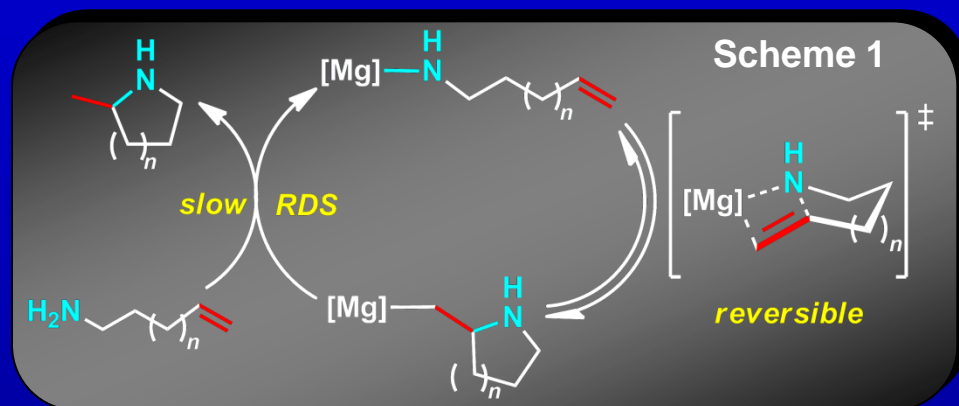


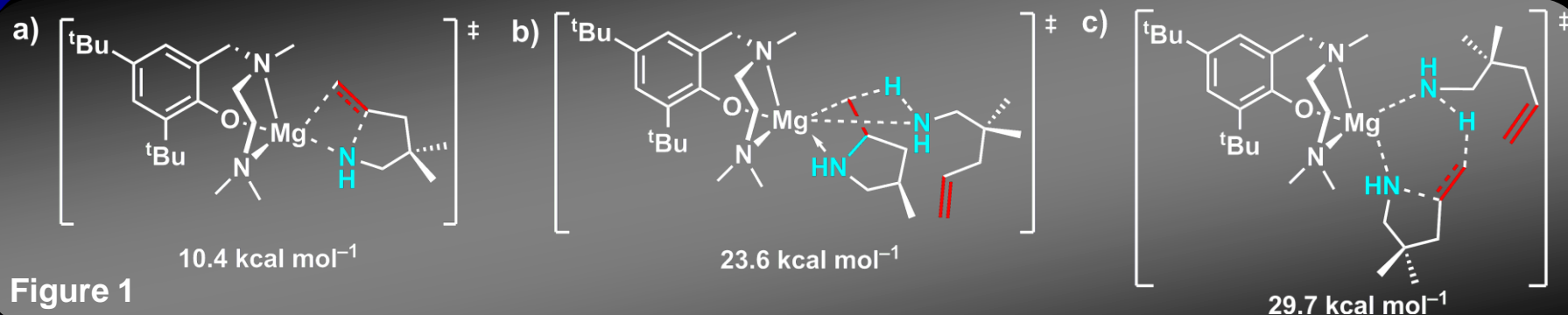
# Mechanistic Study of the Magnesium-Catalyzed Hydroamination of Aminoalkenes

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The hydroamination, a reaction in which an amine N-H bond adds to an unsaturated carbon-carbon bond, is a **highly atom-efficient** and **green process** for the **waste-free synthesis** of **industrially important bulk chemicals, specialty chemicals and pharmaceuticals**. The reaction mechanism of the magnesium-catalyzed process was studied experimentally and theoretically (in collaboration with Dr. Tobisch, University of St Andrews).



The reaction was found to involve a **reversible olefin insertion step** (Scheme 1), as indicated by a low activation barrier (Figure 1a) compared to the higher barrier for the **protolytic cleavage** of the metal-carbon bond (Figure 1b), which becomes the **rate-determining step (RDS)** (Scheme 1).



**Figure 1**

This finding is in contrast to the paradigm for early transition metal-catalyzed hydroamination reactions that always has assumed that the olefin-insertion is rate-determining and the protonolysis is fast. An alternative mechanistic scenario involving a concerted N-C ring-closure/protonolysis pathway (Figure 1c) can be ruled out based on the significant higher activation barrier.



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