

## Transition Metal Catalyzed Hydroboration of Unsaturated Hydrocarbons

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The hydroboration reaction is one of the most versatile methods for the reduction of many unsaturated bonds. The organoboranes formed can be easily converted into other functional groups. In the uncatalyzed reaction, boron adds to the least substituted and thus least sterically congested carbon. In cases where the stereochemistry may be defined, addition is exclusively in a syn fashion.<sup>1</sup>

In 1985, Männig and Nöth reported that addition of catecholborane (1,3,2-benzodioxaborole) to alkenes was greatly accelerated by  $\text{RhCl}(\text{PPh}_3)_3$ .<sup>2</sup> They also demonstrated that a similar reaction of catecholborane with an unsaturated ketone in the presence of the catalyst results in the reduction of the carbon-carbon double bond rather than the carbon-oxygen double bond. This is in contrast to uncatalyzed hydroboration, which results only in reduction of the carbonyl group.<sup>3</sup> In addition to rhodium compounds, other late transition metal complexes have also been shown to catalyze hydroboration.<sup>4</sup>

The advantage of using a transition metal complex over the noncatalyzed hydroboration is that less reactive or thermally sensitive boranes can be induced to react faster under milder conditions. Furthermore, in many cases different chemo-, regio-, and stereoselectivity is observed; this makes these reactions potentially quite useful for organic synthesis.<sup>5,7</sup> The mechanisms that operate in these systems have been the subject of several theoretical<sup>6</sup> and experimental studies.<sup>7,11</sup> Pathways involving oxidative addition/reductive elimination sequences were initially proposed for the Rh catalyst used by Männig and Nöth (Figure 1).<sup>2</sup> The proposed mechanism involves the following steps: initial oxidative addition of B-H to  $\text{RhCl}(\text{PPh}_3)_2$ , alkene coordination to an open site, insertion of an alkene into the M-H bond, and elimination of the organoborane with catalyst regeneration.

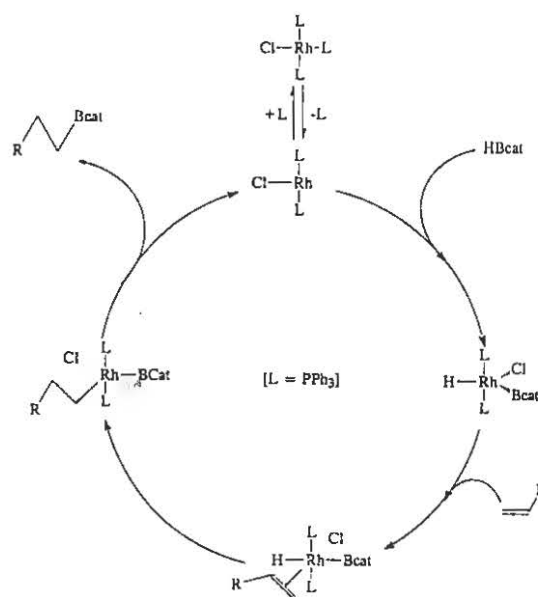


Figure 1

Support for the catalytic cycle shown in Figure 1 is provided by the reaction of  $\text{RhCl}(\text{PPh}_3)_3$  with stoichiometric amounts of catecholborane, which results in formation of  $\text{RhHCl}(\text{BO}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2$ .<sup>8</sup> This compound then reacts with alkenes to give hydroboration products and  $[\text{RhCl}(\text{PPh}_3)_2]_2$ . Efforts to obtain a solid state structure of  $\text{RhHCl}(\text{BO}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2$  have been unsuccessful, but an analogous triisopropylphosphine complex has been characterized via single-crystal X-ray diffraction studies.<sup>9</sup>

Though the cycle proposed by Männig and Nöth accounts for prominent features of the system, there are still differences in opinion over certain details of the mechanism.<sup>4</sup> Side reactions such as the isomerization of the alkene and the catalytic decomposition of catecholborane to  $\text{BH}_3$  makes determination of the mechanism difficult.<sup>10</sup> One proposal suggests that the course followed by the catalyzed hydroboration reaction is substrate dependent.<sup>11</sup> This variability leads to different stereoselectivity-determining steps for different alkenes; for example, the regioselectivity-determining step for the reaction of 1-decene is reductive elimination<sup>11</sup>, whereas for styrene it is hydride migration.<sup>12</sup>

Recently, there have been reports of insertion of an alkene or alkyne into metal-boron bond.<sup>13</sup> This has prompted suggestions that the alkene insertion during hydroboration is not into the metal-hydrogen bond, but into the metal-boron bond. Complexes of early transition metals like titanium, zirconium<sup>14</sup> and lanthanides<sup>15</sup> have also shown catalytic activity, however, their mechanism is likely to be different. Substrates other than catecholborane have also been considered, but detailed studies have yet to be carried out.<sup>16</sup>

There is no question about the importance of hydroboration in organic syntheses: the value of the catalytic variant lies not only in the activation of less reactive boranes, which are therefore easy to handle and store, but also in controlling the selectivity of the reaction.

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