Advances in the Industrially-Relevant Hydosilylation of Siloxanes

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The platinum-catalyzed hydrosilylation of olefinic substrates by hydridosiloxanes is of considerable importance to the silicones industry.[1] Hydrosilylation involving vinyl-substituted siloxane polymers with multifunctional hydridosiloxanes is one of the key crosslinking mechanisms used in several applications such as abhesive paper coatings and injection-molded parts made from Liquid Silicone Rubber (LSR). Hydrosilylation of hydridosiloxanes of various structures with olefinic organic substrates ranging from alpha-olefins to allyl ethers of polyethers or even naturally occurring allylphenols such a Eugenol is the most common path to organofunctional siloxanes, and is used in such diverse applications as hair conditioners, paint additives, polyurethane foam additives, and diesel antifoams. Despite the wide use of this reaction, process chemists are still challenged by issues of reactivity and selectivity.

The present investigation compares a number of traditional and novel platinum catalysts in the reactions of hydridosiloxanes with common organic substrates, such as alpha-olefins and allyl ethers. Deuterosiloxanes are synthesized to probe questions related to the reaction mechanism, and kinetic studies are used to examine issues of reactivity and selectivity. These results are discussed in terms of the Chalk-Harrod mechanism and compared to earlier studies with silanes and siloxanes.[2]

[1] Reviews: a) B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, **1992**. b) B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc, *Hydrosilylation: A Comprehensive Review on Recent Advances,* Springer, London, **2009**. c) H-H. Moretto, M. Schulze, G. Wagner *Silicones* in *Ullmann's Encyclopedia of Industrial Chemistry*, VCH Publishers Inc., Weinheim, **1993**, 57-93.

[2] (a) T. K. Meister, K. Riener, P. Gigler, J. Stohrer, W. A. Herrmann, F. E. Kühn *ACS Catal.* **2016**, *6*, 1274-1284. (b) J. Stein, L. N. Lewis, Y. Gao, R. A. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 3693-3703. (c) X. Coqueret, G. Wegner, *Organometallics* **1991**, *10*, 3139-3145.