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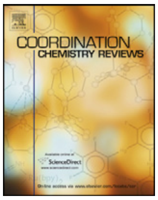

Review

Recent advances and actual challenges in late transition metal catalyzed hydrosilylation of olefins from an industrial point of view

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ABSTRACT

Hydrosilylation of olefins is the key catalytic reaction for the production of industrially important organosilicon compounds such as organofunctional silanes and silicones. Moreover catalytic hydrosilylation is used for crosslinking of silicone polymers to elastomers and silicone-based release coatings, and for coupling of silanes and siloxanes to organic polymers. Industrially relevant aspects of hydrosilylation are dominated by the selectivity, activity (defined by the turnover frequency (TOF)), and stability (defined by the turnover number (TON)) of hydrosilylation catalysts as well as switchable catalyses. Furthermore, the high and volatile price of platinum as the industrially most important catalytic metal is a strong motivation for the reduction of precious metal consumption, such as homogeneous catalyst recycling or increasing the TOF resp. TONs of established hydrosilylation catalysts, or employing lower-priced transition metal catalysts. The selectivity of hydrosilylation determines yield and production costs of functional silanes, e.g. hydrosilylation products of allyl chloride, but is of equal importance for the product quality of silane-modified organic polymers and hybrid polymers. As industrial applications of hydrosilylation curing silicones, such as release coatings and elastomers, continuously move towards higher production speed, this requires catalytic systems capable of very high activity resp. turnover frequencies at temperatures typically above 100 °C, but allowing shelf-stable silicone compositions and therefore requiring suppression of any catalytic activity at ambient conditions prior use. This form of switchable catalysis employs carefully designed catalytic systems, which are activated by heating or photoactivation in a very short period of time, demanding very high standards of industrial hydrosilylation chemistry.

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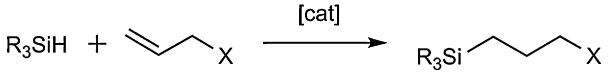
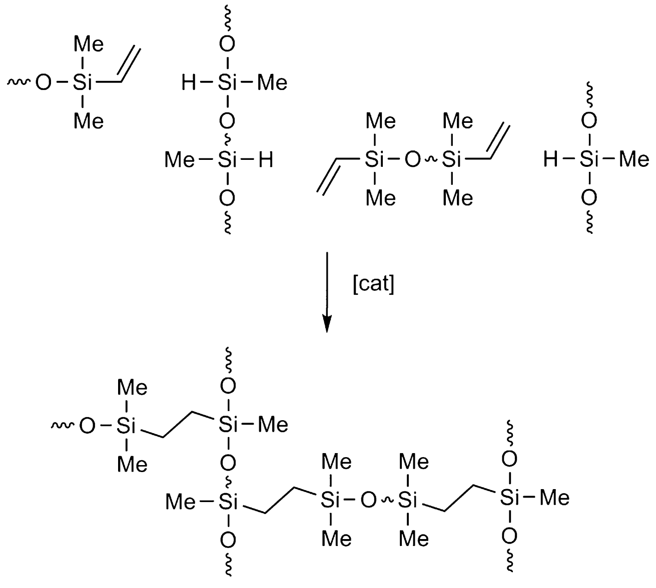


Scheme 1. Formation of γ-substituted propylsilanes by catalyzed reaction of silicon hydrides with allyl compounds.

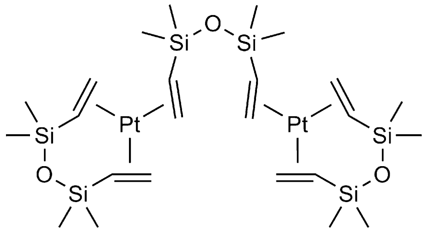
1. Introduction

The catalytic addition of organic and inorganic silicon hydrides to multiple bonds (hydrosilylation or hydrosilation), in particular to C=C or C≡C bonds, has proved to be an efficient method for the formation of organosilicon compounds and represents (in combination with the Direct Process [1]) one of the most important reactions in the silicone industry. The hydrosilylation process is widely applied in the synthesis of industrially employed organofunctional silanes [2] (such as γ-substituted propylsilanes, Scheme 1) and for the production of silicone polymers [3] such as silicon oils, functional siloxanes [4] and silicone resins [5]. Furthermore, hydrosilylation is employed as an important way for crosslinking of multifunctional silicone hydride polymers with multi-vinyl functional silicone polymers, forming a three-dimensional network and resulting in a curing of the silicone composition (Scheme 2). This technology is applied in manufacturing of silicone elastomers [6,7] and silicone-based release coatings [8,9], so these important applications of hydrosilylation reaction are basically used from customers of the silicone industry. Furthermore, catalytic hydrosilylation is used for coupling of silanes and siloxanes to organic polymers, giving polysiloxane copolymers [10] and silane-modified polymers (SMP) [11] which are of interest as adhesive and sealing materials [12]. The economical production of these products with their individual properties requires well-designed catalytic systems for the hydrosilylation process, respectively, which are almost exclusively based on transition metal coordination compounds.

It is important to note that any hydrosilylation catalyst used in crosslinking reactions leads to an immobilization of valuable metal catalysts in the crosslinked product (such as rubber or coatings) and is lost for further reuse, whereas in the production of organofunctional silanes the catalyst can be recovered in most cases. Consequently, high amounts of metal catalyst permanently remain in the silicone polymer products (especially in the production of silicone release coatings), so the search for low-cost hydrosilylation catalysts is an important issue in industrial hydrosilylation research.



Scheme 2. Crosslinking reaction between SiH-functionalized silicone polymers and vinyl-containing polysiloxanes.



Scheme 3. Formula of Karstedt's catalyst.

The first hydrosilylation reaction was reported in 1947 by Sommer in which trichlorosilane and 1-octene reacted in the presence of peroxide in a free-radical mechanism with low selectivity [13]. Some years later, platinum supported on powdered charcoal was observed to be an active and more selective catalyst in the hydrosilylation of trichlorosilane with acetylene or allyl chloride [14]. With the discovery of hexachloroplatinic acid as a very effective homogeneous platinum-based catalyst by Speier in the late 1950s [15], an important milestone in the development of transition metal catalyzed hydrosilylation was achieved, leading to wide application of this process in the silicone industry. Due to the long induction period and the moderate activity of the Speier catalyst system, Karstedt developed in 1973 platinum(0) complexes containing vinyl-siloxane ligands [16] which are characterized by better solubilities in polysiloxane compositions and high catalytic activity. The most prominent example of this type of platinum complexes is Karstedt's catalyst (Scheme 3) which is the most versatile and established catalyst for industrial hydrosilylation processes today and represents the benchmark for other hydrosilylation catalysts [17,18].

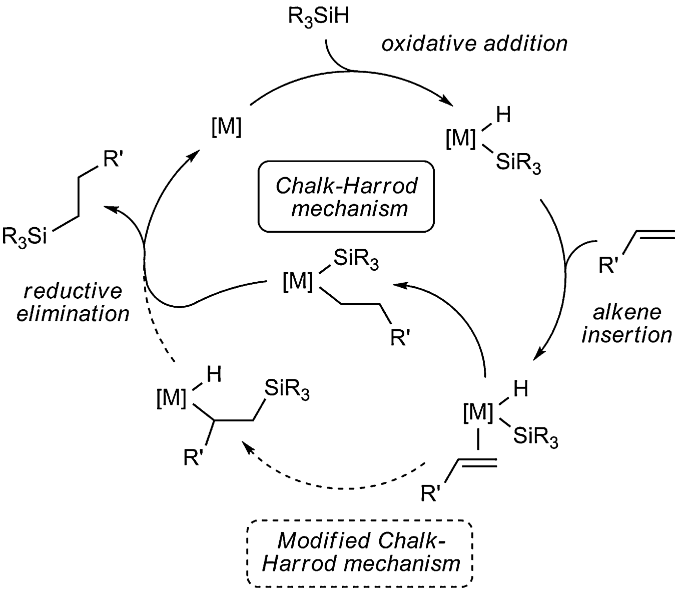
Catalyzed hydrosilylation reactions or selected aspects of these processes are discussed intensively in the scientific literature, and a variety of comprehensive reviews, articles, chapters or books was published in the last twenty years [19]. Very recently, Marciniec reviewed the advances of hydrosilylation processes covering the time between 1990 and 2007 [20,21].

As a supplement and a contribution to the communication between academic and industrial research, this review will address selected industrially relevant aspects of olefin hydrosilylation processes. The main focus is the selectivity, activity, and stability of homogeneous hydrosilylation catalysts as well as switchable catalyses, covering the literature (especially the patent literature) that appeared during the last decade, i.e. 2000–2010. The aim of this review is to discuss the most important issues of industrial hydrosilylation and to emphasize the aspects which are not satisfactorily clarified. We will give indications for future developments to make progress in this field.

2. Selectivity of hydrosilylation reactions

The relevance of the selectivity of catalyzed hydrosilylation strongly depends on the respective application. In the case of the synthesis of organofunctional silanes (Scheme 1), selectivity of hydrosilylation is directly related to the yield of the desired product and the formation of byproducts, and therefore to manufacturing costs of organofunctional silanes. In the discussion of crosslinking polymerization (Scheme 2), high selectivity is required to achieve high crosslinking densities and to minimize residual unreacted functional groups, corresponding to high product quality.

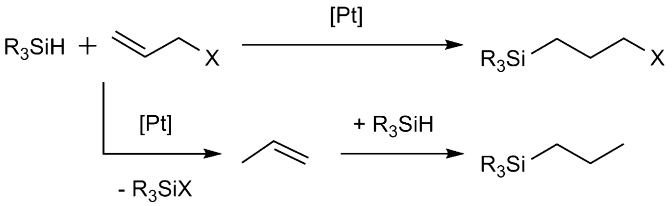
Platinum-catalyzed hydrosilylation of olefins is commonly explained by the Chalk–Harrod mechanism [22] which involves



Scheme 4. Chalk–Harrod and modified Chalk–Harrod mechanism of transition metal catalyzed hydrosilylation of alkenes.

elementary steps such as the oxidative addition of silanes $HSiR_3$ to a metal alkene complex, an insertion of the alkene into the M–H bond, and reductive elimination by Si–C bond formation (Scheme 4). Although the basic aspects of the Chalk–Harrod mechanism enjoy great acceptance, some phenomena, such as an induction period for many (pre)catalysts or the formation of vinylsilanes [23], are not explained by this mechanism. Therefore another mechanism (called the modified Chalk–Harrod mechanism; Scheme 4) was proposed later which involves the alkene insertion in the M–Si bond followed by the C–H reductive elimination. Recent studies including quantumchemical calculations concluded that the Chalk–Harrod cycle in Pt-catalyzed hydrosilylation reactions is energetically preferred over the modified Chalk–Harrod mechanism because the activation barrier of the rate-determining step of the modified Chalk–Harrod mechanism, the olefin insertion in the M–Si bond and isomerization, is much higher than that of the Chalk–Harrod mechanism (isomerization of the ethylene insertion product [Pt(silyl)(alkyl)]) [24]. This result was supported with the synthesis and characterization of the alkene–platinum–silyl complexes $[(R_3Si)Cl(COD)Pt]_2$ (COD = 1,5-cyclooctadiene) and $(COD)Pt(SiR_3)_2$ which has been postulated as hydrosilylation intermediates of the Chalk–Harrod mechanism [25].

Unfortunately, platinum-catalyzed hydrosilylation of alkenes does not quantitatively proceed to the idealized cycle shown in Scheme 4 and is often accompanied by side reactions, leading to significant yield losses of the desired product. The reasons for side reactions can be located in the reactivity of alkenes (isomerization, oligomerization, polymerization, and hydrogenation) as well as in that of silicon hydrides (redistribution and dehydrogenation) and in reactions in which both substrates take part (e.g. dehydrogenative silylation) [26,27]. An additional observation which especially concerns the hydrosilylation of alkynes is its low regio- and stereoselectivity which mostly leads to mixtures of isomeric alkenylsilanes or the formation of bissilylated adducts [28]. Side reactions and the formation of byproducts do not often matter in academic hydrosilylation research, but represent significant issues in industrial processes because they cause additional efforts for purification and separation of the desired products and increase the costs of the production process (e.g. additional consumption of educts, disposal of waste products, etc.). Consequently, there is a great interest in the silicone industry to develop new highly selective catalytic systems. In this section, some selected and industrially important hydrosilylation reactions requiring improved selectivity will be presented.



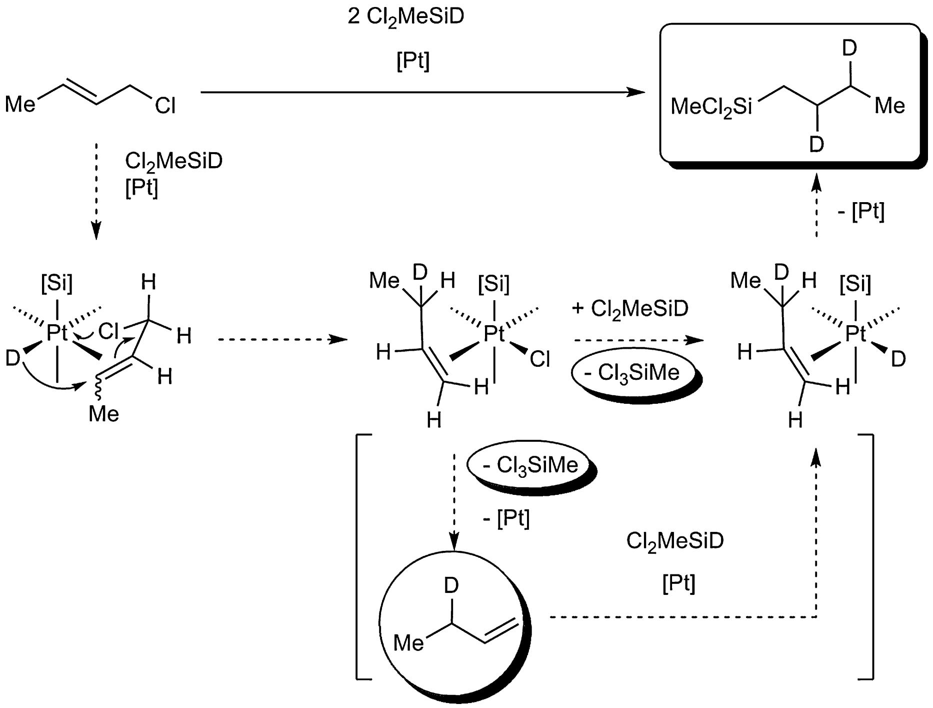
Scheme 5. Hydrosilylation of allyl compounds.

2.1. Hydrosilylation of allyl compounds

The hydrosilylation of allyl compounds is industrially employed for the production of γ-substituted propylsilanes (Scheme 1) and is a well-known example for a hydrosilylation process with rather imperfect selectivity. By using established platinum-based catalytic systems (such as Speier's or Karstedt's catalyst), an H/X redistribution reaction occurs and significant amounts of propene are formed which in a second step can also react with the silicon hydride to *n*-propylsilane as side product (Scheme 5). Mechanistic studies on the system $Cl_3SiH/CH_2{=}CHCH_2Cl$ (Pt/C catalysis) showed that the formation of propene and $SiCl_4$ occurs competitively, whereas the formation of trichloro(*n*-propyl)silane is a consecutive reaction [29]. This result allowed the conclusion that the selectivity of this type of reaction can be partially controlled via the concentrations of the reaction partners and the order of their addition to the reaction mixture.

Most synthetic procedures for the hydrosilylation of allyl compounds (mainly allyl chloride) recommend a sequence in which the silane R_3SiH is mixed with the catalyst, and the alkene is subsequently added to the silane under effective reaction conditions. By using this order, the reaction mixture initially contains a minimum concentration of unreacted olefinic compound in the reaction medium relative to the silane, and thus effectively establishes a very large molar excess of the silane relative to the allyl compound in the reaction medium which promotes the formation of the desired γ-substituted propylsilane [30,31]. In the platinum-catalyzed hydrosilylation of trichlorosilane $HSiCl_3$ with allyl chloride, most experiments were carried out in a small excess (1.1–1.3:1.0) of $HSiCl_3$ which was reported to be the optimum ratio of these two substances [29]. Some industrial processes purposefully use an excess of silicon hydride to achieve higher selectivities for the formation of the desired product. For instance, the excess of the silane (e.g. $HSiCl_3$) can be achieved by using a cascade of several serial-connected tubular reactors [32], dosing proportionate quantities of allyl chloride between the reactors and reacting it in the following reactor in each case [33]. This process is characterized in that $HSiCl_3$ is brought into contact with the catalyst in a 3–100 fold molar excess in relation to allyl chloride, so the yield of the desired trichloro(3-chloropropyl)silane can be increased from 74% to 85% in relation to allyl chloride [33]. A variation of this process is the use of a reaction column [34], in which the silane accumulates and the amount of propene is minimized [35]. The disadvantages of this approach are the lower turnovers due to the decreasing catalyst activity which require a periodic replacement of the catalyst. Furthermore, an excess of the silicon hydride favors the consecutive reaction of propene to the undesired *n*-propylsilane.

Another approach which allows the formation of propene, but suppresses the formation of *n*-propylsilanes, is the use of an excess of the allyl compound by simultaneous removal of the formed



Scheme 6. Proposed mechanism of byproduct formation via allylic rearrangement [19i].

propene [36]. Although the competitive H/X redistribution reaction proceeds at the same scale, the silane component preferentially reacts to the γ-substituted propylsilane due to the higher availability of the allyl compound, so the yield of the final product can be increased. The disadvantage of these processes is the higher consumption of allyl compounds, and the recovery of unreacted substances causes additional costs.

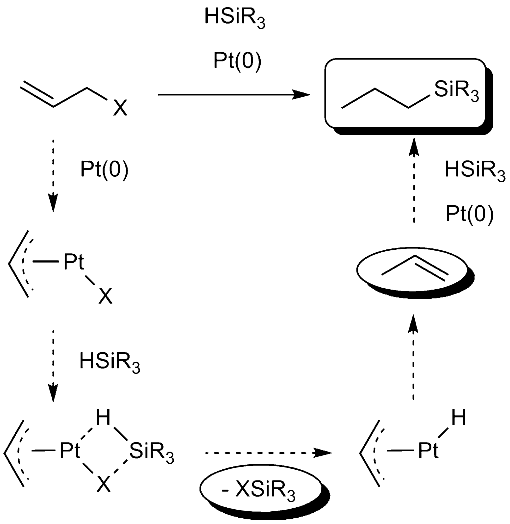
It seems contradictory that the use of an excess of silane as well as an excess of the allyl compound lead in both cases to better selectivities, respectively. This is due to the use of different reference points for the term "selectivity" preventing a direct comparison of these selectivities. From the examples described above it can be concluded that the use of an excess of silane increases the selectivity of the formation of the desired γ-substituted propylsilane *in relation to the allyl compound* and suppresses the formation of propene in the first competitive step, but almost every propene generated reacts in the consecutive step to the undesired n-propylsilane. This approach is recommended for hydrosilylation processes of valuable allyl compounds. On the other hand, the use of an excess of the allyl compound allows the formation of propene, but strongly reduces the reaction of the silane with the propene, so the selectivity *in relation to the applied silane* is improved. This procedure is advisable for reactions based on valuable silicon hydrides. These examples clearly demonstrate that selectivity has to be discussed very carefully, and the fundamental mechanistic comprehension about the catalytic cycle and the formation of main and byproducts is not complete yet. This is aggravated by the fact that only few systematic studies were published until now, and these cannot be compared among each other in most cases due to the large differences in the hydrosilylation systems (e.g. different silanes, allyl compounds, or catalysts used as well as non-uniform reaction conditions, respectively).

From the hitherto published results, two basic approaches for the explanation of byproduct formation can be proposed:

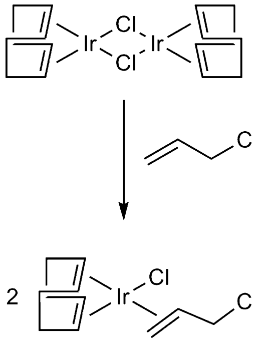
(1) Assuming the oxidative addition of the Si–H bond to be the first step in the catalytic cycle, a platinum-catalyzed allylic rearrangement reaction can occur during hydrosilylation, as it was shown in a study performed by Roy et al. [19i] (Scheme 6).

(2) Another possibility is an oxidative addition of the C–X bond in the first step of the catalytic cycle. It is well known that almost all transition metals react with allyl compounds to η^3-bound allylic complexes due to the easily activated C–X bond [37]. In the next step, reaction with one equivalent of a silicon hydride R_3SiH should lead to the elimination of a silane R_3SiX and the formation of propene, which reacts with a second equivalent of R_3SiH to the related n-propylsilane (Scheme 7) [38].

Both basic mechanisms (1) and (2) give indications for the development of more selective catalytic systems for the hydrosilylation of allyl compounds. In the case of (1), the allylic rearrangement



Scheme 7. Proposed mechanism of the formation of byproducts via η^3-bound allylic complexes [38].



Scheme 8. Coordination of allyl chloride to [(COD)IrCl]$_2$ [44].

has to be suppressed, whereas in the case of (2) the C–X activation and the oxidative addition of the allyl compound to the metal center have to be inhibited. One possibility to influence the course of reaction and to suppress undesired side reactions is the addition of promotors such as carboxylic acids [39], aromatic compounds [30], phosphines [40], or nitrogen-containing compounds [41] which can improve both the selectivity and the activity of the catalysts used.

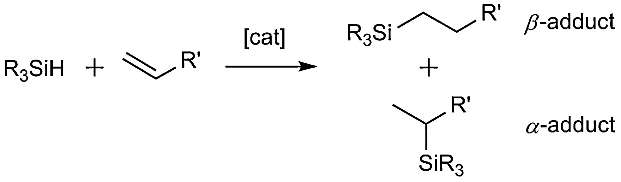
However, the most promising approaches for the economic production of organofunctional silanes generating only small amounts of byproducts are based on hydrosilylation catalysts which contain other transition metals than platinum which are able to coordinate the alkene but are stable against C–X activation. Suitable catalysts are iridium compounds such as $IrCl_3$ hydrate or H_2IrCl_6 [42], but the most established representatives are dimeric iridium complexes of the general formula type [(diene)IrX]$_2$ (X = Cl, Br, I; diene = 1,5-hexadiene, 1,5-COD, 2,5-norbornadiene [43]) which effectively suppress the H/X redistribution reaction and increase in this way the yields of the desired hydrosilylation products. The industrially most important iridium-based catalyst of this type [(COD)IrCl]$_2$ is well-known in the hydrosilylation of allyl chloride reacting only via coordination of the alkene and not via oxidative addition (Scheme 8) [44]. Unfortunately, the lifetime of [(COD)IrCl]$_2$ is very short and its activity rapidly decreases during the hydrosilylation reaction by forming elemental iridium, resulting in low yields and uneconomical high catalyst loads needed (ca. 1000 ppm). It was shown that the addition of a large excess of the free ligand COD as co-catalyst (100–200 mole% related to Ir) suppresses the deactivation of the catalyst and allows a drastic reduction of the Ir-concentration (ca. 100 ppm) along with almost quantitative turnovers and high selectivities (yields 90–95%, purities up to 99%) [43c,43f,45]. As an undesired side effect, a reaction of the free diene with the silane can also occur, leading to the formation of byproducts which are difficult to remove from the target products. This problem can be solved for example by the use of polymeric co-catalysts such as polyenes for continuous or discontinuous reaction processing [46]. Another approach which gets along without excess of diene is the iridium-catalyzed hydrosilylation with [(diene)IrX]$_2$ (preferably [(COD)IrCl]$_2$) in the presence of oxidative co-catalysts which are able to reconvert iridium from a reduced state to an oxidized one (via organic oxidants like aldehydes, ketones, diketones (e.g. 1,2- and 1,4-cyclohexanedione), quinones (e.g. *p*-benzoquinone), or organic peroxides) [47]. Due to the permanent reactivation of the iridium catalyst, its turnover number (TON) can be significantly increased and a continuous production of γ-substituted propylsilanes in an industrial scale may be possible, e.g. by using a loop reactor [48]. However, the formation of new side products due to the presence of these co-catalysts was not discussed in these examples.

The main disadvantages of these iridium-based catalysts are their low turnover frequencies (TOFs), resulting in high catalyst loads needed, and the relatively high price of iridium (also compare Section 3), so they are almost exclusively applied in the selective production of organofunctional silanes allowing for regain of spent iridium.

A promising and low-cost alternative seems to be ruthenium compounds which are far cheaper than iridium and platinum and are also able to catalyze the hydrosilylation reaction of allyl chloride with silanes such as trimethoxysilane under certain conditions [49]. Typical ruthenium-based catalysts which are of interest for the industrial hydrosilylation of allyl compounds are $RuCl_3$ hydrate, $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$, and (COD)$RuCl_2$ [31,50,51] which are sometimes combined with electron-donating promotors such as aromatic compounds (e.g. toluene, ethylbenzene, anisole, biphenyl) for increasing the product yields [30]. Ruthenium complexes containing only triphenylphosphine, hydrido and chloro ligands such as $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3RuHCl$, and $(Ph_3P)_3RuH_2$ are ineffective as catalysts and need additional ligands which are different from hydrogen or chlorine [31], e.g. $[Ru(CO)_3(PPh_3)_2]$ [49]. Therefore, ruthenium carbonyl complexes are the most preferred Ru-catalysts, but they have poor activities and are often dependent on the presence of oxygen for (re)activation which is problematic in industrial processes [31,51]. Another problem in ruthenium-catalyzed hydrosilylation are significant side reactions which are additionally promoted, such as dehydrogenative silylation of alkenes (forming of vinylsilanes [52]), alkene metathesis, alkene reduction, and alkene isomerization [53]. Based on these facts, a special design of suitable ruthenium catalyst is essential for allowing a reasonably selective hydrosilylation of allyl compounds with good yields. The Ru-catalyzed hydrosilylation and its problems and advantages will be embraced more detailed in Section 3.

In addition to the described transition metal catalysts, a remarkable patent application reported the hydrosilylation of allyl chloride with triethylsilane by using neat platinum-free copper-containing catalysts such as copper acetate, copper chloride, and copper sulfate which also eliminated undesired byproducts such as *n*-propylsilane [54]. However, this catalysis did not proceed via a transition metal complex-catalyzed mechanism but is rather based on nucleophilic–electrophilic catalysis [55]. But just like the described ruthenium complexes, these copper-based catalysts do not achieve the high yields and selectivities of the iridium-based hydrosilylation catalysts and clearly need further development for their optimization.

The selectivity of catalyzed hydrosilylation processes including allyl compounds depends not only on the respective catalyst but also on the nature of the alkene itself. A very particular case is the platinum-catalyzed hydrosilylation of primary allyl amines which usually led to the formation of hydrogen and a complex mixture of unidentified products, presumably aminosilanes [56]. In some efforts these hydrosilylation reactions are performed at high reaction temperatures and pressure or are carried out in the presence of reaction promotors [57], but this reaction is incomplete (70–85% yield) and of no industrial use. Improvements have been achieved by using rhodium-based catalysts [58]. This approach is hampered by the extremely high price of rhodium which does not allow a production of primary γ-aminopropylsilanes in an industrial scale (see also Section 3). Although this unexpected behavior of primary allyl amines hydrosilylation is known for over fifty years, no satisfying explanation has been hitherto described. However, it is remarkable that the hydrosilylation of secondary or tertiary *N*-substituted allyl amines does not liberate hydrogen to any noticeable extent [59], so the addition of silicon hydrides to methallyl amines of the general formula type $CH_2{=}C(Me)CH_2NR$ (e.g. R = Me, Pr, Bu, Ph) led to isomeric pure products in high yields and turnovers [60].

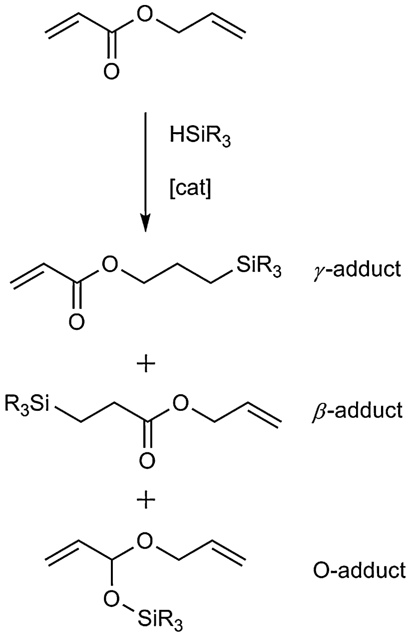


Scheme 9. Formation of α/β hydrosilylation products.

2.2. Hydrosilylation of other olefinic compounds

There are many other aspects concerning the selectivity of hydrosilylation processes which are also of interest from an industrial point of view. An important issue which should be mentioned in the context of C-allylic hydrosilylation is the isomerization of terminal alkenes. Pt-catalyzed hydrosilylation of terminal alkenes containing $CH_2{=}CHCH_2$– moieties is generally accompanied by unwanted isomerization of the allylic C=C bond to its internal isomer $CH_3CH{=}CH$– which is unreactive towards hydrosilylation [26]. This leads to an accumulation of isomerized, unreacted alkene in the process and may cause problems with product purification and quality. For example, levels of isomerization in the hydrosilylation products of allyl-terminated poly(alkeneoxide) are typically in the region of 10–30% [61]. It is possible to reduce the isomerization levels of compounds containing a $CH_2{=}CH{-}CH_2$– moiety to less than 0.1 mole% via procedural methods, e.g. by feeding the silicon hydride and the allyl compound through a reaction zone maintained at a temperature in the range of 115–250 °C (preferably in the range 130–170 °C) via heat exchanger [62] to dissipate the heat from the exothermic hydrosilylation reaction [61]. A similar problem is the isomerization of dienes, in which the C=C bond drifts from a terminal position to an internal one, causing degraded or nonexisting hydrosilylation activities. An example for minimizing these amounts of drifting C=C bonds uses platinum complexes as catalysts in the presence of amino-containing promotors (e.g. octylamine; ratio Pt:N ≈ 1:2) [63]. For instance, in the reaction of 1,5-hexadiene with $HMeSiCl_2$ by using Speier's catalyst, the percentage of isomerization can be reduced from 33 to 5 mole% in this manner [63], clearly demonstrating the selectivity effects of modified catalytic systems. Another approach for suppressing the isomerization of alkenes is the use of a new class of highly selective *N*-heterocyclic carbene platinum(0) complexes (NHC–Pt(0)) which were developed by Markó et al. during the last decade (see also Section 3.1.3) [64,65]. The *N*-heterocyclic carbenes as robust σ-donor ligands increase the electron density at the platinum atom and reduce its activity (=decrease of the TOF). In this way, the selectivity of these NHC–Pt(0) complexes is improved compared to Karstedt's catalyst. For instance, a NHC–Pt(0) catalyst was recently applied in the hydrosilylation of bis(4-(but-3-enyl)phenyl)methylsilane, leading to hyperbranched polycarbosilanes showing only trace amounts of isomerized double bonds [66].

In general, the catalytic cycle of platinum-catalyzed hydrosilylation according to the Chalk–Harrod mechanism (Scheme 4) follows the *anti*-Markovnikov rule and leads (e.g. in the case of 1-alkenes) to the β-hydrosilylated 1-silylalkanes [67]. In most cases, the formation of α-hydrosilylated products is not observed, but with some alkenes such as styrene and its derivatives, significant amounts of adducts with an internal silyl group can be also formed (Scheme 9) [68]. In an example of the hydrosilylation of styrene and triethoxysilane catalyzed by a platinum(0) complex of divinyltetramethyldisiloxane, a β:α ratio of 1.9:1 was reported [69]. This ratio could be improved by the addition of different co-catalysts (e.g. 2-hydroxypyridine, 15:1; trimethylsilylbenzenesulfonate, 19.2:1; trimethylsilylmethanesulfonate, 53:1), demonstrating the wide influence of additives on the hydrosilylation selectivity [69]. Unfortunately, the mode of action of these co-catalysts on the Chalk–Harrod mechanism has not been discussed yet. In another example, $(Ph_3P)_3RuCl_2$ was reported to catalyze the reaction of trichlorosilane with olefinic nitriles (such as acrylnitrile) which selectively led to the desired β-cyanoalkylsilanes which are stable against hydrolysis as opposed to their related α-adducts [70].



Scheme 10. Chemoselectivity of allyl acrylate hydrosilylation.

In some special cases, the α-adduct is the most desired product which can be purposefully produced by using specific catalysts. For instance, the conversion of ω-alkenyl-*N*-carboxamides (e.g. *N*-methyl-*N*-vinylacetamide) with alkoxysilanes $(RO)_3SiH$ applying rhodium catalysts such as $(Ph_3P)_3Rh(CO)H$ yields *N*-[ω-(methyl),ω-(silyl)]alkyl-*N*-organocarboxamides (e.g. *N*-(1-(triethoxysilyl)ethyl)-*N*-methylacetamide) as main product (yields: 73–83%) [71].

Another example of a regioselective hydrosilylation using rhodium-based catalysts is the reaction of 1,1,3,3-tetramethyldisiloxane ($HSi(Me)_2OSi(Me)_2H$) with vinylsilanes which leads selectively to the monohydrosilylated 1-(2-silylethyl)-1,1,3,3-tetramethyldisiloxanes [72].

Apart from that, the chemoselectivity of bisunsaturated alkenes such as allyl acrylate is another aspect in industrial hydrosilylation processes, because allyl acrylate has three reactive groups from which the allyl group and the C=C bond of the acrylate moiety as well as the C=O ester function are active for the addition of silicon hydrides, so three different products can be formed from which the γ-adduct is the desired one (Scheme 10) [40]. The chemoselectivity of this process can be significantly improved by performing this reaction with the Speier catalyst system in the presence of phosphines (e.g. triphenylphosphine, trihexylphosphine) as co-catalysts, so the desired acryloxypropylsilanes which are of interest as silane-coupling agents or as raw materials for acrylate-functionalized polysiloxanes can be obtained in better yields and in higher purity [40]. The effect of the phosphine is not understood completely, but it is believed that this co-catalyst suppresses the formation of colloidal platinum by forming stable Pt-complexes with higher activity and selectivity as it was observed for similar systems using cyclohexanone [73]. Despite that, there is still a great need for better understanding and further optimization of these hydrosilylation processes.

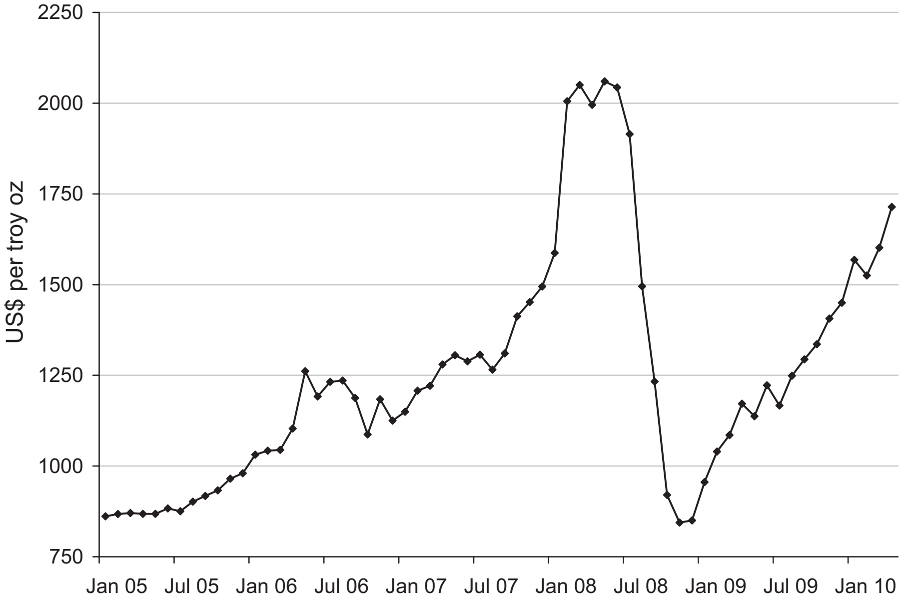


Fig. 1. Price trend of platinum from 2005 to 2010 (data are based on the Johnson Matthey monthly average prices [74]).

3. Low-cost catalysis for hydrosilylation

Almost all industrial used hydrosilylation processes are carried out by platinum-based catalysis, so a significant part of the worldwide platinum consumption is needed for the silicone industry. Unfortunately, most of the applied platinum catalyst quantities remain in the silicone products and cannot be recaptured (see below). Furthermore, platinum represents one of the most expensive precious metals with considerable price fluctuations (Fig. 1).

Three different types of applications of hydrosilylation reactions require individual types of catalysts:

- The majority of the platinum consumption is located in silicon release coating processes which need extremely high production speeds requiring high curing rates and therefore high loads of catalyst (up to 100–200 ppm platinum), so low-cost catalysts with high activity (=high turnover frequencies (TOFs)) are essential. Recovery of the platinum content of silicone release coatings is not established.
- In the production of silicone rubbers, the catalysts also remain in the products, but these curing processes do not require high production speeds and get along with lower catalyst loads, so low-cost catalysts with good stability (=high turnover numbers (TONs)) are preferred.
- On the contrary, platinum as catalyst in different silane productions can be mostly recovered, so the catalyst cost contribution is comparably low, but it has to show excellent selectivities to achieve high yields of organofunctional silanes (see also Section 2).

Consequently, there is a particular interest in highly active catalytic systems for hydrosilylation allowing lower platinum loads or in Pt-free catalysts containing lower priced transition metals. This section deals with recent developments for increasing the catalytic activity and/or stability of established platinum-based catalysts or the application of new special platinum complexes in hydrosilylation (Section 3.1) as well as advances in the development of lower priced transition metal catalysts (Section 3.2).

3.1. Hydrosilylation with platinum-based catalysts

For the reasons given above, it is essential to develop methods for extending the efficiency of catalytic species by increasing the activity (=TOF) and the stability (=TON) of established catalysts.

The TOF of the catalytic process can be improved either by identifying the substrate with the highest TOF for a given catalyst, or by developing the catalyst with the highest TOF for a given substrate. For instance, the use of specific siloxanes such as highly branched siloxanes of the formula type $Si[(-OSiMe_2-)_nOSiMe_2CH{=}CH_2]_4$ [75,76] or silicone oils with a higher quantity of Si–H units ($OSiHR/OSiR_2 \approx 5$) as the crosslinker [77] accelerates the Karstedt-catalyzed crosslinking reaction in comparison to linear siloxanes with a low content of Si–H units, therefore allowing lower loads of this specific platinum catalyst. The second approach to increase the TOF via more active catalytic systems is discussed in the following sections.

Low TONs correspond to fast deactivation of the catalyst and thus raise the consumption of platinum. As described in Section 2, platinum-catalyzed hydrosilylation proceeds commonly along the Chalk–Harrod mechanism (Scheme 4). Extensive studies on hydrosilylation catalysis by using Karstedt's catalyst additionally considered the induction period during which the dimeric Pt(0) catalyst undergoes dissociation of the bridging olefin to form an active mononuclear, two-coordinate complex. Furthermore, the platinum end products are dependent on the concentrations of the alkene and the hydrosilane, leading to a $Pt(olefin)_3$ complex or a multinuclear Pt cluster $[Pt_x(R_3Si)_y]$, respectively, which are both deactivated by the formation of platinum colloids [18]. Platinum colloids are undesired because they minimize the TONs of the corresponding catalyst and also cause yellowish discolorations in the cured products.

Hereafter, some basic approaches for modifying transition metal catalytic systems, mainly platinum-based catalysts, are described.

3.1.1. (Re)activation by using promotors

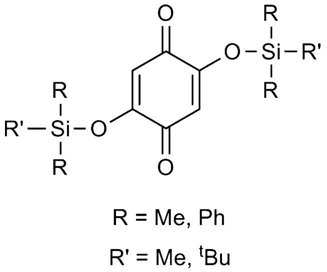
An improvement of the transition metal-catalyzed hydrosilylation was achieved in many cases by adding promotors for increasing the activity of the respective catalyst.

An important promotor which is present in all aerobic hydrosilylation processes is dioxygen which has a co-catalytic effect by modifying the reactivity of platinum-containing intermediates and also preventing irreversible colloid agglomeration [78]. In a proposed mechanism, dioxygen is bound to the active catalyst species without an O–O bond breakage (oxygen is not consumed in the reaction), so it acts as a co-catalyzing ligand which makes the active intermediate more electrophilic [78]. Alternatively, the absence of oxygen can be purposefully used to inhibit the hydrosilylation reaction, leading to curable silicone compositions which can be stored under anaerobic conditions [79] (see also Section 4). A similar co-catalytic effect is performed by the addition of organic peroxides (such as benzoylperoxide, di-*tert*-butylperoxide) [80] or peroxo acids (such as peracetic acid, *meta*-chloroperbenzoic acid) [81] to the reaction mixture which extends the activity (=TOF) and lifespan (=TON) of the respective hydrosilylation catalyst, resulting in its reduced consumption. Further advantages of this promotion are decreased discolorations of the silicone products, lower amounts of immobilized platinum residues, and a significant acceleration of the hydrosilylation process.

The hydrosilylation reaction of dichlorosilane with less reactive internal alkenes (e.g. cycloalkenes) can be promoted by using aldehydes (e.g. benzaldehyde) [82], unsaturated ketones (e.g. α/β-ionone, 4-hexen-3-one, ethylvinylketone) [83], and saturated as well as unsaturated alcohols (e.g. *tert*-butanol, benzyl alcohol, 2-cyclohexen-1-ol, and silylated derivatives, e.g. 2-trimethylsilyloxy-2-methyl-3-butene) in an amount of 0.1–10% (w/w) in relation to the alkene [84]. In all cases, an accelerated reaction was observed during the first hour, mostly to the formation of the monohydrosilylated products $RHSiCl_2$. In the reactions using aldehydes as promotors, the bishydrosilylated adducts R_2SiCl_2 were also formed in significant amounts after 1 h or are the main products, so the TOF of the aldehyde-promoted catalytic system is higher than those of the ketone- or alcohol-promoted ones [82].

Carbonic acids also have a promoting effect on many hydrosilylation reactions often with an additional influence of their selectivity. The preferential formation of β-adducts in the hydrosilylation reaction of styrenes (see also Section 2.2) can be promoted by phosphine-modified platinum catalysts, but their activity is strongly weakened. A solution of this problem can be the addition of carbonic acids for restoring the catalyst activity [85]. The choice of carbonic acid depends on the relative volatility of the promotor and the desired product of the hydrosilylation process, so acetic acid is often the most preferred acidic promotor because it is more volatile than most silane and silicone products and can be removed after reaction [39]. Furthermore, acidic promotors are suitable for hydrosilylation processes whose reactants contain epoxide moieties (such as allyl glycidyl ether) which is not trivial because acids usually attack oxirane groups, and ring-opening can occur. The combination of platinum-based catalysts (such as Speier's or Karstedt's catalyst) with mono- or dicarbonic acids (e.g. formic-, acetic-, and propenoic acid, phenol) enables a faster hydrosilylation reaction without ring-opening of the epoxide [86]. Apart from acidic promotors, an activation of the Speier catalyst by the addition of a base (e.g. sodium carbonate) was also reported [87].

Sometimes, additives which are well-known to act usually as hydrosilylation inhibitors (see Section 4) can promote the hydrosilylation reaction under certain conditions. For instance, the application of elemental sulfur as hydrosilylation promotor was reported, but the sulfur has to be added in very well-defined amounts so as not to work as a hydrosilylation inhibitor [88]. Another example is the use of lactones (e.g. ε-caprolactone) which inhibit the reaction at room temperature, but accelerate the TOF at temperatures above 70 °C [89]. However, the most prominent examples of such type of hydrosilylation promotors are specific amines and phosphines. Amine or phosphine inhibition may be based on their coordination to the catalyst (the modes of action of hydrosilylation inhibitors will be embraced more detailed in Section 4), so as to act as a promotor and not as an inhibitor, their tendency for transition metal coordination has to be suppressed. For that reason, poorly nucleophilic amines (e.g. aniline, benzylamine, hexamethyldisilazane) [90] as well as sterically hindered amines (such as 2,2,6,6-tetramethylpiperidines, -piperidinoles, and -piperidones, di-*tert*-butylamine) and phosphines (such as $^tBu_3P$, Et^tBu_2P) are reported to induce higher reaction rates, decreased side reactions, and a reduced catalyst consumption [91].



Scheme 11. Examples of suitable quinone-based promotors [92a].

Promotor-containing catalyst systems have to feature enhanced activities as well as good solubilities in silicone polymer compositions. These needs are well-fulfilled by quinone additives [92], particularly being silyloxy-substituted for improved solubility in polysiloxane compositions (Scheme 11). In the hydrosilylation of unsaturated ethers containing carbinol moieties (e.g. $CH_2{=}CHCH_2OC_2H_4OH$), volatile cyclic ethers (such as tetrahydrofuran, 1,2-epoxycyclohexane, limonene oxide) were described as promotors which are easy to remove after reaction and do not accumulate by continuous processing via loop- or tube-reactors [93]. These promotors are characterized by a good solubility in the silicone phase which obviates the need for organic solvents, and have no inhibiting effect compared to amines or phosphines.

Another aspect is the essentially quantitative conversion of all SiH units in addition-cured silicone elastomers to prevent uncontrolled hydrolysis or crosslinking reactions which would lead to increased H-linker density and a higher compression set of the polymers [94]. The amount of SiH residues in the product can be minimized by the initial addition of auxiliary alkenes (e.g. ethene, propene, 1-/2-butene, cyclohexene) to the hydrosilylation reaction mixture, generating a highly active platinum catalyst which ensures a quantitative SiH-turnover without additional steps after reaction [95]. As a further effect, the presence of the auxiliary alkene which preferentially contains electron-donating substituents significantly improves the activity of the applied platinum catalyst which results in a lower activation temperature and a quantitative conversion of the SiH units. It is believed that the presence of alkenes initiates a cascade of association and dissociation processes at the catalyst in whose course novel, more active platinum(0) species are generated [95].

Another remarkable approach to increase the activity of platinum-based hydrosilylation catalysts is the combination with another transition metal to generate a synergistic catalyst system. It was shown in the addition of alkenes (e.g. α-methylstyrene) to SiH-containing polysiloxanes that a combination of Speier's catalyst H_2PtCl_6 and $RuCl_3{\cdot}nH_2O$ resulted in a significantly increased catalytic activity which could not be deduced from the independent activities of the single components [96]. In addition to this synergetic interaction of the transition metal components, this type of catalyst system may be also of interest in the context of hydrosilylation catalyst cost reduction.

When a hydrosilylation reaction dies down despite all the care taken, subsequent addition of trihalogenosilanes $RSiX_3$ (R = H, halogen-containing alkyl; X = halogen) such as trichlorosilane as the most preferred one can sometimes affect a reactivation of the catalyst, leading to better turnovers to the desired products and lower amounts of unreacted educts [97].

In summary, it was demonstrated by means of selected examples that a large variety of different additives for (re)activating hydrosilylation catalysts is available. A main problem in the rationalization of hydrosilylation promotors are the big differences relating to their structures and properties, respectively. In most cases, the mechanism of these promotors is not known or not completely established, and no rational guideline can be given which promotor is suitable for a specific hydrosilylation reaction. The promotor performance seems to depend on the type of silicon hydride, alkene, and catalyst used, respectively. Therefore, each specific hydrosilylation reaction requires careful identification of suitable promotors.

3.1.2. *Optimized hydrosilylation process conditions*

Suitable process layouts can often have an additional influence on the catalyst performance. Often, it is recommended to continuously dose the homogeneous catalyst, e.g. in a reactive distillation [98,99]. Due to the continuous dosage of fresh catalyst and the concurrent removal of spent one, the activity of the overall catalytic system is kept up during the whole process, and interruptions due to catalyst change are prevented [98]. The catalytic activity can be further improved by reducing the content of water in the reaction mixture to <1000 ppm (optimal: 0.1–100 ppm) to minimize the formation of hydrogen due to the partial hydrolysis of the SiH units [100]. As opposed to this, fast hydrosilylation reactions in water were also reported [101].

Contrary to the literature which often reports the use of organic solvents such as alcohols and aromatic solvents for hydrosilylation, solventfree reactions are usually preferred in industrial processes. The dilution of hydrosilylation reactions, e.g. for the purpose of lowering the viscosity or better removal of the reaction heat, is better achieved via “self-dilution” with recycled reaction products, so no organic solvents have to be removed after reaction.

While solventfree two-phase hydrosilylation processes are well-known for reactants with a miscibility gap [102], the intentional use of two-phase hydrosilylation processes with ionic liquids, i.e. salts with melting points below 100 °C, allows to reutilize the applied transition metal catalysts for repetitive use via phase-separation [103]. Ionic liquids are characterized by many favorable properties: essentially no vapour pressure, reasonable thermal stabilities, ability to dissolve a wide range of organic, inorganic, and organometallic compounds, immiscibility with selected organic solvents, and are therefore usable in two-phase systems [103]. By carrying out the hydrosilylation reaction in such two-phase systems, the catalyst generally remains in the ionic phase (polar) to be separated from the product phase (nonpolar) [104]. The most preferred ionic liquids for hydrosilylation consist of nitrogen- or phosphorus-containing cations (e.g. substituted ammonium, phosphonium, imidazolium, pyridinium, pyrazolium, triazolium, picolinium, and pyrrolidinium cations) and anions such as halogenides, BF_4^-, $AlCl_4^-$, PF_6^-, RCO_2^-, RSO_3^-, and $ROSO_3^-$ [98,105]. Two-phase systems based on ionic liquids seem to be more effective than heterogeneous catalyzed hydrosilylations [106].

As some catalysts such as Wilkinson’s catalyst $[(PPh_3)_3RhCl]$ do not remain completely in the ionic phase but redistribute partially into the product phase (catalyst-leaching), the catalyst has to be suitably adapted, e.g. by the substitution of the phosphine ligands [105]. Solventfree hydrosilylation reactions followed by subsequent addition of the ionic liquid during or after the reaction can be used to extract the catalyst by *in situ*-formation of the catalyst-containing ionic phase, thus obtaining catalyst-free products without distillation [105].

These selected examples clearly demonstrate a variety of factors to adjust the hydrosilylation catalyst activity by procedural methods. Again, every procedure has to be customized for the respective hydrosilylation reaction and the quality requirements of the desired silicone products.

All hitherto discussed approaches in this section were focused on established platinum-based catalytic systems such as Speier’s or Karstedt’s catalyst. In the next section, recent advances in the development of novel platinum complexes with improved properties will be presented [107].

3.1.3. *Platinum complexes with improved stability*

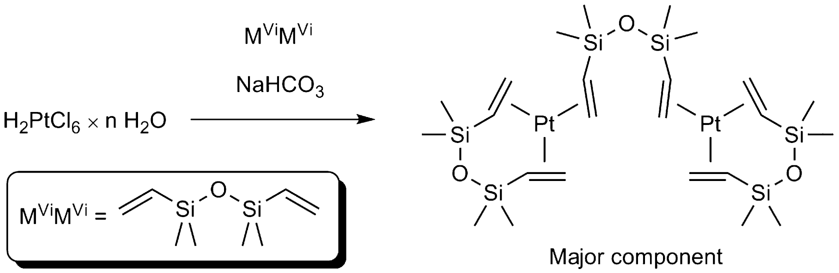
Achieving very high TONs is a prerequisite for low-cost hydrosilylation, but the TON of established platinum-based catalysts such as Karstedt’s catalyst is limited due to precipitation of platinum colloids caused by a reductive deactivation of the catalytic system [18].

Karstedt’s catalyst was originally obtained by the reduction of platinum chlorides (such as $PtCl_2$, H_2PtCl_6) with divinyltetramethyldisiloxane ($M^{Vi}M^{Vi}$) in the presence of sodium bicarbonate which resulted in a complex and dynamic mixture of different Pt(0) and Pt(II) species in which Karstedt’s catalyst is the major component [16,17] (Scheme 12). Better yields are achieved by starting the synthesis from $[Pt(COD)_2]$ in which platinum already has the intended oxidation-state and therefore does not need a reduction by $M^{Vi}M^{Vi}$ [108].

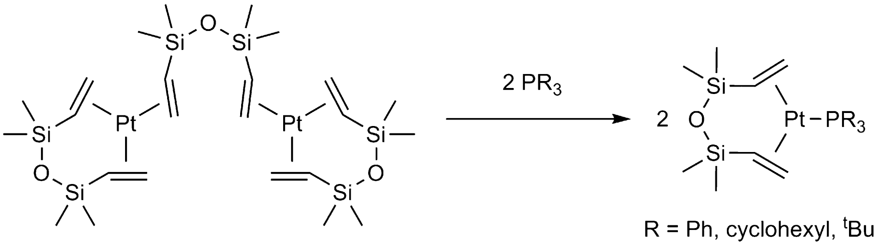
Platinum colloid formation of Karstedt’s catalyst is caused by the $M^{Vi}M^{Vi}$ ligand which is too labile and dissociates rapidly. Consequently, many approaches for derivatives of Karstedt’s catalyst, e.g. by using other alkenyl ligands and modified reaction conditions were reported recently [87,109,110]. In the case of alkenyl polysiloxanes, cycloalkenylpolysiloxanes, and $M^{Vi}Q$ alkenyl polysiloxane resins as ligands for platinum instead of $M^{Vi}M^{Vi}$, new active platinum-based catalysts were obtained which rapidly catalyze the hydrosilylation reaction at lower temperatures, improving the platinum catalyst performance in terms of reduced cure time and reduced amounts of platinum needed [87,110]. Furthermore, it was shown by Markó et al. via novel Karstedt-type complexes with diene ligands, e.g. $Allyl_2O$, that the variation of the diene fragment enables the modulation of the stability of the resulting Pt(0) complexes [109]. Consequently, the nature of the alkene fragment is a key parameter in determining the stability and the hydrosilylating activity of platinum complexes, leading to an expansion of the scope of catalyzed hydrosilylation employing reactive Pt(0) fragments.

Pt(0) catalysts of the Karstedt type can be further stabilized by strongly binding, electron-rich ligands onto the platinum, such as monophosphines (Scheme 13) [111]. Phosphine ligands are known to protect against colloid formation, but the resulting (phosphine)Pt($M^{Vi}M^{Vi}$) complexes are inferior to Karstedt’s catalyst in terms of hydrosilylation reaction rates and selectivities. Furthermore, colloidal platinum is still produced, implying that the phosphine ligand is displaced to some extent during the reaction.

These stability problems could be circumvented by *N*-heterocyclic carbene platinum(0) complexes (NHC–Pt(0)) which were already mentioned in Section 2.2 [64,65,109]. In contrast to $M^{Vi}M^{Vi}$ in Karstedt’s catalyst, the *N*-heterocyclic carbenes (preferentially imidazoyl or benzimidazoyl carbenes, Scheme 14) as robust σ-donor ligands increase the electron density at the platinum atom and reduce its activity (=decrease of the TOF), and the formation of platinum colloids is almost completely suppressed (=increase of the TON) [64]. The Markó-type catalysts show interesting properties such as better stability and tolerance to a wide range of functionalities and protecting groups (e.g. hydroxyl, carbonyl, ester, and epoxide units). They can be applied to the production of silicone oils and compositions crosslinkable into silicone elastomers [112], and

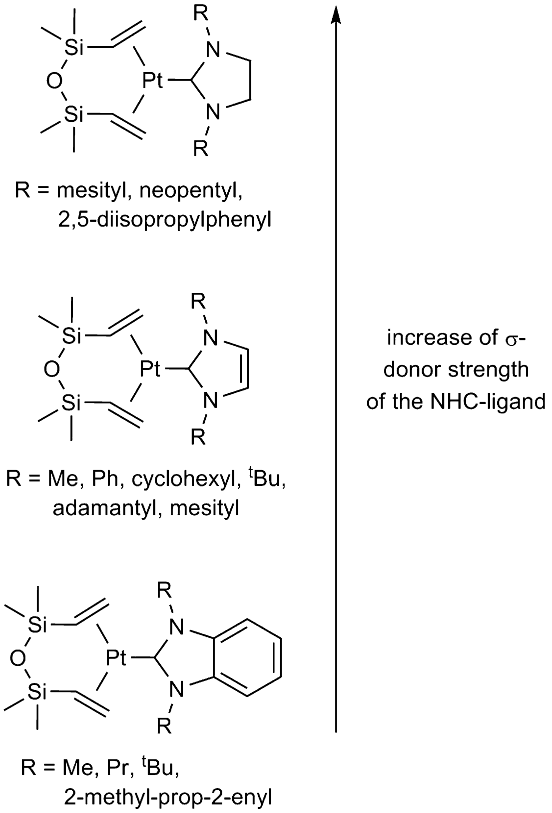


Scheme 12. Formation of Karstedt's catalyst.



Scheme 13. Synthesis of (phosphine)Pt($M^{Vi}M^{Vi}$) complexes.

the catalyst loading can be reduced as low as ~30 ppm [64b]. Furthermore, the NHC ligands can be combined with inhibiting ligands such as dicarboxyacetylene esters to adjust the pot life of the reaction mixtures, leading to storable silicone compositions which are stable at room temperature but rapidly cure at higher temperatures (see also Section 4) [112a].



Scheme 14. Selected examples of suitable NHC–Pt(0) complexes for hydrosilylation [64,107].

3.2. Hydrosilylation with low-cost transition metal catalysts

The use of catalytic active metals other than platinum to catalyze hydrosilylation reactions is well-known [19,113]. Nucleophilic–electrophilic catalysis [55], e.g. by applying aluminium or boron [114], alkaline-earth metals [115], copper [54], or titanium [116], and early transition metal catalysis [117] are currently not used in industrial catalyzed hydrosilylation of olefins due to the usually poor activities and yields. For that reason, late transition metal-catalyzed hydrosilylation is still predominant in industrial research, so this section will focus on this topic.

The industrially most important alternatives to platinum as hydrosilylation active metals are rhodium, iridium, and ruthenium. There are some industrial applications of rhodium-based catalysts, mainly in the area of silicone elastomers which are claimed to show improved product properties such as better temperature resistance, no discolorations, or extended pot life of the rhodium-containing silicone compositions without auxiliary addition of inhibitors [118]. Furthermore, coordination compounds of rhodium can be used in the selective synthesis of organofunctional silanes [71,72] because rhodium-catalyzed hydrosilylation occurs preferentially along the modified Chalk–Harrod mechanism as contrasted to platinum (Scheme 4) and therefore exhibits other selectivities (see also Section 2.2) [119].

As can be seen from Fig. 2, rhodium is more expensive than platinum and characterized by strong price variations. Consequently, rhodium is of little interest for low-cost hydrosilylation catalysts.

Iridium is significantly lower priced than platinum and rhodium showing little price fluctuations (Fig. 2). Unfortunately, lifetime (=TON) and activity (=TOF) of established iridium complexes such as $[(COD)IrCl]_2$ are very poor, so high catalyst concentrations are needed (ca. 1000 ppm) (see also Section 2.1). This compensates the low price of iridium, so iridium-catalyzed hydrosilylation is industrially only applied for selectivity reasons, mainly in the production of organofunctional silanes [42–48]. For applications in which the catalyst remains in products such as silicone rubbers or silicone release coatings, iridium-based catalysts are not used for low-cost hydrosilylations.

As can be seen from Fig. 2, ruthenium is the cheapest of all precious metals useful for hydrosilylation catalysis and has a relatively stable price trend. Therefore, ruthenium seems to be

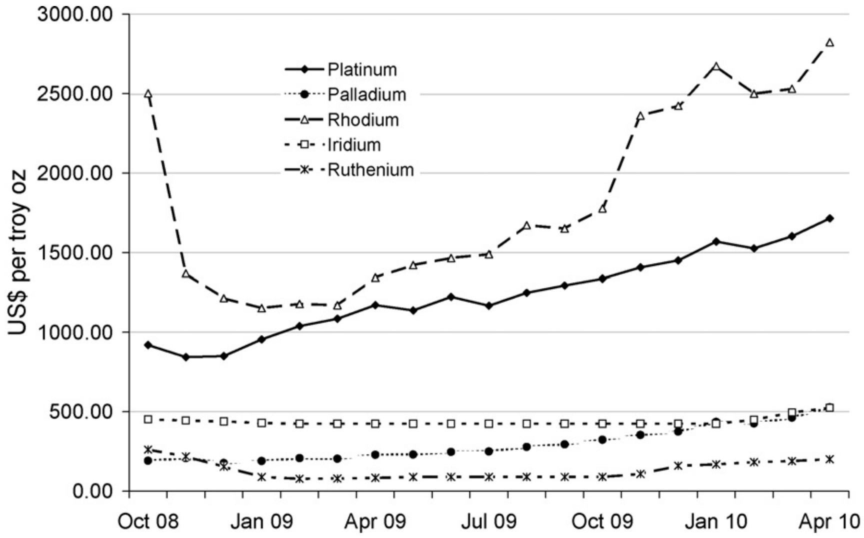
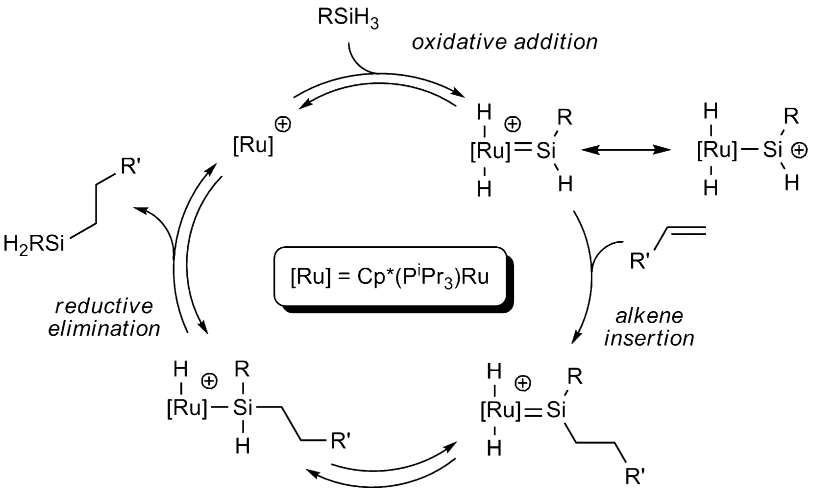


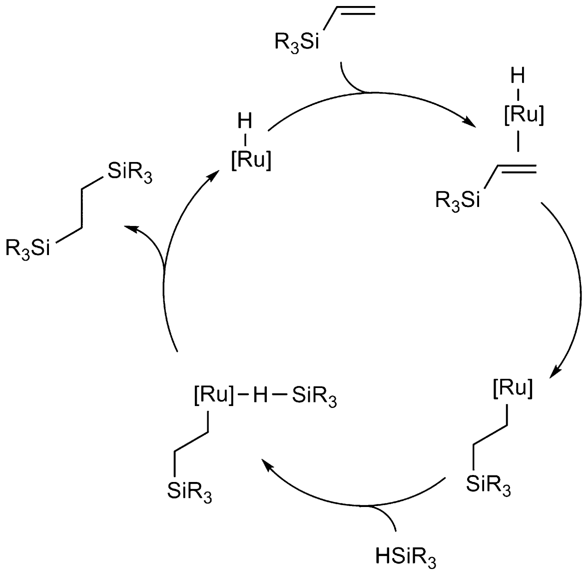
Fig. 2. Price trends of precious metals from October 2008 to April 2010 (data are based on the Johnson Matthey monthly average prices [74]).



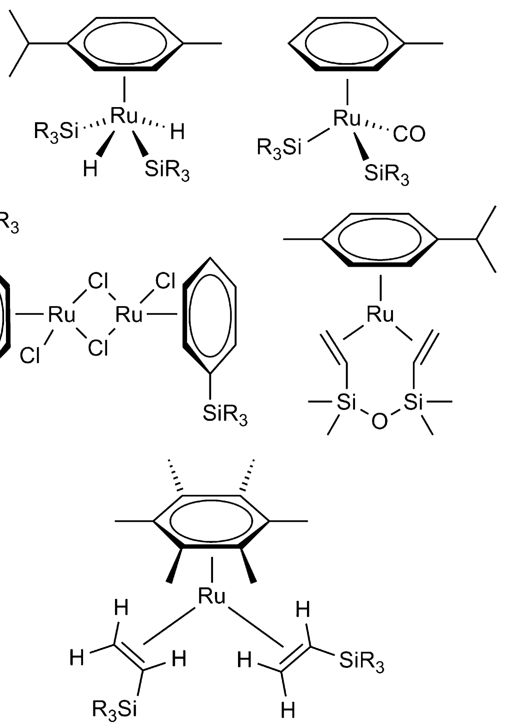
Scheme 15. Glaser–Tilley mechanism for ruthenium-catalyzed hydrosilylation of 1-alkenes [120].

the most promising transition metal as a low-cost alternative to platinum-based hydrosilylation catalysts [53]. Unfortunately, ruthenium-catalyzed hydrosilylation is hampered by some characteristics which will be discussed more detailed in the following.

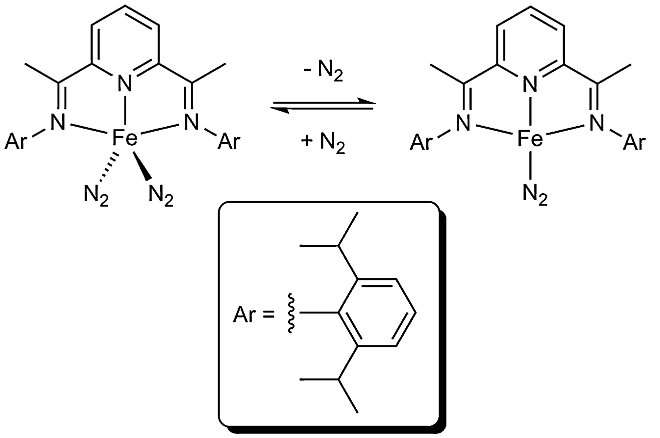
Contrary to electron-rich transition metals such as platinum and rhodium, ruthenium-catalyzed hydrosilylation does not proceed according to the Chalk–Harrod and/or the modified Chalk–Harrod mechanisms but along a new mechanism proposed by Glaser and Tilley (Scheme 15) [120]. Many studies including quantumchemical calculations confirmed the mechanistic implications of the Glaser–Tilley mechanism which unfortunately are only valid for primary silanes $RSiH_3$ [121] and cannot be transferred to hydrosilylation leading to industrially important organosilicon products [53b]. Recently, theoretical studies considering the hydrosilylation of a tertiary silane, $HSiMe(OMe)_2$, with methylvinyldimethoxysilane and different ruthenium-based catalysts (e.g. $RuCl_2(CO)_2(PPh_3)_2$, $[RuCl(N{\equiv}CCH_3)_5]^+$) [122] came to the conclusion that a σ-bond metathesis mechanism (Scheme 16) which is well established for early transition metal catalysts [123] provides the most favorable route in this ruthenium-catalyzed hydrosilylation reaction. Due to this different mechanistic behavior of ruthenium coordination compounds compared to those of platinum or rhodium, ruthenium-catalyzed hydrosilylation is often



Scheme 16. σ-bond metathesis mechanism for ruthenium-catalyzed hydrosilylation of tertiary silanes and vinylsilanes [122].



Scheme 17. Examples of silyl-substituted η^6-arene ruthenium complexes [126].



Scheme 18. Equilibrium of [(pdi)Fe(N_2)$_2$] in solution [130].

accompanied by undesired side reactions, such as dehydrogenative silylation of alkenes (formation of vinylsilanes [52]), dehydrocoupling of trialkylsilanes, alkene metathesis, alkene reduction, and alkene isomerization [53,124]. Frequently, the dehydrogenative silylation is even favored over hydrosilylation, e.g. by using $[RuH_2(H_2)_2(PCy_3)_2]$ as the catalyst [124].

As discussed in Section 2.1, ruthenium carbonyl complexes such as $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$, and $[Ru(CO)_3(PPh_3)_2]$ are active catalysts which can be used in the selective hydrosilylation of allyl compounds, whereas carbonyl-free complexes such as $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3RuHCl$, or $(Ph_3P)_3RuH_2$ are ineffective for such hydrosilylation processes [31,49–51].

The most relevant target for low-cost hydrosilylation is the addition curing of organopolysiloxanes, e.g. of elastomers or release coatings. Novel low-priced ruthenium complexes are therefore required to show significant activity (=high TOF) and stability (=high TON) for these applications.

A promising approach in the development of such ruthenium catalysts is a special class of neutral complexes containing two independent carbon-π-bound ligands such as η^6-bound arenes, η^6-bound trienes, COD, and COT (COT = 1,3,5-cyclooctatriene) [125]. At least one of these two ligands is weakly bound at Ru, so the hydrosilylation catalytic cycle can be started by the displacement of the respective ligand, giving a short induction period in most cases. Furthermore, these ligands stabilize the electronic unsaturated Ru-fragments and are compatible with most substrates used [125]. Selective examples of such catalysts are (COD)Ru(COT), (COD)Ru(2-methallyl)$_2$, (η^6-C_6H_6)Ru(cyclopentadiene), and (COD)RuCl(η^5-Cp*), showing high TONs and good selectivities which are close to those of Karstedt's catalyst (65–87%; Karstedt: 91%). Their low solubility in polysiloxanes can be circumvented with π-bound ruthenium complexes which additionally contain silyl or siloxy units at the ruthenium center or at the ligands (Scheme 17) [126]. These "silicophilic" ligands give complexes with good solubility in polysiloxanes [125] but surprisingly result in lower activity and selectivity. Therefore, new catalysts based on ruthenium(0) sulfoxide complexes were developed (e.g. ($M^{Vi}M^{Vi}$)Ru(CO)(κ-S-DMSO)(κ-O-DMSO), ($M^{Vi}M^{Vi}$)$_2$Ru(κ-S-DMSO), (dmbtd)$_2$Ru(κ-S-DMSO); DMSO = dimethylsulfoxide; dmbtd = 2,3-dimethylbutadiene) [127]. These catalysts were reported to exhibit high selectivities, good solubility in polysiloxane compositions, and high TOFs in silicone curing processes (loads of Ru: 5–500 ppm) compared to other ruthenium-based catalysts. A further advantage is that compositions containing these catalysts are shelf-stable at room temperature but cure rapidly at elevated temperatures, so addition of inhibitors is not necessary [127].

Nevertheless, activity and stability of ruthenium complexes in hydrosilylation reactions cannot yet achieve those of established platinum-based catalysts such as Karstedt's catalyst, but they seem to be the most promising low-cost alternative.

Another remarkable progress towards new low-cost hydrosilylation catalysts is based on iron as the catalytically active metal [53b,128]. The use of iron pentacarbonyl $Fe(CO)_5$ in hydrosilylation reactions is known for many years [23] although being accompanied by the dehydrogenative silylation of alkenes which often cause the production of vinylsilanes as the main products [129]. For that reason, iron complexes were not considered as useful hydrosilylation catalysts. Very recently, Chirik et al. reported their studies of the catalytic activity of the high spin d^8 square pyramidal iron(0) bis(dinitrogen)complex [(pdi)Fe(N_2)$_2$] (pdi = (ArN=C(Me))$_2$$C_5H_3N$, Ar = 2,6-^{i}Pr$_2$-$C_6H_3$) which loses one equivalent of dinitrogen in solution to afford the mono(dinitrogen) adduct (Scheme 18) [130]. It was demonstrated in the reaction of 1-hexene with $PhSiH_3$ or Ph_2SiH_2 catalyzed by [(pdi)Fe(N_2)$_2$] that in both cases a rapid hydrosilylation occurred which exclusively formed the *anti*-Markovnikov product. However, for other alkene and silane substrates, the TOFs are strongly depend on the substrates used (e.g. 2-hexene/$PhSiH_3$, 0.09 mol/h; styrene/$PhSiH_3$, 242 mol/h; 1-hexene/$PhSiH_3$, 364 mol/h) [130a], respectively, so the application of this iron catalyst for industrial hydrosilylations needs further development. The study of further derivatives of [(pdi)Fe(N_2)$_2$] and their catalytic activities is already in progress [131]. Additionally, recent patent applications claiming hydrosilylation reactions catalyzed by iron complexes such as CpFe(CO)$_2$Me, CpFe(CO)SiR$_3$, and CpFeH(CO)(SiR$_3$)$_2$, as well as other iron complexes such as iron(III) acetylacetonate emphasize the current interest in iron-catalyzed hydrosilylation for industrial applications [132].

These examples clearly demonstrate that deliberate design of novel hydrosilylation catalysts and their successive optimization might lead to new promising low-cost alternatives to established platinum-based catalysts. Currently, from an industrial point of view, no alternative to Karstedt's catalyst is implemented, so further studies and developments are essential to create low-cost catalysts for economic hydrosilylation processes.

4. Switchable catalysis

Addition curing systems are based on the platinum-catalyzed hydrosilylation of vinyl-functionalized polysiloxanes with SiH-functionalized oligosiloxanes (crosslinker) (Scheme 2) [3]. In general, hydrosilylation is a fast reaction which proceeds immediately at room temperature in the presence of the catalyst. Addition curable silicone mixtures provided as two-component (2K) formulations (catalyst component and crosslinking component, mostly 1:1) are therefore shelf-stable as long as the components are separated from each other, but cure rapidly when both components are mixed together.

In contrast, industrial applications of hydrosilylation curing silicones with high production speeds, such as release coatings [8], do not allow for 2K systems as the mixing time is too long relative to the required curing speed.

One-component (1K) polysiloxane compositions therefore used for release coatings need to be shelf-stable at room temperature but have to cure extremely fast. Any premature curing of 1K-systems would cause adherence of silicone polymers at machine parts (e.g. rollers), supply tanks, and dosing systems requiring frequent-shutdown for cleaning. Hence, exercising precise control of the catalytic activity of 1K addition curing systems requires a switchable catalysis of the hydrosilylation crosslinking process which can be triggered by energy input, such as thermal activation or irradiation.

This section embraces the field of switchable catalysis with the main focus on inhibitors and thermal activation (Section 4.1) as well as photoactivated hydrosilylation (Section 4.2).

4.1. Thermal activated hydrosilylation

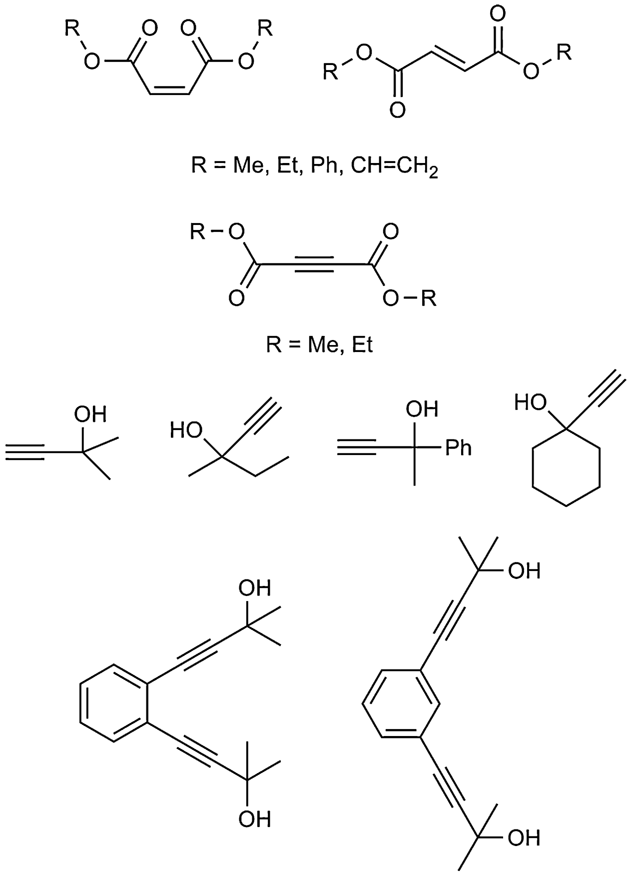
4.1.1. Use of inhibitors

Adding retardants (inhibitors) to reduce, or reversibly inhibit, the low-temperature activity of the platinum catalyst is used to extend the pot-life of hydrosilylation curing silicone compositions while maintaining the required high curing speed [133]. An ideal inhibitor allows for an infinite pot-life at ambient temperature combined with rapid cure at elevated temperature [134]. This cannot be achieved by the Arrhenius-type temperature dependence of the catalytic system but requires a very fast deactivation of the inhibiting system at elevated temperatures.

Furthermore, the evaporation speed of the inhibitor should be low, preventing premature removal of the respective inhibitor, leading to a reactivation of the catalyst and unwanted initiation of the hydrosilylation reaction [135]. This aspect is additionally important for workplace safety because emissions of volatile inhibitors should be prevented. Finally, inhibitors should be dispersible in polysiloxanes [136].

Thermal curable silicone compositions are required to be shelf-stable at temperatures up to 50 °C, and the curing process has to proceed quantitatively within 5–20 s in the temperature range between 120 and 160 °C. Most recent silicone release coatings are produced with coating speeds up to 1000 m/min requiring even faster curing speeds down to ~2 s, demonstrating the high standards of industrial hydrosilylation chemistry.

The most important and most frequently applied inhibitors are maleates, fumarates, and β-alkynoles (Scheme 19) [17,133,137,138] which are typically used in levels of 0.01–10% (w/w) (mostly preferred: 1–5% (w/w)). Their mechanism of action was traced to their ability to act as ligands which block the hydrosilylation reaction by coordination to the metal center, but release the active catalyst under suitable curing conditions [17,137]. This assumption initially enjoyed great acceptance, primarily due to the synthesis of mononuclear platinum complexes containing dimethyl fumarate or maleate as ligands [137]. However, recent density functional computation studies on the Karstedt-catalyzed crosslinking of silicones via hydrosilylation in the presence of inhibitor molecules resulted in semiempirical solubility estimates of commonly used inhibitors such as maleates, fumarates, and β-alkynols. As a result, these inhibitors are insoluble in polysiloxane substrates. Therefore, these authors conclude that the examined inhibitors do not interfere with the hydrosilylation by binding to the platinum center [138]. Their inhibiting effect is rather based on the formation of a second micro phase containing the catalyst being physically separated from the substrate, i.e. the role of an inhibitor is to act as a phase-separator. The temperature-induced deactivation of the inhibitor is supposed to be caused by the vaporization of the inhibitor, so curing rate and activation temperature are expected to depend strongly on the inhibitor's vapor pressure [138].



Scheme 19. Selected examples of inhibitors based on fumarates, maleates, dicarboxyacetylene esters, and alkynols [133].

Therefore, to increase the shelf stability of siloxane compositions containing low loads of less volatile maleates as inhibitor, maleates are claimed in combination with volatile co-inhibitors such as alcohols, diols, triols, 2-methoxyethanol, or tetrahydrofuran [139,140]. Inversely, low-boiling maleates can be combined with high-boiling phosphites for extended shelf stability while maintaining temperature-induced high curing speed [141].

These results complement the concept of metal-coordination of inhibitors but clearly demonstrate that the comprehension of the mechanisms of inhibition in catalyzed hydrosilylation is not complete yet. This is illustrated by the fact that maleates are more efficient inhibitors than fumarates, the activation temperature of maleates depends on the type of ester alkyl groups but does not correlate to the vapor pressure of the maleate, and substantial amounts of maleates are found after the hydrosilylation process within the crosslinked composition.

Very similar to fumarates and maleates are dicarboxyacetylene esters of the general formula types $ROC(O)C{\equiv}CC(O)OR$ (R = Me, Et) which are reported to be effective inhibitors effecting long pot-lives without an impairment of the curing behavior [142]. They are miscible with polysiloxanes and have high boiling points (>200 °C). This type of inhibitor is completely destroyed during the curing process and chemically bound to the siloxanes, so no free inhibitor remains after the curing is finished. Additionally, they can be combined with highly active and selective NHC–Pt complexes (see Section 3.1.3) [112a].

A very important type of inhibitors are β-alkynols such as 2-ethinylisopropanol, 2-ethinylbutan-2-ol, 3-phenyl-1-butin-3-ol, 1-ethinyl-1-cyclopentanol and 1-ethinyl-1-cyclohexanol from which the latter is broadly established in industrial applications [135,136,139,141,143]. These alkynols are more volatile than fumarates and maleates and evaporate partially during the curing process (quantitative determination of remaining 1-ethinyl-1-cyclohexanol in a polysiloxane matrix is possible via gas chromatography [144]). Volatile inhibitors especially at high loads are generally under discussion with respect to workplace safety. For that reason, low vapor pressure alkynols with longer alkyl chains (e.g. 3,5-dimethyl-1-hexin-1-ol, 3-methyl-1-dodecin-3-ol) are preferred, additionally they remain longer in the curing composition, resulting in lower inhibitor amounts needed [145]. Another approach is the use of alkynol group-containing organopolysiloxanes in crosslinkable compositions resulting from the reaction of chlorosiloxanes with polyol alkynols (e.g. 3-methyl-1-butin-3,4-diol) [146]. These inhibitors are not volatile and therefore completely bound to the crosslinked siloxane. Furthermore, bisalkynol-based ligands containing an aromatic core were also reported (Scheme 19) [134].

The inhibition effect of β-alkynols (L) was explained to be based on the formation of the platinum complex PtL_2 (or Pt_2L_2). This complex is stable at ambient temperatures because the hydrosilylation of the ligand L is sufficiently slow. At high temperatures, the rate of consumption of ligand L is increased due to hydrosilylation with the Si–H compound, restoring the active platinum catalyst [134].

Organophosphorous-, organosulfur-, and organonitrogen-based inhibitors enable silicone compositions which are storage-stable under anaerobic conditions but cure rapidly in the presence of dioxygen [147]. The inhibiting effect of these additives is suppressed in the presence of molecular dioxygen, so the hydrosilylation reaction is initiated via contact with air. Typical phosphorous-based inhibitors are organophosphines $R'_nR_{3-n}P$, -phosphinoxides $R'_nR_{3-n}P=O$, and -phosphites $(R'O)_nR_{3-n}P$ (n = 0–3; R = H, alkyl, aryl; R′ = alkyl, aryl) [148,149] which can be combined with free-radical or oxygen scavengers to additionally increase the shelf life of the composition [148]. Recent studies by Marciniec et al. on the effect of triorganophosphites on platinum-catalyzed curing of silicone rubber allowed the conclusion that the effectiveness of these inhibitors requires steric demanding or electron-withdrawing substituents of the phosphite ligands [150]. For that reason, phosphite inhibitors $(R'O)_nR_{3-n}P$ with bulky aromatic groups (R′, R = Ph, 4-*tert*-butylphenyl, 2,4-di-*tert*-butylphenyl, pyridyl, fumaryl, thiophenyl) are commonly preferred [151]. Furthermore, the inhibiting effect of phosphites $(RO)_3P$ can be extended by modifying the organic groups R with other bulky groups such as aliphatic polycycles (R = bicyclo[2.2.1]pentyl, bicycle[3.3.1]nonyl, adamantyl) [152], silyl groups (R = $Si(OPh)_3$, $Si(O^tBu)_3$, $Si(O^iPr)_3$, $Si(OSiMe_3)_3$) [153], or aryl substituted phenyl moieties (R = biphenyl, (2,4-diphenyl)phenyl) [154]. At last, the use of bisphosphinites of the general formula type $(R'O)_2P{-}R{-}P(OR')_2$ (R′, R = aryl) was reported to have a superior inhibiting effect compared to that of monophosphinites [145e,155]. A disadvantage of most of these optimized organophosphorous-based inhibitors is their elaborate synthesis. Therefore, low-cost phosphites (e.g. triphenylphosphite or triethylphosphite) are preferred in combination with co-inhibitors such as β-alkynols, maleates, dicarboxylic acids, or isocyanurates which lead to synergistically inhibiting effects [141]. A modification of this procedure is the use of phosphites in presence of organic peroxides (e.g. *tert*-butylperoxy-3,5,5-trimethylhexanoate, 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane), in which the peroxide decomposes at elevated temperature and oxidizes the phosphite by eliminating its inhibiting effect [156].

Nitrogen-containing inhibitors are originally based on tertiary amines such as tripropylamine or *N*,*N*,*N*′,*N*′-tetramethylethylendiamine [147a/c,148] which usually do not lead to satisfying shelf lives. For that reason, the use of isocyanides (e.g. $^tBuN{\equiv}C$, cyclohexyl$N{\equiv}C$), cyclic polyamine compounds (e.g. 12-azacrown-4, 18-azacrown-6), and imino compounds (e.g. $MeN{=}CHPh$, $PhN{=}CHPh$) as well as amides (e.g. *N*,*N*-dimethylformamide), cyanates, nitriles (e.g. adiponitrile), oximes (e.g. 2-butoxime), and imidazoles (e.g. 2-methyl-1H-imidazole) are claimed [147a/c,157]. Furthermore, azodicarbonyl compounds of the general formula type $RC(O)N{=}NC(O)R$ (e.g. R = Ph, *para*-Me-Ph, NMe_2) are described to significantly extend the shelf life [158]. Further improvements are achieved by applying triazoline dienes (e.g. 4-phenyl- and 4-methyl-1,2,4-triazolin-3,5-dione) [159] as well as heterocyclic aromatic compounds such as 2,2′-bipyridine, 1,10-phenanthroline, chinoxaline, chinoline, and isochinoline [157]. $Ph{-}NH{-}CH_2{-}C_5H_4N$ and its derivatives were reported to reduce the amounts of required inhibitor in silicone curing compositions [160].

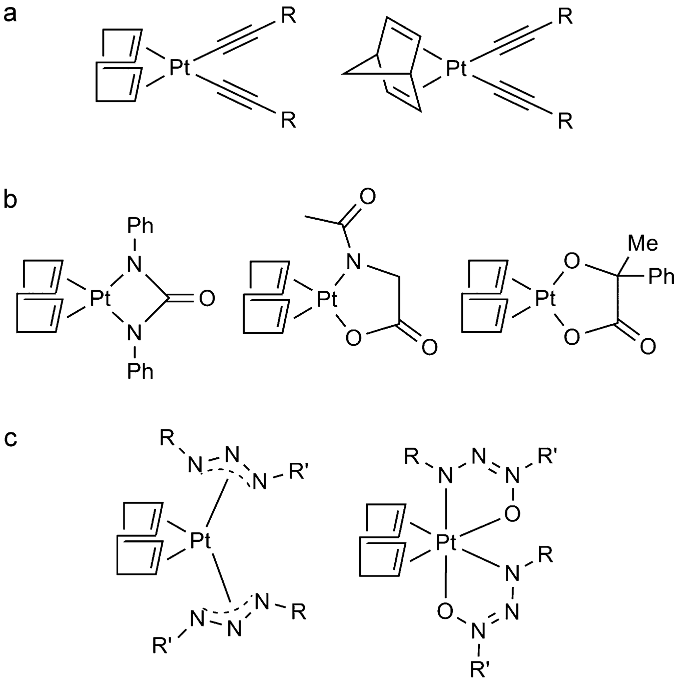
A combination of titanium(IV)-alkoxylates $Ti(OR)_4$ (R = Et, ^nPr, ^iPr) with H-functionalized silanes or siloxanes, such as $(MeO)_3SiH$, $(EtO)_3SiH$, or $Me_3SiOSi(H)(Me)OSiMe_3$, is reported to suppress the activity of platinum catalysts in the absence of air and moisture (up to 100 ppm, respectively) [161]. Its mechanism of action is not clarified yet, but it is supposed that an intermediate formed via dehydrogenation is responsible for the inhibiting effect.

4.1.2. Encapsulation of the catalyst

A completely different approach for provisioning thermally activatable catalyst systems is based on the microcapsulation of platinum group complexes which can be used in one-part polysiloxane compositions which are stable at ambient temperature and release the catalyst only at elevated temperatures [133].

Prominent examples can be generated by the treatment of $(COD)MCl_2$ (M = Pt, Pd, Rh) with cyclodextrines (preferentially β-CD; CD = cyclodextrine) to obtain host–guest complexes CD-M(COD)Cl_2 in which the transition metal catalyst is molecular-encapsulated within one cyclodextrine [162]. Residual free $(COD)PtCl_2$ is removed through washing processes of the β-CD complex [163]. In the case of encapsulated platinum catalyst, shelf stabilities up to 50 °C could be achieved for more than one month, and crosslinking occurred at 200 °C within 85 s. However, the very poor solubility of these platinum–cyclodextrine complexes in organopolysiloxane mixtures causes an inferior curing. A slight improvement of the solubility could be achieved by immobilizing these inclusion complexes on organically modified silica surfaces which can be easily incorporated into storage-stable polysiloxane compositions [164].

Another approach is to enclose the hydrosilylation catalyst in thermoplastic polymers or in crystalline compounds which melt at high temperatures and release the catalyst in this way. This encapsulation can take place in monomer organic compounds (e.g. 3,6-dimethyl-4-octin-3,6-diol, mp. 54 °C; thiochromane-4-



Scheme 20. Selected examples of dormant platinum catalysts based on bisalkynyl (a), carbamide (b), acid (b), triazene (c), and triazeneoxide (c) ligands.

ol, mp. 69 °C; 2-acetyl-1-tetralone, mp. 56 °C) [165], but in most cases the platinum complexes are embedded in thermoplastic organopolysiloxane resin particles which release the catalysts in a temperature range of 40–200 °C. The morphologic variety of the organosiloxane particles enables to adjust the dispersibility of the particles as well as the crosslinking behavior and the pot life of the formulation, respectively, and can be further combined with inhibitors [166] and stabilizing disiloxanes [167]. These systems have to be carefully designed relating to their glass-transition temperature and particle size. Optimally, the glass-transition temperature should be in the range between 40 and 250 °C; and the particle size has to be adjusted in the range of 0.1–20 μm [167,168].

Encapsulated catalysts cause a significant delay during the dissolving process, so they are not applicable in high speed processes such as the production of silicone release coatings. Another disadvantage is that the encapsulated catalysts create a concentration profile of platinum catalyst with high curing rates directly at the encapsulation, leading to ongoing self-encapsulation via the curing process, and therefore slow and uneven curing of the addition curing composition, so these encapsulated catalysts are of minor interest for industrial applications.

4.1.3. *"Dormant" platinum complexes with inhibiting ligands*

An interesting concept are dormant platinum complexes with strong binding ligands which have no hydrosilylation activity at ambient temperature but rapidly catalyze the reaction at elevated temperatures (Scheme 20). For instance, platinum(II) phosphite complexes of the general formula type $R'_2Pt[P(OR)_3]_2$ (R′ = halogen, alkyl, alkoxy) exhibit rather low activation temperatures (100–160 °C) and moreover prevent the formation of platinum colloids, resulting in better color fastness [169]. Similar properties are found with platinum bisalkynyl complexes such as $(COD)Pt(C{\equiv}CR)_2$, (1,5-dimethyl-COD)$Pt(C{\equiv}CR)_2$, or (bicyclo[2.2.1]-hepta-2,5-diene)$Pt(C{\equiv}CR)_2$ [170] (Scheme 20, a). These complexes are well-soluble in polysiloxanes, inactive up to 40 °C, and do not precipitate platinum colloids, so the resulting silicone products are free of color. They have been successfully tested as hydrosilylation catalysts in the silicone coating of paper or textiles [171]. Quantum-chemical calculations using DFT methods studying the activation steps of these complexes came to the conclusion that the activation of the pre-catalyst $(COD)Pt(C{\equiv}CR)_2$ is initiated by oxidative addition of Si–H. The activation energy and activation temperature depend on the substituents R in the alkynyl groups [172].

Further examples for dormant platinum complexes contain bidentate ligands derived from urea (e.g. *N*,*N*-diphenylcarbamide, *N*-(*n*-hexyl)-*N*-phenylcarbamide, *N*,*N*-diacetylcarbamide), acids (e.g. phenylphosphinic acid, *N*-acetylglycine, mandelic acid), and phenylisocyanate (Scheme 20, b) [173]. These complexes were described as easily handled platinum catalysts which exhibit low activation temperature with concomitant rapid curing speed and additionally suppress the formation of platinum colloids as well as isomerization reactions of terminal double bonds.

Platinum complexes of triazenes and their derivatives (e.g. $Pt(PhNNN(CH_2)_5Me)_4$, (COD)Pt((*para*-NO_2-Ph)$NNN(CH_2)_7Me)_2$) were reported to have high activation energies and suppress the hydrosilylation reaction at room temperature without additional inhibitor [174]. A further development are related complexes of triazeneoxide ligands (e.g. (COD)Pt((*para*-CN-Ph)$NNN(O)(CH_2)_5Me)_2$, $Pt(PhNNN(O)Me)_4$) which can be adjusted to their activation energy by the variation of the ligands, respectively [175]. These catalyst systems can be activated by high temperature (50–250 °C) as well as by UV-irradiation (200–400 nm) which extends their potential industrial applicability. The photochemical aspects of these and other platinum-based catalysts which can be used in photoactivated hydrosilylation will be discussed more detailed in the following section.

4.2. *Photoactivated hydrosilylation*

Photogenerated catalysts obtained by the light-induced generation of a ground-state catalyst from a catalytically inactive precursor are also of current interest in industrial hydrosilylation research [176]. They combine the advantages of good shelf stabilities of 1K silicone compositions with rapid curing via irradiation, even at ambient temperature which is advantageous for heat-labile substrates and for low-viscosity formulations. A general disadvantage in photoactivated hydrosilylation might be incomplete crosslinking because the radiation intensity cannot entirely penetrate thick-layered curing compositions.

Initially, photoactivatable hydrosilylation with established platinum complexes has been achieved with a combination of inhibitors (e.g. alkynols, see Section 4.1.1) and photosensitizers (such as benzophenone, acetophenone). The latter are primarily excited by irradiation transferring the energy to the inactive catalyst, leading to the formation of an active catalyst [177].

Commonly, most photoactivatable platinum catalysts show the highest absorbance in the deep UV (below 300 nm) and sometimes in the near UV (300–400 nm). In the visible spectral range (400–800 nm), only low absorbances are obtained in most cases, but the activation of these catalysts can be improved by auxiliary photosensitizers which shift the wavelengths of the radiation into the range needed for activation.

As described in Section 4.1.3, platinum complexes of triazenes and their derivatives (Scheme 20, c) are heat-sensitive as well as photolabile. The photolytic decomposition of $Pt(PhNNN(CH_2)_5Me)_4$ via irradiation with a XeCl* excimer laser (398 ppm) was studied by Wokaun et al. [178]. The results of this study indicate a decomposition of the photolabile ligands which generates reactive, coordinative-unsaturated platinum species. Due to the high activation barrier, compositions containing these triazene-containing complexes are storage-stable up to 6 weeks in the absence of light but cause a rapid curing within 5 min via irradiation [174]. Further components resulting from side reactions such as isomerization of alkenes, dehydrogenative silylation, and formation of α-/β-product mixtures were also observed [178].

The use of (COD)PtMe$_2$ as hydrosilylation catalyst in light-curable silicone elastomer casting compounds was reported (curing via irradiation with an average wavelength of 370 nm) [179]. However, more important complexes of this type are (η^5-cyclopentadienyl)trialkylplatinum(IV) catalysts such as CpPtMe$_3$ whose photolysis in the presence of a reactive silicon hydride HSiR$_3$ results in the formation of a silyl methyl hydride platinum complex CpPtMe(SiR$_3$)H as the crucial intermediate which is partitioned under the reaction conditions between colloidal platinum and a bis(silyl)platinum hydride CpPt(SiR$_3$)$_2$H [180]. These photoactivable catalysts are preferably used in applications such as dental imprints, adhesives, release liners, and sealing compounds [181] as well as in the production of light emitting devices (LEDs) using silicone-based encapsulants [182]. It should be noted that low-molecular platinum complexes such as CpPtMe$_3$ are very volatile [183], which combined with their toxicity is problematic with respect to workplace safety.

To decrease the volatility and to improve the solubility and stability of CpPtR$_3$ complexes in polysiloxanes as well as their curing rates, an interesting approach is the introduction of silyl substituents or alkyl groups at the cyclopentadienyl ligand (e.g. in $(\mathrm{R}'_3\mathrm{Si}-\mathrm{Cp})\mathrm{PtR}_3$, (Me-Cp)PtR$_3$) [184].

Furthermore, to minimize the consumption of CpPtMe$_3$ and its derivatives, their photoactivated hydrosilylation can be accelerated by adding auxiliary radical photoinitiators (e.g. monoketales of α-diketones or α-ketoaldehydes such as PhC(O)C(OMe)$_2$Ph, PhC(O)CMe$_2$OH) for increasing the quantum efficiency [185]. As an additional effect, the photoinitiators shift the wavelengths of the radiation source in the range needed for activation, so photoactivated hydrosilylation can occur by using actinic radiation, i.e. in the range of 200–800 nm. However, these photoinitiators are often incompatible with polysiloxanes, so large amounts are essential to ensure an effective energy transfer from the photoinitiator to the platinum catalyst.

To improve the quantum efficiency of CpPtR$_3$-catalysts, their cyclopentadienyl ligands can be substituted by polyaryl groups (e.g. naphthyl, biphenyl, anthracenyl) which operate as an internal photoinitiator and also improve the shelf life of the curing compositions [186]. Unfortunately, the solubility of the resulting complexes is reduced. Consequently, progress can be achieved via a coincident combination of aryl-substitution at the cyclopentadienyl ligand as well as silyl-substitution of the aliphatic alkyl groups at the platinum (e.g. [naphthyl(Me)Cp]PtMe$_2$(CH$_2$SiMe$_3$)), resulting in photocatalytic systems which have a better solubility in polysiloxanes and do not require additional photoinitiators [187].

Another class of photoactivatable platinum catalysts contains dicarbonyl ligands derived from acetyl acetone such as dimeric trimethyl(β-dicarbonyl)Pt(IV) complexes of the general formula type [Me$_3$Pt(RC(O)CHC(O)R)]$_2$ (R = Me, OEt, Ph, CF$_3$) which can be activated by irradiation of 225–260 nm [188]. These complexes show similar reactivities to CpPtMe$_3$ and are more active than Pt(acac)$_2$ (acac = acetylacetone). During photolysis, catalytically active intermediates are formed which convert to platinum colloids in the course of the catalytic cycle. For that reason, photoactivated hydrosilylation proceeds faster with catalysts showing a high stability against the formation of less active platinum colloids. Further studies on the activity of platinum(II) β-diketonate complexes (e.g. Pt(acac)$_2$, (CH$_2$=CH$_2$)Pt(CF$_3$C(O)CHC(O)CF$_3$)$_2$) as catalysts for hydrosilylation reactions were also recently reported [189]. From these compounds, Pt(acac)$_2$ was mentioned as hydrosilylation catalyst useful for visible light curing of silicone-based encapsulations of LEDs [182].

Furthermore, the photoactivated hydrosilylation of vinylsiloxanes with hydrosiloxanes in the presence of platinum(II) phosphine complexes of the general formula type *cis*-Pt(PR$_3$)$_2$Cl$_2$ (R = Me, Bu, Ph) [190] or platinum(II) alkene and sulfoxide complexes such as Pt(MeCOD)Cl$_2$ and *cis*-Pt(*para*-Me-C$_6$H$_4$SO)$_2$R$_2$ (e.g., R = Cl, Br, NO$_3$, C$_2$O$_4$/2) [191] was reported, from which the oxalate ligand exhibits the most effective catalysis (100% conversion after an irradiation time of 1 min and a curing time of 90 min; catalyst load 1×10^{-5} M in the reaction mixture).

A disadvantage of all photocatalytic processes based on UV-irradiation is the concurrent generation of IR-radiation from the radiation source which requires an expensive dissipation of the heat via water or air cooling. Furthermore, the predominantly applied medium pressure mercury lamps have to be disposed regularly. An interesting alternative can be a hydrosilylation process based on microwave radiation which is reported to reduce the curing time of silicone coating compositions up to 50% [192]. However, this method does not class among photocatalyzed hydrosilylation because it is based on thermal effects.

From an industrial point of view, photoactivated hydrosilylation is hitherto of interest for selected, high-value applications due to significantly higher costs due to the demanding ligand structures. Further improvements might be possible with better knowledge of the mechanistic aspects of the photocatalyzed hydrosilylation using platinum complexes, resulting in even better photocatalysts.

5. Conclusions

Hydrosilylation of olefins is the key catalytic reaction for the production of industrially important organosilicon compounds such as organofunctional silanes and silicones, and industrial research on this topic has made important contributions to the development of novel hydrosilylation catalysts as well as new methods for improving the selectivity, activity, and stability of established catalysts. In the last decade, a variety of new approaches was pursued in industrial as well as in academic hydrosilylation research, and this revealed many important insights into catalyzed hydrosilylation. To complement this specific view on homogeneous catalysis of hydrosilylation, advances in catalyzed heterogeneous hydrosilylation should be also noted [106], e.g. the hydrosilylation of poly(methylhydro)siloxanes or polyolefins catalyzed by platinum-nanoclusters [193].

Partially incoherent results and often non-satisfying rationalization clearly demonstrate that further advancement of the mechanistic aspects of catalyzed hydrosilylation is needed and a deeper understanding has to be developed, e.g. for the real mode of action of promotors and/or inhibitors. Mechanistic and selectivity studies on different hydrosilylation reactions are often hard to compare as they use non-uniform, heterogeneous/multiphase catalytic systems and reaction conditions. Particularly for industrial applications, catalytic systems have to be individually designed to fulfill the requirements of the selected processes and the products obtained, respectively. For instance, the economic production of organofunctional silanes puts higher demands on the selectivity of the applied hydrosilylation reactions, whereas the crosslinking of silicone polymers requires highly active, but low-priced catalysts due to the need for high crosslinking speeds and the impossibility of recovering of the catalyst. Consequently, it is rarely possible to obtain catalysts which are generally applicable for hydrosilylation reactions.

In these authors' opinion, the future of industrial hydrosilylation research should relate to the development of new metal catalysts with higher activities and better selectivities for the desired product, especially for industrial hydrosilylation processes hampered by undesired side reactions which generate byproducts and/or require high catalyst loads. Established expensive catalysts based on Pt, Ir, and Rh in particular have to be used more efficiently, which includes better methods for suppressing deactivation, e.g. by the formation of metal colloids. Additionally, lower loads of precious metal catalysts often induce lower reliability in application due to contaminations, e.g. sulfur or nitrogen compounds, which are often present in the rubber industry. Catalysts with significant improved resistance to sulfur or nitrogen contaminations seem therefore to be an interesting approach.

Substituting platinum as catalytically active metal with lower-priced metals is a specially rewarding approach for industrial hydrosilylation. Ruthenium seems to be the most promising metal-based alternative for low-cost hydrosilylation, but the hitherto evaluated Ru-catalysts do not yet show the required activities and selectivities compared to established Pt-catalysts. For that reason, further optimization of ruthenium-catalyzed hydrosilylation and the development of new commercially viable non-precious metal catalysts is needed. Some promising approaches concerning the use of iron-based catalysts have been started, but are still far away from an industrial application. Therefore, industrial hydrosilylation will continue to rely on the creativity of silicon and catalysis researchers to design better catalytic systems.

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