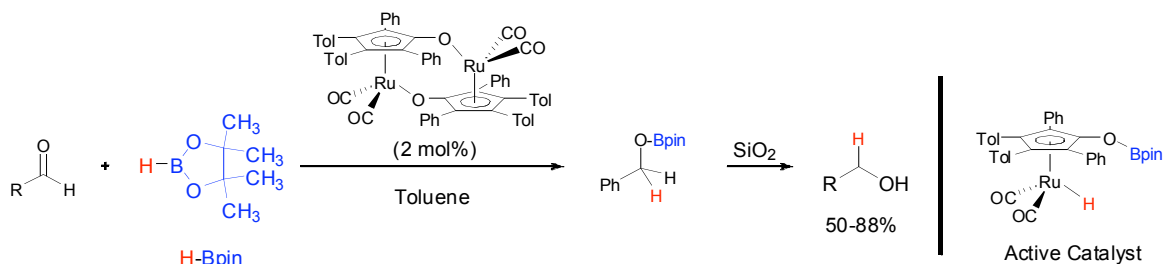


Ruthenium-Catalyzed Hydroboration Reactions of Aldehydes

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The Shvo catalyst $[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COH})\text{Ru}(\text{CO})_2\text{H}]$ is used in the hydrogenation of polarized double ($\text{C}=\text{X}$) and triple ($\text{C}\equiv\text{X}$) bonds and exhibits a unique reaction mechanism. The key mechanistic step involves an interesting outer-sphere, concerted mechanism in which the substrate does not coordinate to the metal prior to addition of hydrogen. Our group is taking advantage of the specific reactivity of the Shvo catalyst to deliver functional groups other than hydrogen. We have limited our attention to boron-substituted analogues of the Shvo catalyst, $[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COH})\text{Ru}(\text{CO})_2\text{BR}_2]$ and $[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COBR}_2)\text{Ru}(\text{CO})_2\text{H}]$, due to the synthetic utility of potential boron-containing organic products. Initial studies were focused on the $[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COBR}_2)\text{Ru}(\text{CO})_2\text{H}]$ catalyst which resulted from the activation of boranes ($\text{R}_2\text{B-H}$). The $[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COBpin})\text{Ru}(\text{CO})_2\text{H}]$, (Bpin = 4,4,5,5-tetramethyldioxaborolane, see below) complex was shown to react with carbonyl compounds, catalyzing the addition of the H-Bpin bond across $\text{C}=\text{O}$ bonds. Current research involves optimizing the reaction conditions and determining the reaction scope with respect to the carbonyl compounds used. Aryl and alkyl aldehydes were shown to participate in catalytic hydroboration after 1–2 days at 50 °C. The electronic effects of substituted aromatic aldehydes were also examined for comparison to standard hydrogenation catalysts (including the Shvo catalyst). Electron withdrawing substituents accelerate hydroboration, providing high yields of the desired alcohols.



References:

1. Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090-1100.