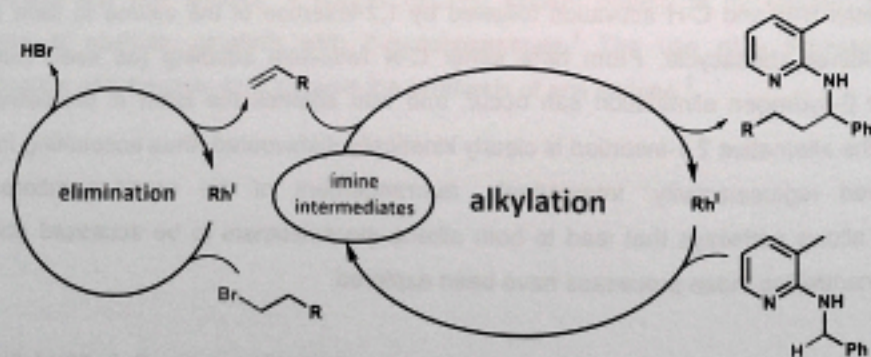


Mechanistic insight into a Rh(I)-catalyzed C-H alkylation of benzylic amines - A seemingly sp^3 - sp^3 coupling proceeding via an sp^2 - sp^2 mechanism

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A new method for direct C-H alkylation of benzylic amines with alkylbromides catalyzed by Rh(I) was developed. From a glimpse at the starting materials this would seem to be a coupling between two sp^3 -hybridized carbon atoms. Detailed mechanistic investigations have been performed and mechanistic information was obtained by extensive kinetic studies and intermediate analysis. Substrate scope experiments reveal this alkylation to proceed via elimination of the alkylbromide to the corresponding alkene and the reaction conditions proved to be even more efficient when alkenes instead of alkylbromides are used. Comparing kinetic profiles for both alkylations shows that elimination of the alkylbromide is the slow process in this reaction. In addition, kinetic evidence for the alkylation using alkenes reveals that the reaction actually proceeds over the corresponding imines making the whole process effectively a coupling between two sp^2 -hybridized carbon atoms. On the basis of our data a detailed kinetic model for the reaction using alkenes is established and the following schematic reaction mechanism for the whole process is proposed:



In addition, the whole reaction using alkenes is shown to be reversible and the formation of two by-products via C-C activation is observed.