

**An Investigation into Rhodium(I) Silyl-Promoted Hydrosilane Reactions of
Olefins and Ketones**

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Abstract

We are introducing a new family of rhodium(I) silyl complexes, $\text{Rh}(\text{NBE})(\text{SiR}_3)(\text{PPh}_3)_2$ [$\text{SiR}_3 = \text{SiMe}_2\text{Ph}$ (**1a**), SiMe_2Et (**1b**), $\text{Si}(\text{OMe})_2\text{Me}$ (**1c**), $\text{Si}(\text{OSiMe}_3)_2\text{Me}$ (**1d**)] that are readily accessed from rhodium(I) complexes $\text{RhX}(\text{PPh}_3)_n$ [$n = 3$, $\text{X} = \text{Cl}$ (**2a**), OOCCH_3 (**5**), H (**4a**); $n = 4$, $\text{X} = \text{H}$ (**4c**)] and $\text{Rh}(\eta^3\text{-cyclohexenyl})(\text{PPh}_3)_2$ (**14**), in the presence of norbornene (NBE) and HSiR_3 . NBE plays the unique role of both sacrificial hydrogen acceptor and trapping agent of $[\text{Rh}(\text{SiR}_3)(\text{PPh}_3)_2]$ (**7**) in the formation of **1a-d**. The reversible ligation of NBE to **7** makes this system well-suited for investigating rhodium(I) silyl-promoted hydrosilane reactions with organic substrates. Compounds **1a-d** are shown to promote (presumably via **7**) the catalytic dehydrogenative silylation of acetophenone (**19**) in the presence of excess NBE. In the absence of NBE or substrate, the 14-electron transient $[\text{RhSiMe}_2\text{Ph}(\text{PPh}_3)_2]$ (**7a**) reacts with available PPh_3 to form a mixture of chelated phosphino(phenylene) silyl rhodium(I) complexes, $\text{Rh}[(\kappa^2\text{-P,Si})\text{-SiMeR-o-phenylenePPh}_2](\text{PPh}_3)_2$ [$\text{R} = \text{Me}$ (**8a**); Ph (**8b**)]. We report the independent preparation, isolation, and characterization of these compounds. Finally, compound **1a** is used to show that $[\text{RhSiMe}_2\text{Ph}(\text{PPh}_3)_2]$ (**7a**) promotes both hydrosilylation and dehydrogenative silylation of styrene (**13**), even when $\text{RhX}(\text{PPh}_3)_3$ [$\text{X} = \text{Cl}$ (**2a**), $\text{X} = \text{H}$ (**4a**)] serves as precatalyst.