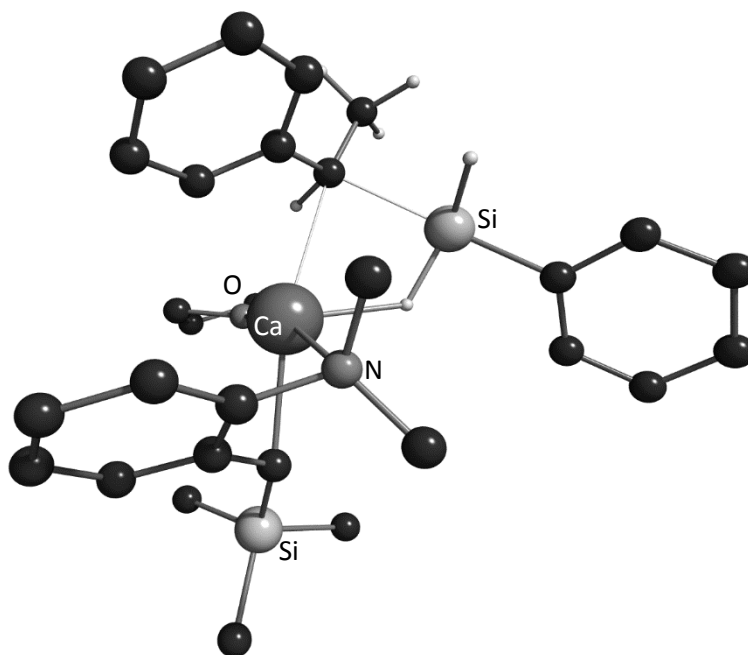


Mechanistical Insight on the Hydrosilylation of Conjugated Alkenes Catalyzed by Early Main-Group Metal Catalysts

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The key to developing highly efficient catalysts is to fully comprehend the reaction mechanism. Computational chemistry allows us to model the reactions and possible alternatives. We here present density functional calculations on the catalysts introduced by Harder *et al.* [1] for the hydrosilylation of conjugated alkenes. The Markovnikov or anti-Markovnikov regiochemistry strongly depends on the catalyst and on the reaction medium. We compare gas-phase and PCM/CPCM solvent model calculations for prototype models and for the full potassium and calcium-based catalysts. These provide mechanistic details and allow the identification of the catalytically active species.



Transition structure for the reaction of [Bz(Me)CaDMATxthf] with PhSiH₃: formation of the hydrosilylated styrene product and regeneration of the [HCaDMATxthf] catalyst (some hydrogen atoms omitted for clarity)

[1] F. Buch, J. Brettar, S. Harder, *Angew. Chem. Int. Ed.* **2006**, 45, 2741