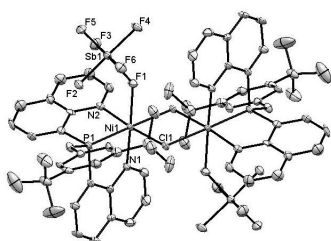


# NEW NICKEL-BASED CATALYST AND NEW MECHANISM FOR ALKENE HYDROSILYLATION PROCESSES

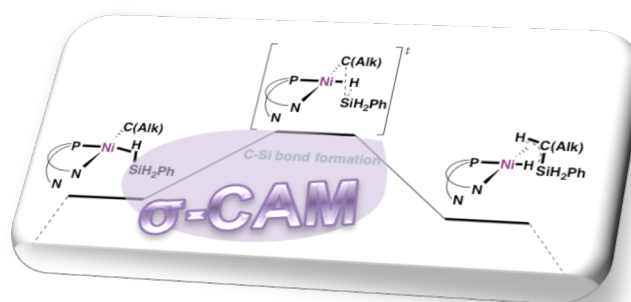
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Hydrosilylation reactions (where a Si-H bond is added across an unsaturated C-C or C-X (X=heteroatom) bond), are fundamental chemical transformations for the synthesis of organosilicon building blocks, which are widely used for constructing silicon-based products. The most common and active hydrosilylation catalysts are based on 2<sup>nd</sup> and 3<sup>rd</sup>-row transition metals (mainly platinum,<sup>1</sup> but also ruthenium and rhodium<sup>2</sup>). Due to the high cost associated with these metals, there is an increasing interest in the utilization of less expensive 1<sup>st</sup>-row and environmental benign transition metals for this aim. However, only a few examples of general and effective 1<sup>st</sup>-row transition-metals catalysts have been reported.<sup>3,4,5</sup> Up to four different mechanisms have been suggested for olefin hydrosilylation processes: Glaser-Tilley (GT),<sup>6</sup> Chalk-Harrod (CH), modified Chalk-Harrod (mCH), and  $\sigma$ -bond metathesis (SBM), the preferred one varying with the catalyst applied.

In this seminar we present a computational study of the hydrosilylation reaction mechanism for a recent Ni catalyst:  $[(\text{Ar}^{\text{tBu}}\text{O-NPN})\text{Ni}(\mu\text{-Cl})_2]^{2+}$ , where  $(\text{Ar}^{\text{tBu}}\text{O-NPN}) = \text{bis}(8\text{-quinlyl})(\text{dimethylamino})\text{phosphine}$ . This catalyst has been reported effective and general for the hydrosilylation of alkenes.<sup>7</sup> The nature of the active species of our catalyst,  $[(\text{Ar}^{\text{tBu}}\text{O-NPN})\text{NiH}]^+$ , prevents it to follow standard CM, mCH, SBM or GT mechanisms for the hydrosilylation reaction. In this work, a new reaction mechanism is presented. The mechanism is plausible and consistent with the available experimental evidences and involves a non-planar  $\sigma$ -CAM metathesis as the rate-limiting step. First hints about the rationalization of the catalyst's selectivity and competing processes are also presented.



**Image:** X-ray crystal structure of  $[(\text{Ar}^{\text{tBu}}\text{O-NPN})\text{Ni}(\mu\text{-Cl})_2](\text{SbF}_6)_2$ .



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<sup>2</sup> (a) Glaser, P.B.; Tilley, T.D. *J. Am. Chem. Soc.* **2003**, 125, 13640-13641. (b) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, 260, 335-346. (c) Kakiuchi, F., Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, 12, 4748-4750.

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<sup>5</sup> Bart, S.C.; Lobkovsky, E.; Chirik, P.J. *J. Am. Chem. Soc.* **2004**, 126, 13794-13807.

<sup>6</sup> (a) Glaser, P.B.; Tilley, T.D. *J. Am. Chem. Soc.* **2003**, 125, 13640-13641. (b) Chalk, A.J.; Harrod, J.F. *J. Am. Chem. Soc.* **1965**, 87, 16-21. (c) Schroeder, M.A.; Wrighton, M.S. *J. Organomet. Chem.* **1977**, 128, 345-358. (d) Crabtree, R.H. *Chem. Rev.* **1995**, 95, 987-1007.

<sup>7</sup> Yang, J.; Lipschutz, M.I.; Fasulo, M.; Tilley, T.D. *Efficient Nickel-Based Catalyst for the Hydrosilylation of Alkenes, Supported by a Bis(8-quinolyl)phosphine (NPN) Ligand* (submitted).