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In Situ Determination of the Active Catalyst in Hydrosilylation Reactions Using Highly Reactive Pt(0) Catalyst Precursors

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Abstract: The mechanism of hydrosilylation using the highly active precatalyst Karstedt's precatalyst (Pt$_x$-(M^{vinyl}M^{vinyl})$_y$, M^{vinyl}M^{vinyl} = divinyltetramethyldisiloxane) was investigated using extended X-ray absorption fine structure (EXAFS), small-angle X-ray scattering (SAXS), and ultraviolet−visible (UV−vis) spectroscopy. Contrary to previous reports suggesting colloidal catalysts, we find that regardless of the stoichiometric ratio of hydrosilane to olefin, the catalyst is a monomeric platinum compound with silicon and carbon in the first coordination sphere. The platinum end product, however, is a function of the stoichiometry of the reactants. At excess olefin concentration, the platinum end product contains only platinum−carbon bonds, whereas at high hydrosilane concentration, the platinum end product is multinuclear and also contains platinum−silicon bonds. The two end products can interconvert by adding additional aliquots of the stoichiometrically deficient reagent. An explanation of the "oxygen" effect is also given. In the absence of oxygen, hydrosilylation of certain olefins does not occur. Oxygen serves to disrupt multinuclear platinum species that are formed when poorly stabilizing olefins are employed. Finally, we discuss the olefin isomerization reaction that may accompany hydrosilylation of terminal olefins. When the hydrosilylation reaction proceeds slowly due to poorly reactive olefins, the olefin isomerization products become significant. EXAFS analysis of solutions after olefin isomerization has occurred shows the presence of platinum−platinum bonded compounds.

Introduction

Many studies have been devoted to the soluble platinum-catalyzed hydrosilylation reaction (eq 1) since its discovery by Speier in the late 1950s.[1] Industrially, this reaction is employed

$$R_3SiH + R'CH{=}CH_2 \xrightarrow{Pt} R_3SiCH_2CH_2R' \qquad (1)$$
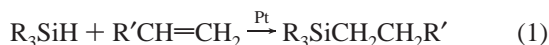
in the synthesis of silane coupling agents and UV screeners. It is also utilized in the formation of three-dimensional networks from the cross-linking reaction of multifunctional silicone hydride polymers with multifunctional silicon vinyl polymers. Product applications include silicone rubbers, liquid injection molding compounds, paper release coatings, and pressure-sensitive adhesives (PSAs).[2]

The Chalk−Harrod mechanism is the most commonly accepted mechanism for platinum-catalyzed hydrosilylation and

is based on elementary steps such as oxidative addition and reductive elimination which are fundamental to organometallic chemistry for processes such as the hydrogenation of olefins.[3−8] There are a number of phenomena not explained by the Chalk−Harrod mechanism, including the induction period of variable length, formation of color bodies particularly at the end of a hydrosilylation reaction, kinetic data which suggest competing equilibria, and a requirement for oxygen in hydrosilylation reactions with certain hydrosilane/olefin combinations. Additionally, the platinum complexes proposed in the elementary steps of the Chalk−Harrod mechanism have not been observed with highly active catalysts. Some mechanistic studies on platinum-catalyzed hydrosilylation have been conducted using phosphine-containing complexes; however, these compounds exhibit poor catalytic activity relative to the Pt(0)−olefin complexes of the present study.[9]

In the 1980s a new mechanism was proposed based on colloids as the active species in the hydrosilylation reaction.[10−15]

† GE Corporate Research and Development.

‡ The University of Georgia.

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According to this proposal, the induction period was attributed to the formation of colloidal species which were also responsible for the color bodies. It was further proposed that, during the induction period, the platinum species is reduced with a hydrosilane to a colloidal species which is stabilized by oxygen. The platinum colloid then reacts with a hydrosilane to form a platinum species coordinated via a three-center two-electron bond to the hydrosilane. In a subsequent step, olefin is directly added to the coordinated hydrosilane to yield the hydrosilylation products. The major issue with this mechanism is that there is no in situ evidence for the formation of colloids during the catalytically active portion of the hydrosilylation reaction.
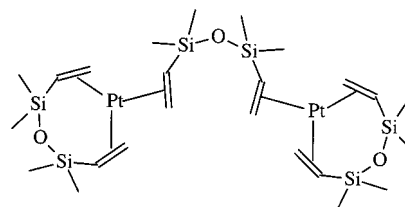
The evidence for the proposal of colloids as intermediates in the hydrosilylation reaction is largely based on transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) of evaporated solutions after completion of the hydrosilylation reaction.[10–13,15,16] The HREM studies typically showed platinum products that were 18–25 Å diameter crystallites with diffraction fringes and electron diffraction patterns in agreement with those reported for crystalline platinum. The only in situ evidence for colloid formation was the generation of a colloidal platinum solution from the reaction of CODPtCl$_2$ with excess triethoxysilane in methylene chloride.[10] Light scattering data on this solution indicated the presence of particles of about 40 Å. When this solution was used to catalyze the hydrosilylation reaction, no induction was noted, whereas an induction period was observed for CODPtCl$_2$. This led Lewis to propose that generation of colloids occurred during the induction period. Additional evidence presented by Lewis included an observation that mercury inhibited hydrosilylation, whereas as dibenzylcyclooctatriene did not.

Mechanistic studies to date have suffered on two accounts. First, due to the complexity of the kinetics of the hydrosilylation reaction,[17–21] there is a dearth of reliable information in this regard. Second, in situ evidence for either mechanism based on colloids or mononuclear species is lacking. We now have data for which platinum species are structurally characterized during hydrosilylation with highly active catalysts. In this paper we describe the results of our in situ investigations of the hydrosilylation reaction using Karstedt's precatalyst.[22–25] Furthermore, the model system we employed in our study is based on polydimethylsiloxanes encountered in platinum-catalyzed cross-linking of siloxanes. We report the results of extended X-ray absorption fine structure (EXAFS) spectroscopy, small-angle X-ray scattering (SAXS) and X-ray photoelectron spectroscopy (XPS) during catalysis.[2,15,26] We now propose a new reaction scheme which incorporates aspects of both the Chalk–Harrod mechanism and the colloid mechanism in which the active species are mononuclear platinum complexes.

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Results

The Induction Period. Often an induction period is observed for the hydrosilylation reaction. The length of the induction period is dependent upon the nature of the platinum precatalyst, the olefin structure, the hydrosilane structure, and the concentration of reagents and platinum precatalyst.

To understand the chemistry occurring during the induction period, the order of reactivity of olefin was determined in both individual and competitive experiments using the Pt(0) precatalyst, Karstedt's precatalyst, where $M^{vinyl}M^{vinyl} = (H_2C=CH)(CH_3)_2SiOSi(CH_3)_2(CH=CH_2)$. M, D, etc. shorthand is described in the Appendix.[25] The structure of Karstedt's catalyst is shown here and was crystallographically determined by the Lappert group.[24]
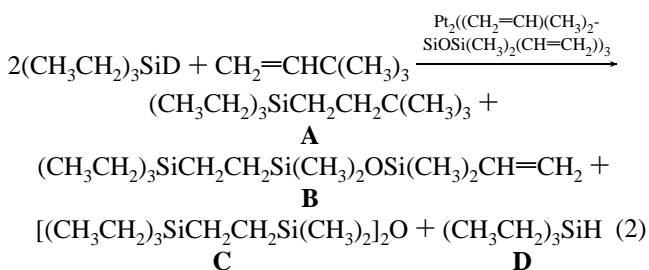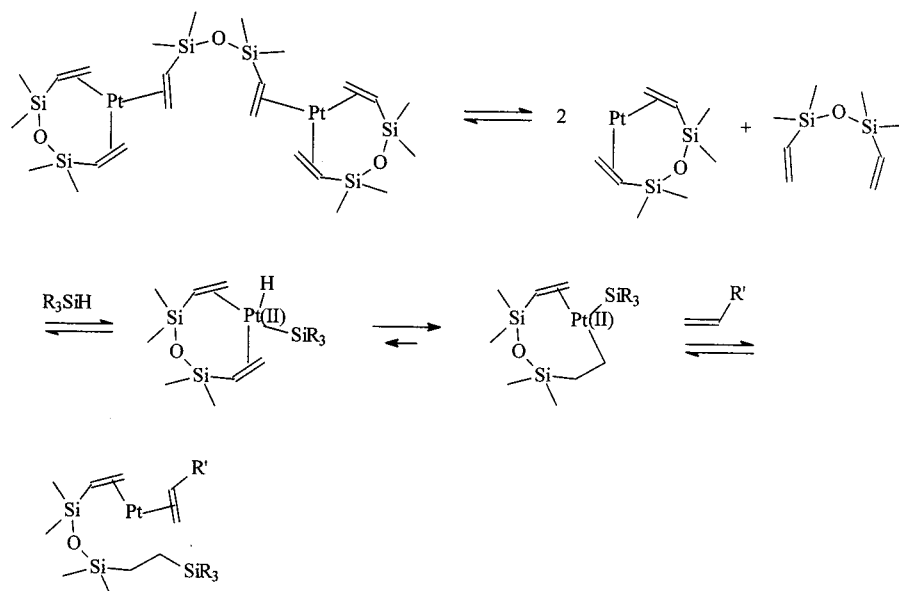

$Pt_2(M^{vinyl}M^{vinyl})_3$

In an individual experiment, an equimolar amount of methylbis(trimethylsiloxy)silane (MD^{H}M) and an olefin were reacted, and the rate of reaction was obtained. The reactivity followed the following order: hexenylmethylbis(trimethylsiloxy)silane (MD^{hexenyl}M) > vinylmethylbis(trimethylsiloxy)silane (MD^{vinyl}M) ≈ vinylpentamethyldisiloxane (M^{vinyl}M) > divinyltetramethyldisiloxane (M^{vinyl}M^{vinyl}). The observed order corresponded to the order predicted on the basis of the electron-donating ability of the group attached to the vinyl group.[27]

However, the results were reversed in a competitive experiment in which two olefins at equimolar concentration were reacted with one molar concentration of hydrosilane. The olefin which can coordinate most strongly is hydrosilylated preferentially and at a rate which is analogous to the rate obtained in the individual case described above: divinyltetramethyldisiloxane (M^{vinyl}M^{vinyl}) > vinylpentamethyldisiloxane (M^{vinyl}M) > vinylmethylbis(trimethylsiloxy)silane (MD^{vinyl}M) > hexenylbis(trimethylsiloxy)silane (MD^{hexenyl}M) > vinyltris(trimethysiloxy)silane (M$_3$T^{vinyl}).

These results suggest that, during the induction period, the divinyltetramethydisiloxane (M^{vinyl}M^{vinyl}) ligand in the starting Karstedt's precatalyst must undergo hydrosilylation or exchange of ligands prior to hydrosilylation of the added olefin. Consistent with these steps as part of the induction period are the results of deuterium incorporation into the divinyltetramethyldisiloxane (M^{vinyl}M^{vinyl}) ligands and other olefins present in the hydrosilylation reaction when a deuterated silane source is used, eq 2.

$$2(CH_3CH_2)_3SiD + CH_2=CHC(CH_3)_3 \xrightarrow{Pt_2((CH_2=CH)(CH_3)_2\text{-}SiOSi(CH_3)_2(CH=CH_2))_3}$$

$$(CH_3CH_2)_3SiCH_2CH_2C(CH_3)_3 +$$
$$\mathbf{A}$$
$$(CH_3CH_2)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH=CH_2 +$$
$$\mathbf{B}$$
$$[(CH_3CH_2)_3SiCH_2CH_2Si(CH_3)_2]_2O + (CH_3CH_2)_3SiH \quad (2)$$
$$\mathbf{C} \qquad\qquad\qquad \mathbf{D}$$

Figure 1. Induction period for hydrosilylation using platinum(0) precatalysts.

The amount of deuterium incorporation into **A** is between 0 and 1, whereas the amount of deuterium incorporation into **B** and **C** is much greater than 1. There was no observed incorporation of deuterium into the alkyl groups in **D**. The high level of deuterium incorporation into **B** and **C** can only be explained by the reactions in eq 3, a series of hydrosilylation and exchange reactions. A set of similar exchange processes has been reported by Pregosin[17] for hydrosilylation of styrene with triethylsilane using Pt(styrene)$_3$.
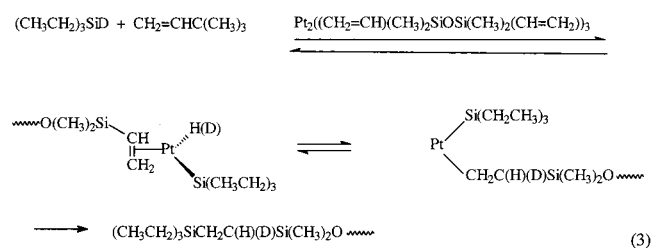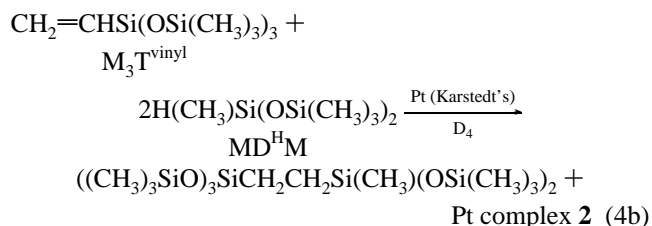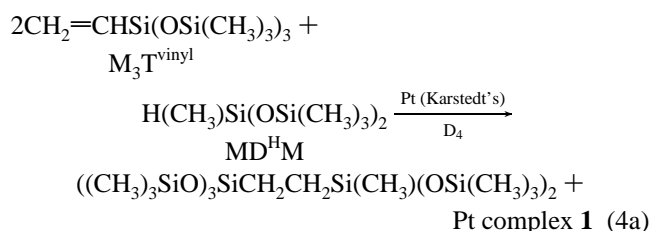

Thus, during the induction period a series of exchange and hydrosilylation processes occur to give rise to the active catalyst (Figure 1). A shorter induction period is seen with Pt(0) precatalysts compared with $K_2Pt(Cl)_4$ or other higher oxidation state platinum precatalysts because they do not need to undergo reduction prior to ligand exchange or hydrosilylation.

The Catalytic Cycle. It is known that mercury selectively alloys with heterogeneous, bulk metal-like materials and renders them inactive for catalytic reactions. Lewis had originally reported that the hydrosilylation reaction using platinum catalysts was suppressed in the presence of mercury.[10] Repetition of these experiments showed that mercury *did not* inhibit hydrosilylation. The discrepancy in these results can be explained as follows. In the original experiments, the platinum complex was contacted with the mercury for 7 h prior to introduction of the reagents. In the second case, the mercury was added to the reagents followed by addition of the platinum complex. In a model

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experiment, Karstedt's precatalyst was stirred with mercury in hexamethyldisiloxane (MM) for 7 h; the solution was then decanted from the mercury and analyzed for platinum by atomic absorption spectroscopy. No platinum was detected in the solution, indicating that the mercury caused decomposition and precipitation of the platinum complex. Therefore, in the original experiments, no active platinum would remain in the solution to catalyze hydrosilylation. The lack of inhibition in the repeated experiments is evidence for catalysis via a homogeneous route.[28,29]

Small-angle X-ray scattering (SAXS) was used to determine if large clusters or colloids were detectable during hydrosilylation. Whereas the reaction product of chloroplatinic acid and excess triethoxysilane contained 20 Å particles (confirmed by TEM), there was no scattering from solutions containing Karstedt's catalyst *during* hydrosilylation.[30]

Hydrosilylation reactions with different stoichiometric ratios of hydrosilane and olefin (eqs 4a,b) were monitored by UV−

$$2CH_2{=}CHSi(OSi(CH_3)_3)_3 +$$
$$M_3T^{vinyl}$$
$$H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4]{Pt\ (Karstedt's)}$$
$$MD^HM$$
$$((CH_3)_3SiO)_3SiCH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 +$$
$$Pt\ complex\ \textbf{1}\ \ (4a)$$

$$CH_2{=}CHSi(OSi(CH_3)_3)_3 +$$
$$M_3T^{vinyl}$$
$$2H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4]{Pt\ (Karstedt's)}$$
$$MD^HM$$
$$((CH_3)_3SiO)_3SiCH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 +$$
$$Pt\ complex\ \textbf{2}\ \ (4b)$$

visible (UV−vis) spectroscopy (Figures 2 and 3, respectively). Pt complexes **1** and **2** are described below. The UV−vis spectrum of the initial Karstedt's precatalyst is essentially featureless except for an absorption tail extending into the visible region. However, during catalysis, the UV−vis spectrum contains a peak with a maximum intensity at 370 nm regardless
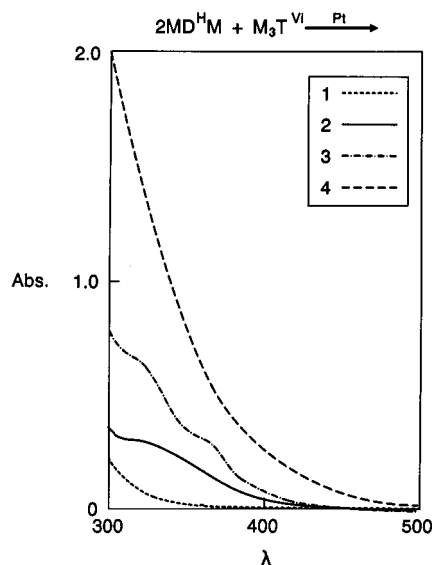
Figure 2. Reaction of 2:1 M_3T^{vi} with MD^HM (eq 4a) monitored by UV−vis spectroscopy. Trace 1 was taken immediately after addition of platinum catalyst, trace 2 was taken during the induction period, trace 3 was measured during the catalytic part of the reaction, and trace 4 was taken at the end of the reaction.

Figure 3. Reaction of 1:2 M_3T^{vi} with MD^HM (eq 4b) monitored by UV−vis spectroscopy. Trace 1 was taken immediately after addition of platinum catalyst, trace 2 was taken during the induction period, trace 3 was measured during the catalytic part of the reaction, and trace 4 was taken at the end of the reaction.
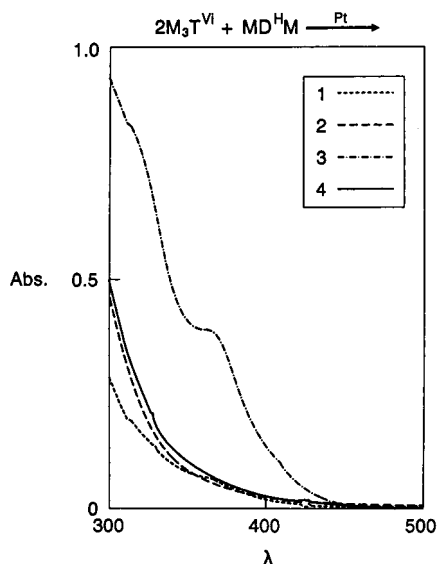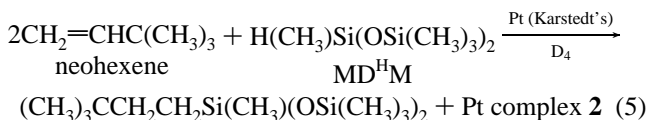
of the initial ratio of hydrosilane to olefin. The UV−vis spectral results imply a common catalyst for hydrosilylation which is independent of the stoichiometry of reagents. The spectrum at the end of the hydrosilylation reaction does depend on the initial ratio of hydrosilane to vinylsilane. With excess olefin, the final spectrum is analogous to that of the starting material, whereas

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with excess hydrosilane, the final spectrum exhibits a highly absorbing tail which extends into the visible region and may result from scattering from small particles (vide infra).

In situ EXAFS analysis of solutions during catalysis was obtained with strongly coordinating olefins at stoichiometric excesses of both hydrosilane and vinylsilane, eqs 4a,b. In addition, EXAFS analysis was obtained during catalysis for the solution from the reaction of an excess of a poorly coordinating olefin and hydrosilane, eq 5. We determined the time period

$$2CH_2=CHC(CH_3)_3 + H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4]{Pt\ (Karstedt's)}$$

$$\text{neohexene} \qquad\qquad MD^HM$$

$$(CH_3)_3CCH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 + Pt\ complex\ \mathbf{2}\ \ (5)$$

during which catalysis was occurring most rapidly using gas chromatography analysis. We then repeated each reaction and froze the solutions in liquid nitrogen during the most active portion of the catalytic cycle and analyzed the frozen samples by EXAFS spectroscopy. The EXAFS analysis of the solutions from eqs 4 and 5 showed the presence of Pt−C (2.18 Å) and Pt−Si (2.32 Å) bonds with a ratio of Pt−C to Pt−Si of about 3:1 and no Pt−Pt bonds. Thus, the bulk of the platinum exists as a mononuclear species during the hydrosilylation reaction regardless of the nature of reagents or stoichiometry.

We were also able to trap the platinum catalyst in a three-dimensional glass prepared from the reaction of tetramethyltetravinylcyclotetrasiloxane (D_4^{vinyl}) and tetramethylcyclotetrasiloxane (D_4^H). The reaction was performed with either a 2-fold excess of vinylsilane or a 2-fold excess of hydrosilane. XRD analysis indicated that the glass from eq 6 was amorphous.
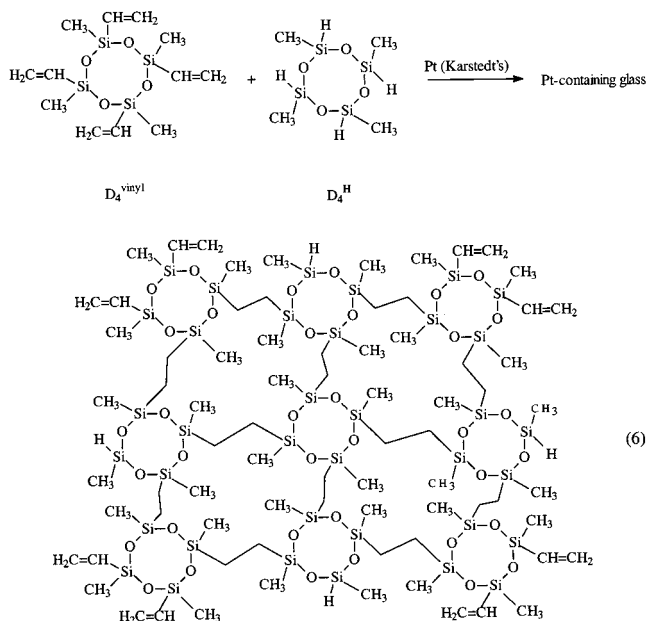
EXAFS analysis of the glass from eq 6 showed that the trapped platinum species contained only Pt−C and Pt−Si bonds regardless of the ratio of vinylsilane to hydrosilane and was analogous to that obtained for the platinum compositions of the reactions in eqs 4a,b. XPS analysis of the glass product from eq 6 gave a Pt ($4f_{7/2}$) binding energy of 73.1 eV, whereas Karstedt's precatalyst had a Pt ($4f_{7/2}$) binding energy of 72.4 eV, which suggests that the trapped Pt catalyst is in the +2 oxidation state.[30]
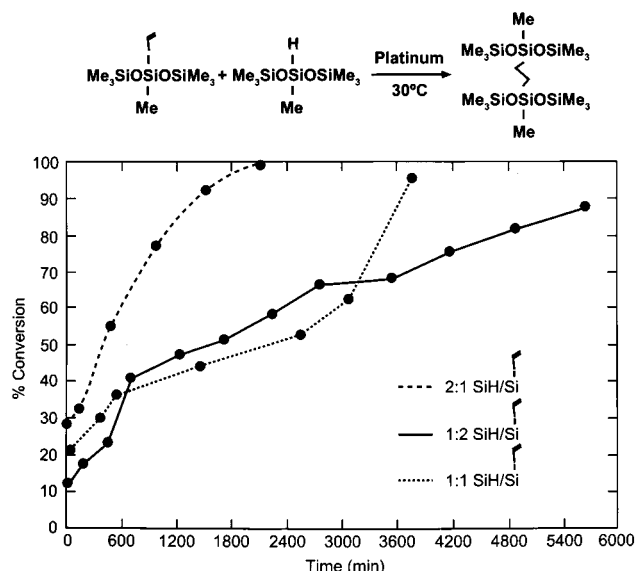
Figure 4. Reaction of MD^{vi}M with MD^{H}M at different stoichiometries (2:1, eq 7a; 1:2, eq 7b; 1:1, eq 7c) monitored by gas chromatography.
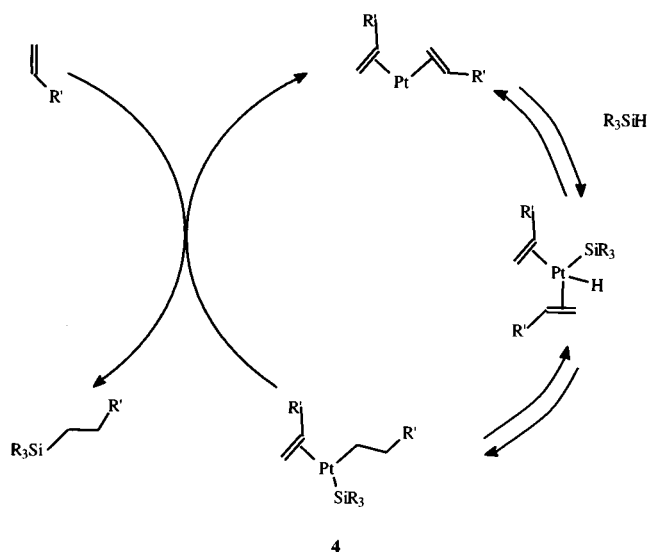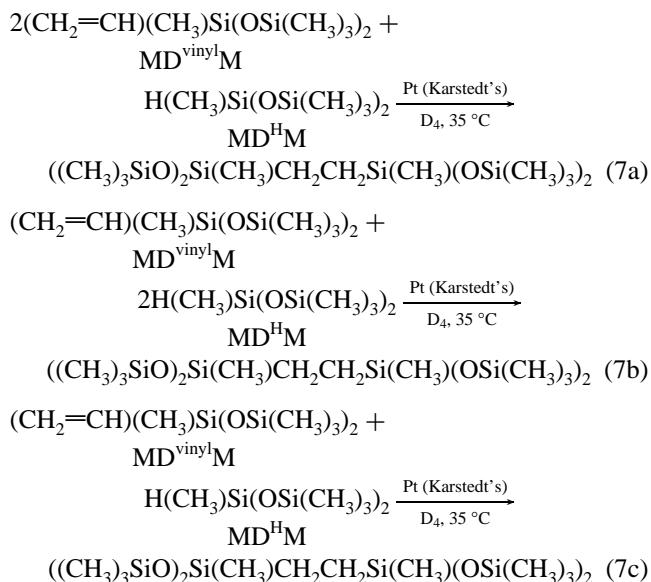

Figure 5. Catalytic cycle of the hydrosilylation reaction.

Although only preliminary kinetic experiments have been performed on these systems (Figure 4), a number of trends are evident. With a stoichiometric excess of hydrosilane (eqs 7a–c), there is a definite rate increase consistent with a positive dependence of the rate on hydrosilane concentration and an inverse dependence on olefin concentration.

Previous kinetic studies on hydrosilylation by Pregosin[18] and others[19–21] were performed with aliphatic and aromatic olefins whose binding to platinum is significantly weaker than that of the silicon olefin reagents used in the present study.[25,31] Pregosin[18] showed that the hydrosilylation reaction was first order in platinum and zero order in olefin and hydrosilane. The origin of the difference between our work and Pregosin's may be attributed to the stronger binding ability of the olefins used in our study.

The kinetic isotope effect for the reaction of equimolar amounts of bis(trimethylsiloxy)silane (MD^{H}M) with vinyltris-

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$$2(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 +$$
$$MD^{vinyl}M$$
$$H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4,\ 35\ °C]{Pt\ (Karstedt's)}$$
$$MD^HM$$
$$((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 \quad (7a)$$

$$(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 +$$
$$MD^{vinyl}M$$
$$2H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4,\ 35\ °C]{Pt\ (Karstedt's)}$$
$$MD^HM$$
$$((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 \quad (7b)$$

$$(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 +$$
$$MD^{vinyl}M$$
$$H(CH_3)Si(OSi(CH_3)_3)_2 \xrightarrow[D_4,\ 35\ °C]{Pt\ (Karstedt's)}$$
$$MD^HM$$
$$((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)(OSi(CH_3)_3)_2 \quad (7c)$$

(trimethylsiloxy)silane (M$_3$T^{vinyl}) was compared to the reaction in which MD^{H}M was replaced by the deuteriosilane, MD^{D}M. The ratio of the rate constants for deuteriosilane vs hydrosilane was 1.8, which suggests that bond breaking occurs prior to or during the rate-determining step and is consistent with a nonlinear transition state.
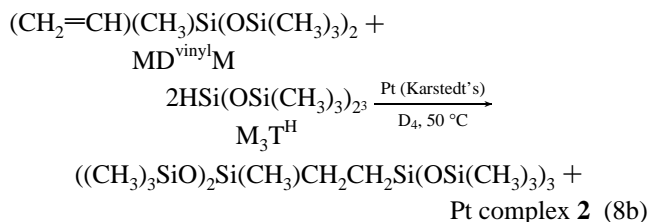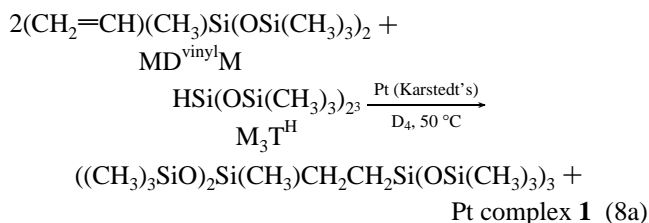
Electronic and steric effects have also been determined for the reactants in hydrosilylation reactions using Karstedt's precatalyst. As reported previously,[11,14,27] electron-donating groups on the olefin increase the rate, electron-withdrawing groups on the hydrosilane increase the rate, and strongly coordinating olefins also decrease the rate. However, steric effects cannot be ignored. On the basis of the amount of positive charge on the silicon atom, the following order of reactivity for the silicone hydride compounds would be predicted: pentamethyldisiloxane (MM^H) < methylbis(trimethylsiloxy)-silane (MD^{H}M) < tris(trimethylsiloxy)silane (M$_3$T^H). However, the order is reversed, which indicates that steric control is extremely important in the hydrosilylation reaction.[27]

The proposed catalytic cycle for hydrosilylation using Karstedt's precatalyst is depicted in Figure 5. The cycle is comprised of elementary steps well-known in organometallic chemistry and is reminiscent of the mechanism proposed by Chalk and Harrod.[8] Dissociation of a ligand occurs to produce a vacant coordination site followed by oxidative addition of the hydrosilane species. Migratory insertion of the olefin into the Pt–H bond then occurs, followed by reductive elimination. Reversible migratory insertion into the Pt–H bond rather than the Pt–Si bond is consistent with the deuterium exchange reactions (vide supra) and with the absence of vinylsilane products. The rate-determining step must be either migratory insertion or reductive elimination and is likely to be reductive elimination on the basis of the irreversibility of that step.

Pt-Containing End Products of the Hydrosilylation Reaction with Karstedt's Precatalyst. The compositions of the platinum end products of the hydrosilylation reaction using Karstedt's precatalyst were determined by EXAFS spectroscopy. EXAFS analysis was performed on solutions in which different stoichiometric ratios of hydrosilane and vinylsilane had been employed. For example, vinylbis(trimethylsiloxy)silane (MD^{vinyl}M) was reacted with tris(trimethylsiloxy)silane (M$_3$T^H)
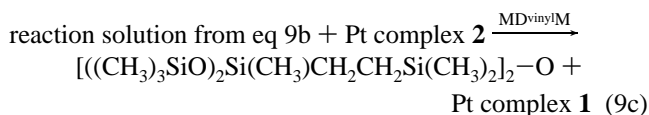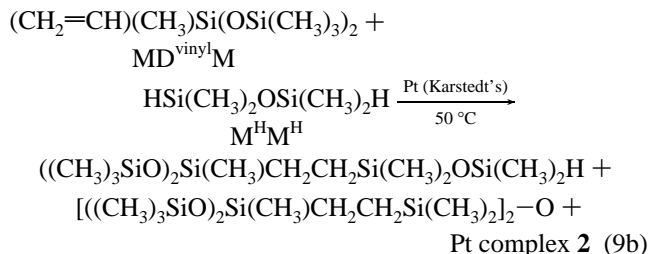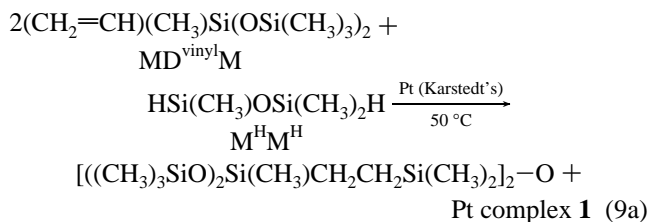
at ratios of 2:1 and 1:2 (eqs 8a,b, respectively). In the presence

$$2(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 + \\ MD^{vinyl}M \\ HSi(OSi(CH_3)_3)_{23} \xrightarrow[D_4, 50\,°C]{Pt\,(Karstedt's)} \\ M_3T^H \\ ((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(OSi(CH_3)_3)_3 + \\ Pt\ complex\ \mathbf{1}\ \ (8a)$$

$$(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 + \\ MD^{vinyl}M \\ 2HSi(OSi(CH_3)_3)_{23} \xrightarrow[D_4, 50\,°C]{Pt\,(Karstedt's)} \\ M_3T^H \\ ((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(OSi(CH_3)_3)_3 + \\ Pt\ complex\ \mathbf{2}\ \ (8b)$$

of excess olefin, the platinum species at the end of the hydrosilylation reaction contained only Pt−C bonds at a distance of 2.18 Å analogous to the starting Karstedt precatalyst. However, in the presence of excess hydrosilane, the platinum species contained Pt−Si bonds at a distance of 2.30 Å and Pt−Pt bonds at a distance of 2.75 Å. Thus, hydrosilylation in the presence of excess olefin yields a platinum product in an olefin rich environment (complex **1**) and in the presence of excess hydrosilane yields platinum in a platinum and silicon rich environment (complex **2**).

In a second experiment, tetramethyldisiloxane (M^HM^H) was reacted with vinylmethylbis(trimethylsiloxy)siloxane (MD^vinyl^M) with either an equimolar ratio of olefin and hydrosilane or a 2-fold excess of hydrosilane to olefin. The Pt EXAFS spectrum of the solution from eq 9a (Figure 6a) was nearly identical to that found for Karstedt's precatalyst, and solved for Pt−C at 2.17 Å (Figure 6b). Pt EXAFS analysis of the solution from eq 9b showed an equal ratio of Pt−Si bonds at 2.35 Å and Pt−Pt bonds at 2.85 Å (Figure 6c). The brown reaction solution from eq 9b was analyzed by gas chromatography, and complete consumption of the MD^vinyl^M reagent was confirmed. A second equivalent of MD^vinyl^M was then added to the solution (eq 9c),

$$2(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 + \\ MD^{vinyl}M \\ HSi(CH_3)OSi(CH_3)_2H \xrightarrow[50\,°C]{Pt\,(Karstedt's)} \\ M^HM^H \\ [((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2]_2-O + \\ Pt\ complex\ \mathbf{1}\ \ (9a)$$

$$(CH_2=CH)(CH_3)Si(OSi(CH_3)_3)_2 + \\ MD^{vinyl}M \\ HSi(CH_3)_2OSi(CH_3)_2H \xrightarrow[50\,°C]{Pt\,(Karstedt's)} \\ M^HM^H \\ ((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2OSi(CH_3)_2H + \\ [((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2]_2-O + \\ Pt\ complex\ \mathbf{2}\ \ (9b)$$

$$\text{reaction solution from eq 9b} + \text{Pt complex } \mathbf{2} \xrightarrow{MD^{vinyl}M} \\ [((CH_3)_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2]_2-O + \\ Pt\ complex\ \mathbf{1}\ \ (9c)$$

which resulted in loss of the brown color and a change in the
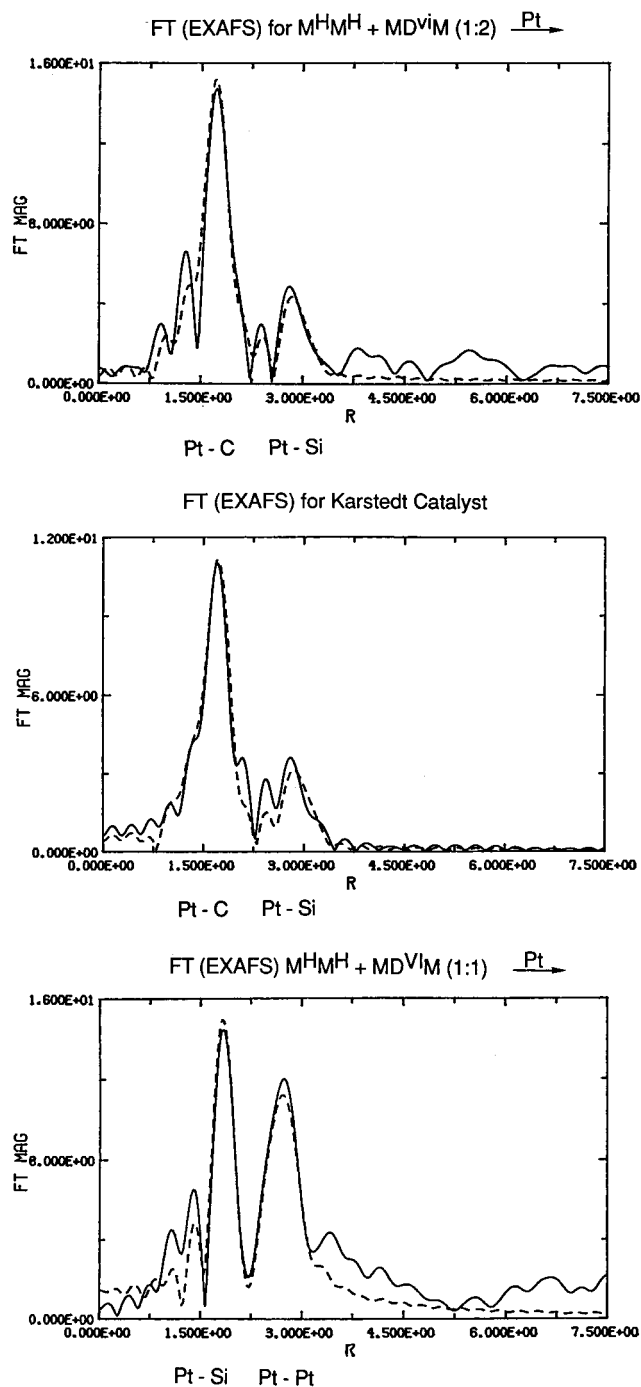
Figure 6. (a, top) Fourier transform of platinum EXAFS for the reaction solution from eq 9a, 2MD^vi^M + M^HM^H in D_4 in the presence of Karstedt's precatalyst, showing Pt−C in the first coordination sphere and second-shell Pt−Si peaks. (b, middle) Fourier transform of platinum EXAFS for Karstedt's precatalyst solution showing Pt−C and second-shell Pt−Si peaks. (c, bottom) Fourier transform of platinum EXAFS the reaction solution from eq 9b, MD^vi^M + M^HM^H in D_4 in the presence of Karstedt's precatalyst, showing Pt−Si and Pt−Pt peaks.

Pt EXAFS spectrum to one resembling that found in eq 9a, namely, a species giving rise to Pt−C peaks at 2.16 Å and no first shell Pt−Si or Pt−Pt bonds. Thus, addition of a strongly coordinating olefin to a solution containing complex **2** resulted in the formation of complex **1**. The two platinum species interconvert most likely through the catalytically active mononuclear platinum species.

Very different results were obtained with poorly coordinating olefins such as hexene (eq 10a) or neohexene (eq 10b). With

both of these olefins, regardless of the stoichiometry of olefin to hydrosilane, the platinum end product contained Pt—Pt and Pt—Si bonds (Pt complex **2**). Thus, poorly coordinating olefins yield a multinuclear platinum end product with silicon ligands completing the coordination sphere.

$$Et_3SiH + H_2C=CHCH_2CH_2CH_2CH_3 \xrightarrow{Pt}$$
$$Et_3SiCH_2CH_2CH_2CH_2CH_2CH_3 + Pt\ complex\ \mathbf{2}\ \ (10a)$$

$$Et_3SiH + H_2C=CHC(CH_3)_3 \xrightarrow{Pt}$$
$$Et_3SiCH_2CH_2C(CH_3)_3 + Pt\ complex\ \mathbf{2}\ \ (10b)$$
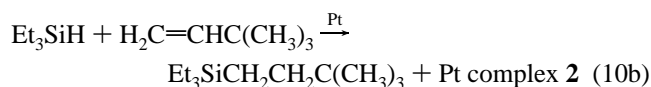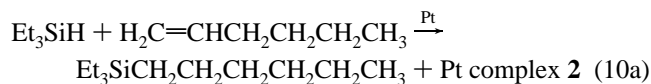
Platinum-Containing End Products of the Hydrosilylation Reaction Using Speier's Catalyst. Speier's catalyst prepared from chloroplatinic acid and 2-propanol is also used industrially as a hydrosilylation catalyst. This platinum(IV) complex shows a much longer induction period than Karstedt's precatalyst. EXAFS analysis of H_2PtCl_6 in 2-propanol showed primarily Pt—Cl bonds at 2.31 Å. However, Pt EXAFS analysis of the platinum products at the end of hydrosilylation with Speier's catalyst shows that they are identical with those obtained using Karstedt's catalyst. The reaction of eq 5 was repeated except that Speier's catalyst was used in place of Karstedt's precatalyst. At the end of the reaction, Pt EXAFS analysis showed that the Pt species contained Pt—Si at 2.25 Å and Pt—Pt at 2.83 Å. In a second experiment, equimolar amounts of tris(trimethylsiloxy)silane (M_3T^H) and vinylmethylbis(trimethylsiloxy)silane ($MD^{vinyl}M$) were reacted in the presence of H_2PtCl_6/2-propanol in octamethylcyclotetrasiloxane (D_4). Pt EXAFS analysis of the resultant solution was identical to that obtained for Karstedt's precatalyst solution, namely, Pt—C bonds in the first coordination shell around platinum. Thus, the platinum products of hydrosilylation are the same regardless of the nature of the starting platinum precatalyst. These results also suggest that both Pt(0) and Pt(IV) starting materials catalyze the hydrosilylation reaction through a series of identical steps.

Structure/Size of Pt Nanoparticles Formed at the End of the Hydrosilylation Reaction. None of the platinum products present at the end of the hydrosilylation reaction showed second-shell Pt—Pt peaks in the EXAFS spectrum. Originally we concluded that the end product at high hydrosilane concentration or with poorly coordinating olefins was a tetramer, due to the absence of second-shell platinum and a Pt to Si ratio of 1:1. However, EXAFS analysis of a citrate-stabilized colloid[16,32] also showed no second-shell platinum. Small-angle X-ray scattering (SAXS) confirmed that the citrate-stabilized platinum colloid had particles with a radius of gyration (R_g) of 24 Å. Therefore, the absence of second-shell platinum peaks in an EXAFS spectrum is *not conclusive* evidence that nanoparticles are not present in solution.

Formation and growth of platinum nanoparticles from reacted solutions of neohexene with methylbis(trimethylsiloxy)silane (as in eq 5) were monitored using SAXS over a period of 22 h (Figure 7). The amount of scattering increased with time for 3 h after the reaction was complete, and then remained constant for the remainder of the 22 h period during which SAXS data
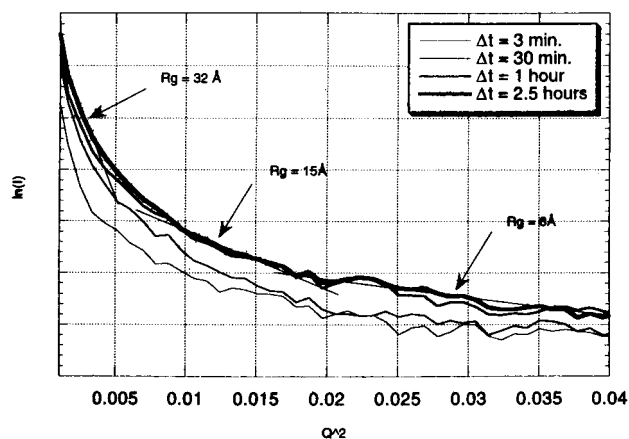

Figure 7. Small-angle X-ray scattering (SAXS) of the reaction mixture of neohexene with methylbis(trimethylsiloxy)silane (MD^{H}M) immediately after complete reaction and until 22 h later.

were collected. Using Gunier analysis, a continuum of particle sizes was calculated which ranged from $R_g = 32$ Å to $R_g = 8$ Å.

Bradley and co-workers[33−37] have shown that nanoparticles can be trapped with carbon monoxide and their size range determined by infrared spectroscopy (IR). These workers have observed an increase in the amount of terminal carbonyl over bridging carbonyl groups with decreasing particle size and have attributed this difference to the ratio of edge sites to face sites increasing with decreasing particle size. The platinum end product from the reaction of 2 equiv of methylbis(trimethylsiloxy)silane (MD^{H}M) with vinylmethylbis(trimethylsiloxy)silane (MD^{vinyl}M) was immediately trapped with carbon monoxide, and the IR spectrum indicated that the platinum complex contained only terminal carbonyls. However, if the reaction mixture was allowed to age for 24 h prior to the addition of carbon monoxide, both bridging and terminal carbonyls were present, suggesting nanoparticle growth during the aging period.[38]

Transmission electron microscopy (TEM) of *evaporated* solutions with high hydrosilane-to-olefin ratios showed the presence of colloidal species. Interestingly, we have now found that even under conditions of high olefin concentration where it is known that the end product is mononuclear, evaporation leads to the formation of colloids! The solutions from the reactions in eqs 8a,b were evaporated and analyzed by high-resolution electron microscopy which showed the presence of platinum crystallites in both cases. The platinum crystallites from eq 8a (excess olefin) were 40 Å (Figure 8a), whereas the particles formed from evaporation in eq 8b (excess hydrosilane) were 25 Å (Figure 8b). The origin of the difference in size is not known.

The Oxygen Effect. The oxygen effect was first noted by Chalk and Harrod who reported that triethoxysilane and 1-alkenes did not react in the absence of air but reacted vigorously upon exposure to air using chloroplatinic acid as the catalyst. They hypothesized that the role of oxygen was to introduce a new oxygen-containing ligand into the coordination sphere of the metal with concurrent loss of chloride ion.[8,39]

(32) Bruno, G. C. *J. Chem. Soc., Faraday Trans.* **1956**, *52*, 1235.

(33) Amiens, C.; deCaro, D.; Chaudret, B.; Bradley, J. S.; Mazel, R.; Roucau, C. *J. Am. Chem. Soc.* **1993**, *115*, 11638.

(34) Bradley, J. S.; Hill, E. W.; Chaudret, B.; Duteil, A. *Langmuir* **1995**, *11*, 693.

(35) Bradley, J. S.; Millar, J.; Hill, E. W.; Behal, S. *J. Catal.* **1991**, *129*, 530.

(36) Bradley, J. S.; Hill, E. W. *Chem. Mater.* **1992**, *4*, 1234.

(37) Bradley, J. S.; Via, G. H.; Bonneviot, L.; Hill, E. W. *Chem. Mater.* **1996**, *8*, 1895.

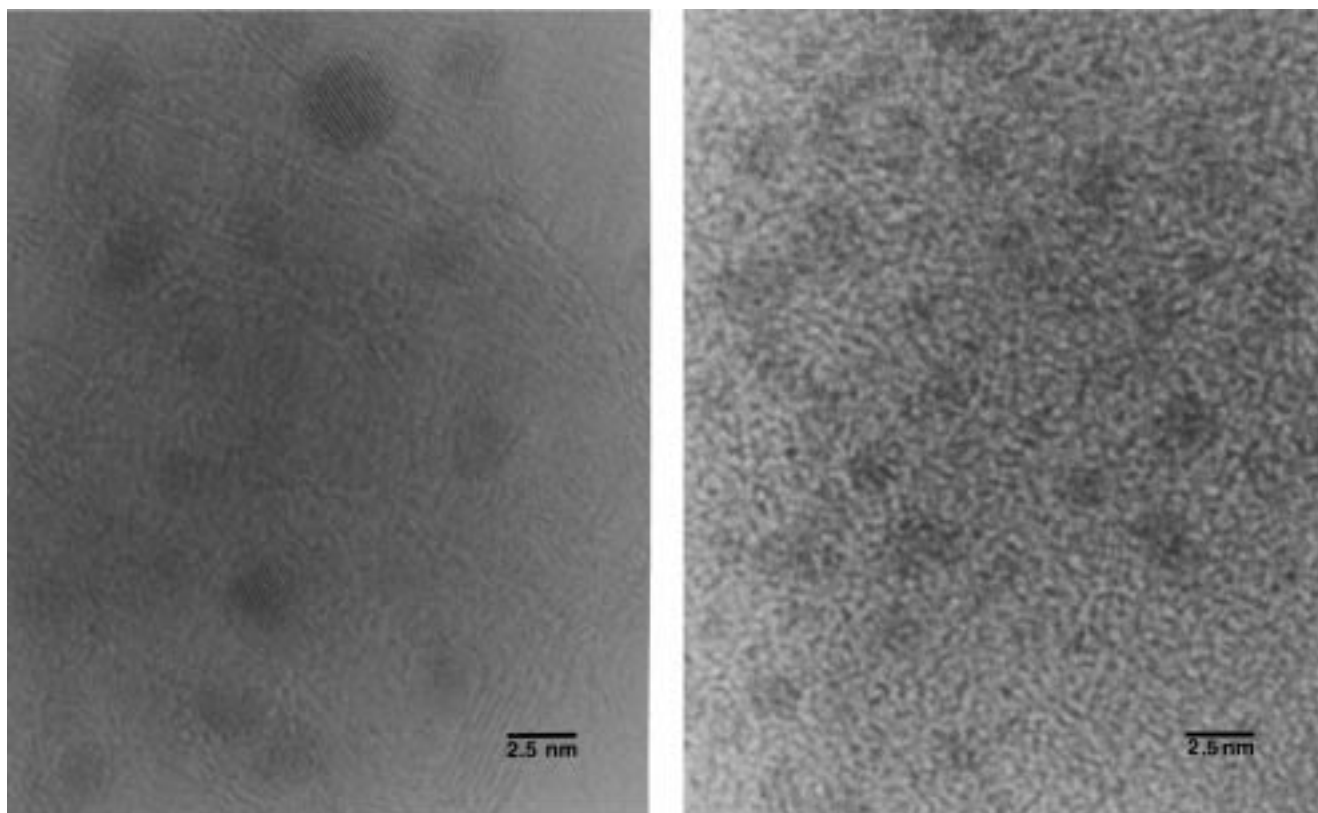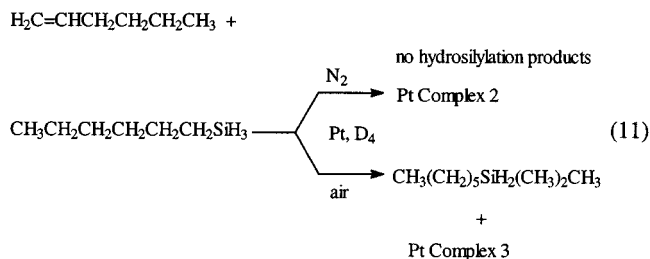(38) Lewis, L. N.; Stein, J. Manuscript in preparation.

Figure 8. (a, left) High-resolution transmission electron micrograph for the evaporated solutions from the reaction of 2MD^{vinyl}M with M$_3$T^H in D$_4$ catalyzed by Karstedt's precatalyst (eq 8a). Note platinum crystallites with diffraction fringes. (b, right) High-resolution TEM for the evaporated solution from the reaction of 2M$_3$T^H with MD^{vinyl}M in D$_4$ catalyzed by Karstedt's precatalyst (eq 8b). Note the smaller size of the platinum crystallites vs those in (a).

Lewis later suggested that oxygen prevented irreversible colloid agglomeration and made the silylated colloid species more prone to nucleophilic attack by olefin.[11] Onopchenko and Sabourin reported that spent catalyst in the synthesis of tetraalkylsilanes via hydrosilylation could be regenerated by air saturation but too much air resulted in siloxane formation.[40] Last, Kleyer disclosed that the hydrosilylation reaction could be controlled by the amount of oxygen in the reaction mixture.[41]

To verify the oxygen effect, 1-hexene was reacted with hexylsilane in the presence of Karstedt's precatalyst under both aerobic and anaerobic conditions (eq 11).[14] In the absence of

$$H_2C=CHCH_2CH_2CH_2CH_3 \ +$$

$$CH_3CH_2CH_2CH_2CH_2CH_2SiH_3 \begin{array}{c} \xrightarrow{N_2} \text{no hydrosilylation products} \\ \text{Pt Complex 2} \\ \xrightarrow{Pt,\ D_4} \\ \xrightarrow{air} CH_3(CH_2)_5SiH_2(CH_3)_2CH_3 \\ + \\ \text{Pt Complex 3} \end{array} \quad (11)$$
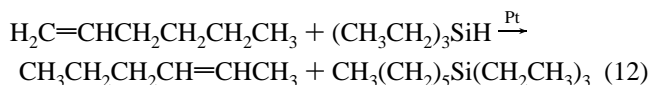
air, no reaction was observed after the reaction was allowed to reflux for 30 min. However, reaction did occur when the solution was allowed to reflux in air for 30 min, indicating that, with poorly coordinating olefinic substrates, oxygen is necessary for

hydrosilylation. The identity of the platinum species present in the above solutions was determined using EXAFS analysis.

The platinum species present after heating hexylsilane with hexene in the presence of Karstedt's precatalyst under N$_2$ contained the Pt−Pt and Pt−Si bonds described earlier for Pt complex **2**. Therefore, multinuclear platinum species were formed under the reaction condiitons of eq 11. However, if reaction of eq 11 is performed in air, a monomeric platinum species forms which contains only Pt−Si bonds. The results from eq 12 indicate that one role of oxygen in these systems is the prevention and/or destruction of multinuclear platinum species.

Alkene Isomerization. Migration of the double bond in a terminal olefin is a frequent (nuisance) reaction in the hydrosilylation of 1-alkenes. The olefin rearrangement frequently occurs when less active hydrosilanes such as trialkylsilanes are employed in the hydrosilylation reaction, eq 12.

$$H_2C=CHCH_2CH_2CH_2CH_3 + (CH_3CH_2)_3SiH \xrightarrow{Pt}$$
$$CH_3CH_2CH_2CH=CHCH_3 + CH_3(CH_2)_5Si(CH_2CH_3)_3 \ (12)$$

The internal olefins thus produced do not typically undergo hydrosilylation. Analysis by EXAFS spectroscopy of solutions during isomerization shows the presence of multinuclear platinum species with Pt−Pt and Pt−Si bonds. The multinuclear platinum species persist after isomerization and do not catalyze hydrosilylation of internal olefins.

Apparently both alkene isomerization and the oxygen effect are related to the presence of multinuclear platinum species. In both cases, these multinuclear species do not catalyze hydrosi-

(39) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.
(40) Onopchenko, A.; Sabourin, E. T. *J. Org. Chem.* **1987**, *52*, 4118.
(41) Kleyer, D. L.; Nguyen, B. T.; Hauenstein, D. E.; Davern, S. P.; Schultz, W. J. U.S. Patent 5,359,111, 1994.
(42) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.
(43) Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308.
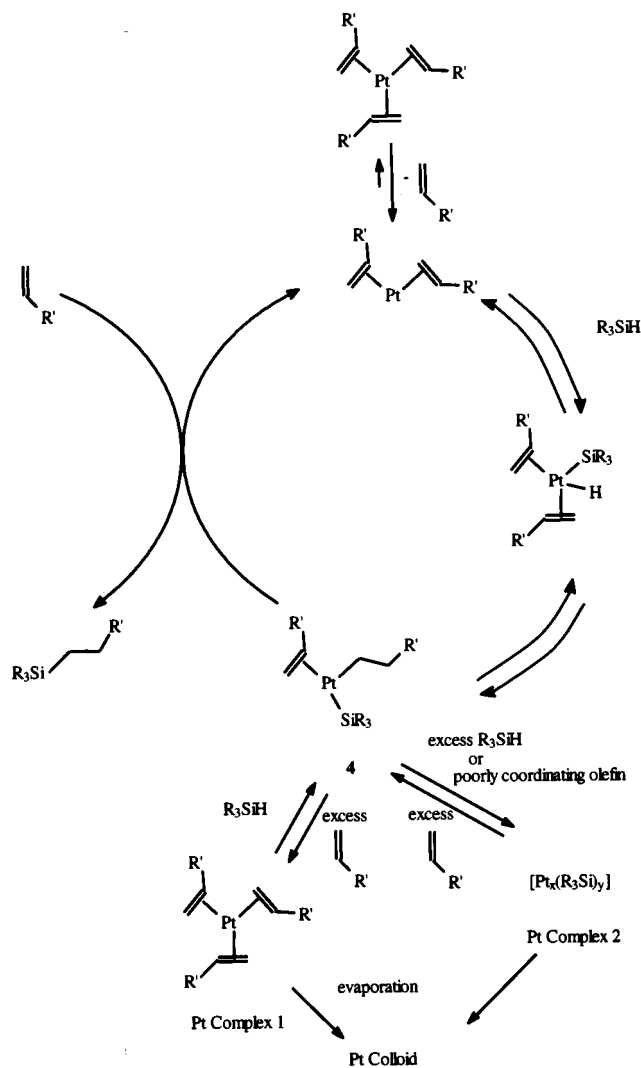
Figure 9. Overall reaction mechanism for hydrosilylation catalyzed by Karstedt's precatalyst.

lylation, which supports the premise that catalysis occurs via a mononuclear, homogeneous pathway and that the multinuclear platinum species are end products.

Mechanism Discussion. An overall reaction scheme is shown in Figure 9. During the induction period, the Pt(0) precatalyst undergoes dissociation of the bridging olefin to form a mononuclear, two-coordinate complex. Oxidative addition of R_3SiH leads to formation of a Pt(II) complex, which is followed by migratory insertion of the olefin into the Pt−H bonds. The reversibility of these steps is supported by the reaction with deuteriosilane in which high levels of deuterium were incorporated into the hydrosilylation products of $M^{vinyl}M^{vinyl}$. After hydrosilylation of the $M^{vinyl}M^{vinyl}$ ligand, which concludes the induction period, the catalytic cycle proceeds with the added olefin. Of course we cannot rule out that olefin exchange may also be occurring during the induction period.

Steps in the catalytic cycle are similar to those occurring during the induction period. Evidence in support of the catalytic cycle includes kinetic data which support a positive order in hydrosilane and an inverse dependence on olefin concentration. In situ EXAFS analysis indicates that the catalyst is mononuclear and contains Pt−C and Pt−Si bonds regardless of the stoichiometry of the reagents. The absence of vinylsilane products is consistent with migratory insertion of the olefin into the Pt−H

bond. The observed kinetic isotope effect suggests that Si−H bond breaking occurs prior or during the rate-determining step. The rate-determining step is most likely reductive elimination since no Pt−H bonds are observe by NMR or IR spectroscopies. We did not observe colloids under any conditions during catalysis. In fact colloids are only observed as an end product.

The platinum end products are dependent on the stoichiometry of the reagents. With high olefin concentration, a $Pt(olefin)_3$ complex is formed. Under conditions of high hydrosilane concentration, a multinuclear Pt cluster is formed with silyl ligands. The products can interconvert by addition of the appropriate reagent probably through the intermediacy of species **4**. Conditions that favor formation of Pt complex **2** (absence of oxygen with poor reagents for hydrosilylation, excess hydrosilane, and poorly coordinating olefins) can result in low conversion and olefin bond isomerization.

Experimental Section

General Procedures. Neohexene and hexene were purified by flash chromatography using activity I alumina followed by distillation. D_4, MD^HM, $MD^{vinyl}M$, and M_3T^{vinyl} were degassed using three freeze/degas/thaw cycles. All of the above reagents were stored in the glovebox over activated 4A molecular sieves. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl.

Reactions were carried out in air or under nitrogen employing Schlenk techniques or in a Vacuum Atmospheres drybox. ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6, on a GE QE-300 instrument at 300.15 and 75.48 MHz, respectively. In addition, ^{13}C, [2]D, ^{29}Si, and [195]Pt NMR spectra were recorded on a GE GN-Omega 500 NMR instrument at 125.8, 76.8, 76.77, and 107.512 MHz, respectively. ^{29}Si NMR spectra were recorded using 1% $Cr(acac)_3$ relaxation reagent and gated decoupling. IR spectra were obtained using a Mattson Instruments Model 6020 Galaxy Series FTIR. GC−MS data were obtained using a JEOL SX 102 high-resolution, double-focusing magnetic sector instrument with a 30 m DB 5 capillary column. UV−vis spectra were recorded on a Unicam Model UV3 spectrometer with 1 cm path length cells. XPS analysis was conducted on a Physical Electronics 5500 spectrometer, employing a monochromatic aluminum Kα X-ray excitation source. Survey scans were acquired using a fixed pass energy of 187 eV, and high-resolution scans of the individual core levels were acquired at a pass energy of 11.7 eV. TEM measurements were made as described previously.[15,16]

Polycarbonate EXAFS cells were 27.2 × 3.77 × 1.77 mm three-dimensional rectangles open at one face; the fourth face was sealed with Mylar tape. Liquid samples were added to the cell, covered with a polycarbonate cap, and then frozen in liquid nitrogen within 60 s. In cases in which a solid glass was formed, a 35 × 24 × 1.5 mm copper plate with a 32 × 4 mm slit was used as a sample holder. Mylar tape was applied to one face of the copper sample holder, liquid reagents were added to the cell, and the sample was allowed to cure to a hard glass which fit in the slit of the sample holder. EXAFS measurements and analyses were performed as described previously.[31]

In situ SAXS experiments were performed at the X3A2 beamline, NSLS, Brookhaven National Laboratory. A pinhole collimated X-ray beam at 1.54 Å with an approximate beam size of 1.0 mm was used, and the SAXS data were collected by a Fuji two-dimensional Image Plate system. The solution samples (olefin, platinum, and hydrosilane) were combined immediately for measurement and injected with a needle syringe in the sample chamber. The sample chamber was sealed with Kapton film on both sides for incident and scattered X-rays. Each measurement took 3 min, and a series of data sets were collected after completion of the reaction. The two-dimensional data were then integrated around the azimuthal angles and converted into one-dimensional data for further analysis.

The background SAXS scattering from the solution and primary incident beam was measured from a sample without Pt and then

subtracted to remove background scattering from all the data sets. In addition, all the data sets were normalized using the intensities in the high Q (or tail) region. To minimize the effects from incident beam intensity changes, all the measurements were taken within a single electron fill of the storage ring.

Dilute solutions were employed (typically $10^{-4}-10^{-5}$ M) in the SAXS experiments. We assumed that the Pt colloids had a spherical shape. The classical Guinier plot method was used to analyze the data, which showed that the colloids were polydispersed. The range of colloid sizes was obtained by fitting a straight line at three locations of the curve.

Synthesis of Et$_3$SiD. LiAlD$_4$ (512 g, 0.12 mmol) was combined with anhydrous diethyl ether (75 mL). Et$_3$SiCl (18 g, 0.119 mmol) in diethyl ether (20 mL) was slowly added to the LiAlD$_4$ mixture with stirring under nitrogen, and the mixture was allowed to stir for 14 h. The mixture was then added to 100 mL of ice containing 10% HCl, and the aqueous layer was extracted with three 100 mL aliquots of diethyl ether. The ether layer was dried with MgSO$_4$. Diethyl ether was removed by distillation (37 °C). Et$_3$SiD was collected at 106– 107 °C; cf. bp of Et$_3$SiH, 107–8 °C (Gelest Catalogue). ^{1}H NMR: δ 0.56 (q, 8 Hz), 0.96 (t, 8 Hz). IR: νSiD 1530 cm^{-1} calcd from the reduced mass equation from νSiH of Et$_3$SiH at 2100 cm^{-1}, 1512 cm^{-1}. GC–MS: 117 amu (M$^+$), 115 amu (M$^+$ – D), 88 amu (M$^+$ – C$_2$H$_5$).

Reaction of Et$_3$SiD with H$_2$C=CHC(CH$_3$)$_3$ in the Presence of Karstedt's Precatalyst. Et$_3$SiD (0.5 g, 4.25 mmol) was combined with H$_2$C=CHC(CH$_3$)$_3$ (0.0.17 g, 2.0 mmol) and Karstedt's precatalyst solution (0.115 g of a 5 wt % platinum solution in xylene, 0.033 mmol of Pt). IR analysis showed the disappearance of the peak at 1530 cm^{-1} with concomitant appearance of a peak at 2100 cm^{-1}. ^{2}H NMR: δ 0.75 (s), 1.0 (m). ^{29}Si NMR: δ 7.36, 16.8. The amount of deuterium in each of the products was determined by GC–MS.

Reaction of 2:1 M$_3$T^{vinyl} and MD^{H}M with Karstedt's Precatalyst. M$_3$T^{vinyl} (6.4 g, 19.9 mmol) was combined with MD^{H}M (2.22 g, 10 mmol) in a 25 mL volumetric flask which was then filled to volume with D$_4$. The reaction was initiated at ambient temperature by addition of Karstedt's precatalyst solution (0.034 g, 1.7 mg of Pt, 8.7 mmol of Pt). The reaction was monitored by GC and UV–vis spectroscopy. The EXAFS cell was filled and frozen 6 min after initiation. GC–MS analysis of the reaction mixture confirmed that ((CH$_3$)$_3$SiO)$_3$SiCH$_2$- CH$_2$Si(CH$_3$)(OSi(CH$_3$)$_3$)$_2$ was the major product on the basis of the observation of a small molecular ion peak at 544 amu and a large M$^+$ – CH$_3$ peak at 529 amu. Further proof of the product was obtained by exact mass spectral analysis of the aforementioned M$^+$ – CH$_3$ fragment, C$_{17}$H$_{49}$O$_5$Si$_7$ calcd 529.1965, found 529.1956.

Reaction of 1:2 M$_3$T^{vinyl} and MD^{H}M with Karstedt's Precatalyst. M$_3$T^{vinyl} (3.23 g, 10.0 mmol) was combined with MD^{H}M (4.44 g, 20 mmol) in a 25 mL volumetric flask which was then filled to volume with D$_4$. The reaction was initiated at ambient temperature by addition of Karstedt's precatalyst solution (0.034 g, 1.7 mg of Pt, 8.7 mmol of Pt). The reaction was monitored by GC and UV–vis spectroscopy. The EXAFS cell was filled and frozen 2 min after initiation.

Reaction of 2:1 Neohexene and MD^{H}M with Karstedt's Precatalyst, Eq 6. Neohexene (1.68 g, 20.0 mmol) was combined with MD^{H}M (2.22 g, 10 mmol) in a 25 mL volumetric flask which was then filled to volume with D$_4$. The reaction was initiated at ambient temperature by addition of Karstedt's precatalyst solution (0.034 g, 1.7 mg of Pt, 8.7 mmol of Pt), and the EXAFS cell was filled and frozen 2 min after initiation.

Reaction of 2:1 D$_4^{vinyl}$ and D$_4$H with Karstedt's Precatalyst, Eq 7. D$_4^{vinyl}$ (3 g, 34.9 mmol) was combined with D$_4$H (1.05 g, 17.5 mmol) in a glass vial in air, and then Karstedt's catalyst solution (0.0166 g, 0.83 mg Pt, 4.2 mmol Pt) was added. A portion of the solution was placed in the copper cell holder. A hard glass formed after 24 h at ambient temperature.

Reaction of 1:2 D$_4^{vinyl}$ and D$_4$H with Karstedt's Precatalyst, Eq 7. D$_4^{vinyl}$ (2.16 g, 25.1 mmol) was combined with D$_4$H (3.0 g, 50.0 mmol) in a glass vial in air, and then Karstedt's precatalyst solution

(0.021 g, 1.05 mg of Pt, 5.4 mmol of Pt) was added. The copper cell holder was filled rapidly, and a hard gel formed within 5 min. *WARNING*: *A violent exotherm was always noted upon addition of platinum, and the contents burst into flames in one case.*

Synthesis of MD^{D}M. The bis(trimethylsiloxy)methylsilyl deuteride was made from bis(trimethylsiloxy)methylsilyl chloride, MD^{Cl}M.

Synthesis of MD^{Cl}M. MD^{H}M (20 g, 90 mmol) was combined with CCl$_4$ (50 g, 325 mmol) and PdCl$_2$ (0.2 g, 1.1 mmol) under nitrogen in a two-necked round-bottom flask equipped with a stir bar, a reflux condenser, and a gas inlet. An exotherm was noted upon addition of PdCl$_2$. The contents of the flask were stirred and then allowed to reflux for 2 h. Analysis of the reaction by GC showed that 75% of the MD^{H}M was converted to a single, higher retention time product. An additional charge of PdCl$_2$ was added, and then reflux was allowed to continue until complete conversion of MD^{H}M to product had occurred (total time ca. 4 h). The CCl$_4$ was removed in vacuo, and the remaining liquid was distilled (45 °C, 0.1 mmHg) to give 23 g of a single product (GC analysis). The imputed MD^{Cl}M from above (10 g, 39 mmol) was combined with anhydrous THF (30 mL), and NaBD$_4$ (5 g, 119 mmol) was slowly added under nitrogen to the stirring solution. The contents were allowed to reflux for 17 h. The THF was removed in vacuo (30 mmHg), and the product was distilled at ambient temperature, 0.1 mmHg (8 g). IR analysis showed that there was 84% enrichment of deuterium in the product. The product was further confirmed by GC– MS analysis.

Kinetic Isotope Effect Study. M$_3$T^{vinyl} (0.65 g, 2.0 mmol) was combined with MD^{H}M (0.44 g, 1.98 mmol) in a 25 mL volumetric flask filled to volume with 25 mL of toluene-d_8 containing benzene as an NMR internal standard. The reaction was initiated by addition of Karstedt's precatalyst solution (30 μL, 1.38 mg of Pt, 7 mmol). The rate of the reaction was monitored by ^{1}H NMR analysis. The above reaction was repeated except that MD^{D}M (0.44 g) was used in place of MD^{H}M.

Reactions of M$_3$T^H and MD^{vinyl}M. (a) 1:2 M$_3$T^H:MD^{vinyl}M. M$_3$T^H (0.452 g, 1.52 mmol) was combined with MD^{vinyl}M (0.765 g, 3.08 mmol) and phenyldodecane (internal GC standard, 0.0731 g, 0.297 mmol) in a 5 mL volumetric flask which was filled to volume with D$_4$ and placed in a 50 °C constant-temperature bath. The reaction was initiated by addition of Karstedt precatalyst (75 μL, 3.45 mg of Pt, 17.7 mmol). The reaction was monitored by GC. Conversion had reached 90% in 24 h.

(b) 2:1 M$_3$T^H:MD^{vinyl}M. M$_3$T^H (0.933 g, 3.14 mmol) was combined with MD^{vinyl}M (0.391 g, 1.57 mmol) and phenyldodecane (internal GC standard, 0.0741 g, 0.301 mmol) in a 5 mL volumetric flask which was filled to volume with D$_4$ and placed in a 50 °C constant-temperature bath. The reaction was initiated by addition of Karstedt precatalyst (75 μL, 3.45 mg of Pt, 17.7 mmol). The reaction was monitored by GC and became yellow-brown (ca. 2 h) when complete conversion to products had occurred. Analysis by GC–MS, exact mass determination, showed 529 amu corresponding to M$^+$ – CH$_3$ for the addition of M$_3$T^H to MD^{vinyl}M, C$_{17}$H$_{49}$O$_5$Si$_7$ calcd 529.1965, found 529.1956.

Reaction of M^{H}M^H and MD^{vinyl}M Followed by Addition of a Second Equivalent of MD^{vinyl}M. M^{H}M^H (0.183 g, 1.37 mmol) was combined with MD^{vinyl}M (0.402 g, 1.62 mmol) in a 10 mL volumetric flask which was filled to volume with D$_4$ and placed in a 50 °C constant-temperature bath. The reaction was initiated by addition of Karstedt precatalyst (50 μL, 2.3 mg of Pt, 11.8 mmol). After 16 h the solution changed from colorless to brown and GC analysis showed that complete consumption of MD^{vinyl}M had occurred. An additional aliquot of MD^{vinyl}M was added (0.418 g, 1.69 mmol). After complete conversion, the sample was frozen for EXAFS analysis. The GC analysis of the solution after the first addition of MD^{vinyl}M showed the presence of two products. The products were analyzed by exact mass GC–MS, which showed that the earlier retention time product had a mass at 381 amu corresponding to the M$^+$ – 1 ion for the single addition of MD^{vinyl}M to M^{H}M^H, C$_{13}$H$_{37}$O$_3$Si$_5$ calcd 381.1589, found 381.1584. The second product at higher retention time had a mass at 615 amu

corresponding to the $M^+ - CH_3$ ion for the double addition product of two $MD^{vinyl}M$ units to M^HM^H, $C_{21}H_{59}O_5Si_8$ calcd 615.2517, found 615.2505.

Reactions with Speier's Catalyst, H_2PtCl_6 in 2-Propanol. MD^HM (0.222 g, 1.0 mmol) was combined with neohexene (0.116 g, 1.38 mmol) in a 5 mL volumetric flask which was filled to volume with D_4. In a separate 5 mL volumetric flask H_2PtCl_6 (0.48 g, 40% Pt, 0.98 mmol Pt) was added, and then the flask was filled to volume with 2-propanol. An aliquot of the 2-propanol solution (39 μL, 7.7 mmol of Pt) was added to the MD^HM/neohexene mixture. Aliquots of the solution were taken at around 50% conversion (as determined by GC analysis) and after the reaction was complete. EXAFS analysis was performed on the completely converted sample.
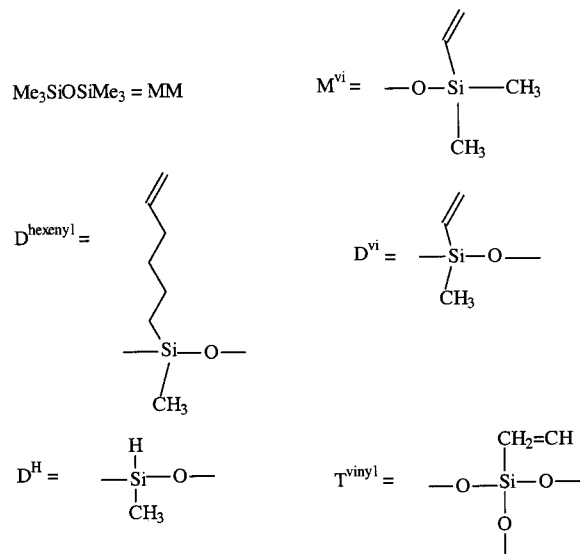
M_3T^H (8.50 g, 28.7 mmol) was combined with $MD^{vinyl}M$ (7.12, 28.7 mmol) in a stock solution. The stock solution (2 g) was placed in a 5 mL volumetric flask which was then filled to volume with D_4. In a second 5 mL volumetric flask H_2PtCl_6 (0.662 g, 1.35 mmol Pt) was added, and the flask was filled to volume with 2-propanol. The 2-propanol solution (25 μL, 6.7 mmol Pt) was added to the M_3T^H/$MD^{vinyl}M$ mixture. After 24 h, GC analysis showed that the reaction was complete, and the solution was frozen for EXAFS analysis.

Reaction of 1-Hexene with Et_3SiH. Et_3SiH (1.25 g, 10.8 mmol) was combined with 1-hexene (0.91 g, 10.8 mmol) and 0.2 mL decane internal standard followed by Karstedt's precatalyst (15 μL, 3.5 mmol of Pt) at 30 °C. Analysis by GC indicated that 40% conversion was achieved after 40 h. No additional conversion to hydrosilylation product occurred after 40 h. ^{1}H NMR analysis showed disappearance of the terminal olefin resonances and formation of a new resonance at 5.4 ppm (internal olefin). Analysis by GC−MS confirmed that an 84 amu species was present in solution as well as the hydrosilylation product as determined by exact mass GC−MS: $M^+ - C_2H_5$ obsd at 171 amu, $C_{10}H_{23}Si$ calcd 171.1569, found 171.1575.

Appendix

The M, D, T, and Q nomenclature is a shorthand for monofunctional, difunctional, trifunctional, and tetrafunctional (quadrifunctional) and specifies the number of oxygen groups around each silicon atom. The shorthand is used because each silicon typically shares one or more oxygens, which makes it tedious to present the specific empirical formulas. All groups around silicon other than oxygen are assumed to be methyl groups. When a methyl is substituted with another group, a superscript is used. The following examples should illustrate the shorthand.