

Metal Silylenes Generated by Double Silicon–Hydrogen Activation: Key Intermediates in the Rhodium-Catalyzed Hydrosilylation of Ketones**

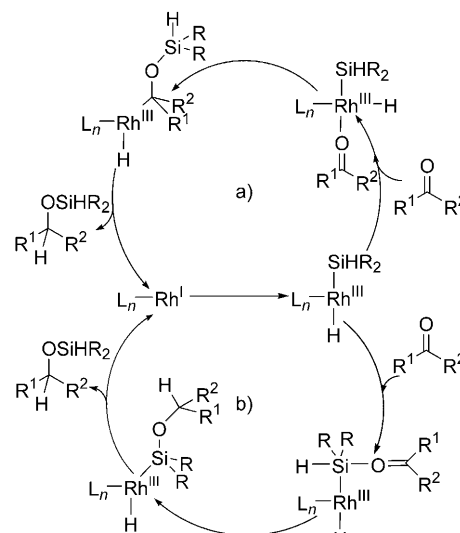
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Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

Although the rhodium-catalyzed hydrosilylation of ketones has been extensively studied, there have been relatively few investigations into the mechanism.^[1] Most catalyst development studies in this area refer to a mechanism proposed by Ojima et al. in 1975 (Ojima mechanism, OM; Scheme 1 a),^[2] in which an oxidative addition of the hydrosilane to a Rh^I complex gives a silyl metal hydride Rh^{III} intermediate. End-on O-coordination of the ketone to the latter, followed by the insertion of the ketone carbonyl function into the Rh–Si bond and, finally, reductive elimination gives the silyl ether and recovers the Rh^I species.

However, this mechanism does not explain several key observations, namely the rate enhancement observed when dihydrosilanes are used instead of monohydrosilanes, the observed kinetic isotope effects and the regioselectivity in the hydrosilylation of α,β -unsaturated carbonyl compounds. Based on such data, Zheng and Chan^[3] proposed an alternative catalytic cycle (Chan mechanism, CM; Scheme 1 b) in which the first step is the same as in the OM. Subsequently, the ketone interacts with the metal-bonded silicon atom and inserts into the Si–H bond to give an alkoxysilylrhodium intermediate in the key step. After reductive elimination, the product is obtained and the active species is recovered.^[4]

Finally, several studies suggest mechanisms that involve Rh^V species. Indeed, Rh^{III} intermediates can undergo a second oxidative addition of another silane molecule, which



Scheme 1. Two catalytic cycles proposed for the rhodium-catalyzed hydrosilylation of ketones: a) Mechanism proposed by Ojima et al. (OM); b) Mechanism proposed by Zheng and Chan (CM) to account for the enhanced rate, different regiochemistry, and KIE observed for secondary silanes R_2SiH_2 compared to tertiary silanes R_3SiH .

facilitates the final reductive elimination step of the product.^[5] Goikhman and Milstein reported an example of α -hydrogen elimination in a Rh–SiPh₂H moiety followed by the elimination of the SiPh₂ group. The silylene molecule was not directly observed but was trapped with a cationic Rh^I complex or with an organic silanol.^[6] In this context, a possible mechanism for the catalytic hydrosilylation of alkenes, which involves a silylene intermediate that results in the double addition of olefins to a silane substrate was proposed.

We recently reported a very efficient enantioselective Rh catalyst system (**2a,b**), derived from the neutral precursor **1a,b**, for the hydrosilylation of both aryl–alkyl and dialkyl ketones by using chiral oxazoline-*N*-heterocyclic carbene chelate ligands.^[7] As the rate law of the catalytic hydrosilylation of acetophenone with **2** was first order in catalyst, ketone, and silane,^[7b] it was compatible with both previously proposed mechanisms. As found previously for other chiral Rh catalysts^[8] complexes **1a,b** proved to be far more active (and selective) in reactions that used secondary silanes, (aryl)₂SiH₂, instead of tertiary silanes, R₃SiH. Furthermore, the temperature dependence of the enantioselectivity dif-

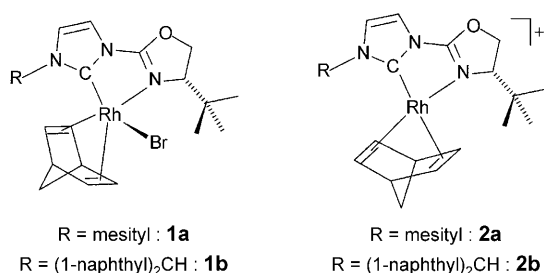
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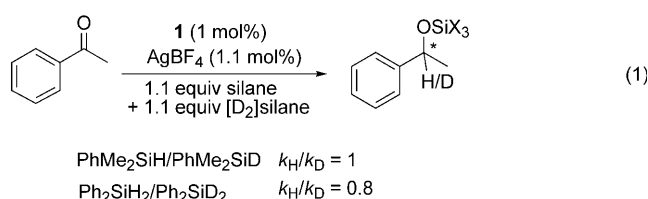
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ferred markedly and characteristically for R_2SiH_2 and R_3SiH (see the Supporting Information). Finally, whereas the hydrosilylation of acetophenone with $PhMe_2SiH$ and $PhMe_2SiD$ displayed no kinetic isotope effect (KIE), the same reaction with Ph_2SiH_2 and Ph_2SiD_2 was found to be characterized by an inverse KIE of 0.8 [Eq. (1)]. The latter observations were



incompatible with the previously postulated mechanistic schemes. The reaction was investigated theoretically by DFT methods to differentiate between the various mechanistic scenarios.^[9] Thus, the OM and CM mechanisms were examined along with other possible pathways that employed a suitable model system.

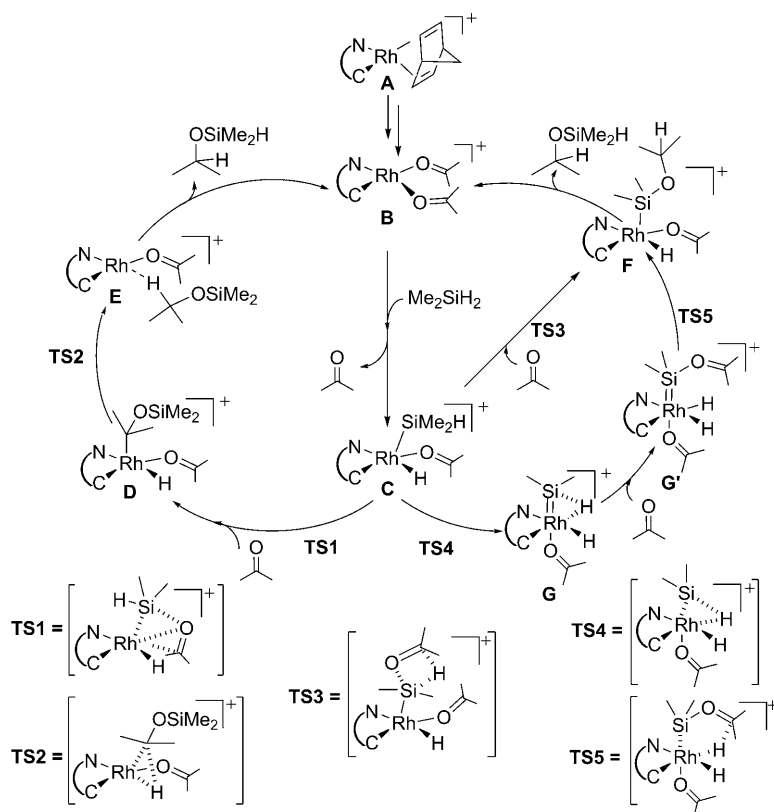
Full catalytic cycles were calculated at the B3LYP/TZVP//BP86/SV(P) level of theory for cationic Rh^I complexes. Me_2SiH_2 was used as the model silane for Ph_2SiH_2 and acetone as the model for acetophenone. The ligand was simplified by replacing the substituents on the imidazolyl ring by a methyl group and by removing the alkyl group of the oxazoline. Thus, the electronic and steric features of the imidazolyl and oxazolyl ring were maintained, whilst the decrease of the overall number of atoms lowered the computational time and enabled the full screening for possible conformers, isomers, and mechanistic pathways.^[10] The activation and rotational barriers connecting these isomers and rotamers of the reaction intermediates were found to be significantly lower in energy compared to the catalytic reaction pathway, and a rapid equilibrium between all possible isomers at each stage of the catalytic cycle could thus be assumed (Curtin–Hammett principle).

In addition to the OM and CM mechanistic pathways that involve alkoxy intermediates such as those found in hydrogenation reac-

tions,^[11] analogues to the Chalk–Harrod or modified Chalk–Harrod mechanisms^[12] as well as double-oxidative-addition products of the silane group were investigated.^[13] Three viable mechanistic pathways could be established. These pathways are all based on the assumption that the precursor complex $[L_nRh^Inbd]^+$ (**A**; nbd = norbornadiene) is initially converted to the species $[L_nRh^I]^+$ (**B**); oxidative addition of the silane results in the Rh–silyl intermediates $[L_nRh^{III}(H)SiHMe_2]^+$ (**C**). According to Scheme 2, these pathways differ in the mode of insertion of the ketone, which takes place either into the Rh–Si bond (**C**→**D** via **TS1** (OM)) or into the Si–H bond (**C**→**F** via **TS3** (CM)).

Alternatively, according to the DFT results, the formation of a silylene intermediate **G** (**C**→**F** via **TS4**, **G**, **G'**, and **TS5**) offers a low-energy channel to the hydrosilylation product. The first two reaction channels (OM and CM) are associated with high activation barriers ($\Delta G^\ddagger = 132.7 \text{ kJ mol}^{-1}$ for **TS1** and $\Delta G^\ddagger = 195.7 \text{ kJ mol}^{-1}$ for **TS3**). In particular, the CM appears to involve a prohibitively high free enthalpy of activation. A silicon–ketone intermediate adduct, as represented in Scheme 1, could not be confirmed as a local minimum species but conversion to **F** potentially occurs by direct external attack and insertion of the ketone into the Si–H bond.

Remarkably, the third mechanistic pathway involves a second Si–H bond cleavage in **C** ($\Delta G^\ddagger = 48.9 \text{ kJ mol}^{-1}$) to



Scheme 2. Three possible mechanistic pathways for the rhodium-catalyzed hydrosilylation of ketones: OM, CM, and a low-activation-barrier pathway that involves double Si–H activation of the secondary silane and silylene intermediates (**C** to **F** via **G** and **G'**, silylene mechanism). C $\square$ N = ligand.

form the silylene complex **G** (Scheme 2).^[14] The imaginary frequency, which characterizes the transition state **TS4**, represents a vibrational motion tilting the silyl ligand, which leads to the formation of the Rh–H bond (Figure 1). The

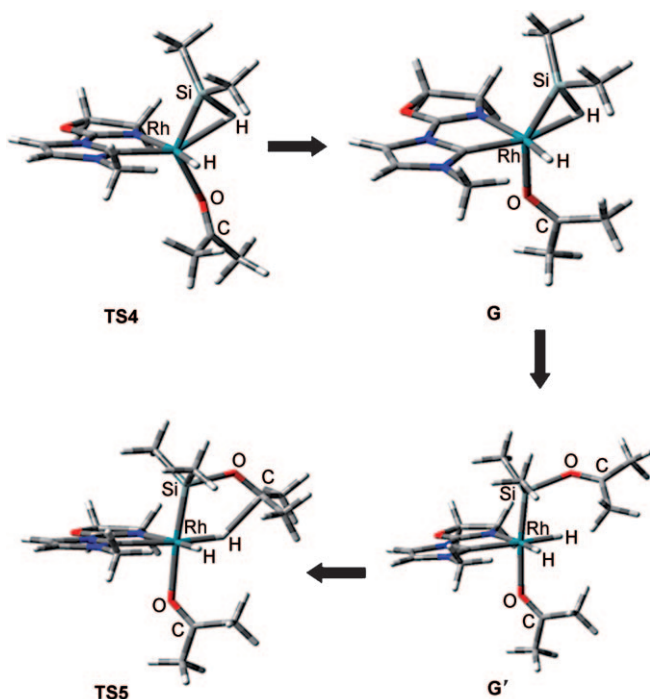


Figure 1. Computed molecular geometries of the key species in the silylene mechanism: The transition state **TS4** that leads to the hydrogen-bridged silylene intermediate **G**, external attack of a ketone at the silicon atom giving the donor adduct **G'**, and, finally, the transition state **TS5** associated with the intramolecular hydride transfer from the metal to the carbon atom of the ketone.

resulting intermediate **G** is characterized by a Rh=Si bond (2.22 Å) which is significantly shorter than the single bond in **C** (2.34 Å).^[15] We note that the silicon- and rhodium-bound hydrogen atom in **G** does not occupy a “classical” terminal position but is almost symmetrically bonded to Rh (1.87 Å) and to Si (1.68 Å). The interaction of an acetone molecule with the intermediate **G** gives the Si/σ complex **G'**. The proximity of the acetone molecule weakens the interaction between the Si and the H atom to give the latter a full hydride character (Rh–H_{trans C} = 1.63 Å, Si–H_{trans C} = 2.63 Å). Despite these structural changes, **G** and **G'** are very similar in energy and no barrier to interconversion could be found.^[16]

The next step in this pathway is the hydride transfer to the acetone molecule via the five-membered transition state **TS5** to generate the same alkoxysilyl intermediate **F**, as implicated in the CM. The intramolecular motion associated with the imaginary frequency of **TS5** represents the breaking of a Rh–H bond and the formation of the C–H bond (Figure 1). In **TS5**, the Rh–Si bond is slightly elongated with respect to **G'** (2.28 Å), whilst the inserting acetone is still planar (angle sum at C_{ins ac} = 357.0°) and the carbonyl C=O bond is only slightly elongated (1.28 Å). The energy of this transition state is only 36.1 kJ mol^{−1} above the intermediate **G'**. As in the CM, the

catalytic cycle is completed by an activation-barrier-free Si–H reductive elimination to liberate the reaction product Me₂CH–OSiMe₂H and regenerate the active species **B**.

The free enthalpy profiles of the three established catalytic cycles are compared in Figure 2. The overall standard free reaction enthalpy is −73.8 kJ mol^{−1}. Both the

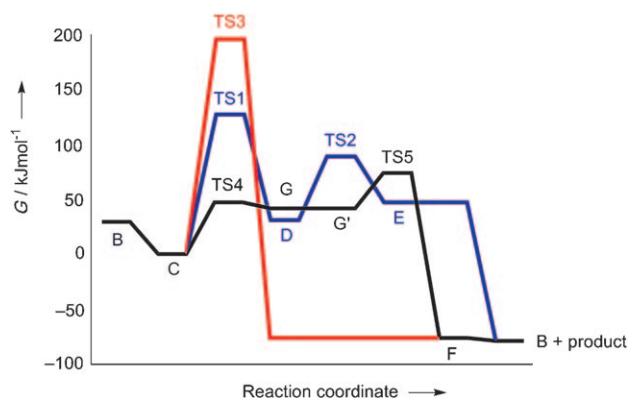


Figure 2. Comparison of the computed free enthalpy profiles (B3LYP/TZVP//BP86/SV(P)) of the three catalytic cycles discussed in this work (blue = OM, red = CM, black = silylene mechanism).

OM and CM involve higher activation barriers than the silylene mechanism discussed above. The highest transition state energies of the OM and CM pathways relative to the common intermediate **C** were found to be 132.7 kJ mol^{−1} and 195.7 kJ mol^{−1}, respectively, compared to a barrier of 77.6 kJ mol^{−1} in the silylene mechanism which provides by far the lowest-energy hydrosilylation pathway.

In the OM, no Rh–H or Si–H bond is broken in the rate-determining step, which accounts for the absence of a KIE; whereas a Si–H bond is broken during the rate-determining step (**TS3**) of the CM, which should give rise to a normal KIE.^[3] There are two significant activation barriers in the silylene mechanism (**TS4** and **TS5** in Figure 3), the second of which is the rate-determining step (**TS5** of step 2); thus, $k_H/k_D = (k_{\text{step2(H)}}/k_{\text{step2(D)}})$. As observed, an inverse KIE can be expected for the overall catalytic cycle because deuterium prefers to be located in the stronger bond, that is, C–D versus M–D.^[17]

The key intermediates in the new mechanistic scheme are transition-metal–silylene complexes, which are known as reactive species in a number of stoichiometric or catalytic reactions, but have also been isolated in several cases.^[18] Although various attempts to trap a Rh–silylene complex have remained unsuccessful in our case, Tilley and co-workers reported the generation of a Rh–silylene complex under conditions which are similar to those discussed in this work.^[19] Moreover, reaction sequences that combine silane Si–H oxidative addition, reductive elimination to open a coordination site, and α-H migration from silicon to a metal center have been developed and exploited in the hydrosilylation of alkenes.^[20,21] Finally, the iridium–silylene complex [Cp*-(PMe₃)₂Ir(SiPh₂)(H)][B(C₆F₅)₄] (Cp* = C₅Me₅) was found to catalyze the hydrosilylation of ketones, even though the

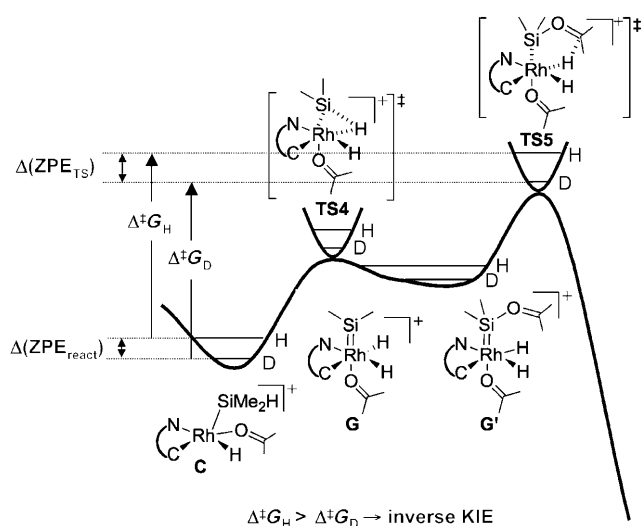


Figure 3. Origin of the inverse kinetic isotope effect in the silylene mechanism.

involvement of a metal-mediated or a Lewis acid mechanism could not be clearly distinguished.^[22]

In summary, a new mechanistic pathway for the rhodium-catalyzed hydrosilylation of ketones is proposed, which involves a silylene intermediate and is therefore only accessible when a secondary silane is used. It accounts for the experimental observations, notably the rate enhancement for R_2SiH_2 over R_3SiH as well as the inverse kinetic isotope effect. The accessibility of multiple reaction pathways which are controlled by subtle features in the reacting substrates but lead to a similar product spectrum probably has to be considered in the mechanistic discussions of many other catalytic transformations.

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