Soc. of the likelihood of directivity in the hydroboration of a homoallylic alcohol olefin hydrogenation were screened for participation in the role of a boron hydride in order to explain anomalous regio and stereoselectivities of directed hydrogenation and ketone reduction serve to illustrate prospects for the development of a directable olefin hydroboration. rhodium-catalyzed variant by Mannig and Noth6 revived the evidence for the chemical fidelity of the reaction, see: Wang, C. H.; Jarvi, E. T.; Rasen, T. D. A.; Hoveyda. As a result, the reacting partners in the transition structure. Recent examples of directed hydrogenation and ketone reduction serve to illustrate this point. Although a number of reactions have been shown to be directed, no general approach to effecting a directed olefin hydroboration with BH3 or alkylboranes has been reported. The lack of success in this area may well arise from constraints inherent to the uncatalyzed hydroboration process.5 The discovery of a rhodium-catalyzed variant by Mannig and Noth6 revived the prospects for the development of a directable olefin hydroboration. Indeed, we reported in 1988 that phosphinites are capable of delivering the rhodium-mediated reaction (eq 1);7 however, because temporary binding a reagent and delivers it to a second functionality result from the multiple contact points that are established between the reacting partners in the transition structure. High levels of regio- and stereocontrol often fall short of accomplishing our goal of developing a catalytic directed hydroboration. In this communication we report that amidic effectively direct the iridium-catalyzed hydroboration in the context of a catalytic directed hydroboration of olefins with catecholborane (CB), an observation that represents a fulfillment of our original objective. As a contrast to this finding, see: Suzuki, H.; Hoveyda, A. H. J. Am. Chem. Soc. 1990, 112, 6447-6449. The studies were supported by NIH Grant GM34509 and Centre National de la Recherche Scientifique (Unité de Recherche Associée 135).

### Amide-Directed, Iridium-Catalyzed Hydroboration of Olefins: Documentation of Regio- and Stereoselective Control in Cyclic and Acyclic Systems

David A. Evans* and Gregory C. Fu†

*Department of Chemistry, Harvard University Cambridge, Massachusetts 02138

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A "directed reaction" is a process in which a functional group transiently binds a reagent and delivers it to a second functionality within the molecule. High levels of regio- and stereocontrol often result from the multiple contact points that are established between the reacting partners in the transition structure. Recent examples of directed hydrogenation and ketone reduction serve to illustrate this point. Although a number of reactions have been shown to be directed, no general approach to effecting a directed olefin hydroboration with BH3 or alkylboranes has been reported. The lack of success in this area may well arise from constraints inherent to the uncatalyzed hydroboration process.5 The discovery of a rhodium-catalyzed variant by Mannig and Noth6 revived the prospects for the development of a directable olefin hydroboration. Indeed, we reported in 1988 that phosphinites are capable of delivering the rhodium-mediated reaction (eq 1);7 however, because stoichiometric quantities of Rh[P(nBu)3]Cl are required, this method fell short of accomplishing our goal of developing a catalytic directed hydroboration. In this communication we report that amidic effectively direct the iridium-diP(CY3)3(py)2PF6-catalyzed hydroboration of olefins with catecholborane (CB), an observation that represents a fulfillment of our original objective. From (1) National Science Foundation Predoctoral Fellow.

A number of functional groups known to direct metal-catalyzed olefin hydrogenation were screened for participation in the analogous hydroboration process with catecholborane.8 From (1) National Science Foundation Predoctoral Fellow.

**Table I. Solvent Effect on the Stereoselectivity of the Amide-Directed Hydroboration (Eq 2)**

<table>
<thead>
<tr>
<th>solvent</th>
<th>0</th>
<th>syn/1:3</th>
<th>Σ(other 3 isomers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>45:55</td>
<td>99:1:1:1 (73)</td>
<td></td>
</tr>
<tr>
<td>ether</td>
<td>52:48</td>
<td>99:1:1:1 (78)</td>
<td></td>
</tr>
<tr>
<td>CICH2CH2Cl</td>
<td>95:5</td>
<td>1.2:1:1 (78)</td>
<td></td>
</tr>
</tbody>
</table>

* Ratios determined by GLC on derived acetates.

**Table II. Amide-Directed, Catalyzed Hydroboration: Acyclic Cases**

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>selectivity (%) yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[R]</td>
<td>+ Σ isomers</td>
<td>(1)</td>
</tr>
<tr>
<td>2</td>
<td>[R]</td>
<td>+ Σ isomers</td>
<td>(2)</td>
</tr>
<tr>
<td>3</td>
<td>[R]</td>
<td>+ Σ isomers</td>
<td>(3)</td>
</tr>
</tbody>
</table>

* Ratio of proximal:distal hydroxylation, as determined by GLC.

The following observations support the assertion that these reactions amide-directed:

**Stereoselectivity.** The catalyzed hydroboration of a variety of other 4-substituted cyclohexenes, which include derivatives such as 2c, 5 equiv of CB, 5% catalyst, 10 h, 20 °C, CICH2CH2CI as the directing group (eq 3).

2a. R = CONH2

2b. R = COOMe

2c. R = OSi(fep-Bu)Me2

The following observations support the assertion that these reactions amide-directed:

**Stereoselectivity.** The catalyzed hydroboration of a variety of other 4-substituted cyclohexenes, which include derivatives such as 2b or 2c, furnish an essentially statistical mixture of the four isomeric reaction products. Predominant formation of the syn-1,3 isomer (eqs 2 and 3) is consistent with the expectation of a directed reaction.12

(1) National Science Foundation Predoctoral Fellow.
(3) Several workers have proposed reaction pathways involving the delivery of a boron hydride in order to explain anomalous regio- and stereoselectivities observed in uncatalyzed olefin hydroboration reactions. For example, see: (a) Suzuki, K.; Miyazawa, M.; Shimazaki, M.; Tsuichihi, G.-I. Tetrahedron 1988, 44, 4061-4072. (b) Welch, M. C.; Breyon, T. A. Tetrahedron Lett. 1989, 30, 523-526.
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 2e. 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.\(^\text{13}\)

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 homopenta- lactic amine such as 3 can also direct the process (eq 4).\(^\text{14}\)

\[
\begin{align*}
\text{HN-CH}_\text{3} & \quad \text{catalyborane} \quad \text{HN-CH}_\text{3} \\
\text{CH}_\text{3} & \quad \text{OH} \quad + \quad \Sigma \text{isomers} (4)
\end{align*}
\]

Hyperbranched Poly(siloxylsiliesales)

Lon J. Mathias* and Terrell W. Carothers

Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

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Startbrind dendrimers, polymers, and arbors were synthesized by Tomalia et al.\(^{1,4}\) 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 polyphenylacetylenes and polyanimes.\(^{6}\) The present report describes the use of hydrolysis 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 allyltribromsilane 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.

\[\text{SiCl}_3 + 3 \text{H}_2\text{SiCl} \xrightarrow{\text{H}_2\text{O}} \text{Si} \quad \text{O} \quad \text{H} \quad \text{O} \quad \text{C}_3 \]

Polymerization of 1 occurred in a 1:1 mixture of acetone/tert 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 \(^{1}H\) NMR spectrum (CDCl\(_3\)) of 1 showed peaks for allyl at \(\delta 1.5\) (allyl CH\(_3\)), \(\delta 4.9\) (vinyl CH\(_2\)), and \(\delta 5.7\) (vinyl OH–CH\(_2\)). The Si–H peak appeared at \(\delta 4.7\), 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 19000. 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.\(^{3}\) 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.