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The Splitting of the Silicon-Carbon Bond by Compounds of Platinum and Palladium

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Reactions involving the splitting of an Si-C bond under the influence of platinum and palladium complexes have been examined, and the mechanisms of these reactions discussed. It has been shown possible to use reactions involving the splitting of the Si-C bond in organic synthesis.
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I. INTRODUCTION

The extensive application of organosilicon compounds in various branches of industry has stimulated the search for new methods of synthesis. The considerable progress in this direction in the last 20–30 years has been related to the use of metal-complex catalysts, in particular compounds of platinum and its analogues, which are the most active catalysts for a wide range of reactions in the synthesis of organosilicon compounds. Among these reactions, a process of the greatest importance is hydrosilylation, which is a general method for the synthesis of organosilicon compounds of different classes. Heterogeneous systems containing platinum and palladium were first proposed as hydrosilylation catalysts in 1953.[1] The use of these catalysts made it possible to carry out the reaction between hydrosilanes and unsaturated compounds with functional groups; this had not been possible before, since the hydrosilylation methods used required high temperatures or the presence of radical initiators. Somewhat later, the use of hydrogen chloroplatinate as a highly effective hydrosilylation catalyst was proposed[2]. In 25 years, the range of catalysts has extended considerably, but even now, H_2PtCl_6 is most frequently used for the hydrosilylation of alkenes and alkynes. Alkene complexes of Pt^{II}, phosphine complexes of Pt^0 and Pd^0, complexes of platinum with silyl ligands and with polymeric ligands, and many others are also widely used[3]. Hydrosilylation can now be applied to practically all unsaturated compounds: simple alkenes and alkenes with functional groups, dienes, alkynes, and carbonyl compounds. Recently, this reaction has been used not only for the synthesis of organosilicon monomers and oligomers, but also for the conversion of linear and branched organosilicon polymers into polymers with a reticular structure. It is also acquiring importance for the synthesis of polycarbo-organosiloxanes[3]. In a number of cases, hydrosilylation is used industrially[4].

As well as the addition of hydrosilanes to unsaturated compounds, reactions involving the replacement of hydrogen on a silicon atom by other groups in the presence of platinum metal complexes are also of preparative importance. These reactions are used to obtain silanols, alkoxy- and aryloxysilanes, silyl ethers, siloxamines, silicon halides, etc.[5–11]

The reactions of hydrosilanes (and also metal-silyl derivatives of silicon) with platinum and palladium complexes form the basis of methods for synthesising complexes of these metals with silyl ligands[12–18]. The interest in platinum metal complexes containing group IVb elements is largely due to the promise of their practical application as catalysts.

Like silicon hydrides, compounds with a silicon–halogen bond can undergo oxidative addition to coordinatively unsaturated transition metal complexes, again giving silyl derivatives of the transition metals[17]. An interesting feature is that the splitting of a carbon–halogen bond under the influence of Pt^0 compounds can also take place in the coordination sphere of the metal, converting silyl complexes into silylene compounds[19].

In recent years, in addition to reactions accompanied by the splitting of Si–H bonds, reactions involving the splitting of Si–Si bonds have been used successfully in organosilicon synthesis. The disproportionation of disilanes to polysilanes in the presence of *trans*-$(Et_3P)_2PtCl_2$ was first detected in 1970.[20] A development of this work was the extensive use of the splitting of Si–Si bonds in disilanes, catalysed by triphenylphosphine complexes of platinum and palladium, "double silylation", to introduce two organosilicon groups into alkenes, 1,3-dienes, alkynes[21–25], and allenes[24].

The ability of Pd^0 complexes to catalyse the disproportionation of disilanes[26] has also been used to convert relatively easily accessible disilanes into monosilanes with functional groups by a reaction involving the combination of disilanes with halogen derivatives[27–29].

The transformations of organosilicon compounds under the influence of platinum and palladium complexes, examined above, include the splitting of both polar bonds Si–M and Si–Cl and non-polar bonds Si–H and Si–Si, and are used chiefly for the synthesis of organosilicon compounds. The last known review in this field is that of Curtis and Epstein[30].

In the last ten years, the activation and splitting of the even more inert Si–C bonds have been increasingly studied. Studies in this direction are opening up new possibilities for the use of organosilicon compounds in organic synthesis and as components of catalytic systems.

The urgency of this task is determined by the following features. Organic derivatives of silicon, unlike organometallic compounds, are stable to oxygen and moisture, do not ignite in air, and are generally non-toxic. On the other hand, organosilicon compounds are fairly readily accessible, and many of them are produced on the industrial scale. Thus the use of organosilicon compounds of the organometallic derivative type in organic synthesis or as components of catalytic systems is a promising field.

II. THE SPLITTING OF SILICON–CARBON BONDS IN ORGANOSILICON COMPOUNDS CONTAINING AN ACTIVATED Si–C BOND

1. The Removal of Unsaturated Groups from a Silicon Atom

The bonds formed by silicon with α,β-unsaturated compounds are more reactive than a silicon–alkyl bond. This is due to the increase in the polarity of the silicon–carbon bond when an alkyl group is replaced by an unsaturated group[31], and also to the instability of the products of the addition of electrophilic reagents to multiple bonds as a consequence of β-decomposition[32]. These bonds can be split by protonic and aprotic acids, halogens, and nucleophiles[32–35]. An important feature, however, is that vinyl-, allyl-, and alkynylsilanes readily undergo reactions which are not accompanied by the rupture of silicon–carbon bonds: hydrogenation, the addition of halogens and hydrogen halides, etc. The vinyl group is not removed from the silicon atom when unsaturated silanes are polymerised in the presence of peroxides, protonic and aprotic acids, and also Ziegler–Natta systems[31].

Studies of the transformations of unsaturated silanes, catalysed by Pt and Pd complexes, were begun more than ten years ago[36]. It has now been shown that a wide range of platinum and palladium complexes bring about the removal of unsaturated groups from the silicon atom. π-Complex formation is the first stage in these reactions, and in a number of cases the corresponding π-complexes of the unsaturated silanes have been isolated as stable products. Allyl-[37–38], vinyl-,[38,39] and ethynylsilanes[36,40] are split by platinum and palladium complexes at the bonds between silicon and the unsaturated groups. For example, allylsilanes react very rapidly with palladium chloride and acetate in proton-containing solvents, forming a π-allyl complex of palladium and organic splitting products[37]†:

$$Me_3SiCH_2CH{=}CH_2 + Li_2PdCl_4 \xrightarrow{MeOH,H_2O} \rightarrow (\pi\text{-}C_3H_5PdCl)_2 + Me_3SiOMe + (Me_3Si)_2O + C_3H_6 + HCl$$
$$32\%\ (81\%) \quad 75\%\ (188\%) \quad 25\%\ (63\%) \quad 56\%\ (140\%)$$

The mechanism proposed by the authors includes the initial exchange of groups between the Si and Pd atoms with the formation of a chlorosilane and a σ-allyl and then a π-allyl complex of palladium:

$$R_3SiCH_2CH{=}CH_2 + PdCl_2 \rightarrow R_3SiCl + [CH_2{=}CHCH_2PdCl]$$
$$[CH_2{=}CHCH_2PdCl] \rightarrow (\pi\text{-}C_3H_5PdCl)_2 \rightarrow \text{products}$$
$$R_3SiCl + R'OH \rightarrow R_3SiOR' + HCl$$
$$R_3SiCH_2CH{=}CH_2 + HCl \rightarrow R_3SiCl + CH_3CH{=}CH_2 .$$

The overall reaction is not catalytic with respect to the palladium salt[37], but formally, the catalytic yield of splitting products, calculated relative to Li_2PdCl_4, is due to the splitting, taking place in parallel, of the allylsilanes under the influence of HCl, formed by the alcoholysis or hydrolysis of the chlorosilane.

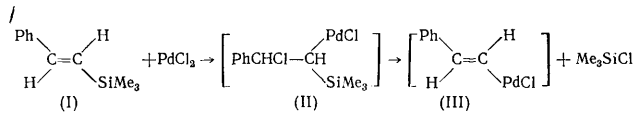
The benzonitrile complex of palladium $(PhCN)_2PdCl_2$ reacts with trimethylallylsilane, forming bis(η^3-allyl)-μ-dichlorodipalladium and trimethylchlorosilane[38]:

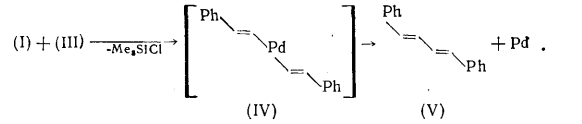
$$2\,Me_3SiCH_2CH{=}CH_2 + 2(PhCN)_2PdCl_2 \xrightarrow[-4PhCN]{} \left(HC\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\!\!>\!\!-Pd-Cl\right)_2 + 2\,Me_3SiCl .$$

The reaction is quantitative in 3 d at 20°.

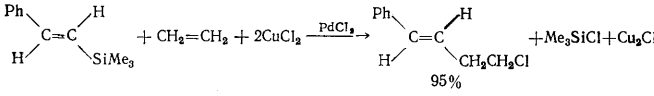
† The yields are given relative to the original silane, and in brackets relative to Li_2PdCl_4.

Interesting transformations take place with vinylsilanes under the influence of palladium chloride. In the presence of palladium chloride at room temperature, oxidative combination of β-trimethylsilylstyrene (I) takes place with the formation of *trans*, *trans*-1,4-diphenyl-1,3-butadiene (V).[39] In the presence of copper(II) chloride, the reaction is catalytic. The authors postulate the intermediate formation of organic derivatives of palladium (II)–(IV):

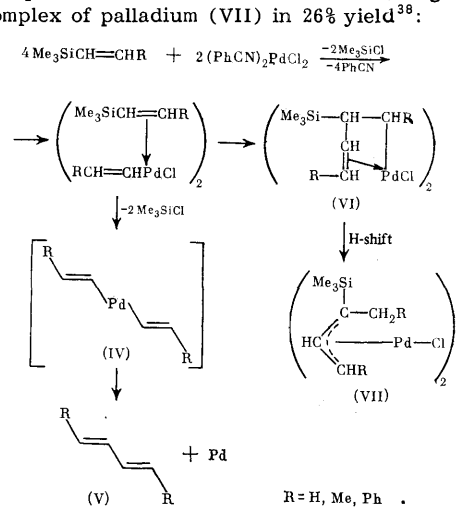




In the presence of an alkene and an excess of copper(II) chloride, chloroethylation products are formed, by analogy with Heck's chloroethylation reactions[41]:



The reaction of vinylsilanes with the benzonitrile complex of palladium in benzene shows an interesting feature: in addition to the products of oxidative combination, it gives a new π-allyl complex of palladium (VII) in 26% yield[38]:



According to the scheme proposed by the authors, the reaction giving divinylpalladium (IV) competes with the insertion of the alkene at the Pd–C bond, which gives an unstable compound (VI). The final π-allyl complex of palladium (VII) is formed as a result of the stabilisation of compound (VI) by a hydrogen shift.

Zeise's salt $K[PtCl_3(C_2H_4)]$ catalyses the removal of vinyl and allyl groups from a silicon atom in boiling absolute ethanol[36]. For the reaction of trimethylvinylsilane with Zeise's salt[42] it was proved that π-bonding is the first stage in the splitting of unsaturated silanes. In acetone, a π-complex containing trimethylvinylsilane has been isolated quantitatively and characterised:

$$Me_3SiCH{=}CH_2 + K[PtCl_3(C_2H_4)] \rightarrow K[PtCl_3(Me_3SiCH{=}CH_2)] + C_2H_4 .$$

In moist acetone this compound undergoes splitting of the Si-vinyl bond to give Zeise's salt and hexamethyldisiloxane:

$$K[PtCl_3(Me_3SiCH{=}CH_2)] + \frac{1}{2}H_2O \rightarrow K[PtCl_3(C_2H_4)] + \frac{1}{2}(Me_3Si)_2O .$$

The formation of π-complexes of vinyl- and ethynylsilanes have also been observed when unsaturated silanes are treated with other Pt^0 and Pt^{II} compounds such as $Pt(C_2H_4)_2(PR_3)$,[43] $(Ph_3P)_2Pt(C_2H_4)$,[40,44] and $PtCl_2(C_2H_4)Py$.[45] A comparison of vinylsilane complexes of Pt^0 and Pt^{II} [44] showed that the Pt^0 complexes are more stable to splitting.

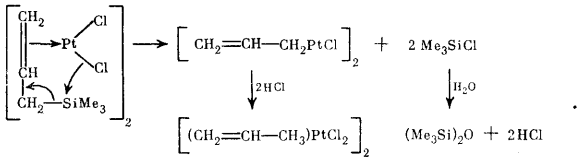
In 1976, French chemists[45] made a detailed study of the reactions of unsaturated silanes with the general formula $Me_3Si(CH_2)_nCH{=}CH_2$ ($n = 0, 1, 2$) with the dimeric platinum complex $Pt_2Cl_4(C_2H_4)_2$. As in most of the reactions described above, the first stage in this case is ligand exchange to give a new Pt^{II} complex containing an unsaturated silane as ligand. The activated silicon–carbon bond is then split. Thus in the reaction of $Me_3SiCH_2CH{=}CH_2$ with $Pt_2Cl_4(C_2H_4)_2$ in the presence of water at 20° (molar ratio silane : platinum complex : water = 2 : 1 : 1), the silane is converted quantitatively into hexamethyldisiloxane and propene:

$$2Me_3SiCH_2CH{=}CH_2 + H_2O \xrightarrow{[Pt]} 2CH_3CH{=}CH_2 + Me_3SiOSiMe_3 .$$

The reaction of allylsilane with $Pt_2Cl_4(C_2H_4)_2$ takes place catalytically at 20° in 10 d (molar ratio silane : complex : water = 20 : 1 : 10). For all the silanes studied, in the stoichiometric reaction with the dimeric platinum complex, a rapid equilibrium is first established, with the formation of the π-complex. At $n = 2$, the crystalline complex of the silane with $PtCl_2$ was isolated:

$$2\,Me_3Si(CH_2)_nCH{=}CH_2 + Pt_2Cl_4(C_2H_4)_2 \rightleftharpoons \left[\begin{array}{l} CH_2 \\ \| \rightarrow PtCl_2 \\ CH \\ | \\ (CH_2)_nSiMe_3 \end{array}\right]_2 + 2C_2H_4 .$$

The splitting of the vinyl- and allylsilanes by the dimeric platinum complex is attributed[45] to the decomposition of an intermediate π-complex in which the platinum atom creates a positive charge in the β-position relative to silicon.

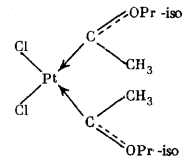


This explains the observed stability of the complex with butenylsilane $Me_3Si(CH_2)_2CH{=}CH_2$, in which a positive centre is created in the γ- and δ-positions relative to the silicon atom. In the proposed scheme, Pt^{II} acts as a π-acid. An interesting feature is that in the splitting of silanes, Pt^{II} has been found to be a stronger acid than protonic acids such as CF_3COOH and HCl. The phosphine complex $Pt_2Cl_4(Ph_3P)_2$ is also active in reactions with $Me_3Si(CH_2)_nCH{=}CH_2$. Its reaction with allylsilane in aqueous $CDCl_3$ at 20° leads to slow splitting of the silane to give hexamethyldisiloxane (90% after 60 h).[45] Pt^{II} complexes can also split Si–C_{sp} bonds[36]. Thus the reaction of $Pt_2Cl_4(C_2H_4)_2$ with $PhC{\equiv}CSiMe_3$ in dry benzene at 20° in an atmosphere of nitrogen gives a deeply coloured complex containing platinum; its infrared spectrum shows a band corresponding to the frequency of the ethyne group $\nu = 2070$–$2110\ cm^{-1}$:

$$2PhC{\equiv}CSiMe_3 + Pt_2Cl_4(C_2H_4)_2 \xrightarrow{60°} 2Me_3SiCl + 2C_2H_4 + 2PhC{\equiv}CPtCl .$$

In boiling alcohol, the ethynyl group is removed from the silicon atom under the influence of catalytic quantities of the complexes $Pt_2Cl_4(C_2H_4)_2$ or $K[PtCl_3(C_2H_4)]$. Under these conditions, allylsilanes are split even more easily[36].

The reactions of ethynylsilanes with platinum complexes are sometimes unusual, and do not reduce to a simple scheme including π-complex formation with the subsequent elimination of unsaturated compounds. An example[46,47] is the interesting transformation of trimethylethynylsilane under the influence of H_2PtCl_6 in isopropyl alcohol at 20° into an alkoxycarbene complex of Pt^{II}, whose structure was established by X-ray diffraction:

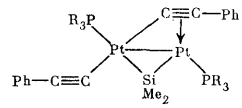


The reaction is accompanied by rupture of the Si–C bond. The resulting complex is a good catalyst for the hydrosilylation of alkynyl compounds.

The reaction of $Me_2Si(C{\equiv}CPh)_2$ with the platinum(0) complex $[Pt(C_2H_4)_2(PR_3)]$ is also extremely unusual[40]. In this case, both phenylethynyl groups are removed from the silicon atom to give a diplatinum complex containing all the fragments of the organosilicon molecule:

$$Me_2Si(C{\equiv}CPh)_2 + 2Pt(C_2H_4)_2(PR_3) \rightarrow [Pt_2(Me_2Si)(C{\equiv}CPh)_2(PR_3)_2] + 4C_2H_4 .$$
$$R = C_6H_{11}$$

X-Ray diffraction showed that the platinum atoms in this complex are not equivalent; one of them (formally Pt^{IV}) is joined by σ-bonds to the dimethylsilyl and two phenylethynyl groups, and the other platinum atom (formally Pt^{II}) is joined by a σ-bond to the dimethylsilyl groups and by a π-bond to one of the phenylethynyl groups:



This reaction is of interest as the first rigorously proved example of the oxidative addition of an Si–C bond to a transition metal atom.

2. The Rupture of Silicon–Carbon Bonds in Strained Cyclic Silanes and Disilanes

Platinum and its derivatives Pt/C, H_2PtCl_6, and $(C_2H_4)_2 . Pt_2Cl_4$ catalyse the splitting on of an Si–C bond in strained organosilicon heterocyclic compounds such as sila- and 1,3-disilacyclobutanes to give telomerisation and polymerisation products[48–50]. Thus silacyclobutanes are converted into polymers by heating with catalytic quantities of Pt/C or H_2PtCl_6 at 50–100° [49]:

$$nR^1R^2Si\begin{array}{l}CH_2\\CH_2\end{array}CHR^3 \xrightarrow{[Pt]} -(-R^1R^2SiCH_2CHR^3CH_2-)_n- .$$

The dimeric ethlene complex $(C_2H_4PtCl_2)_2$ is effective in this reaction even at room temperature[50]. Disilacyclobutanes in the presence of platinum catalysts are polymerised at 100 to 150°:

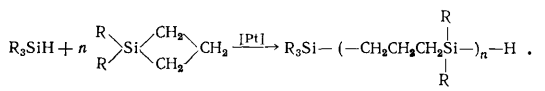
$$nMe_2Si\begin{array}{l}CH_2\\CH_2\end{array}SiMe_2 \xrightarrow[150°]{[Pt]} -(-Me_2SiCH_2-)_n- .$$

In the absence of catalysts, polymerisation does not take place at this temperature.

With 1,1-dimethyl-1-silacyclopentane, polymerisation on platinum does not take place up to 200°, and the silacyclohexanes $CH_2-(CH_2)_4-SiH_2$ and $CH_2(CH_2)_4-SiMeH$ are not split under the influence of platinum and palladium catalysts at

500°.[51] Thus the driving force of the splitting of Si–C bonds in sila- and disilacyclobutanes is the strain in the four-membered ring.

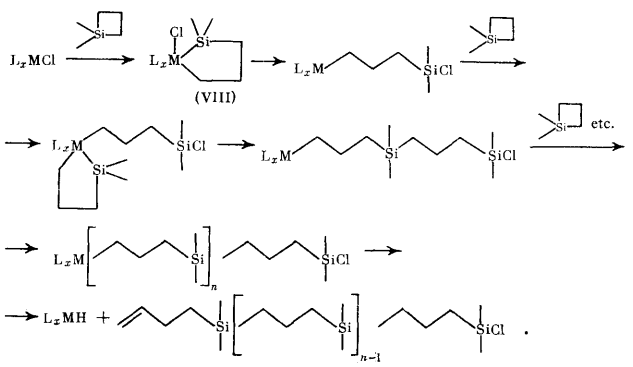
In the presence of platinum catalysts, silacyclobutanes and disilacyclobutanes react with hydrosilanes at 50–100° to give telomers:



$n = 1, 2$

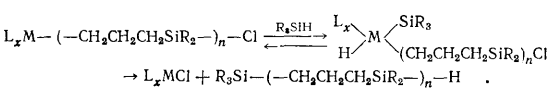
This reaction can be regarded as an example of alkyl-hydrogen ligand exchange at a silicon atom under comparatively mild conditions. Without the catalyst, it takes place at a higher temperature.

The role of the transition metal in the homogeneous catalytic polymerisation of strained organosilicon heterocyclic compounds has been studied[50]. A mechanism including the following successive stages was proposed: the oxidative addition of the silacyclobutane to the transition metal complex to give a metal-containing ring (VIII); splitting of the M–Si bond, accompanied by the migration of halogen from M to Si and opening of the ring; growth of the polymer chain as a result of the insertion of a new molecule of silacyclobutane at the M–C bond; and chain termination by the ejection of a hydrogen atom from the β-position relative to the metal:

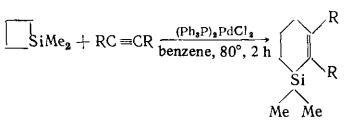


(VIII)

The formation of telomeric products can be explained similarly.



Interesting reactions involving the cyclo-addition of silacyclobutanes to alkynes in the presence of palladium catalysts have also been described[52].



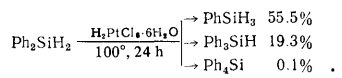
R=COOMe .

Pd^{II} and Pd^{0} complexes are effective in these reactions: $PdCl_2(PhCN)_2$, L_4Pd, L_2Pd(alkene), and metallic Pd. The authors suggest that the driving force of these reactions is again the strain in the silacyclobutane ring, since silacyclopentanes and other non-strained silacyclanes do not react with alkynes.

3. Rupture of Silicon–Carbon Bonds in Hydrosilanes

Hydrosilanes can disproportionate when heated or under the influence of Lewis acids. The ease of the disproportionation of hydrosilanes compared with tetra-alkyl(aryl)-silanes is due to the ease of formation of five- and six-co-ordinate complexes of silicon in the case of the hydrosilanes, since for these the geometric and electronic factors are more favourable than for tetraorganosilanes. In five- and six-co-ordinate complexes of silicon, the rupture of Si–H and Si–C bonds is facilitated. The tendency for these complexes to be formed increases with increase in the number of hydride hydrogen atoms in the molecule and with increase in the acceptor power of the groups joined to silicon.

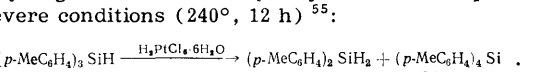
The disproportionation of diphenylsilane in the absence of catalysts is observed at 160°. Lewis acids ($AlCl_3$, $ZnCl_2$) catalyse these transformations under milder conditions[53]. Platinum derivatives also catalyse the disproportionation of hydrosilanes[53]. Thus in the presence of catalytic quantities of H_2PtCl_6 at 100°, diphenylsilane disproportionates to give the following products:



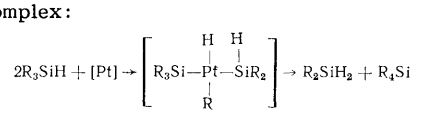
PtO_2 and metallic platinum are also effective in this reaction.

$PhSiH_2Cl$ begins to disproportionate under the influence of H_2PtCl_6 even at room temperature, $PhSiHCl_2$ at 50°, and Ph_2.SiHCl at 200°.[54] K_2PtCl_4 and K_2PtCl_6 also show catalytic activity in these reactions.

The disproportionation of tri-p-tolylsilane in the presence of H_2PtCl_6 to give di- and tetra-p-tolylsilanes takes place under severe conditions (240°, 12 h)[55]:

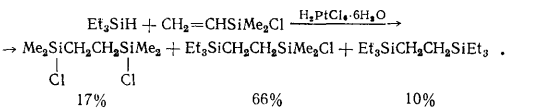


Disproportionation is not observed under these conditions in the absence of H_2PtCl_6. In the authors' opinion, the reaction mechanism includes the rupture of the Si–H and Si–tolyl bonds with retention of these fragments in the sphere of the platinum complex:

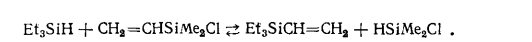


The authors cited[54,55] consider that the hydrosilane not only reduces Pt^{IV} to Pt^{II} but also takes part in the formation of the active complex. The formation of the various products is thermodynamically determined.

Several reactions have been described, in which the hydrosilylation of unsaturated compounds, in addition to the main processes, involves parallel processes with splitting of an Si–C bond. Thus the reaction of Et_3SiH with $CH_2=CHSiMe_2$.Cl in the presence of H_2PtCl_6 [55] gives a mixture of products:



The formation of side products can be explained if it is assumed that vinyl-hydrogen exchange takes place at the silicon atom:



In the reaction of $(Me_3SiO)_2SiMeH$ with hex-2-ene in the presence of $H_2PtCl_6.6H_2O$ at 140°, in addition to the "normal" hydrosilylation product $(Me_3SiO)_2SiMeC_6H_{13}$, the side products $(Me_3SiO)_3SiH$, $Me_3SiOSiMe_2C_6H_{13}$, and $Me_3SiOSiMe_2H$ were detected[56]. To explain the formation of the latter, it must be assumed that intermolecular exchange of Me_3SiO and Me groups takes place at the silicon atom:

$$2(Me_3SiO)_2SiMeH \xrightarrow[140°]{[Pt]} Me_3SiOSiMe_2H + (Me_3SiO)_3SiH$$
$$\downarrow \text{hex-2-ene}$$
$$Me_3SiOSiMe_2C_6H_{13}$$

In the extensive literature devoted to hydrosilylation reactions, however, very little mention is made of the anomalous products obtained by the splitting of Si–C bonds.

III. THE SPLITTING OF SILICON–ALKYL AND SILICON–ARYL BONDS BY Pt AND Pd COMPOUNDS

A silicon–carbon bond not containing activating groups is fairly inert in homolytic and heterolytic reactions. The reactivity of the silicon–alkyl bond resembles most closely that of the carbon–carbon bond in alkanes. In homolytic reactions in tetra-alkylsilanes, as a rule, the carbon–hydrogen bond, and not the silicon–alkyl bond, is broken preferentially[33,51,57]. Tetra-alkylsilanes also have a high thermal stability. Tetramethylsilane decomposes at 700°, and methyldibutylsilane only at 1000°.[57] Substituted alkylsilanes, in particular β-halogenoalkylsilanes, are much less stable to heat[51].

The silicon–carbon bond is more sensitive to electrophilic and nucleophilic reagents than the carbon–carbon bond. This is due to the slight polarity of the Si–C bond and the ability of the silicon atom to increase its co-ordination number, facilitating attack by a base at this atom. Nevertheless, in these reactions also, the silicon–alkyl bond is chemically fairly inert. Thus under ordinary conditions, tetra-alkylsilanes are not affected by alkali metals, organometallic compounds, metal hydrides, and alkalis and acids of medium strength[35,51].

The chemical inertness of the Si–Alk and Si–Ar bonds is greater than that of the vinyl, allyl, ethynyl, and other activated Si–C bonds examined in section II. The problem of the metal-complex activation of Si–Alk and Si–Ar bonds therefore appears most difficult.

1. Transformations of Silanes Under the Influence of Pt^{IV} and Pd^{II} Complexes

The splitting of an Si–Alk bond was first detected[58] by the action of Pt and Pd derivatives on hexamethyldisiloxane. When hexamethyldisiloxane is heated in the presence of 0.01 to 1% of a catalyst, octamethyltrisiloxane is formed:

$$Me_3SiOSiMe_3 \xrightarrow{\text{catalyst}} Me_3SiOSiMe_2OSiMe_3 .$$

Methane is detected in the gas phase.

Under the same conditions in the absence of a catalyst, octamethyltrisiloxane and methane are not formed from the disiloxane. The reaction takes place both in solvents (alcohol, benzene) and without a solvent, and takes place to a slight extent even at 100°. The yield of octamethyltrisiloxane after 10 h at 200° is 10–20%, calculated relative to the original hexamethyldisiloxane. Catalytic activity in this reaction is shown by a fairly wide range of platinum and palladium compounds: $H_2PtCl_6.6H_2O$, $(Ph_3P)_4Pt$, $(Ph_3P)_3Pt$, $PdCl_2$, Pt/C, etc.

Subsequently, the possibility of splitting the Si–C bond under the influence of platinum and palladium complexes in organosilicon compounds not containing functional groups—tetra-alkyl- and trimethylarylsilanes—was studied[59–67]. The transformations of the following silanes were examined: Me_4Si, Me_3SiEt, Me_3SiPr, Me_3SiBu, $Me_3SiC_6H_4X$ (X = H, *p*-Me, *p*-MeO, *p*-Cl, *m*-Me, *m*-MeO, *m*-Cl). Chloro-complexes of platinum and palladium in different oxidation states $PtCl_4$, $H_2PtCl_6.6H_2O$, Na_2PtCl_6, $PtCl_2$, K_2PtCl_4, $(Ph_3P)_2PtCl_2$, $(Py)_2PtCl_2$, $(Ph_3P)_2Pt_2Cl_4$, *trans*-$[Pt(CO)Cl(Ph_3P)_2][ClO_4]$, $Pt_2Cl_4(C_2H_4)_2$, $PdCl_2$, $LiPdCl_3$, Li_2PdCl_4, and $(PhCN)_2PdCl_2$, metallic Pt and Pd, and triphenylphosphine complexes of Pt^0 and Pd^0, $(Ph_3P)_4Pt$ and $(Ph_3P)_4Pd$, were studied. It was found[59–63] that the silicon–carbon bond can be split unexpectedly easily by platinum(IV) and palladium(II) chlorides: $PtCl_4$, H_2PtCl_6, $PdCl_2$, $LiPdCl_3$, Li_2PdCl_4, and $(PhCN)_2PdCl_2$. Compounds of these metals in lower oxidation states ($PtCl_2$, K_2PtCl_4, $(Ph_3P)_2PtCl_2$, $(Ph_3P)_4Pt$, $(Ph_3P)_4Pd$, Pt/C, Pt black) have a low activity or are completely inactive.

Under the influence of $PtCl_4$ or $PdCl_2$ in organic solvents containing a small quantity of water, tetraorganosilanes are split to give the hydrocarbon and the hexa-alkyldisiloxane as main products:

$$2Me_3SiR + H_2O \xrightarrow[60–120°]{MX_n} 2RH + Me_3SiOSiMe_3$$
$$MX_n = PtCl_4, H_2PtCl_6, PdCl_2, LiPdCl_3, Li_2PdCl_4, (PhCN)_2PdCl_2 .$$

Organic chlorides and products of radical decomposition are formed in parallel to a slight extent in a number of cases.

The disiloxane formed is also demethylated under the influence of these complexes. For example, in the reaction of Me_4Si with $PtCl_4.3H_2O$ in benzene at 80°, octamethyltrisiloxane is formed in addition to methane and hexamethyldisiloxane.

Special experiments showed that HCl does not catalyse these reactions, that is in this case metal-complex activation, and not acid activation, of the Si–C bonds take place. The reactions take place under mild conditions, and the degree of conversion reaches 90%.

The role of the solvent is different in the reactions of silanes with Pd^{II} and Pt^{IV} chlorides. With the palladium complexes, silanes react readily in the most varied solvents (alcohols, THF, DMF, MeCN, benzene). In the reactions of silanes with $PtCl_4$, on the other hand, the nature of the solvent is more significant. Thus in the reaction of Me_3SiBu with $PtCl_4.3H_2O$, the degree of conversion of the silane is 80% in $CHCl_3$, 50% in benzene, and 14% in DMF, and the reaction does not take place in EtOH and Et_2O.[62] The passivating influence of donor solvents was attributed to their ability to form stable coordinatively saturated solvates with the metal salt.

An interesting feature is that the splitting of silanes is highly selective: in trimethylarylsilanes the aryl group is removed exclusively, and in mixed trimethylalkylsilanes practically only the methyl group is removed. The authors discuss the possible mechanism of this reaction, and suggest that the splitting of the Si–C bond by platinum and palladium chlorides takes place as an exchange reaction, giving the trialkylchlorosilane and an unstable organic derivative of the transition metal[62]:

$$Me_3SiR + MCl_n \rightarrow Me_3SiCl + [RMCl_{n-1}]$$
$$Me_3SiCl + \frac{1}{2}H_2O \rightarrow \frac{1}{2}Me_3SiOSiMe_3 + HCl .$$

The intermediate organic derivative of the transition metal can decompose further by two routes: it can undergo protolysis with the formation of the hydrocarbon and the regeneration of the metal chloride, or it can give organic chlorides

and the products of radical decomposition#:

$$[RMCl_{n-1}] + HCl \rightarrow RH + MCl_n$$
$$[RMCl_{n-1}] \rightarrow \begin{cases} \rightarrow RCl + MCl_{n-2} \\ \rightarrow R^{\cdot} + MCl_{n-1} \end{cases} .$$

The reactions of Me_4Si with $PtCl_4$ in benzene or of Me_3SiPh with Li_2PdCl_4 in DMF in the presence of alcohols labelled with deuterium (ROD) give the hydrocarbons MeD and PhD respectively, containing a high percentage of deuterium (up to 80% of the theoretical yield). Thus in the presence of a source of protons, the principal direction of the decomposition of the intermediate organometallic compound is its protolysis, leading to the regeneration of the original transition metal complex. This route opens up the possibility of carrying out a catalytic reaction. In fact, in the presence of small quantities of added alcohol or water, the reactions of silanes with Pt and Pd chlorides take place catalytically[62]. A high activity is shown by H_2PtCl_6 in acetonitrile (Table 1) and by palladium(II) chloride in DMF (Table 2).

Table 1. Catalytic reactions of tetraorganosilanes with platinum compounds[62].

Silane	Catalyst	t, °C	τ, h	α	Solvent	A
Me_4Si	$H_2PtCl_6 \cdot 6H_2O$	150	10	100	MeCN *	14
Me_3SiEt	$PtCl_4 \cdot 3H_2O$	80	20	20	$PhNO_2$ *	12
Me_3SiPr	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	4,4
Me_3SiBu	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	6
Me_3SiBu	$PtCl_4 \cdot 3H_2O$	80	20	20	C_6H_6	17
Me_3SiBu	$H_2PtCl_6 \cdot 6H_2O$	120	20	1000	MeCN	20
Me_3SiPh	$H_2PtCl_6 \cdot 6H_2O$	150	20	1000	MeCN	130
Me_3SiPh	Pt/C	100	50	30	EtOH	32

Symbols. Here and in later Tables: τ is the reaction time, α the molar ratio Me_3SiR : catalyst, and A the degree of conversion of the silane, moles per mole of catalyst.

* [EtOH] = 0.5 M.

Although the presence of small quantities of water or alcohol is a necessary condition for catalysis, large quantities of these reagents inhibit the reactions.

The reactions of silanes with Pd^{II} can be converted into catalytic reactions by another method, by oxidising the precipitated metal by external oxidising agents ($CuCl_2$, p-benzoquinone), but the stability of the system is low: the degree of conversion of the silane does not exceed 7 moles per mole of Li_2PdCl_4 (see Table 2).

The behaviour of platinum and palladium compounds towards the silicon–carbon bond differs significantly from that of other transition metals, in particular the metals of the 3*d* series in their principal oxidation states[58–63]. The latter activate chiefly the splitting of arylsilanes, whereas Pt and Pd compounds split both Si–Ar and Si–Alk bonds[61].

For the reactions of silanes with $PtCl_4$, it is apparently necessary to take account of the possibility of the equilibrium $RPtCl_3 + PtCl_2 \rightleftharpoons RPtCl + PtCl_4$, although at a high temperature it is displaced to the left[68].

The kinetics and mechanism of the splitting of the silicon–aryl bond in Me_3SiAr, catalysed by Li_2PdCl_4 in DMF in the presence of 0.7% H_2O, have been studied[63]. At 80–100°, the reactions take place exclusively with the splitting of the Si–Ar bond to give hexamethyldisiloxane and the corresponding aromatic hydrocarbon:

$$2Me_3SiC_6H_4X + H_2O \xrightarrow{Li_2PdCl_4} Me_3SiOSiMe_3 + 2C_6H_5X$$
$$X = H, p\text{-Me}, p\text{-Cl}, p\text{-MeO}, m\text{-Me}, m\text{-Cl}, m\text{-MeO} .$$

The rates of the reactions of trimethylarylsilanes (except $Ar = p\text{-}MeOC_6H_4$) with Li_2PdCl_4 are described by an equation of first order with respect to the silane; the order of the reaction with respect to Li_2PdCl_4 in all cases was 0.5:

$$w = k\,[Me_3SiAr]\,[Li_2PdCl_4]^{0.5} .$$

The catalyst for the reaction is not the original complex, but the complex of $LiPdCl_3$ with DMF, formed by solvolysis[69]:

$$PdCl_4^{2-} + L \rightleftarrows PdCl_3(L)^- + Cl^-$$
$$L = DMF .$$

A characteristic feature of this reaction is that its rate is not sensitive to the nature of the substituent in the aromatic ring.

Table 2. Catalytic reactions of silanes with Pd^{II} compounds at 100°.[62]

Silane	Catalytic system	τ, h	α	Solvent	A
Me_4Si	Li_2PdCl_4	50	200:1	DMF*	150
Me_3SiPh	Li_2PdCl_4	50	1000:1	DMF	200
Me_3SiBu	Li_2PdCl_4	10	10:1	EtOH	2
Me_3SiBu	Pd(II)—$FeCl_3$—LiCl	10	10:1:10:10	EtOH	2
Me_3SiBu	Pd(II)—$C_6H_4O_2$—LiCl	10	10:1:10:10	EtOH	3.5
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	40	10:1:10:10	THF	1.3
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	10	10:1:10:10	EtOH	4.4
Me_3SiBu	Pd(II)—$CuCl_2$—LiCl	20	10:1:10:10	EtOH	7

* $[H_2O] = 0.4$ M.

Table 3. Influence of substituents in the splitting of Si–Ar bonds in $Me_3SiC_6H_4X$ under the influence of Li_2PdCl_4 in DMF at 100° (k'_{rel}) and under the influence of acids (k''_{rel}).

X	k'_{rel} (Ref.69)	k''_{rel} (Ref.70)
m-MeO	0.7	0.01
p-Cl	1.4	0.1
m-Cl	0.7	0.4
H	1	1
m-Me	0.8	2.3 (36.6) *
p-Me	2.6	23 (116,3) *
p-MeO	(1.2) **	1510

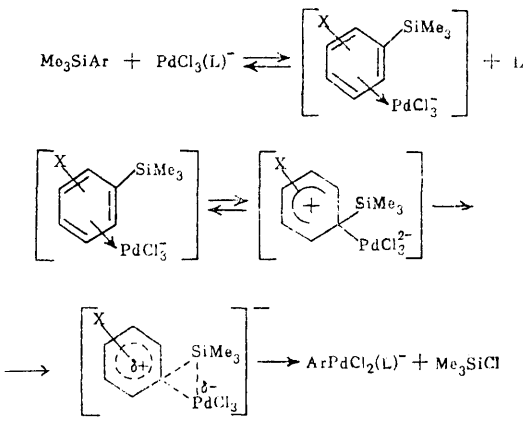
* Figures in brackets for the reaction with $FeCl_3$ in MeCN.[71]

** Ratios of the average reaction rates after 2 h taken.

Table 3 gives the relative rates of the splitting of trimethylarylsilanes under the influence of Li_2PdCl_4 in DMF and under the influence of electrophilic reagents. It can be seen from Table 3 that the position and nature of the substituents

have very little influence on the rate of splitting of the silanes under the influence of Li_2PdCl_4: silanes of the *meta*-series react at practically identical rates, irrespective of the nature of the substituent (*m*-Me, *m*-Cl, *m*-MeO). Substituents in the *para*-position, both electron donors (*p*-Me) and electron acceptors (*p*-Cl), increase the reaction rate slightly relative to non-substituted phenylsilanes. On the other hand, the rate of the acid splitting of the Si–Ar bond is extremely sensitive to the nature of the substituent, and the values of ρ in this case reach −5. An even greater influence of the substituents is observed in the reaction of trimethylarylsilanes with $FeCl_3$.

The following scheme was proposed for the splitting of Si–Ar bonds under the influence of Li_2PdCl_4 in aqueous DMF [69]:



$$2\,Me_3SiCl + H_2O \longrightarrow Me_3SiOSiMe_3 + 2\,HCl$$

$$ArPdCl_2(L)^- + HCl \longrightarrow ArH + PdCl_3(L)^-$$

L = DMF.

According to this scheme, the reaction involves the formation of a cyclic intermediate state with a low polarity. This suggestion agrees with the levelling of the influence of substituents, the low value of the enthalpy of activation (20.1 kcal mole^{-1}), the fairly high negative orientational entropy of activation (−27.2 e.u.), and the fact that the reaction rate is independent of the ionic strength of the solution, observed for the reaction of Me_3SiPh with Li_2PdCl_4 in DMF at 80–100°.

The authors suggest that the specific character of the action of the Pd^{II} complex on the Si–Ar bond is due to its biphilic character, that is its ability not only to accept electrons from the carbon atom but also to take part in a co-ordinative interaction with the silicon atom, as a result of which palladium simultaneously activates both atoms of the Si–C bond. Special calculations for geometric models of the corresponding σ-complexes showed that the Pd–Si distance in them is 3.20 Å, which is much less than the sum of the van der Waals radii of Pd and Si, equal to 4.25 Å. Thus the calculation of the model is consistent with the suggestion that there is a co-ordinative Pd–Si interaction[69].

The subsequent stages of the reaction involve the formation of an aryl palladium complex, which undergoes protolytic decomposition to give the final products and regenerate the catalyst. The intermediate formation of the σ-organic derivative of palladium is confirmed by the methylation and phenylation of alkenes by organosilicon compounds[59,60]. Thus in the presence of $PdCl_2$, the hydrogen at the double bond in styrene and cyclohexene is replaced by the methyl or phenyl group of an organosilicon compound:

$$R_3SiR' + PdCl_2 \rightarrow R_3SiCl + [R'PdCl]$$

$$[R'PdCl] + \underset{H}{\overset{}{\rangle}}C{=}C\langle \rightarrow \underset{R'}{\overset{}{\rangle}}C{=}C\langle + HCl + Pd$$

R′=Me, Ph.

The reactions take place very slowly even at room temperature, and at 100° and above, the yields of the products may be fairly high. Thus styrene can be methylated by tetraorganosilanes (Me_4Si, Me_3SiEt), silazane, and siloxanes. The methylating power of organosilicon compounds changes in approximately the same sense as the ease of splitting of the Si–C bond by electrophilic reagents:

$$Me_4Si\,(66\%),\ Me_3SiEt\,(66\%) > Me_3SiNHSiMe_3\,(52\%) > > Me_3SiOSiMe_3\,(34\%) > Me_3SiCH_2Cl\,(32\%) > > (Me_2SiO)_3\,(3\%) > Me_3SiCl\,(0\%)$$

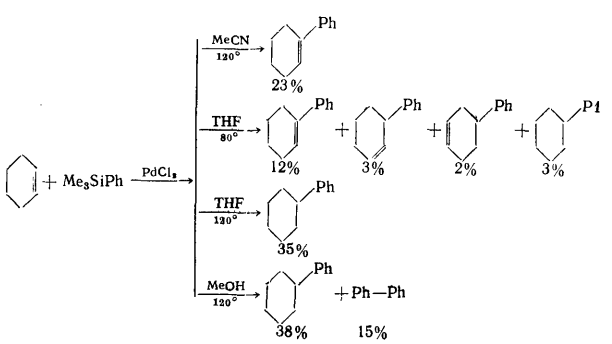
The chief product is that formed by the replacement of the β-hydrogen of styrene. The phenyl group in Me_3SiPh is removed more readily than the methyl group. It is also more readily transferred to the alkene. Examples of the phenylation of alkenes under the influence of Me_3SiPh are given in Table 4.

Table 4. Phenylation of alkenes under the influence of Me_3SiPh*. [60]

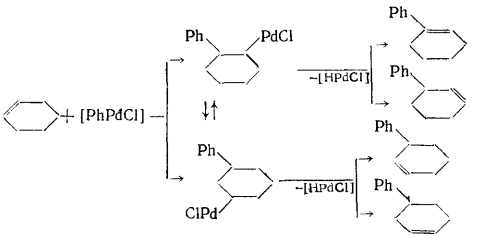
Alkene	Palladium compound	Solvent	*t*, °C	τ, h	Product	Yield, % calculated relative to the silane
Styrene	Li_2PdCl_4	THF	20	100	*trans*-stilbene	20**
Styrene	Li_2PdCl_4	THF	60	6	*trans*-stilbene	17
Styrene	Li_2PdCl_4	MeOH	60	6	*trans*-stilbene	20
Styrene	Li_2PdCl_4	THF	120	10	*trans*-stilbene	94
Styrene	$LiPdCl_3$	MeCN	120	10	*trans*-stilbene	65***
Styrene	Li_2PdCl_4	MeOH	120	10	*trans*-stilbene	47
Cyclohexene	Li_2PdCl_4	THF	120	10	phenylcyclohexane	35
Cyclohexene	$LiPdCl_3$	MeCN	120	10	1-phenylcyclohexene	23
Cyclohexene	Li_2PdCl_4	MeOH	120	10	phenylcyclohexane	38
					biphenyl	15

* Molar ratio $[Me_3SiPh] : [alkene] : [Pd^{II}] = 1 : 2 : 1$.
** + 5% β-methylstyrene.
*** + 8% β-methylstyrene.

Cyclohexane is phenylated less readily than styrene. The formation of 1-phenylcyclohexene, the "normal" product of the phenylation of cyclohexene, as the only product is observed only in acetonitrile. The reactions in THF and MeOH are complicated by side reactions—isomerisation, hydrogenation, and disproportionation:



Thus the reaction of Me_3SiPh with cyclohexene in the presence of Li_2PdCl_4 in the THF at 80°, in addition to the main product, 1-phenylcyclohexene, also gives 3- and 4-phenylcyclohexenes and phenylcyclohexane. The formation of the isomeric phenylcyclohexenes is attributed[60] to the isomerisation of the intermediate phenylcyclohexylpalladium chloride, since 1-phenylcyclohexenes do not isomerise under the reaction conditions:



At 120° in THF, the only product of the reaction of Me_3SiPh with cyclohexene is phenylcyclohexane. Under the same conditions in methanol, a mixture of phenylcyclohexane and biphenyl is formed. The formation of the latter is attributed to the disproportionation of 1-phenylcyclohexene under these conditions by a reaction of the irreversible Zelinskii catalysis type[60].

The above reactions involving the transfer of organic compounds to alkenes in the presence of Pd^{II} compounds are analogous to the familiar Heck reactions[41,72-76]. In the Heck reactions, organic derivatives of Hg, Sn, and Pb are used as alkylating and arylating agents.

The possibility of using organosilicon compounds in these reactions is of preparative interest, particularly for the methylation of alkenes, since organosilicon compounds are non-toxic and stable to air and moisture.

2. The Splitting of Silanes Under the Influence of Pt^{II} Compounds

Dimeric alkene complexes of Pt^{II} are active in the splitting of tetra-alkylsilanes[64-66].

The reactions of the silanes Me_3SiR (R = Ph, Me) with $Pt_2Cl_4(alkene)_2$ complexes take place even at room temperature. In $CHCl_3$ in the absence of water, the reaction gives Me_3SiCl and the corresponding σ-organic derivative of Pt^{II}, identified by ^1H NMR:

$$Me_3SiR + Pt_2Cl_4(C_2H_4)_2 \rightarrow Pt_2Cl_3(C_2H_4)_2R + Me_3SiCl .$$

In an excess of Me_3SiR, the reaction may proceed further:

$$Me_3SiR + Pt_2Cl_3(C_2H_4)_2R \rightarrow Pt_2Cl_2(C_2H_4)_2R_2 + Me_3SiCl .$$

The rate of the removal of different groups from the Si atom in Me_3SiR under the influence of $Pt_2Cl_4(C_2H_4)_2$ at 20° in $CHCl_3$ changes in the following order:

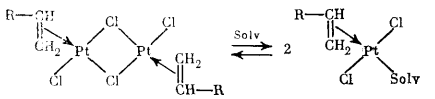
$$CH_2{=}CH > CH_2{=}CH{-}CH_2 > Ph \gg Me .$$

In the presence of water, the process becomes catalytic with respect to the Pt^{II} complex. As in reactions catalysed by Pd^{II} and Pt^{IV} complexes, the catalyst is regenerated by the protolytic splitting of the σ-organic derivative of the metal:

$$2Me_3SiCl + H_2O \rightarrow Me_3SiOSiMe_3 + 2HCl$$
$$[Pt_2Cl_2(C_2H_4)_2R_2] + 2HCl \rightarrow [Pt_2Cl_4(C_2H_4)_2] + 2RH .$$

In the reaction with Me_3SiPh, a wide range of monomeric *cis*- and *trans*-complexes of Pt^{II} containing phosphines, pyridines, biallyl, thiols, and ethene as ligands have been studied. All were inactive under the conditions studied (20°, 24 h). Among the dimeric complexes $Pt_2Cl_4L_2$, the collidine and phosphine complexes are also inert.

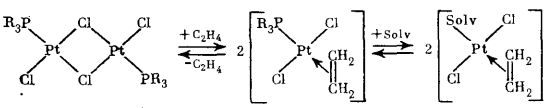
The high activity of dimeric alkene complexes of Pt^{II} in reactions with silanes was attributed[66] to the ease of formation of the intermediate coordinatively unsaturated Pt^{II} complex obtained by the dissociation of $Pt_2Cl_4(alkene)_2$:



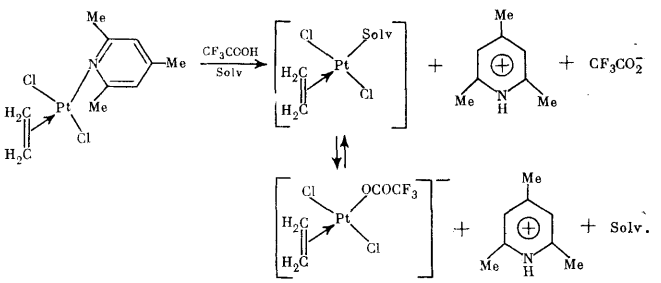
Solv = solvent .

In agreement with this, the rate of the splitting of silanes under the influence of the complexes $Pt_2Cl_4(C_2H_4)_2$ depends significantly on the solvent. Thus after 20 h, Ph is removed from Me_3SiPh to the extent of 100% in $CHCl_3$, 60% in benzene, 10% in acetone, and 2% in MeOH.[66] Thus solvents which form stable solvates decrease the coordinative unsaturation of the intermediate monomeric complex $PtCl_2(C_2H_4)$, and hinder the reaction.

The suggestion that an active three-coordinate Pt^{II} complex is formed agrees with the fact that the phosphine complexes $Pt_2Cl_4L_2$ [L = PPh_3 and $P(n\text{-}Bu)_3$], which are inert in reactions with silanes, react with them in the presence of ethene. The replacement of ethene by argon stops the reaction, and saturation again with ethene renews it. These facts are explained by ligand exchange in the presence of ethene.



Similarly, the ethene complex of Pt^{II} with the collidine ligand, *trans*-$PtCl_2(C_2H_4)(Me_3C_5H_2N)$, which is inactive in reactions with silanes, reacts with them in the presence of CF_3COOH at room temperature[64]. It has been proved that in the presence of CF_3COOH, protonation and removal of the collidine ligand take place to give the complex $PtCl_2(C_2H_4)$.



The unique activity of the complex $[PtCl_2(C_2H_4)Solv]$ is attributed to the increased electrophilic character of Pt^{II} in the presence of the π-acceptor, and the coordinative unsaturation of this complex.

The nature of the ethene ligand in the dimeric complex $Pt_2Cl_4(alkene)_2$ also influences its activity with respect to the Si-C bond. With increase in the size of the group R at the co-ordinated multiple bond, the rate of the splitting of silanes decreases in the order: ethene > styrene > propene > pentene > 3,3'-dimethyl-1-butene. This is attributed to the decrease in the accessibility of the metal with increase in the volume of the group R.

Low activity in the reaction with Me_3SiPh is also shown by the dimeric complex $Pt_2Cl_4(S\text{-}Bu_2\text{-}n)_2$, which has bridging ligands and can be converted into the three-coordinate complex $PtCl_2(S\text{-}Bu_2\text{-}n)$.

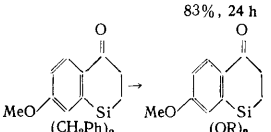
In the authors' opinion, Pt^{II} complexes can bring about either electrophilic splitting of the Si–C bond or oxidative addition of the silanes at the Si–C bond with the subsequent reductive elimination of R_3SiCl.[65]

3. The Splitting of the Si–C Bond by Metallic Pt and Pd

Metallic palladium in the presence of hydrogen is able to split the $Si\text{–}CH_2Ph$ bond[77]. Thus various benzyl- and dibenzylsilanes in the presence of the catalytic complexes Pd/C in alcohol in an atmosphere of hydrogen are converted into alkoxysilanes and toluene. The reactions take place slowly at room temperature:

$$PhMe_2SiCH_2Ph \xrightarrow[67\%,\ 24\ h]{} PhMe_2SiOMe$$

$$m\text{-}MeOC_6H_4Si(Et)(CH_2Ph)_2 \xrightarrow[83\%,\ 24\ h]{} m\text{-}MeOC_6H_4Si(OEt)_2Et$$



$$C_6H_{11}Me_2SiCH_2Ph \xrightarrow[10\%,\ 9\ d]{} C_6H_{11}Me_2SiOMe$$

The method can be used to synthesise alkoxysilanes difficult to prepare, for example dialkoxysilatetralins. Electron-donor groups in the benzene ring facilitate the reaction, and acceptor groups (CF_3) hinder it. This feature led the authors to the conclusion that complex formation by the benzyl π-system with metallic Pd is the limiting stage of the process. The activated Si-benzyl bond is then split by alcohol (by an S_NSi mechanism) to give the alkoxysilane and benzylpalladium hydride, after which the latter is reduced by hydrogen to toluene and Pd^0. Platinum is inactive in this reaction. It has been shown, however, that the Si–Ph bond in Me_3SiPh is split very slowly under the influence of Pt/C in ethanol at 100°. The degree of conversion of the silane after 50 h corresponds to 32 moles per g-atom of platinum[62].

The triphenylphosphine complexes L_4Pt and L_4Pd are inert with respect to silanes on prolonged heating in benzene at 150°.[62] The apparent explanation is that the metal atom in these complexes is completely shielded, and is inaccessible to attack. The dissociation of L_4M gives the complexes L_3M and L_2M, in which the metal is still fairly well shielded by the molecules L and is still not readily accessible to attack by the silicon atom, which in turn is shielded by four organic groups[78].

4. Electrochemical splitting of the Si–C Bond.

Tetra-alkyl- and trialkylarylsilanes are oxidised at a Pt anode at 2.63 V in the presence of the fluoride anion in absolute MeCN.[79] The reaction is accompanied by the formation of fluorosilanes and the elimination of the most stable radical:

$$R_3SiR' \xrightarrow[H_3F_4^-,\ MeCN]{Pt,\ 2.63\ V} R_3SiF + R'^{\cdot}$$

50–80%

$R' = Me, Et, CH_2Ph$.

Silanes are not oxidised in the absence of the fluoride anion. In the authors' opinion, this reaction takes place by a mechanism involving one-electron oxidation with the nucleophilic co-operation of the fluoride anion. The transfer of the electron from Si takes place in step with the attack by F^- at the Si atom.

The proposed mechanism is confirmed by the selectivity of the splitting of the Si–C bonds and the nature of the products formed. Thus in the anodic oxidation of Me_3SiPh and $Me_3SiC_6H_4F$, the methyl group is eliminated exclusively, whereas in the case of trimethylbenzyl- and triethylbenzylsilanes, only the benzyl group is eliminated. The anodic oxidation of Me_3SiEt is accompanied by the preferential replacement of the ethyl group. Thus the ease of the removal of the radicals decreases in the order: $PhCH_2$ > Et > Me. The resulting radical then dimerises, or removes hydrogen from the solvent ($Me^{\cdot}$), or undergoes further anodic oxidation to the cation ($Et^{\cdot}$, $PhCH_2^+$).

It is of interest to compare the selectivity of the splitting of the Si–C bond under the influence of Pd^{II} and Pt^{IV} on the one hand and in electrochemical splitting at a platinum anode on the other. In the first case, in trimethylarylsilanes, the aryl group is removed exclusively, whereas in the mixed trimethylethyl-, trimethylpropyl-, and trimethylbutylsilanes, practically only the methyl group is removed. Unlike the Ph and Me groups, the benzyl group is not removed from the Si atom under the influence of the complex $Pt_2(C_2H_4)_2Cl_4$. The opposite relationships are observed for the electrochemical oxidation of silanes.

5. The Reactions of Siloxanes with Platinum and Palladium Complexes

Of particular interest is the splitting of the silicon–oxygen bond in siloxanes, which would open up the possibility of using the readily accessible siloxanes in organic synthesis. On the other hand, the selectivity of the replacement of organic groups in siloxanes by polar groups provides a method for the directed modification of siloxanes in the absence of aggressive media.

The siloxane bond is fairly strong, and is split only by strong acidic and basic reagents[80]. There are several published examples, indicating the stability of siloxanes to the action of Pt and Pd complexes. Thus the reactions of substituted acetylenes with dihydrodisiloxanes in the presence of the Speier catalyst or Pt/C at 110° in toluene gives five-membered organocyclosiloxanes[81], that is, the reaction takes place without rupture of the SiOSi unit:

$$XC{\equiv}CX' + HR'RSiOSiRR'H \xrightarrow{catalyst} \underset{\displaystyle XHC\text{—}CHX'}{\overset{\displaystyle O}{R'RSi\quad SiRR'}}$$

50–70%

X = H, Ph; X′ = Ph;
R = R′ = Me; R = Me, R′ = Et .

When hexamethyldisiloxane is heated for a prolonged period with trichlorosilane at 150° in the presence of $H_2PtCl_6.6H_2O$, $PtCl_2$, or $Pt_2Cl_4(C_2H_4)_2$, selective exchange takes place between the methyl group and chlorine, and the siloxane bond is not affected[82]:

$$Me_3SiOSiMe_3 + HSiCl_3 \xrightarrow[150°,\ 24\ h]{catalyst} ClMe_2SiOSiMe_2Cl + HClSiMe_2 .$$

When 1,1,3,3-tetramethyldisiloxane is boiled with $L_2Pt(C_2H_4)$ in benzene, a disila-ring containing the metal is obtained[83]:

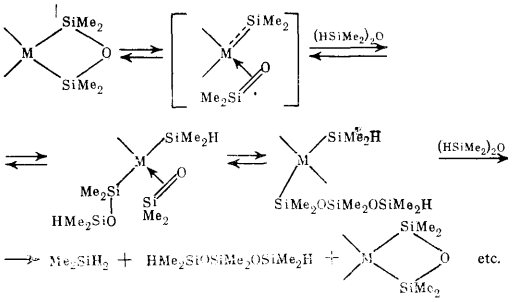
$$(HMe_2Si)_2O + L_2Pt(C_2H_4) \xrightarrow[C_6H_6]{20\text{–}80°} L_2Pt\underset{\displaystyle Me_2Si}{\overset{\displaystyle Me_2Si}{\diagup\ \diagdown}}O + C_2H_4 + H_2$$

L = Ph_3P .

In this case, selective splitting of the Si–H bonds is observed, and rupture of the siloxane bond is not observed. The palladium, iridium, and rhodium analogues of these complexes were subsequently obtained[84]. Metal-containing rings of the type $L_2M(Me_2SiOSiMe_2)$ even at room temperature catalyse the disproportionation of 1,1,3,3-tetramethyldisiloxane to give dimethylsilane and higher siloxane oligomers:

$$n\,(HSiMe_2)_2O \xrightarrow{\text{catalyst}} Me_2SiH(OSiMe_2)_nOSiMe_2H + n\,Me_2SiH_2$$
M=Ir, Rh, Pt, Pd.

The platinum and palladium metal-containing rings are poor catalysts for these reactions, but the iridium and rhodium complexes show a high activity[84]. The authors suggest that the disproportionation of the disiloxane involves the participation of intermediate complexes of dimethylsilylene and dimethylsilanone, co-ordinated to the transition metal atom:



The dimeric ethene complex of platinum $Pt_2Cl_4(C_2H_4)_2$ in the presence of water brings about the slow hydrolysis of hexamethyldisiloxane at room temperature to give polysiloxanes[64]. The composition of the products was not determined.

It was noted above that the hydrosilylation of hex-2-ene under the influence of $(Me_3SiO)_2SiMeH$ at 140° in the presence of H_2PtCl_6 is complicated by a side process, which is also accompanied by the splitting of the siloxane bond[56]. The platinum and palladium compounds $PdCl_2$, $PtCl_4$, $H_2PtCl_6.6H_2O$, $(Ph_3P)_2PtCl_2$, $(Ph_3P)_4Pt$, and $(Ph_3P)_4Pd$, and also metallic Pt and Pd at 80–100°, activate both the Si–C bond and the Si–O bond in hexamethyldisiloxane. Linear and cyclic siloxanes are formed. The chief product is octamethyltrisiloxane, the yield of which corresponds to 10 moles per mole of catalyst[58, 60,61]. In the reaction of hexamethyldisiloxane with $PdCl_2$ (molar ratio 2:1, 150°, 10 h, in the absence of a solvent), methane, methyl chloride, and ethane are formed in the molar ratio 70:10:1 together with chlorine derivatives and higher linear and cyclic siloxanes[85].

In solvents (aqueous THF, MeCN, and MeOH), hexamethyldisiloxane reacts with Pd^{II} salts at 120° to give octamethyltrisiloxane, decamethyltetrasiloxane, and hexamethylcyclotrisiloxane. In the presence of $CuCl_2$, this reaction becomes catalytic. Thus 1 mole of Li_2PdCl_4 at 120° after 10 h converts approximately 5 moles of disiloxane. Metallic Pt and Pd are also active in the splitting, and the reaction with Pt/C takes place even at 80°. The products are methane and $Me_3SiOSiMe_2OSiMe_3$. The degree of conversion of the disiloxane after 10 h amounts to 10 mole per g-atom of Pt.[85]

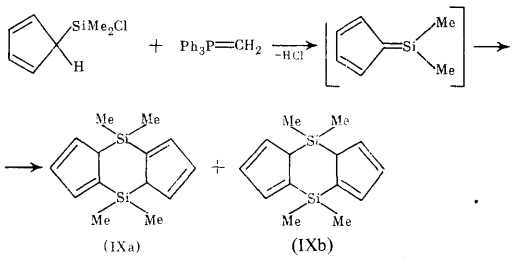
Unlike metallic platinum and palladium, the triphenylphosphine complexes of these metals, $(PPh_3)_4Pt$ and $(Ph_3P)_4Pd$, do not react with hexamethyldisiloxane in benzene even at 150°. The reaction with these complexes was observed only at 200°, that is under conditions in which decomposition of the complex to the metal is possible[85]. A significant feature is that the formation of cyclic siloxanes from hexamethyldisiloxane under the influence of platinum and palladium compounds or the corresponding metals is observed not only in aqueous solvents, but also under anhydrous conditions and in the initial stages of the reaction.

To explain the formation of cyclic dimethyldisiloxanes under anhydrous conditions, the authors assumed the intermediate formation of silacetone $Me_2Si=O$, stabilised by complex formation with a transition metal compound. Its polymerisation gives cyclic siloxanes, and insertion into linear and cyclic siloxanes at the Si–O bond gives higher linear and cyclic oligomers:

$$Me_3SiOSiMe_2OSiMe_3 + ML_n \rightleftarrows Me_3SiOSiMe_3 + Me_2SiO\cdot ML_n$$
$$Me_2SiO\cdot ML_n \xrightarrow{\text{polymerisation}} (Me_2SiO)_n$$
$$Me_2SiO\cdot ML_n \xrightarrow{Me_3Si(OSiMe_2)_nMe} Me_3Si(OSiMe_2)_{n+1}Me$$
$$Me_2SiO\cdot ML_n \xrightarrow{(Me_2SiO)_n} (Me_2SiO)_{n+1}.$$

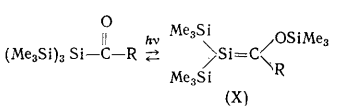
Until recently, it was considered that compounds containing a silicon atom forming multiple bonds did not exist. The formation of unstable organosilicon compounds with a double $(p-p)_\pi$-bond at the silicon atom is now well established. Thus the formation of short-lived silicon analogues of the unsaturated compounds $R_2Si=CH_2$,[86–90] $R_2Si=O$,[87,91] $R_2Si=SiR_2$,[92,93] $R_2Si=NR$,[94] and $R_2Si=S$[95] has now been proved.

Recently, several groups of research workers have attempted to synthesise stable silaethylenes. Thus with the idea of stabilising structures of the type C=E by delocalisation of the π-bond and an increase in the steric hindrance at the C and E atoms, attempts have been made[96] to synthesise silafulvenes, which, according to quantum-mechanical calculations[97], should be the most stable systems. The reaction of $C_5H_5SiMe_2Cl$ with triphenylmethylenephosphorane, however, instead of the expected silafulvene, gave a mixture of its dimers (IXa) and (IXb) with sp^3 hybridisation of the silicon atoms. The authors consider that the intermediate products of this reaction—silafulvenes—are too reactive, and are converted exceptionally readily into the thermodynamically stable dimers:



(IXa) (IXb)

Silaethylenes (X), relatively stable at room temperature in argon, were first obtained by the photolysis of acylpolysilanes[88]:



R=CMe$_3$, CEt$_3$, 1-adamantyl, etc.

With R = 1-adamantyl, a solid compound stable in argon, and characterised from its infrared, Raman, NMR (^1H, ^{13}C, ^{29}Si), and mass spectra, was isolated. Its structure (X) was confirmed by X-ray diffraction. Attempts to stabilise the intermediate unstable species of the silaethylene $R_2Si=CH_2$[98] and sila-allyl $R_2Si=CH=CH_2$[99–101] type by co-ordination to complexes of transition metals (Fe, Mo, W) has as yet, unfortunately, been unsuccessful.

Thus the new branch of metal-complex catalysis in organosilicon chemistry has arisen and developed successfully in the last ten years.

In this period it has been found that platinum and palladium complexes are effective catalysts for the splitting of Si–C bonds in vinyl-, allyl-, and ethynylsilanes, strained

sila- and disilacyclobutanes, silyl hydrides, and alkyl- and arylsilanes. These studies are being carried out with a view to investigating the mechanism of the activation of Si–C bonds by Pt and Pd complexes, and also using the splitting of these bonds in synthesis.

The removal of unsaturated groups from the Si atom is preceded by complex formation at the multiple bond. The driving force of the splitting of the Si–C bonds in cyclosilanes is their strain. In the splitting of Si–C bonds by Pd complexes, a significant feature is the ability of the Pd atom both to accept an electron pair from the carbon of the Si–C bond and to take part in a co-ordinative interaction with the silicon atom.

The splitting of Si–C bonds opens up new possibilities for the use of organosilicon compounds in synthesis: for the vinylation, methylation, phenylation, and chloroethylation of alkenes, the polymerisation of sila- and disilacyclobutanes, the preparation of organosilicon compounds not readily obtained, by the direct replacement of organic group on Si, the synthesis of platinum and palladium complexes containing organic and organosilicon groups on the metal, etc. The splitting of Si–C bonds in siloxanes is opening up new possibilities for the modification and oligomerisation of siloxanes.

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