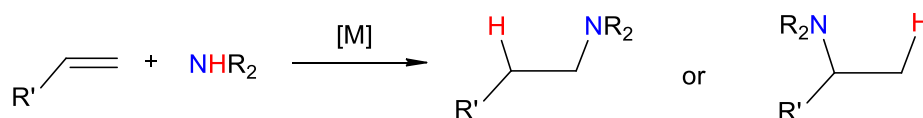


# ORIGIN OF REGIOSELECTIVITY IN METAL-CATALYZED HYDROAMINATION REACTIONS

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Hydroamination reaction on unsaturated molecules is one of the most economical pathways (in terms of price and atom economy) for synthesis of nitrogen containing compounds such as amines, imines and enamines.<sup>[1]</sup> This reaction is thermodynamically accessible but activation energies use to be quite high. This makes necessary the use of catalysts, and transition metals are proven to be very efficient. Regarding the regioselectivity of the process, anti-Markovnikov hydroamination of olefins catalyzed by transition metals was named as one of 10 challenges for homogeneous catalysis (Scheme 1).<sup>[2]</sup> Progress has been made, but a lot of work is still needed.



*Scheme 1.* Schematic representation of the regioselective addition of amines to terminal alkenes.

The reaction mechanism for several catalysts based on Rh and Au transition metals will be here described.<sup>[3]</sup> The two main proposed mechanisms of hydroamination reaction mechanisms (amine activation and alkene activation) will be evaluated. One of the major competitive side reactions yielding the enamine product, oxidative amination, will be also investigated.

The origin of the regioselectivity for the addition process (Markovnikov vs anti-Markovnikov nucleophilic attack) will be analyzed in detail. Interesting correlations between catalyst-alkene coordination mode and the regioselective outcome will be discussed.

## References:

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