4300 *Organometallics* **2002,** *21,* 4300−4302

Synthesis and Characterization of (Perfluoroaryl)borane-Functionalized Carbosilane Dendrimers and Their Use as Lewis Acid Catalysts for the Hydrosilation of Acetophenone

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Received July 2, 2002

Summary: Carbosilane dendrimers capped with 4, 8, and 12 perfluoroarylborane Lewis acids are prepared via a self-catalyzed silation of the aryl ether **1** *with the appropriate Si−H terminated dendrimer scaffold. The dendrimers were fully characterized by spectroscopic methods and MALDI-TOF mass spectrometry and tested as catalysts for the hydrosilation of acetophenone using triethylsilane, exhibiting only slightly inferior activities in comparison to* $B(C_6F_5)_3$.

Dendrimers are aesthetically pleasing macromolecules formed in iterative synthetic protocols which build branches from a geometrically defined core such that the final structures are essentially monodisperse.[2] In recent years, research on dendrimers has evolved from form to function in that well-defined dendrimeric scaffolds can be adorned at the periphery with groups that serve some chemical purpose: e.g. catalysis,[3] light harvesting,[4] or (as in carborane-containing dendrimers) neutron capture therapy.[5] In the catalysis area, the focus has mainly been on incorporation of transition-metal-based catalysts, and several examples of the preparation and behavior of dendritic catalysts with well-defined mononuclear organometallic analogues has been achieved. In general, activities of the dendrimeric catalysts are comparable to (or even better than[6]) those of the parent mononuclear systems, but "dendritic effects" which lower activity have been observed in some systems. These effects include leaching of the active metal away from the dendrimeric support,[7] dimerization of active sites on the periphery of the dendrimer,[8] and other steric effects resulting from a high local density of catalyst sites.

While transition-metal-functionalized dendrimers have received much attention, few if any examples of dendrimers adorned with main-group Lewis acids have appeared.[9] Our interest in the chemistry of the strong organometallic Lewis acid $B(C_6F_5)_3$ [10] as a catalyst for organic reactions such as hydrosilation[11] and allylstannation[12] of carbonyl functions, as well as its important role as a cocatalyst in olefin polymerization by single-site catalysts,[13] led us to prepare dendrimeric versions of this catalyst to explore their behavior in these areas. Since $B(C_6F_5)_3$ is a relatively expensive Lewis acid, the possibility of implementing removable dendritic versions of this catalyst is a primary motivation of this work.

In addition to the above-mentioned reactions, $B(C_6F_5)_3$ is also an efficient catalyst for the silation of aryl methyl ethers ArOMe to form $ArOSiR_3$ and CH_4 in high yields and with trivial workup procedures.[14] This is thus an ideal reaction for capping the well-known carbosilane dendrimers with (perfluoroaryl)borane groups, provided a suitable borane-functionalized ArOMe reagent can be prepared. The mechanism of this ether silation reaction involves the activation of the silane by $B(C_6F_5)_3$ through partial abstraction of the silane hydride, followed by nucleophilic attack of the developing silylium ion by the

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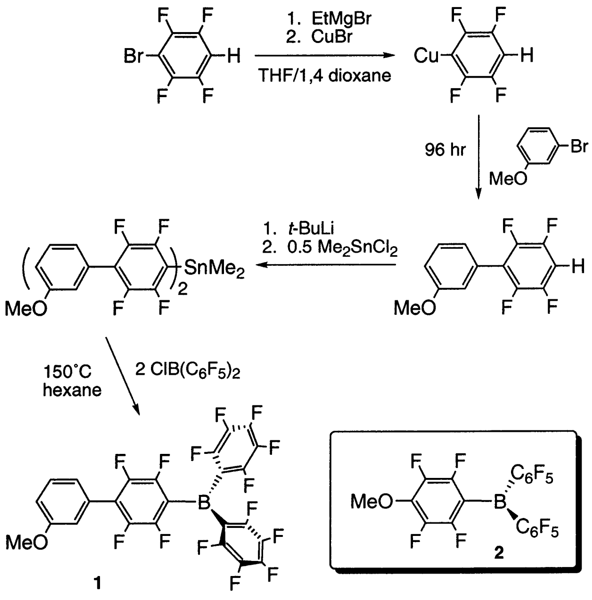
10.1021/om0205187 CCC: $22.00
Publication on Web 09/17/2002

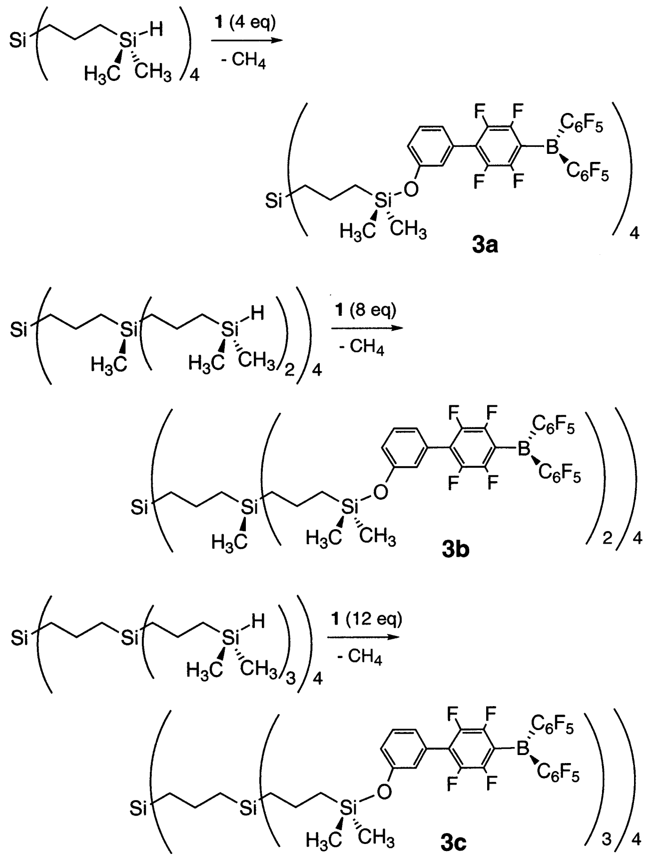
Scheme 1



ether substrate.[15] Loss of methane from $[Ar(Me)O\rightarrow SiR_3]^+[HB(C_6F_5)_3]^-$ gives the $ArOSiR_3$ product and regenerates the borane. It follows from this mechanistic picture that, in addition to a strongly Lewis acidic borane catalyst, this reaction also requires a sufficiently nucleophilic ArOMe substrate to proceed efficiently.

With these considerations in mind, we prepared low-generation dendrimers incorporating 4, 8, and 12 borane centers using the appropriate carbosilane dendrimer framework and the borane **1**, synthesized as shown in Scheme 1. The installation of a phenyl linker between the −OMe and (perfluoroaryl)borane functions was necessitated by the fact that the ArOMe function in the borane **2** was not basic enough to engage in the silation reaction. Use of a phenyl spacer and positioning the −OMe group in the meta position minimized the possibility of conjugation between the aryl ether group and the boron center.[16] The aryl ether was synthesized using standard copper coupling methodology,[17] while the B−C bond-forming step utilized transmetalation with the Ar_2SnMe_2 reagent[18] and $ClB(C_6F_5)_2$.[19] Although other reagents were explored (Ar_2Zn, for example), this tin-based route produces **1** cleanly with no aryl group redistribution and is therefore the method of choice thus far, although forcing conditions are required to drive this step to completion. Multinuclear NMR data for **1** (e.g. ^{11}B NMR, 59.7 ppm) are consistent with its formulation as a three-coordinate borane and do not point to any intermolecular aggregation involving −OMe coordination to the boron center. Furthermore, by the Childs method,[20] **1** has a Lewis acid strength essentially identical with that of the parent borane $B(C_6F_5)_3$.

Scheme 2



Coupling of borane **1** with carbosilane dendrimers[21] terminated by Si−H functions proceeds smoothly with evolution of CH_4, as shown in Scheme 2, to give the polyfunctional boranes **3a**−**c**, containing 4, 8, and 12 borane functions, respectively. In these reactions, the borane serves as its own catalyst, and since it is present in essentially 100% loading, the reactions smoothly proceed to completion (8 h at room temperature), giving essentially quantitative yields of high-purity (>95%) dendrimers. The dendrimeric products are readily soluble in both saturated hydrocarbon and arene solvents and have been fully characterized using ^1H, ^{11}B, ^{13}C,^{19}F, and ^{29}Si NMR spectroscopy and provide samples for which elemental analyses are consistent with the expected empirical formulas. In the case of **3c**, the 500 MHz HMQC spectrum accumulated with a cryoprobe reveals a highly monodisperse structure, with only trace signals attributable to defect structures detectable. Negative ion MALDI-TOF mass spectrometry confirms that molecules of mass *m*/*z* 2769 (**3a**), 5850 (**3b**), and 8532 (**3c**) are the products of these reactions (Figure 1). The parent ion peaks are detectable but much less intense than peaks which arise from the dendrimers plus a fluoride ion, or an equivalent of LiF. This pattern is apparent in all three spectra; in addition, peaks arising from the loss of a branch (*m*/*z* 569) via C−O bond cleavage are apparent, particularly in the spectrum for **3a**. All three compounds are moderately stable in air

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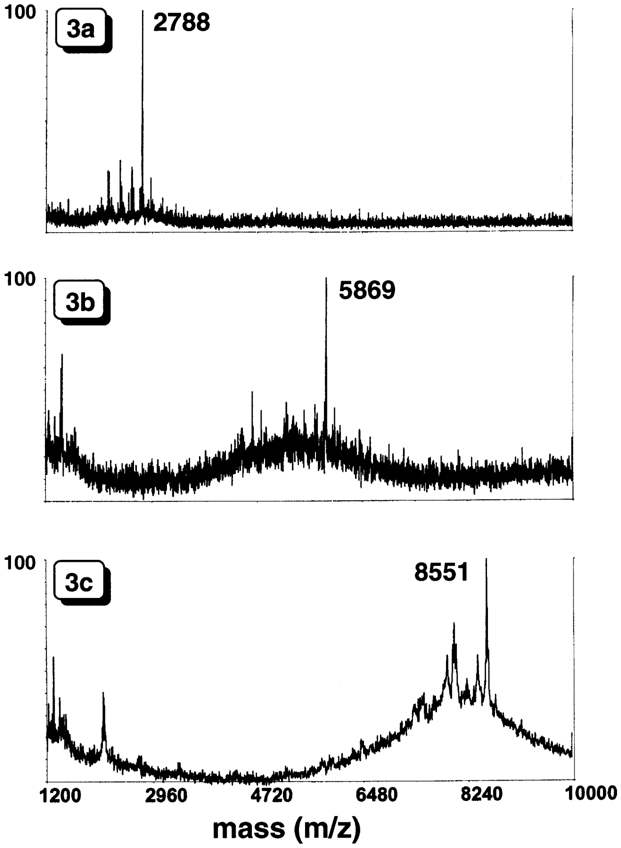

Figure 1. MALDI-TOF spectra for dendrimers **3a**–**c** accumulated using a benzo[*a*]pyrene matrix. The most intense peaks shown are actually doublets corresponding to the dendrimer plus a fluoride ion and the dendrimer plus LiF.

but are seriously hygroscopic and aquo adducts are formed readily.[22] Thus, the samples for MALDI-TOF were prepared under air-free and anhydrous conditions.

To test the efficacy of these (perfluoroaryl)borane-functionalized dendrimers in comparison to the parent borane $B(C_6F_5)_3$, we examined the hydrosilation of acetophenone by $HSiEt_3$ as a test reaction.[11] This hydrosilation proceeds cleanly to essentially 100% conversion over the course of several minutes at 5% catalyst loadings at room temperature. To conveniently monitor the reaction by ^{1}H NMR spectroscopy and compare the various catalysts, the reaction was followed at −35 °C over the course of a few hours. As Figure 2 shows, the dendrimers perform well in comparison to the parent borane at these loadings, with **3a** and **3b** retaining ~80% of the activity. The more crowded **3c** operates at a somewhat slower rate but is still an effective catalyst under these conditions. These results suggest that each boron center in the dendrimers is functioning as an independent catalyst for this hydrosilation reaction and that, under the conditions of the reaction, deleterious dendrimer effects are minimal. It should be noted, however, that in the absence of ketone substrate the dendrimers do react with triethylsilane over the course of several hours in ways which are as yet not fully understood. Boron–carbon bond cleavage to form B–H moieties[19b] or silation of the Si–O bonds[15] present at the linking point are two possible degradation reactions. The former process may be prevented by incorporating perfluoroborole groups[23] instead of $-B(C_6F_5)_2$ termini, while to address the latter scenario, routes to (perfluoroaryl)borane dendrimers without these Si–O bonds are currently being developed.

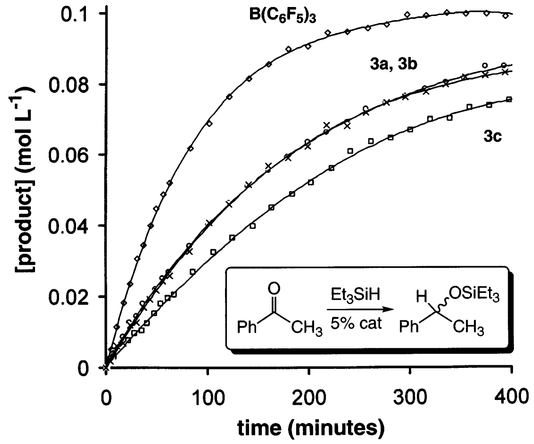

Figure 2. Hydrosilation of acetophenone as followed by the appearance of product over time using $B(C_6F_5)_3$ (diamond), **3a** (circle), **3b** (crosshatch), and **3c** (square) at 5% catalyst loading ([B] normalized) and −35 °C.

In conclusion, we have prepared the first examples of low-generation dendrimeric molecules functionalized by an important class of (perfluoroaryl)*borane*. While perfluoroaryl*borate* dendrimers have appeared,[24] the dendrimers reported herein are more versatile by virtue of the many applications that $B(C_6F_5)_3$ has in both organic[25] and organometallic[13] chemistry. In addition to further exploring the organic chemistry preliminarily discussed here, we are evaluating these dendrimers as olefin polymerization cocatalysts and developing procedures aimed at recycling the catalyst.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of a Postdoctoral Fellowship to R.R., a Discovery Grant to W.E.P., and an E. W. R. Steacie Fellowship to W.E.P. (2001–2003). We gratefully acknowledge Prof. Susan Lees-Miller and Mr. Mohamed Bader (Biological Sciences, University of Calgary) for the use of their MALDI-TOF mass spectrometer, Dr. Randy Whittal (University of Alberta) for MALDI-TOF analysis of dendrimers, and Prof. Hans Vogel and Dr. Deane Mcintyre (Biological Sciences, University of Calgary) for the use of their 500 MHz NMR spectrometer.

Supporting Information Available: Text giving full experimental details for the synthesis of all new compounds, plus spectroscopic and other characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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