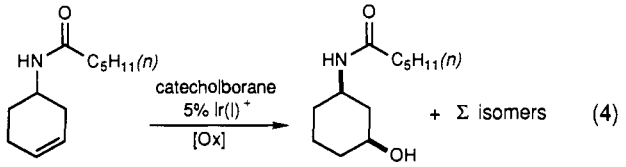
Enhanced Reactivity. In a competition experiment, *N*-benzylcarboxamide **2a** is over 1 order of magnitude more reactive toward iridium-catalyzed hydroboration than is silyl ether **2c**. Given the remoteness of the substituent from the olefin, a steric or an electronic effect is unlikely to be the origin of this disparity in relative reaction rates.[13]

Solvent Effect on Stereoselectivity. The data in Table I for the hydroboration of amide **1** reveal an inverse relationship between the Lewis basicity of the solvent and the level of diastereoselectivity observed. This trend may readily be rationalized if the amide is delivering the metal through Lewis acid–base complexation: When the solvent is better able to compete with the amide for complexation to the metal, the directed pathway becomes less favorable, and an erosion in stereoselectivity results.

Additional examples serve to illustrate the generality of amide delivery of the iridium-catalyzed hydroboration reaction. For example, we have found that amides derived from cyclic homoallylic amines such as **3** can also direct the process (eq 4).[14]



3 *diastereoselection 88 : 12 (69%)*

The directing ability of the amide moiety is also evident in acyclic systems (Table II). Iridium-catalyzed hydroboration of the illustrated β,γ-unsaturated amide (entry 1) affords the β-hydroxy amide with >99:1 selectivity, while the analogous reaction of a homologue (entry 2) is only slightly less regioselective (99:1). In fact, the amide directing group is capable of turning over the normal regiochemical preference of the iridium-catalyzed hydroboration of a terminal olefin. Whereas 1-hexene undergoes hydroboration with 98:2 selectivity favoring formation of the primary alcohol, reaction of the 3-butenamide (entry 3) affords the *secondary* alcohol as the major product (1.2:1).[15]

In conclusion, this study demonstrates that amides effectively direct the $[Ir(cod)(PCy_3)(py)]PF_6$-catalyzed hydroboration of olefins with catecholborane, producing hydroxy amides with high levels of regio- and stereochemical control; this reaction represents the first application of iridium-catalyzed hydroboration to organic synthesis. In contrast to the rhodium-mediated, phosphinite-directed process uncovered earlier, the amide-directed reaction proceeds in the presence of a *catalytic* quantity of the metal complex. Further studies of diastereo- and enantioselective amide-directed hydroboration are planned.

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Supplementary Material Available: Selected experimental procedures, as well as spectral and analytical data for all reaction products (4 pages). Ordering information is given on any current masthead page.

(13) We have also shown separately that, in contrast to the hydroxyl-directed, $[Ir(cod)(PCy_3)(py)]PF_6$-catalyzed olefin hydrogenation reaction (ref 2c), the amide-directed, $[Ir(cod)(PCy_3)(py)]PF_6$-catalyzed hydroboration process is *not* ligand-decelerated.

(14) Yield based on recovered starting material.

(15) Typical procedure: Catecholborane (300 mg, 2.50 mmol) was added to a mixture of **2a** (108 mg, 0.50 mmol) and $[Ir(cod)(PCy_3)(py)]PF_6$ (20.1 mg, 0.025 mmol) in 2.0 mL of $ClCH_2CH_2Cl$. The resulting homogeneous, pale yellow solution was stirred at 20 °C for 10 h and then subjected to an oxidative workup [1.0 mL of EtOH:THF (1:1), 1.0 mL of pH 7.00 buffer (0.05 M potassium phosphate monobasic sodium hydroxide), and 1.0 mL of 30% H_2O_2] for 12 h at 20 °C. The oxidized mixture was isolated by extraction, and then the unpurified reaction product was acetylated in order to ease diastereomer analysis. GLC analysis of an aliquot revealed a 91:9 [syn-1,3:$\sum$(other isomers)] mixture of acetates. The acetates were purified by flash chromatography, which afforded 106 mg (77%) of the acetylated hydroxy amides.

Hyperbranched Poly(siloxysilanes)

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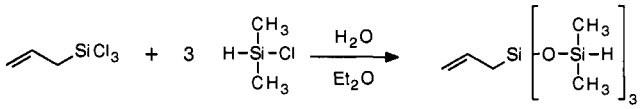
Starburst dendrimers, polymers, and arborols were synthesized by Tomalia et al.[1,2] and Newkome et al.,[3] respectively. These materials have precisely determined branch contents and branch lengths, but synthetic requirements are demanding and time-consuming. An alternative is to use multifunctional step-growth monomers, AB_n, where n determines the number of branches per repeat unit.[4] Two recent reports describe the synthesis of hyperbranched polyphenylenes[5] and polyamines.[6] The present report describes the use of hydrosilation to obtain highly branched polymers containing silane and siloxane groups. During the lengthy evaluation of our manuscript, a communication appeared on materials structurally very similar.[7]

The monomer chosen for initial study contains an allyl moiety and three Si–H groups. Monomer synthesis involved addition of allyltrichlorosilane to 3 equiv of dimethylchlorosilane in a mixture of ether and water. Yields of **1** were surprisingly good (>50%, >98% pure after distillation) in view of possible side reactions. Spectral and physical data confirm the structure.



1

Polymerization of **1** occurred in a 1:1 mixture of acetonitrile and ether under N_2 using hydrogen hexachloroplatinate(IV) hydrate (Aldrich). Stirring was continued at 52 °C for 8 h. Polymer isolation by addition of water gave **2** in the organic layer and catalyst in the aqueous phase. The FTIR spectrum of **2** shows essentially complete disappearance of the vinyl peak (1635 cm^{-1}) and reduction of the Si–H peak (2200 cm^{-1}).

The ^1H NMR spectrum ($CDCl_3$) of **1** showed peaks for allyl at δ 1.5 (allyl CH_2), δ 4.9 (vinyl β-CH_2), and δ 5.7 (vinyl α-CH). The Si–H peak appeared at δ 4.7 as a multiplet (coupling to two CH_3's). **2** showed almost no vinyl peaks. Integration of Si–H vs repeat unit peaks indicated chain extension to the third or fourth generation (average MW 11 000–35 000). Size-exclusion chromatography (THF) gave a single, narrow peak corresponding to a polystyrene standard of 19 000. Formation of this polymer was rapid, and addition of more catalyst did not increase its molecular weight, suggesting sterically inhibited chain extension. Molecular simulations of polyamide starburst dendrimers illustrate such outer-surface steric crowding.[8] Clearly, facile formation of polymer is possible with this system, although the absolute molecular weight, molecular weight distribution, and uniformity of branching have not yet been determined.

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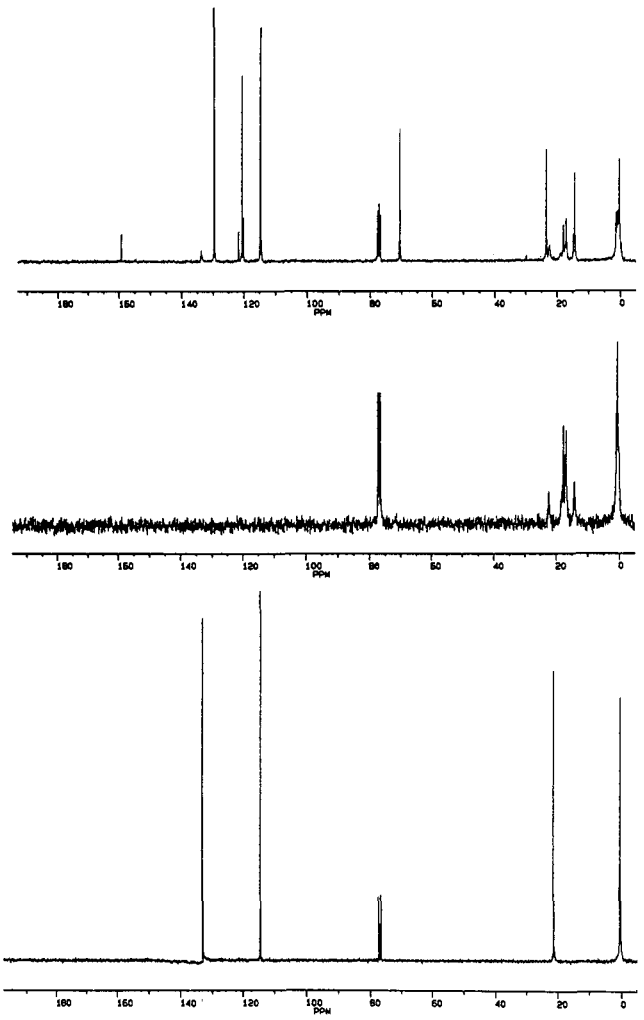
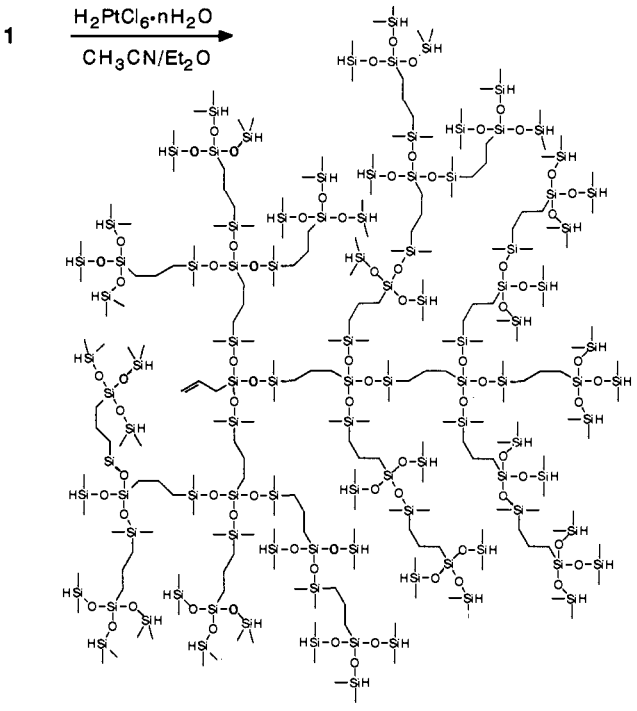


Figure 1. ^{13}C NMR spectra (in $CDCl_3$) of monomer **1** (bottom trace), polymer **2** (middle trace), and end-capped polymer **3** (top trace).



2 gradually became insoluble due to coupling of Si–H bonds through Si–O–Si formation.[9] Reaction of fresh **2** with allyl phenyl ether as end capper[10] gave polymer **3**. ^{13}C NMR spectra ($CDCl_3$) of **1**, **2**, and **3** confirm polymer formation (disappearance of alkenes) and end capping (appearance of aromatic and CH_2–O peaks without associated allyl ether peaks) (Figure 1). Alternative addition of an allyl-terminated oligomer of oxyethylene gave material with a hydrophobic core and hydrophilic exterior.

The one-pot polymerization and end-group reaction have been repeated several times to confirm facility of formation of terminally derivatized hyperbranched polymers. This approach makes available single-molecule structures with tailored interior and exterior functionality.

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Poly(thionylphosphazenes): A New Class of Inorganic Polymers with Skeletal Phosphorus, Nitrogen, and Sulfur(VI) Atoms

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The synthesis of new inorganic and organometallic polymers is attracting considerable current attention because these macromolecules often provide access to physical, chemical, preceramic, or biomedical properties that are difficult or impossible to achieve with conventional organic systems.[1] In principle, the ring-opening polymerization of cyclic inorganic compounds offers an attractive route to new macromolecular species. However, to date, relatively few examples of the successful use of this approach have been reported.

Cycloheterophosphazenes are an interesting class of inorganic species which are formally derived from the well-studied, polymerizable cyclic phosphazenes by the replacement of a skeletal phosphorus atom by an atom of a heteroelement.[2] Many examples of these small-molecule compounds are now known, and in the last two years the successful polymerization of species with skeletal carbon, molybdenum, or tungsten atoms to yield stable macromolecular products has been described.[3,4] Most recently, the ring-opening polymerization of a cyclic thiophosphazene (**1**) which contains a skeletal sulfur(IV) atom was reported.[5] However, in

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