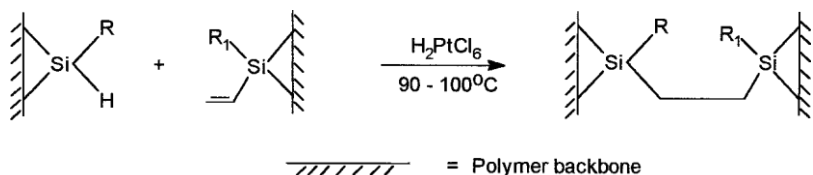
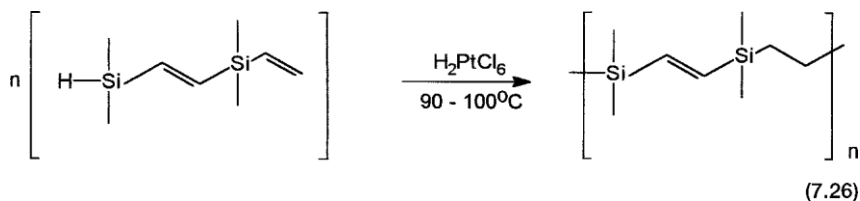


HYDROSILYLATION

The addition of a silicon compound such as R_3SiH to alkene functionality, as shown by reaction 7.25, is used widely in silicone polymer manufacture and is called the hydrosilylation reaction. Although hydrosilylation was discovered in 1947, the first homogeneous catalyst, H_2PtCl_6 (1– 10%), in 2-propanol was reported in 1957 from the laboratories of Dow Corning.

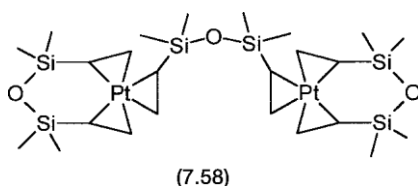


The importance of hydrosilylation reaction in the context of homogeneous catalysis is twofold. First, the hydrosilylation reaction is very important in the “curing” of silicone rubber. Such curing leads to cross-linking of the polymer chains and turns a “syrupy” polymer to a “gum” rubber or a “soft” polymer to a “hard” one. Reactions 7.26 and 7.27 show the formations of new bonds that can bring about these changes in the polymer properties. Hydrosilylation reactions have also been used to give nitrile or a CF_3 group containing monomers. These monomers in turn can be used to give silicone polymers of special properties.



(7.27)

Second, the formal dividing line between homogeneous and heterogeneous catalysis becomes blurred in the case of hydrosilylation reactions. In a number of such reactions, recent evidence shows that metal colloids as well as homogeneous catalytic intermediates may be involved. The involvement of metal colloids is well established for all H_2PtCl_6 plus isopropanol-based reactions. Like the Zeigler catalysts, most of these catalytic systems are therefore closer to heterogeneous ones. In fact, even with fully characterized soluble platinum complexes of the type 7.58, under the conditions of the hydrosilylation reaction colloidal platinum is eventually generated. However, there is evidence to show that with these precatalysts mononuclear catalytic intermediates are also involved.



In reaction systems where the ligands prevent colloid formation, the hydrosilylation reaction probably occurs via true homogeneous catalytic intermediates. Many such systems, including one based on Wilkinson's catalyst, have been reported. An interesting aspect of such reactions is that hydrosilylation of $-\text{C}=\text{O}$ and $-\text{C}=\text{N}$ bonds could be effectively carried out. Such transformations may have potential applications in the syntheses of fine chemicals and intermediates.

Catalytic Cycle and Mechanism

The first mechanistic proposal for the hydrosilylation reaction where mononuclear homogeneous catalytic intermediates are assumed is known as the Chalk-Harrod mechanism. The catalytic cycle in a slightly modified form is shown in Fig. 7.16. All steps of this catalytic cycle belong to organometallic reaction types that we have encountered many times before. Thus conversions of 7.60 to 7.61, 7.61 to 7.62, and 7.62 to 7.59 are

examples of oxidative addition of HSiR_3 , insertion of alkene into an M–Si bond, and reductive elimination, respectively.

As already mentioned, the highly active hydrosilylation catalysts derived from H_2PtCl_6 has been shown to be colloidal in nature. Colloid formation from the precatalyst $(\text{COD})\text{PtCl}_2$ takes place according to reaction 7.28. This reaction obviously is not a stoichiometric one. The products cyclo-octene and cyclo-octane are formed by hydrogenation of 1,5-COD catalyzed by the platinum colloid. The hydrogen generated in the reaction comes from the silane reagent.

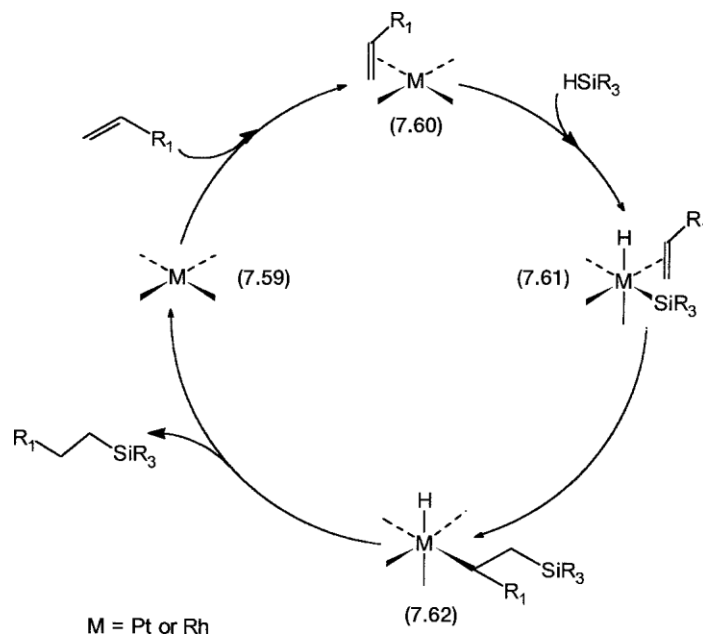
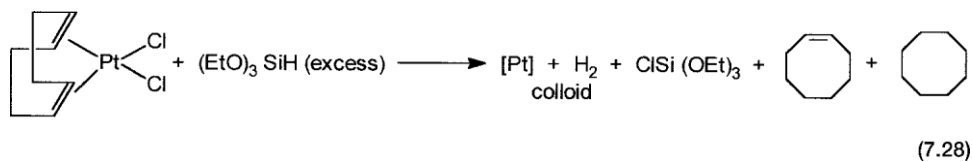


Figure 7.16 Proposed hydrosilylation mechanism with soluble catalysts of platinum or rhodium.



In recent years a variety of spectroscopic and other techniques have been employed to investigate and monitor hydrosilylation reactions. The techniques include multinuclear NMR, transmission electron microscopy, extended X-ray absorption fine structure (EXAFS), etc. Results from these experiments indicate that depending on the precatalyst, colloids and/or mononuclear complexes take part as catalytic intermediates.