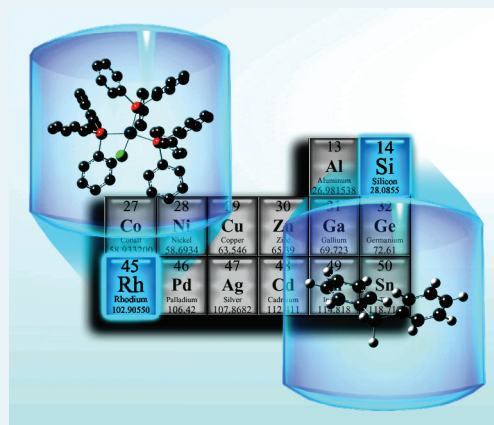


Rhodium-Catalyzed Hydrosilylation of Ketones: Catalyst Development and Mechanistic Insights

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ABSTRACT: The current status of rhodium-catalyzed hydrosilylation of ketones is reviewed, focusing on development milestones leading to state of the art chiral ligand systems and mechanistic understanding. Four ligand classes are discussed: phosphorus-, nitrogen-, mixed-donor ligand- as well as N-heterocyclic carbene-based ligand systems. Results relevant for a mechanistic understanding of the reaction are presented, starting from the initial investigations by Ojima, limitations of the first mechanistic picture leading to the Zheng-Chan mechanism, which was recently replaced by a silylene-based mechanism introduced by Hofmann and Gade.

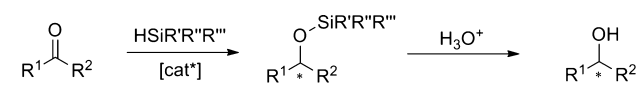


KEYWORDS: asymmetric catalysis, homogeneous catalysis, hydrosilylation, ketones, mechanism, rhodium

1. INTRODUCTION

The development of efficient stereoselective reactions has been one of the biggest challenges in synthetic chemistry over the past decades. In this regard, the field of transition metal catalysis has become very important because of the stereochemical control by suitable chiral ligands attached to the metal center. Therefore, a wide variety of chiral ligands have been developed. Rhodium-catalyzed hydrosilylation of ketones using chiral ligands, followed by hydrolysis of the silyl ethers, provides an efficient route to chiral alcohols, which are of great significance in agrochemicals and pharmaceuticals as well as in fine chemicals (Scheme 1).

Scheme 1. Asymmetric Hydrosilylation of Ketones and Hydrolysis to the Corresponding Chiral Alcohols



The catalytic hydrosilylation of unsaturated carbon-element bonds has been a topic of several reviews.^{1–9} In this perspective article, fundamental principles of rhodium-catalyzed hydrosilylation of ketones are in the focus, including the state of the art catalysts and a comparison of the mechanistic considerations suggested to date. Three models are presented including the Ojima, Zheng-Chan, and the most recent silylene-based mechanism suggested by Hofmann, Gade et al. Although, the catalyst part is focused on the asymmetric hydrosilylation of ketones, the mechanistic perspective also includes results on the

hydrosilylation of α,β -unsaturated carbonyl compounds for a more complete picture.

2. CATALYST DEVELOPMENT

Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ was the first rhodium-containing catalyst employed in the hydrosilylation of carbonyl compounds reported by Ojima in 1972.¹⁰ Shortly thereafter, the first variants applying chiral ligands were reported by the groups of Ojima, Kumada, and Kagan.^{11–13} Phosphines were the first chiral ligands used, but monodentate $\text{P}(\text{BnMePh})$ only gave moderate asymmetric induction in the hydrosilylation of acetophenone with Me_2PhSiH .¹¹ In the following years, a lot of effort was put into the development of new catalysts. Besides ketones different carbonyl compounds such as α,β -unsaturated carbonyls and α -keto esters were applied as substrates in the asymmetric hydrosilylation.^{14–17}

Over the past couple of decades, research focused on four predominant classes of ligand systems: phosphorus-, nitrogen-, mixed heteroatom-, and NHC-based ligands, with the most important achievements shown in Figure 1.^{18–22}

2.1. Nitrogen-Based Ligands. The first major contributions to asymmetric rhodium-catalyzed hydrosilylation of ketones by Brunner and co-workers involved the use of chiral Schiff-bases and thiazolidine ligands.^{19,23} In the hydrosilylation of acetophenone with diphenylsilane, the chiral alcohol could be obtained in up to

Received: November 3, 2011

Revised: February 22, 2012

Published: February 23, 2012

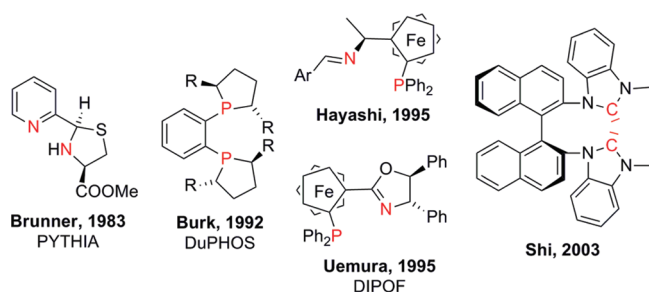
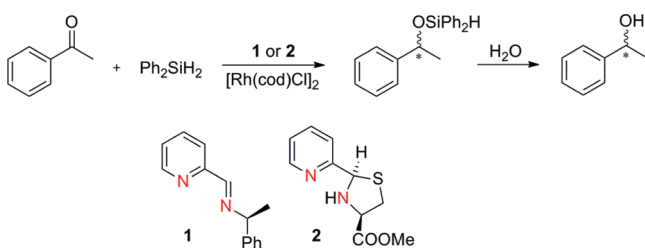


Figure 1. Important ligand motifs in asymmetric, rhodium-catalyzed hydrosilylation of ketones.

87% enantiomeric excess (ee) and almost quantitative yield with a catalyst loading of 1 mol % (Scheme 2).

Scheme 2. Brunner's Catalyst Systems



The main drawback of the systems was the 10-fold excess of ligand necessary to facilitate the asymmetric induction. The use of stoichiometric amounts showed activity, but no preference for one enantiomer. Although an excess of the ligand is needed for a successful catalytic reaction, the ligand syntheses are inexpensive and facile compared to the phosphine systems. Interestingly, racemized ligand **2** at the 2-position gave almost the same ee's as the pure diastereomer.²⁴

These achievements led to the development of C2-symmetrical terdentate PYBOX ligands by Nishiyama et al.,²⁵ which yielded 90% of silyl ether with 94% ee using 1 mol % of $[\text{Rh}(\text{3})\text{Cl}_3]$ and additional 4 equiv of ligand **3** (Figure 2).

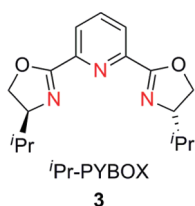


Figure 2. Nishiyama's PYBOX ligand **3**.

The reaction did not work without Lewis acids, but addition of 2 mol % of AgBF_4 gave the desired results in the hydrosilylation of acetophenone with Ph_2SiH_2 .

More nitrogen-based ligands have been developed, and the most promising ones are shown in Figure 3.^{26–30}

These N-based ligands have contributed significantly to the field of rhodium-catalyzed hydrosilylation. Although the reaction conditions (temperature, solvent, reaction time, metal/ligand ratio) have been optimized, utilizing a broader scope of reactants, that is, dialkyl ketones and cheaper, nonaryl silanes, has still to be accomplished.

2.2. Phosphorus-Based Ligands. The first chiral phosphine which led to ee's of up to 93% was bidentate

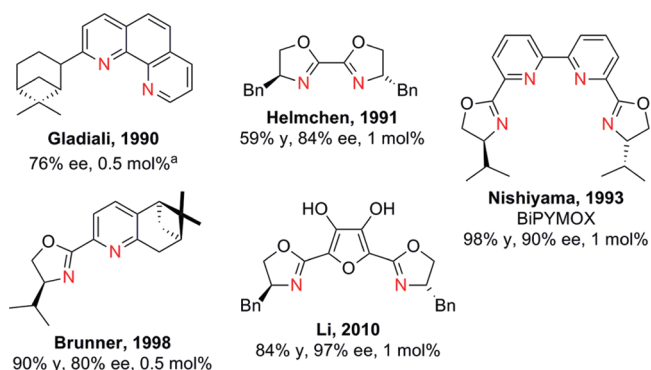
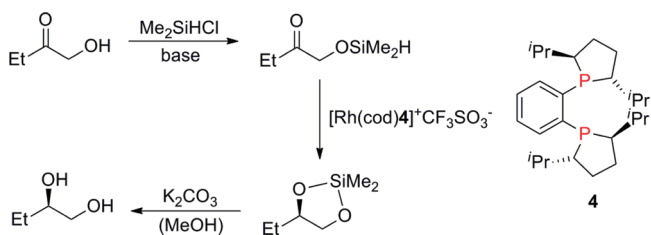


Figure 3. Developments on N-based ligands in the hydrosilylation of acetophenone with Ph_2SiH_2 (yield and enantiomeric excess of silyl ether, catalyst loading based on Rh); ^ayield was not determined.

DuPHOS (**4**) by Burk et al.¹⁸ (Scheme 3). Over 75% yield was achieved using 0.3 mol % of the catalyst in the hydrosilylation

Scheme 3. Hydrosilylation of Hydroxyketones Using *i*-Pr-DuPHOS (**4**) by Burk et al.



of hydroxyketones. An increased steric demand of the substituents on the phosphorus atoms of DuPHOS led to higher asymmetric induction whereas this particular reaction gave only poor results with other chiral phosphines such as CHIRAPHOS and BINAP.^{31,32}

Compared to the nitrogen-based ligands, no excess of chiral phosphines was necessary for the enantioselective transformation. This advantage is somewhat attenuated by the more challenging synthesis of the chiral phosphorus-based ligands, which could not be obtained by simple condensation but by multistep reactions.³³

The ligand motif was further improved by Ito and co-workers to chiral, chelating ferrocenyl phosphines (**5**, Figure 4), available in a 6-step synthesis.^{34,35}

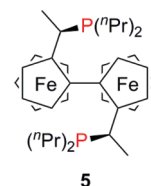


Figure 4. Ito's *i*-Pr-TRAP (**5**).

The reaction of acetophenone with Ph_2SiH_2 gave 92% ee and a yield of 89% with 1 mol % of $[\text{Rh}(\text{cod})_2]\text{BF}_4/\mathbf{5}$ (1/1). The best results were achieved with linear alkyl groups on the phosphorus compared to branched alkyl or aryl groups. P-based ligands are used for a broader variety of substrates than the N-based ones, but major progress has not been made since the

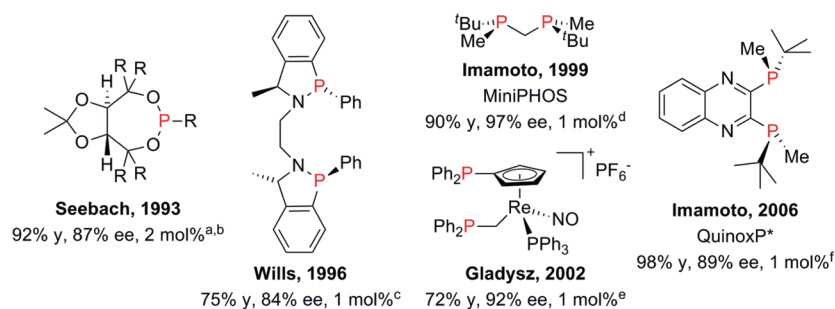


Figure 5. Improved phosphorus-based ligand systems (yield and enantiomeric excess of silyl ether, catalyst loading based on Rh); ^aR = 2-naphthyl; ^b1'-acetonephthone, Ph₂SiH₂; ^c2'-bromoacetophenone, Ph₂SiH₂; ^d1'-acetonephthone, 1-NpPhSiH₂; ^ePhCO(CH₂CH₂CH₂Cl), Ph₂SiH₂; ^facetophenone, 1-NpPhSiH₂.

discoveries by Burk and Ito.^{18,34} The ligand systems that have contributed to the field are shown in Figure 5.^{36–40}

Similar to the nitrogen-based ligands, the phosphorus-based ligands have only been established in the transformation of aryl methyl ketones with aryl silanes.

2.3. Mixed Heteroatom-Based Ligands. Mixed heteroatom-based ligands have had the biggest impact on rhodium-catalyzed hydrosilylation of ketones and started with two independent publications by the groups of Hayashi and Uemura (Figure 6).^{20,21} The ligands were synthesized by a

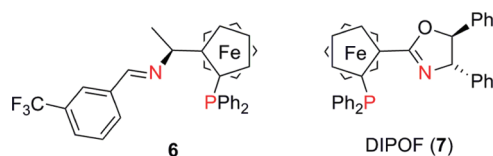


Figure 6. Hayashi's *P,N*-based ligand **6** and Uemura's DIPOF (**7**).

multi step reaction sequence, again more complicated than for the nitrogen-based ligands.

The new chiral oxazolinylerocenes gave ee values and yields of around 90% in the hydrosilylation of acetophenone with Ph₂SiH₂, 1 mol % of rhodium precursor or lower and 2–3 equiv of ligand, whereas the active catalyst was generated in situ.

The main contribution to the mixed heteroatom-systems was made by Fu et al.⁴¹ who used a slightly modified version to Hayashi and Uemura and designed a new class of planar *P,N*-based ligands. Ligand **8**—obtained in a linear 5-step synthesis after chiral HPLC separation—not only showed excellent yields and ee values in the hydrosilylation of alkyl aryl ketones but also worked very well with dialkyl ketones (Table 1).

These systems have led to a variety of new mixed heteroatom-based ligands (Figure 7).^{42–45}

Although all mixed heteroatom-based ligands mentioned before showed good results in the hydrosilylation of acetophenone, only the ligands by Fu and Evans gave significant enantiomeric induction in the transformation of dialkyl ketones.

2.4. *N*-Heterocyclic Carbene-Based Ligands. In the past 15 years, chiral ligand systems based on *N*-heterocyclic carbenes (NHCs) have been developed.⁴⁶ The unique properties of NHCs to form strong bonds to late transition metals are thought to be advantageous for chiral ligand scaffolds since they do not dissociate from the metal center during the catalysis and therefore no excess of ligand is needed.⁴⁷

As early as the 1970s and 1980s, Nile and Lappert reported the first rhodium NHC systems for the hydrosilylation of acetophenone with Ph₂SiH₂.^{48,49}

Table 1. Selected Results by Fu et al. in the Hydrosilylation of Ketones Using Ligand **8 and 1 mol % [Rh(cod)Cl]₂**

ligand	ketone	silane	yield	ee
 8		MesPhSiH ₂	94%	98%
		MesPhSiH ₂	95%	98%
		<i>o</i> -Tol ₂ SiH ₂	91%	94%
		<i>o</i> -Tol ₂ SiH ₂	98%	82%

In 1996, Herrmann and co-workers carried out the first asymmetric application with a chiral monodentate *N*-heterocyclic carbene derived from the enantiopure amine.⁴⁷ Enders later used axially chiral triazolinylenes.⁵⁰ Even though the chiral center in both systems is in close proximity to the metal center, the achieved ee's were moderate (Figure 8).

A couple of modified ligand architectures, both monodentate and bidentate, have been published since the initial reports,^{51–55} yet the mark of 90% ee was not reached until 2003, when Shi and co-workers reported the use of a chiral biscarbene ligand derived from BINAM.²² Although, the overall yield of the respective rhodium(III) complex was only moderate (Figure 9), the asymmetric hydrosilylation of various aryl methyl ketones gave ee values of up to 98%, excellent yields of around 90% with a catalyst loading of 2 mol % and also enantiopure alkyl methyl alcohols could be generated in high yields and ee's.

Gade et al.⁵⁶ reported the use of chiral, bidentate oxazoline-NHC ligands in 2004 and their use in the asymmetric hydrosilylation of aryl and alkyl methyl ketones with Ph₂SiH₂ which gave good to excellent yields and ee (Figure 9). The synthesis of the rhodium(I) catalyst was achieved in good yields, and 1 mol % of the complex in combination with 1.2 mol % of AgBF₄ to abstract the bromide gave the active catalyst.

The systems by Shi and Gade are still the best systems known in the asymmetric hydrosilylation of ketones using NHC-based ligands, which can even compete with the mixed-heteroatom-based ligands with regards to the variety of substrates used, especially dialkyl ketones.

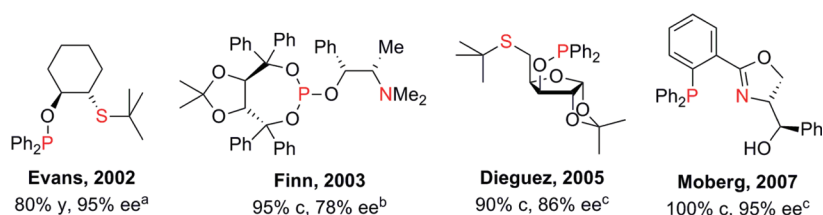


Figure 7. Further mixed heteroatom-based, bidentate ligands (yield/conversion and enantiomeric excess of silyl ether, catalyst loading of 1 mol % based on Rh); ^aacetophenone, 1-NpPhSiH₂; ^b1'-acetonaftone, Ph₂SiH₂; ^cacetophenone, Ph₂SiH₂.

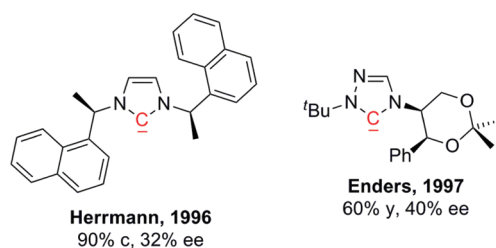


Figure 8. First chiral NHC ligands for asymmetric rhodium-catalyzed hydrosilylation of acetophenone with Ph₂SiH₂ by Herrmann and Enders (yield/conversion and enantiomeric excess of silyl ether, catalyst loading of 1 mol % based on Rh).

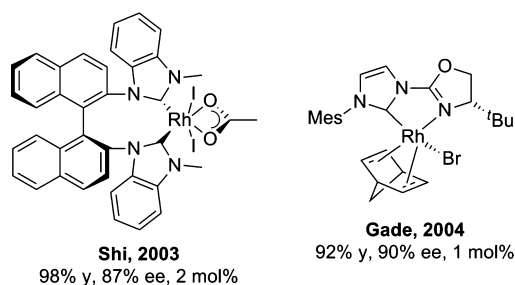


Figure 9. NHC rhodium complexes bis-NHC BINAM by Shi and oxazoline-NHC by Gade for the hydrosilylation of acetophenone with Ph₂SiH₂ (yield and enantiomeric excess of silyl ether).

2.5. Comparison of the Ligand Classes. To compare the presented ligand classes above, Table 2 summarizes the performance of each catalyst system in the hydrosilylation of acetophenone with Ph₂SiH₂, giving reaction temperature, catalyst loading, yield and ee.

The reaction temperatures of the catalytic reactions range from -60 to 25 °C with catalyst loadings of up to 5 mol %. Since in most cases kinetic studies have not been presented, the different reaction times are more a result of the protocols used rather than a measure for the activity of the catalysts. Therefore, the turnover number (TON) and turnover frequency (TOF) values are often lacking. All presented ligand classes have experienced significant development over the past decades and show good results in the asymmetric hydrosilylation of acetophenone with Ph₂SiH₂. In addition, the optimized ligand-to-metal ratios and the scope of the reactants successfully applied for each catalyst system have already been mentioned (see above).

2.6. Special Developments. Special applications of rhodium-catalyzed hydrosilylation of ketones have been of current interest. Gladysz et al.^{57,58} reported the hydrosilylation of cyclohexanone using a modified version of Wilkinson's catalyst carrying fluorinated phosphine ligands (Scheme 4).

Catalyst **9** was easily accessible by the reaction of [Rh(cod)Cl]₂ with a fluorinated phosphine and was insoluble in dibutyl ether.⁵⁹ However, a homogeneous phase was formed

Table 2. Catalytic Hydrosilylation of Acetophenone with Ph₂SiH₂

temp.	catalyst	time	yield	ee	ref.
<i>a</i>	1 mol %	41 h	95%	57%	Scheme 2 ²³
0 → 20 °C	0.5 mol %	38 h	99%	83%	Scheme 2 ¹⁹
0 °C	1 mol %	2 h	91%	94%	Figure 2 ²⁵
0 → r.t.	0.5 mol %	18 h	<i>a</i>	76%	Figure 3 ²⁶
0 °C	1 mol %	<i>a</i>	59%	84%	Figure 3 ²⁷
5 °C	1 mol %	2 h	98%	90%	Figure 3 ²⁸
0 °C → r.t.	0.5 mol %	18 h	90%	80%	Figure 3 ²⁹
-5 °C	1 mol %	72 h	84%	97%	Figure 3 ³⁰
-40 °C	1 mol %	5 h	89%	92%	Figure 4 ³⁴
0 → 20 °C	2 mol %	10–15 h	99%	84%	Figure 5 ³⁶
25 °C	1 mol %	1 h	75%	63%	Figure 5 ³⁹
r.t.	1 mol %	2 h	22%	71%	Figure 5 ⁴⁰
20 °C	1 mol %	<10 min	90%	90%	Figure 6 ²⁰
25 °C	0.5 mol %	15–25 h	100%	91%	Figure 6 ²¹
-30 °C	5 mol %	18 h	<i>a</i>	80%	Table 1 ⁴¹
r.t.	1 mol %	<5 min	90%	86%	Figure 7 ⁴²
-30 °C → r.t.	5 mol %	15 h	<i>a</i>	84%	Figure 7 ⁴³
-15 °C	1 mol %	1 h	90% ^b	86%	Figure 7 ⁴⁴
0 °C	1 mol %	16 h	100% ^b	95%	Figure 7 ⁴⁵
-34 °C	1 mol %	2 d	90% ^b	32%	Figure 8 ⁴⁷
11 °C	1 mol %	6 d	60%	40%	Figure 8 ⁵⁰
15 °C	2 mol %	24 h	98%	87%	Figure 9 ²²
-60 °C	1 mol %	10 h	92%	90%	Figure 9 ⁵⁶

^aNot determined/mentioned. ^bConversion.

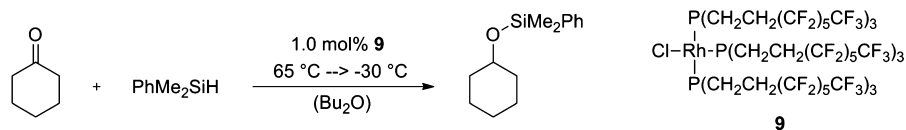
upon heating to 65 °C, which was cooled to -30 °C after the reaction to recover the precipitated catalyst. The hydrosilylation gave 98% yield of the corresponding silyl ether with 1 mol % of **9**, and the same results were obtained in four consecutive runs after recycling of the catalyst. The system was further developed and the catalyst could be recovered by precipitation on the surface of common Teflon tape upon cooling which made the recycling of the catalyst even easier.⁵⁷

Sawamura and co-workers published immobilized phosphine ligand [silica]-SMAP (**10**) which was synthesized in a 4-step route and gave excellent results in the hydrosilylation of sterically hindered dialkyl ketones (Scheme 5).⁶⁰

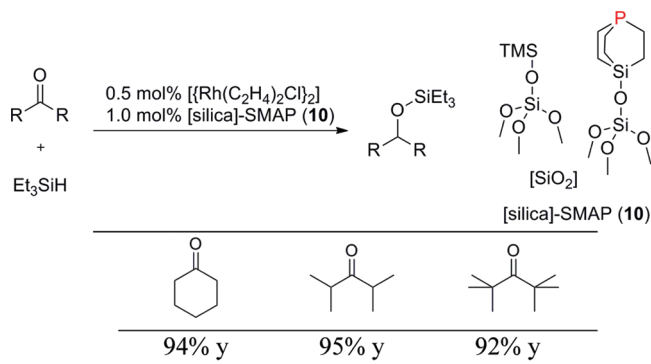
Neither self-aggregation of the catalyst nor leaching was observed with the immobilized system. The reported data and further experiments provided evidence for a rhodium species only coordinated by one phosphine of [silica]-SMAP (**10**).^{61,62} This trend was also seen in other publications where very bulky monodentate phosphines and isocyanides were used in homogeneous systems and proved to be very efficient ligands in rhodium-catalyzed hydrosilylation of ketones.^{63–66}

Very recently, research has focused on the application of rhodium-catalyzed hydrosilylation in ionic liquids.^{67–70} Good yields were achieved at very low catalyst loadings, which could

Scheme 4. Modified Wilkinson's Catalyst in the Hydrosilylation of Cyclohexanone by Gladysz et al.



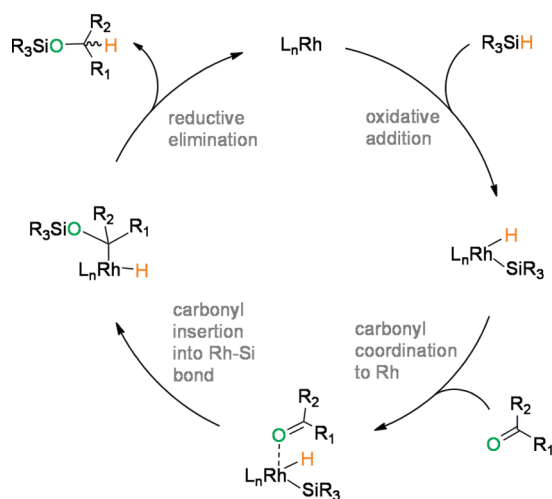
Scheme 5. Synthesis and Application of Sawamura's [silica]-SMAP (10)



be recovered and reused without a loss in catalytic activity. So far, only alkenes have been used as substrates, but this reaction system provides a new outline for future applications also in the hydrosilylation of ketones.

3. MECHANISTIC PERSPECTIVE

With the initial report of Wilkinson's catalyst in the hydrosilylation of carbonyl compounds,¹⁰ Ojima and co-workers adopted a modified version of the mechanism proposed by Chalk and Harrod for the hydrosilylation of alkenes (Scheme 6).^{17,71}

Scheme 6. Proposed Mechanism for the Hydrosilylation of Carbonyl Compounds by Ojima^a

^aL_n denotes any number of ligands, n may change during the catalytic cycle.

In the first step of the mechanism, a rhodium(III) species is formed via oxidative addition of the silane R₃SiH. Then, a ketone coordinates to the metal center before it inserts into the Rh–Si bond to form a rhodium(III) alkyl hydride species. These steps are followed by reductive elimination to yield the product R¹R²CH–O–SiR₃ and regenerate the catalyst L_nRh. The

isolation of [RhCl(H)(SiEt₃)(PPh₃)₂] provided experimental evidence for the existence and formation of the first intermediate of this catalytic cycle.¹⁰ Using a chiral analogue of Wilkinson's catalyst, a strong influence of the silane on the optical yield was observed.¹¹ Additionally, the opposite stereoconfiguration was obtained compared to the mechanistically similar hydrogenation reaction using the same catalyst.⁷² Therefore, according to the modified Chalk–Harrod mechanism, the insertion into the Rh–Si bond was proposed. This mechanism is generally referred to as the Ojima mechanism. In 2002, Prock and Giering published an extensive kinetic study on rhodium-catalyzed hydrosilylation of acetophenone with monohydro silanes, which supported the Ojima mechanism and also discussed the formation of byproduct.⁷³

Experimental results obtained by replacement of monohydro silanes by dihydro silanes, however, did not support the Ojima mechanism. Considerable rate enhancement was observed, and the product selectivities for the hydrosilylation of α,β-unsaturated ketones differ significantly for mono- and dihydro silanes, with monohydro silanes undergoing 1,4-addition exclusively.^{17,74} A kinetic isotope effect of two (KIE = 2) was determined in case of dihydro silanes, which—along with the above-described differences—led to the proposal of a different mechanism for the hydrosilylation of ketones with dihydro- and trihydro silanes by Zheng and Chan⁷⁴ (Scheme 7).

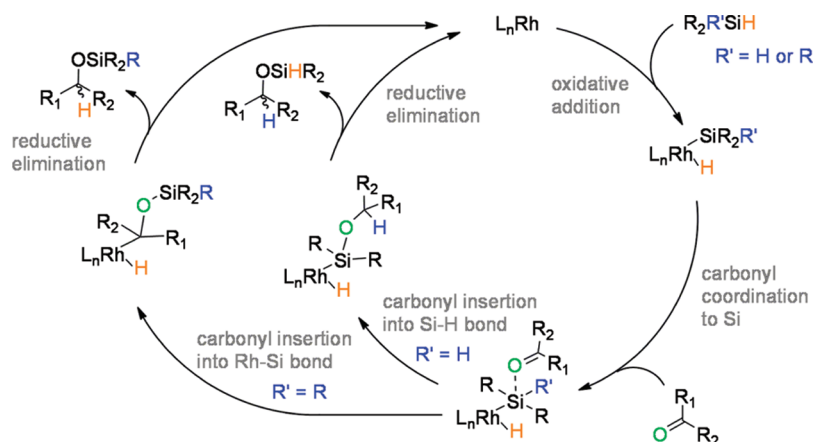
After oxidative addition of the silane R₂R'SiH and coordination of the ketone to the silicon atom, the insertion into the Si–H bond yields a rhodium(III) silyl hydride intermediate. In the last step, reductive elimination generates the hydrosilylation product and recovers the catalyst. The coexistence of the Ojima and Zheng–Chan mechanism therefore seemed to explain the different reaction rates for mono- and dihydro silanes. The observed kinetic isotope effect of KIE = 2 for dihydro silanes was not seen with monohydro silanes (KIE = 1) and therefore neither a Si–H nor a Rh–H bond is cleaved in the rate-determining step.

For the 1,2- and 1,4-selective hydrosilylation of α,β-unsaturated ketones, the mechanism suggested by Zheng and Chan was also applied. It involves a σ-coordination of the ketone to the silicon atom and a π-coordination of the double bond to the metal center (Scheme 8).

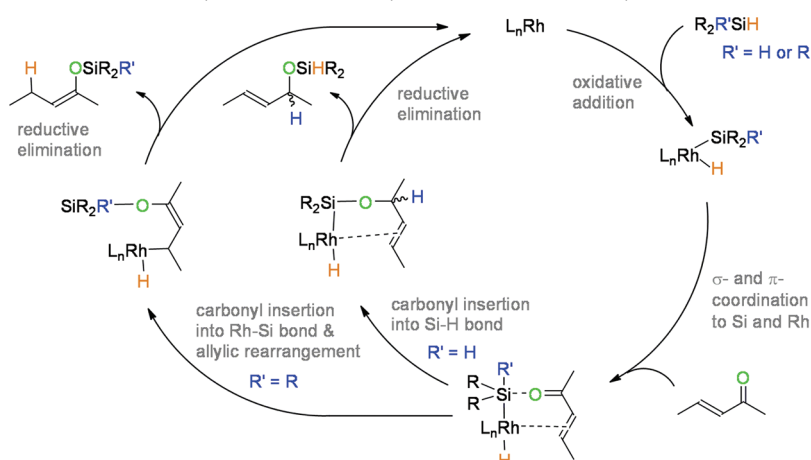
For di- and trihydro silanes, insertion of the carbonyl into the Si–H bond yields the 1,2-hydrosilylation product after reductive elimination. In case of monohydro silanes, a rearrangement of the σ,π-coordination intermediate gives the silyl enol ether after reductive elimination. In both cases, the formation of the σ,π-coordinated complex was expected to be the rate determining step, which is in accordance to the absence of a kinetic isotope effect.

In 2004 Gade et al.⁵⁶ reported the enantioselective hydrosilylation of ketones catalyzed by a rhodium(I) complex bearing a chelating chiral NHC–oxazoline ligand (Figure 9). In addition to the aforementioned rate enhancement, they determined an inverse kinetic isotope effect (KIE = 0.8) for dihydro silanes,^{75,76} which could not be explained by the Zheng–Chan mechanism. Therefore a third, silylene-based

Scheme 7. Mechanism Suggested by Zheng and Chan for the Hydrosilylation of Ketones with Di-/Trihydro Silanes (Inner Cycle) Compared to the Ojima Mechanism for Monohydro Silanes (Outer Cycle)

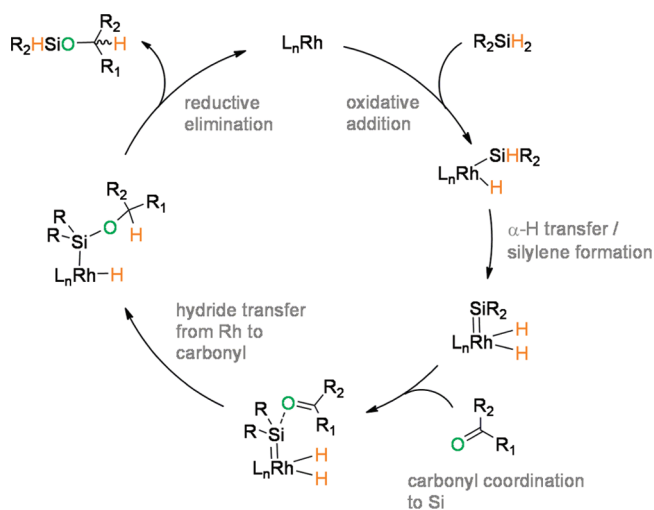


Scheme 8. Zheng's and Chan's Mechanism Accounting for the 1,2- and 1,4-Selectivity in the Hydrosilylation of α,β -Unsaturated Ketones with Monohydro Silanes (Outer Cycle) or Di-/Trihydro Silanes (Inner Cycle)



mechanism was proposed for the hydrosilylation with di- and trihydro silanes (Scheme 9), supported by theoretical studies.^{56,75}

Scheme 9. Hofmann-Gade Mechanism for the Hydrosilylation of Ketones with Di- and Trihydro Silanes



According to the calculations by Hofmann, Gade et al. from 2009, the silylene-mechanism involves the lowest activation

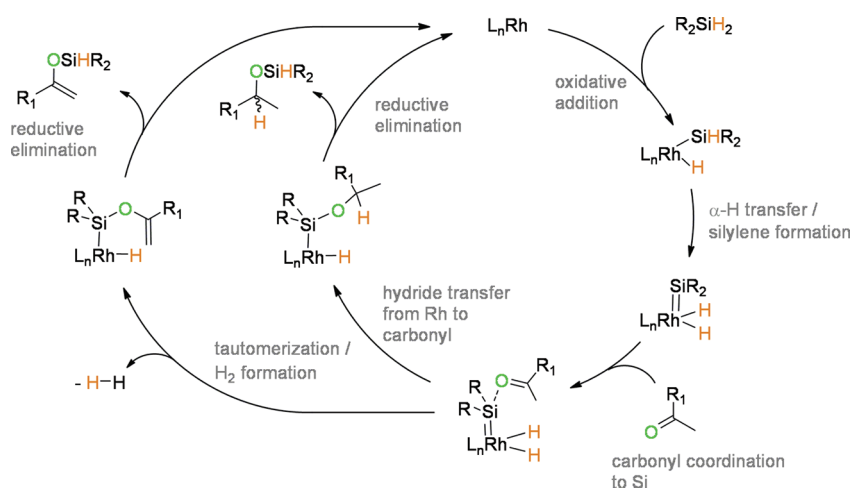
barrier for the rate-determining step. Whereas the oxidative addition of the silane R_2SiH_2 is consistent with both mechanisms discussed before, the second step involves the transfer of a second hydrogen atom from the silyl ligand to the rhodium center and thus the formation of a silylene rhodium(III) dihydride species. The ketone coordinates to the electron deficient silicon atom and after a hydride transfer from the metal to the carbonyl carbon, the catalytic cycle is closed by reductive elimination of the product.

The existence of such a silylene species was discussed earlier in rhodium-catalyzed dehydrogenative coupling reactions.^{77–79} Goikman and Milstein were the first to provide evidence for a rhodium silylene species by reacting a diphosphine rhodium triflate complex with a stoichiometric amount of diphenylsilane.⁸⁰ Since the silylene species could not be observed directly, it was trapped with $tBuMe_2SiOH$ and the corresponding rhodium(III) dihydride complex was isolated.

Recently, experimental evidence for the formation of a rhodium silylene intermediate in the hydrosilylation of ketones with dihydro silanes and a biscarbene rhodium(I) catalyst was given by our group leading to an extended silylene-based mechanism (Scheme 10).⁸¹

The inner cycle corresponds to the Hofmann-Gade mechanism, whereas the outer cycle leads to the formation of silyl enol ether as a side product. The oxidative addition of the silane to the cationic rhodium(I) center is again the first step in

Scheme 10. Extended Silylene-Based Mechanism for Acetophenone, also Accounting for the Formation of Silyl Enol Ether as a Side Product



the catalytic cycle. In a stoichiometric reaction of the catalyst with diphenylsilane, the formation of small amounts of cyclooctane and dihydrogen, as well as oligomeric diphenylsilane species—typical products of dehydrogenative coupling—were observed, while the addition of equimolar amounts of diphenylsilane and 1,5-cyclooctadiene led to the reduction of cyclooctadiene to cyclooctene and also 1,3- and 1,4-isomers of cyclooctadiene were formed. Since α -H transfer of the second silicon–hydrogen to the rhodium atom and concomitant formation of the silylene rhodium dihydride was expected to be the key step of the mechanistic cycle, Ph_2SiHD together with an equimolar amount of 1,5-cyclooctadiene under catalytic conditions should give different product distributions for intra- and intermolecular reaction pathways. The reaction did not show any DD-hydrogenation products and therefore supported an intramolecular hydride transfer. A silylene-trapping experiment with $^t\text{BuMe}_2\text{SiOH}$ resulted in vigorous evolution of hydrogen and the formation of disiloxane when using dihydro silanes, whereas no conversion occurred with monohydro silanes over a period of several days, thus supporting the existence of a silylene rhodium(III) dihydride as a key intermediate.

As an effect of the Lewis-acidity of the silylene Si atom, the ketone coordinates to the silicon atom instead of the rhodium center. Two possible pathways arise: reduction of the carbonyl via H-transfer from the metal center (inner cycle, Scheme 10) or formation of silyl enol ether as the side product (outer cycle, Scheme 10). This requires a tautomerization of the ketone after coordination to the Si atom to form the silyl enol complex and the release of hydrogen, which is the driving force for the formation of the undesired side product. This reaction pathway can be suppressed by performing the reaction under H_2 pressure as Compte et al.⁸² showed for analogous systems. Another approach is to reduce the Lewis-acidity of the electron-deficient silicon atom to favor the keto tautomer. Replacement of the noncoordinating solvent methylene chloride by coordinating tetrahydrofuran resulted in a slight increase in product selectivity (68% \rightarrow 74%). The same trend was observed when diphenylsilane was replaced by the more electron-rich *ortho*-methoxy-substituted diphenylsilane (68% \rightarrow 92%). Therefore the Lewis-acidity of the silylene species seemed to be responsible for the formation of high amounts of side product. Accordingly, Ph_2MeSiH did not yield any side product because no silylene species can be formed.

Hofmann, Gade et al.^{75,76} assigned the hydride transfer as the rate-determining step. An inverse kinetic isotopic effect of 0.57 in unison with the absence of a Hammett correlation, when using different *para*-substituted diphenyl silanes, confirmed the rate-determining step.

In summary, three mechanisms for the hydrosilylation of ketones with rhodium complexes have evolved: While the Ojima-mechanism from 1975 is still accepted for monohydro silanes,¹⁷ the Zheng-Chan mechanism from 1995 was replaced by the Hofmann-Gade mechanism in 2009, which is the most reasonable mechanism in rhodium-catalyzed hydrosilylation of ketones with di- and trihydro silanes.^{74–76} Recent work by our group considers multiple reaction pathways in parallel to the Hofmann-Gade mechanism.⁸¹ Although, the silylene-based mechanism has been well studied, some aspects are still not fully understood and require additional research. Further effort should focus on the direct observation of the silylene-intermediate as well as the influence of the solvent and the steric properties of the silane. In addition, recently published articles could be of potential help to further develop a complete mechanistic picture.^{83–85}

4. CONCLUSION

Rhodium-catalyzed hydrosilylation of ketones has been a versatile tool in organic synthesis for almost 30 years. Because of the very mild reaction conditions, catalytic hydrosilylation became an interesting alternative to the common reduction methods of ketones to chiral alcohols. This led to intensive research in the field after the initial discovery by Ojima et al. in 1972. Although rhodium-catalyzed hydrosilylation is somewhat limited because of the need of expensive, mainly aryl silanes as hydride donors and rhodium being the most expensive transition metal, the mechanism is well understood and therefore provides insight and fundamental understanding of these types of catalytic transformations. The transfer of these concepts to other, environmentally benign and cost efficient metals has proven to be difficult since there is increasing proof in literature that the hydrosilylation of ketones with catalysts based on early and middle transition metals proceeds via pathways different than those established for rhodium.⁸⁶ Nevertheless, the achievements in rhodium-catalyzed hydrosilylation of ketones have led to a mechanistic picture, which clearly benefits the development of new catalyst systems. This

should be seen as an incentive to focus more on the understanding of mechanistic details in the recent catalyst systems based on cheaper metals. Several simple iron salts and nitrogen donor ligands or phosphines were used to generate active iron catalysts in situ for the hydrosilylation of ketones.^{87–89} Also copper(I) hydride complexes have been successfully applied for the hydrosilylation of carbonyl compounds by Brunner, Nolan, and Lipshutz.^{90–100} At the moment, research is being focused on the development of catalyst systems based on Fe, Cu, and other comparable cheap metals. However, no profound mechanistic understanding for these types of complexes has been developed so far. Besides the mechanistic investigations, rhodium systems also provide high TONs of up to 50,000 h⁻¹ which are comparable to those of the most active catalysts based on copper,^{101,102} but still the research on rhodium-catalyzed hydrosilylation of ketones might seem a little outdated because of reasons mentioned earlier. Nevertheless, potential in the field of immobilization of rhodium hydrosilylation catalysts as well as applications in “new” solvent media like fluorous phase or ionic liquids and in the synthesis of fine chemicals is clearly visible.

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Funding

We are grateful for financial support of the Wacker Chemie AG (Ph.D. grants for M.P.H. and P.G.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Mathias Esser for the graphical abstract and Dr. Mirza Cokoja for proof-reading of the manuscript.

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