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Short Review

Recent advances in catalytic hydrosilylation *

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1. Introduction

This short review deals with reports published in the last 2 years concerning catalytic, mechanistic, synthetic and stuctural aspects of hydrosilylation as well as asymmetric syntheses involving hydrosilylation. (However, reports on the application of these processes in polymer chemistry are not covered.) It is to be regarded as a supplement to the recently published book entitled *Comprehensive Handbook on Hydrosilylation* [1] which surveyed publications appearing from 1965 up to early 1990. (Another monograph, in Russian, surveying papers and conference abstracts of the last 15 years up to 1989 has recently appeared [2].)

The great interest in the additions of silicon hydrides to multiple bonds—one of the most important methods for synthesis of organosilicon compounds—has resulted in over 40 reviews which provide surveys of publications and/or discuss particular aspects of the reaction.

The great contribution of Professor Voronkov and his group in this area of organosilicon chemistry comprises numerous books and reviews as well as many original research papers. It should be noted that Voronkov has carried out remarkable work on the reactivity of the Si–H bond generally, including not only hydrosilylation but also a wide range of other processes such as dehydrocondensation. His work has led to new catalytic systems and to new methods of synthesis of alkyl and carbofunctional compounds by hydrosilylation.

Our handbook [1] consists of two basic parts. The first descriptive part covers the catalytic, mechanistic, structural and synthetic aspects of hydrosilylation as well as its applications in organic, organosilicon and polymer chemistry. The second part consists of tables summarizing information on the relevant reactions of selected trisubstituted silanes from more than 2000 papers and patents published in the 25 years up to 1990.

The present review covers the most important relevant contributions appearing in the last 2 years, presented in a form corresponding to that in the first part of our handbook. However, in contrast with the latter, this survey does not deal with the numerous reports (mainly patents) concerned with the application of hydrosilylation in polymer chemistry, *e.g.* curing and modification of polyorganosiloxanes and the modification of unsaturated organic polymers.

2. Catalytic and mechanistic aspects of hydrosilylation

Since 1957 when J.L. Speier showed chloroplatinic acid to be a very effective catalyst for homogeneous hydrosilylation, there have been many studies of catalysis of hydrosilylation by transition metal (predominantly platinum) complexes. At present, work in this field is mainly directed towards the search for new catalytic complexes of Pt, Rh, Co, Ru, Pd, Ni and some other metals, and to establishing the composition and structure of key intermediates, which lead to more accurate description of the individual steps and to elucidation of the detailed mechanism. The latter is mainly based on the suggestions of Chalk and Harrod, but recently olefin insertion into M–Si bonds has been shown also to provide a good explanation of dehydrogenative silylation depicted in the general equation

$$X_3SiH + 2\,RCH{=}CH_2 \longrightarrow X_3SiCH{=}CHR + RCH_2CH_3 \quad (1)$$

where R = H, alkyl, fluoroalkyl, phenyl and silyl groups. Although a wide range of catalysts has been studied for

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* Dedicated to Professor M.G. Voronkov in recognition of his distinguished contribution to organosilicon chemistry.

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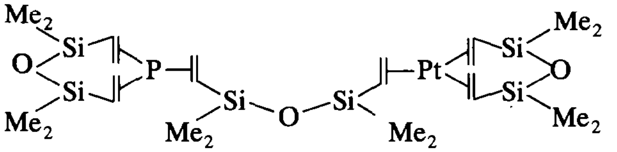
hydrosilylation, most research and industrial syntheses are carried out in the presence of Pt complexes, with H_2PtCl_6 commonly used as the initial precursor. Karstedt's catalyst, obtained by treating hexachloroplatinic acid with vinylsiloxane, has been most used in recent years. Reaction of $Pt(cod)_2$ with tetramethyldivinyldisiloxane in diethyl ether afforded colourless crystals of a complex whose structure was shown by X-ray crystallography to be **I** [3]. Other Pt catalyst systems for hydrosilylation were prepared by treating Pt complexes and salts with alkadienes, norbornodienes and cycloolefins [4].



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Kinetic studies of the action of dichloro(dicyclopentadiene) platinum(II) as a catalyst precursor for hydrosilylation of allyl ethers revealed changes in the apparent order of reaction with respect to Pt with a change in the nature of the olefin and led to a suggested mechanism involving a dinuclear homogeneous catalyst [5]. The strong effect of the σ-electron-donating properties of tertiary phosphines L in the PtL_2X_2 complex in hydrosilylation of 1-heptene by methyldichlorosilane is reflected in the following reactivity order: $Ph_3P > (C_6H_5O)_2PPh > PhMe_2P > Et_3P > Pr_3P > Bz_3P > Bu_3P > {}^iPr_3P$ [6].

Many specific complex catalysts have recently been used for hydrosilylation and dehydrogenative silylation. Organometallic catalysts generated from zirconocene dichloride and two equivalents of butyllithium were used in the hydrosilylation of olefins such as styrene, 1-hexene and 2-pentene by diphenylsilane [7,8]. The formation of vinylsilane during the hydrosilylation of styrene, as well as rapid H–D exchange and olefin isomerization of 2-pentene, attests to the complexity of this catalytic system. Possible mechanisms for allylsilane and vinylsilane formation were discussed [7].

A highly regioselective zirconium-catalysed hydrosilylation of 1-alkene by diphenylsilane which seems to be of general synthetic utility has been reported [9] and is as follows:

$$RCH{=}CH_2 + H_2SiPh_2 \xrightarrow{CpZrR'_2} RCH_2CH_2SiHPh_2 \qquad (2)$$

where $R = {}^nHex, {}^nOct, Ph$ *etc.* and $R' = Et$ or ${}^nBu$. A doubly hydrido-bridged dimer of $Cp_2Zr(H)SiHPh_2$ (a direct precursor of the respective monomer) was isolated and identified by X-ray crystallography [9].

In contrast, detailed studies of the reactions of $PhMeSiH_2$ with cyclic and acyclic olefins in the presence of $Cp_2MCl_2 + {}^nBuLi$ (M = Ti, Zr, Hf) catalysts have revealed the occurrence of a range of reactions, including hydrosilylation, olefin isomerization of internal olefins followed by their hydrosilylation of the new isomers, dehydrocoupling of the silane to form silicon oligomers and dehydrocoupling of the silane with olefin to form vinylsilanes [10].

Dimeric μ-hydride complexes of the general formula $Q^+[(CO)_5M(\mu\text{-}H)M(CO)_5]^-$ where $Q = Et_4N$ or $(PPh_3)_2N$ and M = Cr, Mo and W have been shown to be regiospecific and/or stereospecific catalysts for hydrosilylation of aldehydes, acetylenes and conjugated olefins [11]. Manganese acyl complexes $L(CO)_4MnCOR$ (where L = CO, $R = CH_3$, Ph, $L = PPh_3$, PEt_3) were found to be effective catalysts for hydrosilylation of organomanganese and acyliron compounds [12].

Catalysts of a new type, namely 1,1-bis(benzylthio)-ferrocene platinum and rhodium complexes, have been used for the hydrosilylation of olefins with triethoxysilane [13].

A comprehensive study by Ojima *et al.* of catalysis of hydrosilylation by carbonyl clusters resulted recently in the application of $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ in the hydrosilylation of 1-hexyne [14], isoprene, cyclohexanone and cyclohexenone [15] by trisubstituted and disubstituted silanes. Mechanistic considerations were discussed. Less common Ir^I, Ir^{III} and Ir^V complexes stabilized by O-donor ligands have been reported to be selective catalysts for dehydrogenative silylation and hydrosilylation of ethylene by triphenylsilane and diphenylmethylsilane [16]. The complex $IrCl(CO)(PPh_3)_2$ was used for hydrosilylation of phenylacetylene [17].

Complexes of Group 10 elements containing bidentate ligands also showed unusual activity. The complexes $MCl_2(2{,}6\text{-}Me_2C_6H_3NC)_2$ (where M = Pt, Pd, Ni) as well as rhodium isocyanide were used in the hydrosilylation of α-methylstyrene and ketones [18]. Bis(diphenylphosphino)methane complexes of Pd were used for the addition of trichlorosilane to 1-hexene, styrene and vinyltrichlorosilane [19]. $Ni(acac)_2$ and other Ni complexes were shown to be catalysts for the unusual reactions of vinyltrisubstituted silanes with triethoxysilane to give products of dehydrogenative silylation, hydrosilylation and hydrogenative dimerization [20].

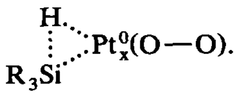
The first examples of organolanthanide-catalysed hydrosilylation have been reported. The complexes $[(C_5Me_5)_2NdH]_2$ and $(C_5Me_5)_2NdCH(SiMe_3)_2$ effectively catalyse the hydrosilylation of alkenes with disubstituted and monosubstituted silanes at 30–80°C [21]. Catalysts of the general formula Cp_2MR (where R is a hydroxycarbyl or silyl group and M = Y, Sc or a rare earth metal) have been used for hydrosilylation and dehydrocondensation of silicon hydrides [22].

In the rhodium(II)-perfluorobutyrate-catalysed hydrosilylation of 1-alkene, styrene and ethylacrylate, the mode of addition determines the products formed. When the alkene is added to triethylsilane, "normal" hydrosilylation occurs, but reverse addition results in the formation of allylsilanes or vinylsilanes [23]. In hydrosilylation of 1-alkynes catalysed by this complex, either allylsilanes or vinylsilanes are formed, again depending on the mode of addition of reagents [24].

Many catalytically active intermediates in hydrosilylation have been isolated [25–29], strongly supporting the proposed mechanisms for the catalysis. $CpRh(C_2H_4)(SiR_3)H$ was isolated and tested in hydrosilylation of ethylene, providing support for the generation of a complex in the Rh^V oxidation state as a key intermediate in the reaction, although no explanation was given for the formation of unsaturated products formed when an excess of alkene was present [25]. $OsHCl(CO)P^iPr_3$ was found to be a very active and highly selective catalyst for the hydrosilylation of phenylacetylene by triethylsilane. The catalytic path involves the silyl dihydrogen intermediate $Os(SiEt_3)Cl\text{-}(\eta^2\text{-}H_2)CO(P^iPr_3)$ [26]. Similarly, $(C_5H_5)Fe(CO)(SiHPh_2)H$ was identified as an active intermediate in the hydrosilylation of acetophenone by diphenylsilane catalysed by iron cyclopentadienyl complex [27].

Various mechanistic suggestions have been advanced for $Pt(CH_2{=}CH_2)(PPh_3)_2$-catalysed dehydrogenative double silylation of olefins and dienes by *o*-bis(dimethylsilyl)benzene [28]. Silyleneplatinum species have been proposed as key intermediates in this reaction also. Cluster carbonyl complexes of osmium have been isolated and structurally characterized for the first time as intermediates in the hydrosilylation of alkynes by trialkoxysilanes [29].

Recent studies by Lewis and coworkers have shown that various widely used hydrosilylation catalysts derived from platinum [30–32] rhodium [31,33] and other metal [31] halides are colloidal in character. In metal cluster complexes, bridging involving interactions with oxygen atoms provides a type of coordination that can be extended to large clusters and even to colloids [34]. The proposed mechanism for metal-colloid-catalysed hydrosilylation involves the formation of the following metal colloid–R_3SiH intermediate [32]:



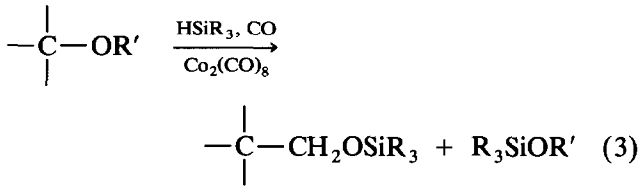
$$\begin{matrix} H \\ \vdots \\ R_3Si \end{matrix} \!\!\cdot\!\!\cdot Pt_x^0(O{-}O).$$

As in homogeneously catalysed hydrosilylation by Ru and Rh complexes [1], molecular O_2 acts as a true co-catalyst (*i.e.* it is not consumed in the reaction). The function of the O_2 is to prevent irreversible colloid agglomeration (colloids of larger particle size had reduced activity) and to make the Pt/SiH complex more electrophilic, *i.e.* more susceptible to nucleophilic attack by olefins. A recent study in this field has revealed an essential difference between the morphologies of the Pt colloid formed under particular conditions in the hydrosilylation of various olefins by Et_3SiH in the presence of Karstedt's catalyst [30].

Although among heterogeneous catalysts it is mainly the precious metals that promote hydrosilylation at a useful rate, recent work by Boudjouk *et al.* [35] has shown that activated Ni powder produced by Li or Na reduction of nickel iodide in tetrahydrofuran effectively catalyses the hydrosilylation of various olefins. Sonication during reduction increases the rate of reduction as well as that of hydrosilylation. A search has been made for efficient Pt and Rh complexes immobilized on polymer matrices functionalized with CN, sulphide and phosphine ligands [36]. The activity of the catalysts examined in the hydrosilylation of olefins depends strongly on the structure of the support used [37]. A Pd complex supported on a modified asbestos was used for synthesis of 1,1-bis(trichlorosilyl)ethane [37].

Little new information on non-transition metal complex catalysts of hydrosilylation has appeared in the last two years. Radiation-induced addition of methyldichlorosilane to vinyl acetate occurs by a radical-chain mechanism [38]. Photodissociation of the Si–H bond to form silyl radicals depends markedly on the substituents on Si [39]. Inorganic solid acids and bases, such as Fe^{3+}-ion-exchanged montmorillonite and hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, catalyse the hydrosilylation of carbonyl compounds [40].

Hydrosilylation in the presence of transition metal complexes can be accompanied by many side reactions because of the occurrence of ligand exchange at the metal centre [1]. Some of these side reactions reported recently can in themselves be of great research and industrial importance. Work on silylformylation of olefin catalysed by Rh and Co carbonyls has been continued by Murai and coworkers [41]. This reaction in the case of 1-hexyne in the presence of Rh and mixed Rh–Co carbonyl clusters was studied by Ojima *et al.* [42]. In the presence of $[RhCl(CO)_2]_2$ the reaction of enamines with hydrosilanes and carbon monoxide resulted in regioselective attachment of CO to the α-C atom to give α-(siloxymethylene)amines [43], which can be readily converted into α-siloxy ketones by hydrolysis. A new catalytic reaction of siloxymethylation of oxygen-containing compounds (oxiranes, oxetanes, five-membered cyclic ethers, β-lactones, glycosyl acetates, acetals and ortoesters) can be formulated generally as follows [44]:



$$-\overset{|}{\underset{|}{C}}-OR' \xrightarrow[Co_2(CO)_8]{HSiR_3,\ CO} -\overset{|}{\underset{|}{C}}-CH_2OSiR_3 + R_3SiOR' \quad (3)$$

Novel catalytic hydrosilanolysis of alkenyl acetates by triethylsilane was found to be catalysed by rhodium carboranes according to the following equation [45]:

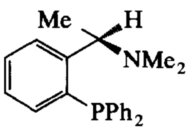
$$CH_2{=}C(R)OC(O)CH_3 + R'_3SiH \xrightarrow{\text{catalyst}} CH_2{=}CHR + R'_3SiOC(O)CH_3 \quad (4)$$

where $R = CH_3$, C_6H_5; $R' = C_2H_5$.

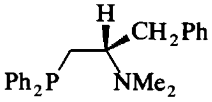
3. Asymmetric hydrosilylation

In the last few years, many papers on asymmetric hydrosilylation have been published describing new catalytic systems (mainly new optically active ligands) and new synthetic applications of the reaction.

New phosphates [46] and diphosphines [47] can be used as chiral ligands, but most reports come from Brunner's laboratory, where additional non-phosphine-based chiral ligands have been synthesized. The remarkable activity of $[RhCl(cod)]_2$ with chiral phenanthroline ligands has been reported [48]; the enantioselectivity increases as the chiral substituent is moved closer to the N atom. Among the useful new ligands reported were compounds **II** and **III** [46,49], products of the addition of the optically active amines to diphenyl vinylphosphine oxide or DPPE sulphide [50] and others [51]. N-centred ligands are usually derived from the inexpensive and readily available pool of optically pure amines and, despite the fact that over 200 chiral bidentate N-based ligands had been synthesized in the previous decade [52], further new ones have been reported. For example, new chiral C_2 symmetrical bisoxazolines, bis(oxazolinyl)pyridines and bithioazolines were used very effectively with Rh precursors [53,54], especially in the case of Rh^{III} complexes [54] (above 90% EE for $PhCOCH_3$ reduction with Ph_2SiH_2). The use of the $[RhCl(cod)]_2$-pyridineoxazoline ligand system was studied in some organic solvents [55]. The so-called "CCl_4 effect" was observed (higher reactivity and EE); a stoichiometric amount of CCl_4 with respect to the Rh precursor was optimal. On the basis of the EE dependence on the excess of the ligand, the solvent, and the concentrations of the substrate and of the catalyst, Brunner and Brandl [56] proposed a structure for the intermediates and suggested a detailed reaction mechanism. A polymer-bound catalyst of this type gave even higher EE than did the homogeneous catalyst in the addition of Ph_2SiH_2 to $PhCOCH_3$ [57]; after eight to ten runs of catalyst reusage, its activity decreased markedly but, surprisingly, the EE rose to 92%.



(II)



(III)

Most catalysts are still based on Rh complexes, but some Pd complexes with optical active ferrocenylmonophosphine [58] or bis(anthracenyl)phosphine [59] ligands, and also Co^I complexes with the pyridineoxazoline ligand [60], have been described. Bis(dihydrooxazolyl) derivatives of Cu, Ir and Pd precursors also provide new attractive and (owing to their accessibility and high structural variability) very promising catalysts for asymmetric hydrosilylation [61].

From the synthetic point of view, catalytic asymmetric intramolecular hydrosilylation is currently the most extensively studied [47,62–65]. In the first wholly systematic attempt to achieve the highest possible EE's, Bosnich and coworkers [62] studied the effect of silicon substituents on silicon and of various olefinic fragments in $CH_2{=}C(CH_3)CH_2OSiHRR'$. A mechanism for the reaction was proposed [65]; $Rh(diphosphine)^+$ was used as catalyst and specifically labelled deuterated substrates were employed. Oxidative addition of the Si–H bond to the catalyst precursor is very fast and reversible. A silyl metal olefin hydride complex is suggested to be the major diastereomeric intermediate [65]. Asymmetric hydrosilylation of β-silylketones [63] was performed in the presence of the superacid catalyst $TfOH_2^+B(OTf)_4^-$, offering organic chemists an attractive new route to optically active diols. The synthesis of dioxasilanes from β-silyloxyketones using cationic rhodium chiral [47] or superacid [63] catalyst is noteworthy. It provides a new route to $R'-\overset{|}{C}-OSiMe_2OCH_2$-type compounds with asymmetric centres.

Hydrosilylation of the C=C bond with a high degree of stereoselectivity is still much more demanding than that of the C=O bond described in almost all the above mentioned studies. The positive results in Cl_3SiH addition to conjugated dienes (with over 60% EE) [58] and terminal alkenes in the presence of Pd systems published by Hayashi [59] are particularly noteworthy. In this case the process represents the first successful conversion of terminal olefins into optically active secondary alcohols (with an EE higher than 94%). The steric effect seems to be the most critical in intramolecular addition. Variation of aryl groups at the Si atom in

$CH_2{=}C(CH_3)CH[OSiR_2H]C(CH_3){=}CH_2$ revealed the most significant effects [64]. With the sterically demanding *o*-tolyl substituent the reaction under study proceeded with poor selectivity and low chemical yield, whereas *m*- and *p*-tolyl derivatives gave both high chemical and high optical yields.

4. Synthetic and structural aspects of hydrosilylation

Hydrosilylation offers a great many synthetic opportunities for organic chemists. Since a large number of different multiple bonds may be involved, it can provide a useful method for synthesis of a whole family of Si-containing organic molecules and/or a convenient way of reducing organic compounds.

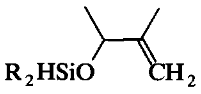
Alkylsilanes (or arylsilanes) are usually the products of hydrosilylation of alkenes [6,7,21], which may give both linear and cyclic alkylsilanes. For a series of chlorosilanes, in the reaction with 1-heptene [6] (yielding heptylsilanes) it was found that the rate increased (with a significant elongation of the induction period) on decrease in the number of Cl atoms in a silane molecule, *i.e.* $Me_2ClSiH > MeCl_2SiH > Cl_3SiH$. Products of reactions of this type are useful as materials for modified silicones [66]. Hydrosilylation of cyclopentene in the presence of a Cl-deficient chloroplatinic acid catalyst gives cyclopentylsilane in good yield [67]. Hydrosilylation of styrene and its regioselectivity has been often used in examination of the effect of the silane structure on the hydrosilylation rate. Usually the reaction gives the linear silylation product $PhCH_2CH_2Si\equiv$ irrespective of the silane involved. However, in the presence of a Nd-based catalytic system the branched product $PhCH(CH_3)Si\equiv$ dominates (72/16) for $PhSiH_3$, whereas for $HexSiH_3$ almost the inverse ratio is observed (11/56) [21]. For less sterically hindered silanes there is competition from a coupling reaction, yielding an oligomeric product; $PhSiH_3$ yields only alkylsilane, and Ph_3SiH only vinylsilane [7].

The natures of the silane and catalytic system determine the regioselectivity of this process, and the proper choice of these can lead directly to the product needed. The addition of hydrosiloxanes to tricyclodecenes (in the presence of Speier's catalyst) yields new dicyclopentadiene derivatives, substrates for biologically active elastomers used in agriculture [68]. Similar derivatives can be efficiently prepared from indene [69]. Hydrosilylation of 1-hexene with monosilane provides a route to trihydroorganosilanes [70,71], which are new materials for the organosilicon industry as precursors for polycrystalline Si and amorphous Si. Dienes (*e.g.* 1,5-hexadiene) are also used in these reactions [70].

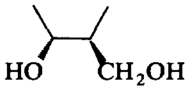
Alkenes and their derivatives may be converted into silylated products by a free-radical mechanism [72]. The success of hydrosilylation (in competition with telomerization) depends, however, on the electronegativity of the olefin substituents [73,74].

Rh and Ru–Co carbonyl clusters show high selectivity and give highly regioselective products in hydrosilylation of isoprene by HMe_2SiPh [15]. Similarly, in the presence of a Ni precursor, cis-2-butenyldimethylchlorosilane was exclusively formed in Me_2ClSiH addition to butadiene [75]. Larger cyclic molecules can be prepared from the dienes. For example the addition of diphenylsilane to norbornadiene catalysed by a Rh-based catalyst with phosphine ligands gave 8,8-diphenyltricyclo[2.2.1.1]-8-silaoctane in 59% yield [76]. Hydrosilylation of tetraenes provides a convenient method for the preparation of ring systems bearing a pendant allyl moiety [58].

Several reports have appeared on the hydrosilylation of functionally substituted alkene derivatives which lead to the formation of molecules with additional heteroatoms or a new functionality. Voronkov has recently shown that vinyloxysilanes $HR_2SiCH_2CH_2OCH{=}CH_2$ in the presence of Speier's catalyst yield five- and six-membered cyclic products [77]. The regioselectivity of this process depends to some extent on the nature of the substituents on Si, but it is mainly controlled by thermodynamic factors, which favour primary formation of the Pt-containing six-membered cyclic intermediates, resulting in production of the five-membered cyclic products. Bis(dimethylsilyl)benzene and bis(dimethylsilyl)ether react with olefin derivatives to yield different, more extended, cyclic products [78]. Intramolecular hydrosilylation can also be useful for functionalization of an enol ether [79]. The substrate fragment



forms two isomers:



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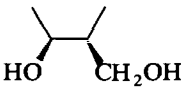
and



(B)

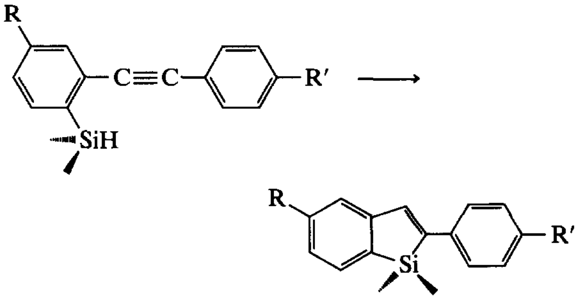
The selectivity depends mainly on the catalyst used; $Rh(acac)(C_7H_8)$ yields an A-to-B ratio of 92/8 whereas Karstedt's Pt catalyst yields almost the inverse ratio, 9/91. Most work on the hydrosilylation of the C=C bond in the presence of heteroatoms in a substrate molecule is directed towards the synthesis of silane coupling agents. Their wide application is reflected in the broad patent literature in this field [80–89]. New compounds or new methods of their preparation have been patented, namely cyclopentadiene derivatives [68,69], alkenyloxy functional organosilicon compounds [80,81], β-acetoxyl(ethyl)silanes [82], aminopropylalkoxysilanes [83] and other aminosilanes [84], mercaptosilanes [85] and hydrosilyl derivatives [86]. Methacryloxypropylsilanes are still used as silane coupling agents [87]. Silaacrylates have been efficiently prepared by H_2PtCl_6-catalysed hydrosilylation of allyl methacrylate and acrylate with organochlorosilanes [88]; phenothiazine was used as a free-radical polymerization inhibitor. The effect of the silane structure was also studied in the case of methyl methacrylate hydrosilylation in the presence of a Pt catalyst [89]; the linear product $R_3SiCH_2CH(CH_3)COOCH_3$ dominated for all the silanes used.

The preparation of F-containing organic silicon compounds (new coupling agents and materials for functional polymers) has been reported [89]. F-containing organic Si monomers of the type $[CH_2SiR_1R_2X]_2$ have been prepared by hydrosilylation of vinylsilane [90]. The use of hydrosiloxanes in direct addition to perfluoroallylethers led to the formation of anionic fluoro surfactants [91]. A study of the Pt-catalysed hydrosilylation of disilylethenes with high boiling hydrosilanes revealed the formation of various products arising from the redistribution and subsequent addition of the redistribution products to the disilylethenes [92].

The hydrosilylation of alkynes still provides the most convenient and direct route to vinylsilanes, which are very important as reagents in organic synthesis and as intermediates for cross-linked silicones. The stereochemistry of this reaction, which gives 1-silylalkenes (in both *cis* and *trans* forms) has given rise to much controversy in recent years [1]. Ojima *et al.* reported recently that hydrosilylation of 1-hexyne catalysed by Rh, Co carbonyls and by Wilkinson's catalyst gives a mixture of the *cis* and *trans* isomers and the α-isomer. The *cis*-to-*trans* ratio depends on the concentration of catalyst as well as on the substituents in the hydrosilane used [14]. *Cis*- and *trans*-$PhCH{=}CHSiEt_3$ can be selectively obtained, in good yields, in the presence of Os complexes depending on the reaction conditions [26]. Some Rh complexes of general formula $Rh(C_2H_4)_2L$ (L = acac or hfa) catalyse the hydrosilylation of phenylacetylene with R_3SiH to produce $PhC(Si{\equiv}){=}CH_2$ selectively [93].

In an elegant study, Lewis *et al.* [94] obtained interesting results on the hydrosilylation of alkynes with highly active Pt^0 olefin species as catalysts [94]. The effect of steric and electronic factors in both substrates on the product selectivity was investigated. The presence of a bulky group near the α position give rise to exclusive formation of the β product, although all silanes in the series $Ph_{3-x}Me_xSiH$ ($x = 0$–2) give β and α products in the same ratios. The effect of the coordination of organosilane at the open coordination site of a transition metal catalyst on the outcome of the reaction in the presence of Rh(II) perfluorobutyrate and H_2PtCl_6 has been studied [24].

Vinyltrimethoxysilane can be produced directly from acetylene and alkoxysilane in the liquid phase [95]. Vinyltrichlorosilane was synthesized successfully by hydrosilylation of acetylene with a polymer-protective immobilized Pt complex as catalyst, by the gas-phase flow method [96]. Additional new racemic vinylsilanes have been obtained by hydrosilylation of acetylene and monosubstituted alkynes with ($\pm$)α-NpPhMeSiH and ($\pm$)$N(CH_2CH_2O)_3SiCH_2PhMeSiH$ in the presence of Pt precursors [97]. Under certain conditions (depending on substituent at the C≡C bond, the catalyst and the reaction temperature) the reaction occurs regiospecifically to give exclusively the β-*trans* adduct. Hydrosilylation of phenylthioacetylenes followed by oxidation gives the corresponding silylvinylsulphones [98]. The C≡C triple bond in substituted tolanes may be activated in the presence of a $H_2PtCl_6 + CH_2Cl_2$ catalyst to yield a bicyclic product [99], as follows:



(5)

One-pot coupling of a substituted propargylamine derivative with triorganosilane and CO catalysed by Rh carbonyls has been shown to provide a novel route to α-silylmethylene-β-lactams via silylcarbonylation [100].

Catalytic hydrosilylation of aldehydes and ketones to give silyl ethers is a useful method for reversible protection of the C=O function or for its reduction to the corresponding alcohols. The reactions of cyclohexanone with $HSiEt_3$ catalysed by Rh and Rh–Co carbonyls give (cyclohexyloxy)triethylsilane [15], whereas the reactions with $HSiMe_2Et$ or Ph_2SiH_2 afford a mixture of cyclohexyloxysilane (major) and (cyclohex-1-enyloxy)silane (minor). Reductive silylation of quinones by Et_3SiH catalysed by Wilkinson's catalyst provides an easy method for protecting the highly reactive quinonic groups of naturally occurring macromolecules and others of high biological importance [101]. Bis-silyl ethers readily undergo oxidative desilylation or acid hydrolysis to give the parent quinones and corresponding hydroquinone derivatives, respectively. It is noteworthy that Me_2PhSiH reacts readily with the C=O bond in solvents (of low polarity) in the presence of catalytic amounts of alkali metal fluorides and crown ethers as phase-transfer agents [102]. This method is considerably simpler, milder and more convenient than previously reported procedures, especially those using transition metal complexes.

The reduction of the carbonyl group by hydrosilylation has been successfully used for the conversion of esters into primary alcohols [103] and acyl–transition metal complexes M–C(O)R, leading to the corresponding α-siloxyalkyl complexes $M–CH(OSiHPh_2)R$ [104]. Hydrosilylation of α,β-unsaturated carbonyl compounds followed by hydrolysis provides a novel and effective method of reduction to give the corresponding saturated carbonyl compounds or allylic alcohols. Hydrosilylation of linear and (in the presence of Rh precursor) cyclic α,β-unsaturated ketones leads to 1,4-addition products [18]. For α,δ-unsaturated ketones, 1,2-addition to the C=C bond occurs, to give corresponding silylketones. Bis(hydrosilanes) react with vinylketenes [105] and ketones [106] to yield cyclic bis(sila)-adducts. The reaction of cyclohexenone with $HSiMe_2Ph$ catalysed by Rh and Rh–Co carbonyls yields the 1,4-addition product exclusively [15]. *Cis–cis*-dimethylmuconate can be converted with complete regioselectivity in the presence of $RhCl(PPh_3)_3$ as a catalyst into novel ketene silyl acetals possessing moderate electrophilic properties [107]. The synthesis of methoxysiladioxane from β-silyloxyesters containing $(^iPr)_2HSi$ groups [108] is an example of intramolecular hydrosilylation involving the carbonyl bond.

New amines and imines of synthetic interest can be produced by hydrosilylation of C=N and C≡N bonds. A facile reduction of various Schiff bases with Cl_2SiH_2 and Cl_3SiH in the presence of BF_3Et_2O has been reported [109]. The resulting amines are highly active herbicides. Dehydrogenative double silylation of nitriles and azirine derivatives via addition of *o*-bis(dimethylsilyl)benzene yields silyl enamines and imines [110]. A hydrosilane can act as an H source and chain carrier in radical deoxygenation of primary alcohols occurring via (to our knowledge) the first successful hydrosilylation of a C=S bond [111].

References

1 B. Marciniec, J. Guliński, W. Urbaniak and Z. W. Kornetka, in B. Marciniec (ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, 1992, pp. 758.
2 V. B. Pukhnarevich, E. Lukevics, L. I. Kopylova and M. G. Voronkov, in E. Lukevics (ed.), *Perspectives of Hydrosilylation*, Institute of Organic Synthesis, Riga, 1992, pp. 383 (in Russian).
3 P. Hitchcock, M. F. Lappert and N. J. W. Warhurst, *Angew. Chem., Int. Ed. Engl., 30* (1991) 438.
4 G. Friedmann, Y. Shreim and J. Brossas, *Eur. Polym. J., 28* (1992) 271; *Jpn. Patent 91 157 138*; *Chem. Abstr., 116* (1992) 83921p; *Ger. Patent 3 906 514* (1989).
5 X. Cogueret and G. Wegner, *Organometallics, 10* (1991) 3139.
6 N. K. Skvortsov, A. E. Trofimov, K. E. Timov, V. N. Spevak and V. V. Vasil'ev, *Zh. Obshch. Khim., 61* (1991) 574.
7 M. R. Kesti and R. Waymouth, *Organometallics, 11* (1992) 1095.
8 M. R. Kesti, M. Abdulrahman and R. M. Waymouth, *J. Organomet. Chem., 417* (1991) C12.
9 T. Takahashi, *J. Am. Chem. Soc., 113* (1991) 8564.
10 J. Y. Corey and X. H. Zhu, *Organometallics, 11* (1992) 672.
11 T. Fuchikami, Y. Ubukata and Y. Tanaka, *Tetrahedron Lett., 32* (1991) 1199; *Yuki Gosei Kagaku Kyohashi, 48* (1990) 1022; *Chem. Abstr., 114* (1991) 122440m.
12 P. K. Hanna, B. T. Gregg and A. R. Cutler, *Organometallics, 10* (1991) 31; B. T. Gregg, P. K. Hanna, E. J. Crawford and A. R. Cutler, *J. Am. Chem. Soc., 113* (1991) 384.
13 Y. Chen, J. Ni and J. Yao, *Gaodeng Xuexiao Huaxue Xuebao, 12* (1991) 830; *Chem. Abstr., 116* (1992) 174221b.
14 I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics, 9* (1990) 3127.
15 I. Ojima, R. J. Donovan and N. Clos, *Organometallics, 10* (1991) 2606.
16 R. S. Tanke and R. H. Crabtree, *Organometallics, 10* (1991) 415.
17 L. I. Kopylova, V. B. Pukhnarevich and M. G. Voronkov, *Zh. Obsch. Khim., 61* (1991) 2606.
18 T. Hagiwara, K. Taya, Y. Yamamoto and H. Yamazaki, *J. Mol. Catal., 54* (1989) 165.
19 J. Guliński and B. R. James, *J. Mol. Catal., 72* (1992) 167.
20 B. Marciniec, H. Maciejewski and J. Mirecki, *J. Organomet. Chem., 418* (1991) 61.
21 T. Sakakura, H.-J. Lautenschlager and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, (1991) 40.
22 *US Patent 4 965 836* (1990); *US Patent 4 973 643* (1990).
23 M. P. Doyle, G. A. Devora, A. O. Nefedov and K. G. High, *Organometallics, 11* (1992) 549.
24 M. P. Doyle, K. G. High, C. L. Nesloney, T. W. Clayton, Jr., and J. Lin, *Organometallics, 10* (1991) 1225.
25 S. B. Buckett and R. N. Perutz, *Organometallics, 11* (1992) 90.
26 M. A. Esteruelas, L. A. Oro and C. Valero, *Organometallics, 10* (1991) 462.
27 H. Brunner and K. Fisch, *J. Organomet. Chem., 412* (1991) C11.
28 M. Tanaka, Y. Uchimaru and H.-J. Lautenschlager, *J. Organomet. Chem., 428* (1992) 1.
29 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, *Organometallics, 11* (1992) 2.
30 L. N. Lewis, R. J. Uriarte and N. Lewis, *J. Catal., 127* (1991) 67.
31 L. N. Lewis and R. J. Uriarte, *Organometallics, 9* (1990) 621.
32 L. N. Lewis, *J. Am. Chem. Soc., 112* (1990) 5998.
33 L. N. Lewis, R. J. Uriarte and N. Lewis, *J. Mol. Catal., 66* (1991) 105.
34 R. D. Adams, J. E. Cortopassi and M. P. Pompeo, *Inorg. Chem., 30* (1991) 2960.
35 P. Boudjouk, B.-H. Han, J. R. Jacobsen and B. J. Hauck, *J. Chem. Soc., Chem. Commun.*, (1991) 1424; P. Boudjouk, A. B. Rajkumar and W. L. Parker, *J. Chem. Soc., Chem. Commun.*, (1991) 245.
36 Z. M. Michalska, B. Ostaszewski, J. Zientarska, B. N. Kolarz, M. Wojaczyńska, *React. Polym., 16* (1991/1992) 213; X. Lu, Z. Zhong and Y. Chen, *Gaodeng Xuexiao Huaxue Xuebao, 11*

(1990) 561; *Chem. Abstr., 114* (1991) 43114e; L. Meng, Z. Zhong, A. Ke and Y. Chen, *Yingyong Huaxue, 8* (1991) 49; *Chem. Abstr., 116* (1992) 129040f.

37 *Pol. Patent 150 376* (1986).

38 Yu. M. Lugovoi, N. P. Tarasova, G. Bourgeois, N. V. Bryantseva, V. V. Kostikov, C. Filliatre and A. G. Shostenko, *React. Kinet. Catal. Lett., 43* (1991) 177.

39 U. Muller and E. Popowski, *Z. Phys. Chem., 271* (1990) 703.

40 Y. Izumi, H. Nanami, K. Higuchi and M. Onaka, *Tetrahedron Lett., 32* (1991) 4741.

41 Y. Seki, K. Kawamoto, N. Chatani, A. Hidaka, N. Sonoda, K. Ohe, Y. Kawasaki and S. Murai, *J. Organomet. Chem., 403* (1991) 73.

42 I. Ojima, P. Ingallina, R. J. Donovan and N. Clos, *Organometallics, 10* (1991) 38.

43 S. Ikeda, N. Chatani, Y. Kajikawa, K. Ohe and S. Murai, *J. Org. Chem., 57* (1992) 2.

44 N. Chatani, T. Murai, S. Ikeda, T. Sano, Y. Kajikawa, K. Ohe and S. Murai, *Tetrahedron, 48* (1992) 2013.

45 H. Kang and M. F. Hawthorne, *Organometallics, 9* (1990) 2327.

46 E. Yu. Zhorov, V. A. Pavlov, Yu. D. Koreshov and E. I. Klabunovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1990) 1951.

47 M. J. Burk and J. E. Feaster, *Tetrahedron Lett., 33* (1991) 2099.

48 S. Gladiali, L. Pinna, G. Delogu, E. Graf and H. Brunner, *Tetrahedron Asymm., 1* (1990) 937.

49 E. Yu. Zhorov, K. N. Gavrilov, V. A. Pavlov, L. S. Gorshkova and E. I. Klabunovskii, *Izv. Akad. Nauk SSSR*, (1991) 1464.

50 H. Brunner and S. Limmer, *J. Organomet. Chem., 417* (1991) 173.

51 Ch. Dobler and A. Kinting, *J. Organomet. Chem., 401* (1991) C23.

52 M. E. Wright and S. A. Svejda, *Polyhedron, 10* (1991) 1061.

53 G. Helmchen, A. Krotz, K.-T. Ganz and D. Hansen, *Synlett*, (1991) 257.

54 H. Nishiyama, M. Kondo, T. Nakamura and K. Itoh, *Organometallics, 10* (1991) 500.

55 H. Brunner and Ch. Hubert, *Z. Naturforsch., Teil B, 46* (1991) 1145.

56 H. Brunner and P. Brandl, *Tetrahedron Asymm., 2* (1991) 919.

57 H. Brunner and P. Brandl, *Z. Naturforsch., Teil B, 47* (1992) 609.

58 T. Hayashi, Y. Matsumoto, I. Morikawa and Y. Ito, *Tetrahedron Asymm., 1* (1990) 151.

59 Y. Uozumi and T. Hayashi, *J. Am. Chem. Soc., 113* (1991) 9887.

60 H. Brunner and K. Amberger, *J. Organomet. Chem., 417* (1991) C63.

61 C. Bolm, *Angew. Chem., Int. Ed. Engl., 30* (1991) 542.

62 S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc., 114* (1992) 2121.

63 S. Anwar, G. Bradley and A. P. Davis, *J. Chem. Soc., Perkin Trans. I*, (1991) 1383.

64 K. Tamao, T. Tohma, N. Inui, O. Nakayama and Y. Ito, *Tetrahedron Lett., 31* (1990) 7333.

65 S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc., 114* (1992) 2128.

66 *Jpn. Patent 91 294 282; Chem. Abstr., 116* (1992) 174432w.

67 *Eur. Patent 460 589* (1991).

68 *Ger. (East) Patent 294 027* (1990).

69 *Ger. (East) Patent 294 026* (1990).

70 M. Itoh, K. Iwata, R. Takeuchi and M. Kobayashi, *J. Organomet. Chem., 420* (1991) C5.

71 *Jpn. Patent 91 181 488; Chem. Abstr., 116* (1992) 59629d.

72 M. Ballestri, C. Chatgilialoglu, K. B. Clark, D. Griller, B. Giese and B. Kopping, *J. Org. Chem., 56* (1991) 678.

73 C. Chatgilialoglu, M. Guerra, A. Guerrini, G. Seconi, K. B. Clark, D. Griller, J. Kanabus-Kaminska and J. A. Martinho-Simoes, *J. Org. Chem., 57* (1992) 2427.

74 C. Chatgilialoglu, *Acc. Chem. Res., 25* (1992) 188.

75 *Jpn. Patent 90 290 886; Chem. Abstr., 114* (1991) 185744j.

76 H. Brunner and F. Prester, *J. Organomet. Chem., 411* (1991) C1.

77 M. G. Voronkov, S. V. Kirpichenko, V. V. Keiko and A. I. Al'banov, *J. Organomet. Chem., 427* (1992) 289; M. G. Voronkov, S. V. Kirpichenko, A. T. Abrosimova, V. V. Keiko and A. I. Al'banov, *Zh. Obshch. Khim., 61* (2033) 1991.

78 *Eur. Patent 448 334* (1991); *Jpn. Patent 91 258 788; Chem. Abstr., 116* (1992) 194583h.

79 N. R. Curtis and A. B. Holmes, *Tetrahedron Lett., 33* (1992) 675, 671.

80 *Eur. Patent 396 130* (1990).

81 *Jpn. Patent 90 286 688; Chem. Abstr., 114* (1991) 185742g.

82 M. Hong, Ch. Chen, Q. Fang and X. Wei, *Xiamen Daxue Xuebao, Ziran Kexueban, 28* (1989) 618; *Chem. Abstr., 114* (1991) 122487g.

83 *Eur. Patent 382 258* (1990).

84 *Jpn. Patent 91 190 888; Chem. Abstr., 115* (1991) 280281k; *US Patent 5 030 746* (1990); *Jpn. Patent 90 300 192; Chem. Abstr., 114* (1991) 229142t.

85 X. Lu, J. Mei, Y. Zhang and Y. Chen, *Wuhan Daxue Xuebao, Ziran Kexueban*, (1990) 61; *Chem. Abstr., 115* (1991) 233534k.

86 *Jpn. Patent 91 151 393; Chem. Abstr., 115* (1991) 256375y.

87 *Eur. Patent 472 438* (1991).

88 Yu. T. Efimov, T. A. Tandura, V. M. Kopylov, S. I. Anbrosenko and M. I. Shkol'nik, *Zh. Obshch. Khim., 61* (1991) 2244; A. K. Saxena, C. S. Bisaria and L. M. Pande, *Indian J. Technol., 29* (1991) 310.

89 *Jpn. Patent 91 106 888; Chem. Abstr., 115* (1991) 183576c; *Jpn. Patent 91 106 889; Chem. Abstr., 115* (1991) 183577d; *Ger. Patent 4 024 720.*

90 *Eur. Patent 465 177.*

91 G. Sonnek, Ch. Rabe, G. Schmaucks, R. Kaden and I. Lehms, *J. Organomet. Chem., 405* (1991) 179.

92 T. Suzuki and P. Y. Lo, *J. Organomet. Chem., 391* (1990) 19; *396* (1990) 299.

93 F. Wada, S. Abe, N. Yonemaru, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn., 64* (1991) 1701.

94 L. N. Lewis, K. G. Sy, G. L. Bryant and P. E. Donahue, *Organometallics, 10* (1991) 3750.

95 *US Patent 5 041 595* (1990).

96 B. Marciniec, Z. Foltynowicz and M. Lewandowski, *Appl. Organomet. Chem.*, in press; *Pol. Patent P-295 177* (1991).

97 V. Gevorgyan, L. Borisova, J. Popelis, E. Lukevics, Z. Foltynowicz, J. Guliński and B. Marciniec, *J. Organomet. Chem., 424* (1992) 15.

98 A. Herunsalee, M. Isobe and T. Goto, *Tetrahedron, 47* (1991) 3727.

99 G. Marki and K.-P. Berr, *Tetrahedron Lett., 33* (1992) 1601.

100 I. Matsuda, J. Sakaibara and H. Nagashima, *Tetrahedron Lett., 32* (1991) 7431.

101 M. N. Bakola-Christianopoulou, *J. Mol. Catal., 65* (1991) 307.

102 Yu. Goldberg, E. Abele, M. Shymanska and E. Lukevics, *J. Organomet. Chem., 410* (1991) 127.

103 S. C. Berk, K. A. Kreutzer and S. L. Buchwald, *J. Am. Chem. Soc., 113* (1991) 5093.

104 M. Akita, O. Mitani, M. Sayama and Y. Moro-oka, *Organometallics, 10* (1991) 1394.

105 *Jpn. Patent 91 258 791; Chem. Abstr., 116* (1992) 174427y.

106 *Jpn. Patent 91 258 793; Chem. Abstr., 116* (1992) 174428z.

107 K. Yamamoto and T. Tabai, *J. Organomet. Chem.*, *428* (1992) C1.
108 A. P. Davis and S. C. Hegarty, *J. Am. Chem. Soc.*, *114* (1992) 2745.
109 H. Okamoto and S. Kato, *Bull. Chem. Soc. Jpn.*, *64* (1991) 3466.
110 N. P. Reddy, Y. Uchimaru, H.-J. Lautenschlager and M. Tanaka, *Chem. Lett.*, (1992) 45; *Jpn. Patent 91 258 789; Chem. Abstr.*, *116* (1992) 174426x.
111 D. H. R. Barton, P. Blundell, J. Dorchak, D. O. Jang and J. Cs. Jaszberenyi, *Tetrahedron*, *47* (1991) 8969.