

Platinum Catalysis Revisited—Unraveling Principles of Catalytic Olefin Hydrosilylation

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Supporting Information

ABSTRACT: Hydrosilylation of C–C multiple bonds is one of the most important applications of homogeneous catalysis in industry. The reaction is characterized by its atom-efficiency, broad substrate scope, and widespread application. To date, industry still relies on highly active platinum-based systems that were developed over half a century ago. Despite the rapid evolution of vast synthetic applications, the development of a fundamental understanding of the catalytic reaction pathway has been difficult and slow, particularly for the industrially highly relevant Karstedt's catalyst. A detailed mechanistic study unraveling several new aspects of platinum-catalyzed hydrosilylation using Karstedt's catalyst as platinum source is presented in this work. A combination of ²H-labeling experiments, ¹⁹⁵Pt NMR studies, and an in-depth kinetic



study provides the basis for a further development of the well-established Chalk–Harrod mechanism. It is concluded that the coordination strength of the olefin exerts a decisive effect on the kinetics of the reaction. In addition, it is demonstrated how distinct structural features of the active catalyst species can be derived from kinetic data. A primary kinetic isotope effect as well as a characteristic product distribution in deuterium-labeling experiments lead to the conclusion that the rate-limiting step of platinum-catalyzed hydrosilylation is in fact the insertion of the olefin into the Pt–H bond rather than reductive elimination of the product in the olefin/silane combinations studied.

KEYWORDS: hydrosilylation, platinum catalysis, mechanism, silanes, Karstedt's catalyst, isotopic labeling, kinetic study, deactivation

■ INTRODUCTION

Hydrosilylation ranks among the most important industrial applications of homogeneous catalysis, providing access to organofunctional silanes and silicones, which are commonly used for the production of adhesives, cross-linkers, and polymers.¹ The reaction is characterized by its high atom-efficiency, broad substrate scope, and widespread application, facilitating a plethora of synthetic pathways.^{1,2} Recent efforts have been directed toward the development of new commercially viable nonprecious metal catalysts.^{1j,3} However, owing to their unparalleled catalytic activity, industry still relies largely on platinum-based systems (Scheme 1).^{1j,4}

Of these, Karstedt's catalyst is the most versatile and established catalyst for industrial hydrosilylation to date and remains the benchmark system for new hydrosilylation catalysts.^{1j,8} Considering that this reaction has been commonly practiced for over 50 years, the development of an understanding of the underlying catalytic cycle has been arduous and slow mainly due to the elusive nature of intermediates formed by highly active catalysts.⁹ The initial model proposed 50 years ago

in a pioneering study by Chalk and Harrod in 1965 continues to be widely accepted for platinum catalysis (Scheme 2).¹⁰

It comprises four elemental steps: I_{CH} , oxidative addition of the hydrosilane; II_{CH} , coordination of the olefin; III_{CH} , migratory insertion of the olefin into the Pt–H bond; and IV_{CH} , reductive elimination of the hydrosilylation product (CH = Chalk–Harrod). Steps I_{CH} –III_{CH} are believed to be reversible, whereas step IV_{CH} is considered to be the rate-determining, irreversible step. The formation of Pt⁰ particles is associated with catalyst deactivation. ^{1b,j,8b} The fundamental mechanistic work of Lewis and Stein,^{8b} Roy,¹¹ and others¹² provides valuable insights that can be incorporated into the basic steps of the Chalk–Harrod mechanism according to Scheme 2. It has been established that (1) the reaction proceeds homogeneously,^{8b} (2) the active species contains Pt–Si and Pt–C bonds,^{8b} (3) olefin insertion into the Pt–Si bond is not facile,¹¹ (4) hydrosilylable olefins are

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^{*a*}*i*PrOH = *iso*-propanol, dvtms =1,3-divinyl-1,1,3,3-tetramethyldisiloxane, NHC = *N*-heterocyclic carbene. For Speier's catalyst, the species formed in the solution in situ is drawn.⁷

Scheme 2. Chalk–Harrod (CH) Mechanism for the Platinum-Catalyzed Hydrosilylation of Alkenes^{1h,8b,11} (See^a)



^{*a*}The reaction proceeds along the following steps: $I_{CH\nu}$ oxidative addition of HSiR₃; $II_{CH\nu}$ coordination of olefin; $III_{CH\nu}$ insertion of the olefin into the Pt–H bond; $IV_{CH\nu}$ reductive elimination of alkylsilane. Steps I_{CH} –III_{CH} are believed to be reversible.

resistant to insertion into the Pt–Si bond but not to isomerization and hydrogenation if no excess silane is present,¹¹ and (5) that oxygen exerts a beneficial effect on hydrosilylation of poorly coordinating olefins through prevention and/or destruction of multinuclear platinum species associated with catalyst deactivation.^{1b,8b} All of these findings strongly support the validity of the Chalk–Harrod mechanism for platinum-catalyzed hydrosilylation rather than the modified variant¹³ comprising the insertion of the olefin into the Pt–Si bond. This is in agreement with the results of a number of theoretical investigations, suggesting the prevalence of the Chalk–Harrod mechanism in platinum-catalyzed hydrosilylation and supporting the notion that step IV_{CH} is rate-limiting.¹⁴

The mechanistic studies mentioned above typically focus on identifying the active catalyst species, which has remained elusive for a long time. It has been concluded by Stein, Lewis et al.,^{8b} and

Roy et al.¹¹ that it contains Pt–Si and Pt–C bonds, whereas no Pt–H bonds could be detected so far. It is believed to look similar to the structure shown in Figure 1.



Figure 1. Proposed (generic) structure of the active catalyst species in platinum-catalyzed hydrosilylation according to the literature. ^{8b,11}

While a plethora of mechanistic studies has been presented on less-active transition metals, detailed investigations of platinumbased systems remain comparatively scarce due to their high activity and the highly sensitive nature of the corresponding intermediates.⁹ In addition, the industrially fundamentally important Karstedt's catalyst has been largely disregarded in academic research due to its inconvenient characteristics detrimental to common laboratory techniques: it is not a solid, but usually distributed as a highly diluted solution owing to its tendency to form platinum black without excess olefin ligand.^{4b,5} Unfortunately, this renders many of the typical experiments for the investigation of a reaction mechanism such as isolation and characterization of intermediates painstakingly difficult, if not impossible. Only one in-depth study of this catalyst's behavior in hydrosilylation catalysis has been published in recent years, focusing on the nature of the active catalyst species.^{8b} A detailed kinetic investigation of this system has not been put forth to date, even though the elucidation of the underlying kinetic principles might be highly advantageous for a better understanding of the catalytic cycle.

Furthermore, little attention has been paid to the hydrosilylation of internal double bonds so far, which are generally known to be far less reactive toward hydrosilylation than terminal olefins. ^{1a,b,j} This has been attributed solely to steric aspects in the past, which does not adequately account for the ready hydrosilylation of, for example, norbornene under relatively mild conditions,¹⁵ while cyclohexene is reluctant to undergo hydrosilylation. ¹⁶ This illustrates that not the internal position of the olefinic double bond per se is decisive for successful hydrosilylation and that other factors must exert an influence.

Bearing this in mind, a detailed mechanistic investigation of the hydrosilylation of selected internal olefins using Karstedt's catalyst is presented. In order to relate all observed phenomena to common hydrosilylation substrates and for better comparison of the obtained parameters, oct-1-ene was included in the substrate scope of this study.

RESULTS AND DISCUSSION

1. Substrate Scope. The set of substrates chosen for this study is shown in Figure 2. Norbornene seems to be an ideal probe for hydrosilylation, considering it is easily hydrosilylable



Figure 2. Substrate scope of this study: norbornene, cyclopentene, *cis*-hex-3-ene, cyclohexene, oct-1-ene, *trans*-oct-2-ene, and *cis*-oct-2-ene.

but does not allow for isomerization or the formation of vinylsilanes according to Bredt's rule.¹⁷ Cyclohexene, cyclopentene, and *cis*-hex-3-ene have been chosen to mimick selected structural aspects of norbornene and to compare their proneness to hydrosilylation to that of norbornene. Oct-1-ene is a typical model substrate for hydrosilylation reactions^{4e} and was employed as a benchmark system for the internal linear octenes, that is, *trans*-oct-2-ene and *cis*-oct-2-ene (Figure 2). (Note: The utilization of olefin substrates comprising electron-withdrawing substituents at the allylic position was deliberately omitted to avoid excessive byproduct formation via allylic rearrangement.⁹)

Trichlorosilane was chosen by virtue of its known high reactivity in hydrosilylation, which was expected to help overcome the reluctance of internal alkenes toward hydrosilylation.¹⁸ The reactions were typically performed on NMR scale at 333 K using Karstedt's catalyst as platinum source and monitored in situ via ¹H NMR (Scheme 3).

Scheme 3. Hydrosilylation of Olefins in This Work^a

^{*a*}The experimental conditions were chosen as follows: NMR scale, 1.86 M solution of olefin in toluene- d_{sv} aerobic conditions in order to take advantage of the oxygen effect. Typically Pt:olefin:silane = 1:8000:16000, corresponding to 125 ppm [Pt] with respect to the olefin. The identity of R and R' depends on the chosen substrate (see Figure 2).

2. Particle Formation Depending on Platinum Concentration. Initially, all reactions were carried out at a concentration of [Pt] = 500 ppm with respect to the olefin (T = 333 K). While the observed conversion rates were surprisingly high considering that internal olefins have been described in the literature as being unreactive toward hydrosilylation, ^{1a,j} a curious effect was observed when varying the catalyst concentration in a series of experiments with oct-1-ene (Figure 3).

It is evident that at platinum concentrations over 125 ppm, an increase in catalyst concentration does not concur with either a mounting initial reaction rate or augmenting total conversion



Figure 3. Hydrosilylation of oct-1-ene with $HSiCl_3$ at 313 K and different [Pt] (see also Figure S4 and Figure S5). The platinum concentration is given with respect to oct-1-ene; [oct-1-ene] = 1.86 M in toluene- d_8 .

after 4 h. On the contrary, these parameters actually decrease at $[Pt] \ge 250 \text{ ppm at } 293 \text{ K}, 313 \text{ and } 333 \text{ K}$ (see also Figure S4 and Figure S5). Analysis of the reaction mixtures during catalysis by dynamic light scattering (DLS) reveals substantial particle formation at [Pt] = 250 and 500 ppm, while no particles are observed at 125 ppm and below (Table S1 and Figure S1-S3). The size distribution is multimodal in all samples, and the average particle size increases with platinum concentration. This illustrates that at platinum concentrations over 250 ppm, rapid formation of colloids occurs even during catalysis and potentially influences catalytic results. In the 1980s, a hydrosilylation mechanism with platinum colloids as the active species was proposed.¹⁹ Later, it was concluded that the particles that had been observed form after deactivation of the catalyst and represent its inactive form.^{8b} Hence, the comparatively low activities of solutions with high colloid concentrations are in good agreement with previous findings. The results above illustrate that the formation of platinum particles is not only symptomatic of deactivated catalyst but can also be minimized (at least temporarily) by choosing appropriate reaction conditions. To avoid undesired effects related to particle formation, which is strongly influenced by the solubilization characteristics of the chosen olefins, all subsequent experiments were carried out at $[Pt] \leq 125$ ppm.

3. Hydrosilylation of Chosen Substrates. Figure 4 shows the time—conversion plots for the set of substrates chosen at [Pt] = 125 ppm (see also Table 1 as well as Figure S6 and S7 for [Pt] = 63 ppm).

High conversion is achieved using norbornene and oct-1-ene, while the remaining internal substrates investigated react only reluctantly or not at all. (Note: The description of the reactivity of the different substrates applies first and foremost to the reaction conditions chosen in this study. It is not intended to imply that these substrates do not undergo hydrosilylation in general, although a general trend in reactivity can be deduced. Therefore, when appropriate (more drastic) reaction conditions are chosen, cyclopentene,²⁰ cyclohexene,^{16,20} and *endo-2,3*dicarboxylic anhydride²¹ as well as maleic anhydride²² (see Section 4) are hydrosilatable.) Especially the efficient reaction of norbornene is startling considering its structural similarity to the entirely inactive cyclopentene and cyclohexene. It appears that not the ring strain but either the substitution pattern at the α -C (does not allow for isomerization) or the possible agostic interaction of the bridging methylene protons might exert a beneficial effect. To further probe this phenomenon, cis-5norbornene-endo-2,3-dicarboxylic anhydride was used in a sample hydrosilylation reaction under identical conditions (Figure 5).

No conversion was detected, suggesting that the successful reaction of norbornene may not solely depend on structural features in direct vicinity to the double bond but rather a combination of beneficial structural features and electron density at the double bond.

Even though the hydrosilylation of oct-1-ene with Karstedt's catalyst is quite fast, significant isomerization of the double bond occurs and notable formation of the corresponding oct-2-enes is evident. In fact, isomerization is observed immediately after the reaction is started (t = 3.0 min, see Figure S8 and Figure S9). This illustrates that the time scale for isomerization is similar to hydrosilylation, even though the formation of trichloro(octyl)-silane remains the predominant reaction. The internal olefin—generated in situ from the terminal olefin—reacts very slowly to



Figure 4. Time–conversion plots for hydrosilylation reactions with different olefin substrates. Pt:olefin:HSiCl₃ = 1:8000:16000 (corresponds to 125 ppm [Pt] with respect to olefin); T = 333 K; solvent = toluene- d_8 . Note that the conversion is equal to product formation for all investigated substrates except oct-1-ene, for which the product formation is shown. See Table 1 for selectivities and SI for determination of error bars.

the same reaction product, trichloro(octyl)silane (Scheme 4), just like *trans*-oct-2-ene and *cis*-oct-2-ene when used directly.

Thus, both internal octenes are expected to react along the same reaction pathway (i.e., first isomerizing to the terminal octene and then undergoing hydrosilylation). In light of these results, it appears feasible that the reductive elimination step IV_{CH} is truly rate-limiting in these cases as indicated by the

Table 1. I	Hydrosil	ylation of	Selected	Substrates [*]
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Figure 5. Structure of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride.

Scheme 4. Hydosilylation and Competing Isomerization of Oct-1-ene



Chalk–Harrod mechanism (Scheme 2) and that IV_{CH} proceeds fastest for terminal olefins.

4. ¹⁹⁵Pt NMR Study. ¹⁹⁵Pt NMR was used to investigate the coordination strength of the substrates chosen for this study. Hydrosilylation has been reported to depend on the ability of the olefin to coordinate to the Pt center, with weaker donors reacting slower when employed alone. When used in competitive experiments with more reactive, electron-rich olefins, a higher activity is observed for weak donors which has been attributed to the higher potential of these olefins to coordinate to Pt.¹ In a typical experiment, Karstedt's catalyst and 10 equiv of the respective olefins (i.e., 5 equiv per Pt center) were diluted in toluene- d_8 , followed by ¹⁹⁵Pt NMR investigation at 293 and 333 K. The comparison of the resulting ¹⁹⁵Pt NMR spectra to that of pure Karstedt's catalyst allowed for an estimation of the degree to which an exchange of the dvtms ligand had taken place. The stepwise replacement of dvtms in Karstedt's catalyst may be described by two consecutive equilibria according to Scheme 5 and is in line with a report by Stein, Lewis, and co-workers disclosing the formation of a $[Pt(olefin)_3]$ complex (3) at an excess of olefin.8

The corresponding equilibrium constants *K* are given by the following equations:

$$K_{1} = \frac{[\mathbf{2}]^{2} [\text{dvtms}] [\text{olefin}]^{4}}{[\mathbf{1}] [\text{olefin}]^{6}} = \frac{[\mathbf{2}]^{2} [\text{dvtms}]}{[\mathbf{1}] [\text{olefin}]^{2}}$$
$$K_{2} = \frac{[\mathbf{3}]^{2} [\text{dvtms}]^{3}}{[\mathbf{2}]^{2} [\text{dvtms}] [\text{olefin}]^{4}} = \frac{[\mathbf{3}]^{2} [\text{dvtms}]^{2}}{[\mathbf{2}]^{2} [\text{olefin}]^{4}}$$

substrate	product	selectivity ^b	yield ^c	$\delta_{ m product}~(^{29}{ m Si~NMR})^d$
norbornene	trichloro(norbornyl)silane	100%	89.7 ± 8.07	11.24
cyclohexene	n/a^e	n/a ^e	0%	n.a. ^e
cyclopentene	n/a^e	n/a ^e	0%	n.a. ^e
cis-hex-3-ene	trichloro(hexyl)silane ^f	100%	33.1 ± 1.49	13.32
oct-1-ene	trichloro(octyl)silane ^f	92% ^g	92.3 ± 1.85	13.40
cis-oct-2-ene	trichloro(octyl)silane ^f	100%	28.0 ± 1.82	13.40
trans-oct-2-ene	trichloro(octyl)silane ^f	100%	18.1 ± 0.81	13.40

^{*a*}Reactions were performed at 333 K in toluene- d_{sv} Pt:olefin:HSiCl₃ = 1:8000:16000 (corresponds to 125 ppm [Pt] per olefin). ^{*b*}Selectivity was determined by ²⁹Si NMR. ^{*c*}Yield was determined by ¹H NMR after 4 h. ^{*d*}Chemical shifts are given in ppm vs tetramethylsilane (TMS). ^{*e*}Could not be determined since no product was observed. ^{*f*}The identity of these products was confirmed by DEPT135 spectra. ^{*g*}Due to isomerization of the terminal alkene, selectivity was determined by a combination of ²⁹Si, ¹H and DEPT135 NMR. Please see Figures S9–S19 for the relevant NMR spectra.

Scheme 5. Ligand Exchange of Karstedt's Catalyst When Exposed to Olefin Substrates a



"The stoichiometry was chosen to account for full replacement of dvtms in two consecutive equilibrium reactions. $2a = [Pt(dvtms) (norbornene)]; 2b = [Pt(dvtms) (oct-1-ene)]; 3a = [Pt-(norbornene)_3]; 3b = [Pt(oct-1-ene)_3]. The identity of R and R' depends on the chosen substrate (see Figure 2).$

$$K_{\text{total}} = K_1 \times K_2 = \frac{[\mathbf{3}]^2 [\text{dvtms}]^3}{[\mathbf{1}] [\text{olefin}]^6}$$

No ligand exchange was observed with olefins that exhibit little or no activity in hydrosilylation such as cyclohexene, cyclopentene, *cis*-hex-3-ene, *cis*-oct-2-ene and *trans*-oct-2-ene at 293 and 333 K. (Note: No exchange of dvtms was observed when *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride was applied, either (see also Section 3).) Likewise, the highest reaction rates are found with those substrates that prompt Karstedt's catalyst to undergo ligand exchange of dvtms for the respective olefin, i.e. norbornene and oct-1-ene (Table S2, Figure 6 and S12).

Norbornene and oct-1-ene were chosen as model substrates for the following in-depth mechanistic study due to their high reaction rates and conversion, which allow for adequate observation of kinetic effects in subsequent experiments. In a first step, the coordination strength of both olefins was explored in more detail by applying 1.0, 5.0, and 50 equiv per Pt (Figure 6 and Figure S22). It is evident that norbornene is bound much more strongly to Pt than oct-1-ene. At Pt:norbornene = 1:50, it replaces not only the bridging but also the chelating dvtms ligand (step 2 in Scheme 5: formation of 3). Using the obtained ¹⁹⁵Pt NMR data, the relative equilibrium constants can be estimated:

$$\frac{K_{1(\text{norbornene})}}{K_{1(\text{oct}-1-\text{ene})}}(333 \text{ K}) \approx 2 \cdot 10^5$$

Considering that the catalytic reaction is carried out at a much higher ratio of olefin to platinum, a full replacement of dvtms for

2a + 1.0 equiv Norbornene + 5.0 equiv Norbornene + 50 equiv Norbornene 3a + 1.0 equiv Oct-1-ene + 5.0 equiv Oct-1-ene 2b + 50 equiv Oct-1-ene -5700 -5800 -5900 -6000 -6100 -6200 -6300 -6400

Figure 6. ¹⁹⁵Pt NMR spectra of ligand exchange reactions of Karstedt's catalyst (1) with oct-1-ene and norbornene at 333 K. The signal at $\delta = -6130$ ppm is typical for pure Karstedt's catalyst (1) at this temperature. Note that addition of the electron-rich norbornene results in an upfield shift of the ¹⁹⁵Pt resonance, while the corresponding oct-1-ene-substituted species is shifted downfield compared to Karstedt's catalyst. **2a** and **3a** denote the substituted platinum species of Karstedt's catalyst with norbornene according to Scheme 5, **2b** denotes the corresponding substitution product of oct-1-ene. See Table S2 for chemical shifts.

both olefins is likely, with norbornene bonding to Pt several orders of magnitude stronger than oct-1-ene.

It appears that a certain degree of coordination ability under the given conditions is beneficial for rapid hydrosilylation. However, if the olefin in question is bound too strongly to the Pt center, the reactivity suffers as well. This was observed for maleic anhydride, which causes the original peak of Karstedt's catalyst to vanish completely at Pt:olefin = 1:5, but is not converted at all under the typical hydrosilylation conditions applied in this study (Figure S20). It is apparent that it is advantageous for the course of the reaction if the substrate's coordination ability to Pt is *just right* (i.e., if the resulting η^2 -alkene bond is neither too strong nor too weak). This is consistent with observations made by the groups of Osborn²³ and others²⁴ regarding the replacement of the bridging dvtms ligand by other olefins in Karstedt's catalysti.

5. Deuteration Experiments. (a). 1,2-Dideuterocyclohexene. A series of ²H-labeling experiments was carried out to pinpoint the rate-limiting factors of the platinum-catalyzed hydrosilylation and identify crucial steps and barriers. 1,2-Dideuterocyclohexene was employed to elucidate the pronounced difference in reactivity observed for cyclohexene and norbornene despite their structural similarity. The intention was to determine whether this cyclic substrate does not react at all under the reaction conditions, or whether at least isomerization of the double bond about the cycle actually does take place, providing evidence for successful insertion of cyclohexene into the Pt–H bond. Indeed, it was found that the double bond scrambles about the C_6 cycle, illustrating that the limiting step in this particular setup is the reductive elimination of product (Scheme 6 and Scheme 7, Figure S23).

It is noteworthy that isomerization occurs only after the addition of $HSiCl_3$ (i.e., the silane is necessary for the formation of the active species).

(b). DSiCl₃. A second set of experiments was conducted using deuterated trichlorosilane, DSiCl₃. If the Chalk–Harrod mechanism is accurate and steps I_{CH} –III_{CH} are truly reversible (as has been suggested by the literature to date), ^{1j,8b} scrambling

Scheme 6. Hydrosilylation Experiment Using 1,2-Dideuterocyclohexene as Substrate^a



⁴Only isomerization of the double bond about the cycle was observed, and no hydrosilylation product was detected. Isomerization takes place only if silane is added to the reaction mixture.

Scheme 7. Result of the Deuteration Experiment with 1,2-Dideuterocyclehexene on the Basis of the Chalk–Harrod Mechanism^a



^{*a*}No reaction is observed without silane (i.e., the silane is necessary for the formation of the active species). Only isomerization and no hydrosilylation takes place at T = 333 K, [Pt] = 125 ppm with respect to 1,2-dideuterocyclohexene.

of deuterium about the olefinic methylene and methine groups of oct-1-ene and norbornene should be observed (Scheme 8).

Scheme 8. Step III_{CH} of the Chalk–Harrod Mechanism (See Scheme 2) Adapted for Deuterated Silanes $D-SiR_3^a$



^{*a*}If step III_{CH} is truly reversible, scrambling of deuterium about the olefinic positions would be expected.

However, after hydrosilylation (deuterosilylation) of oct-1ene, deuterium is detected solely at C2 of the product and the terminal CH_3 group of the isomerization product oct-2-ene, but not at the olefinic positions (Scheme 9, Figure S24).

Likewise, no deuterium is observed at the CH=CH group of norbornene after the reaction (Scheme 9, Figure S25). This is rather surprising and indicates that the reversibility of these steps in the catalytic cycle might not be given as expected. It appears that olefin insertion into the Pt–H bond *cannot* be considered reversible but rather that the insertion step is immediately followed by two alternative, competing reactions, namely, hydrosilylation (IV_{CH}) or isomerization (IV_{IS} and V_{IS} , Scheme 10).

Scheme 10. Proposed Mechanism of Pt-Catalyzed Hydrosilylation Accounting for the Product Distribution Using DSiCl_3^a



^{*a*}Note that III_{CH} and III_{IS} are identical for C₂ symmetric olefins and that IV_{IS} is not feasible for non-isomerizable olefins such as norbornene (IS = isomerization). After elimination of the isomerization product (step V_{IS}), the corresponding platinum hydride rather than the deuteride would be formed (omitted for clarity).

Which of these reactions follows is determined by the overall energy profile, which seems to be favorable for isomerization in the case of 1,2-dideuterocyclohexene and for hydrosilylation in the case of oct-1-ene. This may be attributed to the possibility for 1,2-insertion of oct-1-ene, which is not given in the case of 1,2dideuterocyclohexene. Scheme 10 appears to be more appropriate than the classical Chalk-Harrod mechanism to account for the products observed in all deuteration experiments. Data reported previously by Stein, Lewis, and co-workers mirrors the depicted reaction steps.^{8b} In their study, they also employ a deuterated silane and observe a high degree of deuteration (>1) in the hydrosilylation product of the dvtms ligand of Karstedt's catalyst (see Scheme 1). Owing to the structure of the dytms ligand, a degree of deuteration of 2 is to be expected in two subsequent hydrosilylations (deuterosilylations) of both vinyl groups of the ligand. The second hydrosilylable olefin present in

Scheme 9. Observed Products in Hydrosilylation Reactions Using Deuterated Trichlorosilane, $DSiCl_3^{a}$





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the reaction mixture, hex-1-ene, incorporates only one deuterium, which is again in line with irreversible migratory olefin insertion. While the group of Lewis and Stein interpreted their results in the spirit of the state of the art at the time, taking them as indicative for reversible olefin insertion, the presented data actually supports a reaction scheme similar to Scheme 10. Therefore, the results of Stein, Lewis, and co-workers^{8b} should not be considered as contradictory to the observations presented here, but should rather be interpreted in a different manner. Hence, it can be concluded that the migratory insertion of the olefin (Scheme 8: III_{CH} ; Scheme 10: III_{CH} and III_{IS}) is irreversible.

Considering the reaction pathway for oct-1-ene as an example, the following steps are expected to lead to the observed products: (a) irreversible 1,2-insertion of the olefin into the $Pt-^{2}H$ bond and subsequent product formation, yielding trichloro(2-deuterooctyl)silane; or (b) irreversible 2,1-insertion of the olefin into the $Pt-^{2}H$ bond followed by β -hydride elimination and formation of the isomerization product, 1-deuterooct-2-ene.

6. Kinetic Isotope Effect. The connotation that the insertion of the olefin into the Pt-H bond is not truly reversible is further substantiated by the determination of the kinetic isotope effect (KIE) of the hydrosilylation reaction of both norbornene and oct-1-ene with H/DSiCl₃. The values obtained amount to $k_{\rm H}/k_{\rm D}$ = 2.4(1) (norbornene) and 3.9(4) (oct-1-ene, Figure S26 and S27). (Note: The reaction is slowed down so significantly that the overall conversion of the respective olefin is quite low. The values for the KIE listed here can be considered as lower limit, substantiating the primary nature of the KIE. The KIE was determined by running two parallel reactions with HSiCl₃ and DSiCl₃, respectively. Additional experiments with a mixture of HSiCl₃ and DSiCl₃ were carried out to eliminate the possibility that an impurity in the freshly prepared DSiCl₃ was responsible for the extremely low conversion.) This illustrates that for both substrates, the KIE is primary, implying that an X-H bond (X = Pt, Si) contributes to the rate-determining step (rds) of the reaction.²⁵ This is in good agreement with the work of Pregosin reporting a primary KIE of 3.6(2) for the hydrosilylation of styrene with Et₃SiH using cis-[PtCl₂(PhCH $= CH_2_2$ as platinum source.¹²⁴

In their extensive mechanistic study, Stein, Lewis, and coworkers report a KIE of 1.8 in the hydrosilylation of tris(trimethylsiloxy)vinylsilane with heptamethyltrisiloxane using Karstedt's catalyst, which they interpret as indicative for Si-H bond breaking prior or during the rate-limiting step.^{8b} However, considering that Karstedt's catalyst is a 16 VE complex, it should be expected that oxidative addition of H-SiR₃ occurs readily to form the 18 VE Pt(II) complex [Pt(H) (SiR₃)- $(olefin)_3$. (Note: It is worth mentioning that the reversibility of the addition step I_{CH} appears to be given even after formation of the 18 VE complex. See also Duckett, Perutz et al.²⁶) The fact that 1,2-dideuterocyclohexene was isomerized only after the addition of silane substantiates this notion further, indicating that the formation of the active catalyst species entails a facile reaction of Pt and silane. In addition, a ¹⁹⁵Pt NMR experiment reveals the full disappearance of the original peak of Karstedt's catalyst after addition of 5 equiv silane per Pt in conjunction with a rapid color change of the solution from colorless to bright yellow (Figure S21). This corresponds to previously published literature reporting a rapid reaction of Karstedt's catalyst with hydrosilane, eliminating the oxidative addition of hydrosilane I_{CH} as rds for the reaction.²⁷ Therefore, it seems highly unlikely that Si-H bond breaking is involved in the rds as suggested by Lewis, Stein

and co-workers.^{8b} By contrast, the observed KIE should be interpreted as symptomatic of the rate-limiting nature of the *insertion step* III_{CH}, which is in line with the absence of scrambling products 1-deuterooct-1-ene, 2-deuterooct-1-ene and 1-deuteronorbornene in these deuteration experiments (Scheme 9 and Scheme 10). Thus, we conclude that the rds of the hydrosilylation reaction is in fact the insertion of the olefin into the Pt– H bond. (Note: In cases where isomerization of the olefin but not hydrosilylation is feasible (e.g., cyclohexene), the competitive nature of the subsequent reaction steps *after* migratory insertion is decisive.)

7. Observation of $Pt-^{2}H$ Species. If the migratory insertion of the olefin (III_{CH}) is truly rate-limiting, the predominant metal species in situ should be a platinum hydride species. Deuterated silane was used in order (a) to trap the $Pt-^{2}H$ species by virtue of the significantly lowered reaction rate (see Section 6) and (b) to provide a viable spectroscopic probe that would not vanish due to large signals of the highly diluted solution of Karstedt's catalyst. Such a Pt-²H species was observed in a set of experiments where Karstedt's catalyst was exposed to 5 equiv of norbornene or oct-1-ene, respectively, and 10 equiv of DSiCl₃. This mixture was prepared on NMR scale at 77 K, carefully warmed to room temperature for a few seconds and immediately transferred to the NMR (cooled to 193 K) after a color change from colorless to lemon-yellow was observed. Timing is crucial in these experiments because the reaction is completed within seconds at such a high platinum concentration, which in turn is necessary for the observation of these species. The signals of these platinum hydrides (deuterides) are observed at $\delta = -26.3$ ppm (oct-1-ene) and -29.3 ppm (norbornene, Figure 7), thus lying in the typical range of platinum hydrides.²⁸

The observation of such a $Pt-^{2}H$ species corresponds well to the in situ observation of a large Pt-H coupling constant of 605 Hz during styrene hydrosilylation using *cis*-[$PtCl_2(PhCH = CH_2)_2$] by Pregosin and co-workers, which they attributed to a



Figure 7. In situ ²H NMR of 1:5:10 mixtures of Karstedt's catalyst with norbornene (top) or oct-1-ene (bottom) and DSiCl₃ in toluene-*d*₈ at 193 K. The absence of a second set of signals with visible ¹*J*_{Pt,H} coupling (natural abundance of ¹⁹⁵Pt = 33.7%)²⁹ is due to the low signal-to-noise ratio of these spectra.

 ${}^{1}J_{Pt,H}$ coupling and thus the presence of a hydride or η^{2} -HSiCl₃ species (Figure 8).^{12a}

Figure 8. Proposed in situ Pt hydride species in hydrosilylation reactions put forth by Pregosin et al. $^{\rm 12a}$

The fact that Lewis and Stein^{8b} did not observe Pt—H bonds in their EXAFS analysis of frozen samples is probably due to the fleeting nature of these hydrides compared to the corresponding deuterides. In addition, the prerequisite high catalyst concentrations result in very short reaction times and rapid formation of platinum colloids, further impeding the observation of hydride species.

8. Kinetic Study. In order to gain further insight into the molecular processes governing hydrosilylation, a kinetic study was conducted using the model substrates oct-1-ene and norbornene. The rate law for the hydrosilylation reaction is given by (M = catalyst):

 $r = k_{\rm HS} \times [\mathbf{M}]^m \times [{\rm HSiR}_3]^n \times [{\rm olefin}]^q$

The results of this series of experiments are shown in Table 2 and Figures S28–S35.

Table 2. Results of the Kinetic Study^a

parameter	norbornene ^b	oct-1-ene ^c
т	0.85 ± 0.03	1.18 ± 0.08
n	1.33 ± 0.09	2.26 ± 0.15
9	0.01 ± 0.13	-1.28 ± 0.23
p = n + q	1.23 ± 0.04	0.98 ± 0.08
E_{A}^{d}	$138.6 \pm 7.5 (\text{kJ mol}^{-1})^e$	$60.2 \pm 3.5 (\text{kJ mol}^{-1})^{f}$

^{*a*}Reactions were performed at [Pt] = 125 ppm with respect to the olefin on NMR scale using naphthalene as internal standard. ^{*b*}Reactions were performed at 333 K, [Pt] = 125 ppm for the determination of the reaction order regarding the substrates. ^{*c*}Reactions were performed at 313 K, [Pt] = 63 ppm for the determination of the reaction order regarding the substrates. ^{*d*}The activation barrier was determined via Eyring plots, thus $E_A = \Delta G^{\uparrow}$. ^{*e*}Determination at 313 K, 318 K, 323 K, 328 K, 333 K, [Pt] = 125 ppm via Eyring plot. ^{*f*}Determination at 293 K, 303 K, 313 K, 323 K, 333 K, [Pt] = 63 ppm via Eyring plot. The reaction conditions were chosen to ensure sufficient conversion for the determination of the reaction rate.

The observed activation barriers E_A illustrate that oct-1-ene $(E_A = 60.2 \pm 3.5 \text{ kJ mol}^{-1})$ is much more prone to hydrosilylation than norbornene $(E_A = 138.6 \pm 7.5 \text{ kJ mol}^{-1})$, reflecting the reluctance of most internal olefins to undergo this reaction. The observed orders of reaction can best be explained when considering them in conjunction with the results of the ¹⁹⁵Pt NMR study and the deuteration experiments. The coordination equilibria about the Pt center can be described according to Scheme 11a.

At very low olefin concentrations, **A** might be the predominant form of appearance, but typically, Pt(0) is coordinated by three olefins (**B**). This species **B** is expected to be particularly stable if the respective olefin binds well to the platinum center; if the interaction is weak and the alkene is only loosely bound, the oxidative addition of H–SiR₃ with concomitant loss of one alkene ligand (formation of **C**) seems more likely. The equilibrium constant K_{BC} of this equilibrium **B** \leftrightarrows **C** can be written as follows: Scheme 11. (a) Different Proposed Platinum Species Depending on the Coordination Strength of the Respective Olefin; (b) Pt-Catalyzed Hydrosilylation According to the Results of the Deuteration Experiments Described above^a</sup>



^{*a*}The coordination strength of the olefin in question determines the nature of **M**, i.e. $\mathbf{M} = \mathbf{C}$ for oct-1-ene (weakly coordinating olefin) and $\mathbf{M} = \mathbf{B}$ for norbornene (strongly coordinating olefin). The coordination geometries about the platinum center in (a) are typical for Pt(0) complexes (Pt(II) in case of **C**) and have been suggested previously;^{8b,30} however, additional spectator ligands as suggested by Roy (hemilabile cyclooctadiene)¹¹ cannot be excluded and should be thought of as part of the species denoted as [Pt]. The depicted alkene may represent both dvtms and the olefin substrate for hydrosilylation.

$$K_{\rm BC} = \frac{[\mathbf{C}][\text{olefin}]}{[\mathbf{B}][\text{HSiR}_3]}$$

Assuming that the coordination strength of the olefin in question exerts a strong influence on this dynamic equilibrium, we propose that depending on the olefin, either **B** or **C** will be predominant, and either one of these species will enter the catalytic hydrosilylation cycle as active species **M** (Scheme 11b). In the following, we will go through the implications of this proposal for both our model substrates step by step.

a). Oct-1-ene. Oct-1-ene has been shown to coordinate weakly to Pt (Figure 6). Therefore, we can assume that C is the predominant platinum species in hydrosilylation of oct-1-ene (i.e., $\mathbf{M} = \mathbf{C}$, Scheme 11). Rearrangement of the formula for the equilibrium constant $K_{\rm BC}$ gives

$$K_{\rm BC} = \frac{[\mathbf{C}][\text{olefin}]}{[\mathbf{B}][\text{HSiR}_3]} \Leftrightarrow [\mathbf{C}] = \frac{K_{\rm BC}[\mathbf{B}][\text{HSiR}_3]}{[\text{olefin}]}$$

Taking into account the evidence for the rate-limiting nature of the olefin insertion step (II_{HS}, Scheme 11b) presented above, the olefin concentration [olefin] is not part of the equation for the rds in a first approximation, since the olefin appears only *after*

the rds in the cycle (III_{HS} , Scheme 11b). Consequently, the rate law is simplified to

 $r = k_{\text{HS}} \times [\mathbf{M}] \times [\text{HSiR}_3] = k_{\text{HS}} \times [\mathbf{C}] \times [\text{HSiR}_3]$

 $(k_{\rm HS}$ = rate constant for the overall hydrosilylation reaction)

[C] should be expressed using [B], which is equivalent to the used concentration of Karstedt's catalyst at the low platinum to olefin ratios used in catalysis. Using $K_{\rm BC}$ to express [C], the rate law can be written as follows:

$$\mathbf{r} = \mathbf{k}_{\text{HS}} \times \underbrace{\frac{\mathbf{K}_{\text{BC}}[\mathbf{B}][\text{HSiR}_3]}{[\text{olefin}]}}_{[\acute{\text{C}}]} \times [\text{HSiR}_3]$$

$$r = k_{\rm HS} \times \frac{K_{\rm BC}[\mathbf{B}][\rm HSiR_3]^2}{[\rm olefin]}$$

Consequently, applying the principles laid out in Scheme 11, the expected reaction order with respect to the different reagents would be first order with respect to [Pt], second order with respect to silane [HSiR₃] and negative order with respect to [olefin]. In fact, this corresponds well to the values determined experimentally that are listed in Table 2. This clearly illustrates how the principles derived from the mechanistic study (¹⁹⁵Pt, ²H experiments) can be used to improve our understanding of the kinetic laws of the platinum-catalyzed hydrosilylation reaction.

b). Norbornene. In the case of norbornene, the relevant species for the hydrosilylation cycle is expected to be B since coordination to Pt is strong in this case (M = B, Scheme 11). Therefore, the rate law can be written as follows:

$$r = k_{\text{HS}} \times [\mathbf{M}] \times [\text{HSiR}_3] = k_{\text{HS}} \times [\mathbf{B}] \times [\text{HSiR}_3]$$

 $(k_{\rm HS}$ = rate constant for the overall hydrosilylation reaction)

Again, since the recoordination of the olefin occurs *after* the rate-limiting step II_{HS} (Scheme 11b), the olefin concentration [olefin] does not need to be included. Therefore, a first-order reaction in both [Pt] and [HSiR₃] is to be expected, which again matches the experimental values displayed in Table 2.

The reported values regarding the reaction order correspond well to previously published, preliminary results for Karstedt's catalyst^{8b} and for a Pt(II) precatalyst.^{12a} They also reflect the prevalence of a mononuclear rather than a binuclear mechanism, which has been reported by Stein, Lewis, and co-workers.^{8b} This study illustrates how solving the rate law can give important information on structural features of the active species in platinum-catalyzed hydrosilylation. In conjunction with the ¹⁹⁵Pt and ²H NMR studies, this allows for a further development of the widely accepted Chalk–Harrod mechanism for platinumcatalyzed hydrosilylation (Scheme 12).

9. Overall Mechanistic Picture. As a result of the mechanistic investigations presented above, we propose a revised version of the Chalk–Harrod mechanism for platinum-catalyzed hydrosilylation (Scheme 12).

The cycle includes the following steps: I_{HS} , oxidative addition of the hydrosilane; II_{HS} , migratory insertion of the olefin into the Pt–H bond; and III_{HS} , reductive elimination of the hydrosilylation product concomitant with recoordination of the olefin. Depending on the olefin, II_{HS} and III_{HS} might compete with or be substituted by an isomerization reaction II_{IS} – IV_{IS} to form the corresponding internal olefin rather than the hydrosilylation product, depending on the overall energy profile of the reaction. On the basis of the experimental data, it is concluded that not reductive elimination of the hydrosilylation product but migratory insertion of the olefin is rate-limiting in this reaction.





^{*a*}Decomposition pathways are omitted for clarity, see Stein, Lewis, and co-workers.^{8b} The proposed mechanism comprises the following steps (HS = hydrosilylation): I_{HS}, oxidative addition of silane; II_{HS}, migratory olefin insertion and III_{HS}, reductive elimination of product and recoordination of olefin. Olefin isomerization (IS = isomerization) proceeds via I_{HS}, oxidative addition of silane; II_{IS}, migratory olefin insertion; III_{IS}, *β*-H elimination and IV_{IS}, elimination of isomerization product and recoordination of olefin. Note that for C₂ symmetric olefins, II_{HS} and II_{IS} are identical. Contrary to previous reports, we propose that migratory olefin insertion into the Pt–H bond is rate-limiting.

The nature of the active catalyst species \mathbf{M} as well as the rate law for the hydrosilylation reaction appear to be linked to the coordination strength of the olefin substrate.

A detailed study of platinum-catalyzed hydrosilylation using Karstedt's catalyst comprising both a mechanistic and a kinetic investigation of the reaction pathway has been presented. As a result of comprehensive ¹⁹⁵Pt NMR and ²H-labeling experiments as well as a kinetic study, a revised version of the widely accepted Chalk-Harrod mechanism for platinum-catalyzed hydrosilylation is proposed. It constitutes a successful continuation of the principles evoked by Roy¹¹ and corresponds well to the mechanistic picture put forth by Stein and Lewis.^{8b} Important new features of the revised mechanism include (1) the assignment of the rds to the insertion of the olefin into the Pt–H bond (step II_{HS} in Scheme 12), (2) the introduction of a separate bypath for the isomerization of terminal olefins, and (3) the unraveling of a connection between the coordination strength of the olefin in question and the rate law governing the conversion of that olefin as well as structural features of the active species [M]. For the systems investigated in this study, ¹⁹⁵Pt NMR proves to be a valuable tool for the estimation of the reactivity of a target substrate in hydrosilylation. This study may serve as incentive for other mechanistic investigations to utilize a combination of isotope labeling and kinetic experiments to decode veiled reaction pathways.

EXPERIMENTAL DETAILS

General Remarks. All reactions were performed in aerobic conditions in order to take advantage of the so-called oxygen effect.^{1j,8b,9} Toluene- d_8 , norbornene, oct-1-ene, *cis*-oct-2-ene, *trans*-oct-2-ene, *cis*-hex-3-ene, cyclopentene, cyclohexene, Na₂SO₄, 1,2-cyclohexanedicarboxylic anhydride, [Pb(OAc)₂] (OAc = acetate), D₂SO₄, and silicon powder were purchased from Sigma-Aldrich, Deutero or ABCR and used without further purification. DSiCl₃ was synthesized according to a modified

literature procedure, using DCl instead of HCl (formed in situ, see also Figure S36).³¹ 1,2-Dideuterocyclohexene was prepared according to a previously published procedure.³² Karstedt's catalyst was kindly provided by Wacker Chemie AG as a solution (2 wt % Pt) in toluene, a mixture of xylenes and dvtms. NMR spectra were acquired on a Bruker Avance Ultrashield 400 MHz spectrometer. All ¹H, ²⁹Si, and ¹³C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak serving as internal reference,³³ whereas ¹⁹⁵Pt NMR shifts are reported relative to K₂[PtCl₆].

Dynamic Light Scattering (DLS). DLS measurements were performed in a quartz cuvette using a Dyna Pro NanoStar from Wyatt. Toluene was used as solvent. Samples were prepared according to the general procedure for hydrosilylation reactions (see below). For measurement and analysis the software Dynamics V7 was used. One measurement represents a statistic analysis of the results of 8 single measurements, which were performed using 10 acquisitions, each given 5 s acquisition time. A regression fit for multimodal samples was implemented on the autocorrelation function for the analysis of the measurements. Data was presented using mass distribution.

¹⁹⁵Pt NMR Study. In a typical experiment, an NMR tube was equipped with Karstedt's catalyst in toluene- d_8 and 5 equiv (1 equiv, 50 equiv) of the respective olefin and immediately investigated by ¹⁹⁵Pt NMR. Fresh samples were used for all spectra (i.e., individual samples were used for the same olefin at 293 and 333 K).

Hydrosilylation Experiments. In a typical experiment, a pressure NMR tube was equipped with the respective olefin (0.93 mmol, 1.0 equiv), trichlorosilane (1.86 mmol, 2.0 equiv), naphthalene (40 mg, 0.31 mmol), and 300 μ L of toluene- d_8 . After a zero-point ¹H NMR, catalysis was started by injection of the catalyst in 200 μ L of toluene- d_8 . The reaction was monitored by in situ ¹H NMR (D1 (relaxation delay) = 1 s; Ns (number of scans) = 16). Selectivity was determined by a combination of ²⁹Si NMR (D1 = 5 s; Ns = 128), DEPT135 (D1 = 2 s; Ns = 256) and ¹H NMR.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02624.

DLS data, time–conversion plots of hydrosilylation experiments, ¹⁹⁵Pt and ²H NMR spectra of substitution and deuteration experiments, results of the kinetic study, photos of particle solutions after catalysis, and the experimental setup for DSiCl₃ synthesis (PDF)

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Notes

The authors declare no competing financial interest.

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