Carbon-Carbon Single Bond Activation for Nucleophilic Addition to Michael Acceptors

Catherine Calyore
Janelle Kirsch
Erik Phipps
Jeffery B. Johnson

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Background- Alkene Insertion Carboacylation

The reaction of a quinolinyl ketone with a rhodium catalyst results in the activation of a carbon-carbon single bond and the insertion of the alkene into this activated bond. This reaction was first reported by Douglas and coworkers (Dreis, A. M.; Douglas, C., J. Am. Chem. Soc. 2009, 131, 142) and has been analyzed in depth by past Johnson group members with mechanistic and kinetic studies.

Catalytic Cycle of Carboacylation

Kinetic Studies

The reaction occurs with several rhodium(I) catalysts and proceeds at varying rates. Research was done to see how different Rh(I) catalysts affected the rate of the reaction, specifically the initial rate of the reaction. The initial rate was determined from the first 15% of the reaction. A table of results is shown below.

<table>
<thead>
<tr>
<th>Rh(I) Catalyst</th>
<th>Initial Rate (M•s⁻¹)</th>
<th>kₚ, 67°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(COD)₂OTf</td>
<td>6.52 x 10⁻⁶</td>
<td>3.922 x 10⁻⁴</td>
</tr>
<tr>
<td>[Rh(nbd)₂BF₄]</td>
<td>1.85 x 10⁻⁶</td>
<td>8.322 x 10⁻⁴</td>
</tr>
<tr>
<td>[Rh(C2H4)₂Cl]²</td>
<td>5.47 x 10⁻⁶</td>
<td>2.813 x 10⁻⁴</td>
</tr>
<tr>
<td>RhCl(PPh₃)₃</td>
<td>2.03 x 10⁻⁶</td>
<td>2.813 x 10⁻⁴</td>
</tr>
<tr>
<td>Rh(acac)(COD)</td>
<td>6.3 x 10⁻⁷</td>
<td>2.33 x 10⁻⁴</td>
</tr>
</tbody>
</table>

* Calculated from initial rate [Rh]₀

Intermolecular Reaction

In attempts to make the alkene insertion successful with intermolecular conditions an unexpected product was formed involving the carbon-carbon bond activation and nucleophilic addition to these Michael acceptors. This reaction is observed with ortho-substitution on the quinolinyl ketone. Ortho-substituted fluorne was used based on prior Johnson group research involving rhodium(I) carboacylation using palladium catalysis (Bour, et. al. J. Org. Chem. 2013, 78, 1665).

Proposed Catalytic Cycle

Future Research

• Work toward synthesizing the intermolecular carboacylation product
• Change conditions leading to optimization of both the carboacylation and nucleophilic addition reactions
• Expand alkene scope and work toward alkyne insertion

Preliminary¹H NMR Kinetic Study

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