

Synthesis and Characterization of a Series of Monodisperse, 1,3,5-Phenylene-Based Hydrocarbon Dendrimers Including C₂₇₆H₁₈₆ and Their Fluorinated Analogues

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Abstract: The convergent synthesis of a series of monodisperse aromatic dendrimers having molecular diameters of 15–31 Å is described. These materials consist of 4, 10, 22, or 46 benzene rings linked symmetrically by σ -bonds. Increasingly large dendrimer arms are prepared stepwise via palladium-catalyzed coupling of arylboronic acids to 3,5-dibromo-1-(trimethylsilyl)benzene. The aryltrimethylsilane is subsequently converted to a new arylboronic acid by reaction with boron tribromide followed by hydrolysis. Coupling of arylboronic acid dendrimer arms to 1,3,5-tribromobenzene or 1,3,5-tris(3,5-dibromophenyl)benzene is the final step in the synthesis. A series of dendrimers consisting of 4, 10 and 22 phenyl rings symmetrically arranged in which the outer phenyl rings are fluorinated is synthesized by a similar sequence of reactions. The largest hydrocarbon dendrimer is soluble to the extent of 190 g/L in toluene and is stable to 500 °C. Depending upon their thermal history, dendrimers having more than 10 phenyl rings can be crystalline or amorphous. Enthalpies and entropies of fusion and glass-transition temperatures where applicable have been measured. These materials are single molecules having high symmetry and thermal stability and utility as standards in size-exclusion chromatography.

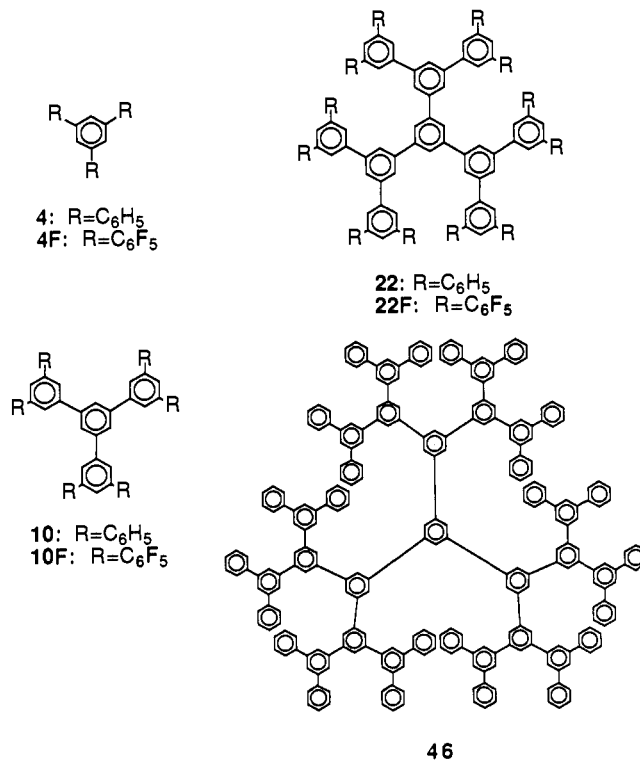
Introduction

Many useful properties of polymeric materials take advantage of their linear nature. The technological applications of thickening agents, lubricating fluids, and thermoplastics revolve around the propensity of these linear chains to coil in solution or in the melt.¹ High-strength liquid crystalline polymers,² conducting polymers,³ and polymers for nonlinear optical applications⁴ depend in turn upon a highly ordered parallel arrangement of linear chains for their bulk properties. Increasingly, there has been interest in the development of rational routes to polymers having architectures other than linear chains. Important examples include ladder, star, and comb polymers, all of which have some two-dimensional character.⁵ Recently, a family of polymers consisting of hyperbranched⁶ chains prepared by multiplicative growth from a central core has attracted much attention. These materials, named "starburst dendrimers" by Tomalia,⁷ are unique in that the arrangement of polymer chains gives rise to spherical structures. Furthermore, since the polymer chains branch geometrically with successive generations, the concept of densely packed systems arises, in which further growth is precluded by steric constraints imposed by the previous generation. This approach to polymer synthesis leads to the interesting new concept of a macroscopic particle comprising a single molecule.⁸ Several others have recently reported syntheses of hyperbranched polymers.^{9–13}

While the commercial applications of hyperbranched polymers have been confined to their use as molecular size standards,¹⁴ we believe that three-dimensional polymers will increasingly find technological applications. Indeed, materials of this type have been suggested as the building blocks of nanotechnology, in which three-dimensional structures may be constructed on a molecular level.¹⁵

Two distinct approaches to dendrimer synthesis have evolved from the pioneering work of Vogtle and Denkwalter.^{16,17} Tomalia⁷ and Newkome⁹ developed the divergent route in which the synthesis is begun at the center of the dendrimer. Thus, reaction of a core with two or more moles of a reagent containing at least two protected branching sites, followed by removal of the protecting groups and subsequent reaction of the liberated reactive sites, leads to the first-generation dendrimer. The process is repeated until a dendrimer of the desired size has been prepared. The disadvantage of this approach is that successive generations require that a geometrically increasing number of reactions be carried out on the growing dendrimer. Circumvention of this problem necessitates large excesses of reactants and forcing conditions and causes difficulty in purification.

Scheme I



We¹⁸ and others¹⁰ have developed the convergent route in which the synthesis begins at what will become the outer surface of the

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: London, 1981.

(2) *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L. L., Ed.; Elsevier: London, 1985.

(3) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vols. 1 and 2. Billingham, N. C.; Calvert, P. D. *Adv. Polym. Sci.* 1989, 90, 1.

(4) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987; Vols. 1 and 2. *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Eds.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.

(5) Webster, O. W. *Science* 1991, 251, 887. Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* 1990, 2, 649.

[†] Undergraduate Summer Research Program participant.

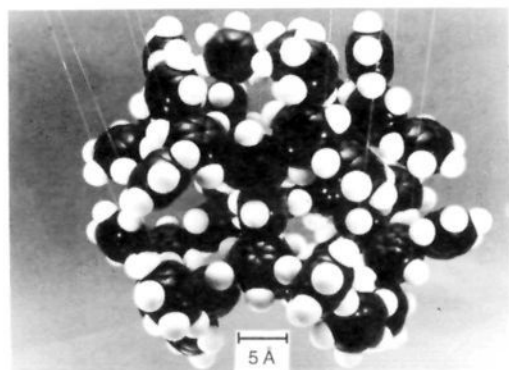


Figure 1. Space-filling molecular model of 46.

dendrimer. Progressively large dendrimer arms are prepared by the attachment of a small number (typically two) of smaller arms to a molecule having two functional groups, X and Y. Each arm has a single functional group, Z, which reacts with only one of the two functional groups, e.g., X. The unchanged functional group Y in the new larger arm must then be converted to the functional group Z, permitting further iterations. Finally, the completed dendrimer arms are coupled to a core containing a small number (typically three) of the functional group X. The advantages of the convergent approach have been discussed and include the ability to precisely control molecular weights as well as to make materials having functionalities in precise positions and numbers within these materials.^{10c}

Here we describe the preparation and characterization of a series of monodisperse dendrimers based upon 1,3,5-trisubstituted benzenes. They consist of 4, 10, 22, or 46 benzene rings symmetrically attached to one another (Scheme I). These materials are the first all-hydrocarbon dendrimers, with the largest ($C_{276}H_{186}$) being one of the highest molecular weight, pure, synthetic hydrocarbons known.¹⁹ We also report on a series of dendrimers consisting of 4, 10, and 22 aromatic rings, again linked symmetrically, in which the outer tier of phenyl rings is perfluorinated.

(6) The working definition of hyperbranched polymers has come to mean polymers in which every monomer except terminal monomers is a branch site. See, for example, refs 7, 9, and 10.

(7) For an extensive review of starburst dendrimers, see: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(8) For the synthesis of a monodisperse rigid rod of 50 Å in length, which is observable as a single species by transmission electron microscopy, see: Miller, L. L.; Kenny, P. W. *J. Chem. Soc., Chem. Commun.* **1988**, 84.

(9) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2004. Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.

(10) (a) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Hawker, C. J.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (c) Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **1990**, *23*, 4726.

(11) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077.

(12) Rengan, K.; Engel, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1084. For a related low molecular weight dendrimer system based upon polyarylamines using a protect/deprotect scheme with 2,4-dinitrofluorobenzene as the starting material, see: Hall, H. K.; Polis, D. W. *Polym. Bull.* **1987**, *17*, 409.

(13) Kim, Y. H.; Webster, O. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(14) Starburst dendrimers based upon poly(alkylamides) have recently become commercially available from Polysciences, Warrington, PA, under license from Midland Macromolecular Institute.

(15) For a discussion of nanotechnology (which has been defined as the preparation and manipulation of devices with dimensions and tolerances in the 0.5–100 nm range), see: Franks, A. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1442. See also: Drexler, K. E. *Engines of Creation*; Anchor Press: New York, 1986. Webb, T. H.; Wilcox, C. S. *J. Org. Chem.* **1990**, *55*, 363.

(16) Buhleier, E.; Wehner, W.; Vogtle, F. *Synthesis* **1978**, 155.

(17) Denkwalter, R. G.; Kolc, J.; Luskasavage, W. J. U.S. Patent 4,289,872, 1983. Aharoni, S. M.; Crosby, C. R., III; Walsh, E. K. *Macromolecules* **1982**, *15*, 1093.

(18) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346.

(19) For the synthesis of some very interesting linear *n*-alkanes prepared by Wittig chemistry including C_{246} and C_{390} , see: Bidd, I.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 543. For the synthesis of linear alkanes prepared by oxidative oligomerization of 1,2,3-tetracosadiyne, see: Lee, K. S.; Wagner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 203.

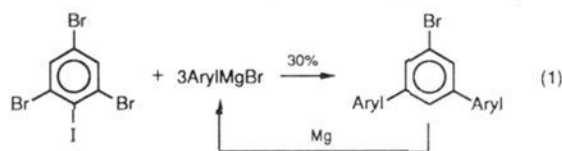
These materials are of interest because they may be more hydrophobic and volatile than their hydrocarbon analogues. We used an entirely convergent route, as described previously, to prepare the smaller dendrimers¹⁸ and a convergent/divergent approach using an expanded core to prepare the largest two.

Several features distinguish our dendrimers from those previously prepared. Ours have among the highest (ideally D_{3h}) symmetry of any and contain no flexible methylene linkages.²⁰ There is therefore less ambiguity about the spatial distribution of portions of the dendrimer chains, and our molecules should adopt approximately spherical shapes at earlier generations (Figure 1). We have measured diameters of our dendrimers from space-filling molecular models and by calculation of the length of maximum extension of a dendrimer arm. These diameters are 15, 20, 25, and 31 Å and 15, 20, 28, and 35 Å for **4**, **10**, **22**, and **46**, respectively. Diameters (space-filling molecular models) for the fluorinated dendrimers are 16, 22, and 28 Å for **4F**, **10F**, and **22F**, respectively. Finally, our dendrimers are extremely thermally stable and resistant to aggregation. Because of the cumbersome systematic nomenclature for these materials, we have adopted a simple notation for these compounds. The number of phenyl rings in a molecule is indicated by the compound number. A following "F" indicates that the exterior phenyl rings are fluorinated, and for instance "-TMS" indicates the other functionality present in the molecule. For instance, 3,5-bis(pentafluorophenyl)phenylboronic acid is named **3F-B(OH)₂**.

Results and Discussion

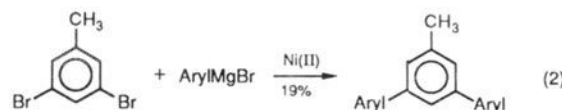
Early Synthetic Approaches. Since compound **4** (Scheme I) is commercially available, the first synthetic target was **10**, and we envisioned that the last step in the synthesis would be reaction of three substituted *m*-terphenyls with a trifunctional benzene. The immediate objective was, therefore, finding a synthetic route to a symmetrical *m*-terphenyl having a functional group that would permit coupling to, or formation of, a central benzene ring. Since iterative approaches demand that high yields be obtained in each step, we evaluated several existing methodologies for the formation of aryl-aryl bonds.

The first route (eq 1) involves the reaction of 3 mol of an aryl Grignard reagent with 1 mol of 2,4,6-tribromiodobenzene. This reaction, developed by Hart²¹ and co-workers, yields 3,5-diphenylbromobenzene where aryl is phenyl. We planned to replace



the bromine with acetylene and cyclotrimerize the resulting arylacetylene to yield **10** and substitutional isomers. Larger arms should be accessible by reaction of 3,5-diphenylbromobenzene with Mg, yielding a new aryl Grignard reagent. In our hands, the yield of 3,5-diphenylbromobenzene was typically 30%, making this reaction unacceptable for large-scale preparation.

We explored the reaction of phenylmagnesium bromide with 3,5-dibromotoluene using Kumada's procedure (eq 2).²² This reaction also gave an unacceptably low yield and produced a large number of side products resulting from transmetalation and reduction of the carbon-halogen bond.



The third strategy for linking benzene rings depended upon the Suzuki coupling²³ of arylboronic acids with aryl halides catalyzed

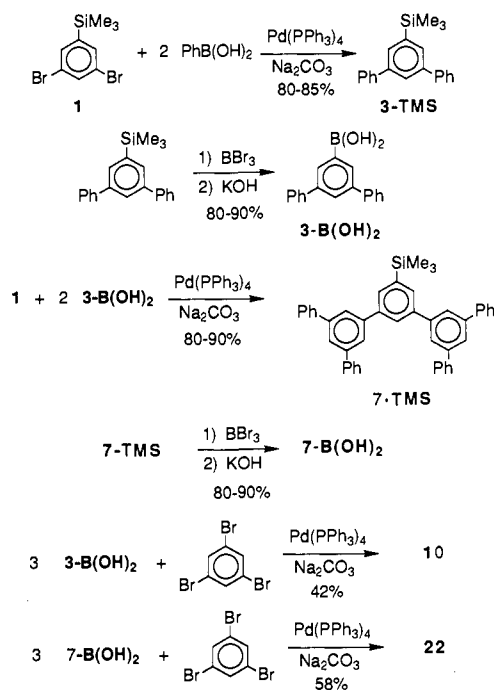
(20) A polyether dendrimer system described by Hall and Tomalia ideally has T_d symmetry but contains aliphatic linkages. Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.* **1987**, *52*, 5305–5312.

(21) Du, C.-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162.

Ghosh, T.; Hart, H. *J. Org. Chem.* **1988**, *53*, 3555.

(22) Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1978**, *58*, 127.

Scheme II



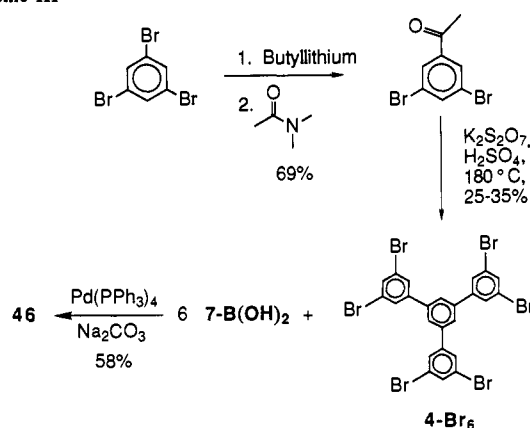
by Pd(PPh₃)₄, which had been successfully used by Kim and Webster.¹³ It is known that an aryltrimethylsilane can be transformed in one step into an arylboronic acid by treatment with BBr₃²⁴ followed by hydrolysis. By combining these two high-yield reactions, we devised a scheme that allowed us to prepare increasingly large dendrimer arms in a controlled iterative way, a critical step in preparing monodisperse dendrimers.

Syntheses of 10 and 22. The key intermediate in the synthesis of our dendrimers was 3,5-dibromo-1-(trimethylsilyl)benzene²⁵ (1), which was prepared in 79–85% yield by treatment of 1,3,5-tribromobenzene with butyllithium at –78 °C and reaction of the resulting aryllithium with Me₃SiCl. Typically, we prepared 1 in 25-g quantities. Reaction of 2 mol of phenylboronic acid with 1 under Suzuki coupling conditions yielded 3,5-diphenyl-1-(trimethylsilyl)benzene (3-TMS) in 80–85% yield (Scheme II). We tried without success to improve the yield by increasing the amount of palladium catalyst or the amount of excess phenylboronic acid. Treatment of 3-TMS with BBr₃ in CH₂Cl₂ yielded the aryl-dibromoborane which was not isolated but hydrolyzed with aqueous base yielding (3,5-diphenylphenyl)boronic acid, (3-B(OH)₂), which was used in successive steps without purification.²⁶ The next dendrimer arm, 7-B(OH)₂, was prepared by a second round of coupling and treatment with BBr₃ (Scheme II). The yields of both reactions in the second round were similar to those observed in the first.

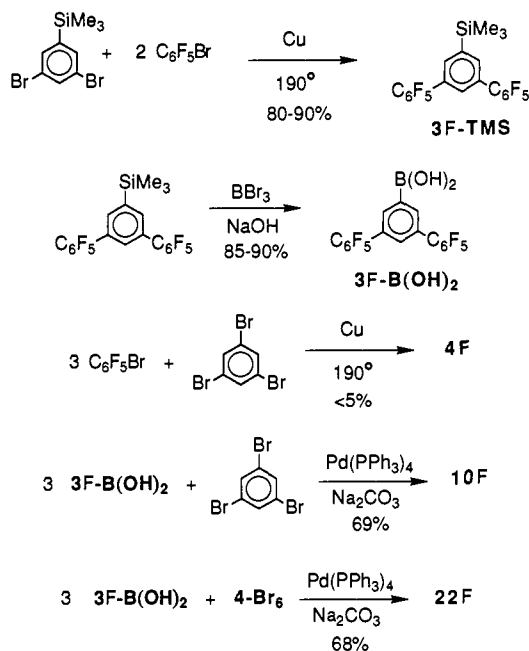
The final step in the syntheses of 10 and 22 required coupling 3 mol of 3-B(OH)₂ or 7-B(OH)₂ with 1 mol of 1,3,5-tribromobenzene (Scheme II). The course of all of the coupling reactions was monitored by TLC or HPLC using size-exclusion columns. The disappearance of 1,3,5-tribromobenzene was rapid, but complete substitution of the final bromine often did not proceed to completion. The yields in this step were moderate, primarily due to difficulties in purification which required careful column chromatography followed by recrystallization.

Synthesis of 46. The preparation of 15-TMS proceeded without difficulty as expected on the basis of our ability to prepare 22. However, we were unable to convert the TMS group to a useful

Scheme III



Scheme IV



functionality. Reaction of 15-TMS with BBr₃ occurred only at ca. 90 °C and primarily yielded the hydrocarbon derived by protonolysis of the TMS group. Reaction of 15-TMS with Br₂ occurred readily at 50 °C, but also appeared to yield only the protonolysis product. 15-TMS did not react with ICl at all,²⁷ even at 80 °C.

We devised an alternate route to 46 which circumvented 15-B(OH)₂ (Scheme III). This strategy was based upon coupling 6 mol of 7-B(OH)₂ with a core having 4-phenyl rings and 6 bromines. We regard this as a convergent/divergent approach. We prepared the known 1,3,5-tris(3,5-dibromophenyl)benzene, 4-Br₆, by a variation of the literature procedure.²⁸ Reaction of (3,5-dibromophenyl)lithium with *N,N*-dimethylacetamide yielded 3,5-dibromoacetophenone,²⁹ which was condensed with K₂S₂O₇/H₂SO₄ at 180 °C. Having 4-Br₆ in hand, we explored its coupling chemistry.

Analysis by TLC of a Suzuki coupling reaction of 4-Br₆ with 8 mol of 7-B(OH)₂ indicated that the replacement of three bromines was rapid and that successive replacement of the rest was slow. This result is not surprising since, in such large molecules, the rate of bond formation is greatly reduced by nonproductive

(23) Miyaura, N.; Yanagai, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.(24) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1.(25) Benkeser, R. A.; Hickner, R. A.; Hoke, D. I.; Thomas, O. H. *J. Am. Chem. Soc.* **1958**, *80*, 5289.

(26) The boronic acids were contaminated with small amounts of the corresponding polyaryls formed by protonolysis of the trimethylsilyl group. These contaminants were removed in subsequent chromatography steps.

(27) There is good precedence in the literature for the replacement of trimethylsilyl by iodine in the reaction with iodine chloride. See: Felix, G. F.; Dunogues, Piscioti, F.; Calas, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 488.(28) Sharnin, G. P.; Molsak, E. E.; Gryazin, E. E. *J. Appl. Chem. USSR* **1970**, *43*, 1659.(29) Brüning, W. *J. Recl. Trav. Chim. Pays-Bas* **1922**, *41*, 655.

collisions. Indeed, this rate reduction may be a fundamental limitation to the convergent synthesis of large molecules. We obtained **46** in 58% yield and 26% overall yield based on **1** and **4-Br₆** after purification by column chromatography and recrystallization.

Synthesis of 4F, 10F, and 22F (Scheme IV). We attempted the preparation of (pentafluorophenyl)boronic acid by lithiation of bromopentafluorobenzene and reaction of the resulting aryllithium with triethyl borate but were unable to obtain the desired (pentafluorophenyl)boronic acid. We prepared **4F** in low yield by Ullmann coupling of pentafluorobromobenzene and 1,3,5-tribromobenzene.³⁰ In contrast, Ullmann coupling of pentafluorobromobenzene and **1** yielded 3,5-bis(pentafluorophenyl)-1-(trimethylsilyl)benzene, **3F-TMS**, in high yield. Reaction of **3F-TMS** with BBr_3 at 180 °C in CCl_4 followed by hydrolysis with aqueous base yielded [3,5-bis(pentafluorophenyl)phenyl]boronic acid, **3F-B(OH)₂**, in 90% yield. Suzuki coupling of **3F-B(OH)₂** with 1,3,5-tribromobenzene or with **1** yielded **10F** and the arylsilane, **7F-TMS**, respectively. Reaction of **7F-TMS** with BBr_3 proceeded normally except that the arylboronic acid decomposed upon attempted isolation. We do not understand whether the instability is thermal or caused by O_2 or H_2O . We, therefore, synthesized **22F** in 68% and 49% overall yield based on **1** and **4-Br₆** by reaction of 6 mol of **3F-B(OH)₂** with **4-Br₆**.

Physical and Chemical Characterization of the Dendrimers. All of the dendrimers except **10F** are moderately to highly soluble in typical organic solvents such as THF, toluene, CH_2Cl_2 , or CHCl_3 . Compound **10F** is only soluble to the extent of 0.05 g/L in toluene at room temperature. Its insolubility is puzzling; however, we speculate that it can adopt a pancake-like conformation in which all of the benzene rings are approximately in a plane, which should crystallize well. The dendrimers **4**, **10**, **22**, **46**, **4F**, and **22F** are soluble to the extent of 70, 2.5, 120, 190, 26, and 0.56 g/L, respectively, in toluene at room temperature. Curiously, the 10 phenyl ring dendrimers in each series are the least soluble. Thus, the solubility of these materials does not diminish with increasing molecular weight as with most linear polymers. We attribute the increased solubility of **22** and **22F** over **10** and **10F** to the fact that **22** and **22F** cannot be planar since the outer benzene rings on different arms would occupy the same space. The solubility of our dendrimers is in sharp contrast to the solubility of linear oligomers of benzene. The solubilities of *p*-terphenyl, *p*-tetraphenyl, and *p*-quinquaphenyl are 7.4, 0.12, and <0.005 g/L, respectively, in toluene at room temperature.³¹

We characterized the dendrimers by ^1H and ^{13}C NMR spectroscopy, size-exclusion chromatography, mass spectrometry, and elemental analysis. Due to the low solubility of **10F**, we characterized it by mass spectrometry and elemental analysis alone. Because of the high (ideally D_{3h}) symmetry of these molecules, ^1H NMR spectroscopy (Figure 2) is particularly useful in their characterization. At 360 MHz the proton resonances in **4**, **10**, and **22** are distinguishable and assignable. In **46** the resonances for protons on the first three tiers of benzene rings are distinguishable from tier to tier, but the two different types of protons on a given benzene within a tier are indistinguishable even at 500 MHz. There are several other interesting observations to be made from the ^1H NMR spectra of **4**, **10**, **22**, and **46**. Protons nearer the interior of the dendrimers resonate downfield of protons farther from the interior. There are significant upfield shifts in the resonances of the terphenyl units from **10** to **22** to **46**. We believe that this shift is caused by the proximity of terphenyl units attached to different arms. The ^1H NMR spectra of **4F** and **22F** show a single peak and 5 peaks, respectively. ^{13}C NMR spectroscopy, despite its much larger chemical shift dispersion, resolves fewer resonances. Two of the resonances for carbons in **22** are unresolvable at 90.5 MHz.

FAB mass spectra of our dendrimers confirmed their molecular weights. Elemental analyses are correct for all except **10F**, which

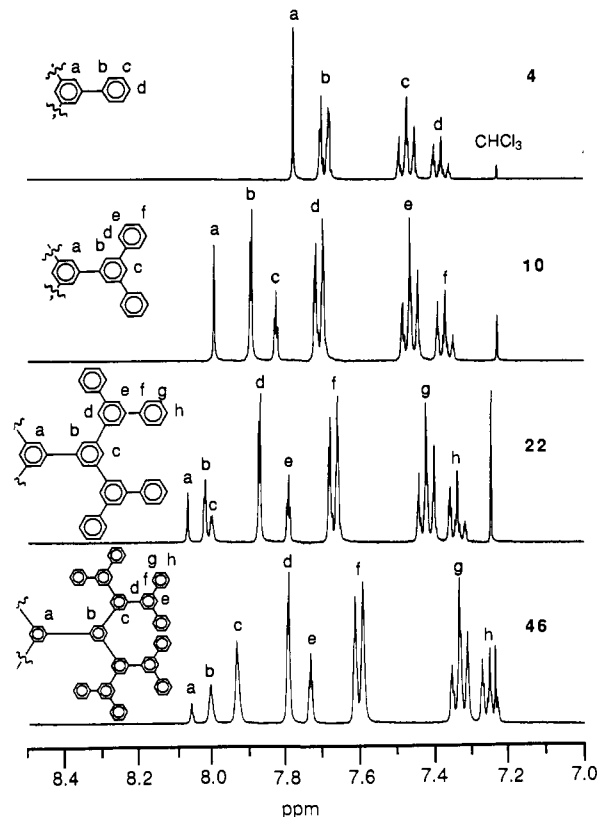


Figure 2. ^1H NMR spectra of hydrocarbon dendrimers at 360 MHz in CDCl_3 .

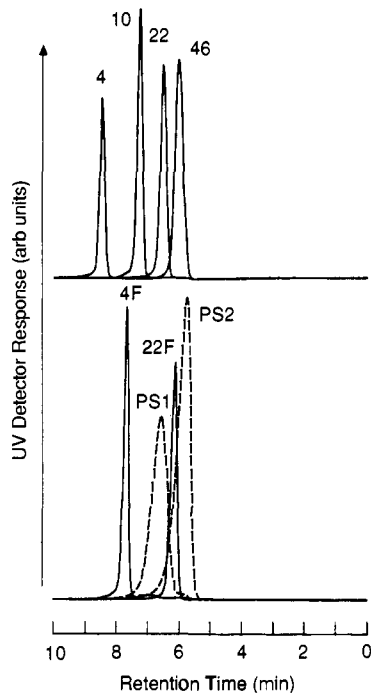


Figure 3. A composite of gel permeation chromatograms of dendrimers using a μ -Spherogel 100-Å column with CH_2Cl_2 as the eluant. PS1 and PS2 are polystyrene molecular weight standards having MW = 1350 and 3650 and $M_w/M_n = 1.08$ and 1.07, respectively.

we have been unable to completely purify because of its insolubility. Elemental analysis is unfortunately not useful in distinguishing dendrimers of different generations because of the minute differences in elemental composition, e.g., **4** ($\text{C}_{24}\text{H}_{18}$), C = 94.08% vs **46** ($\text{C}_{276}\text{H}_{186}$), C = 94.70%.

Size-exclusion chromatograms of our dendrimers support the assertion that they are single compounds (Figure 3). The

(30) Fanta, P. E. *Synthesis* 1974, 9.

(31) Rothe, M.; Rothe, I. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p IV/92.

Table I. Thermal Properties of Dendrimers

compd	$T_{95\%}^a$ (°C)	T_g^b (°C)	ΔC_p^c (J °C ⁻¹ g ⁻¹)	T_m^d (°C)	T_p^e (°C)	ΔT (°C)	ΔH_f^f (J g ⁻¹)	ΔH_f (kcal mol ⁻¹)	ΔS_f^g (cal mol ⁻¹ K ⁻¹)
C ₆ H ₆				5.0	7.3	2.3	126.7	2.36	8.49
4	219			174.0	175.7	1.7	105.5	7.73	17.3
10	442	126	0.28	271.2	274	2.8	88.6	16.2	29.7
22	554	190	0.22	338.9	341.6	2.7	44.3	17.7	29.0
46	574	220	0.11	511.5	513.7	2.2	2.6 ^h		
C ₆ F ₆				5.2	7.1	1.9	62.5	2.78	9.98
4F	210			231.4	233.9	2.5	80.7	11.1	22.0
10F	371			410.3	418.6	8.1	90.6	28.2	41.3
22F	505	183	0.183	354.3	355.9	1.6	82.4	54.3	86.5

^a $T_{95\%}$ is the temperature to which the material retains 95% of its mass when heated at 8 °C/min under nitrogen. ^b The glass-transition temperature is the midpoint of the glass transition at a heating rate of 15 °C/min. ^c ΔC_p is the change in specific heat accompanying the transition from a glassy to a liquid state. ^d The melting point is defined to be the onset of melting at 15 °C/min. ^e The end of the melting process at 15 °C/min. ^f ΔH_f is the heat of fusion. ^g ΔS_f is the entropy of fusion. ^h This is the observed heat of fusion for a partially crystalline sample.

chromatograms show single sharp peaks whose retention times decrease with increasing molecular weight. The SECs of the (trimethylsilyl)aryls are also single sharp peaks. The monodispersity of these dendrimers compares quite favorably with those of polystyrene molecular weight standards. Since upper limits to the radii of the dendrimers are easily established from simple geometric considerations, they may be useful as size standards in SEC.

Thermal Gravimetric Analysis. Thermal gravimetric data for 4 and 4F indicate that they volatilize intact (Table I) since we observed the molecular ion in a TGA/MS analysis of 4. Dendrimers 22, 22F, and 46 begin to decompose above 500 °C, and 10 and 10F probably volatilize with some decomposition. Fluorination increased the volatility but slightly lowered the thermal stability. As expected for polymers composed entirely of benzene rings, the dendrimers are exceedingly thermally stable. TGA/MS analysis of 46 showed that the major volatile products evolved at 600 °C were benzene, biphenyl, and terphenyl and that approximately 50% by weight of the sample is recovered as a carbonized residue. This result is in agreement with the result of a preparative-scale (102.0 mg) thermolysis of 46 under helium at 950 °C. The resulting black, shiny residue weighed 42.3 mg and was analyzed as C_{13.7}H_{1.00}.

Differential Scanning Calorimetry. We studied the thermal behavior of these materials because of their unique structures and because they are at the interface between small molecules and high polymers. In general, melting temperatures (T_m) and glass-transition temperatures (T_g) increased with molecular weight for all but 10F, which melts 56 °C higher than 22F (Table I). The width of the melting peaks for all of the dendrimers except 10F is quite narrow (1.7–2.7 °C) and is further evidence of the high purity of these materials.

Compounds 4, 4F, and 10F showed simple melting and recrystallization behavior characterized by single melting and crystallization transitions. The larger members of each series showed highly complex thermal phenomena. Prototypical is the behavior observed for 10 (Figure 4). The compound as prepared is highly crystalline with a small exotherm ($\Delta Q = 4.0$ J/g, ca. 4% of the heat of fusion) between 165 and 203 °C, which is indicative of a small amount of crystallization on the first heating. On further heating, the compound melts sharply at 271 °C, but crystallization of the sample from the melt was not observed at a cooling rate of 15 °C/min. Instead, vitrification occurred with a discontinuity in the specific heat near 130 °C, which we attribute to a glass transition. This glass transition was observed again on a second heating, followed by two recrystallization exotherms with maxima at 187 and 226 °C. Subsequently, the sample melted sharply at 271 °C as in the first heating. The area under the two crystallization exotherms together equaled the area under the melting endotherm, which indicates that after cooling at 15 °C/min the sample is completely amorphous. The structures of the two crystalline forms of 10 are presently unknown. Cooling of the sample from the melt at 0.2 °C/min caused crystallization to occur in two steps beginning at 201 °C.

The thermal behaviors of 22 and 46 are similar to that of 10. Neither compound was completely crystalline as prepared, and

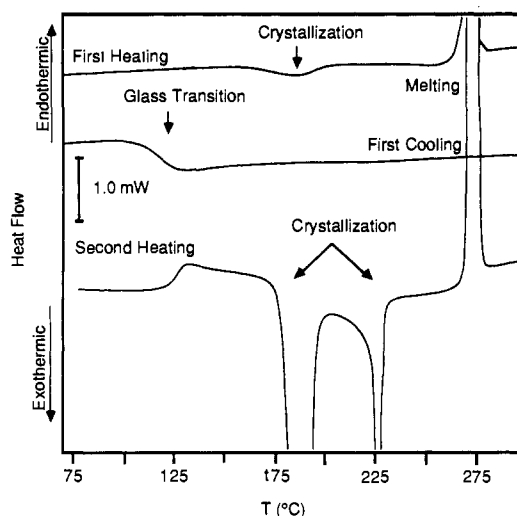


Figure 4. Differential scanning calorimetric traces for successive heating and cooling of 10. The heating rate is 15 °C/min, and the cooling rate is 40 °C/min.

46 could not be completely crystallized by thermal treatment. DSC analysis of 22 showed that on the first heating crystallization occurred near 200 °C. Cooling of the sample even at 0.1 °C/min from the melt gave no sign of crystallization. Annealing the sample at 310 °C resulted in a completely crystalline sample, as evidenced by the absence of a glass transition or crystallization exotherm on cooling or heating after annealing. In the first DSC scan of 46, we observed a glass transition at 220 °C with a ΔC_p of 0.11 J °C⁻¹ g⁻¹ and no sign of crystallization up to 460 °C. When this sample was held at 205 °C for 15.5 h, cooled to 100 °C, and reheated to above T_g , a large endotherm was observed astride the discontinuous change in C_p at T_g . This physical aging phenomenon is consistent with the known behavior of glasses.³² Annealing 46 at 330 °C for 20 h increased the size of the melting endotherm at 512 °C by about 25%, but the DSC still showed a significant ($\Delta C_p > 0.10$ J g⁻¹) glass transition.

The fluorinated dendrimers melt from 15 to 140 °C higher, and the molar heats of fusion are 1.4 to 3 times larger than those of their hydrocarbon analogues. Curiously, the T_g value for 22F is lower than the T_g for 22. The thermal behavior of 22F is very similar to that of 10. When cooled at 15 °C/min, it vitrifies below 180 °C and crystallizes in two steps on subsequent heating. It always melted sharply at 355 °C.

The enthalpies and entropies of fusion summarized in Table I deserve comment. In general, the molar enthalpies (ΔH_f) and entropies (ΔS_f) of fusion increase with increasing molecular weight. A similar trend occurs in ΔH_f and ΔS_f for linear alkanes.³³ The ΔS_f values for the dendrimers are quite large and thus indicate

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a great increase in disorder accompanying melting. The ΔS_f for **22F** is among the highest ΔS_f values that we are aware of. The ΔS_f 's for the fluorinated molecules increase linearly with molecular weight, but those for the hydrocarbons do not. At the simplest level, we expected that ΔS_f should increase linearly with the number of freely rotating σ -bonds in the molecules. The ΔS_f 's for the four fluorinated molecules fit this model well, with a value of 3.4 cal mol⁻¹ K⁻¹ per σ -bond. Despite the structural simplicity and similarity of the two series of compounds, their thermodynamic data are not readily explained. The low solubility of **10F**, the inversion of melting points of **10F** and **22F**, and the high value for the heat of fusion per gram of **10F** point to an anomaly in the structure of either **10F** or **22F**.

The thermal behavior of the dendrimers can be summarized as follows:

1. Dendrimers up to 22 phenyl rings can be obtained in completely crystalline form.
2. Dendrimers **4**, **4F**, and **10F** cannot be vitrified, while **10** vitrifies on rapid cooling and crystallizes on slow cooling.
3. Dendrimer **46** is mainly amorphous.

Conclusions

We have used a convergent synthetic strategy beginning at what will become the outside surface of the structures to prepare gram quantities of poly(1,3,5-phenylenes) using two high-yield reactions: coupling of arylboronic acids to aryl bromides and conversion of aryltrimethylsilanes to arylboronic acids. These materials possess simple symmetrical molecular structures and are monodisperse, soluble, and very thermally stable. They may be useful as size standards in gel permeation chromatography and as models for high polymers.

Experimental Section

General. All reactions were performed under an atmosphere of dry argon. All reagents and solvents, unless otherwise specified, were obtained from Aldrich Chemical Co. and were used without further purification. Melting points were obtained on a Mel-Temp melting point apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 360 spectrometer at 360.1 and 90.5 MHz, respectively, and were referenced to tetramethylsilane. Analytical TLCs were run on commercial Merck plates coated with silica gel GF254 (0.25-mm thick). Analytical GPC analyses were obtained using a Beckman solvent delivery system, a 100-Å μ -Spherogel column, and an adjustable wavelength UV/vis detector usually operated at 254 nm, using CH₂Cl₂ (Aldrich, HPLC grade) as the eluant. Solubilities were measured by weighing 10–50 mg of a compound and adding toluene slowly while vigorously magnetically stirring until complete dissolution occurred.

Compounds **10F** and **22F** were stirred with toluene for ca. 1 h. The resulting suspension was filtered, and the quantity of compound in solution was determined by concentrating the solution in vacuo and weighing.

Thermal gravimetric analysis was carried out under nitrogen in a Perkin-Elmer TGA-7 using a heating rate of 8 °C/min. The calorimetric data were obtained on a Perkin-Elmer DSC-7 at a scanning rate of 15 °C/min under a flow (20 cc/min) of nitrogen. The temperature scale was calibrated using the melting points of indium and zinc and is accurate to ± 0.1 °C. Samples typically weighed 3.5–4 mg, and aluminum containers were used if scans did not exceed 490 °C. If scans exceeded 490 °C, gold containers were used. If the T_m value for a material appeared to exceed its vaporization temperature, it was hermetically sealed in a metal container prior to measurement. The bulk-scale thermolysis of **46** was carried out in a ceramic boat inside a quartz tube in a Kiethley tube furnace.

3,5-Diphenyl-1-(trimethylsilyl)benzene (3-TMS). **Procedure A.** A 200-mL Schlenk flask equipped with a magnetic stirring bar, condenser, and an Ar inlet was charged with 3,5-dibromo-1-(trimethylsilyl)benzene (**1**) (6.16 g, 20.0 mmol), brought into an Ar-filled drybox, and charged with Pd(PPh₃)₄ (1.39 g, 1.20 mmol). The glassware was assembled and removed from the drybox. Solutions of phenylboronic acid (5.36 g, 44.0 mmol) in EtOH (25 mL) and Na₂CO₃ (2 M, 25 mL) in H₂O were prepared and deoxygenated with a stream of Ar. These solutions and 40 mL of deoxygenated toluene were added to the reaction vessel, and the mixture was refluxed under Ar for 6 h. The reaction mixture was poured into a mixture of 100 mL of H₂O and 100 mL of ether, and the two phases were separated. The aqueous phase was washed with ether, and the organic phases were combined and washed with 1 M NaOH followed by brine. The ethereal solution was dried over MgSO₄ and concentrated by rotary evaporation. The crude product was passed through 100 g of

silica gel using *n*-hexane as the eluant, and the resulting material was recrystallized from EtOH (5.18 g, 86%): mp 80–83 °C; ¹H NMR (CDCl₃) δ 7.77 (t, *J* = 1.6 Hz, 1 H), 7.70 (d, *J* = 1.6 Hz, 2 H), 7.63–7.67 (m, 4 H), 7.44–7.50 (m, 4 H), 7.34–7.41 (m, 2 H), 0.35 (s, 9 H); ¹³C NMR (CDCl₃) δ 141.6, 141.5, 141.1, 131.2, 128.8, 127.4, 127.3, 126.9, –1.0. Anal. Calcd for C₂₁H₂₂Si: C, 83.38; H, 7.33; Si, 9.29. Found: C, 82.99; H, 7.35; Si, 9.10.

(3,5-Diphenylphenyl)boronic Acid (3-B(OH)₂). **Procedure B.** A 200-mL, two-necked, round-bottomed flask was fitted with a reflux condenser, Ar inlet, and rubber septum. To this flask was added **3-TMS** (10.0 g, 33.1 mmol) and reagent grade methylene chloride (40 mL). The flask was immersed in a dry ice/acetone bath, and a solution of BBr₃ (50 mL of a 1 M solution in methylene chloride, 1.5 equiv) was added dropwise with a polypropylene disposable syringe through the rubber septum. A faint yellow color was observed in the reaction mixture. The solution was stirred at –78 °C for 1 h, allowed to warm to room temperature over a period of approximately 3 h, and finally heated to 40 °C for 18 h. The solution was cooled to –78 °C, and a solution of KOH in water (40 mL of a ca. 5 M solution, excess) was added through the top of the condenser. The solution was allowed to warm to room temperature, and the two-phase solution was filtered to remove the potassium salt of (3,5-diphenylphenyl)boronic acid. The wet salt was suspended in a mixture of diethyl ether and 2 M HCl (150 mL of each) and stirred vigorously for 2 h. After this period, two clear layers had formed. The aqueous layer was discarded, and the organic layer was washed with 100 mL of 2 M HCl, followed by distilled water (2 volumes of 150 mL each), and finally washed with brine (100 mL). The ethereal solution was dried over MgSO₄, and the solvent was removed to yield a white solid (7.25 g, 81% yield): ¹H NMR (THF-*d*₆) δ 8.06 (d, *J* = 2 Hz, 2 H), 7.88 (m, 1 H), 7.69 (m, 4 H), 7.43 (m, 4 H), 7.35–7.27 (m, 4 H); ¹³C NMR (THF-*d*₆) δ 142.6, 141.6, 132.7, 129.4, 128.1, 127.9, 127.8. Anal. Calcd for C₁₈H₁₅BO₂: C, 78.87; H, 5.52; B, 3.94. Found: C, 84.36; H, 5.28; B, 2.95.

10. This compound was synthesized using procedure A with 5.19 g (18.95 mmol) of **3-B(OH)₂** in 25 mL of EtOH/THF, 1.82 g (5.74 mmol) of 1,3,5-tribromobenzene in 25 mL of toluene, 0.60 g (0.52 mmol) of Pd(PPh₃)₄, and 9 mL of 2 M Na₂CO₃. **3-B(OH)₂** is difficult to dissolve in THF or EtOH alone but dissolves readily in a mixture of the two. The solution was prepared by dissolving it in ca. 200 mL of warm 20% EtOH in THF and concentrating the resulting solution to 25 mL. The reaction mixture was refluxed for 1 day, allowed to cool, and poured into a flask containing H₂O and CH₂Cl₂. The aqueous and organic phases were separated, and the aqueous phase was washed with CH₂Cl₂. The CH₂Cl₂ solutions were combined, washed with brine, dried over MgSO₄, and concentrated to a yellow solid weighing 6.04 g. The solid was chromatographed on silica gel (250 g) using CCl₄ as the eluant. The crude product was applied to the column as a solution in the minimum quantity of warm CHCl₃. The major impurity is *m*-terphenyl, which has a slightly higher *R_f* than the product. Fractions containing product and *m*-terphenyl were chromatographed three more times for a total yield of 2.63 g. This material was recrystallized from hot CCl₄ (80 mL). The final yield after drying in vacuo (105 °C and 20 μ mHg) was 1.84 g (42%): mp 272–274 °C; ¹H NMR (CDCl₃) δ 8.01 (s, 3 H), 7.91 (d, *J* = 1.4 Hz, 6 H), 7.85 (t, *J* = 1.4 Hz, 3 H), 7.71–7.74 (m, 12 H), 7.46–7.51 (m, 12 H), 7.36–7.42 (m, 6 H); ¹³C NMR (CDCl₃) δ 142.65, 142.57, 142.19, 128.87, 127.61, 127.42, 125.85, 125.85, 125.61, 125.40. Anal. Calcd for C₆₀H₄₂: C, 94.45; H, 5.55. Found: C, 94.24; H, 5.28.

7-TMS. This compound was synthesized using procedure A with 6.69 g (24.4 mmol) of **3-B(OH)₂** in 30 mL of EtOH/THF, 3.42 g (11.1 mmol) of **1** in 30 mL of toluene, 0.540 g (0.467 mmol) of Pd(PPh₃)₄, and 15 mL of 2 M Na₂CO₃. The reaction mixture was refluxed for 2 days and worked up by dilution with CH₂Cl₂ and H₂O. The phases were separated, and the aqueous phase was washed with CH₂Cl₂. The combined organic solutions were washed with brine, dried over MgSO₄, and concentrated. The resulting viscous oil was flushed through ca. 10 g of silica gel using 4:1 CCl₄/CH₂Cl₂. The yellow solid was recrystallized from EtOAc/EtOH, yielding 5.46 g (81%) of a white solid: mp 203–207 °C; ¹H NMR (CDCl₃) δ 7.95 (t, *J* = 2 Hz, 1 H), 7.81–7.84 (m, 8 H), 7.69–7.73 (m, 8 H), 7.46–7.52 (m, 8 H), 7.37–7.42 (m, 4 H), 0.38 (s, 9 H); ¹³C NMR (CDCl₃) δ 142.71, 142.47, 142.08, 141.28, 141.13, 131.61, 128.88, 127.58, 127.42, 127.31, 125.47, 125.41, –0.94. Anal. Calcd for C₄₅H₃₈Si: C, 89.06; H, 6.31, Si, 4.63. Found: C, 88.97; H, 6.48; Si, 4.58.

7-B(OH)₂. This compound was synthesized from **7-TMS** using procedure B. The workup procedure was similar except that the potassium salt was dissolved in a 2:1 (v/v) mixture of THF and diethyl ether before being treated with dilute HCl. Thus, 5.4 g (8.9 mmol) of **7-TMS** yielded 4.15 g (82%) of **7-B(OH)₂**, which was a white microcrystalline solid: ¹H NMR (THF-*d*₆) δ 8.24 (d, *J* = 2 Hz, 2 H), 8.19 (t, *J* = 2 Hz, 1 H), 7.97 (d, *J* = 2 Hz, 4 H), 7.87 (t, *J* = 2 Hz, 2 H), 7.79–7.76 (m, 8 H),

7.41–7.48 (m, 10 H), 7.36–7.32 (m, 4 H); ^{13}C NMR (THF- d_6) δ 143.8, 143.3, 142.9, 142.2, 141.9, 133.3, 129.6, 128.1, 125.9. Anal. Calcd for $\text{C}_{42}\text{H}_{31}\text{BO}_2$: C, 87.20; H, 5.40. Found: C, 84.41; H, 5.36.

22. This compound was synthesized using procedure A with 3.33 g (5.76 mmol) of 7-B(OH) $_2$ in 40 mL of THF, 0.50 g (1.44 mmol) of 1,3,5-tribromobenzene in 40 mL of toluene, 0.17 g (0.143 mmol) of Pd(PPh $_3$) $_4$, and 3 mL of 2 M Na $_2$ CO $_3$. The reaction mixture was refluxed for 2 days and worked up by dilution with CH $_2$ Cl $_2$ and H $_2$ O. The organic and aqueous phases were separated, and the aqueous phase was washed with CH $_2$ Cl $_2$. The organic solutions were combined, washed with brine, dried over MgSO $_4$, and concentrated. The resulting solid was chromatographed on 250 g of silica gel with CCl $_4$ as the eluant. The eluant was gradually changed to 10% CH $_2$ Cl $_2$ in CCl $_4$. Impure fractions were combined and chromatographed, again yielding a total of 2.01 g. The resulting solid was recrystallized from CCl $_4$ /EtOH, yielding 1.56 g (58%) of a colorless crystalline solid: mp 342–347 °C; ^1H NMR (CDCl $_3$) δ 8.07 (s, 3 H), 8.02–8.04 (m, 6 H), 7.99–8.02 (m, 3 H), 7.88 (d, J = 1.4 Hz, 12 H), 7.80 (t, J = 1.4 Hz, 6 H), 7.65–7.70 (m, 24 H), 7.40–7.45 (m, 24 H), 7.32–7.38 (m, 12 H); ^{13}C NMR (CDCl $_3$) δ 142.79, 142.74, 142.54, 142.07, 140.99, 128.83, 127.56, 127.38, 126.27, 126.00, 125.91, 125.58, 125.38. Anal. Calcd for C $_{132}$ H $_{90}$: C, 94.59; H, 5.41. Found: C, 94.29; H, 5.23.

15-TMS. This was synthesized using procedure A with 9.50 g (16.4 mmol) of 7-B(OH) $_2$ in 50 mL of THF, 2.30 g (7.46 mmol) of 1, 0.525 g (0.226 mmol) of Pd(PPh $_3$) $_4$, and 5 mL of 2 M Na $_2$ CO $_3$. The reaction mixture was refluxed for 3 days and worked up by dilution with toluene and H $_2$ O. The aqueous and organic phases were separated, and the aqueous phase was washed with toluene. The toluene solutions were combined, washed with brine, dried over MgSO $_4$, and concentrated. The crude product was recrystallized from toluene/EtOAc/EtOH, yielding 6.1 g (67%): mp 316–322 °C; ^1H NMR (CDCl $_3$) δ 7.97–8.01 (m, 3 H), 7.95 (d, J = 2 Hz, 4 H), 7.89 (d, J = 2 Hz, 8 H), 7.86 (t, J = 2 Hz, 2 H), 7.83 (t, J = 2 Hz, 4 H), 7.68–7.72 (m, 16 H), 7.43–7.49 (m, 16 H), 7.35–7.41 (m, 8 H), 0.37 (s, 9 H); ^{13}C NMR (CDCl $_3$) δ 143.11, 142.62, 142.53, 142.33, 142.23, 141.35, 140.99, 131.82, 128.86, 127.59, 127.38, 126.07, 125.76, 125.53, 125.42, –0.92. Anal. Calcd for C $_{93}$ H $_{70}$ Si: C, 91.88; H, 5.80; Si, 2.31. Found: C, 91.59; H, 5.52; Si, 2.46.

3,5-Dibromoacetophenone. A two-necked 500-mL flask fitted with a rubber septum, magnetic stirring bar, and a low-temperature thermometer was charged with 1,3,5-tribromobenzene (10 g, 31.7 mmol). Dry diethyl ether (250 mL) was added, and the solution was cooled with a dry ice-acetone bath. To this solution was added *n*-butyllithium (19.8 mL of a 1.6 M solution, 31.7 mmol). A pale yellow color immediately developed in the reaction mixture. The solution was stirred at –78 °C for 45 min, whereupon *N,N*-dimethylacetamide (3.03 g, 34.8 mmol) was added dropwise with a syringe. The solution was allowed to warm to room temperature overnight. The reaction was quenched with dilute HCl (10%, 200 mL). The organic layer was separated, washed with brine, and dried over MgSO $_4$. The solvent was removed at reduced pressure, and the residue was recrystallized from 95% ethanol. A total of 6.1 g (69%) was recovered: mp 61–63 °C; ^1H NMR (CDCl $_3$) δ 8.00 (d, J = 2 Hz, 2 H), 7.85 (t, J = 2 Hz, 1 H), 2.59 (s, 3 H); ^{13}C NMR (CDCl $_3$) δ 195.2, 139.6, 138.2, 130.1, 123.5, 26.6.

1,3,5-Tris(3,5-dibromophenyl)benzene (4-Br $_6$). A 50-mL round-bottomed flask was charged with 3.00 g (10.8 mmol) of 3,5-dibromoacetophenone, 194 mg (1.98 mmol) of concentrated H $_2$ SO $_4$, and 3.5 g (14 mmol) of K $_2$ S $_2$ O $_7$. The solid mixture was heated to 180 °C for about 12 h. The resulting solid was allowed to cool and subsequently refluxed in EtOH (50 mL) for 1 h. The liquid was decanted, and the resulting solid was refluxed in H $_2$ O (50 mL) for 1 h. The crude product was isolated by filtration and purified by recrystallization from hot CHCl $_3$, yielding 0.98 g (35%) of an off-white solid: mp 313–15 °C; ^1H NMR (CDCl $_3$) δ 7.72 (bs, 9 H), 7.65 (bs, 3 H); ^{13}C NMR (CDCl $_3$) δ 143.6, 140.3, 133.4, 129.2, 125.9, 123.5.

46. This compound was synthesized using procedure A with 4.68 g (8.08 mmol) of 7-B(OH) $_2$, 0.790 g (1.01 mmol) of 4-Br $_6$, 0.2 g (0.2 mmol) of Pd(PPh $_3$) $_4$, and 3.5 mL of 2 M Na $_2$ CO $_3$ in 120 mL of 1:1 THF/toluene. After 1 day no 4-Br $_6$ remained, and there were three closely spaced spots in the TLC. The highest spot was the largest. As the reaction progressed, the lowest spot became larger, the uppermost spot disappeared, and the middle became faint. We believe that replacement of three of the bromines, presumably one of the two on each of the three phenyl rings, occurs quickly, and the three spots we observe are the product and intermediates having four and five arms attached. Size-exclusion chromatography was not useful for following the extent of this reaction because the intermediates were not resolvable. In a small-scale preparation, each of the intermediates was isolated by column chromatography in nearly pure form and analyzed by size-exclusion chromatography. The retention times for the intermediates decreased with decreasing R_f 's. The reaction mixture was heated for 42 h. Workup

as above in the preparation of **22** yielded 5.09 g of a brown solid, which was chromatographed on 250 g of silica gel with CCl $_4$ as the eluant. The eluant was gradually changed to 10% CH $_2$ Cl $_2$ in CCl $_4$. The impure fractions were combined and chromatographed again, yielding a total of 2.22 g of chromatographically pure product. The resulting white solid was recrystallized from ca. 40 mL of CCl $_4$ /EtOH, yielding 2.06 g (58%). At 230–250 °C the compound softens and becomes glassy: ^1H NMR (CDCl $_3$) δ 8.06 (bs, 3 H), 8.01 (bs, 9 H), 7.94 (bs, 18 H), 7.80 (d, J = 1.3 Hz, 24 H), 7.74 (t, J = 1.3 Hz, 12 H), 7.58–7.63 (m, 48 H), 7.30–7.37 (m, 48 H), 7.22–7.30 (m, 24 H); ^{13}C NMR (CDCl $_3$) δ 142.69, 142.62, 142.48, 142.06, 140.93, 128.78, 127.51, 127.33, 126.0–126.3, 125.90, 125.51, 125.34. Anal. Calcd for C $_{276}$ H $_{186}$: C, 94.65; H, 5.35. Found: C, 94.70; H, 5.22.

4F. A thick-walled glass tube was charged with 1,3,5-tribromobenzene (12.8 g, 40.7 mmol), bromopentafluorobenzene (50 g, 202 mmol), and copper bronze (38.5 g, 0.607 mol). The tube was cooled in dry ice acetone, evacuated, and sealed. It was placed in an oil bath, and the temperature was slowly raised to 205 °C. Heating was continued for a total of 5 days. The tube was cooled and opened (CAUTION: contents may be under pressure). The products were washed from the tube with hot hexane and filtered to remove excess copper metal. The hexane was removed under reduced pressure, and the residue was placed in a sublimator. Sublimation at 50 °C and 1 mmHg removed perfluorobiphenyl formed by the homocoupling of bromopentafluorobenzene. When all of the biphenyl had been removed, the residue was recrystallized once from EtOH and once from EtOAc/EtOH, yielding 0.60 g (2.6%): mp 232–236 °C; ^1H NMR (CDCl $_3$) δ 7.63 (s, 3 H); ^{13}C NMR (CDCl $_3$) δ 144.1 (d, J = 248 Hz), 138.2 (d, J = 253 Hz), 138.0 (d, J = 244 Hz), 132.6, 127.8, 113.9. Anal. Calcd for C $_2$ H $_3$ F $_{15}$: C, 50.02; H, 0.53; F, 49.46. Found: C, 49.93; H, 0.80; F, 49.80.

3,5-Bis(pentafluorophenyl)-1-(trimethylsilyl)benzene (3F-TMS). A thick-walled glass tube fitted with a Teflon stopcock was charged with 35 g (0.552 mmol) of copper bronze. Bromopentafluorobenzene (16.4 g, 66.6 mmol) and 1,3-dibromo-5-(trimethylsilyl)benzene (6.85, 22.2 mmol) were added to the tube, and the contents of the tube were degassed by two freeze–pump–thaw cycles. The stopcock was closed and the tube was slowly heated to 200 °C. Heating was continued for 5 days. The tube was cooled and opened. The contents were washed from the tube into a Büchner funnel with diethyl ether, and the residue that collected on the frit was exhaustively washed with diethyl ether and methylene chloride. The washings were combined, and the solvents were removed under reduced pressure. An off-white solid was recovered which was placed in a sublimator and heated at 40 °C at 1 mmHg to remove perfluorobiphenyl. When no further biphenyl was collected on the cold-finger, the sublimator was opened and the residue (10.8 g) dissolved in the minimum amount of hexanes. The solution was passed through 100 g of silica gel using hexanes as the eluant. Removal of the solvent and recrystallization of the product from absolute ethanol (ca. 60 mL) yielded 8.9 g of white needles (83%): mp 134–138 °C; ^1H NMR (CDCl $_3$) δ 7.63 (s, 2 H), 7.47 (s, 1 H), 0.34 (s, 9 H); ^{13}C NMR (CDCl $_3$) δ 144.2 (d, J = 248 Hz), 142.5, 140.7 (d, J = 244 Hz), 139.2 (d, J = 244 Hz), 135.8, 132.0, 126.4, 115.3 (t, J = 19 Hz), –1.3. Anal. Calcd for C $_{21}$ H $_9$ F $_{10}$ Si: C, 52.28; H, 2.49; F, 39.42. Found: C, 52.34; H, 2.44; F, 39.31.

[3,5-Bis(pentafluorophenyl)phenyl]boronic Acid (3F-B(OH) $_2$). A 100-mL Schlenk flask equipped with a Teflon valve was charged with 8.76 g (18.2 mmol) of 3F-TMS and 65 mL of CCl $_4$. BBr $_3$ (3.5 mL, 9.1 g, 36 mmol) was added via syringe, and the resulting solution was freeze–pump–thaw degassed through two cycles. The valve was closed and the reaction was slowly heated to 177 °C. The reaction was held at 177 °C for 2 h and allowed to cool. Progress of the reaction was monitored by TLC by disappearance of the starting material. The reaction mixture was cooled and transferred via cannula to a 250-mL Erlenmeyer flask containing 150 mL of 1 N NaOH, whereupon a white precipitate immediately formed. The resulting mixture was filtered, and the solid was washed with H $_2$ O and CH $_2$ Cl $_2$. The white solid was transferred to a 500-mL Erlenmeyer flask containing 100 mL of 1 N HCl and 200 mL of ether. The mixture was stirred until two clear layers were obtained. The phases were separated, and the aqueous phase was washed with ether. The etheral solutions were combined, washed with brine, dried over MgSO $_4$, filtered, and concentrated to a white solid weighing 7.07 g (87%): ^1H NMR (DMSO- d_6) δ 8.43 (bs, 2 H), 8.04 (bs, 2 H), 7.72 (bs, 1 H); ^{13}C NMR (DMSO- d_6) δ 143.7 (d, J = 244 Hz), 137.3 (d, J = 244 Hz), 136.3, 134.5 (d, J = 262 Hz), 125.7, 114.9 (t, J = 19 Hz). Anal. Calcd for C $_{18}$ H $_3$ BF $_{10}$ O $_2$: C, 47.61; H, 1.11; F, 41.85. Found: C, 48.85; H, 1.24; F, 43.70.

10F. This compound was synthesized using procedure A with 1.73 g (3.82 mmol) of 3F-B(OH) $_2$, 0.344 g (1.09 mmol) of 1,3,5-tribromobenzene, 113 mg (0.098 mmol) of Pd(PPh $_3$) $_4$, 1.5 mL of 2 M Na $_2$ CO $_3$, and 30 mL of 2:1 THF–EtOH/toluene. Here, as with 3-B(OH) $_2$, 3F-

B(OH)₂ was dissolved in ca. 200 mL of warm 3:1 THF/EtOH and concentrated to about 20 mL before using. The reaction mixture was heated for 6 h, during which a white precipitate formed. The white precipitate was isolated by filtration and extracted with hot CH₂Cl₂ followed by hot toluene, yielding a white powder weighing 0.98 g (69%): mp 415–422 °C; mass spectrum (EI) *m/z* 1302/1303. (1.0/0.64). Anal. Calcd for C₆₀H₁₂F₃₀: C, 55.32; H, 0.93; F, 43.76. Found: C, 54.30; H, 0.81; F, 45.08.

7F-TMS. This compound was synthesized using procedure A with 7.09 g (15.6 mmol) of **3F-B(OH)₂**, 2.85 g (7.09 mmol) of **1**, 0.49 g (0.42 mmol) of Pd(PPh₃)₄, 3.5 mL of 2 M Na₂CO₃, and 90 mL of 2:1 THF–EtOH/toluene. The reaction mixture was refluxed for 2 days and worked up by dilution with CH₂Cl₂ and H₂O. The aqueous and organic phases were separated, and the aqueous phase was washed with CH₂Cl₂. The organic phases were combined, washed with brine, dried over MgSO₄, and concentrated. The crude brown solid was chromatographed on 250 g of silica gel using hexane as the eluant. The resulting white solid was recrystallized from EtOAc/EtOH, yielding 6.85 g (75%): mp 198–202 °C; ¹H NMR (CDCl₃) δ 7.75 (bs, 7 H), 7.51 (bs, 2 H), 0.37 (s, 9 H); ¹³C NMR (CDCl₃) δ 144.2 (d, *J* = 144 Hz), 142.7, 140.8 (d, *J* = 261 Hz), 139.8, 138.0 (d, *J* = 251 Hz), 132.1, 130.7, 130.1, 127.7, 127.1, 114.9 (t, *J* = 19 Hz), –1.10. Anal. Calcd for C₄₅H₁₈F₂₀Si: C, 55.91; H, 1.88; F, 39.31; Si, 2.91. Found: C, 55.85; H, 1.68; F, 38.96; Si, 3.22.

22F. This compound was synthesized using procedure A with 2.00 g (4.41 mmol) of **3F-B(OH)₂**, 0.429 g (0.55 mmol) of **4-Br₆**, 75 mg (0.065

mmol) of Pd(PPh₃)₄, 2 mL of 2 M Na₂CO₃, and 30 mL of 2:1 THF–EtOH/toluene. The reaction mixture was heated for 20 h, and the resulting mixture was worked up as above. The crude product (2.01 g) was chromatographed on 100 g of silica gel, beginning with 1:1 CCl₄/hexane and gradually changing to 2:1 CCl₄/hexane. The resulting white solid (1.04 g 68%) was analytically pure after pumping on it to remove traces of volatiles: mp 357–359 °C; ¹H NMR (CDCl₃) δ 7.96 (s, 3 H), 7.91 (d, *J* = 1.5 Hz, 6 H), 7.83 (t, *J* = 1.5 Hz, 3 H), 7.81 (bs, 12 H), 7.53 (bs, 6 H); ¹³C NMR (CDCl₃) δ 144.2 (d, *J* = 248 Hz), 142.8, 142.0, 141.5, 140.9 (d, *J* = 273 Hz), 138.0 (d, *J* = 260 Hz), 131.1, 130.0, 127.9, 126.5, 126.1. Anal. Calcd for C₁₃₂H₃₀H₃₀F₆₀: C, 57.53; H, 1.10; F, 41.37. Found: C, 57.24; H, 1.26; F, 41.02.

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Registry No. **1**, 17878-23-8; **3-TMS**, 128388-53-4; **3-B(OH)₂**, 128388-54-5; **3F-TMS**, 137897-05-3; **3F-B(OH)₂**, 137915-47-0; **4F**, 61371-30-0; **4-Br₆**, 29102-67-8; **7-TMS**, 128388-55-6; **7-B(OH)₂**, 128388-56-7; **7-B(OH)₂** (homopolymer), 137897-11-1; **10**, 137897-08-6; **10F**, 137897-06-4; **22**, 137897-09-7; **22F**, 137897-07-5; **PhB(OH)₂**, 98-80-6; Pd(PPh₃)₄, 14221-01-3; C₆F₅Br, 344-04-7; 1,3,5-tribromobenzene, 626-39-1; 3,5-dibromoacetylbenzene, 14401-73-1; *N,N*-dimethylacetamide, 127-19-5.

Olefin Polymerization at Bis(pentamethylcyclopentadienyl)zirconium and -hafnium Centers: Chain-Transfer Mechanisms

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Abstract: Chain transfer via β-CH₃ elimination by a homogeneous bimetallic Ziegler–Natta propylene polymerization catalyst is reported. Propylene is converted by Cp*₂MCl₂/MAO catalysts (Cp* = pentamethylcyclopentadienyl; M = Zr, Hf; MAO = methylalumoxane) to atactic propylene oligomers and low polymers. GC–MS and ¹H and ¹³C NMR analyses of the oligomers obtained at 50 °C (*P_n* ≈ 4.5 for Zr, 3.4 for Hf) show these products to be mainly allyl- and isobutyl-terminated (1/1 ratio). The allyl/vinylidene ratio is 92/8 for Zr and 98/2 for Hf. No other unsaturated end groups could be detected. This end group structure is produced by first monomer insertion into the M–CH₃ bond and then chain transfer by β-CH₃ elimination. On the contrary, Cp*₂MCl₂/MAO promotes 1-butene polymerization with the chain transfer being exclusively β-H elimination and transfer to Al: no β-ethyl elimination could be detected. The behavior of these catalysts toward propylene and 1-butene is compared with known Cp₂MCl₂/MAO catalysts.

Introduction

Homogeneous olefin polymerization by means of group 4 metallocene–methylalumoxane¹ systems is undoubtedly the most versatile route to polymers with controlled structures: the broad electronic and steric variability of Cp-type ligands allows the design of catalyst precursors that are able to direct the polyinsertion reaction to form regioregular (1,2 insertion²) and stereoregular (isotactic³ or syndiotactic⁴) polyolefins with unprecedented selectivity. The present knowledge of the mechanistic details of the olefin insertion step has reached a high degree of accuracy thanks to extensive ¹³C NMR analysis of the polymers, the use of model organometallic compounds, the elegant work of Grubbs⁵ and Pino,^{2c} and the calculations done by Corradini and Guerra.⁶ The cationic nature of the active site, postulated as early as 1961,⁷ has gained strong support from the synthesis of a now wide series of model cationic titanocene, zirconocene, and hafnocene alkyls and the proven ability of some of them to polymerize olefins in the absence of any added cocatalyst.⁸

Chain transfer normally occurs via facile β-H elimination,⁹ which is the main reason for the much lower molecular weights

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