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Titel des Beitrags: Olefin Hydrosilylation Catalyzed by a Bis-N-Heterocyclic Carbene Rhodium Complex. A Density Functional Theory Study

Abstract: Using a density functional theory method, we explored four reaction mechanisms of hydrosilylation of silane and ethylene as model substrates, catalyzed by a Rh(I) complex with a bidendate ethylene-bridged bis-N-heterocyclic carbene ligand. We examined in detail the energy profiles of the Glaser-Tilley, Chalk-Harrod, and modified Chalk-Harrod mechanisms, as well as of sigma-bond metathesis. The Chalk-Harrod mechanism and sigma-bond metathesis were determined most favorable, with the calculated highest relative activation enthalpies of 9.3 and 8.6 kcal mol\(^{-1}\), respectively. We also studied a potential side reaction in the sigma-bond metathesis that leads to the formation of ethane; its rate-limiting activation enthalpy is sufficiently high, 20.9 kcal mol\(^{-1}\) (14.6 kcal mol\(^{-1}\) higher than the competing barrier on the main pathway), not to be competitive. The feasibility of crucial reaction steps, C-H and C-Si bond formation, was found to correlate with the ease of conformational changes of the bis-N-heterocyclic carbene ligand, thus providing a hint at optimum ligand design.

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