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REVIEW

Silicometallics and catalysis[†‡]

Bogdan Marciniec
Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Several processes of silicon substrates (such as hydrosilylation, dehydrogenative silylation and double silylation of alkenes and alkynes, silylative coupling versus cross-metathesis of vinylsilanes with alkenes, polycondensation of divinyl-substituted silicon compounds versus ADMET polymerization, dehydrocoupling of hydrosilanes and silylformylation of acetylene) by transition-metal complexes are briefly overviewed. All the reactions occur via a mechanism involving intermediates containing metal–silicon (i.e. silicometallics versus organometallics) and metal–hydrogen bonds, only occasionally accompanied (sided) by intermediates including metal–carbon bonds. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: metal–silicon bond; hydrosilylation; bis-silylation; silylformylation; dehydrocoupling; silylative coupling

INTRODUCTION

Organometallic compounds (organometallics) are defined as materials in which there is a bond (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecules and the atoms from the Main Group, transition, lanthanide or actinide metals. The making and breaking of metal–carbon bonds play a fundamental role in homogeneous and heterogeneous catalysis.[1] Numerous reactions of organic compounds catalyzed by transition-metal complexes have been developed during the last 50 years (e.g. olefin oxidation as in the Wacker Process, hydroformylation, carbonylation, hydrogenation, metathesis, Ziegler–Natta polymerization and oligomerization of olefins) in which reactivity of M–C bonds of the active intermediate is a crucial step of the complicated process. Therefore, it is not unusual that the keynote and plenary lectures of the recent most representative international conferences (the 11th International Symposium on Homogeneous Catalysis, St Andrews, UK, 1998; the 18th International Conference on Organometallic Chemistry, Munich, Germany, 1998; the Presymposium of the 10th Symposium on Organometallic Chemistry Directed Towards Organic Synthesis—Organometallics and Catalysis, Rennes, France, 1999) were dominated by topics focused on the relations between organometallics and catalysis. At present, intensive studies, in which representatives of both fields are cooperating, are aimed at finding catalytic reactions attractive for synthetic organic and organometallic chemistry.

Organic derivatives of silicon, as well as other metalloids (boron, germanium, arsenic), are also included in the class of organometallic compounds, and the Si–C bond is the basis of organosilicon monomers and polymers of great industrial application.

On the other hand, if such metalloids (*p*-block) replace the carbon atom in the metal–carbon bonding, then they really form metal–nonmetal bonding. Such compounds are the subject of the new field of study recently called 'inorganometallic chemistry'.[2] In particular, compounds containing *d*-block–*p*-block element bonds, which although closely related to organometallics yet are distinctly different from them, can play a significant role as catalysts in transformations of *p*-block compounds. Since silicon is the most common and useful element among *p*-block elements, the reactivity of metal–silicon and particularly transition metal–

* Correspondence to: Bogdan Marciniec, Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.
E-mail: marcinb@main.amu.edu.pl
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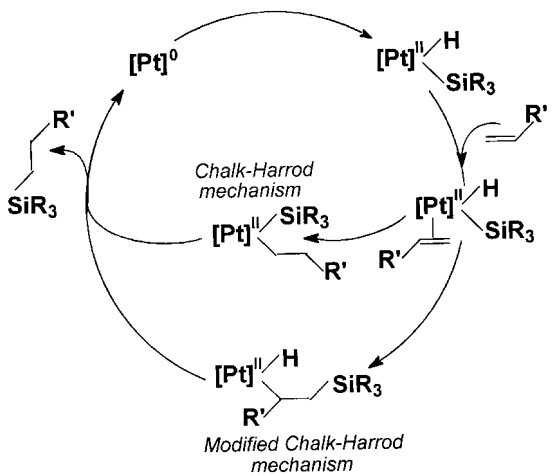
silicon bonds is a key point in most conversions of silicon compounds catalyzed by transition-metal complexes. Numerous developments have been the subject of comprehensive reviews in synthetic, stoichiometric and catalytic chemistry of metal–silicon bonding in recent years.[3–6]

Therefore, although in catalytic conversions of (organo)silicon compounds only hydrosilylation reactions are well known as processes of industrial importance,[7–10] since 1985 other reactions of silicon compounds catalyzed by transition-metal complexes have been revealed and spectacularly developed. Most of them occur via a mechanism involving metal–silicon and metal–hydrogen bonds, only occasionally accompanied (or sided) by metal–carbon bonds.

The aim of this overview is to present the main types of conversions in which intermediates with a metal–silicon bond (i.e. silicometallics versus organometallics) play a decisive role in mechanistic implications of the new and well-known catalytic reactions of silicon-containing substrates.

HYDROSILYLATION AND DEHYDROGENATIVE SILYLATION OF ALKENES AND ALKYNES

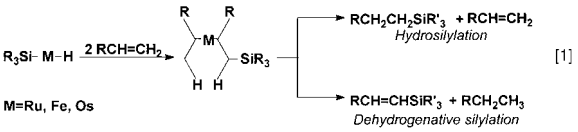
Many reviews and publications explain the mechanism of catalysis of hydrosilylation by transition-metal complexes proposed in 1965 by Chalk and Harrod. This mechanism, originally derived from studies of chloroplatinic acid as a precursor (platinum catalyst) provided a qualitative rational generalization for other transition-metal complexes.[11] The mechanistic scheme presents conventional oxidative addition–reductive elimination steps to explain the hydrosilylation. The oxidative addition of trisubstituted silanes, $HSiR_3$ to a metal–alkene complex configuration (usually with d^8 and d^{10}) is followed by migratory insertion of alkene into an M–H bond and the resulting metal(silyl)(alkyl) complex undergoes reductive elimination by Si–C bond formation and regeneration of the metal–alkene complex in excess of alkene. Since a facile reductive elimination of silylalkane from alkyl–[M]–SiR_3 species was not well established in stoichiometric reaction, a modified Chalk–Harrod mechanism was proposed[12] to explain the formation of an unsaturated (vinylsilane) organosilicon product, which involves alkene insertion into the metal–silyl bond followed by C–H reductive elimination (Scheme 1).[13]



Scheme 1 Chalk–Harrod mechanism for hydrosilylation of alkenes.

Recent detailed theoretical studies of platinum-catalyzed hydrosilylation of ethylene[13,14] led to a conclusion that this process proceeds through the Chalk–Harrod mechanism. The rate-determining step in this mechanism is the isomerization of the Pt(silyl)(alkyl) complex formed by ethylene insertion into the Pt–H bond, and the activation barrier of this step is 23 kcal mol^{-1} for R = Me and −26 kcal mol^{-1} for R = Cl). In the modified Chalk–Harrod mechanism, however, the rate-determining step is ethylene insertion into the Pt–SiR_3 bond and its barrier is 44 kcal mol^{-1} for R = Me and 60 kcal mol^{-1} for R = Cl.

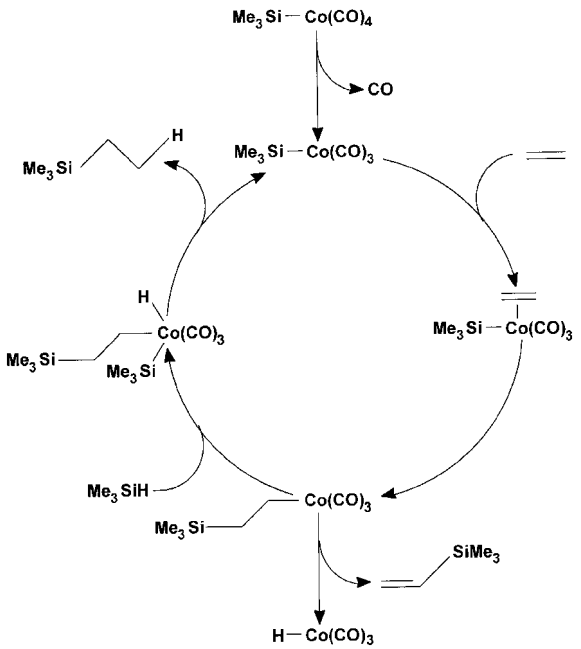
In contrast to the platinum-catalyzed hydrosilylation, the complexes of the iron (iron, ruthenium, osmium) and cobalt (cobalt, rhodium, iridium) triads catalyze dehydrogenative silylation (formation of vinylsilanes) competitively with the hydrosilylation (see Eqn [1]).[12,15,16]



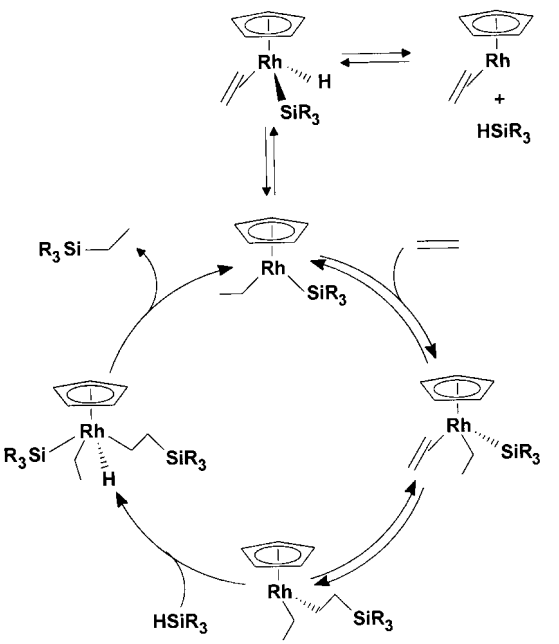
[1]

The reaction occurs via potential formation of a complex containing σ-alkyl and σ-silylalkyl ligands. The β-H transfer from the two ligands to the metal proceeding concurrently is a decisive step for two alternative reactions, i.e. hydrosilylation and/or dehydrogenative silylation of olefins; the catalytic and synthetic aspects of this reaction have recently been reviewed.[17]

The migratory insertion (silyl migration) of



Scheme 2 Seitz–Wrighton mechanism for hydrosilylation and dehydrogenative silylation of alkenes.



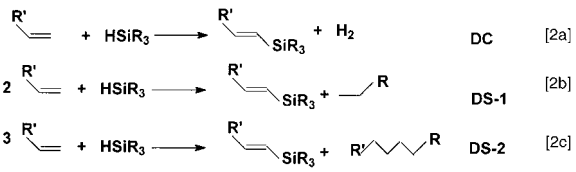
Scheme 3 Duckett–Perutz 'two-silicon cycle' mechanism for hydrosilylation of alkenes.

alkene into the M–Si bond is a key step for the dehydrogenative silylation catalyzed by late transition-metal complexes. The first convincing results for mechanistic pathways involving this step were presented by Seitz and Wrighton (Scheme 2) and obtained in a photochemical study of the reaction with the $Me_3SiCo(CO)_4$ complex.[15] The insertion of ethylene into the Co–$SiMe_3$ bond was confirmed spectroscopically.

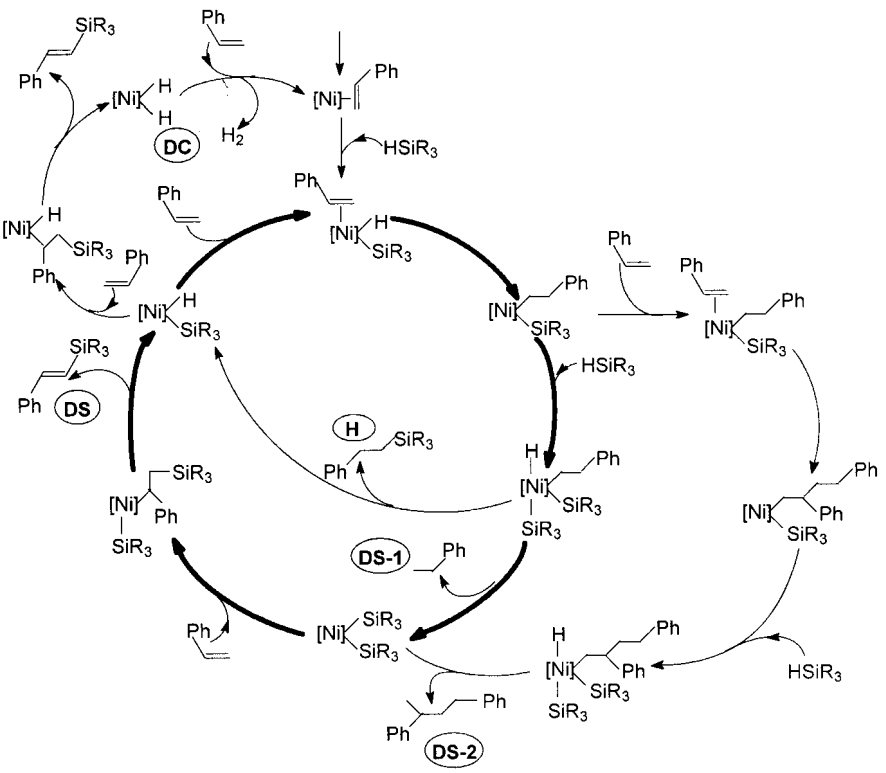
Duckett and Perutz used the same system but with $CpRh(C_2H_4)(SiEt_3)H$ as a precursor, finally proposing an alternative mechanism based on a 'two-silicon cycle' as illustrated in Scheme 3.[18] This mechanism includes the initial formation of $CpRh(C_2H_5)SiEt_3$ (Cp = cyclopentadienyl), followed by ethylene insertion (silyl migration step), but the integrity of the original ethene ligand is proved to be retained. The oxidative addition of Et_3SiH would generate a rhodium(V) intermediate containing two silyl groups. Such rhodium(V) intermediates (e.g. η^5-$C_5Me_5Rh(H)_2(SiEt_3)_2$) were earlier proposed by the Maitlis group.[19,20] Numerous examples of olefin insertion into M–Si bonds, which have been demonstrated for iron,[16] cobalt,[15] ruthenium[21] and rhodium[18,22] complexes, support the evidence for the generality of this reaction.

Dehydrogenative silylation has recently become a useful method for synthesis of unsaturated organosilicon compounds although its drawback is the formation of a mixture of both types of products.[23] However, some reactions involving exclusive or highly selective formation of vinylsilanes have also been reported, particularly in the presence of ruthenium, iron and rhodium complexes [recent examples are $RuH_2(H_2)_2(PCy_3)_2$[24] (Cy = cyclohexyl) and $Rh(cod)_2BF_4$[26] (cod = cyclo-octadiene). The mechanism of these reactions occurring in the presence of the latter cationic complex also involves the insertion of olefin into Rh–H and Rh–Si bonds as the crucial pathway of catalysis.

In the presence of nickel complexes, the dehydrogenative silylation of vinylsilanes,[27,28] styrene[28,29] and other olefins[29] proceeds via three steps yielding the unsaturated product and the respective hydrogenated products of direct dehydrogenation (DC) and olefin hydrogenation (DS-1), as well as hydrogenated dimerization (DS-2) according to Eqns [2a]–[2c].[28]



The nickel equivalent of the Karstedt catalyst

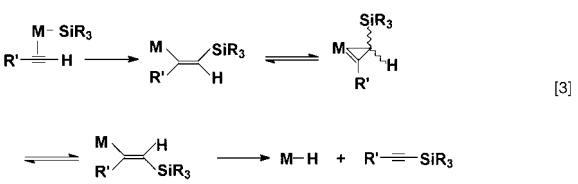


Scheme 4 Mechanism for dehydrogenative silylation of alkenes in the presence of the nickel equivalent of the Karstedt catalyst.

[{Ni(η-CH_2=CHSiMe_2)$_2$O}$_2${(μ)-(η-CH_2=CHSiMe_2)$_2$O}] (1) appeared to be a very efficient catalyst for the dehydrogenative silylation of vinyl derivatives. Synthesis of bis(triethoxy(silyl) divinyltetramethyldisiloxane) nickel complex (3) and particularly the first documented insertion of olefin (styrene) into the Ni–Si bond of this complex as well as all the catalytic data allowed us to propose a scheme of catalysis of this reaction.[28] This scheme shows that all the reactions occur as a consequence of the insertion of vinylsilane into Ni–Si, Ni–H and Ni–C bonds (Scheme 4).

Recently, interesting variations and extensions of dehydrogenative silylation have been reported, e.g. rhodium-catalyzed reaction of trisubstituted silanes with divinyldiorganosilanes,[30] platinum complex-catalyzed dehydrogenative double silylation of dienes with bis(hydrosilane) compounds[31] and the reaction of 1-alkenes with disilanes.[32]

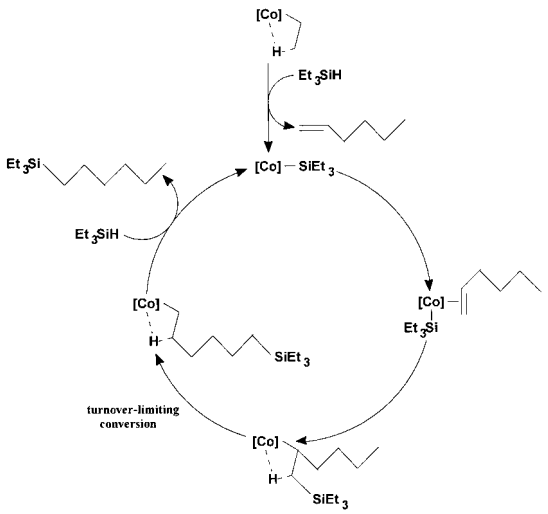
Dehydrogenative silylation of alkynes also may become a predominant route under optimum conditions.[7–10,23] According to the Crabtree concept, in the presence of (for example) the cationic iridium complex [IrH(H_2O)(bq)L_2]SbF_6 (L= PPh_3, bq = [7,8]benzoquinolinato), the above process occurs via the migratory insertion of the C≡C bond into the M–Si bond followed by isomerization of the vinylic ligand according to Eqn [3].[33]



[3]

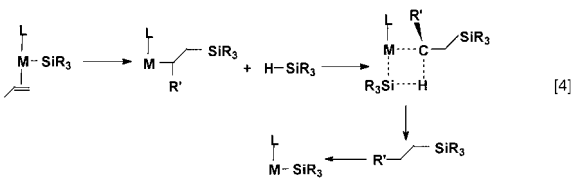
Whereas the hydrosilylation and dehydrogenative silylation catalyzed by late transition metals is explained by insertion of the alkene (alkyne) into M–Si and M–H bonds the olefin hydrosilylation catalyzed by early transition metals occurs via a σ-bond metathesis reaction, i.e. through a concerted four-center transition state.[34]

In zirconium-catalyzed hydrosilylation, an alkyl-



Scheme 5 Brookhard and Grant mechanism for silyl migration mechanism of the hydrosilylation catalyzed by cobalt(III) cationic complex.

silane may be formed via the preliminary insertion of the alkene into the M–Si bond followed by σ-bond metathesis with hydrosilanes, also regenerating the M–Si complex (Eqn [4]).

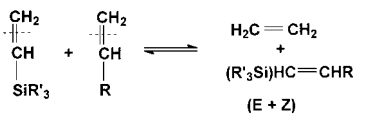


[4]

Direct evidence for the silyl migration mechanism operative in a catalytic hydrosilylation pathway was presented by Brookhart and Grant[35] using the electrophilic cobalt(III) cationic complex. The pathway shown in Scheme 5 involves insertion of hexene into the Co–Si bond $\{[Cp^*Co[P(OMe)_3]CH_2CH_2\text{-}\mu\text{-}H]^+[BAr_4]^-$ where $Ar = 3,5\text{-}(CF_3)_2C_6H_3\}$; Cp^* = pentamethyl cyclopentadienyl. A comprehensive mechanistic study (deuterium labeling and spectroscopic experiments as well as kinetics) has supplied a proof for formation of a secondary alkyl–cobalt complex with agostic (μ-H) bonding (2) and its unexpected isomerization to the primary alkyl(silyl)cobalt complex with (μ-H) bonding (3) (see Scheme 5). The latter is a turnover-limiting step of the whole process. The final step yielding the Si–C compound can occur either via oxidative addition of silane at a cationic cobalt(III) center to yield a cationic cobalt(V) intermediate (as in the case of Duckett and Perutz[18] and Maitlis[19,20] mechanisms) or alternatively via the σ-bond metathesis process mentioned above.

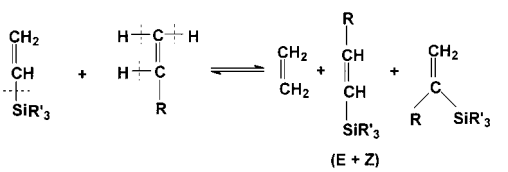
SILYLATIVE COUPLING VERSUS CROSS-METATHESIS OF VINYLSILANES WITH ALKENES

Although many metallacarbenes e.g. of molybdenum, tungsten and rutherium catalyze the metathetical conversion of silicon-containing olefins, neither effective self-metathesis not acyclic diene metathesis (ADMET) polymerization of vinyl-substituted organosilicon olefins and dienes (e.g. vinylsilanes, divinyldiorganosilanes) occurring even in the presence of well-defined molybdenum, tungsten or ruthenium complexes has been reported yet.[36,37] Inactivity of metallacarbene initiators in productive homometathesis of vinylsilanes is accounted for by steric effects and a relative stability of the silyl-substituted carbenes bonded to the metal.[38] However, the successful cross-metathesis of vinyl-substituted silsesquioxanes with alkenes,[39] and above all our recent experiments on the efficient cross-metathesis of vinyltrialkoxysilanes and vinyltrisiloxysilanes with styrene[40]—all occurring in the presence of ruthenium carbenes—may be the proper route for finding circumstances for generalization of the reaction which proceeds according to Eqn [5].



[5]

On the other hand, recent reports on disproportionation of vinyl-substituted silicon compounds and their co-disproportionation (*trans*-silylation, silyl group transfer) with olefins, catalyzed by ruthenium,[41–43] rhodium[44] and cobalt[45] complexes containing (or generating) M–H and M–Si bonds, have shown that new reactions occur through the cleavage of the =C–Si bond of vinylsilane and the =C–H bond of the olefin (also of vinylsilane in the self-disproportionation) according to Eqn [6].



[6]

The latter reaction is conceptually related to

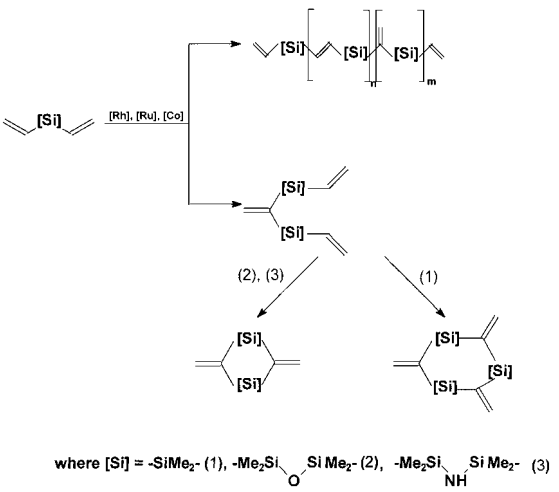
dehydrogenative silylation since the basic reaction involves the silylation of a substrate such as styrene by vinylsilane instead the hydrosilane.

A mechanistic scheme of this new type of silylolefin conversion involves the migratory insertion of styrene (or vinylsilane) into an M–Si bond (where M = Ru,[41–43] Rh,[44] Co[45]) or vinylsilane into an M–H bond, followed by β-H (and β-Si) elimination to give E–phenylsilylethene (and ethylene) (see Scheme 6 for M = Ru).

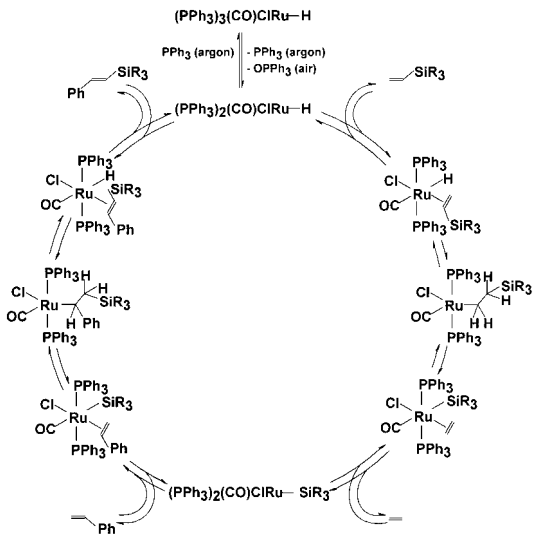
This mechanism of catalysis was proved by insertion of ethylene,[41] vinylsilane[42,45] or styrene[43] into M–Si (where M = Ru, Rh, Co) bonds by the stoichiometric reactions as well as, above all, by a new diagnostic tool in this type of the reaction, i.e. mass-spectrometric (MS) study of the product of the deuterated styrene with vinylsilane,[43,44] or deuterated vinylsilane with vinyl alkyl ethers.[46]

A recent contribution to this field is a discovery of new catalytic reactions of vinylsiloxanes, namely their silylative homocoupling and their heterocoupling with styrene[47] in the presence of ruthenium,[47] rhodium[48] and cobalt.[45]

Moreover, similarly to the case for monovinyl-substituted silanes and siloxanes, divinyl-substituted silicon compounds undergo efficient cross-coupling polycondensation to yield linear oligomers (mostly, if ruthenium complexes are used as catalysts)[49–51] or cyclic dimers[52,53] and trimers[54] particularly if a rhodium catalyst is applied) (Scheme 7). Under the optimum conditions the reaction gives silylene-vinylene,[49] siloxylene-vinylene[50] and silazanylene-vinylene[51] oligomers (M_w/M_n ~1500 – 2400). M_w/M_n = 1.16–1.21) identified by the ^{1}H NMR DEPT method to determine a chain with *trans*-1,2 and 1,1 isomers. The presence of the latter and inactivity of metal carbenes in the above reaction in the homometathesis (ADMET) polymerization of divinyl derivatives of silanes and siloxanes confirm a non-metallacarbene mechanism for this reaction and it is further evidence for the mechanism given above (Eqn [6]). This new, efficient route for preparation of organosilicon linear and cyclic oligomers as an extension of the silylative coupling (*trans*-silylation) of alkenes to dienes has recently been overviewed separatedly.[55]



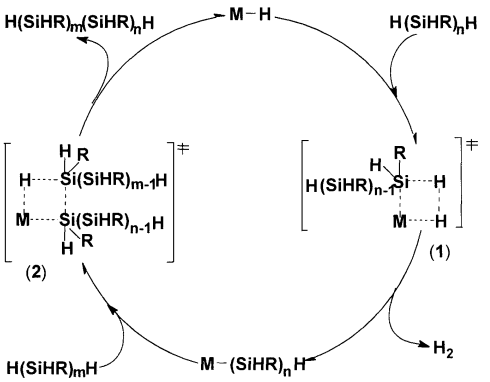
Scheme 7 Polycondensation versus intermolecular cyclization of divinyl-substituted silicon compounds catalyzed by ruthenium, rhodium and cobalt complexes.



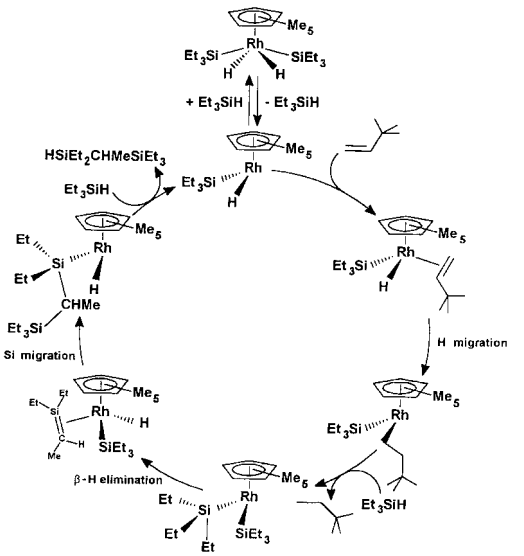
Scheme 6 Mechanism for silylative coupling of vinylsilanes with styrene catalyzed by Ru–H and/or Ru–Si complexes.

DEHYDROGENATIVE COUPLING OF SILANES

Dehydrocoupling of primary silanes to produce an Si–Si bond began in practice with the discovery made by Harrod and co-workers that Cp_2MMe_2 (where M = Ti, Zr) initiated (poly)condensation of $PhSiH_3$ to produce short polymers.[56,57] Tilley's[58,59] and Corey's[60,61] groups developed and utilized other active catalytic systems, mainly the Group 4

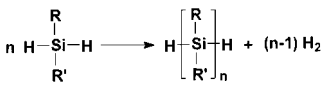


Scheme 8 The σ-bond metathesis mechanism for dehydrocoupling of primary silanes.



Scheme 9 Berry mechanism for dehydrocoupling of Et_3SiH catalyzed by ruthenium and rhodium complexes.

metallocenes (but recently lanthanide metallocenes also, as reported by Marks group[62]) for mechanistic and synthetic studies (e.g. $Cp_2TiMe_2Cp)ZrH_2$.[58–61]. The dehydrocoupling occurs according to Eqn [7]. The reaction constitutes the only alternative to Wurtz coupling for the formation of Si–Si bonds and can therefore be used successfully to produce pre-ceramic materials.[63] The condensation of secondary silanes requires more rigorous conditions and no catalyst yet has been reported to couple tertiary silanes efficiently.[61]



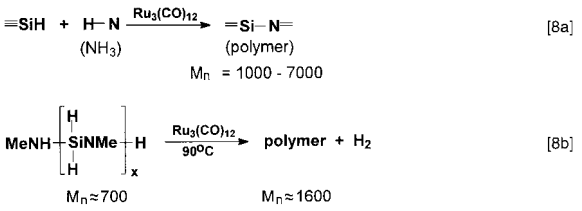
[7]

R = H, Me, Bu, Ph; R' = Me, Ph

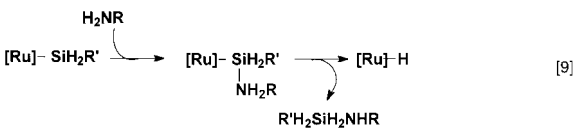
Two mechanisms have been suggested for the dehydrocoupling of silanes. The first, originally presented by Harrod, is based on the oxidative addition and reductive elimination sequences with the intermediacy of transition-metal silylene complexes, but it requires that secondary silanes terminate at the disilane stage (which is not the case). The currently accepted mechanism for the dehydropolymerization of hydrosilanes to polysilanes, as catalyzed by early transition-metal metallocene derivatives, was formulated by Tilley on the basis of the chemistry of CpCp*M[Si$(SiMe_3)_3$]Cl (M = Zr, Hf).[64] This mechanism (Scheme 8) is based on two σ-bond metathesis reactions that pass through four-center transition states, i.e. (1) the dehydrometallation of silane with a metal hydride to give hydrogen and an M–Si intermediate and (2) coupling of the latter metal–silyl derivative with hydrosilane to produce (oligo)silane and regenerate the active metal hydride catalyst.

Quite unusual functionalization of C–H bonds catalyzed by ruthenium and rhodium complexes was found by the Berry group.[65] The (η^6-arene)ruthenium complexes and isoelectronic (η^5-C_5Me_5)Rh analogues catalyze the dehydrocoupling of Et_3SiH to a carbosilane dimer in the presence of hydrogen acceptors such as alkenes (Scheme 9). Only traces of the products of the hydrosilylation and dehydrogenative silylation of alkene analogous to those observed by Duckett[18] and Maitlis[19,20] for their catalysts were found. Therefore, many steps in the mechanism proposed by Berry are identical to those presented in Scheme 3 but the crucial step of this new example of Si–C bond formation is a β-hydrogen elimination from a silyl ligand followed by an insertion of η^2-silene coordinated to the metal into the M–Si bond (silyl migration to silene carbon). Addition of Et_3SiH to the metal and elimination of the bulkier silane complete the catalytic cycle.

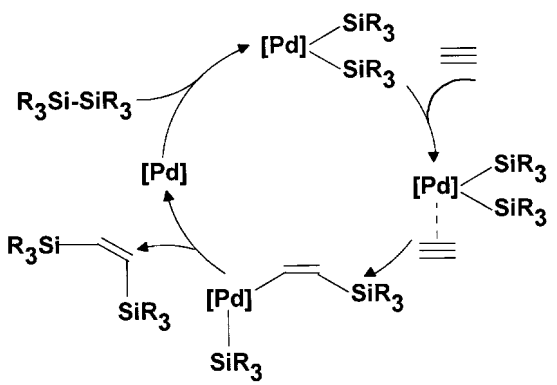
Some attempts were made to prepare polysilazanes via dehydrogenative coupling of diorganosilanes with ammonia[66] and dehydrogenative polymerization of oligosilazanes,[67] using $Ru_3(CO)_{12}$ as a catalyst (Eqns [8a], [8b]).



These two reactions produce materials that are precursors for the pyrolytic generation of silicon nitride. By comparison with the Tilley mechanism for dehydrogenative homocoupling of hydrosilanes (see Scheme 8), in the case of its heterocoupling with NH_3 or RNH_2 the first step is oxidative addition of the hydrosilane with evolution of H_2 and formation of an M–Si intermediate. But the Si–N bond formation is due to nucleophilic attack of the amine at the silicon (M–Si) intermediate, eliminating silazane and regenerating the M–H intermediate according to Eqn [9].



The latter intermediate undergoes intermolecular polymerization according to the mechanism of dehydroheterocoupling summarized in Eqn [8b].



Scheme 10 Mechanism for bis-silylation of alkynes catalyzed by palladium complexes.

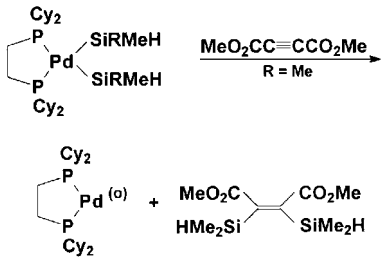
BIS-SILYLATION OF UNSATURATED ORGANIC COMPOUNDS

The catalytic addition of the Si–Si bond to unsaturated organic compounds such as alkynes, alkenes, dienes, α,β-unsaturated ketones and isocyanides has been developed since 1985 to provide new methodologies for the effective synthesis of organosilicon compounds.[68–71] Since the bond energy of the Si–Si bond (74–80 kcal mol^{-1}) is similar to that of the Si–H bond (88–92 kcal mol^{-1}), it is reasonable to assume that the oxidative addition of an Si–Si bond would also be a facile process and would offer the potential for formation of bis(silyl), silyl(silylene), silylene and disilane complexes often at equilibrium with each other.[68] The general trends of catalysis in this area have been reviewed recently[69–73] to emphasize a wide range of potential catalytic processes which can be arranged. Some of them are mentioned below.

Interest in this area began with the preliminary reports by Kumada on the addition of Si–Si bonds to acetylenes[74] but the finding by the Tanaka group[75] that $Pd(PPh_3)_4$ is an effective catalyst of the addition of substituted disilane to ethylene resulted in the common application of many palladium and platinum complexes in bis-silylation of other olefins. The reaction proceeds readily only when the Si–Si bonds are activated by electronegative groups or ring strain. To overcome this drawback, several new catalytic systems have been devised for the reactions of acetylenes, dienes and dicarbonyl compounds with non-activated Si–Si bonds.[69]

The catalysis of bis-silylation of alkynes and alkenes proceeds similarly i.e. via oxidative addition of the disilane to a palladium complex followed by insertion of alkyne (or alkene) into one of the resulting Pd–Si bonds, and finally reductive elimination of 1,2-bis(silyl)ethylene (or the respective bis-silylethane) from the silyl(β-silylethylene)-[or silyl(β-silylethyl]-palladium intermediate (see Scheme 10 for the bis-silylation of alkynes).

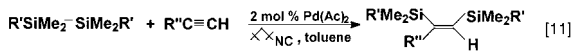
Synthesis and isolation of stable palladium–bis(silyl) complexes by Fink's group and effective stoichiometric insertion of dimethylacetylene dicarboxylate into one of the Pd–Si bonds giving the expected bis-silylation product (Eqn [10]) appeared to be spectacular evidence for migratory insertion of an unsaturated compound into a Pd–Si bond during bis-silylation.[76]



[10]

Examples of reactions catalyzed predominantly by palladium and platinum (some by nickel) complexes illustrate the reactivity of the Si–Si bond in intermolecular (Eqns [11]–[13] and intramolecular[79] (Eqns [14],[15]) bis-silylation reactions.

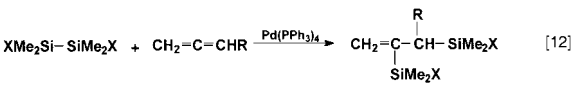
Alkynes[77]



[11]

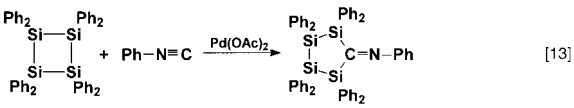
R' = Me, Ph; R'' = H, n-hex, Ph

Allenes[78]



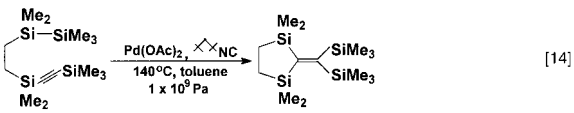
[12]

Isonitriles[79]



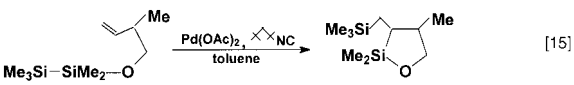
[13]

Alkynes[80]



[14]

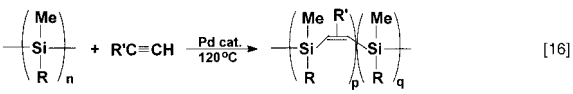
Alkenes[81]



[15]

Much attention has been directed towards modification or synthesis of silicon-containing polymers via insertion of an unsaturated compound into Si–Si bonds of the polymer backbone, e.g.:

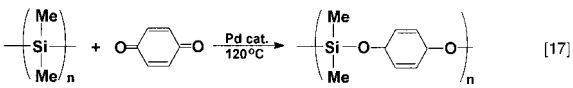
(a) insertion of alkynes to polymers to give a soluble polymer consisting of alternating dimethylsilylene and hexylvinylene units (Eqn [16]);[72]



[16]

R = Me, Pr; R' = hexyl

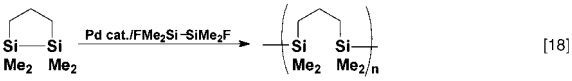
(b) insertion of dicarbonyl compounds (Eqn [17]);[72]



[17]

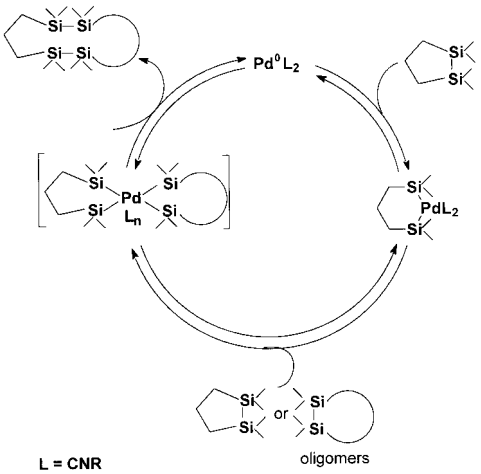
Pd cat. = $PdCl_2(PEt_3)_2$

(c) ring-opening polymerization of cyclic organodisilanes (Eqn [18]);[82]



[18]

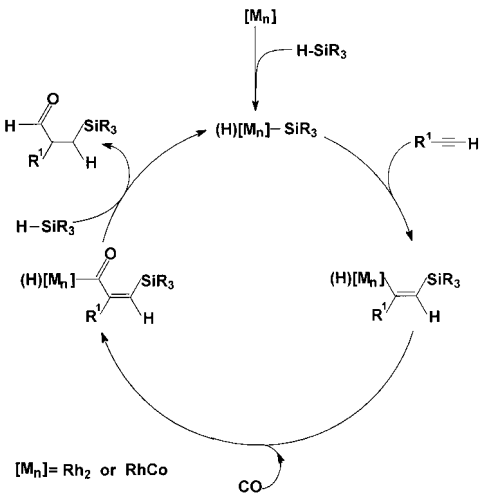
(d) ring-enlargement oligomerization[83] (see Scheme 11).



Scheme 11 Mechanism for ring-enlargement oligomerization of cyclic organodisilanes.

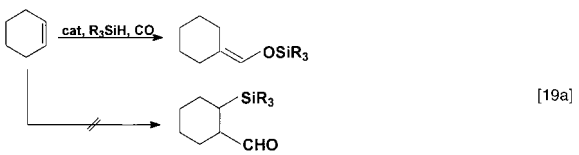
SILYLFORMYLATION OF ALKYNES

Catalytic silylformylation is defined as the addition of silyl and formyl groups across various types of bonds with use of a silane (R_3SiH) and CO. The reaction was discovered by Colleuille[84] and latter

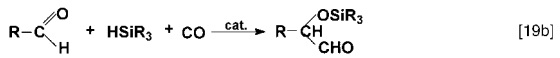


Scheme 12 Mechanism for silylformylation of alkynes catalyzed by Rh_2 and Rh–Co clusters.

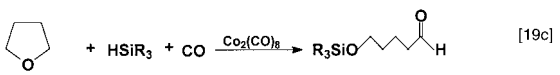
developed by Murai[85,86] as a $Co_2(CO)_8$-catalyzed silylformylation of aldehydes, epoxides and cyclic ethers. In the case of alkenes formation of the silyl enol ether of the formylated alkene is observed (Eqns [19a]–[19c]) instead of silylformylation.



[19a]

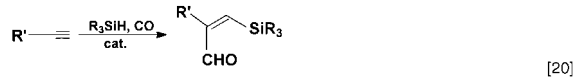


[19b]



[19c]

By contrast to carbonylation of olefin derivatives, a real silylformylation of alkynes was revealed independently by Matsuda's[87,88] and Ojima's[89] groups to yield silylvinyl aldehydes in the presence of rhodium complexes and rhodium–cobalt clusters[90] (Eqn [20]).



[20]

cat. = $Rh_2Co_2(CO)_{12}$; $(t\text{-BuNC})_4RhCo(CO)_4$, $Rh_4(CO)_{12}$;
$Rh_4(CO)_{12}/NEt_3$, $Rh_2(pfb)_4$; $Rh(COD)(\eta^6\text{-}C_6H_5BPh_3)$
pfb = perfluorobenzene

A generalized catalytic cycle for the silylformylation of 1-alkynes catalyzed by rhodium–cobalt clusters is illustrated in Scheme 12. The reactions include the extremely regio-, stereo- and chemoselective insertion of 1-alkyne into the (M)–Si bond of the silyl(hydrido)metal intermediate to form 2-silylvinyl-(M_n) complex, followed by a facile insertion of CO into the vinyl–metal bond to create a 3-silylacryloyl(H)$(M)_2$ complex. A subsequent hydride shift gives the silylformylation product and, in an excess of hydrosilanes, the (HM–silyl)metal species is regenerated.

In the course of a study on alkyne silylformylation, the related reactions of silylative cyclocarbonylation of alkynes, silylcarbocyclization of alkenynes, dyens and other related transformations of C≡C bonds in the presence of $HSiR_3$ and CO were revealed.[91–96] Most of them occur via the insertion of the C≡C bond into the M–Si bond followed by the insertion of CO into the metal–vinyl bond.

CONCLUSIONS

1. Recent achievements in synthesis and characterization of complexes containing metal–silicon bonds and, in particular, their reactivity in stoichiometric reactions, form the basis for their application as intermediates in many reactions of silicon substrates.
2. Mechanisms of all the catalytic reactions overviewed—such as hydrosilylation, dehydrogenative silylation and double silylation of alkenes and alkynes, silylative coupling versus cross-metathesis of vinylsilicon compounds with alkenes and polycondensation of divinylsubstituted silicon compounds versus ADMET polymerization, dehydrocoupling of hydrosilanes and silylformylation of alkynes versus that of alkenes—can be explained by formation of active intermediates containing metal–silicon bonds and metal–hydrogen bonds only occasionally accompanied (or sided) by the intermediates including metal–carbon bonds.
3. The collected experimental material on catalysis by transition-metal complexes exemplified in this overview can be regarded as an initial step in the search for new catalytic conversions of silicon- and carbon-containing substrates or, generally, *p*-block element – carbon containing substrates, occurring via intermediates involving metal–silicon or metal – *p*-block element bonds, respectively.

Acknowledgements My warmest thanks are due to the talented co-workers whose names appear in the references. Our recent research was partly supported by the State Committee for Scientific Research in Poland, Project no. 3T09A07413.

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