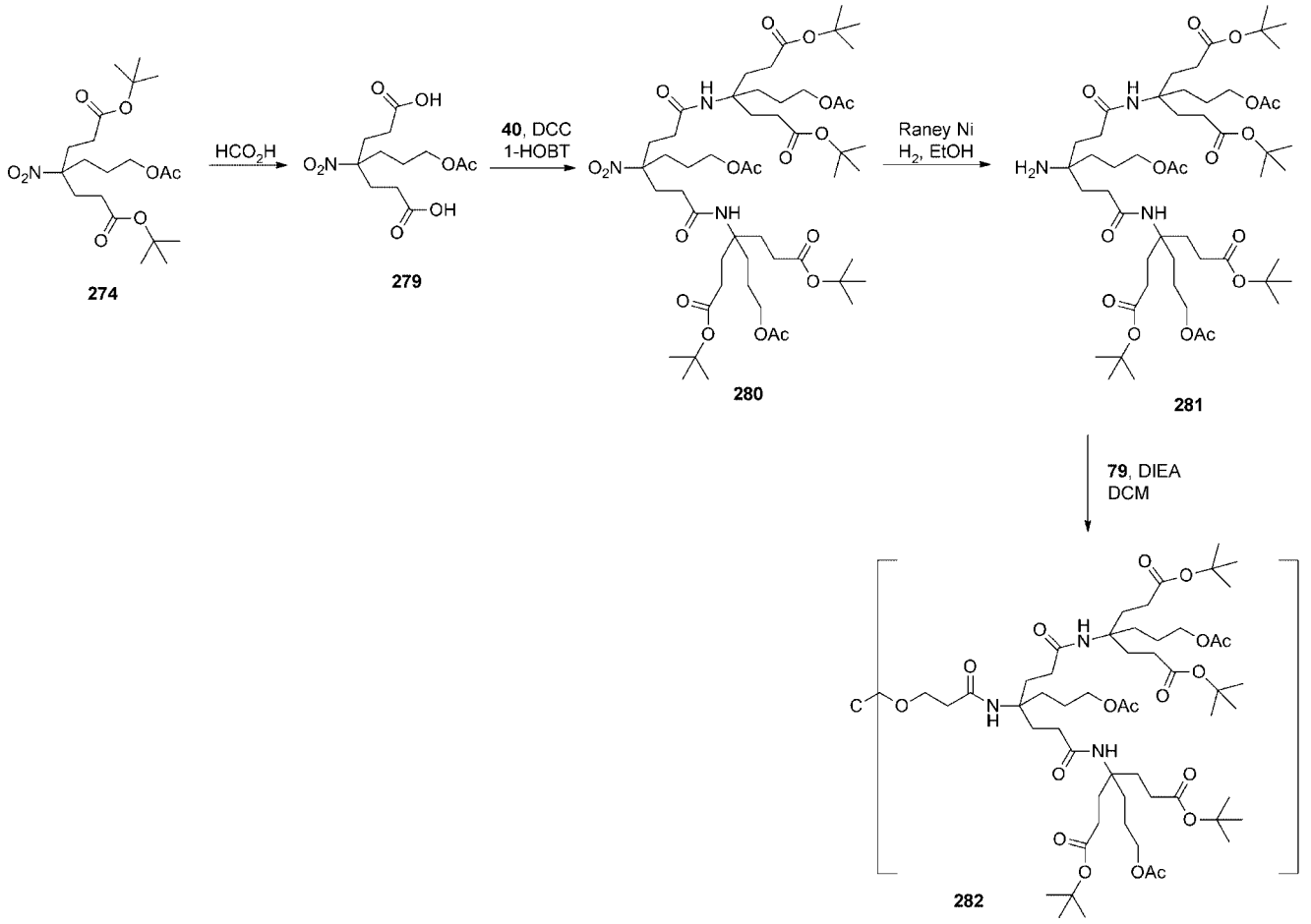
275a n = 1
275b n = 3

Scheme 64. Construction of 1 → (2 + 1) Dendrimers[859] with a Unique Functional Group at Each Tier



(**310**) or four-directional (**311**) core, respectively. The alcohol termini of ammonium chloride **311** were treated with excess tosyl chloride with pyridine in MeCN, followed by excess **309** in MeCN to give (>90%) the G1 pentaammonium dendrimer. Following two iterations, the G2 dendrimer **312** possessing 17 ammonium branching centers and 36 terminal hydroxyl groups was prepared.[872] Attaching these polyammonium polyols to a polymeric backbone, that is, the commercially available Merrifeld resin, generated a high capacity ion exchange substrate.[873] Similar polyammonium architectures have utilized chloromethylstyrene−methyl methacrylate supported on montmorrillonite[874] in which the hydroxyl termini were chloroacetylated, then capped with either triethylamine or triphenylphosphine. Examination of these polyammonium salts as phase-transfer catalysts for nucleophilic substitution reactions (e.g., SCN^- reacting with BuBr) revealed them to be highly activating with conversion yields approaching 100% in relatively short reaction times at reflux temperatures.

4. 1 → 3 P-Branched

4.1. 1 → 3 P-Branched, Alkyl Connectivity

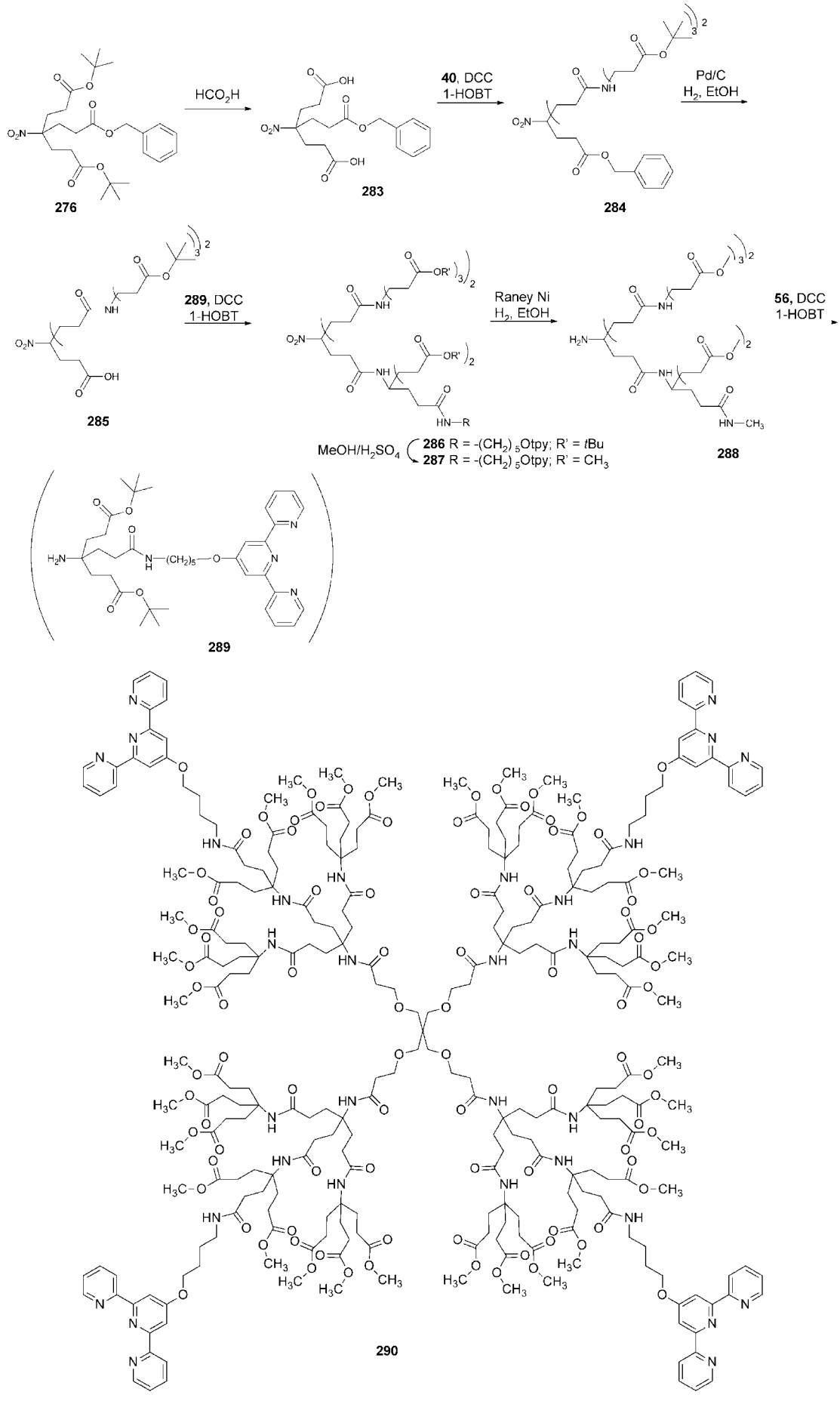
Engel and Rengan[870,875−877] reported and reviewed[871] the preparation of polyphosphonium cascade polymers (Scheme 70). The desired tetradirectional phosphonium core **315** was synthesized (7%) via treatment of phosphine **313** with 4-(methoxymethyl)bromobenzene (**314**) in dry MeOH with anhydrous $NiBr_2$. The tetramethoxy core **315** in dry MeCN was transformed (Me_3SiI) to the tetraiodide and subsequently reacted with phosphine monomer **313** to generate (23%) the G1 pentaphosphonium dendrimer **316**. The G2 **317** possessing 17 phosphonium moieties was generated (93%) by a similar iterative procedure and shown to possess good solubility in common organic solvents (e.g., MeCN, $CHCl_3$). Related three-directional dendrimers were similarly prepared via reaction of phosphine **313** with methyl, benzyl, or $C_{18}H_{37}$ halides to yield the starting core.

A related series of phosphonium dendrimers was constructed by Engel et al.[878] starting with tris(*p*-methoxymethyl)phenylphosphine (**313**) possessing (trivalent) phosphine and (pentavalent) phosphorane cores. These P dendrimers were prepared via oxidation (H_2O_2, AcOH) of building block **313** to give the corresponding P-oxide **318** (Scheme 71). Treatment of this methoxybenzyl ether with Me_3SiI in MeCN generated the desired benzyl iodide, which was followed by the addition of phosphine **313**. After two iterations, the central phosphine oxide of dendrimer **320** was reduced (Cl_3SiH) to afford (99%) the trivalent phosphine dendrimer **321**. Treatment of phosphine **321** with $NaAuCl_4$ gave (97%) the mono gold chloride−phosphorus dendrimer complex.

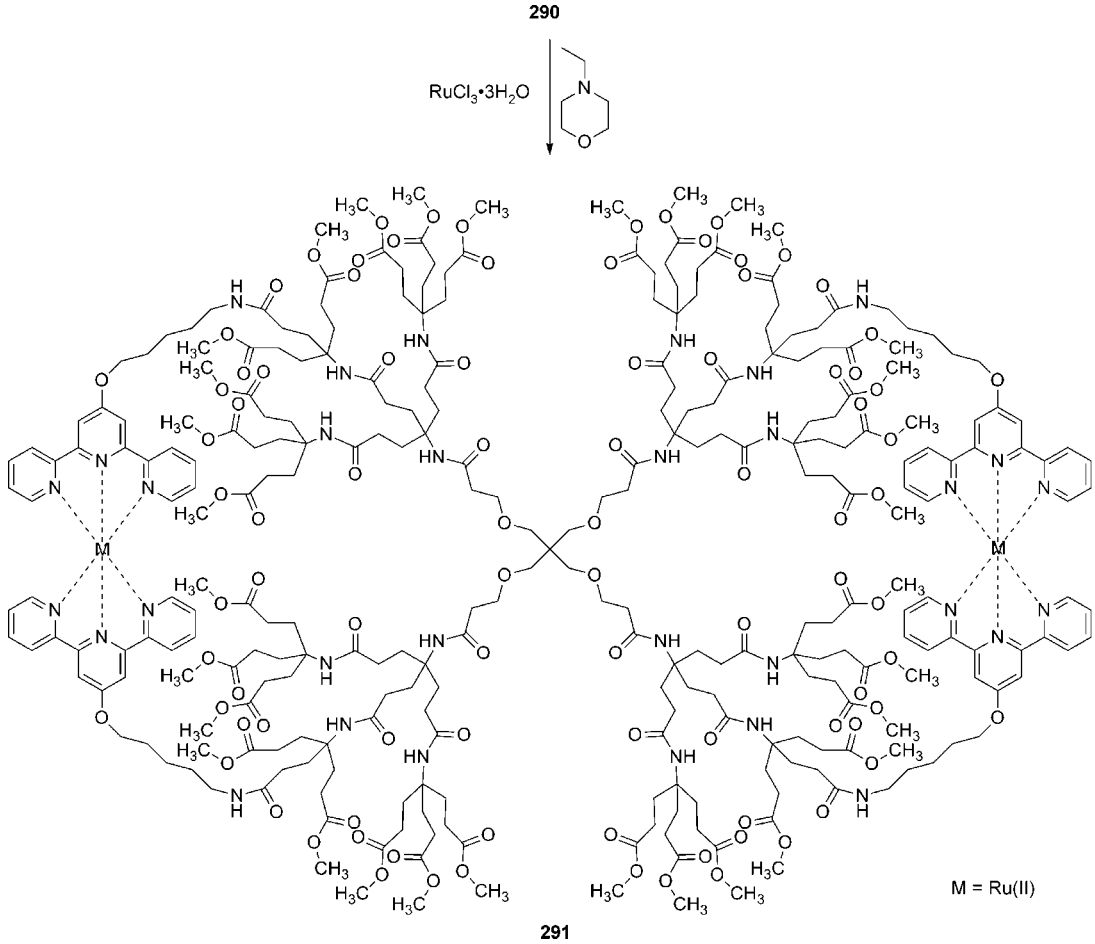
The neutral phosphorane core **322** was generated from the treatment of tetrakis(*p*-methoxymethyl)phenylphosphonium bromide (**315**)[878] in Et_2O under an argon atmosphere with 4-lithiobenzylmethyl ether. This pentavalent core was subjected to the previously described procedures to generate (83%) the unique five-directional G1 dendrimer **323** (Scheme 72).

Treatment of $C(CH_2OCH{=}CH_2)_4$ with $HP(CH_2CH_2C_6H_5)_2$ gave (90%) $C[CH_2OCH_2CH_2P(CH_2CH_2C_6H_5)_2]_4$, and addi-

Scheme 65. Construction of a 1 → (2 + 1) G2 Dendron[859] with a Single Unique Site on Its Outer Rim



Scheme 66. Assembly[860] of the Dendrimer Possessing the Four Unique Moieties Its Surface and Its Macrocyclization



tion of 1-bromomethylnaphthylene gave (99%) C[CH_2-$OCH_2CH_2P^+(CH_2CH_2C_6H_5)_2(CH_2C_{10}H_7)]_4(4Br^-)$.[879]

5. 1 → 3 Si-Branched

The formation of the 1 → 3 branched Si dendrimers appeared at about the same time (early 1990s) from several research groups, and the chemistry was based on very similar, high yield, iterative procedures [two steps, the Pt-catalyzed C−$SiCl_3$ formation, followed by either vinylation (−CH═CH_2) or allylation (−CH_2CH═CH_2)]. The C_2- and C_3-connectivity series were herein separated since, although the chemistry is similar, there is a different on-set of dense packing or crowding at the peripheral centers; see reviews in refs 80, 120, and 239.

Different substituted carbosilane-based dendrimers have been compared with the PAMAM counterparts using molecular mechanics in order to evaluate the shape and steric interactions with increasing generations.[880] The shape of the Si dendrimers is generally more spherical than PAMAMs, and at higher generations they can afford a greater number of termini at the macromolecule's surface without increasing the surface density leading to the ability to build higher generations of more completely branched dendrimers.

5.1. 1 → 3 Si-Branched, C_2 Connectivity

In 1994, Seyferth et al.[881,882] prepared a series of Si-based dendrimers up to G4 with −CH_2CH_2− connections between Si-branching centers. Employing the tetravalent nature of silicon, these macromolecules possessed a tetrahedral, four-directional core, as well as 1 → 3 Si-branching centers. The divergent strategy (Scheme 73) utilized two repetitive transformations: Pt-catalyzed alkyl trichlorosilane formation and vinylation using CH_2═CHMgBr. Reaction of the core, tetravinylsilane **324**, with H_2PtCl_6•$6H_2O$ and Cl_3SiH afforded (ca. 100%) tetrakis(trichlorosilane) **325**, which was treated with CH_2═CHMgBr to produce (63%) the corresponding G1 dodecavinylsilane **326**. Hydrosilylation of silane **326** via similar catalytic conditions resulted in the formation of impure products; however, satisfactory yields of the G1 dodeca(trichlorosilane) **327** were obtained using the Karstedt catalyst;[820] further vinylation gave good yields of the G2 dodeca(trivinylsilane) **328**.

Attempted transformation of vinylsilane **330** to the corresponding 36-trichlorosilane **331** using the Karstedt-catalyzed hydrosilylation led to impure products; however, changing the solvent from THF to Et_2O gave the desired G2 dendrimer **328** and suppressed unwanted side reactions. Conversion of the G3 trichlorosilane to the corresponding trivinylsilane proceeded smoothly, while the construction of the G4 108-trichlorosilane **332** (Scheme 74) required forcing reaction conditions (excess $HSiCl_3$, Karstedt catalyst, Et_2O, 140 °C, 45 h, Pyrex sealed glass vessel) due to the on-set of dense packing at the surface.

Reduction ($LiAlH_4$) of the G3 poly(trichlorosilane) **332** gave the terminal poly(trihydridosilane) **333** as a clear, hard solid. Similar reduction of the G1−3 trichlorosilanes afforded the related hydrido-terminated silanes (e.g., **329** and **328**; see Scheme 73). Interest in these materials for ceramic applications provided the impetus for cross-linking experi-

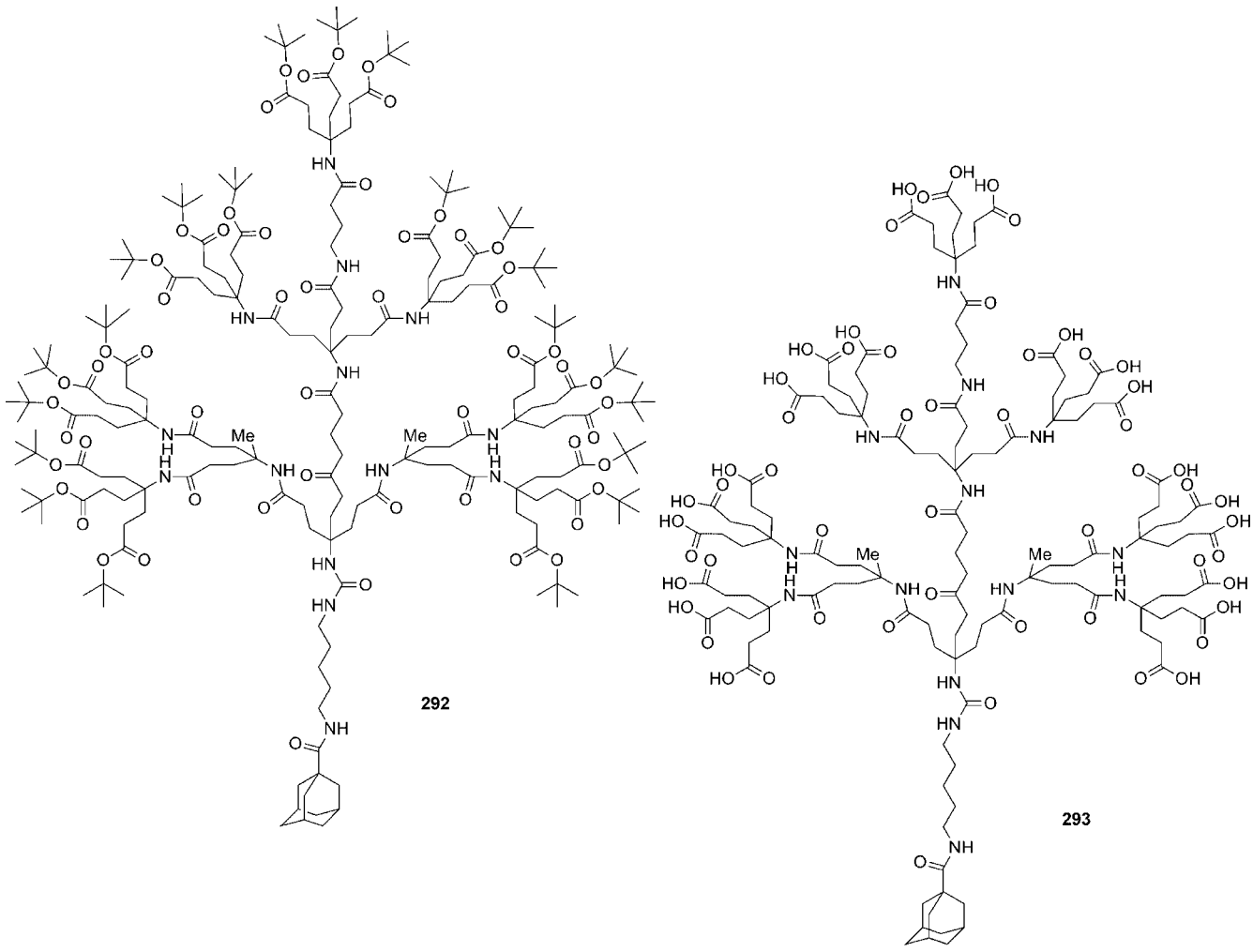


Figure 11. Assembled conifer trees.[460]

ments with the hydrido-terminated series; in particular, the readily available G1 dendrimer **329** was examined. Use, however, of a Zr-cross-linking agent resulted in the formation of products that were insoluble in most common organic solvents. X-ray crystallographic data and the corresponding structures were reported for the G1 polyhydrido **328** (Figure 12). These vinyl carbosilanes were surface-functionalized with (1) $-SiMe_2C{\equiv}CH$ moieties that were subsequently reacted with dicobalt octacarbonyl,[883] (2) terminal phosphines, (3) metallocenes, and (4) surface amines and sulfonic acid groups in order to enhance water solubility.

Friedmann et al.[884] employed similar technology for the construction of the G1−2, Si-based dendrimers with bulky triphenylsilane termini; the crystal structure of the smaller dendrimer was obtained, and the NMR data supported solvent exchange and the formation of inclusion compounds in higher generations in this series. The crystal structure of the dendrimer/THF inclusion complex was later reported.[885]

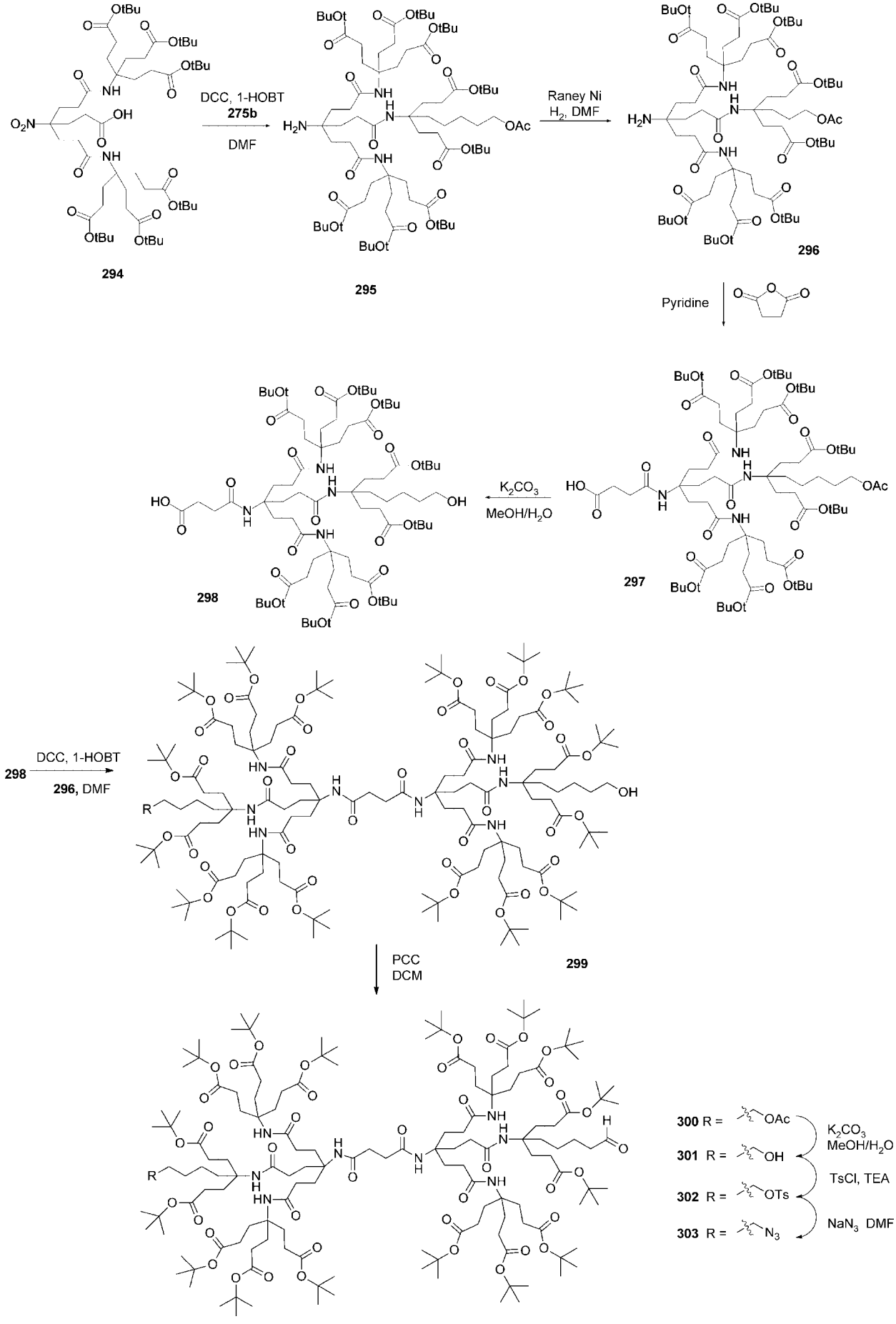
These 1 → 3 branched carbosilanes using polyhedral silsesquioxane (POSS) cores have been reported;[886] a single-crystal X-ray structure was obtained for the 24-vinyl-terminated dendrimer **334** (Figure 13), revealing disorder in the vinyl moieties. Treatment of the trichlorosilane surface groups with $LiCH_2PR_3$ (R = Me, hexyl, or Ph) gave the desired POSS capped with phosphine moieties;[887] these were shown to catalyze hydroformylation reactions. The P-containing dendrimers (i.e., with either a $-CH_2PR_2$ or $-CH_2CH_2PR_2$ surface) were converted to Rh complexes that were used for the hydrocarbonylation of alkenes in polar solvents;[888] the conversions were very high and "the reactions were found to proceed mainly via the formation of the corresponding aldehydes".

The nonpolar fluorinated carbosilanes, for example, $Si[CH_2CH_2Si[(CH_2)_3OCH_2C_8F_{17}]_3]_4$ and $Si[CH_2CH_2Si-[CH_2CH_2Si[(CH_2)_3OCH_2C_8F_{17})_3]_3]_4$, have been prepared and analyzed by atmospheric pressure chemical ionization mass spectroscopy, MALDI TOF MS, and SAXS, as well as T_g and TGA.[889]

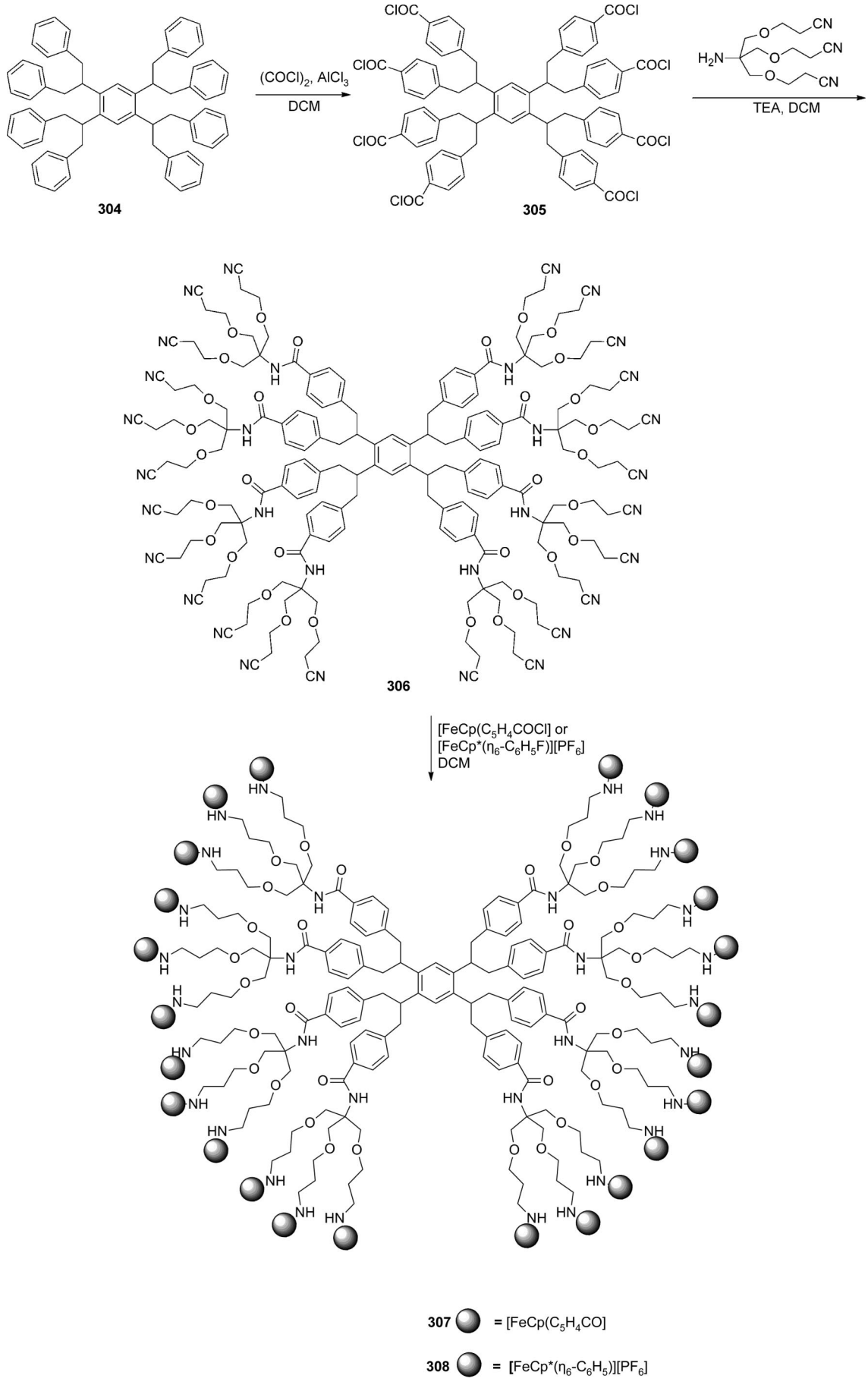
The vinyl-generated G1 and G2 carbosilanes having surface methoxysilanes and arborols with octadecyl and phenyl groups were used in a polycondensation [sol−gel process] to generate porous and nonporous hybrid xerogels, respectively.[890] Additional reports on the preparation of similar "stargels",[891] using the corresponding core silanes, for example, $Si[CH_2CH_2Si(OEt)_3]_4$, are available.

In a study of hyperbranched poly(carbosilanes), 2-bromo-5-trivinylsilylthiophene was prepared (58%) from 2-bromothiophene and $ClSi(CH{=}CH_2)_3$ with *n*BuLi and diisopropylamine; a similar procedure was used to generate (64%) the related furan derivative.[892] Dendrons of either $(Et_3SiCH_2CH_2)_3SiCl$ or $(Ph_2MeSiCH_2CH_2)_3SiCl$ were reacted with $K(C_5H_5)$ then KH affording $K[(Et_3SiCH_2CH_2)_3Si(C_5H_4)]$ or $K[(Ph_2MeSiCH_2CH_2)_3Si(C_5H_4)]$, respectively. These dendronized cyclopentadienides were then transformed into mixed ring titanocenes $[[(Et_3SiCH_2CH_2)_3Si(C_5H_4)]-(C_5R_5)TiCl_2]$ or $[[(Ph_2MeSiCH_2CH_2)_3Si(C_5H_4)](C_5R_5)TiCl_2]$

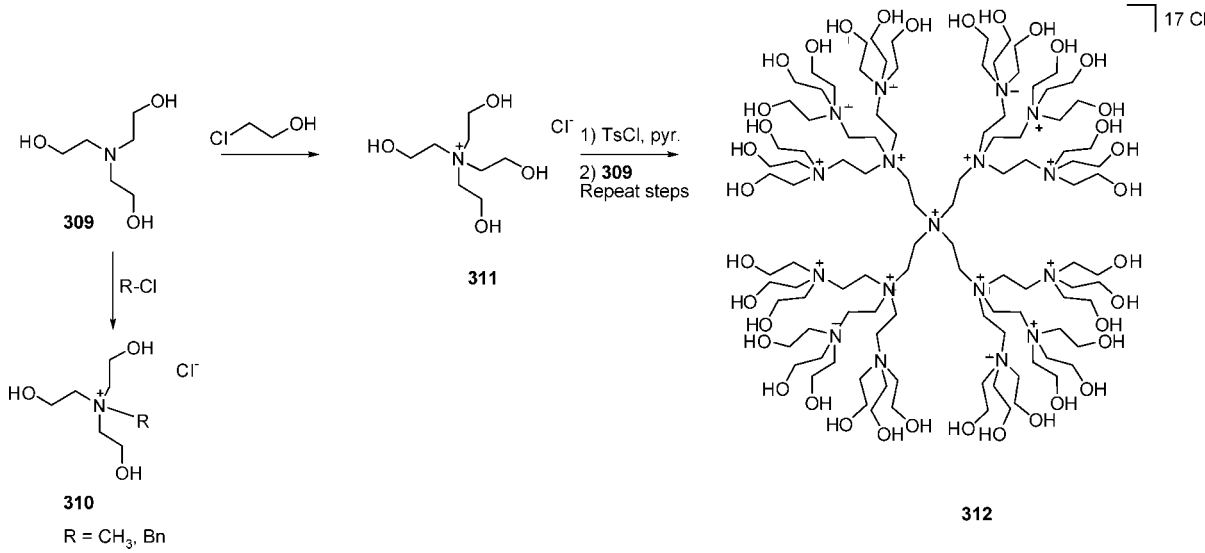
Scheme 67. Construction of an Unsymmetrical Two-Directional Dendrimers[863]



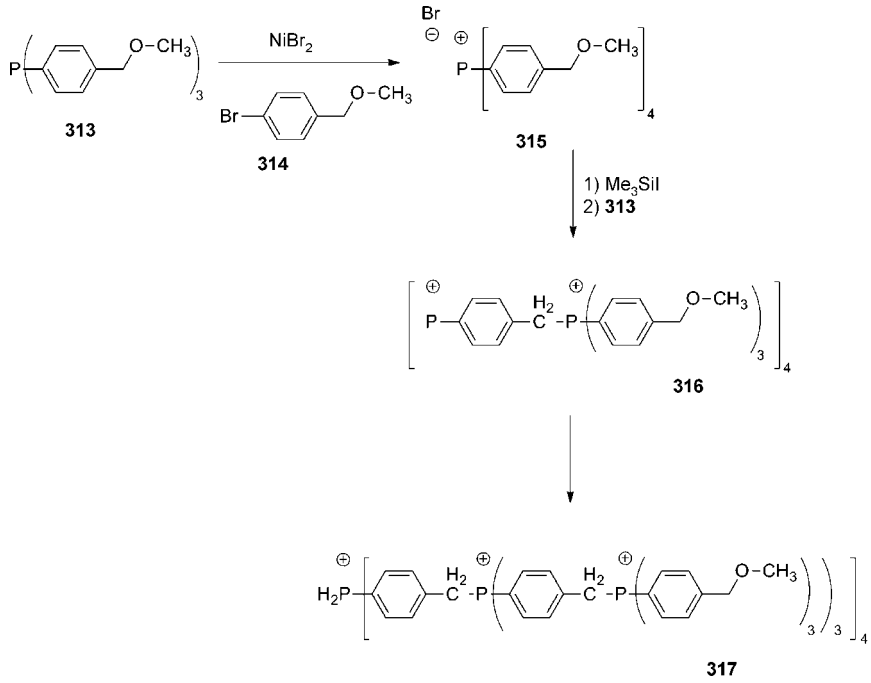
Scheme 68. Formation of Polycationic Metallodendrimers[868]



Scheme 69. Dendrimers Possessing 1 → 3 N-Branching Centers[870]



Scheme 70. Preparation of Charged P-Based Dendrimers[870,875,876]



(R = H or Me), as well as symmetrically substituted metallocenes $[[(Ph_2MeSiCH_2CH_2)_3Si(C_5H_4)]_2MCl_2]$ (M = Ti or Zr).[893] The cyclopentadienyl(β-diketiminato)titanium or zirconium chlorides, $(\eta^5\text{-}C_5H_5)MCl_2[CH[C(NC_6H_4\text{-}4\text{-}OR)Me]_2]$ (M = Ti or Zr), where R = $Si(CH_2CH_2SiMePh_2)_3$, have been created.[894]

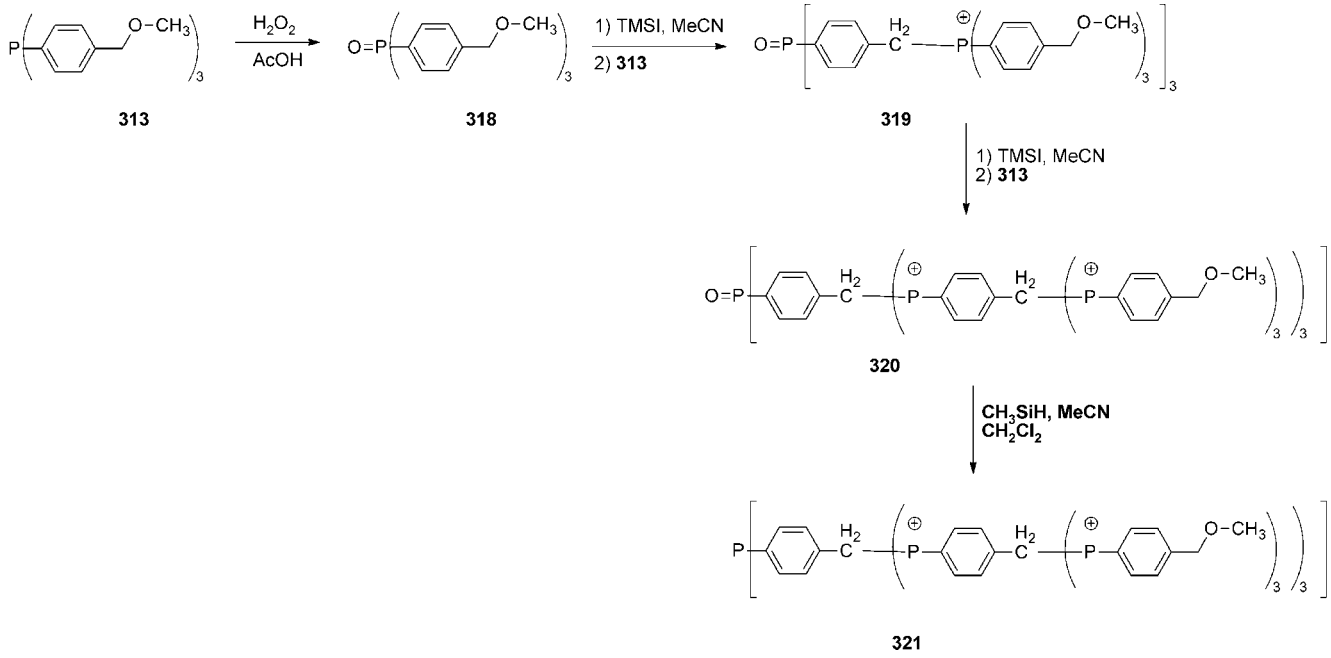
Landskron and Ozin have reported[895] a class of materials called mesoporous dendrisilicas that are based on $Si[CH_2CH_2Si(OEt)_3]_4$, $Si[CH_2CH_2Si[CH_2CH_2Si(OEt)_3]_3]_4$, and $CH_2[Si(CH_2CH_2Si(OEt)_3)_3]_2$, which were prepared from the corresponding chlorides in the presence of EtOH.[896,897] Either acid- or base-catalyzed hydrolysis of the trialkoxysilyl groups and subsequent template-directed condensation generated an ordered dendrisilica nanocomposite; then the template was removed affording the desired periodic mesoporous dendrisilica.

Treatment of 1,3,5-tris[4-(1,12-dicarba-*closo*-dodecaboran-1-ylmethyl)phenyl]benzene with *n*-BuLi, followed by $ClSi(CH{=}CH_2)_3$, gave (51%) the hexa(trivinylsilyl) derivative, which offered an interesting core to construct higher order carbosilanes by the above procedures.[898]

5.2. 1 → 3 Si-Branched, Vinyl Connectivity

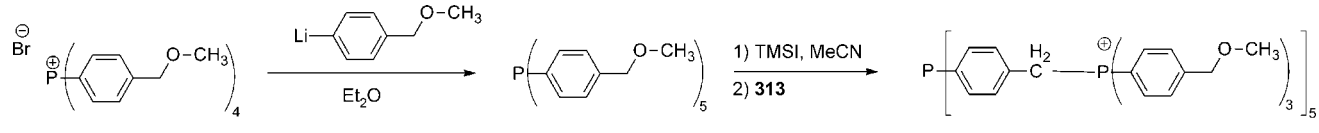
The G1,2 vinyl-connected carbosilane dendrimers were initially synthesized using alkynylation−hydrosilylation steps with $C_6H_5C{\equiv}CLi$ and the 1 → 2 branching $HSiMeCl_2$, as building blocks and tetrakis(phenylethynyl)silane, as a core molecule.[899−901] Application of this procedure to the 1 → 3 branching motif has appeared[901] in which 1,3,5-tribromobenzene was treated with $Me_2Si(CH{=}CH_2)MgCl$, followed by $HSiCl_3$ with Pt/C catalyst to generate the desired activated core (**336**, Scheme 75); treatment with $C_6H_5C{\equiv}CLi$ generated **337**, which was transformed to the G2 product **338** via the same simple two-step process.[902] Attempts to attain G3 failed to give a uniform product. This synthetic procedure using the original 1 → 2 branching

Scheme 71. Construction of P-Dendrimers with Neutral Trivalent P Cores[878]



313 318 319 320 321

Scheme 72. Cascade Synthesis Employing the Novel Pentavalent, Neutral P Core 322[878]



315 322 323

pattern was also conducted on a 1 → 3 Si-branching core, $(SiOMeCH_2CH_2SiCl_3)_4$, to reach the G4 level,[903] as well as $[CH_2Si(CH_2CH_2CH_2SiMeCl_2)_3]_2$.[904]

5.3. 1 → 3 Si-Branched, C_3 Connectivity

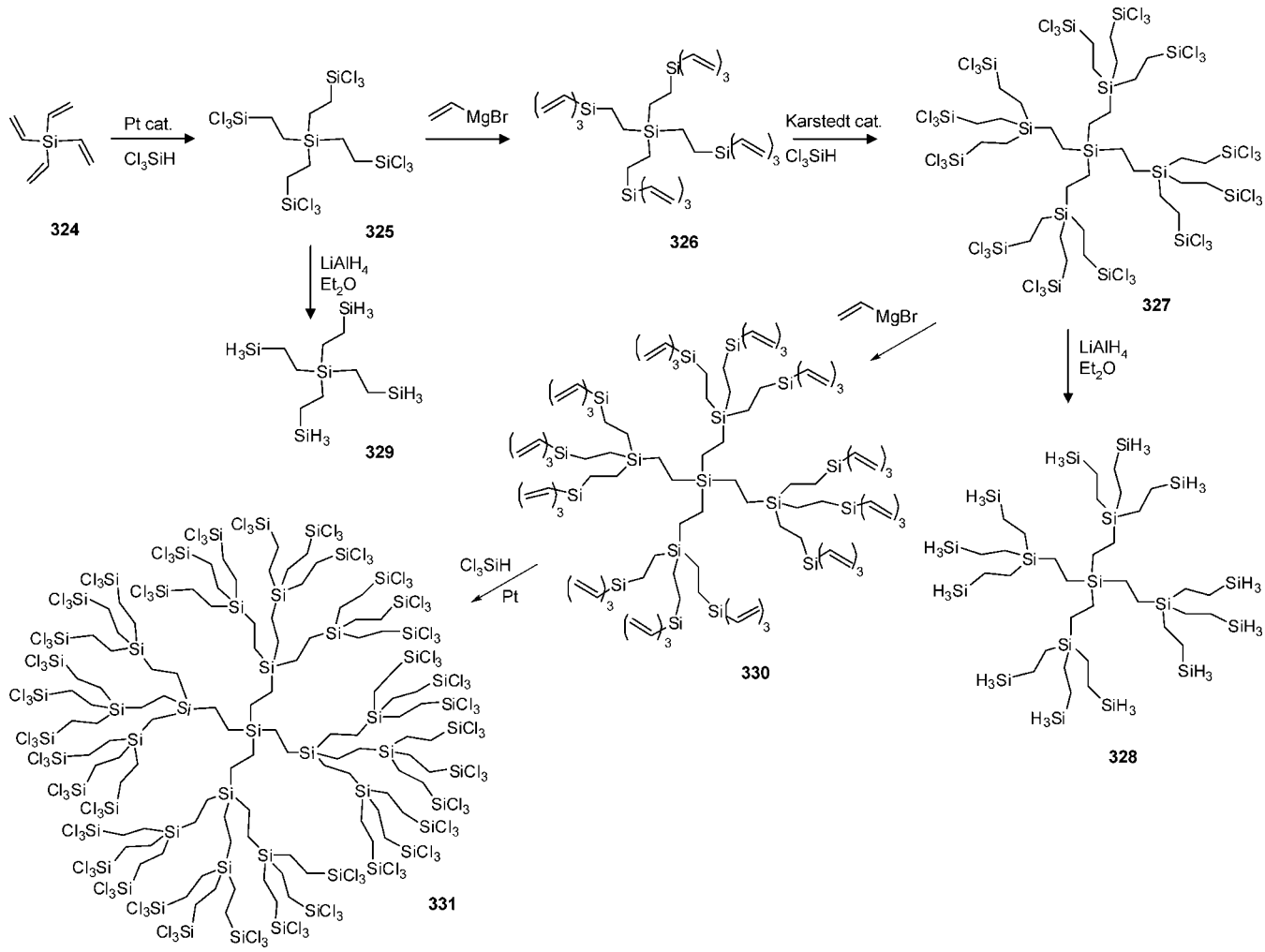
In 1992, van der Made and van Leeuwen reported[896,905] the synthesis of Si-based dendrimers via a repetitive hydrosilylation and alkenylation sequence (Scheme 76). Hence, the zeroth tier tetraalkene **339**, prepared (99%) from $SiCl_4$ and $CH_2{=}CHCH_2MgBr$, was treated with Cl_3SiH in the presence of a Pt catalyst to give (100%) the G1 tetrakis(trichlorosilane) **340**. Subsequent exhaustive alkylation with a 10% excess of $CH_2{=}CHCH_2MgBr$ afforded dodecaalkene **341**. This simple two-step procedure was used iteratively to give up to the G5 dendrimer. Repetitive 1 → 3 branching employing tetravalent Si gave the G5 dendrimer ideally possessing a molecular weight of 73 912 amu and 972 peripheral groups.

Employing similar chemistry for carbosilane construction, van Leeuwen et al.[906] prepared up to G3 of dendritic wedges possessing an alkyl bromide focal group. Reaction with excess ammonia afforded the corresponding alkyl amine moieties, which were reacted with 1,3,5-tris(chlorocarbonyl)benzene to give the desired trisamide aryl-cored dendrimer. Binding studies of these materials using Fmoc-glycine, *Z*-glutamic acid 1-methyl ester, and propanoic acid as guests were performed; 1:1 complexes were observed based on H-bonding. Their use of $[[R_3Si(CH_2)_3]_3Si(CH_2)_3]_3Si(CH_2)_3NH_2$ with polyisocyanopeptides gave access to novel block copolymers, which were characterized and shown to respond to the addition of Ag^+ ions generating nanowires possessing [111] orientated crystalline silver.[907]

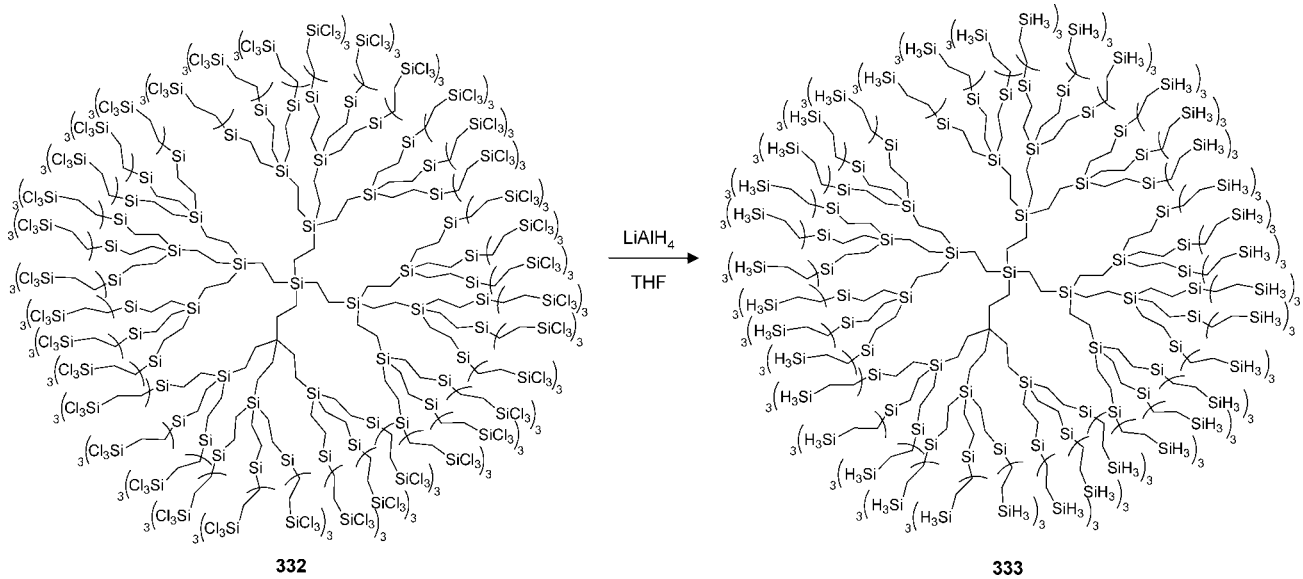
Frey et al.[908,909] employed the same method,[496,905,910] as well as others,[881,911−913] for the preparation of the G1−3 1 → 3 Si-branched dendrimers possessing 12, 36, and 108 termini, respectively. An excellent review by Frey and Schlenk[914] that deals exclusively with Si dendrimers is available. Each dendrimer was peripherally modified with mesogenic cholesteryl groups[908,915] by surface hydroboration;[915,916] then treatment of the terminal OH groups with cholesteryl chloroformate yielded carbonate-based attachment; G1 was completely substituted, while G2 and G3 were determined to possess distribution of 32−36 and 92−108 moieties, respectively. Ultrathin films (5−15 nm) of these carbosilane dendrimers were examined by AFM; films formed via high concentration solutions possessed a thickness of two to four dendrimers, whereas films obtained from low concentration solutions possessed monolayer thickness or irregular hole patterns. For films formed by both G1 and G2 (in the liquid crystalline phase), a molecular "reorientation" upon annealing was observed as manifested in a gradual coalescence of the holes. It was postulated that the mesogenic groups reorient from perpendicular to parallel juxtaposition relative to the surface due to more favorable carbon−mica interaction(s). Frey et al. prepared a series of analogous carbosilane dendrimers bearing hydroxy termini,[917] as well as rigid cyanobiphenyl mesogenic termini;[918] see Goodby's reviews of mesogenic molecular crystalline materials.[919,920]

The synthesis of a surface of chiral moieties has been undertaken as shown in Scheme 77 in which chiral β-amino alcohols (i.e., **343**) have been incorporated; these were shown to be efficient catalysts for the enantioselective addition of diethyl zinc to aldehydes.[921]

Scheme 73. Preparation of Carbosilane Dendrimers[881] Based on C_2 Connectivity



Scheme 74. Reduction of Terminal Trichlorosilane Moieties to Trihydridosilane Units[881]



Kim et al.[916] prepared a G4 carbosilane dendrimer possessing a reported 162 allyl end groups (Scheme 78), starting from bis(allyl)methylphenyl silane (**345**). The initial bis(trichlorosilane) **346** was treated with 2 equiv of Cl_3SiH (Pt, THF, heat), followed by 6 equiv of $CH_2{=}CHCH_2MgBr$ to give hexaalkene **347**. Subsequent hydrosilylation afforded the corresponding poly(trichlorosilane) **348**. Repetition of the sequence afforded the G4 dendrimer **349**. The poly(trichlorosilane) precursor was reduced (LAH) to yield the poly(silane) possessing 54 SiH_3 terminal moieties. Attempts to construct the G5 level were unsuccessful presumably due to dense packing limitations. These authors also noted that dendrimer viscosity increased with increasing generation. Muzafarov et al. have recently reported the successful

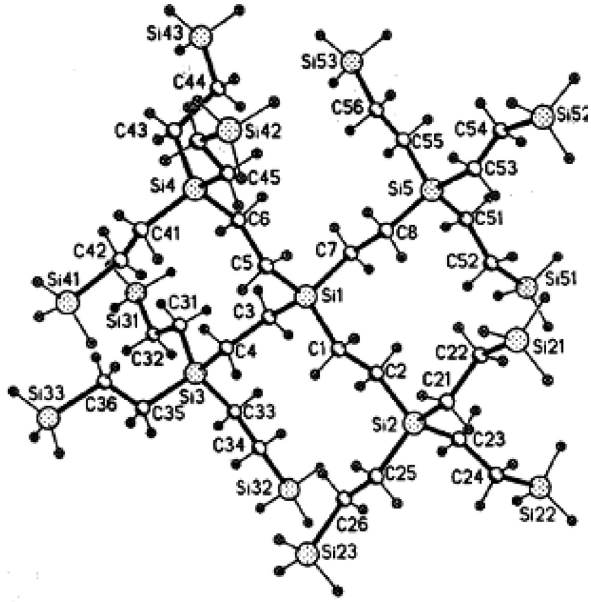
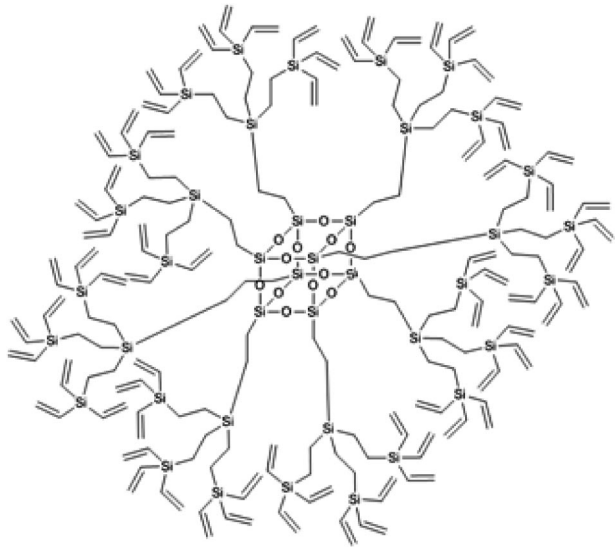


Figure 12. X-ray structure of a dendrimer possessing silicon-based superstructure. Reprinted with permission from ref 881. Copyright 1994 American Chemical Society.



334

Figure 13. 24-Vinyl-terminated, POSS-based dendrimers **334**.[886]

synthesis up to the G6 level of the parent carbosilane dendrimers and that difficulties were experienced at G7, and they suggested that this is due to a dualistic nature of these materials possessing macromolecular and nanoparticle properties.[922] A modified route to these siloxanes has been reported[923] in which nucleophilic substitution was accomplished using allyl alcohol. A new class of amphiphilic−dendritic diblock copolymers, based on hydrophilic linear PEO (focal group) and hydrophobic dendritic carbosilane possessing allyl termini, has been reported.[924,925] Méry et al.[926] reported the formation of worm-like dendrimers starting from a poly(methylhydrosiloxane) core and attaching short propylsilane trees by the above procedure; due to the enhanced onset of steric congestion, only the G2 level was reached (see section 5.6).

Carbosilane dendrons have been focally modified with pyrene and investigated using time-correlated single-photon counting and steady-state fluorescence spectroscopy.[927] Similarities were observed for pyrenyl excimer formation on dendrons of differing generations.

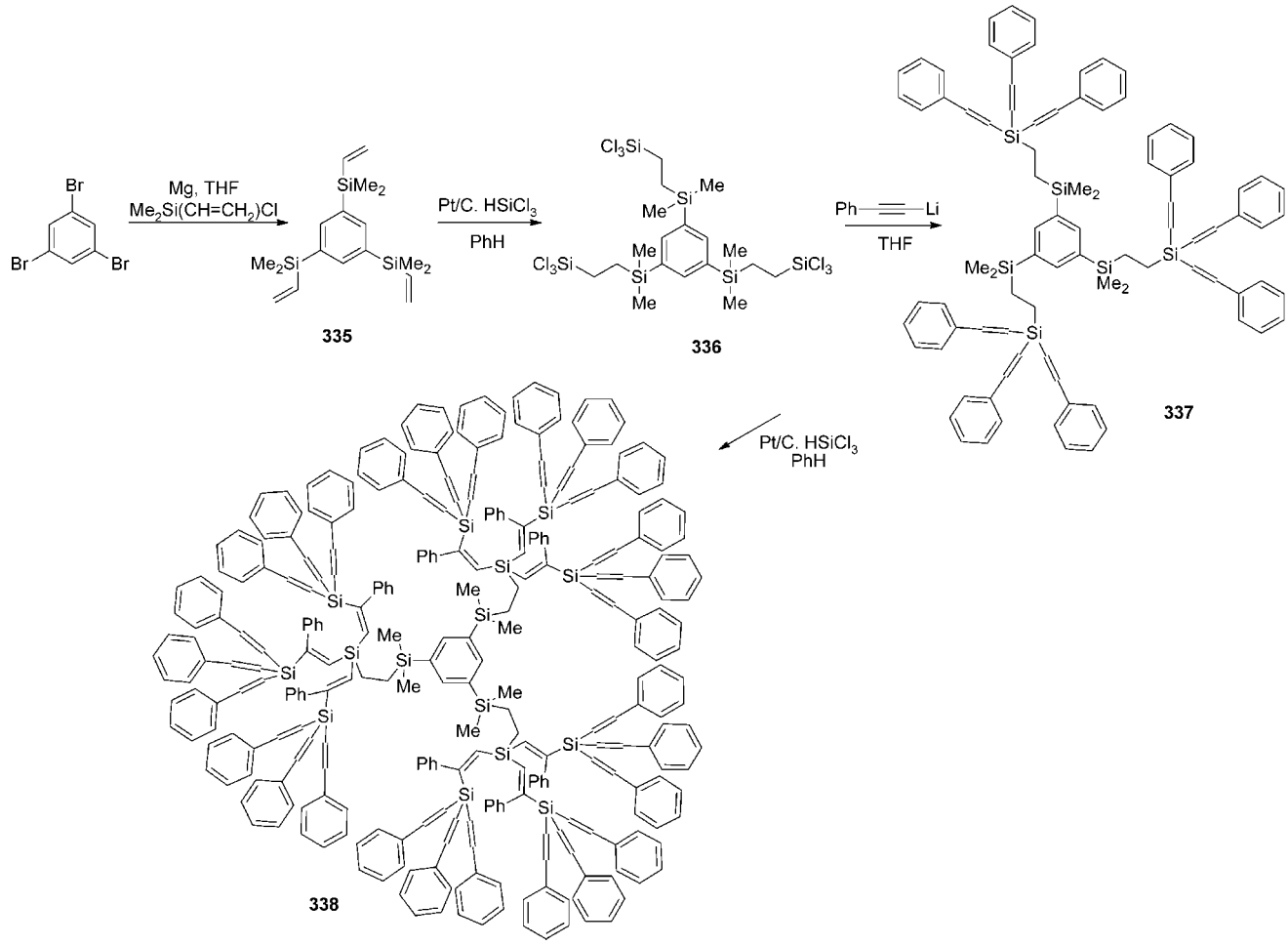
Frey et al.[928,929] coated this type of branched scaffolding possessing allyl termini via free-radical addition with 3,3,4,4,-5,5,6,6,7,7,8,8,8-tridecafluoro-*n*-octylmercaptan. The G1 carbosilane with the perfluoroalkyl surface exhibited a highly ordered smectic mesophase in the −15 to −30 °C temperature range, while the G2 and G3 formed hexagonally ordered columnar arrays. Increased dense packing was postulated to account for the generation-dependent thermal properties. A segmental dynamics study of these terminal perfluorinated (C_6F_{13}) carbosilanes using quasielastic neutron scattering and X-ray scattering was undertaken.[930,931] As a result of end group and carbosilane microphase separation, generation-dependent superstructures were observed, whereby helical end chains formed layers between branched framework domains. The dielectric relaxation of these perfluorinated materials has been examined;[932] a fast β relaxation was observed possessing Arrhenius behavior, while the dominant α-process was found to be comprised of fast and slow components. Piers et al. attached *m*-[-$OC_6F_4B(C_6F_5)_2$], using *m*-$MeOC_6F_4B(C_6F_5)_2$, to $Si[(CH_2)_3Si[(CH_2)_3SiMe_2H]_3]_4$ by simply mixing for 8 h at 25 °C to give a quantitative yield in >95% purity with the loss of CH_4;[933] the product was used as a catalyst for the hydrosilylation of acetophenone using triethylsilane.

Frey et al. undertook a molecular force field study pertaining to the host properties of carbosilane dendrimers.[934] Core structural variations were examined, as well as outer shell denseness. Inner cavity dimensions (5−15 Å) were determined, while higher generation constructs possessed peripheral holes of the order of 2−3 Å. A surface fractal dimension of 2.1 was calculated. Neutron spin echo spectroscopy revealed a relaxation time that was attributed to form fluctuations of particles of these fluorinated carbosilanes.[935]

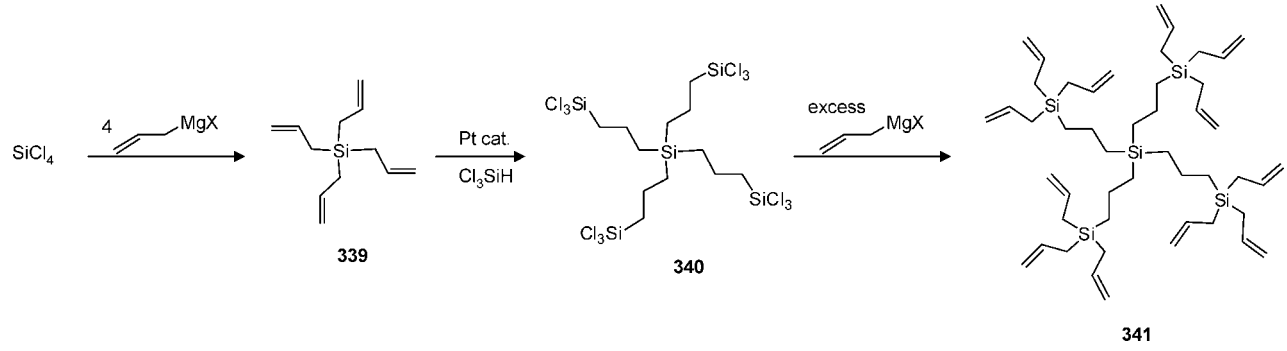
Kriesel and Tilley[936−938] reported the preparation of dendrimer-based xerogels using the G2,3 triethoxysilyl-terminated carbosilanes. Gel formation was achieved by acid-catalyzed (HCl) hydrolysis, followed by solvent removal. The observed small pore volumes suggested a denser xerogel structure than that obtained using hard spheres of comparable size. These xerogels have been examined as new catalyst supports,[939] and they were shown to be very selective as well as significantly more active (yield and initial rate) than the Shell catalyst [silica with $Ti(OiPr)_4$].

von Koten et al.[940−943] used their $Si[(CH_2)_3Si(CH_2CH{=}CH_2)_3]_4$[881,896,905] to generate the $Si[(CH_2)_3Si[(CH_2)_3SiMe_2Cl]_3]_4$ core, which was treated with $HO(CH_2)_4OCONC_6H_2(3,5\text{-}CH_2NMe_2)$ (4-Br) to afford (67%) the desired dodeca(aryl-termini) that were transformed to the 12 Ni(II) centers capable of regiospecific catalytic activity for the Kharasch addition[944] of polyhaloalkanes to carbon−carbon double bonds. The novel surface group functionalization of $Si[(CH_2)_3Si(CH_2)_3SiMe_2\text{-}[4\text{-}(3\text{-bromopyridine})]_3]_4$, in which the heteroaromatic bromine was chemically transformed to different moieties, for example, 4-C_6H_4Me, $-CH{=}CHCO_2Et$, or $-C{\equiv}CC_6H_5$, has appeared.[945] The related air-stable $Si[(CH_2)_3Si[(CH_2)_3SiMe_2C_6H_4CH_2OC_6H_4PdMe(bpy\text{ or }TMEDA)]_3]_4$ have been prepared, and their reactivity has been evaluated.[946] The use of G2 core but terminating with $-C_6H_4CH_2NMe_2$ permitted the generation of $Si[(CH_2)_3Si[(CH_2)_3Si[(CH_2)_3SiMe_2C_6H_3CH_2NMe_2PdpyrCl]_3]_3]_4$, which

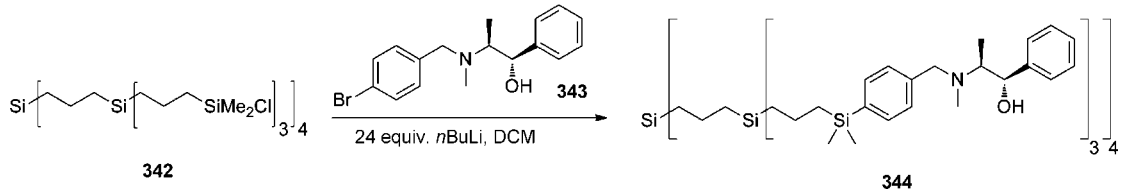
Scheme 75. The Synthesis of Unsaturated Carbosilane Dendrimers[902]



Scheme 76. Dendrimers Prepared Using a Tetraallyl-Substituted Silicon Core Based on C_3 Connectivity[896,905]



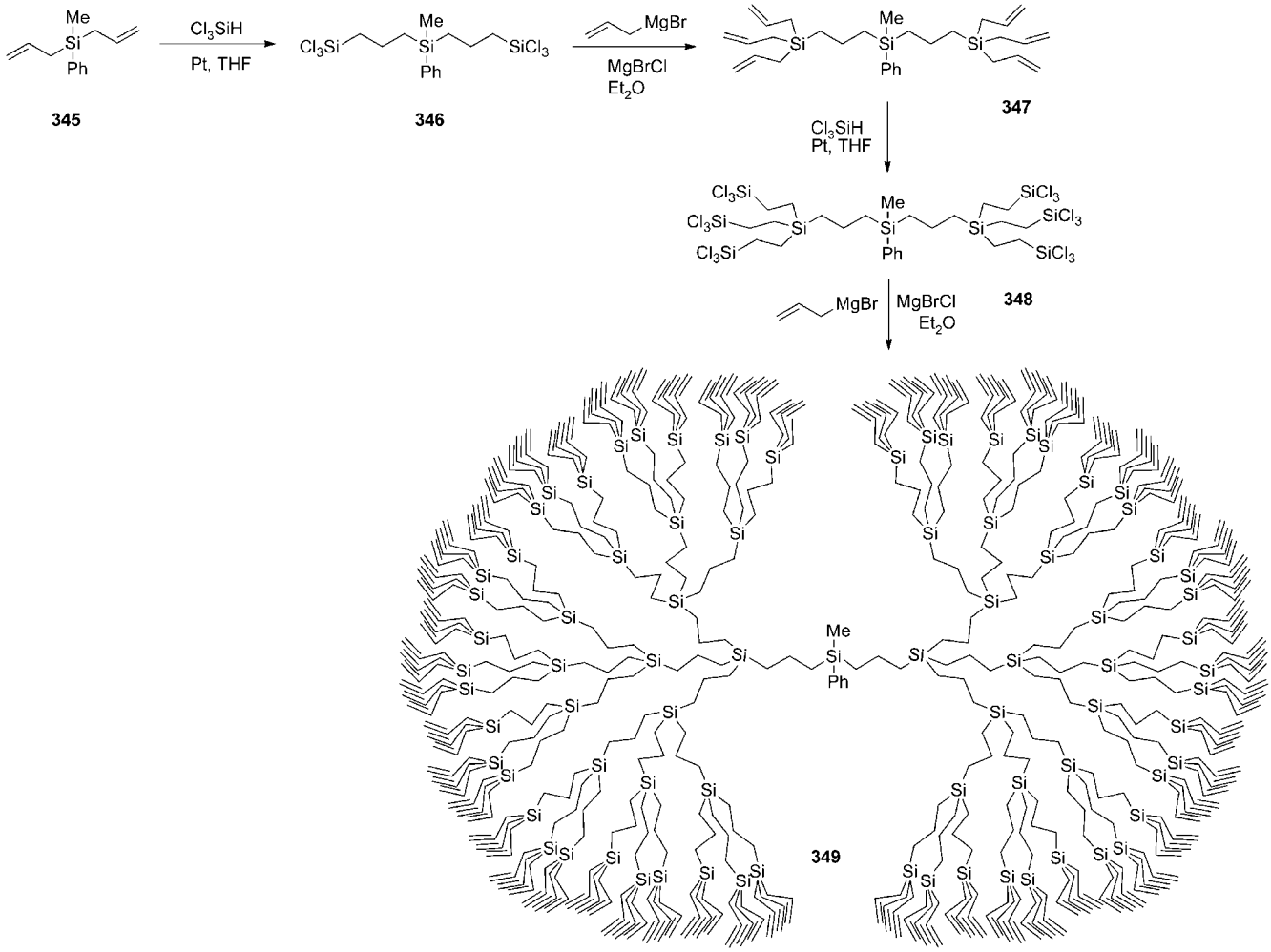
Scheme 77. Synthesis of Chiral-Coated Carbosilane Dendrimers[921]



with $AgBF_4$ in wet acetone gave the related polycationic Pd(II) metallodendrimers.[947]

The addition of 5-[3-(1,1,3,3-tetramethyldisiloxy)propyl]-25-hydroxy-26,27,28-tris(benzoyloxy)calix[4]arene to the above dodecaalkene generated the dodecacalixarene-capped carbosilane dendrimer.[948] Tilley et al.[949] prepared $Si[(CH_2)_3Si[(CH_2)_3Si[CH_2CH_2SiMe(CH_2C_6H_5)_2]_3]_3]_4$, which with excess $\langle [Cp^*Ru(NCMe)_3]^+ OTf^- \rangle$ in $ClCH_2CH_2Cl$ at 95 °C for 5 days gave (77%) the corresponding polycationic metallodendrimer possessing $[Cp^*Ru^+]$ termini. Treatment of $Si(CH_2CH{=}CH_2)_4$ or $Si[(CH_2)_3Si(CH_2CH{=}CH_2)_3]_4$ with $HSiMe_2CH_2SC_6H_5$[950] in the presence of Pt(0) gave the corresponding $Si[(CH_2)_3SiMe_2CH_2SC_6H_5]_4$ or $Si[(CH_2)_3Si[(CH_2)_3SiMe_2CH_2SC_6H_5]_3]_4$, which with a slight excess of lithium naphthalenide[951] afforded the reactive $Si[(CH_2)_3SiMe_2CH_2Li]_4$ or $Si[(CH_2)_3Si[(CH_2)_3SiMe_2CH_2Li]_3]_4$;[952] these

Scheme 78. Preparation of a Carbosilane Dendrimer[916] with a Purported 162 Allylic Termini



lithio reagents readily react with D_2O, $ClXMe_3$ (X = Si or Sn), or $ClSnBu_3$ to label or cap these carbosilanes.

Gade et al.[953] surface-functionalized $Si[(CH_2)_3Si-[(CH_2)_3SiMe_2Cl]_3]_4$ with 4-(3-butynoxy)-10-methyl-bis(2-pyridinylimino)isoindolate via an alkynyl linker; these terminal moieties were subsequently reacted with $[PdCl_2(PhCN)_2]$ to generate the pallada-dendrimers.

A novel organosilane 4-triallylsilylphenol dendron that can be used either convergently or divergently was developed by van Koten et al.;[954] the G1[955,956] and G2[957] levels were also prepared. Facile core attachment (Et_3N) of the dendron was demonstrated using 1,3,5-tris(chlorocarbonyl)benzene; the X-ray crystal structure was obtained.[955] Amide connectivity has also been derived from this same acid chloride except using related 1 → 3 Si dendrons with an amino focal group, which was prepared from the corresponding bromide.[906] Multidentate carbosilane films were prepared by thermally induced hydrosilylation of this G1−3 bromide family of allyl-surfaced dendrons on hydrogen-terminated silicon(111) surfaces.[957] van Koten and others have recently used this 1 → 3 Si core to build reactive organometallic reagents,[958−962] as well as tertiary phosphine catalysts.[963]

The incorporation of a 1,1′-bis(diethylphosphonite)ferrocene, xantphos, or PCl_3 core has been accomplished by means of a simple convergent approach using $RSiR'_3$, $RSi[(CH_2)_3SiR'_3]_3$, or $RSi[(CH_2)_3Si[(CH_2)_3SiR'_3]_3]_3$, where R = $BrC_6H_4CH_2CH_2-$ and R′ = Me or $-CH_2CH=CH_2$, shown in Figure 14 (**350** and **351**). The rhodium complexes of the P ligands were made and evaluated as catalysts for both hydroformylation and hydrogenation.[964]

The axially chiral BICOL backbone, based on a chiral monodentate phosphoramidite ligand or carbazole analogue of BINOL,[965] was functionalized with two *N*,*N*′-$(CH_2)_3Si[(CH_2)_3Si[(CH_2)_3Si[(CH_2)_2CH_3]_3]_3]_3$ dendrons; high enantioselectivities were obtained when these monodentate ligands were applied in the rhodium-catalyzed asymmetric hydrogenation of methyl 2-acetamidocinnamate.[966] The synthesis of the $P[(2\text{-}HOC_6H_4)(4\text{-}RC_6H_4)_2]$, where R= $-CH_2CH_2Si[(CH_2)_3Si[(CH_2)_3SiMe_3]_3]_3$, and its transformation to the internal nickel catalyst used in ethylene oligomerization have been reported.[967]

The two-directional 1,6-dihydroxyhexane was transformed to the bis-allyl ether, which was used to generate the G3 allyl-terminated dendrimer by the alternating hydrosilylation−allylation procedure.[968] Two-directional dendrimers, for example, $[Me(CH_2)_2[Si(CH_2)_3[Si(CH_2)_3]_3]_3]_3Si(CH_2)_3N=C=N(CH_2)_3Si[(CH_2)_3Si[(CH_2)_3Si[(CH_2)_2CH_3]_3]_3]_3$, were synthesized[969] in a divergent way, starting from allyl chloride and a repetitive sequence of hydrosilylation with $HSiCl_3$ and $CH_2=CHCH_2MgBr$, followed by reduction of the terminal double bonds; the dendritic carbodiimide was used to mediate the lactamization of dipeptides.

These 1 → 3 branched carbosilanes, using POSS cores, have been noted above[886] with a C2 connection between the POSS core and the initial Si-branching point; then step growth with $CH_2=CHCH_2MgBr$ gave rise to the C3 fam-

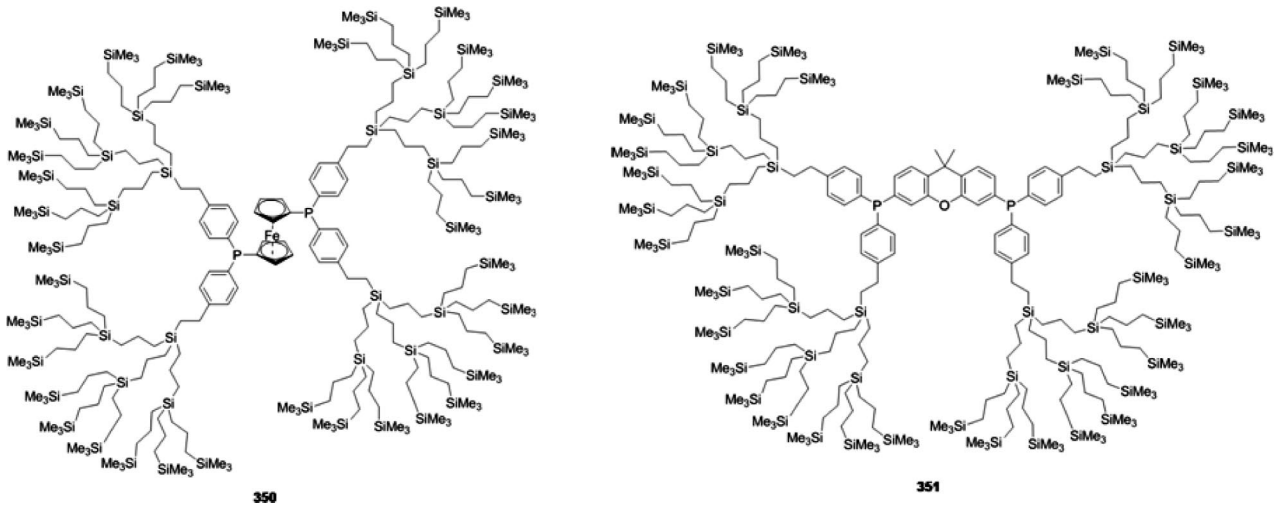
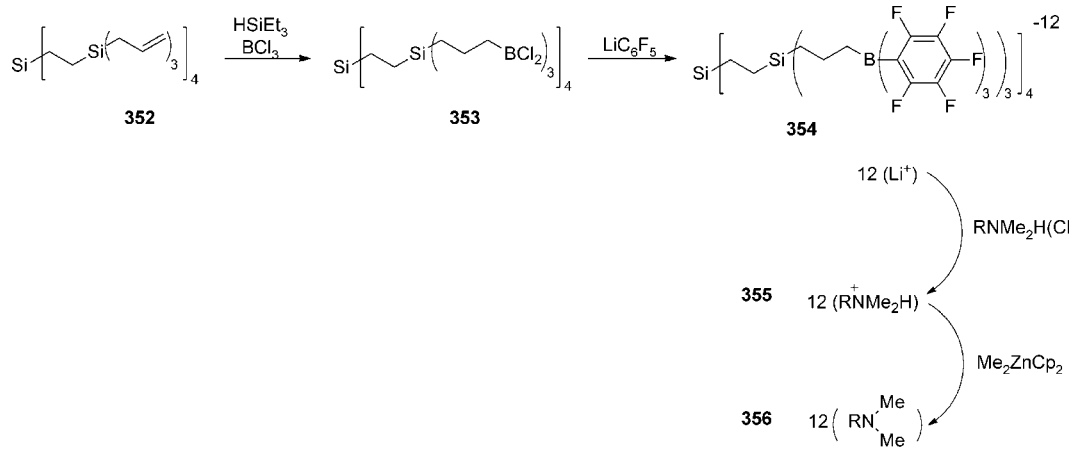


Figure 14. Phosphine-cored silane dendrimers **350** and **351**.[964]

Scheme 79. A Route to Polyborates[971]



ily;[970] hydroboration of the terminal olefin groups generated the hydroxyl surface, and molecular modeling studies were conducted.

The first example of effective polyanionic cocatalysts for the metallocene-catalyzed polymerization of olefins has appeared;[971] the carbosilane core was derived from C_2 connectivity, whereas the surface used C_3 connectivity. Treatment of **352** with $HBCl_2$ generated *in situ* from $HSiEt_3$ and BCl_3 at −60 °C gave the polyalkyl dichloroboranes, for example, **353**, as colorless oils or waxes that rapidly hydrolyze in air (Scheme 79). These reactions are quantitative and regioselective, whereas with the vinyl analogues, considerable α-addition occurred. Treatment of **353** with C_6F_5Li, prepared *in situ* from C_6F_5Br with BuLi at −70 °C, gave the desired **354** as the Li salt, which with *N*,*N*-dimethylundecylammonium chloride generated the soluble ammonium salt **355**. This polyborate was reacted with different dimethylzirconenes, which abstracted a methyl group giving the catalytically active metallocene cations **356**.

The G0 and G1 carbosilane dendrimers have been partially or fully surface-functionalized with a tertiary alkyl bromide and investigated as potential initiators for the Cu(I)Br/*N*-(*n*-octyl)-2-pyridinylmethanimine-mediated living radical polymerization of methyl methacrylate.[972] The larger G1 initiator throughout polymerization produced star−star couplings. The initial formation of dendronized polymers, based on polystyrene, possessing two allyl-terminated carbosilane dendrons was described;[973] then each allyl groups was transformed, $-(CH_2)_3R$, where R = $(SiMe_2O)_3Me$, $S(CH_2)_2C_6F_{13}$, $S(CH_2CH_2O)_3Me$ or OH.[974]

An interesting assembly of tri- or tetravalent carbosilane cores functionalized with three or four β-cyclodextrins using monodeoxy-monomercapto-β-cyclodextrin, respectively, has been reported;[975] the synthesis involved a single-pot Birch reduction, followed by an S_N2 displacement. Kuzuhara et al.[976,977] generated $Me_2Si[(CH_2)_3Si[(CH_2)_3S(CH_2)_3$-carbohydrates$]_3]_2$ in a one-step reaction in liquid ammonia, via a Birch reduction; the dendritic products possessing the trisaccharide groups (globotriaosyl ceramide) were examined as host receptors for verotoxins; also see refs 975 and 978−982 for related examples. The smaller "SUPER TWIG", possessing six trisaccharides, is a therapeutic agent against infections by Shiga toxin-producing *Escherichia coli*.[983] The galabiose unit, prepared from penta-*O*-acetyl-β-D-galactopyranose, was linked with carbosilane dendrimers of three different shapes to afford acetyl-protected glycodendrimers in good yields;[984−986] deprotection (NaOMe) was accomplished, and the biological activities toward Shiga toxins were evaluated. A series of mannose derivatives has been attached to a carbosilane dendritic core of G0 and G1 level; it was found that the products bound more efficiently to concanavalin A than to free mannose and mannobiose.[987] The use of $C_6H_5Si[(CH_2)_3Br]_3$[976] with a carbohydrate possessing a single mercaptan site[988] led to a facile coupling via the formation of the sulfide linkage.[980] A novel glycocluster peripherally functionalized by globotriaose (Galα1−4Galβ1−4Galβ1-)

possessing a silole moiety as the luminophor[989] has been prepared;[990] fluorescence quenching detection of peanut agglutinin, a lactose-binding lectin,[991] and the analytical aspects[992] have been reported for these systems.

The $C_6H_5Si[(CH_2)_3Si[(CH_2)_3Si[(CH_2)_3SiCl_3]_3]_3]_3$ was prepared[993] from $C_6H_5SiCl_3$ using sequential allylation and hydrosilylation divergent procedures, but when a thin film of this dendrimer was place on mica, it spontaneously formed well-defined, submicrometer rings over the surface. These dendritic films polymerized upon curing to give robust, highly stable nano-"O"-rings with the rims of all rings possessing a similar average width ($L \approx 150$ nm) and height of ~4−6 nm.[994,995] This organosilane series was also spin-cast onto mica, and the surface properties, for example, wettabilities, surface tensions, works of adhesion with diverse liquids, pore size, and surface coverage, have been evaluated.[996] The height images of monolayers of $C_6H_5Si[(CH_2)_3Si[(CH_2)_3SiCl_3]_3]_3$[993,997] containing disk structures changed substantially using a lighter tapping mode in the AFM; later the dome-shaped structures were shown to be membranous bubbles filled with air.[998] These bubbles were probably composed of a bilayer of the dendron molecules bound face-to-face with the peripheral silvanol moieties. The authors[998] caution about the use of amplitude/phase vs displacement curves for interpreting tapping mode AFM images. Multidentate organosiloxane thin films were prepared using SiO_2/Si surfaces by solution-phase deposition of these $SiCl_3$-surfaced dendrons with the bromophenyl focal group; the films were analyzed by contact angle goniometry, ellipsometry, and XPS.[999] The p-$BrC_6H_4(CH_2)_2Si[(CH_2)_3Si[(CH_2)_3Si(CH_2CH{=}CH_2)_3]_3]_3$, as well as the smaller G1 and G2 dendrons, were reacted with tetraethyl ferrocene-1,1′-diylbis(phosphonite) to give the corresponding metallodendrimer possessing a ferrocene core.[1000]

The related $C_6H_5Si[(CH_2)_3Si[(CH_2)_3SiMe_3]_3]_3$ has been reported and shown to undergo acidolysis[1001] removing the phenyl group to generate $TfOSi[(CH_2)_3Si[(CH_2)_3SiMe_3]_3]_3$ thus activating the focal position for subsequent substitution; treatment of the dendron triflate with silylated ligands, for example, R−C≡C−$SiMe_2$(*t*-Bu) gave (71%) the R−C≡C−Si(dendron).[953] Similarly, the Si−Ph bond in $PhSi[(CH_2)_3SiMe_2Bn]_3$ was cleaved with triflic acid to give $TfOSi[(CH_2)_3SiMe_2Bn]_3$, which generated either $ClSi[(CH_2)_3SiMe_2Bn]_3$ or $(C_5H_5)Si[(CH_2)_3SiMe_2Bn]_3$ when treated with Et_3NHCl or potassium cyclopentadienide, respectively; the G2 and G3 members were also prepared, and treatment of the G1 cyclopentadienide dendron with $TiCl_4$ or $ZrCl_4 \cdot 2THF$ gave the corresponding dendritic metallocenes.[1002]

Terminated AB_3-type hyperbranched carbosilanes were prepared via the hydrosilylation and continual addition of phenylethynyl, amines, bis(trimethylsilyl)amine, and cholesterol.[1003] The initial monomer $HSi(CH_2CH{=}CH_2)_3$ was treated with $[COD)PtCl_2]$ at 40 °C for 4 days to generate the hyperbranched polytriallylsilane support, which was subsequently surface-modified to afford $-SiMe_2Cl$; then treatment with 3,5-bis[(dimethylamino)methyl]phenyllithium generated the desired precursor, which was transformed to the desired Pd catalyst.[962]

5.4. 1 → 3 Si-Branched, $(CH_2)_2S(CH_2)_3$ Connectivity

Rissing and Son recently reported[1004] the introduction of thioether functionality throughout the Si dendrimers in which $Si(CH{=}CH_2)_4$ was treated with $HS(CH_2)_3Si(OMe)_3$ in MeOH with irradiation to afford $Si[(CH_2)_2S(CH_2)_3SiOMe)_3]_4$, which was subjected to $CH_2{=}CHMgBr$ in THF to generate $Si[(CH_2)_2S(CH_2)_3Si(CH{=}CH_2)_3]_4$. The sequence of reagents was repeated to afford in excellent yields (78−94%) the dendrimers up to the G5 level with vinyl termination. The capping of these vinyl termini to give Si dendrimers possessing hydroxyl functionality was accomplished by their treatment with excess $HSCH_2CH_2OH$ in THF with irradiation.

5.5. 1 → 3 Si-Branched, 1,4-(C_6H_4) Connectivity

A series of rigid core aryl carbosilanes has been reported[1005] in which a basic Si core was prepared from 4-lithiobromobenzene via a one-pot reaction[1006] with either $SiCl_4$ affording (85%) the desired $Si(C_6H_4Br)_4$ or $HSiCl_3$ giving (ca. 95%) the $MeOSi(C_6H_4Br)_3$ and $ClSi(C_6H_4Br)_3$ wedges depending upon workup. By combination of reagents, $[-C_6H_4Si(C_6H_4Br)_3]_2$ (90%) and 1,3,5-$C_6H_3[C_6H_4Si(C_6H_4Br)_3]_3$ (40%) were prepared. By conversion of the arylbromo termini to the corresponding lithio derivative and subsequent treatment with $BrSi(CH_2CH{=}CH_2)_3$, an interesting combination of aryl and alkyl Si-branching patterns can be generated, such as $Si[C_6H_4Si(CH_2CH{=}CH_2)_3]_4$ in 80% yield. In a series of steps, Tour et al. transformed $EtOSi(C_6H_4I)_3$ into $RSi(C_6H_4C{\equiv}CC_6H_4CH_2SCH_2CH_2TMS)_3$, where R = HC≡$CC_6H_4$− or HC≡$CC_6H_4N{=}NC_6H_4C{\equiv}CC_6H_4$−;[1007] these intermediates were subsequently transformed into a series of fullerene-terminated oligo(phenylene ethynylene)s for potential use in electronic or optoelectronic device monolayers.

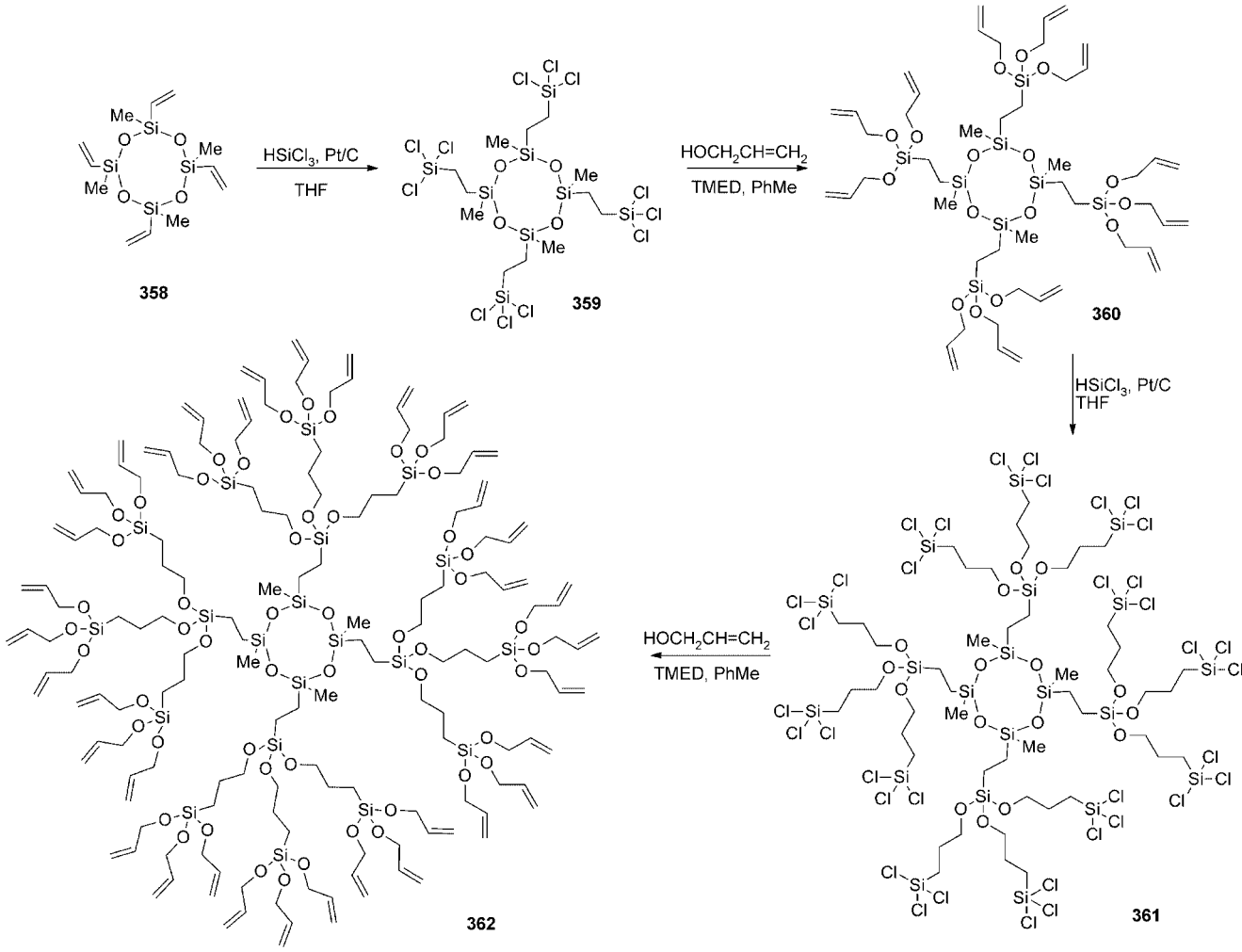
5.6. 1 → 3 Si-Branched, Si Connectivity

Lambert et al.[1008,1009] reported the preparation of the first dendritic polysilane consisting of an all silicon framework. The small dendrimer can be visualized by considering the following formula: $MeSi[SiMe_2Si(SiMe_3)_3]_3$ [methyl[tris(permethylneopentasilyl)]silane] (**357**). Impetus for its construction stems from the electronic, optical, and chemical properties of oligo- and polymeric silanes [i.e., $(-SiR_2-)_n$]; however, Si−Si bond liability can, under specific conditions, adversely affect these properties. Branched silane structures might inhibit internal Si−Si bond scission and thereby maintain bulk properties. Lambert et al.[1010] delineated the first use of two-dimensional $^{29}Si-^{29}Si$ INADEQUATE NMR for unequivocal structural verification of the small Si-based $[(Me_3Si)_2SiMeSiMe_2]_3SiMe$[1009] construct. Its failure to crystallize, preventing single-crystal X-ray confirmation, provided the rationale for the development of this technique. The related tris[2,2,5,5-tetrakis(trimethylsilyl)hexasilyl]methylsilane, $MeSi[SiMe_2Si(SiMe_3)_2SiMe_2SiMe_2Si(SiMe_3)_3]_3$, has been convergently prepared[1011] and characterized by $^{29}Si-^{29}Si$ INADEQUATE NMR in which the entire Si−Si connectivity pattern was assigned.[1012]

Preparation of the branched silane **357** began with the reaction of tris(trimethylsilyl)silane with $CHCl_3$ (CCl_4) and MeLi to afford the peralkylated methyl[tris(trimethylsilyl)]-silane.[1008] Subsequent treatment with $AlCl_3$ and $ClSiMe_3$ gave the trichlorosilane, which was reacted with tris(trimethylsilyl)silyllithium to yield the final silane dendrimer.

Seven silicon nuclei comprised the silane chain that was repeated 27 times. X-ray crystallography confirmed a 3-fold axis-of-symmetry with respect to the core Si−C bond. Suzuki et al.[1013] reported another slightly modified synthesis of silane $[(Me_3Si)_3Si(Me_2Si)]_3SiMe$.

Scheme 80. Construction of Siloxane Dendrimers[923]



A comparative study of a related series of oligosilanes, for example, $Si(SiMe_3)_4$, $[Si(SiMe_3)_3]_2$, $SiMe_2[Si(SiMe_3)_3]_2$, $SiMe_2[(SiMe_2)Si(SiMe_3)_3]_2$, and $[SiMe_2(SiMe_2)Si(SiMe_3)_3]_2$, was conducted by means single-crystal X-ray crystal data; the study gave insight to the influence of the sterically crowded tris(silyl)silyl moieties on the Si−Si framework.[1014]

5.7. 1 → 3 Si-Branched, S/Se/Te Connectivity

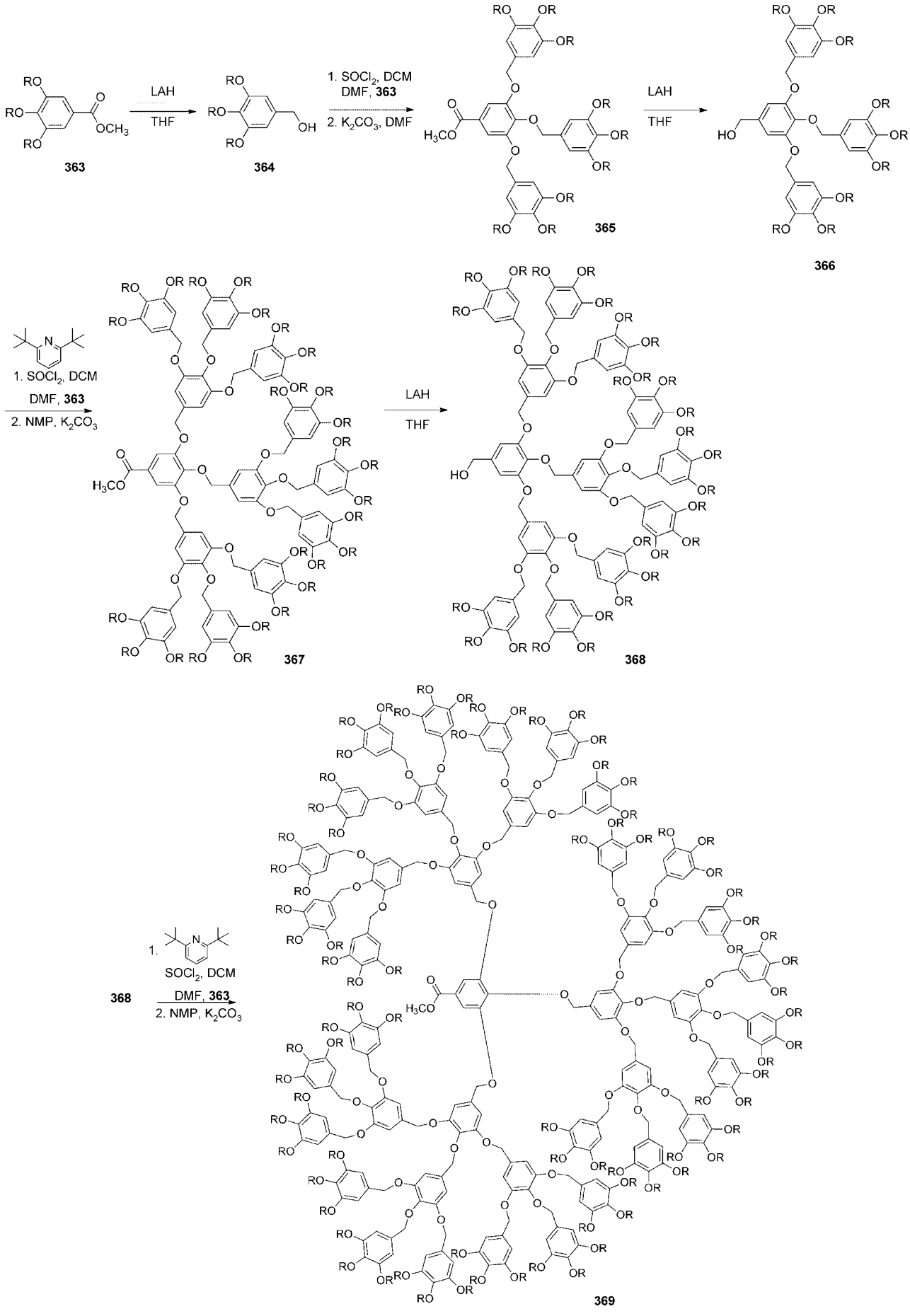
The reaction of $(Me_3Si)SiEK$ (where, E = S, Se, or Te) with organochlorosilanes $R_{4-x}SiCl_x$ (R = Me, Ph; $x = 1-4$) and methylchlorodisilanes (e.g., Si_2Me_5Cl, 1,2-$Si_2Me_4Cl_2$) gave the organosilicon hypersilylchalcogenolates $[(Me_3Si)_3SiE]_xSiR_{4-x}$ ($x = 1-4$) and $[(Me_3Si)_3SiE]_xSi_2Me_{6-x}$ ($x = 1, 2$). Starting with $[(Me_3Si)_3SiE]K$ and $SiCl_4$ gave $[(Me_3Si)_3SiE]_4Si$; similar reaction occurred with $RSiCl_3$, R_2SiCl_2, and R_3SiC giving three-, two- or one-directional dendrimers.[1015]

5.8. 1 → 3 Si(O)-Branched, Alkyl Connectivity

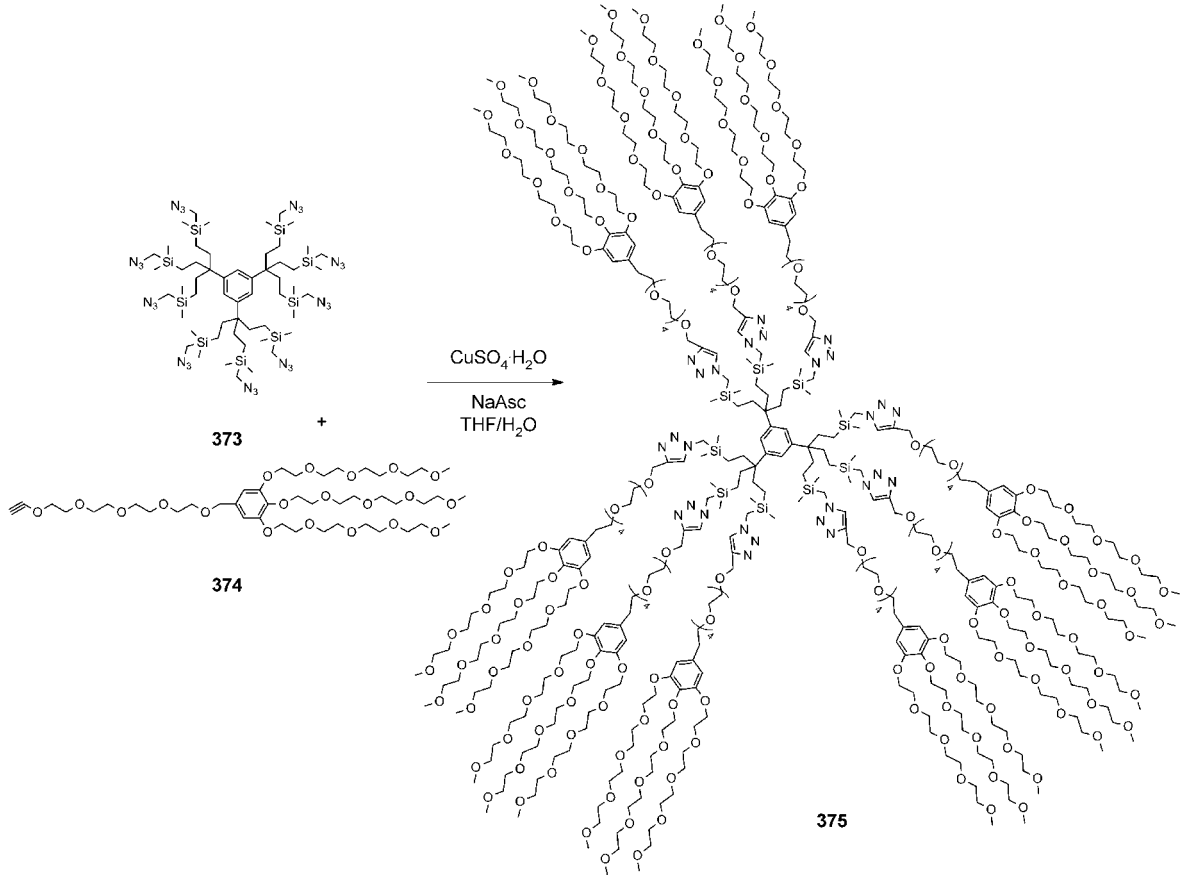
The treatment of siloxane tetramer G0 $[Me(CH_2{=}CH)SO]_4$ (**358**) with $HSiCl_3$ and a Pt catalyst generated the starting tetra(trichlorosilane) core (**359**) for further elaboration (Scheme 80). Reaction with allyl alcohol gave (62%) **360**,[1016−1018] repetition of the simple two-step process gave (~37%) the G2 dendrimer **362**.[923] Attempts to grow this into the product with 108 SiCl bonds were unsuccessful. The related G4 dendrimer with 48 SiCl groups constructed from the 1 → 3 Si branched core but with 1 → 2 Si branching thereafter was capped by treatment with lithiated ferrocene to create a CO gas sensor.[1019] This procedure was further utilized to dendronize a siloxane polymer $\langle Me_3SiO-[MeSi(H)O]_n-SiMe_3\rangle$ as the core, by applying this hydrosilylation/alcoholysis to generate the G1, then G2 level.[1020] The surface of these polymers and related structures derived from $[(Cl_2MeSiCH_2CH_2CH_2O)_3SiCH_2CH_2MeSiO]_4$[1021] was coated with allyl alcohol, cholesterol, 8-hydroxyquinoline, 5-(2-hydroxyl)-4-methylthiazole, 4-pyridinepropanol, or 4-pyridinealdoxime, as well as ferrocenyl moieties.[1022] Similarly, $\langle[(RO)_3SiCH_2CH_2CH_2O]_3SiCH_2CH_2MeSiO\rangle_4$ was prepared in which R = farnesyl; the family (G1−4) of carbosilane dendrimers has been synthesized,[1023] and interesting chemistry has been conducted on the surface in which multiple Diels−Alder reactions were conducted.[1024] Coating these carbosilane dendrimers with diene moieties, that is, 2,4-hexadienyl-1-oxy, permitted a click assembly to occur upon treatment with different active enes, for example, *N*-ethylmaleimide, 1,4-naphthoquinone, and tetracyanoethene.[1024] The larger dendronized polymer was also prepared $\langle[(CH_2{=}CHCH_2O)_3SiCH_2CH_2CH_2O]_3SiCH_2CH_2MeSiO\rangle_4$ by similar procedures.[1020] The reaction of $[CH_2Si(OCH_2CH{=}CH_2)_3]_2$ with $HSiCl_3$ and a Pt catalyst failed to give the desired uniform product;[1025] whereas, a uniform product was accomplished with the related $HSiMeCl_2$.

A one-step synthesis of poly(siloxysilanes) was reported by Mathias and Carothers[1026−1028] in which they treated

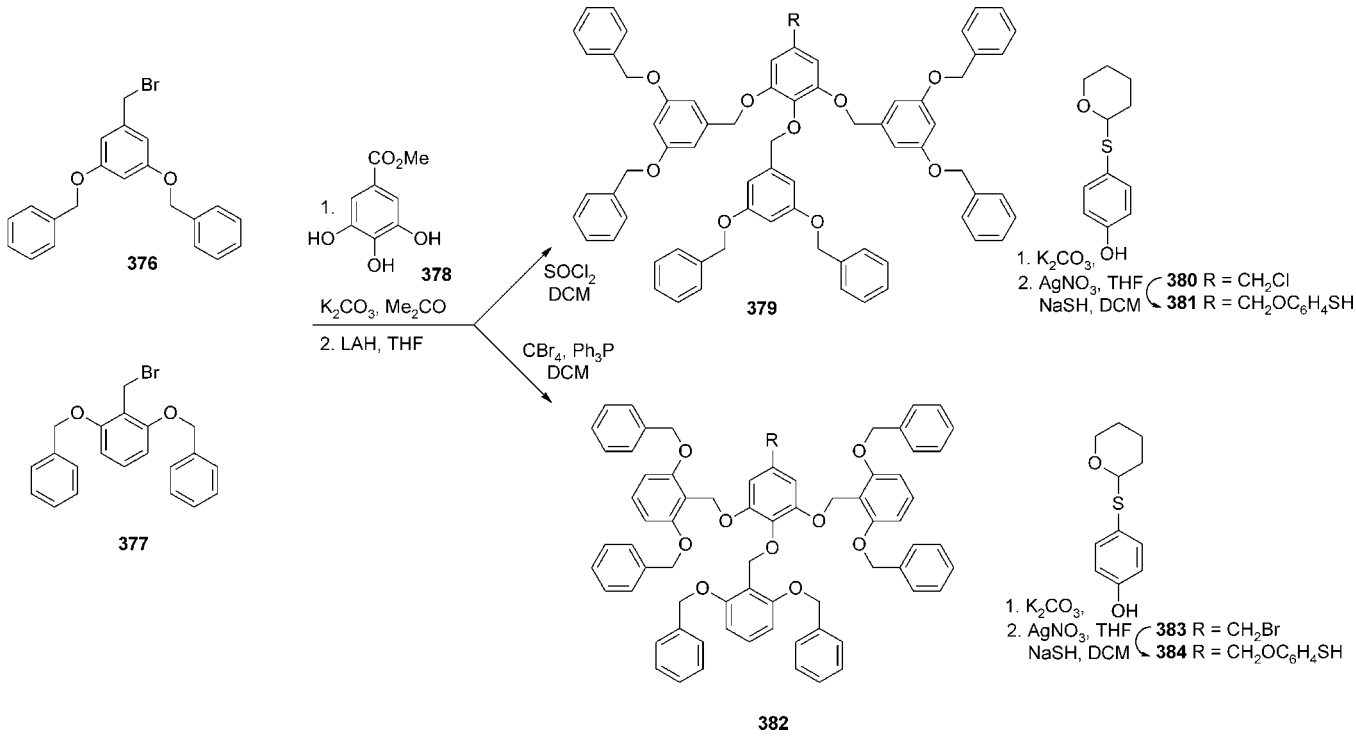
Scheme 81. The Preparation of CH_2O-Connected 1 → 3 Aryl Branching Dendrons[1048]



Scheme 82. An Example of a PEGed Dendrimer[623]

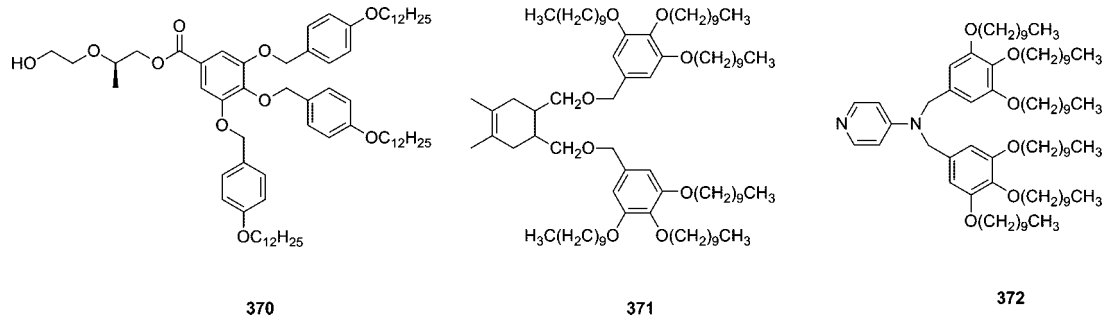


Scheme 83. Extended and Back-Folded Dendrons[1130]



$CH_2{=}CHCH_2Si(OSiMe_2H)_3$ in Et_2O/MeCN (1:1) with $H_2PtCl_6{\cdot}nH_2O$ under nitrogen giving the hyperbranched poly(siloxysilane)s possessing (almost) no vinyl peaks and notable reduction of the Si−H peak. An early review of their work appeared.[1029] The $Si(OCH_2C{\equiv}CH)_4$, as a simple core, has appeared and has been subsequently used in click connectivity to generate a robust C-sialoside multimers.[642]

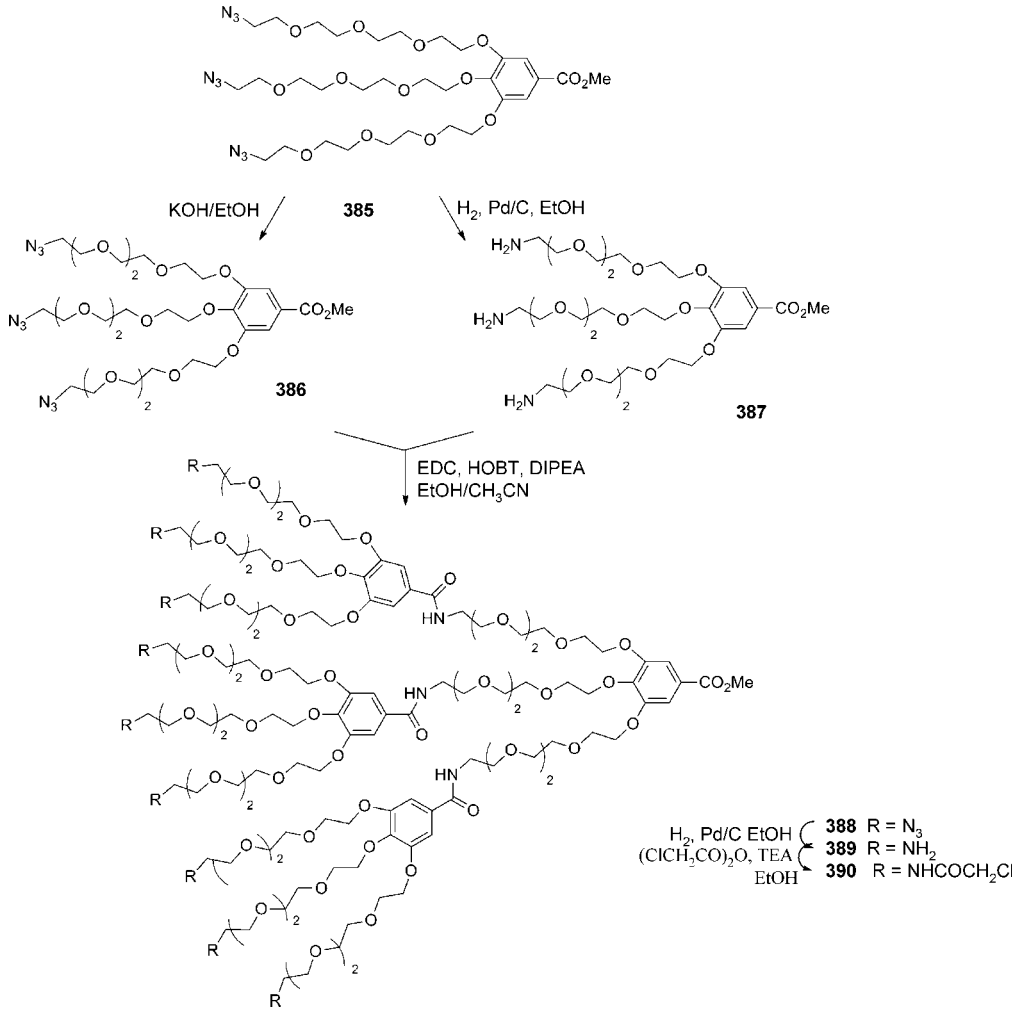
The synthesis, magnetic separation, and characterization of magnetic nanoparticles utilized a polydimethylsiloxane, specifically either $Me(CH_2)_3[SiMe_2O]_nSi[(CH_2)_2SCH_2CO_2H]_3$



370 371 372

Figure 15. Elongated alkoxyaryl dendrons.

Scheme 84. Formation of a PEG-Connected 1 → 3 Aryl Dendron[1143]

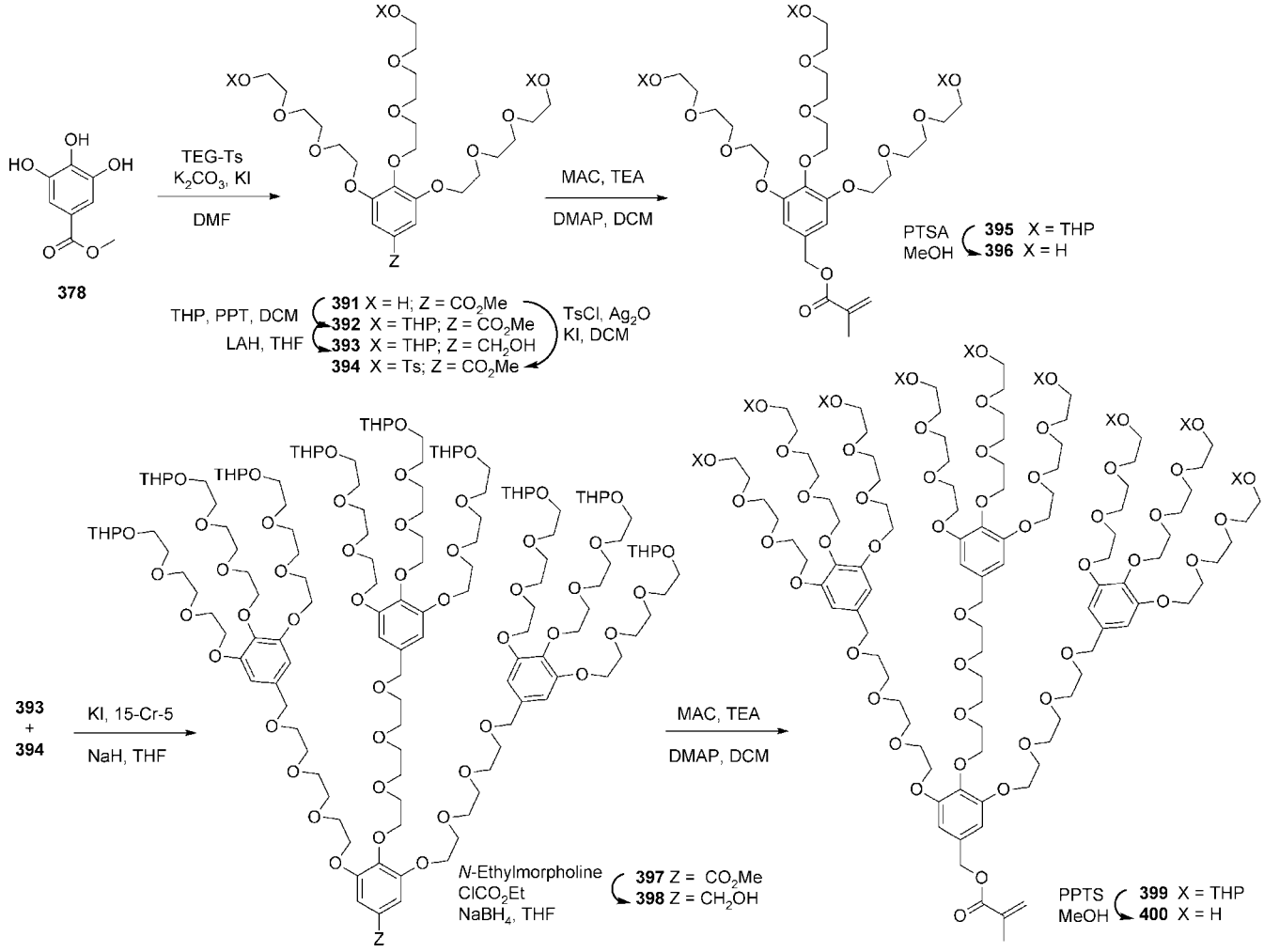


or $Me(CH_2)_3[SiMe_2O]_nSi[(CH_2)_2SCH(CO_2H)CH_2CO_2H]_3$;[1030−1032] these PDMS−magnetite nanoparticle complexes were formed by interfacial adsorption of the carboxylic acid functionalized PDMS stabilizers onto magnetite nanoparticles in slightly acidic media.

5.9. 1 → 3 Si(O)-Branched, Si(O) Connectivity

A series polysiloxane dendrimer-like polymers was constructed from $MeSi(OSiMe_2OSiMe_2Ph)_3$ as the three-directional core and the 1 → 2 branching $HOSiMe_2OSiMe(OSiMe_2Ph)_2$ as the building block. Treatment of the core with bromine gave $MeSi(OSiMe_2OSiMe_2Br)_3$, which was transformed to the corresponding diethylamino derivative, $MeSi(OSiMe_2OSiMe_2NEt_2)_3$; further reaction with the branching building block gave $MeSi[OSiMe_2OSiMe_2OSiMe_2OSiMe_2OSi(OSiMe_2Ph)_2]_3$.[1033] The related $HOSiMe_2OSi(OSiMe_2Ph)_3$ as the building block should give the related 1 → 3 series. The rapid assembly of 3D siloxane architectures was reported in which $Si(OEt)_4$ was treated with $HSiMe(OSiMe_3)_2$ in the presence of $B(C_6F_5)_3$ giving $EtOSi[OSiMe(OSiMe_3)_2]_3$, which with $C_6H_5Si(OSiMe_2H)_3$ or hydrosilane-terminated poly(dimethyl)siloxanes gave $C_6H_5Si[OSiMe_2OSi(OSiMe(OSiMe_3)_2)_3]_3$ or $[(Me_3SiO)_2MeSiO]_3SiO(SiMe_2O)_nSi[OSiMe(OSiMe_3)_2]_3$, respectively.[973] Treatment of $HSiMe(OSiMe_3)_2$ with $Si(OEt)_4$ in the presence of $B(C_6F_5)_3$ gave $EtOSi[OSiMe(OSiMe_3)_2]_3$, which with $C_6H_5Si(OSiMe_2H)_3$ generated $C_6H_5Si[OSiMe_2OSi[OSiMe(OSiMe_3)_2]_3]_3$.[1034] The formation of two- and three-dimensional hybrid mesostructures from $RSi[OSi(OR')_2OSi(OR')_3]_3$, where R = alkyl, R′ = Me, has recently appeared.[1035]

Scheme 85. Synthesis of the PEGed Dendrons[1146]



6. 1 → 3 B-Branched, S Connectivity

The reaction of three $LiCH_2SC_6H_5$ with $PhBCl_2$ in the presence of $(Bu_4N)Cl$ gave $\langle[C_6H_5B(CH_2SC_6H_5)_3]^-(NBu_4)^+\rangle$, which is soluble in chlorinated hydrocarbons, THF, acetone, and MeCN and readily reacted with $[Cu(MeCN)_4]BF_4$.[1036]

7. 1 → 3 Ge-Branched

An early example of polyphenylenegermane was reported using $GeH(C_6F_5)_3$;[1037] however, no pure dendrimers were reported; rheological properties of highly branched poly(fluorophenylene germane) were later reported.[1038] Both of the simple $[(C_6H_5)_3Ge]_2$ and $(Et_3Ge)_2$ members of this family

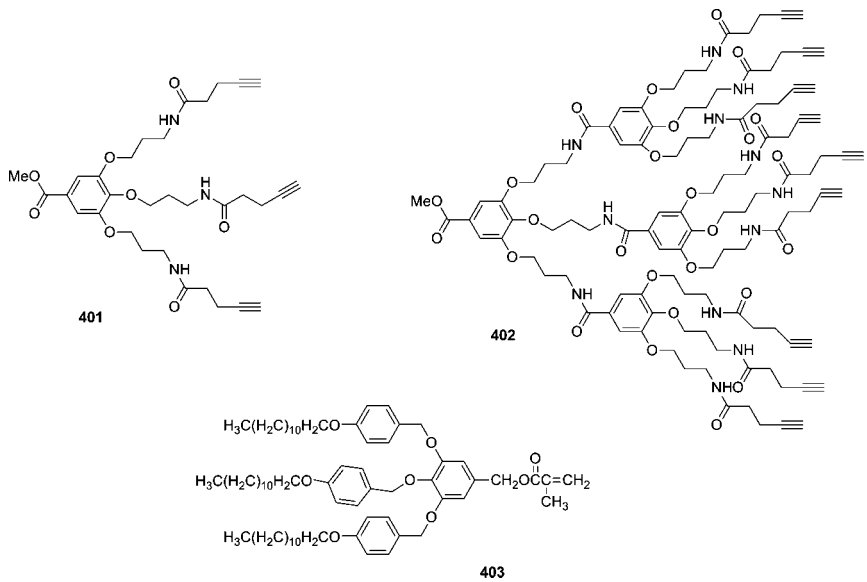
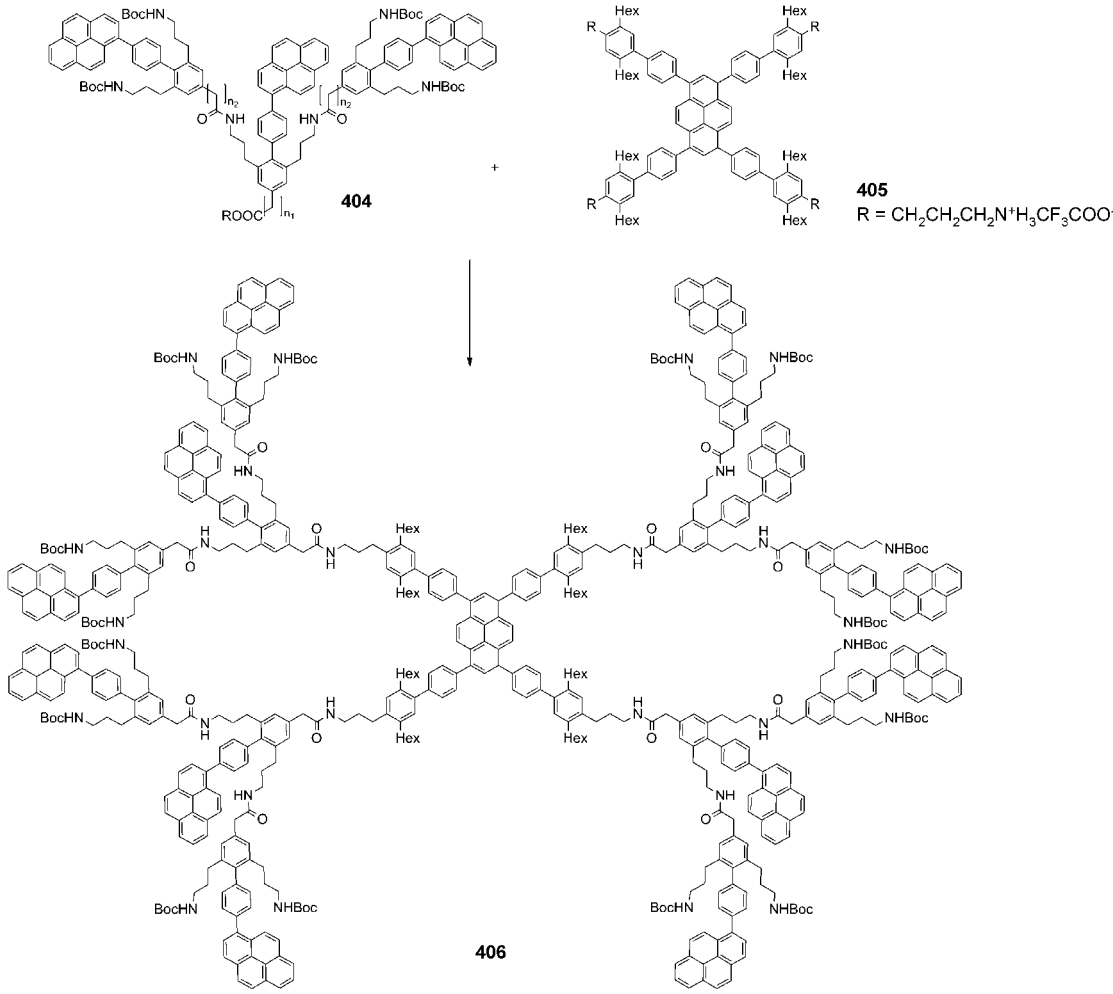


Figure 16. (1 → 3) 3,4,5-Aryl-branched dendrons.

Scheme 86. Creation of a Novel 1 → (2 + 1) Aryl-Branching Series[1164]



are commercially available and proposed for being photoinitiators for radical and cationic polymerization.[1039] The general topic of linear and branched oligogermane structures has been reviewed.[202]

Mazerolles et al.[1040] reported the first stepwise route to the desired Ge dendrimers and dendrons. In procedures analogous to that of Si construction, $GeCl_4$ was treated with either $CH_2{=}CHMgBr$ or $CH_2{=}CHCH_2MgBr$ to give $Ge(CH{=}CH_2)_4$ or $Ge(CH_2CH{=}CH_2)_4$, respectively. Hydrogermylations with $GeHCl_3$ afforded the corresponding $Ge(CH_2CH_2GeCl_3)_4$ or $Ge(CH_2CH_2CH_2GeCl_3)_4$; interestingly, unlike hydrosilylation, which needs a catalyst, hydrogermylation occurred rapidly, exothermically, and without the need for a catalyst. Notably, $GeHCl_3$ is, however, less stable and in equilibrium with dichlorogermylene; the germanium−carbon bonds are also readily cleaved with electrophiles.

Both divergent and convergent procedures have been utilized to generate the G1, but only the divergent route was successful to attain the G2 dendrimer.[1040] Thus, $CH_2{=}CH(CH_2)_4MgCl$ with $GeCl_4$ gave $Ge[(CH_2)_4CH{=}CH_2]_4$, the addition of $GeHCl_3$ followed by the same Grignard reagent gave $Ge\langle(CH_2)_6Ge[(CH_2)_4CH{=}CH_2]_3\rangle_4$, and repetition afforded the desired G2 $Ge\langle(CH_2)_6Ge[(CH_2)_6Ge[(CH_2)_4CH{=}CH_2]_3]_3\rangle_4$. Similarly, the G2 predendron $Cl(CH_2)_6Ge\langle(CH_2)_6Ge[(CH_2)_4CH{=}CH_2]_3\rangle_4$ was prepared, but its Grignard failed to react with $GeCl_4$. The treatment of $(n\text{-}Bu)_3GeNMe_2$ with MeCN at 85 °C gave rise to the intermediary $(n\text{-}Bu)_3GeCH_2CN$, which with $(C_6H_5)_3Ge_3H$ generated either $(n\text{-}Bu)_3GeGe(C_6H_5)_3$ (81%) or $C_6H_5Ge[Ge(n\text{-}Bu)_3]_3$ (98%).[1041]

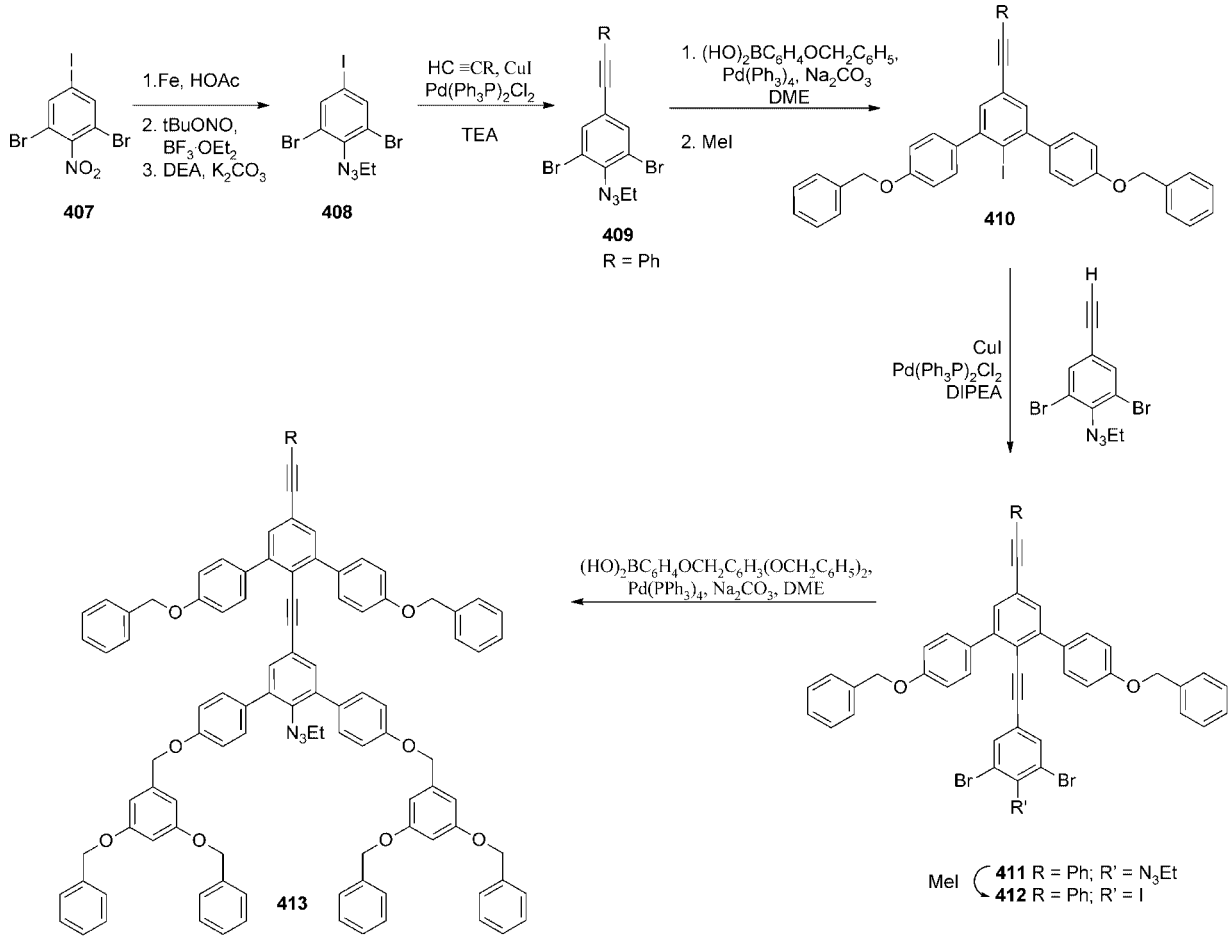
The treatment of CBr_4 with 4 equiv of GeX_2·dioxane (X = Cl or Br) in toluene gave $C(GeBrCl_2)_4$ (79%) or $C(GeBr_3)_4$ (94%);[1042] interestingly, unlike in the preparation[1043] of $C(SiH_3)_4$, $C(GeBr_3)_4$ with $LiAlH_4$ gave $C(GeH_3)_4$ and $HC(GeH_3)_3$ in very low yields.

A related series of Si,Ge dendrimers have been synthesized by the treatment of $Me(PhMe_2Ge)_2SiLi$ with $PhMe_2GeCl$ to give $MeSi(GeMe_2Ph)_3$, which with TfOH followed by $Me(PhMe_2Ge)_2SiLi$ gave $MeSi[GeMe_2SiMe(GeMe_2Ph)_2]_3$. Subsequent reaction with TfOH afforded $MeSi[GeMe_2SiMe(GeMe_2OTf)_2]_3$, which was transformed to the corresponding chloride, then with MeMgI in THF to $MeSi[GeMe_2SiMe(GeMe_3)_2]_3$ possessing the polymethylated surface.[1044]

8. 1 → 3 Sn-Branched

Treatment of $Si(CH_2CH_2SnH_3)_4$ with methyl acrylate with AIBN in toluene gave $Si[CH_2CH_2Sn(CH_2CH_2CO_2Me)_3]_4$, which can be readily saponified to the carboxylate, reduced with $LiAlH_4$ to the terminal alcohol, or treated with 2-aminoethanol to partially form the amide.[1045] The use of other reagents, such as $CH_2{=}CHCO_2CH_2CH_2OR$, where R= H, CO_2-*tert*-Bu, $-(CH_2)_2OH$, or $-SiMe_2$-*tert*-Bu, formed similar products instilling water solubility into these tin-based metallodendrimers.

Scheme 87. Assembly of a Novel (1 + 2) Dendron[1166]



9. 1 → 3 Aryl-Branched

The 1 → 3 aryl-branched dendrons have, for the most part, been used as terminal groups, but herein are numerous examples in which the G2 and G3 dendrons have been created and utilized as internal units. Although not directly within this 1 → 3 aryl-branched family, a novel series of "dendroids" was created[1046] in which "differentially substituted 1,8-naphthalene and 1,2,3-trihydroxybenzene were prepared and represent a family of a → (b + c) → [(d + e) + (f + g)]".[1047]

9.1. 1 → 3 (3,4,5-)Aryl-Branched, Ether-Connectivity Dendrons

Percec et al.[1048,1049] prepared the simplest G1−G3 (1 → 3)-aryl branching series from methyl gallate (methyl 3,4,5-trihydroxybenzoate) in a convergent procedure shown in Scheme 81. This series generally possesses a long chain alkoxide (C_{12})[691,1050−1081] at the termini, but other alkyl lengths,[700,1055,1082−1091] fluoroalkyl groups,[1092,1093] chiral alkyl groups,[1078,1094] benzyloxy moieties,[1075,1095−1097] naphthalene and biphenyl,[1098] PEG,[847,1099,1099−1104] and combinations of substituents[1055,1059,1061,1104−1110] can also be employed. The reaction of alkynes with 3,4,5-tris(decyloxy)phenylazide has been reported.[1111] This simply gives a cross-section of references to the ethereal Percec dendron; it is not a comprehensive list due to their common usage, ease of construction, and ability to instill either hydrophobic or hydrophilic character to their attachment. A comprehensive review by Percec et al. concerning the "dendron-mediated, self-assembly, disassembly, and self-organization of complex systems" has recently appeared;[1112] many references cited therein are based on these ethereal dendrons, and their conversion to uniform "dendrimersomes" has recently appeared.[1113]

Percec et al.[1114] have synthesized a related series of elongated dendrons from methyl 3,4,5-trihydroxybenzoate via similar multistep procedures, where a −[$(CH_2)_3$O]− connection[1115] has been utilized or benzyl ether extenders have been incorporated possessing the basic structure 3,4,5-RO[$(C_6H_4)CH_2O]_nC_6H_2CH_2O[C_6H_4CH_2O]_m$H, where n = 1−3 and m = 0−3, in different combinations.[1116] Convergently, selected members of this family were transformed into the G2 dendrons; ultimately these dendrons were self-assembled into unique libraries possessing different nanoscale motifs. These polyethereal dendrons have been used by numerous research groups to instill bulk at one or more loci within the macromolecular assembly;[1117] the theoretical aspects have also been probed.[1118] Related alkoxyaryl dendrons with extended focal esters have also been reported and connected to a 1,3,5-trihydroxybenzene core to give columnar liquid crystals.[1119] Chiral dendrons, for example, **370** (Figure 15), have been shown to self-assemble by two-dimensional ordering at the liquid−solid interface.[1120] The use of 3,4,5-tri(*n*-decan-1-yloxy)benzyl chloride[1121] with 4-aminopyridine or 4,5-dimethyl-*cis*-Δ^4-tetrahydrophthalyl alcohol gave rise to the dendrons **371** and **372**, respectively (Figure 15); a complex was generated from **372** and OsO_4, followed by oxidation with NMO to give the desired osmium catalyst, which was recyclable and reusable for dihydroxylations.[1122]

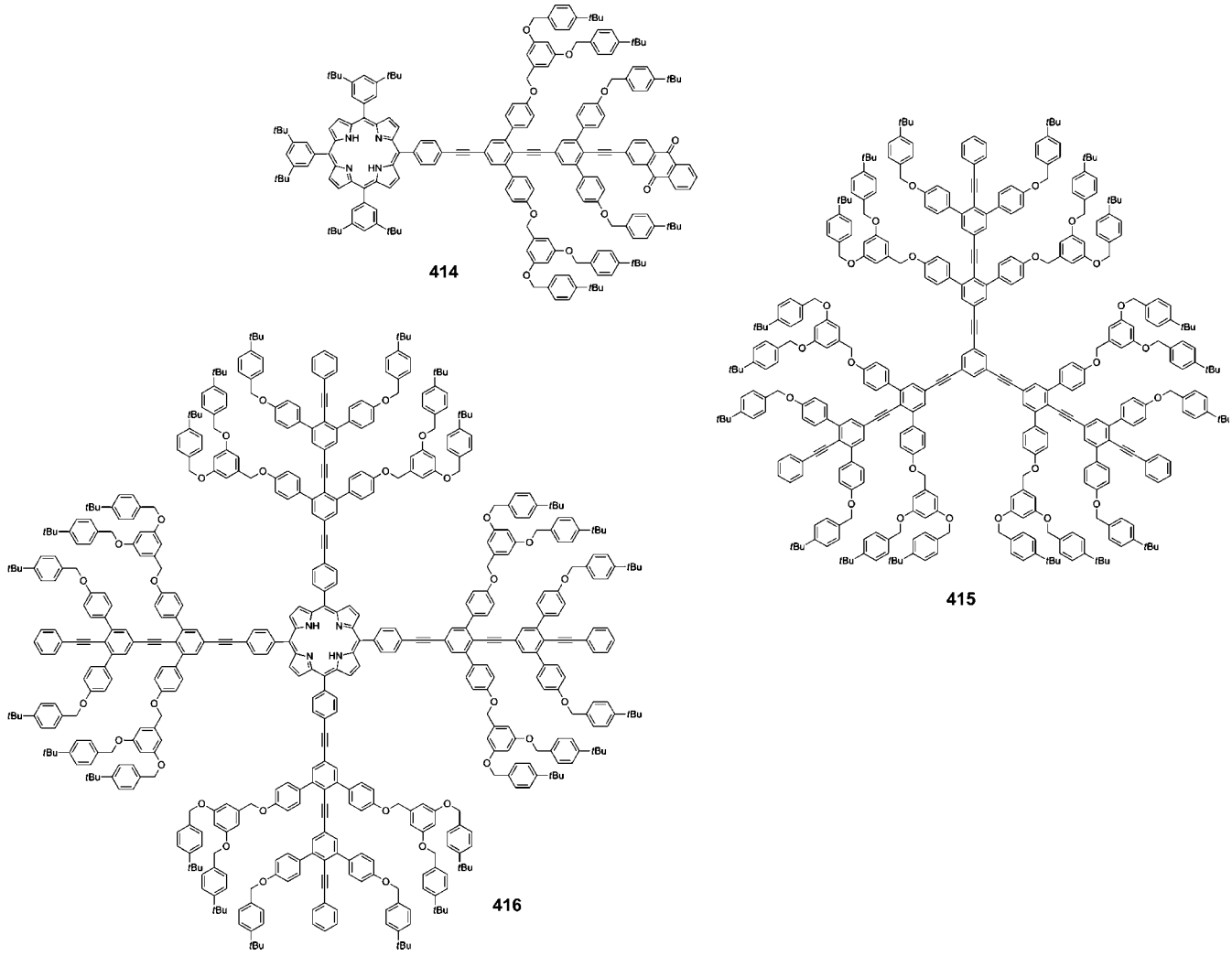


Figure 17. Different dendrimers from combinations of rigid dendrons.

3,4,5-Trihydroxybenzoic acid has also be converted in four steps to 3,4,5-tribenzyloxybenzyl chloride,[1123] which was attached to hydroxymethyl-3,4-ethylenedioxythiophene and subsequently electropolymerized.[1124] The pentafluorophenyl 3,4,5-tris(tetraethyleneoxy)benzoate, as a facile acylating agent, was shown to react with PPI dendrimers to form water-soluble dendrimers capable of molecular encapsulation.[1125] Recently, Tsuji et al.[1126] have used the $TsO(CH_2CH_2O)_{\sim 12}Me$, derived from the commercially available poly(ethylene glycol) monomethyl ether, with methyl 3,4,5-trihydroxybenzoate to give (84%) the tris-dodecaPEGed ester, which was sequentially reduced (LAH, 91%), transformed ($SOCl_2$, 46%) to the chloromethyl derivative, attached (K_2CO_3, 96%) to tris(4-hydroxyphenyl)phosphine oxide, and last reduced ($PhSiH_3$, 89%) to the free phosphine, which showed enhanced efficiency in the Pd-catalyzed Suzuki−Miyaura coupling; also see ref 1127 for the related tetra(ethylene glycol) counterparts.

Two sulfonated dendrons possessing a 3,4,5-alkoxyaryl substitution pattern with a focal sulfonic acid group were prepared from known dendron precursors;[1048] all connectivity within the dendrons was ethereal, and these dendrons were used to prepare polyaniline emeraldine base nanostructures.[1128]

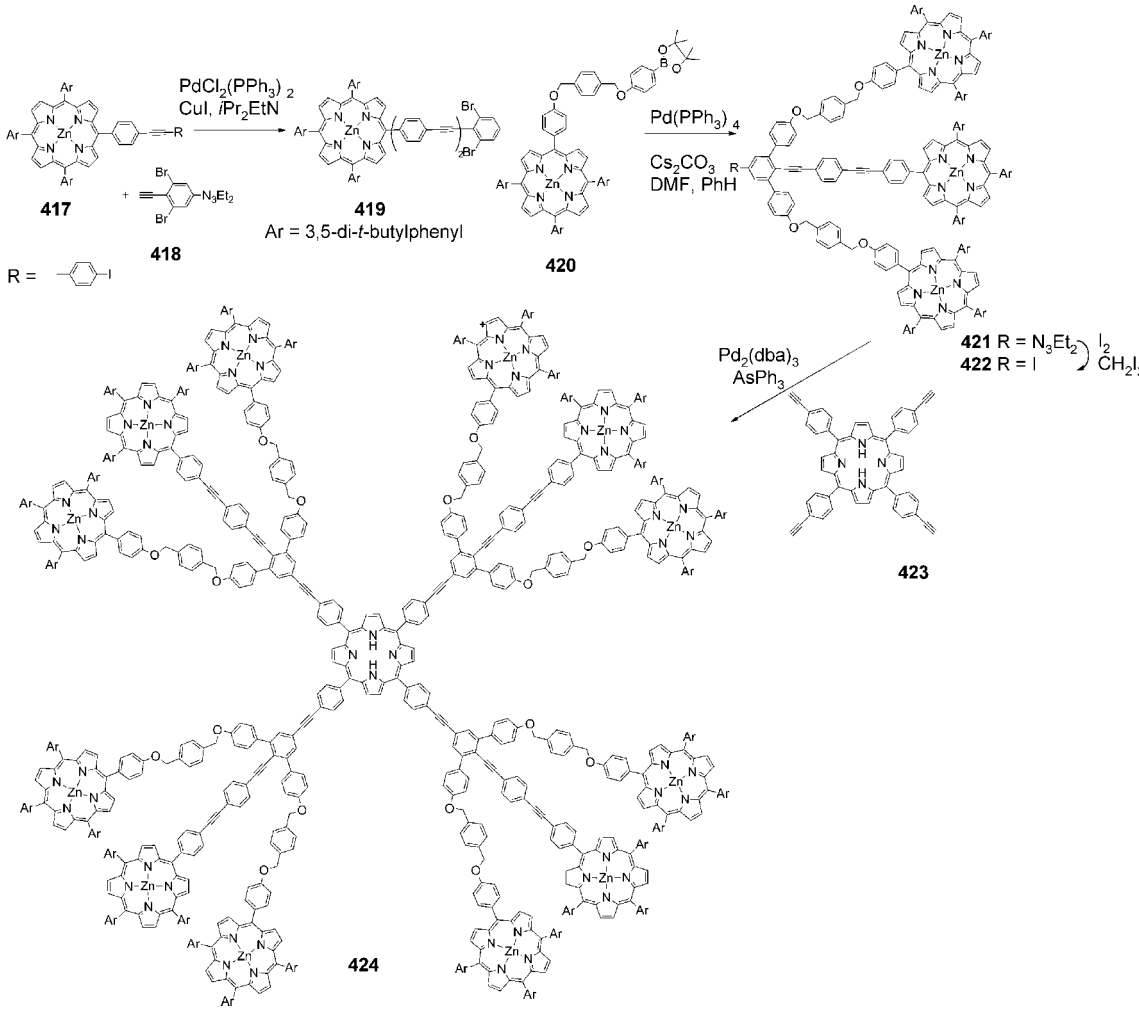
The treatment of methyl 3,4,5-trihydroxybenzoate with $HC{\equiv}CCH_2Br$ in acetone gave (K_2CO_3, 93%) the tris-alkynyl product, which was reduced (LAH, 70%) to HOH_2-$CC_6H_2(OCH_2C{\equiv}CH)_3$ and then transformed (PBr_3, 77%) to the trisubstituted benzyl bromide;[840] the elongation was accomplished (92%) by reaction with hydroquinone in DMF with K_2CO_3. This dendron was shown to be an ideal alkyne source for the click reaction.[614,840]

Astruc et al. recently reported[623] the "click" approach to functionalize their azide-terminated dendrimers[624] (e.g., **373**), which were described earlier, $HC{\equiv}CCH_2O(CH_2CH_2O)_4CH_2C_6H_2[O(CH_2CH_2O)_3Me]_3$ (**374**) (Scheme 82). Initial coating of gold nanoparticles with dodecanethiolate ligands, then ligand substitution with 1-bromoundecanethiolate (using a 10-fold excess), gave the partially coated nanoparticles with a brominated surface; then substitution with NaN_3 gave the desired azido surface, which was clicked with this dendron possessing the alkyne focal moiety.[1129]

Gorman et al.[1077,1130,1131] created a novel set of extended (**380**) and back-folded (**383**) dendrons, based on the substitution pattern. Scheme 83 shows the methodology to dendrons; their focal connection was elongated (**382** and **384**, respectively) and then attached to Fe_4S_4 or Re_6Se_8 cluster cores (Scheme 83).

Lee et al.[1132] transformed 2,6-dimethoxyphenol to 3,4,5-trialkoxy-1-bromobenzene in three steps and then to the corresponding boronic acid derivative, which underwent a Suzuki-coupling reaction[1133,1134] with cyanuric acid to generate (33%) the 2,4,6-triaryltriazine.

Scheme 88. The Synthesis of a Rigid 1 → (2 + 1) Dendron Possessing Three Porphyrin Moieties[1169]



Rissanen et al.[1135] prepared an interesting Janus-type dendrimer from pentaerythritol in which the bow-tie had two 1 → 3 aryl groups with dodecaalkoxy substituents and the other half used 1 → 2 C-branched ester dendrons with ultimately alcoholic termini.

Cossio and Lopez et al.[1136] prepared a series of related dendrimers possessing a central trialkylamine core with increasing degrees of internal congestion using three single linear benzyl ether arms, Fréchet-type ethereal dendrons, or the G1 or G2 (3,4,5-benzyloxy)aryl-branched dendrons; the series was used to evaluate the catalytic activity of these amines in a Henry reaction between 2-nitroethanol and benzaldehyde; as expected, as the size increased, the catalytic activity decreased.

9.2. 1 → 3 (3,4,5-)Aryl-Branched, Ester-Connectivity Dendrons

Treatment of 3,4,5-trihydroxybenzoic acid with $CH_2{=}(Me)C(=O)(OCH_2CH_2)_nOCCl$ in pyridine gave the 3,4,5-tris-ester; then esterification (EDC, DMAP, HOBT) with poly(ethylene glycol) generated the PEG benzoate product,[1137] which was subsequently attached to a core derived (90%) from butane−1,2,3,4-tetra(carbonyl chloride) and L-aspartic acid. The use of 4′-(3,4,5-trioctyloxybenzoyloxy)-benzoic acid appended to a poly(styrene)-*block*-poly(4-vinylpyridine) microdomain has been reported.[1138] The 3,4,5-tribenzyloxybenzoyl chloride, prepared from methyl 3,4,5-trihydroxybenzoate in three steps, was treated with different polyphenols to give the benzoate products and then debenzylated to give the polyphenolic outer surface.[1139] The G2 ester-connected dendrons possessed decyloxy termini and a 3-hydroxy-4-formylphenyl focal group so that coupling to either a PAMAM or PPI surface can be managed.[1140] Aida et al.[1141,1142] created a family of 1 → 3 dendrons and dendrimers possessing increasing degrees of complexity to which a bis-meso-connected porphyrin was incorporated; for an overview of their excellent work, see refs 82 and 128.

9.3. 1 → 3 (3,4,5-)Aryl-Branched, PEG, Amide- or Ester-Connectivity Dendrons

Roy et al. was preparing dendritic lactosides and used gallic acid as the 1 → 3 aryl branching motif.[1143] Tetra(ethylene glycol) was ditosylated (81%) and transformed (39%) to the monoazide, which was treated with methyl 3,4,5-trihydroxybenzoate to give (68%) triazido ester (**385**). This key reagent was either saponified (100%) to **386** or reduced (93%) to the triamine **387** (Scheme 84); the combination of these two monomers gave (83%) the G2 PEGed dendron **388**, whose termini were reduced (100%) to the nonaamine **389**, and last activated (70%) with chloroacetic acid anhydride to give G2 **390**. This activation also applies to the G1 series with **387**. The attachment of either thiolactoside[1143]

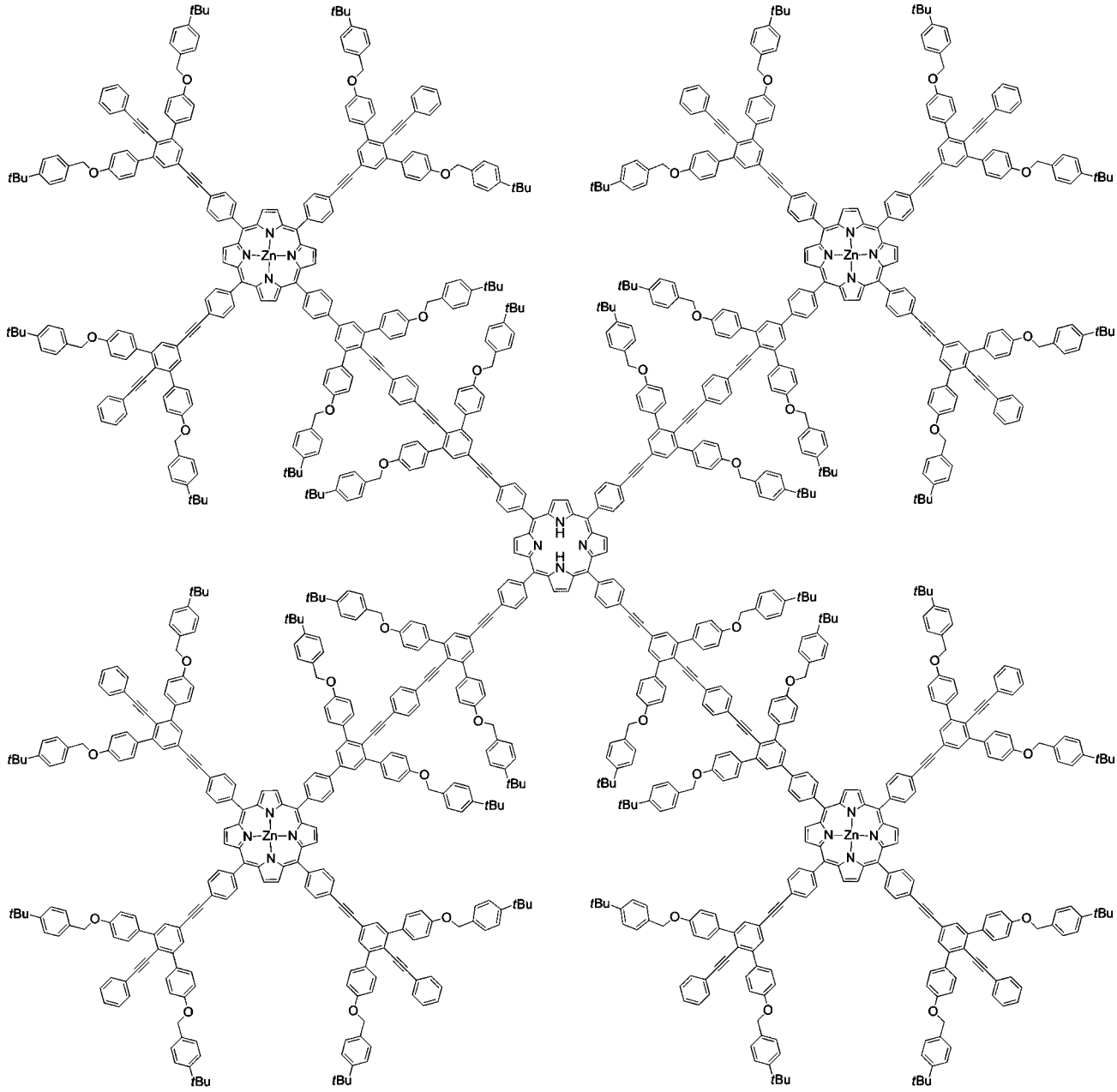


Figure 18. A dendrimer possessing a snow-flake shape.[1170]

or thioacetylated sialic acid[1144] was easily accomplished in high yields. Roy et al.[1145] used similar methodology with the shorter tri(ethylene glycol); also, see other examples, refs 1146−1152. Later Riguera et al.[1153−1155] expanded this procedure to the G3 dendron level and then utilized the terminal azides in click chemistry to attach functionality at the termini. Chen and Wang et al. recently reported[1156] the preparation of a 1 → 3 aryl-branched galactoside-capped nanohybrid with a ZnS/CdSe nanoparticle core using click chemistry for assembly; this was used as a hydrophilic, fluorescent, multivalent probe for metastatic lung cancer cells.

Schlüter et al.[1146] constructed a series of G1 and G2 water-soluble dendronized polymers derived from methyl 3,4,5-trihydroxybenzoate (**378**) with tri(ethylene glycol) monotosylate with KI and K_2CO_3, followed by either termini protection (THP) and reduction to the hydroxymethyl derivative **393** or tosylation to give **394**; combination of **393** and **394** gave (57%) the G2 **395**, which was reduced to **396**. Both the G1 and G2 hydroxymethyl derivatives were subjected to methacroyl chloride, then the termini were deprotected (PTSA or PPTS, MeOH; ∼85%) affording the desired monomers for polymerization (Scheme 85). Thermo-responsive dendronized polymers were made using different terminated dendrons,[1148] or their attachment to a three-directional core was shown to decrease cytotoxicity.[1147] The G1 3,4,5-(methyl-terminated, tetra- and penta-PEGed)aryl moiety was attached to a triazine and oligo(*p*-phenylene) core for studying the different single-stranded DNA templated self-assemblies.[1157]

The construction of the series G1−G4 1 → 3 aryl-branched dendrons possessing an ester focal moiety and a short connector between aryl-branching centers has been reported in order to instill extreme congestion into the resultant structure.[1158−1160]

Click chemistry was utilized to connect azido-carbohydrates to terminal alkynyl dendrons by a Cu(I)-catalyzed [3 + 2] cycloaddition using microwave irradiation;[1161] the acetylene dendrons **401** and **402** are shown in Figure 16.

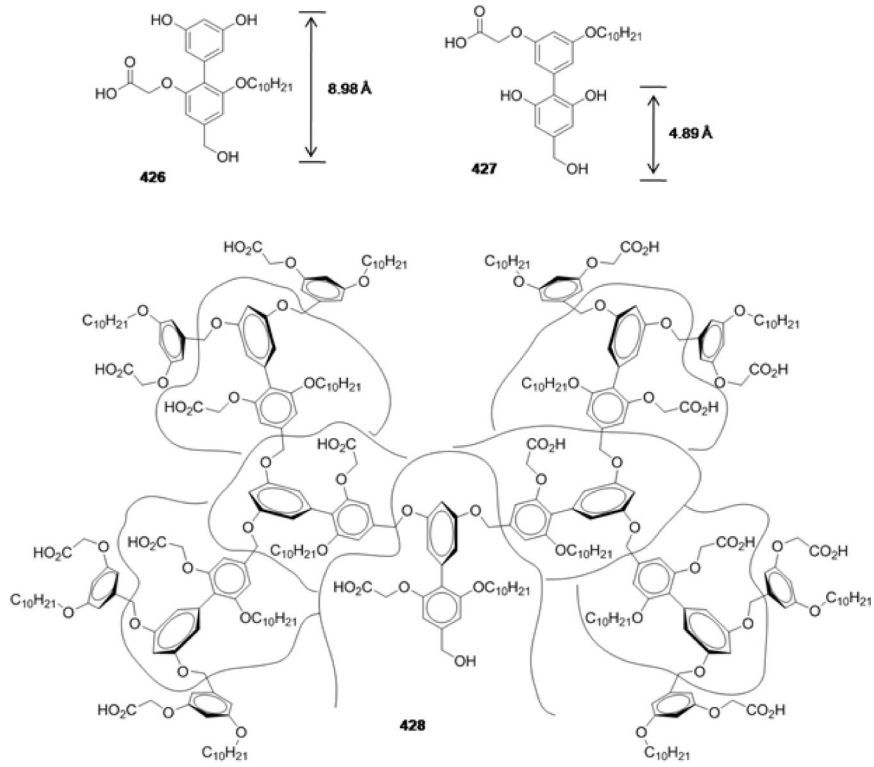
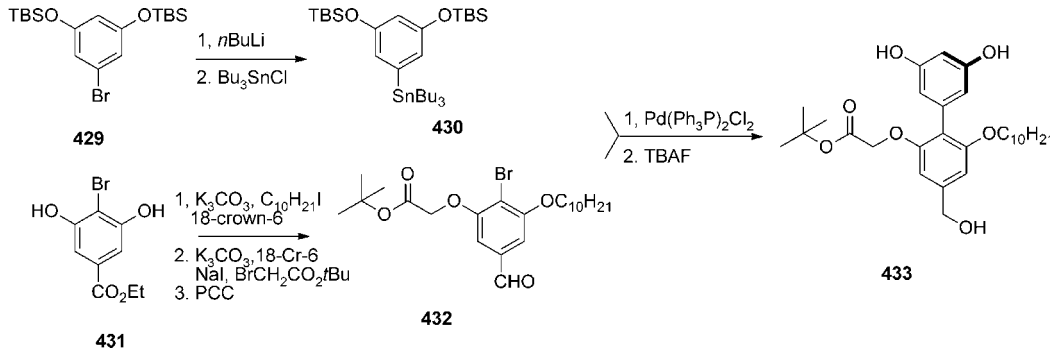


Figure 19. Polyfunctionalized monomers and their introduction into hyperbranched products.[1172]

Scheme 89. Access to the Key Monomer for a Novel Series of Nanocontainers[1177]



Highly ordered honeycomb films with a quasi-horizontally paralleled double-layered structure were fabricated[1162] via an on-solid surface spreading procedure, using dendronized block copolymer (PEO_{113}-*b*-$PDMA_{82}$) in which the dendron methacrylate was **403**.[1163]

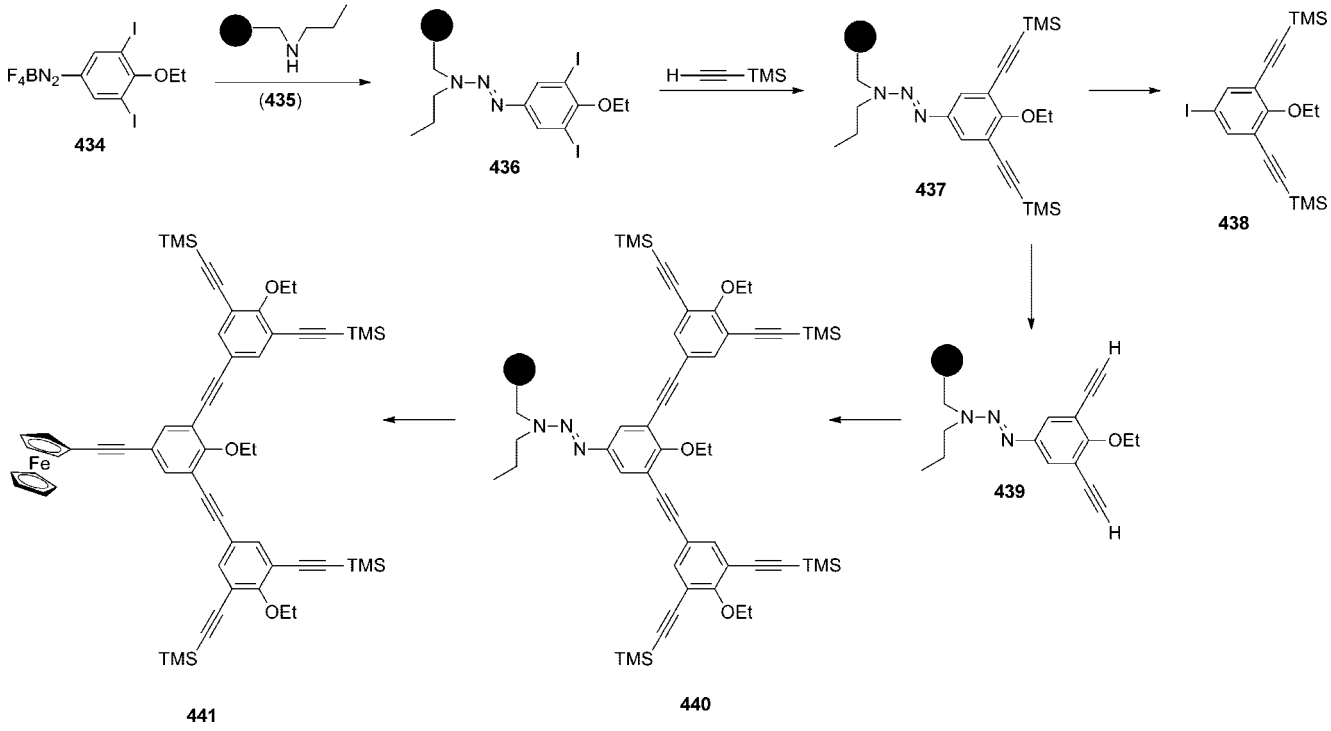
9.4. [1 → (2 + 1)] (3,4,5-)Aryl-Branched Dendrons

Schlüter et al.[1164] synthesized a novel series of dendrons possessing a 1 → (2 + 1) branching pattern in which 3,5-dibromo-4-iodophenyl-acetic acid or -propionic acid were converted into **404** via several steps then coupled to the core **405** to generate the desired G2 dendrimer **406** (Scheme 86). They also created a related series starting from ethyl 3,4,5-trihydroxybenzoate by treating it with $Br(CH_2)_3X$, where X = NHBoc, NHCbz, or OBn;[1165] this permitted access to the symmetric 3,5-dihydroxy-4-(elongated protected amino)benzoate, which was subsequently treated with an OEGylated glycerol derivative. This (2 + 1)-benzoate was then further modified at either the 4-position or the focal site or both.

Kozaki, Okada, et al.[1166−1170] created an innovative 1 → (2 + 1)-branching system in their route to a light-harvesting array made up of porphyrins and a rigid backbone. The key sequence of reaction is shown in Scheme 87 in which 4-iodo-2,6-dibromonitrobenzene (**407**) was transformed to predendron **409** and then to dendron **410**.[1166] The recombination of these monomers permitted the construction of predendron **412**, which can be modified at the apical position or at its focal point. Their elegant procedure is a simple series of chemical additions and subtractions to logically assemble the final dendron and then their attachment to the three-directional core.[1166] Application of this stepwise assembly gave rise to related dendrons possessing a unique cap (or star) of an anthraquinone at the pinnacle position.[1167] Figure 17 shows the variety of structures, for example, with a core porphyrin **416**,[1168] a porphyrin with a single anthraquinone on the dendron's termini **414**,[1167] and a snowflake pattern **415**,[1166] that have been made by simple modifications of their procedures. 3,5-Di(PEG)-4-(R-aminopropoxy)benzoyl derivatives have also been used in the preparation of platinum(II) dendrimer conjugates.[1171]

In Scheme 88, the above monomers were put together in different ways leading to the decaporphyrin starting

Scheme 90. Preparation of Novel 1 → (1 + 2) Polyfunctionalized Dendrons[1181]



with the iodide **417**, which was reacted with the key protected branching component **418**, followed by Suzuki−Miyaura coupling[845] with **420** in an amazing 82% yield.[1169] The desired dendron **421** was deprotected and coupled with the tetradirectional porphyrin core **423** to give (23%) the light-harvesting array **424**, as a purple solid. Use of such bidirectional monomers permitted the construction of the cross-shaped assembly **425** possessing a 12 nm diagonal dimension and a mass of 16 552 amu (Figure 18).[1170]

Thayumanavan et al. recently reported[62,1172−1175] the construction of unsymmetrical dendrimers of the Fréchet-type but instilled either 1 → (1 + 2) (**426**) or 1 → (1 + 1 + 1) (**427**) connectors that permitted the control of the internal hydrophobic−hydrophilic characteristics. These types of amphiphilic dendrimers demonstrated environment-dependent assemblies; interestingly, these constructs were shown to be kinetically trapped in the solvent in which they were initially created.[1176] Figure 19 shows the connecters and their introduction into the hyperbranched products (**428**). Such internal functionality permitted the introduction of spectroscopic probes at precise locations. Difunctionalized bromobenzene **429** was transformed to the tin derivative **430**, which was coupled with trifunctionalized benzaldehyde **432**, derived from ethyl 4-bromo-3,5-dihydroxybenzoate in four steps, to give the desired polyfunctional biphenyl **433**, as shown in Scheme 89.[1177] In order to start to understand the effect of placing a specific functionality at an encapsulated interior location within their dendritic family, the site-specific incorporation of a ferrocene moiety at different locations was demonstrated; interestingly, the redox potentials for the ferrocene at intermediate layers were different from those at the core or periphery.[1178] The incorporation of enzyme-sensitive functionalities onto the lipophilic surface permitted subsequent disassembly and guest release, upon interaction with an enzyme.[1179,1180]

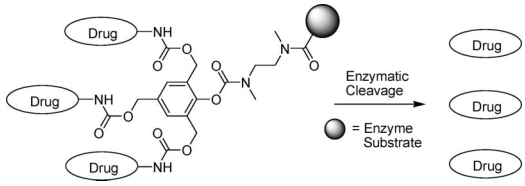


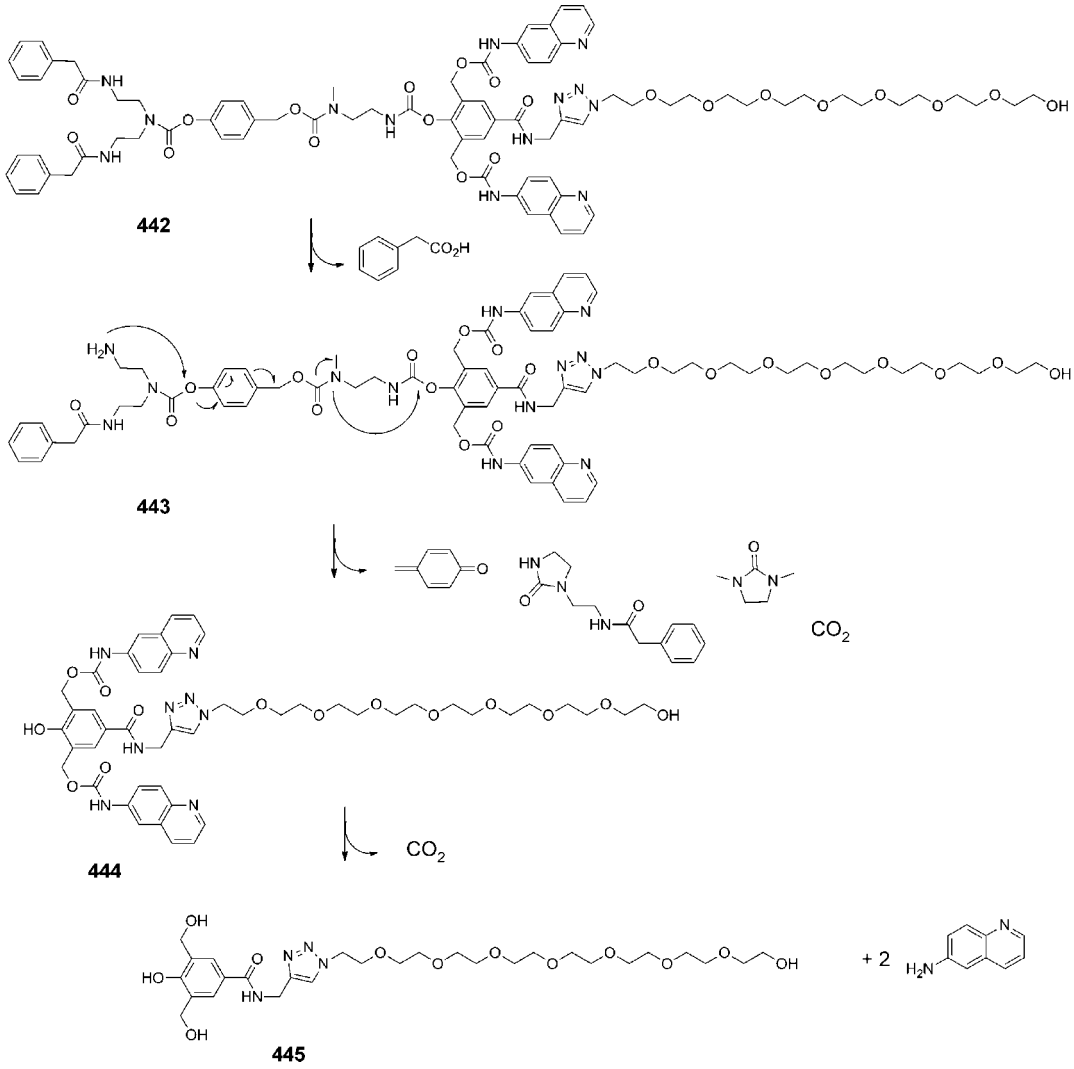
Figure 20. The key 1 → 3 branching unit leading to structural fragmentation.[154]

Wang et al.[1181] synthesized a series of dendronized ferrocenes via the procedure shown in Scheme 90, in which the diazonium tetrafluoroborate salt **434** of 3,5-diiodo-4-ethoxyaniline was reacted with (*n*-propylaminomethyl)polystyrene (**435**) to generate the functionalized resin **436**. This resin was treated with trimethylsilylacetylene in the presence of a Pd catalyst[1182] generating the key resin-protected reagent **437**, which was deprotected to give **438** or transformed into the corresponding iodo monomer **439**. Reaction of the resin **438** with the iodo monomer gave **440**, which was deprotected and with monomer **439** converted into the next generation dendron. In view of the freedom of these dendrons from the resin, the resultant iodo compound was reacted with the ethynylferrocene to generate the desired product, for example, **441**.

9.5. (1 → 3) 2,4,6-Aryl-Branched, Carbamate-Connectivity Dendrons

Shabat et al. have utilized a dendron based on 2,4,6-tris(hydroxymethyl)aniline, which possesses a drug[1183] or reporter[1184] at the dendron's surface and an enzyme substrate or H_2O_2 trigger at the focal position. Similar fragmentations were derived from 2,4,6-tri(formyl)phenol, which was transformed to a very novel 1 → 6 or the 1 → (3 + 2) branching motif.[1185] Shabat[154] presented a highlight entitled "Self-Immolative Dendrimers as Novel Drug Delivery Platforms",[1186] which gives an overview of the self-destruction of these dendron structures (Figure 20); also see section 9.6, the 1 → (2 + 1) (2,6;4)-aryl-branched dendrons.

Scheme 91. The Structural Degradation of 442 with PGA[1187]



9.6. 1 → (2 + 1) (2,6;4)-Aryl-Branched, Amide- and Carbamate-Connectivity Dendrons

Shabat et al.[1187] created a molecular receiver attached to a molecular amplifier that is shown in Scheme 91. The simplest example is when **442** is initiated by the enzymatic cleavage of the phenylacetamide portion of the receiver using penicillin G amidase. The fragmentation rapidly disassembles the original molecule giving eventually **445**. The initial **442** and larger dendrons were described in detail in this article; also see refs 1188−1192.

9.7. 1 → (2 + 1) (3,5;4)-Aryl-Branched, Olefin- and Ether-Connectivity Dendrons

Weng and Zhang[1193] started with 3,5-di(hydroxymethyl)-4-hydroxytoluene in a six-step series to generate monomer **453**, which with 4-cyanobenzaldehyde, followed by hydrolysis, gave the di(olefinic arylnitrile) dendron **454**; the larger generations were similarly prepared (Scheme 92). Reaction of dendron **454** and the cyclen (1,4,7,10-tetraazadodecane) core generated the second generation octa(olefinic arylnitrile) dendrimer **455**. The acid-terminated structures were also prepared, as well as their corresponding Ni(II) complexes.

10. 1 → 3 Adamantane-Branched

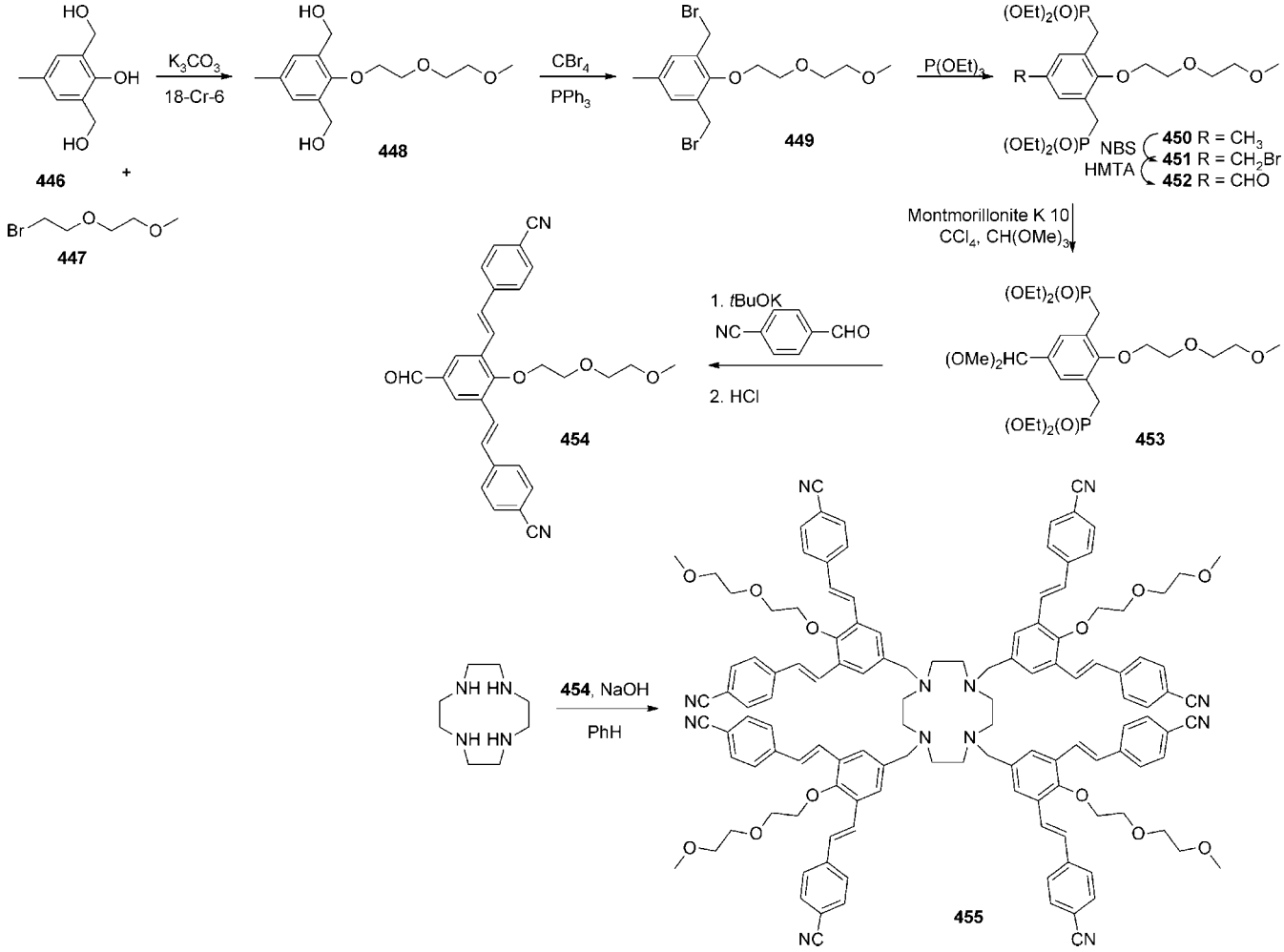
10.1. 1 → 3 Adamantane-Branched, Ester Connectivity

Chapman et al.[1194] reported in a communication the formation of "polycules" **458**, which were generated from "quasi-atoms", specifically, substituted 1,3,5,7-tetraphenyladamantanes and the related diadamantanes. Treatment of the tetraacyl core **456**[1195−1197] with the 1 → 3 adamantyl building block **457** gave the desired tetraester **458** (Scheme 93). This example only appeared in a meeting abstract, and the details were not reported.

10.2. 1 → 3 1,3,5-Triazaadamantane-Branched, Amide and Ether Connectivity

Kohman and Zimmerman recently published[1198] a clever route to degradable dendrimers synthesized from a 1,3,5-triazaadamantane, which was prepared from $HOCH_2$-$C(CH_2NH_2)_3$ and an activated benzaldehyde, as shown in Scheme 94. The alkyne monomer **463** was reacted with $MeC[C_6H_4O(CH_2)_3N_3]_3$ (**464**), the terminal chlorides were transformed to azide moieties, and the procedure was repeated. Addition of HCl to these fragile dendrimers in THF/MeOH led to rapid degradation.

Scheme 92. Synthesis of Cyclen-Cored Dendrimers[1193]



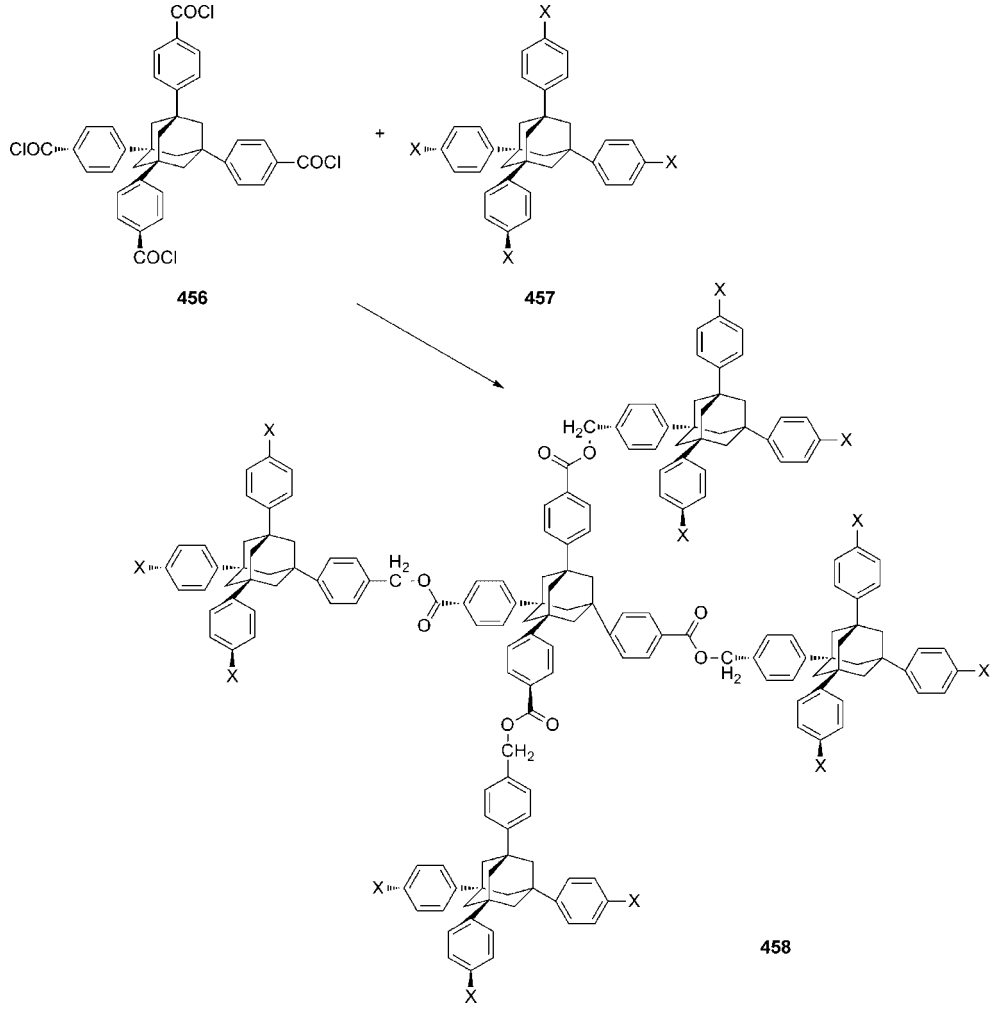
10.3. 1 → 3 Adamantane-Branched Monomers

The use of related adamantanes offers a novel approach to rigid dendrimers that will remain globular upon removal of solvent. When a mixture of 1-adamantanecarboxylic acid and oxalyl chloride was irradiated, followed by methanolysis, the previously synthesized[218,1199] 1,3,5,7-tetrakis(methoxycarbonyl)adamantane was prepared (20−30%) by a simple one-pot reaction.[469] This identical photolytic procedure was applied to 1-nitroadamantane to generate the 1-nitro-3,5,7-tris(methoxycarbonyl)adamantane,[1200] which was catalytically reduced to give the 1-amino-3,5,7-tris(methoxycarbonyl)adamantane (**470**) in low overall yields (Scheme 95);[1201] interestingly, this is a rigid analog to Behera's amine.[217] Similarly, when 1-bromoadamantane was irradiated in the presence of $(COCl)_2$, followed by methanolysis, 1-bromo-3,5,7-tris(methoxycarbonyl)adamantane was isolated in 24% yield.[1202] Alternatively, 1,3,5,7-tetraphenyladamantane **471** was oxidized and esterified to the tetramethyl ester **472**, which was selectively saponified (90%) to the monoacid, then subjected to the Curtius reaction[1203] and selectively deprotected to give **470** in 83% yield.[1204] Maison et al.[1205] also reported the synthesis of tris-(bis-homologue), 1-amino-3,5,7-tris(3-propionic acid)adamantane, from adamantane; the use of such adamantane scaffolds for affinity maturation of prostate cancer specific ligands has been described.[1205] The related 1-amido-3,5,7-tricarboxy- and 1-carboxy-3,5,7-amidoadamantanes have been isolated from a mixture by the treatment of 1,3,5,7-tetrakis(chlorocarbonyl)adamantane with aminofluorescein.[1206] Selective substitution on adamantane has been reported, but as expected, mixtures have resulted from which the specific product must be isolated. For example, when 1,3,5,7-tetrakis(aminomethyl)adamantane was treated, via "stoichiometric restriction... with unimpressive results", with 1 equiv of ethyl trifluoroacetate then 3.5 equiv of 2,3-dimethoxybenzoic acid and BOP (Castro's reagent[1207]), the desired 1 → 3 product was isolated (32%); the initial use of trityl chloride helped slightly giving 40% of the related 1 → 3 substitution pattern.[1208]

Treatment of tetrakis(4-iodophenyl)adamantane[692] with *t*-BuLi, followed by CO_2, hydrolysis, and CH_2N_2, generated in low yield (6−10%) the 1-(4-iodophenyl)-3,5,7-tris(4-methoxycarbonylphenyl)adamantane.[1209] Also 1-(4-ethynylphenyl)-3,5,7-tris[4-(methoxycarbonyl)phenyl {or 4-cyanophenyl}[1210]]adamantane[1209] has been synthesized from this tetraiodophenyl starting material. Stilbenoid moieties have been similarly attached by Pd-catalyzed Heck conditions[1211] to 4-substituted tetraphenyladamantane, tetraphenylmethane, or tetraphenylsilane cores; structural and optical properties were evaluated.[1212]

The synthesis of ethyl 2,4,9-trithiaadamantane-7-carboxylate was accomplished in three steps (25% overall) from diethyl 2,2-diallylmalonate via selective monodeesterification, followed by alkylation to generate $EtO_2CC(CH_2CH{=}CH_2)_3$, which is treated with ozone, then hydrogen sulfide; reduction ($LiBH_4$) gives (100%) 2,4,9-trithiaadamantane-7-methanol.[1213]

Scheme 93. Construction of Adamantane-Based Dendrimers[1194]



11. 1 → 3 Tetraazamacrocycle-Branched, Amide Connectivity

The use of specifically substituted tetraaza[6.1.6.1]paracyclophane has opened the door to novel dendritic polycyclophanes. Scheme 96 demonstrates the unlimited opportunities if one expands the 1 → 3 branched monomer perspective.[1214] The selected substitution of **473** with protected β-alanine (3 equiv) in the presence of DCC gave (33%) tris(Boc-β-alanyl)-1,6,20,25-tetraaza[6.1.6.1]paracyclophane (**474**).[1215,1216] Activation of the remaining free amino site was conducted with succinic anhydride to give acid **475**, which can be coupled with amine **474** to afford the two-directional biscyclophane (**476**) or coupled (pyBOP) to the activated tetraamine core[1217,1218] **477** to give the pentacyclophane **478**. Removal of the protecting groups and introduction of carbohydrates enhances the water solubility of the products; the host−guest properties were considered using the hydrophobic dye 6-*p*-toluidinonaphthalene-2-sulfonate. Details concerning these water-soluble cyclophane heptadecamers coated with galactose and glucose termini have been reported.[1219] The N,N,N,N-attachment of four resorcinarene groups possessing heptacarboxylic acid on the tetraaza[6.1.6.1]paracyclophane core was an interesting use of a larger 1 → 7 branching moiety.[1214,1219−1222]

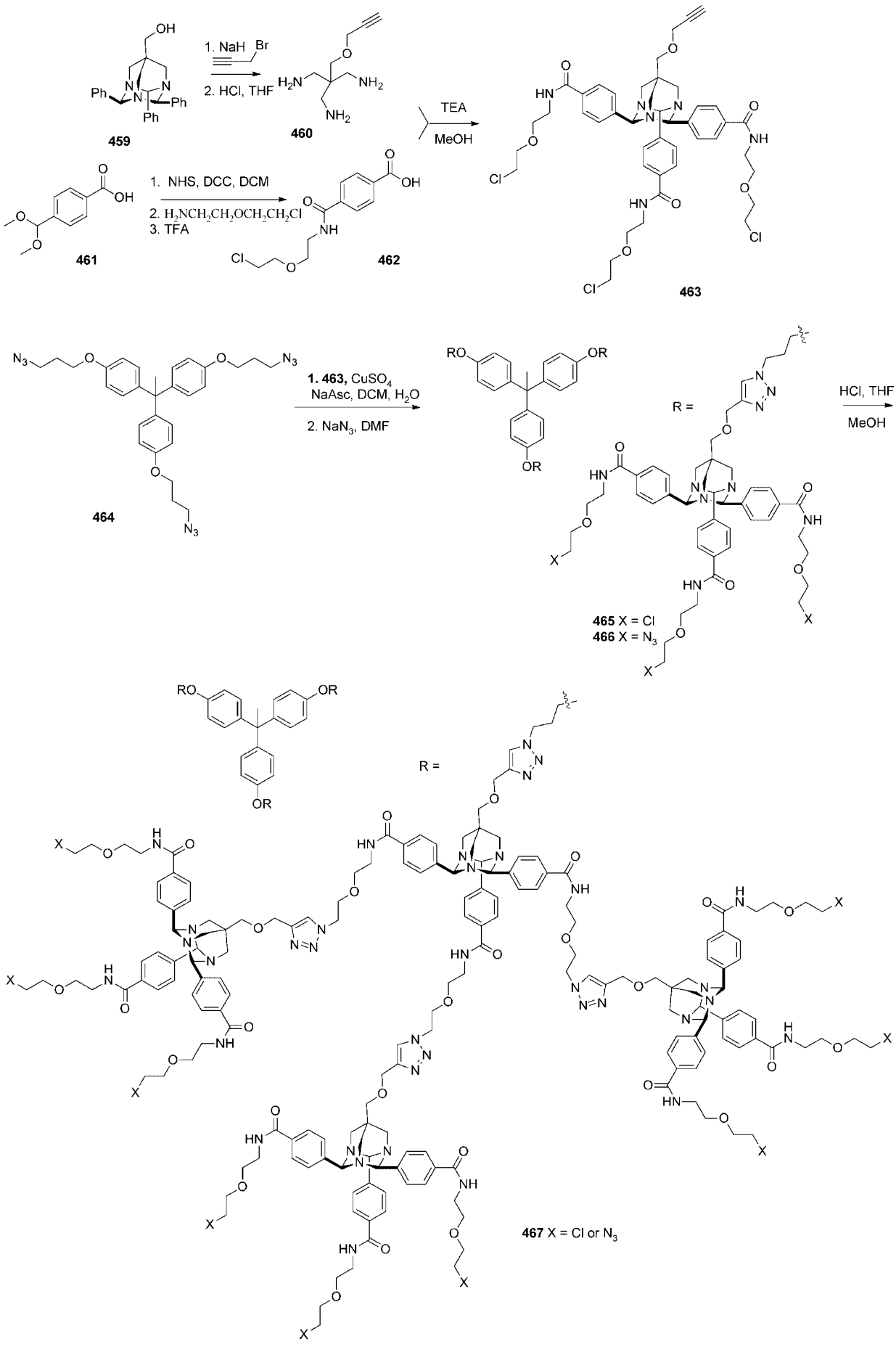
DOTA has been well-known to form a lanthanide chelate, and thus the 1 → 3 monomer **482** offers a convenient reagent for dendrimer construction. Cyclen (1,4,7,10-tetraazadodecane) **479** was monoalkylated with ethyl bromoacetate; then 3 equiv of *tert*-butyl bromoacetate were added to generate (84%) the (1 → 3) tetraester **481**, which was treated with neat ethylenediamine to give (68%) the desired amine **482** (Scheme 97).[1223] This amine **482** was transformed into a 1 → 2 N-branched dendrimer and hydrolyzed to release the *tert*-butyl esters. The specific synthesis of the related 1 → 3 monomers of 1- or 8-monofunctionalized 1,4,8,12-tetraazacyclopentadecanes created from unsymmetrical synthons has been reported.[1224] In a reverse manner, 1,4,7,10-tetraazadodecane **479** was trialkylated with $BrCH_2CO_2CMe_3$ with DMA, then de-esterified (TFA) and treated with 1,2-epoxybutane or -octane to give access to another 1 → 3 branched monomer;[1225] also see refs 1226 and 1227 for other examples.

12. 1 → 3 Porphyrin-Branched

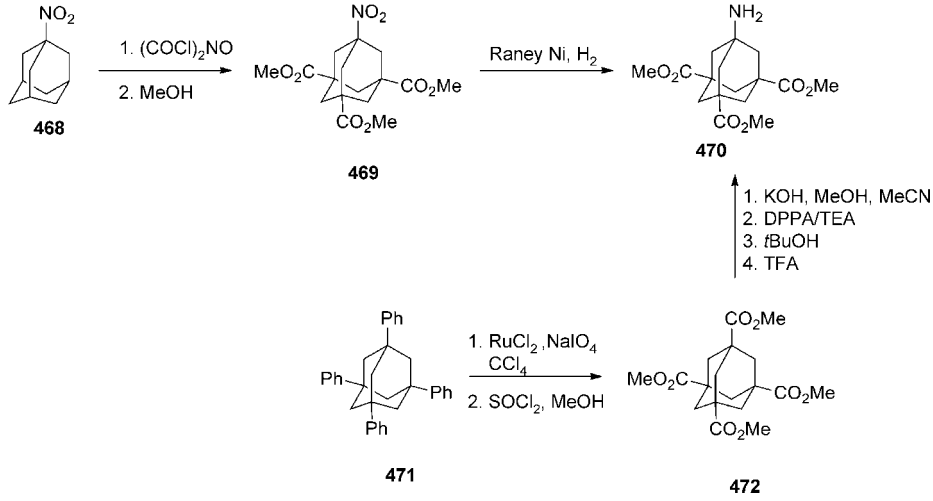
12.1. 1 → 3 Porphyrin-Branched, Porphyrin Connectivity

Sakata et al.[1228] created two of the more inventive 1 → 3 branching monomers necessary to synthesize the porphyrin henicosamer possessing 20 nickel centers with a central metal-free core. The overall structure is square planar with 21 porphyrins measuring 6.5 nm per side. It was constructed (Scheme 98) from two different starting porphyrins, **483** and **484**, which were separated (12% and 3%) from a mixture of condensation product that was generated from the reaction

Scheme 94. A Facile Route to Degradable Dendrimers[1198]



Scheme 95. Preparation of 1-Amino-3,5,7-tris(methoxycarbonyl)adamantane[1200,1201,1204]



of 3,5-di(iso-amyloxy)benzaldehyde, pyrrole, and methyl 4-formylbenzoate in propanoic acid. The external 1 → 3 branching component **487** was derived (25%) from the reaction of **485** (3 equiv) and **486** (1 equiv) with pyrrole and $BF_3 \cdot OEt_2$ in EtOH. Reduction of the remaining function $-CH_2OCOEt$ moiety on **487** to a formyl group permitted access to the final central ring by again treatment of **488** with pyrrole and $BF_3 \cdot OEt_2$ in $EtOH/CH_2Cl_2$ giving (44%) **489**. The overall yield of **489** was 0.15% in 17 steps; it possessed a molecular weight of 20 061 amu for $C_{1244}H_{1350}N_{84}Ni_{20}O_{88}$, a remarkable synthetic venture.

Yeh et al.[1229] recently synthesized a "waterwheel"-shaped porphyrin pentamer by the reaction of tetrabromoporphyrin[1230] (**490**) with 4,4,5,5-tetramethyldioxaborolane in the presence of a palladium catalyst, followed by demetalation generating **492** (Scheme 99). Treatment of the zinc porphyrin **492** with the iodoporphyrin **493** in the presence of $[Pd(PPh_3)_4]$ and Cs_2CO_3 using DMF/toluene gave (3%) **494**; whereas, different combinations of reagents increased the yield of a related pentaporphyrin **495** to 15%.

12.2. 1 → 3 Porphyrin-Branched, Ether Connectivity

A dodecaporphyrin disk was synthesized from hexa(3,5-dibromomethylphenyl)benzene[1231] with a 1 → 3 porphyrin possessing a reactive *meso*-4-hydroxyphenyl and three 4-dodecalkoxyphenyl moieties;[1232] this disk-like structure self-assembled to generate well-ordered and molecularly resolved columnar stacks, as shown by liquid STM. The porphyrin 1 → 3 branched monomer **498** was readily prepared[1233] in one-step from the Fréchet-dendronized 5-(4-hydroxyphenyl)dipyrromethane (**496**), 5-(4-methoxycarbonylpyenyl)dipyrromethane (**497**), and dendronized benzaldehyde in the presence of $BF_3 \cdot OEt_2$ at 25 °C, followed by oxidation (DDQ), incorporation of platinum, and last hydrolysis (Scheme 100).[1234,1235] Treatment of **498** with KH followed by $ErCl_3$ and terpyridine afforded the Er cored metallodendrimer **499**.

12.3. 1 → 3 Phthalocyanine and 1 → 3 C-Branched, N and S Connectivity

Metal-free phthalocyanines, as well as those possessing either Zn(II) or Co(II), were prepared by the condensation of 4-nitrophthalonitrile and 4-(2-dimethylaminoethylsulfanyl)phthalonitrile; the amines were quaternized with MeI; then the nitro moiety was reduced to the free amine giving **500**,[1236] which was reacted with cyanuric chloride in the presence of K_2CO_3 generating **501**, which was further transformed to **502** by the treatment with $NaC(CO_2Et)_3$, followed by TRIS to give **503** (Scheme 101). Completely reversible sensor signals for CO_2 were obtained for the Zn(II) complex.

13. 1 → 3 Calixarene-Branched, Ether Connectivity

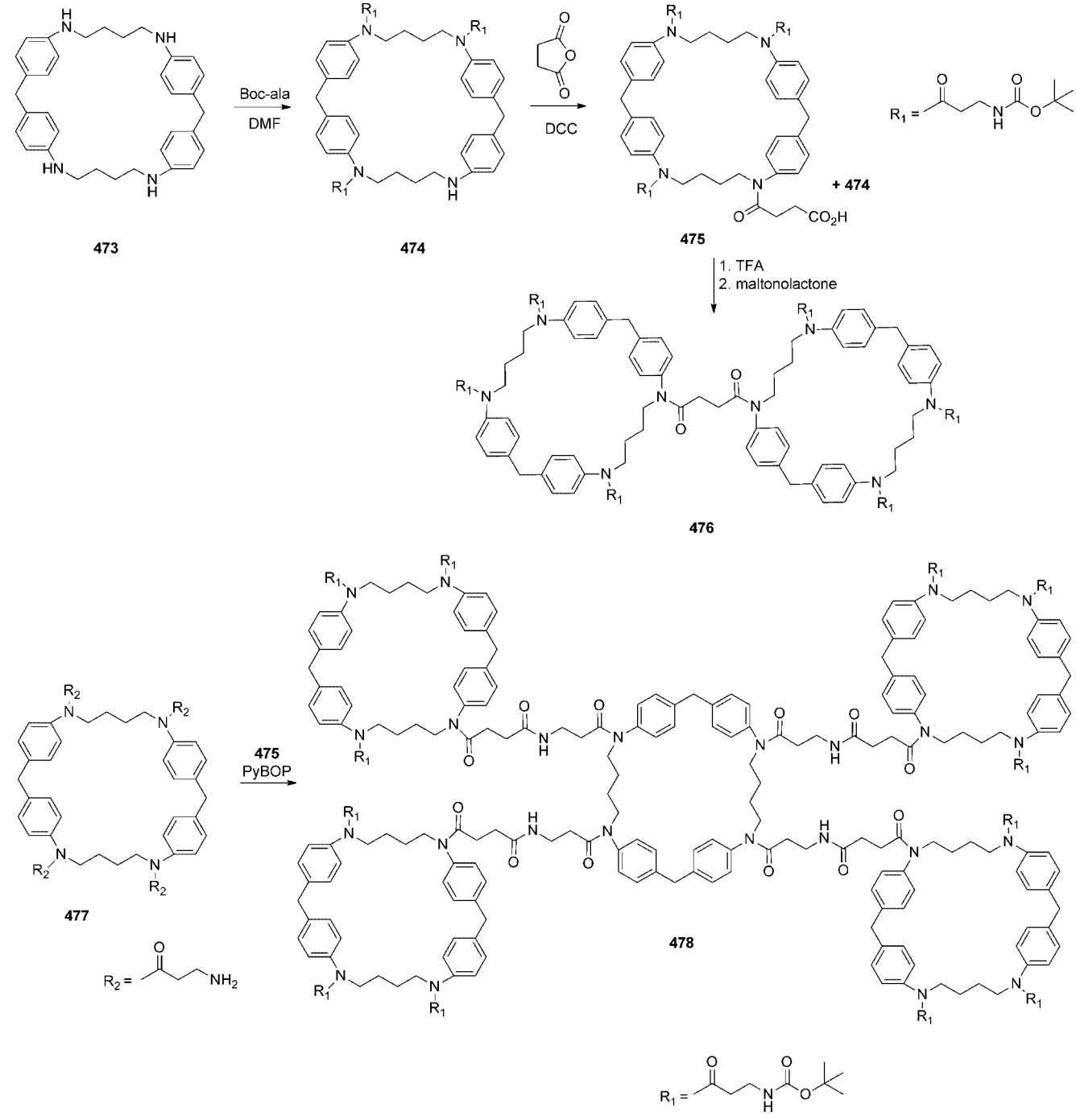
The limited protection of 25,26,27,28-tetrahydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene was readily accomplished by its alkylation with propyl bromide in the presence of $Ba(OH)_2/BaO$ in THF giving the tripropoxy-substituted calix[4]arene **505**, which was subjected to an excess of α,ω-dibromoalkanes in DMF at 55 °C generating $[(CH_2)_n$, $n = 2$, 51%; $n = 3$, 81%; $n = 6$, 76%] the extended monomer **506** or with 0.5 equiv to form ($n = 3$, 70%; $n = 6$, 76%; $n = 10$, 86%) the desired two-directional dendrimers **507** in one step (Scheme 102).[1237] By treatment of **505** with the initial starting tetrahydroxycalix[4]arene, the desired pentakiscalix[4]arene **508** (with *tert*-butyl groups on the core and $n = 6$, 7%; without *tert*-butyl groups on the core, $n = 6$, 38%) was prepared demonstrating the steric congestion caused by the bulky *tert*-butyl moieties. Since in the initial alkylation step the mono- and two dialkylated derivatives were also isolated, other interesting polycalixarenes were reported.[1237]

An overview of hyperbranched calixarenes describing predominately Professors Kin and Vicenes work in this topic has recently appeared.[1238]

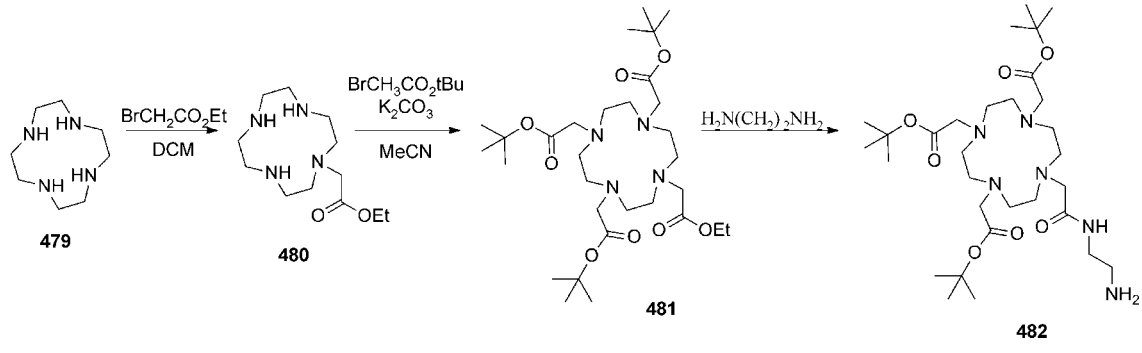
14. 1 → 3 (3,7,12-)Cholic Acid-Branched Dendrons, Ester Connectivity

The treatment of 3α,7α,12α-triacetyloxy-5β-cholanic acid (**509**) with 1-naphthylmethyl 3α,7α,12α-trihydroxy-5β-cholan-24-ate (**510**) generated the tetramer **511**, which was hydrolyzed to the free acid dendron **512**; then reaction of **512** with 3 equiv of monomer **510** afforded the desired dendrimer **513** (Scheme 103).[1239,1240] The chloroacetyl group was used to synthesize the G1 and G2 bile acid dendrons possessing multiple hydroxyl groups.[1241] The unimolecular

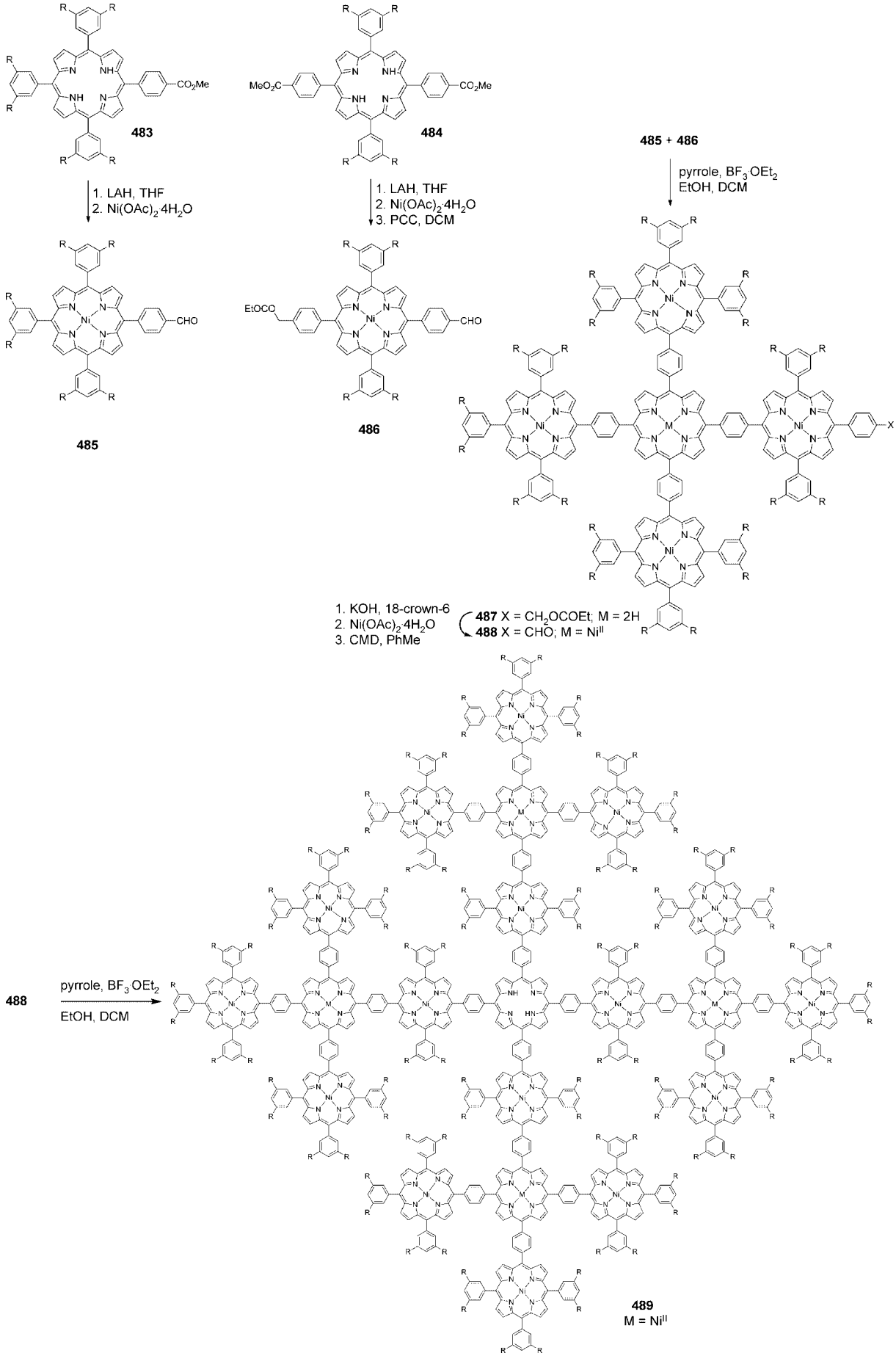
Scheme 96. 1 → 3 Cyclophane Monomers and Core[1214]



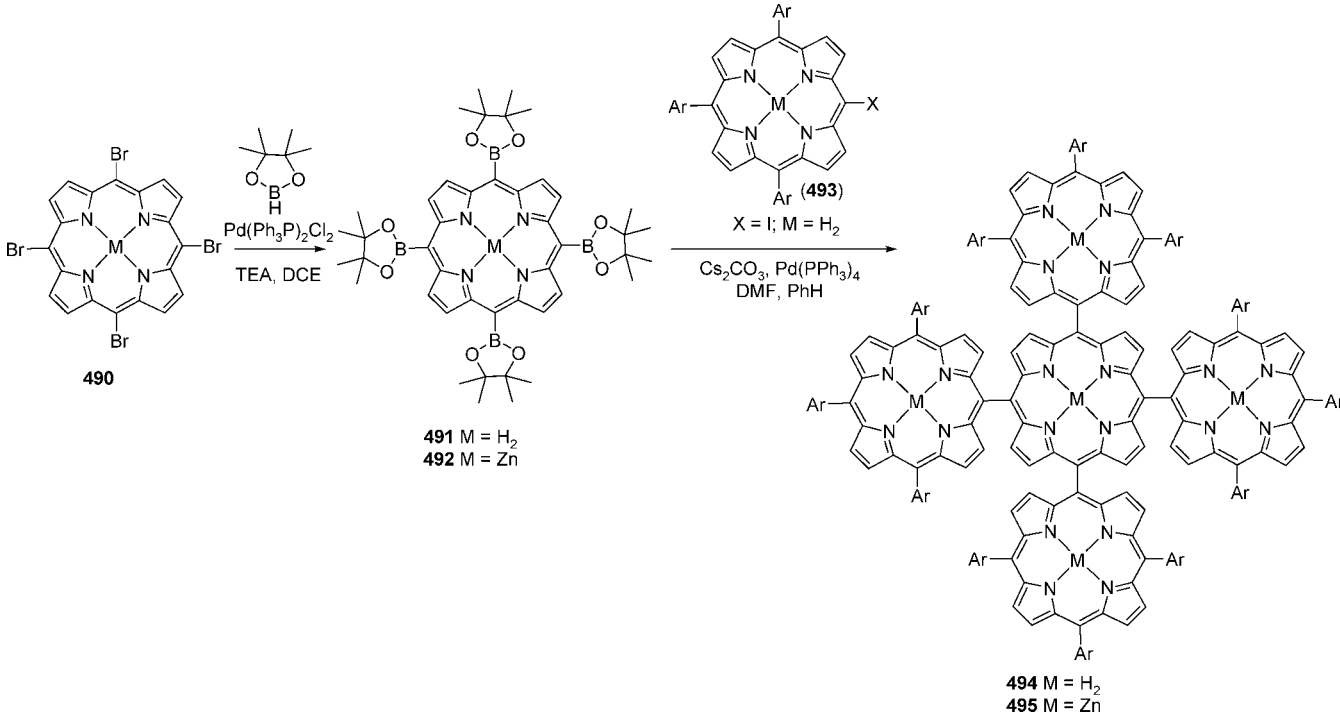
Scheme 97. The Generation of the 1 → 3 Tetraazacyclododecane-Branched Monomer for Dendrimer Construction[1223]



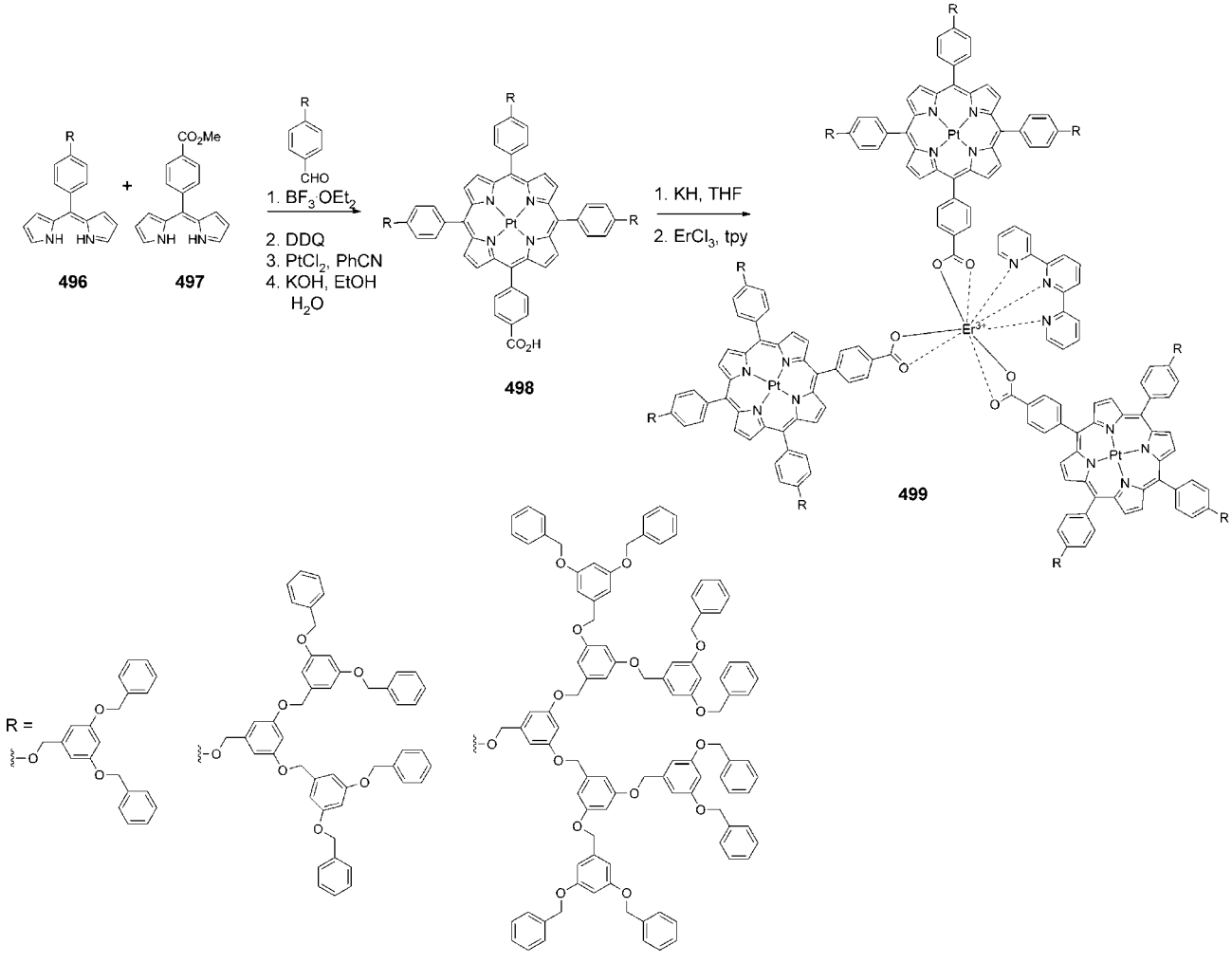
Scheme 98. The Synthesis of the Porphyrin Henicosamer from Two Different 1 → 3 Branching Porphyrin Monomers[1228]



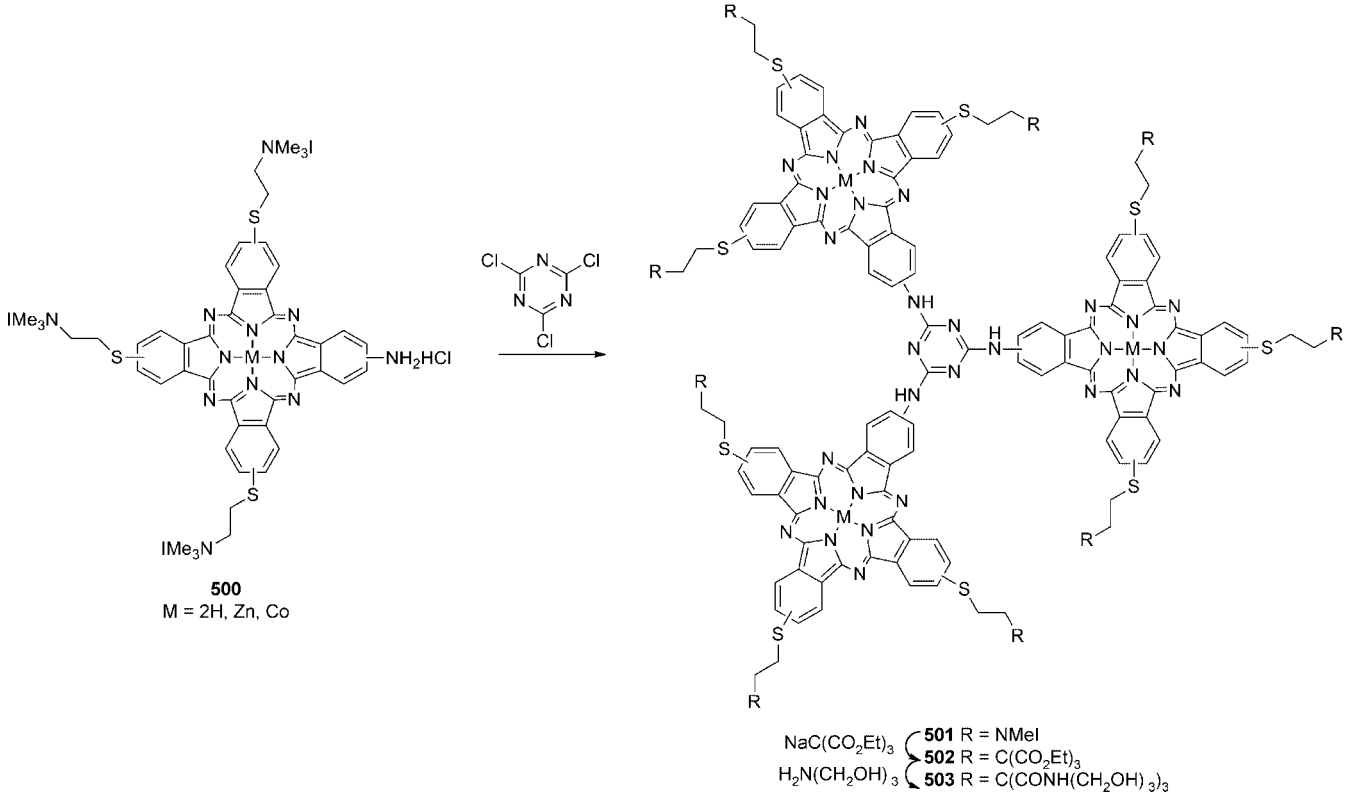
Scheme 99. The Construction of *meso*−*meso*-Linked Pentaporphyrins[1229]



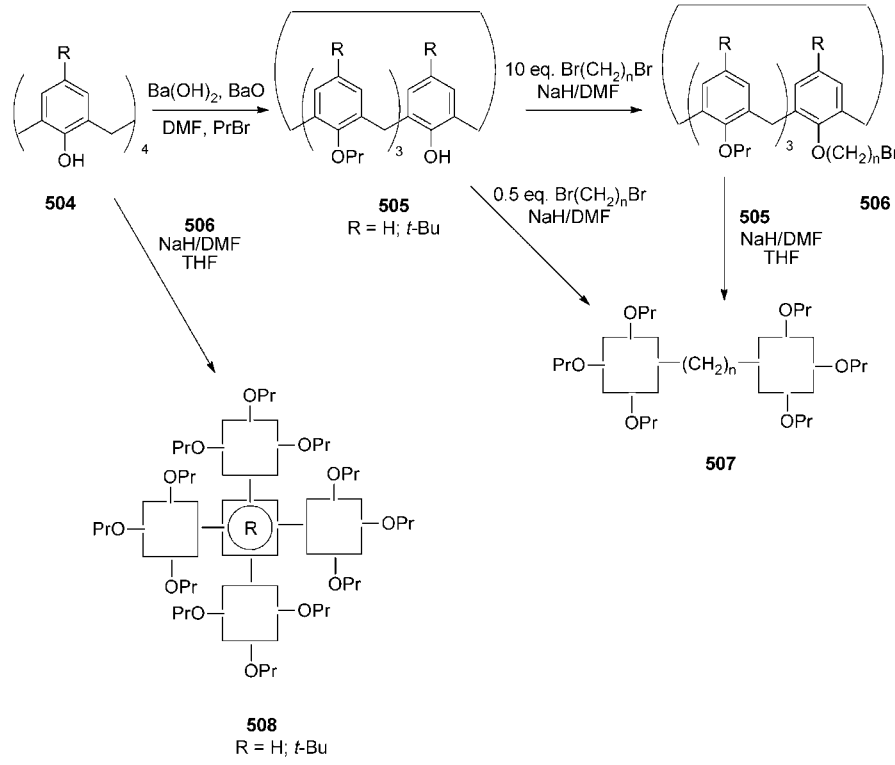
Scheme 100. The Construction of the Metallodendrimer Possessing the 1 → 3 Branched Porphyrin[1233]



Scheme 101. The Combination of Different Modes of Constructing Dendritic Phthalocyanines[1236]



Scheme 102. The Synthesis of Dendritic Species Derived from 1 → 3 Branched Calix[4]arenes[1237]

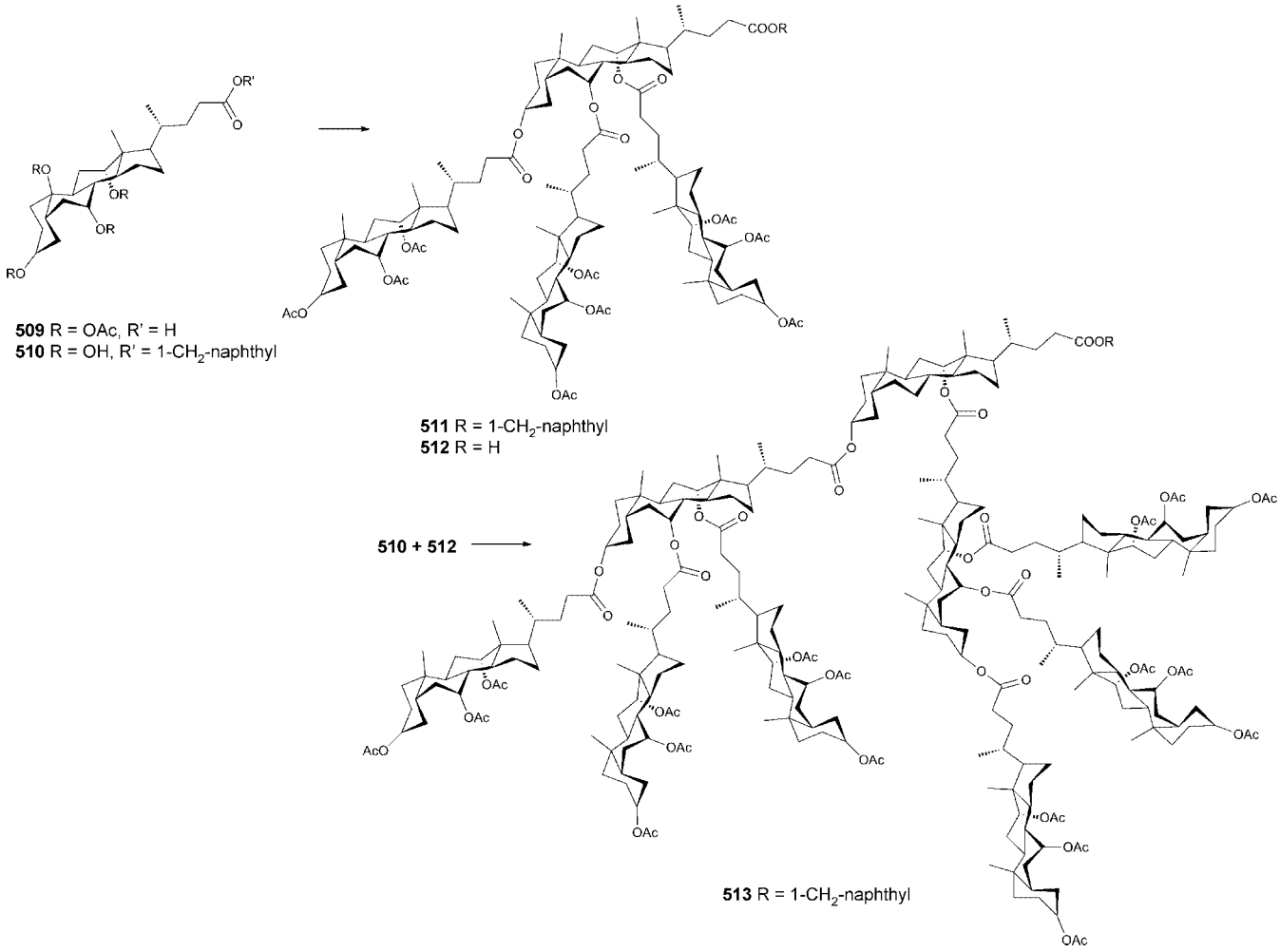


micelle properties of related dendrons have also been demonstrated.[1242] This is the first such example using branched bile acid to construct different oligomers. In view of the multiple naproxen groups on the dendritic structures and the single focal site, anthracene has been placed at the focal position and (*S*)-(+)-2-(6-methoxy-2-naphthyl)propanoic acid moieties have been placed at the 3α,7α,12α-loci.[1243] Their photophysical properties have been studied by both steady-state and time-resolved techniques; these nonconjugated dendrimers were shown to act as molecular light harvesters.[1244]

15. 1 → 3 (3,6,8-)Pyrene-Branched

Müllen et al. recently reported the novel use of the activated 1,3,6,8-centers on pyrene to create the unusual all

Scheme 103. Construction of the First Bile Acid Derived Chiral Dendrimers[1239,1240]



hydrocarbon G1 and G2 dendrimers.[1245] The first generation dendrimer possessing five pyrene moieties was prepared by the borylation of 7-*tert*-butyl-1-bromopyrene with bis(pinacolato)diboron under Suzuki−Miyaura conditions affording 7-*tert*-butylpyrene-1-borate pinacol ester, which was then treated with 1,3,6,8-tetrabromopyrene to generate (42%) 1,3,6,8-tetrakis(7-*tert*-1-pyrenyl)pyrene. The second generation was assembled in a similar manner, except the above reaction was conducted with a 3:1 ratio of the boronic acid reagent and the same tetrabromide giving the desired predendron, 1-bromo-3,6,8-tris(7-*tert*-butylpyren-1-yl)pyrene, which was converted (98%) to the corresponding boronate intermediate; its subsequent treatment with the tetrabromo core gave (38%) the desired 1,3,6,8-tetrakis(7-*tert*-butylpyren-1-yl)pyrene, possessing 17 pyrene units.

16. Outlook

The novel features of these fractal-like molecular architectures are their rich chemistry associated with the untapped internal regime(s) as well as limitless uniform and combinatorial surface possibilities. There is unlimited potential for a wide range of utilitarian applications. Since these 1 → 3 branched dendritic assemblies generally utilize branching centers associated with the starting monomer, the creation of new novel functionalized monomers and their subsequent combination to generate different synthetic patterns will open doors to vast new families of synthetically generated structural organic architectures. The creation of new monomers will afford new avenues to specific nanostructures that will spark the imagination of future inventors.

17. Glossary

AIBN	azobisisobutyronitrile
AFM	atomic force microscopy
amu	atomic mass units
AZT	3′-azido-3′-deoxythimidine
BICOL	bicarbazolediol
BINOL	2,2′-dihydroxy-1,1′-binaphthyl
Bn	benzyl ($C_6H_5CH_2-$)
Boc	*tert*-butyloxycarbonyl
BOP	benzotriazolyl*N*-oxytris(dimethylamino)phosphonium hexafluorophosphate (Castro's reagent)
bpy	2,2′-bipyridine
cBz	benzyloxycarbonyl
CD	circular dichroism
CDI	1,1-carbonyldiimidazole
Cl-tpy	4′-chloroterpyridine
cmc	critical micelle concentration
Co^+	cobalticinium
COD	cyclooctadiene
COSY	correlation spectroscopy
Cp	cyclopentadiene
CV	cyclic voltammetry
CW	continuous wave
DCC	1,3-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone

DHP	3,4-dihydro-2*H*-pyran
DMA	*N*,*N*-dimethylacetamide
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
DOSY NMR	diffusion-ordered spectroscopy nuclear magnetic resonance
DOTA	1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane
DSC	differential scanning calorimetry
EDC	1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride
ENDOR	electron nuclear double resonance
EPR	electron paramagnetic resonance
EXSY	two-dimensional exchange spectroscopy
FAB MS	MS fast atom bombardment mass spectroscopy
Fc	ferrocenyl
Fmoc	9-fluorenylmethoxycarbonyl
FT-IR	Fourier transform infrared spectroscopy
G*n*	generation level or number
HATU	2-(1*H*-7-azabenzotriazole-1-yl)-1,1,3,3-tetramethyl uronium hexafluorophosphate methanaminium
HFBI	heptafluorobutyryl isobutyl
HIV	human immunodeficiency virus
HOBT	1-hydroxy-1*H*-benzotriazole
HYSCORE	hyperfine sublevel correlation
ITO	indium tin oxide
LAH	lithium aluminum hydride
MALDI TOF MS	matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy
MD	molecular dynamics
MDI	methylphenyldiisocyanate
MS	mass spectroscopy
NMO	*N*-methylmorpholine *N*-oxide
OEG	oligo(ethylene glycol)
PAAm	poly(allyl amine)
PAMAM	polyamidoamine
PDMS	polydimethylsiloxane
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PGA	penicillin G amidase
PMB	*p*-methoxybenzyl-
PMMA	poly(methyl methacrylate)
PMMI	poly(monomethyl)itaconate
POM	$[PO_4[WO(O_2)_2]_4]_3^-$
POSS	silsesquioxane (S_8O_{12})
PPI	polypropylenimine
PPTS	pyridinium toluenesulfonate
PPV	poly(*p*-phenylene vinylene)
PTSA	*p*-toluenesulfonic acid
PVA	poly(vinyl alcohol)
pyBOP	benzotriazol-1-yloxytripyrrolidinophosphonium hexaphosphate
SAXS	small-angle X-ray scattering
SDS	sodium dodecylsulfate
SEC	size-exclusion chromatography
SWNT	single-wall nanotube
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TOCSY	total correlation spectroscopy
tpy	terpyridine
tris	three in nomenclature
TRIS	tris(hydroxymethyl)aminomethane
TTF	tetrathiafulvalene
UV	ultraviolet
xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
Z	protecting group

18. Acknowledgments

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