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Hydrosilylation on Photoactivated Catalysts

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Abstract—The review considers hydrosilylation of C=C, C≡C, and C=O bonds in the presence of photoactivated catalysts.

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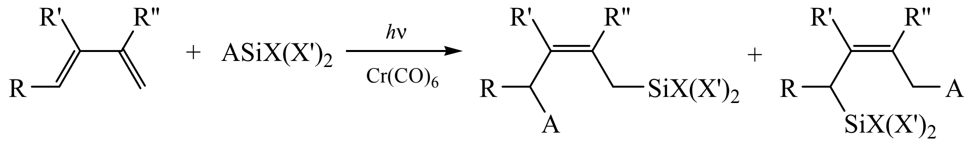
The distinction of the photoactivated metallocomplex catalysis from the usual dark catalytic reactions is manifested in the specific selectivity and the rate of the process, shortening of the induction period of reaction, and sometimes preparation of materials whose formation is impossible in thermal reactions. Noteworthy is that light or catalyst has no appreciable effect on the course of such reactions separately. Monographs, reviews and books [1–9] were describing the hydrosilylation of unsaturated compounds, but the problem of the influence of photoirradiation on hydrosilylation catalysts so far received less attention than it deserved.

The most studied is the photoactivation of carbonyl metallocomplexes. At the irradiation of the pre-catalysts of this type the elimination occurs of one or more CO ligands and the formation of coordinatively unsaturated centers interacting with a reagent or substrate to form the true catalysts.

The photoactivation of metallocomplexes was first applied for varying the rate of catalytic hydrosilylation in [10]. It has been shown that photolysis by UV light of degassed benzene solution of equimolar amounts of 1,3-diene and silane in the presence of chromium(0) hexacarbonyl leads to the 1,4-hydrosilylation affording the products of *cis*-structure [10].

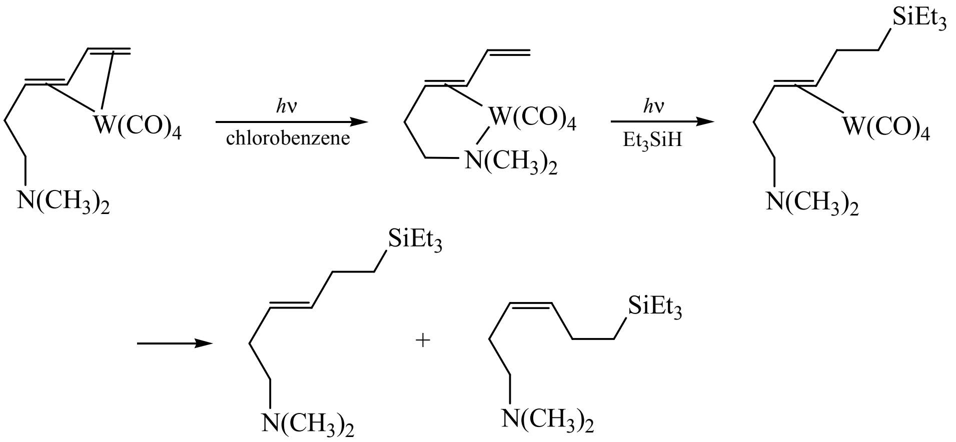


R = R' = R" = A = X = H; X' = Me, Ph; R = R' = R" = A = H; X = X' = Me, OEt; R = R" = H; R' = X = X' = Me; A = H, D; R = X = X' = Me; R' = R" = A = H; R = A = H; R' = R" = X = X' = Me; R = A = H; R' = R" = Me; X = X' = Me.

To maintain the metallocomplex in a catalytically active form a long exposure is not required, but the conversion of diene is strongly dependent on the light intensity, temperature, and the molar ratio of the starting materials [10, 11], as well as on the structure of the parent compounds. For example, *cis*-penta-1,3-diene and *trans*, *trans*-hexa-2,4-diene do not react with $HSiEt_3$ in the presence of photoactivated $Cr(CO)_6$ [10, 11], while hydrosilylation of 1,3-butadiene with $HSiEt_3$ in the presence of $Cr(CO)_6$ or $Mo(CO)_6$ at the irradiation leads to *cis*-1-triethylsilyl-2-butene [12]. Interaction of 2-methylbut-1,3-diene with $HSiMe_3$ or $DSiMe_3$ in the presence of $Cr(CO)_6$ gives *cis*-1-trimethylsilyl-2-methylbut-2-ene in ~60% yield, in the case of 1-methylbut-1,3-diene the yield of *cis*-1-trimethylsilyl-4-methylbut-2-ene was 90%. The rate of hydrosilylation of *s*-*trans*-penta-1,3-diene is slightly less than 2-methyl- and 2,3-dimethylbuta-1,3-diene, indicating a minor hindrances due to the steric and electronic effects of substituents in the substrates as compared with the electronic nature of silanes [10, 11].

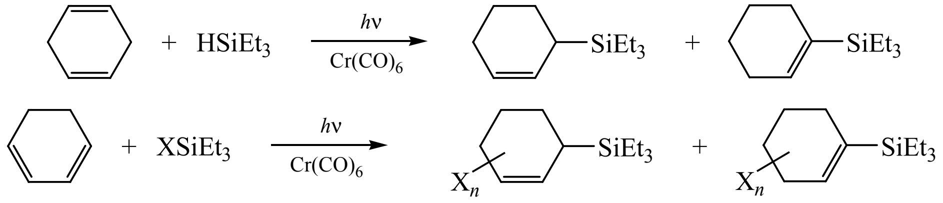
Later it was shown [13] that prolonged exposure at the hydrosilylation of 1,3-dienes (buta-1,3-diene, *s-trans*-penta-1,3-diene, 2,3-dimethylbuta-1,3-diene, 2-methylbuta-1,3-diene, *trans*-2-methylpenta-1,3-diene, and cyclopenta-1,3-diene) with triethylsilane in the presence of $Cr(CO)_6$ or $Mo(CO)_6$ in some cases led to the appearance in the reaction products of *cis*-1-triethylsilylpent-2-ene and *trans*-4-triethylsilylpent-2-ene (the ratio *cis*:*trans* = 25:1), which is not consistent with earlier studies on $HSiMe_3$. This, together with experiments on hydrosilylation of cyclohexa-1,3-diene and *trans*-penta-1,3-diene with $DSiEt_3$ allowed a suggestion that in the presence of chromium carbonyls 1,2-addition occurs together with 1,4-reaction. This is accompanied by deuterium exchange between the silane and diene leading to the formation of alkenylsilanes containing several deuterium atoms and $HSiEt_3$ (deuterium content in triethylsilane decreases from 100 to 0% when the conversion reaches 75%), but in the case of buta-1,3-diene deuterium exchange does not occur.

Elegant selective formation of products of 1,2-addition takes place at the intra-coordinative hydrosilylation in the process of the flash photolysis of (η^3-2-methyl-2-aza-5,7-octadiene)tetracarbonyltungsten(0) in Et_3SiH [14]. As a result of rupture of the W–N bond and the formation of new intramolecular bond η^2-alkene, followed by hydrosilylation of 2-methyl-2-aza-5,7-octadiene, formed exclusively the isomers corresponding to 1,2-addition.



In the dark, in contrast to the photo-irradiation, the W–N bond cleavage did not occur, but the cleavage of the η^2-alkene bond was noted, and the hydrosilylation was not observed [14].

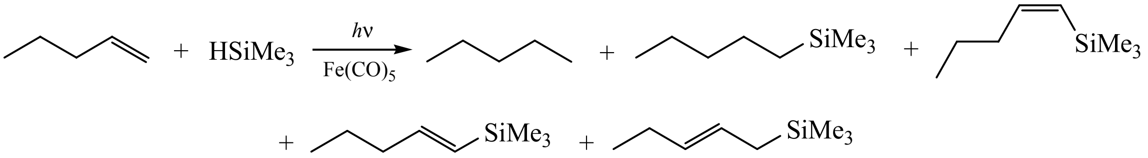
Reaction of isoprene with $HSiEt_3$ leads to *cis*-1-triethylsilyl-2-methyl- and 1-triethylsilyl-3-methylbut-2-ene (yield 76 and 22% respectively), while in the case of cyclohexa-1,3-diene 1-triethylsilylcyclohex-2-ene and 1-triethylsilylcyclohex-1-ene are formed [13]. The hydrosilylation of cyclohexa-1,4-diene with the photoactivated $Cr(CO)_6$ gives the same products as the hydrosilylation of cyclohexa-1,3-diene, however, cyclohexa-1,3-diene is not formed in any stage of the reaction. This suggests that the formation of 1-triethylsilylcyclohex-1-ene is a result of the migration of double bond in the course of hydrosilylation. By the way, the thermal hydrosilylation of cyclohexa-1,4-diene on $Cr(CO)_3$(η^4-nor-bornadiene)-(η^2-ethylene) produces the same mixture as in the photoactivated hydrosilylation on chromium hexacarbonyl [13].



n = 0, 1, 2, 3; X = H, D.

Similarly the hydrosilylation proceeds in the presence of photoactivated chromium(0) carbonyl complexes with pyridine or phosphine ligands [PMe_3, $P(OMe)_3$, PPh_3, $P(C_6H_{11})_3$] [15]. The activity of the catalysts, estimated as the time of reaching 50% conversion, decreases in the order: $Cr(CO)_6 > Cr(CO)_5\cdot(PMe_3) > Cr(CO)_5[P(OMe)_3]$. The complexes $Cr(CO)_5\cdot(PPh_3)$ and $Cr(CO)_5[P(C_6H_{11})_3]$ were inactive in the hydrosilylation of 1,3-dienes, and the conversion of buta-1,3-diene in the presence of $Cr(CO)_5(Py)$ was not higher than 3%. An advantage of $Cr(CO)_5(PMe_3)$ and $Cr(CO)_5[P(OMe)_3]$ as compared with $Cr(CO)_6$ is that the reaction rate at their exposure remains unchanged, whereas in the case of $Cr(CO)_6$ it decreases [15].

Activity of dienes estimated as the time of reaching 20% conversion, decreases in the series [15]: Buta-1,3-diene >> 2-methylbuta-1,3-diene > 2,3-dimethylbuta-1,3-diene > *s-trans*-penta-1,3-diene. Relatively low selectivity of addition of trimethyl- and triethylsilane to ethylene, propene, but-1-ene, pent-1-ene, cyclopentene, 3,3-dimethylbutyl-1-ene and 2-methylbut-1-ene was observed when iron(0) pentacarbonyl was taken as a catalyst. Products ratio depends on the structure of the silane and the silane:alkene ratio [16, 17]. For example, at the hydrosilylation of ethylene with triethylsilane the reaction products contained above 99% of alkylsilane, and in the reaction of $HSiEt_3$ with but-1-ene formed 40% of butane, 20% of trimethylbutylsilane, and 40% of three geometric isomers of trimethylsilylbutene. Increase in the alkene concentration or the temperature negatively affects the process, as in this case increases the fraction of alkenylsilanes in the reaction product [16].



The quantum yield of the reaction of pent-1-ene and trimethylsilane reaches the maximum at a temperature of 7–25°C, the reactants ratio 1:1, and the catalyst concentration 0.01 mol l^{-1}. The silicon hydride excess and lower temperature affect positively the selectivity (the yield of alkylsilane), but simultaneously a decrease is observed in the rate of photocatalytic reaction.

At the same time, when instead of linear terminal alkenes (propene, but-1-ene, and pent-1-ene) the alkenes with less accessible double bond (cyclopentene, *t*-butylethylene, isobutylene) were used, the content of alkylsilanes in the reaction product increased and the conversion of raw material decreases markedly [16]. The reaction of cyclohexene or cyclopentene with triethylsilane proceeds very slowly: The conversion of alkene is only few percent in a week.

The action of trimethyl-, triethyl- and triphenylsilanes on buta-1,3-diene and dimethylbuta-1,3-diene in the presence of iron carbonyl complexes is less selective than in the presence of $Cr(CO)_6$: not only the three geometric isomer of butenylsilane, but butylsilane and 4 isomers of bis(trimethylsilyl)butene are formed [18]. Similarly proceeds the reaction with isoprene and 2,3-dimethylbuta-1,3-diene. This is due to the high activity of the iron carbonyls in the isomerization reactions, in particular, at irradiation. In addition, with the iron carbonyls in the case of deuterosilanes there is the isotope exchange, which is possible only in the presence of alkene [18].

Due to the fact that the irradiation of iron carbonyls at room temperature leads to the formation of inactive aggregates of the metal [11], the studies are interesting [19, 20], where the metallocomplexes such as $(PPh_2Ar)_{5-n}[Fe(CO)\ _n]$ are imobilized on a polymer substrate (n = 3, 4; Ar = Ph or $C_6H_4CH_2CH_2$; phosphorylated microporous styrene polymer), and the iron carbonyl is bound to the polymer through the phosphine ligand. The advantage of these catalysts is that they do not form inactive aggregates by the reaction of the catalyst molecule with each other. The investigation of photochemical behavior of model complexes of $Fe(CO)_{5-m}(PPh_3)_m$ (m = 0–2) showed [19, 20] that the carbonyl ligand suffers photodissociation, while elimination of phosphine requires a prolonged photolysis.

$$Fe(CO)_{5-m}(PPh_3)_m \xrightarrow{h\nu} Fe(CO)_{4-m}(PPh_3)_m + CO.$$

Interaction of pent-1-ene with triethylsilane on such photoactivated catalysts leads to a mixture of *cis*- and *trans*-pent-2-enes, pentane, (*n*-pentenyl)triethylsilane, and several isomers of pentenyltriethylsilane [like the catalysis in the presence of photo-induced $Fe(CO)_5$]. The termination of the irradiation finishes the reaction, while renewal of irradiation results in the reaction reinitiation.

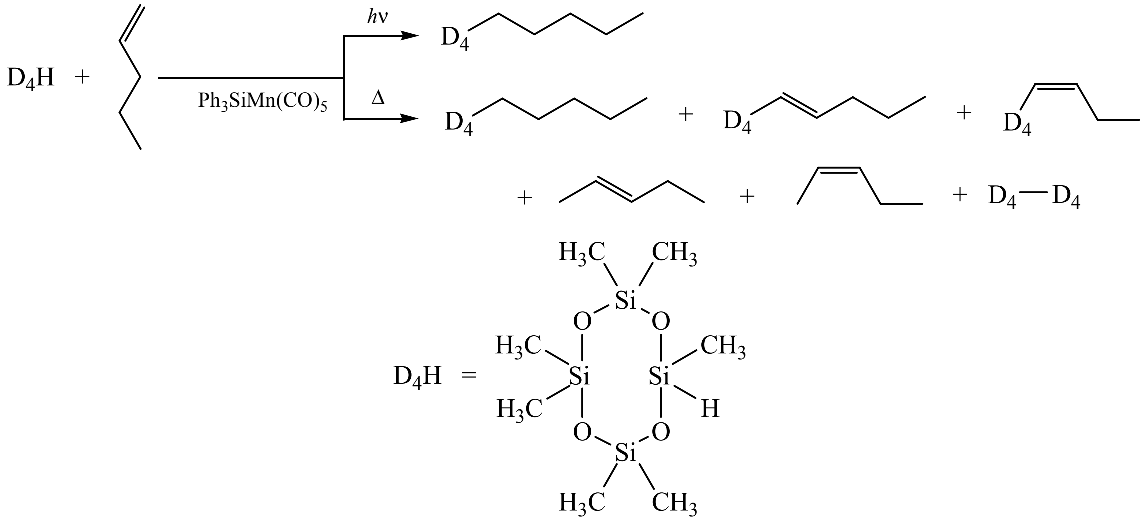
Varying the photoinduced iron catalyst has little effect on the regiospecificity of silanes addition. The catalysts are ordered by the decrease in the selectivity of the catalyzed addition of triethylsilane to pent-1-ene (solutions of the reagents in benzene and isooctane) as follows [19]: $Fe(CO)_4PPh_3$ > *trans*-$Fe(CO)_3(PPh_3)_2$ > polymer substrate-$(Ar\text{-}PPh_2)_{5-n}[Fe(CO)_n]$ > $Fe(CO)_5$.

Cobalt carbonyls used as a pre-catalysts show even lower selectivity (30%) than $Fe(CO)_5$ [21–24]. The order of decreased selectivity of cobalt catalysts in the hydrosilylation of pent-1-ene with triethylsilane is as follows [22]: $Et_3SiCo(CO)_3 > Ph_3SiCo(CO)_4 >> Co_2(CO)_8$. In the case of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ only the isomerization of the alkene was observed, while hydrosilylation does not occur at all [25].

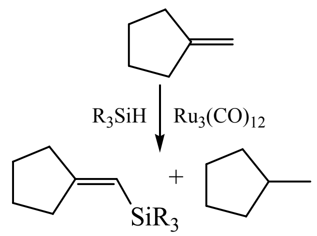
The products of pent-1-ene hydrosilylation with triethylsilane in the presence of cobalt complex [polymer]≡Si–$Co(CO)_4$ fixed on the SiO_2 or Al_2O_3 surface are *n*-pentane, *cis*- and *trans*-pent-2-enes, and triethyl(*n*-pentyl)silane [24], that is, the reduction, isomerization and hydrosilylation occur. The rate of the process varies proportionally to the intensity of irradiation, therewith, the rate of isomerization is higher than that of hydrosilylation. The catalytic activity of [polymer]≡Si–$Co(CO)_3(P(OPh)_3)$ is less than that of [polymer]≡Si–$Co(CO)_4$, and also the quantum yield and the ratio of *trans*- and *cis*-isomers of pent-2-ene are lower.

In general, photoactivated [polymer]≡Si–$Co(CO)_4$ shows an activity quite similar to that of the thermally activated $Co_2(CO)_8$. This is ascribed to the removal of $Co(CO)_4$ after the initial CO photodissociation and by the interaction of the residue with Et_3SiH which finally gives a homogeneous $Et_3SiCo(CO)_3$ [24].

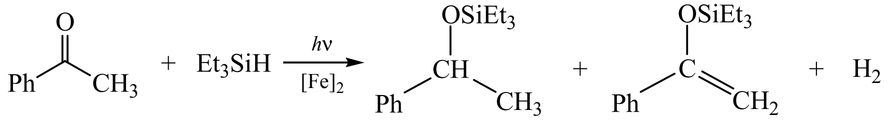
With regard to the activity of manganese carbonyls it is known [26] that at the photo-assisting the reaction of equimolar mixture of heptamethylcyclotetrasiloxane with pent-1-ene in the presence of $Ph_3SiMn(CO)_5$ affords only the product of the terminal addition at the double bond, whereas in the dark the hydrosilylation (180°C) produces a mixture of the product of the terminal addition (55%) and the isomers from dehydrogenative silylation (25%), isomers of pent-2-ene (10%, the ratio of *cis*:*trans* 7:3), and bis(heptamethylcyclotetrasiloxane) (20%):



The irradiation of a mixture of triethylsilane and pent-1-ene in the presence of trinuclear complexes $M_3(CO)_{12}$ (M = Fe, Ru, or Os) [27, 28], as in the case of mono- and binuclear coordination carbonyl compounds, leads to the formation of the products of hydrosilylation, isomerization, and hydrogenation [similarly to the catalysis with iron(0) pentacarbonyl]. The same result was obtained with the mixed-ligand carbonyl complexes of type $M(CO)_n(PPh_3)_{5-n}$ (M = Fe, Ru; *n* = 3–5), $M_3(CO)_{12}$ (M = Fe, Ru, Os), $Ru_3(CO)_3 \cdot (PPh_3)_3$, and $Co_2(CO)_8L_2$ [L = PBu_3 or $P(OPh)_3$] [29]. The ratio of the components in the product depends on the ratio of reactants (increase in the ratio of pent-1-ene:triethylsilane increases the yield of pentyltriethylsilane) and the nature of the metal [30]. $Os_3(CO)_{12}$ yields mainly the pentyltriethylsilane, $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ produce mainly the pentenyltriethylsilane isomers. The comparison of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ shows that both catalysts give the product with a very similar distribution of the components, and the ratio of the products of pentene isomerization is virtually identical [28]. $Ru_3(CO)_{12}$ is a sufficiently selective catalyst for the dehydrogenative silylation of methylenecyclopentane [28].



The carbonyl complexes have been used in the hydrosilylation of compounds at the C=O bond [25, 31, 32]. For example, hydrosilylation of acetophenone with triethylsilane in the presence of methylamino-bis (difluorophosphine) dimers of cobalt or iron occurs only at the irradiation, and the quantum yield depends on the amount of triethylsilane [25]. The activity of the catalysts decreases in the sequence: $[CH_3N(PF_2)_2]_2Fe_2\cdot(CO)_5 > [CH_3N(PF_2)_2]_3Co_2(CO)_2 > [CH_3N(PF_2)_2]_3Co_2\cdot(PPh_3)_2$, and the less active cobalt dimers are more selective and lead to a single product of hydrosilylation, whereas in the case of the iron dimer the silyl enol ether was found. Carrying out the reaction in the CO atmosphere in the presence of $[CH_3N(PF_2)_2]_3\cdot Co_2(CO)_2$ causes a decrease in selectivity (the formation of two products), whereas in the case of $[CH_3N(PF_2)_2]_3Co_2(PPh_3)_2$ the selectivity remains unchanged (one product).

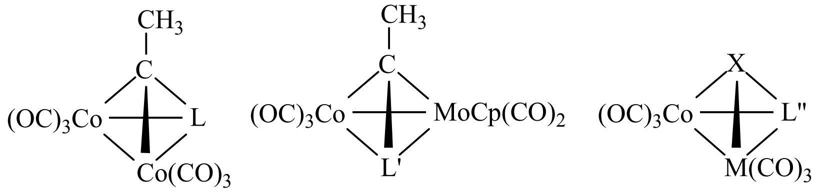


The analysis of the phototransformation of the degassed mixture of triethylsilane with acetone, heptane-2-one, butanal, or hex-1-ene in the presence of transition metal carbonyl complexes showed [31] that a good yield of the acetone silyl ether is reached in the presence of the Re, Ir, Os or Ru complexes; in the case of heptane-2-one Ir and Re complexes were the most active. In some cases dark hydrosilylation occurs after the cessation of exposure (the most effective catalysts for the thermal hydrosilylation are Ru and Os complexes).

At the same time there is a significant difference in the catalytic hydrosilylation of ketones, *n*-butanal and 1-alkenes [31]: the complexes in one case of hydrosilane addition may be inactive in other cases. For example, with ketones only trace amounts of propan-2-ol and heptan-2-ol [were detected 31], while at the hydrosilylation of alkenes the products of complete reduction formed in a good yield [28]. The quantum yield of photodissociation of the complexes falls in the series: $Re_2(CO)_{10} > Os_3(CO)_{12} > Ru_3(CO)_{12}$, but this sequence does not correlate with the activity of carbonyl complexes, which in the acetone hydrosilylation decreases in the series [31]: $Re_2(CO)_{10} > Ru_3(CO)_{12} > Ir_4(CO)_{12} \gg Co_4\ (CO)_{12} > Co_2(CO)_8 \approx Cr(CO)_6 \gg Fe_3(CO)_{12} \approx W(CO)_6 \approx Mn_2(CO)_{10} \gg Mo(CO)_6$. In the reaction with heptane-2-one the change in quantum yield coincides with the sequence of activity of the complexes: $Re_2(CO)_{10} > Ir_4(CO)_{12} \gg Os_3(CO)_{12} > Ru_3(CO)_{12} \gg Fe_3\ (CO)_{12}$, but in the case of *n*-butanal again the sequence of the pre-catalysts by activity is not the same: $Co_4(CO)_{12} > Co_2(CO)_6(PPh_3)_2 \gg Re_2(CO)_{10} \gg Cr\ (CO)_6 > Fe_3(CO)_{12} > Ir_4(CO)_{12}$.

The photoirradiation of the solution of benzaldehyde and triethylsilane in C_6D_6 in the presence of $Ru(CO)_4(PPh_3)$ and $Ru(CO)_3(PPh_3)_2$ leads to benzylsilyl ether, benzyl alcohol, and some unidentified products [32].

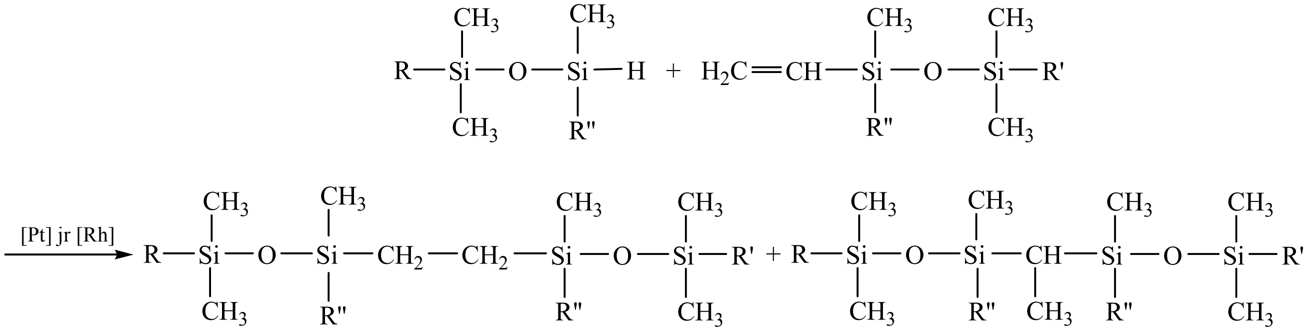
Catalytic behavior of the mixed type μ_3-carbonyl clusters of Mo, Co, Ni, and Fe discussed above is very different from that of mono-, bi- and trinuclear carbonyl complexes (with the same complexing atom). For example, hydrosilylation of phenylacetone under photoirradiation in the presence of most clusters give silyl enol ether of acetophenone and only in some cases a product of the normal addition is also formed [33]. The quantum yields on the clusters are low (from 0.028 to 0.17), the chiral complex do not lead to asymmetric induction (racemate yield 16%).



L = MoCp(CO)$_2$, NiCp; L' = Co(CO)$_2$P(OCH$_3$)$_3$, NiCp; L" = WCp(CO)$_2$, X = CH, M = Co; L" = MoCp(CO)$_2$, X = S, M = Fe; L" = Fe(CO)$_3$, X = PPh, M = Co.

Unlike this, the photochemical hydrosilylation of acetophenone with diphenylsilane catalyzed by a bridging complex Fe[(η^5-Cp)$_2$Fe$_2$(μ-H)(μ-P{Menthyl$_2$})·(CO)$_2$], allows achieving an enan-tiomeric excess (33% *ee* with respect to 1-phenyl-ethanol) [34].

Another direction of the study of photoinducing action of light is the irradiation of the platinum(II) and rhodium(I) sulfoxide, alkene, and phosphine complexes at the hydrosilylation of vinylsiloxanes [35–37] in an environment where iron pentacarbonyl does not work, or of ethylene [38].


$$R-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{R''}{\overset{CH_3}{Si}}-H + H_2C{=}CH-\underset{R''}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-R'$$

$$\xrightarrow{[Pt]\ jr\ [Rh]} R-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{R''}{\overset{CH_3}{Si}}-CH_2-CH_2-\underset{R''}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-R' + R-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{R''}{\overset{CH_3}{Si}}-\underset{CH_3}{CH}-\underset{R''}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-R'$$

R = H, R" = CH$_3$; R = CH$_3$, R" = CH$_3$, OSi(CH$_3$)$_3$; R' = CH=CH$_2$, R" = CH$_3$; R' = CH$_3$, R" = CH$_3$, OSi(CH$_3$)$_3$.

The photoirradiation can reduce the induction period of reaction in the case of phosphine platinum catalysts [36] and increase the rate of hydrosilylation with phosphine rhodium [35, 36], alkene and sulfoxide platinum complexes [37] compared with the dark process. A significant increase in the efficiency of irradiation of the phosphine catalysts is reached in the presence of oxygen due to the oxidation of phosphine and elimination of poorly coordinated phosphine oxide (in the absence of oxygen, the phosphine only dissociates), but in the case of alkene and sulfoxide complexes the oxygen content has no effect on the catalysis.

$$R_3PO + [M(R_3P)_{3-n}Cl_n] \xleftarrow[O_2]{h\nu} [M(R_3P)_{4-n}Cl_n] \xrightleftharpoons{h\nu,\ Ar} [M(R_3P)_{3-n}Cl_n] + R_3P$$

M = Pt, Rh; n = 1, 2.

The quantum yield of the photooxidation (secondary photoreaction at the irradiation) falls in going from phosphines to phosphites, and reaches a minimum with P(OPh)$_3$ (0.0001). Apparently this explains the too low activity of [Rh(POPh$_3$)$_3$Cl] in the hydrosilylation [35]. The complexes derived from alkylphosphites presumably have a binuclear structure, and their activity decreases in going from tributylphosphite to triethyl phosphite [35].

Among rhodium catalysts, the maximum efficiency shows [HRh(Ph$_3$P)$_2$Cl(SiMe$_2$Cl)] (generated thermally or by irradiation from the Wilkinson catalyst with Me$_2$SiHCl), and it does not depend on the temperature (25–70°C) and irradiation. The activity in the hydrosilylation of the irradiated Wilkinson catalyst is comparable to that of [HRh(Ph$_3$P)$_2$Cl(SiMe$_2$Cl)] (70°C) [35], but it is significantly lower than the activity of the phosphine platinum complexes [Pt(R$_2$R'H)$_2$Cl$_2$]

(X = P, R = Me, R' = Ph; X = P, As, Sb, R = R' = Ph or Bu) [36].

The optimal with respect to the hydrosilylation rate in the presence of phosphine platinum complexes is a one-minute exposure, and the influence of ligands on the efficiency of the photoactivated catalyst is markedly different from the dark process, for example, by a sequence of decrease in the reaction induction period [36]: $Ph_3P > Bu_3P >> Me_2PhP$. The ability of concurrent reduction of the complexes by organosilicon compounds decreases in the series [36]: $HMe_2SiOSiMe_3 > (HMe_2Si)_2O >> MeSiHCl_2 >> [(CH_2{=}CH)Me_2Si]_2O$.

The irradiation of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ in deuterobenzene in the presence of trimethyl- or triethylsilane leads to the coordination of silanes. At the ethylene hydrosilylation with triethylsilane in the presence of such a catalyst tetraethylsilane and triethylvinylsilane are formed, and in the case of trimethylsilane are formed ethyltrimethylsilane, vinyltrimethylsilane and 1,2-bis(trimethylsilyl)ethane. The hydrosilylation of vinyltrimethylsilane, in its turn, gives 1,2-bis(trimethylsilyl)ethane [38].

The change in the irradiation duration at the hydrosilylation in the presence of platinum(II) complexes of general formula $[Pt(L)(L')Py(X)_2]$ [L = methyl-*p*-tolylsulfoxide, L' = methyl-*p*-tolylsulfoxide, $CH_2{=}CH_2$, Py; L = L' = methyl-*p*-tolylsulfoxide or Et_2SO; X = NO_3, Cl, Br or $1/2(C_2O_4)$] or $[Pt(MeCOD)Cl_2]$ has almost no effect on the selectivity of hydrosilylation but increases the rate of formation of the product of double addition (β,β-addition due to the two functional groups in tetramethyldisiloxane), which is proportional to the photoactivation duration [37]. The photolysis of these complexes causes the dissociation of the neutral ligand, the greatest effect of irradiation is observed for $[Pt(MeCOD)Cl_2]$. The activation energy of hydrosilylation in the presence of $[Pt(MeCOD)Cl_2]$ is equal to 11.2±0.5 kJ mol^{-1} ($\ln k_0 = 2.5$) [37], which is 3 times lower than the E_a in the dark process [33.6±1.6 kJ mol^{-1} ($\ln k_0 = 10.72$)] [39].

The effect of the nature of other neutral ligands in these complexes at the photoirradiation is not so expressed as in the case of the platinum(II) phosphine complexes. Among sulfoxide catalysts, a higher activity exhibit the *cis*-bis-sulfoxide complexes, because of their greater sensitivity to the quantum of light, while the photoactivation of *trans*-(–)-[Pt(methyl-*p*-tolylsulfoxide)$PyCl_2$] is inefficient because of its inability to photodissociation [37]. The activity of platinum(II) complexes in hydrosilylation of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with 1,1,3,3-tetramethyldisiloxane decreases along the series of the neutral ligands: Methyl *p*-tolyl sulfoxide ≈ $CH_2{=}CH_2$ > MeCOD > Et_2 SO > Py.

The maximum effect of photoirradiation on the rate of hydrosilylation is observed in the presence of bis-sulfoxide complexes containing oxalate ligand as a second photosensitive center. The effect of anionic ligand environment on the activity of photoactivated bis-sulfoxide catalysts decreases in the sequence [37]: $C_2O_4^{2-} > NO_3^- > Cl^- >> Br^-$.

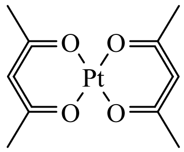
Reactions of methyldichlorosilane with hept-1-ene, *trans*-pent-2-ene and pent-1-ene, and triethoxysilane, triethylsilane and triphenylsilane with hept-1-ene can be carried out successfully in the presence of immobilized phosphine–oxalate platinum(II) complexes [40]. However, the light in this case acts on anionic ligand, leading to the formation of highly active 14-electron platinum center. Fixation of this complex on a surface through the interaction of silanol groups of silica with a phosphine ligand $(Me_3O)_3Si(CH_2)_2PEt_2$ allows avoiding the transformation of the immobilized bimolecular complex into the metal platinum and $Pt(phosphine)_4$ or $Pt(phosphine)_3$.

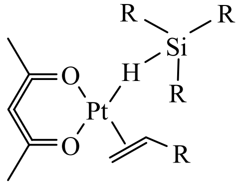
Fixed phosphine–oxalate complex is a quite active photoinducible catalyst, exceeding its not fixed analogue $[Pt(PEt_3)_2C_2O_4]$ that catalyzes the reaction only after ~8 h induction period (after 40 min of irradiation). Irradiation of oxalate complex in the solution of silane in noncoordinating solvents hexane or cyclohexane gives a more effective catalyst than similar solutions in an alkene (the second reactant is added after the photolysis).

Optimal exposure in the terms of the hydrosilylation rate is 45 min. The use of a tenfold excess of alkene compared with silane inhibits the reaction, whereas at low concentrations of alkene the rate does not depend on its concentration (zero order reaction with respect to olefin and first order on the silane). Excess phosphine, like the coordinating solvents, retards the hydrosilylation. Oxygen slowly poisons the catalyst.

The following series of activity of silanes at the hydrosilylation of hept-1-ene in the presence of fixed catalyst is observed [40]: $MeSiHCl_2 > (EtO)_3SiH > Et_3SiH >> Ph_3SiH$.

Such a good effect of a photon on the anion generated a significant amount of work on the photoactivated hydrosilylation in the presence of β-dicerbonyl complexes. They include the hydrosilylation in the presence of bisacetylacetonate platinum(II) complex [41–45], trimethyl(β-dicarbonyl)platinum(IV) [46–49] or other bis(β-diketonates) [42, 50]. Complexes with bis(β-diketonates) activated by UV light yield homogeneous catalyst losing a bidentate ligand in the presence of the silicon hydride or olefin (their presence is usually necessary for the effective formation of the active form of platinum catalyst [42]). The resulting new complex is the active primary catalyst, and further reaction takes place without light. Also, the formation of less active heterogeneous catalyst consisting of Pt^0 colloid (both the work of two catalysts [42], and the formation of platinum colloids after hydrosilylation [41] has been assumed).

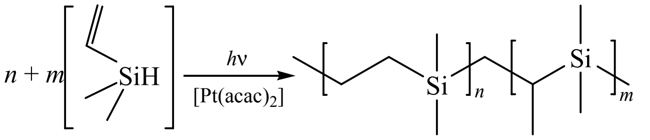




Typically, oxygen, mercury, and dibenzocyclooctatetraene inhibit addition. This relates to the testes showing a homogeneous nature of the formed catalyst.

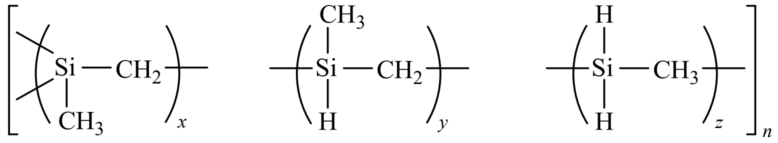
Reductive photoelimination of acetylacetonate in a platinum(II) complex under irradiation with visible light causes the formation of a gel in the mixture of vinylpolydimethylsiloxane bearing terminal active groups with polymethylhydrosiloxane with terminal trimethylsilyl groups [43].

Photolysis of a mixture of $[Pt(acac)_2]$ with vinyldimethylsilane leads after a short induction period (5 min) to a fast consumption of the vinyl substrate due to polymerization in the hydrosilylation, dimerization (formation of 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane and 1,1,4,4-tetramethyl-1,4-dicyclohexane) and oligomerization [41] reactions. The molecular weight of polymer formed is the higher, the shorter exposure time.



$n > m$

Catalytic activity of the catalyst is comparable to the activity of the hexachloroplatinic acid [41].The reaction at low concentrations of silane (0.5 mol l^{-1}) is inhibited not only by mercury, but also by DMF, however, it does not depend on the presence or absence of oxygen. Additionally, at mixing the monomer and the catalyst an intermediate 1,1,4,4-tetramethyl-1,4-disilahex-5-ene is formed, which in 10 min after the reaction beginning is consumed completely [41].



$x = 29\%$, $y = 39\%$, $z = 32\%$.

The cross-coupling in the reaction of hydrosilylation of oligo(methylsilylmethylene) and tetravinylsilane can be successfully performed in the presence of photoactivated mixture of *cis* and *trans* isomers of the platinum(II) bis(β-diketonate) complexes: dibenzoylmetanate $[Pt(dbm)_2]$, 1-benzoylacetonate $[Pt(bac)_2]$, 1,1,1-trifluoro-2,4-pentandionate (triftoracethylacetonate) $[Pt(tfac)_2]$, 1,1,1,5,5,5-hexafluoro-2,4-pentandionate (hexafluoroacetylacetonate) $[Pt(hfac)_2]$, and 4,4,4-trifluoro-1-phenyl-1,3-butadionate (benzoyltrifluoroacetonate) $[Pt(btfac)_2]$, or acetylacetonate catalysts [50, 51]. However, the catalysts are capable of photodegradation, the photodegradation rate decreases in the series of the complexes: $[Pt(bac)_2] > [Pt(dbm)_2] > [Pt(btfac)_2] \approx [Pt(hfac)_2] > [Pt(tfac)_2] > [Pt(acac)_2]$.

The hydrosilylation is characterized by high initial rate followed by deceleration. The cross-coupling is realized through a SiH group. In the case of $[Pt(acac)_2]$ and $[Pt(bac)_2]$ both SiH groups of oligomer are involved, while in the presence of $[Pt(acac)_2]$ the addition is more selective. The reaction mixture hardens during the process (the transformation of the polymer from a liquid to a solid state takes several minutes), the minimum exposure time for curing the composition varies for the photirradiated catalysts in the following order: [Pt(hfac)$_2$] > [Pt(tfac)$_2$] > [Pt(btfac)$_2$] > [Pt(acac)$_2$] > [Pt(bac)$_2$] > [Pt(dbm)$_2$]. Activity of the catalysts, estimated from SiH consumption, decreases in the series ($\lambda > 340$ nm): [Pt(bac)$_2$] > [Pt(acac)$_2$] > [Pt(hfac)$_2$] > [Pt(tfac)$_2$] > [Pt(btfac)$_2$] > [Pt (dbm)$_2$]. An increase in the radiation wavelength of the source ($\lambda > 400$ nm) has little effect on the activity of the complexes, except for [Pt(acac)$_2$], which is less active than [Pt(hfac)$_2$], but more than [Pt(tfac)$_2$]. High activity of irradiated [Pt(hfac)$_2$] apparently is due to its ability to catalyze the process not only during the irradiation, but also in the dark [50].

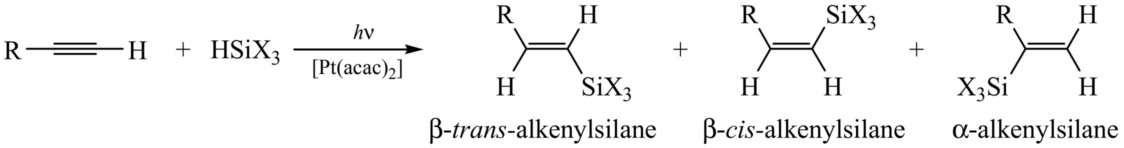
The irradiation of triethylsilane and triethylvinylsilane in the presence of [Pt(acac)$_2$] leads along with the product of hydrosilylation of $Et_3SiCH_2CH_2SiEt_3$ to a small amount of the reduced and silylated olefins (<2%) [42]. For this system a ten-minute exposure is the best (although after 10 min the yield is less than 5%), followed by the dark reactions (30–40 min), but at the generation of complex in the $HSiEt_3$ medium the best results were obtained at 30–60 min photolysis.

The rate of the triethylvinylsilane hydrosilylation in the presence of photoactivated platinum β-diketonates decreases in the order: [Pt(acac)$_2$] ≥ [Pt(bac)$_2$] ≥ [Pt(dbm)$_2$] >> [Pt(hfac)$_2$]. The irradiation of nickel and palladium acetylacetonates leads to destruction of the complexes to H(acac) and metal, which do not catalyze the reaction [42].

The nature of hydrosilane and vinylsilane has a significant effect on the hydrosilylation rate, which in the presence of [Pt(acac)$_2$] and [Pt(benzoylacetonate)$_2$] decreases in the series of the silicon hydrides: $(EtO)_3SiH > MeHSiCl_2 > Et_3SiH > Bu_3SiH >> Ph_3SiH >>$ *i*-PrSiH, and in the series of the vinyl substrates in the sequence [42]: $ViEt_3Si > ViSiCl_3 >$ styrene > methyl methacrylate >> 1-hexene.

Hydrosilylation of 1-, 2-, and 3-hexynes, phenylacetylene, diphenylacetylene, hex-1-ene with the silanes Ph_3SiH, Et_3SiH, $(EtO)_3SiH$, Et_2SiH_2, Me_2ClSiH, and triisopropylsilane in the presence of photoactivated [Pt(acac)$_2$] was investigated in [44]. The initial photoreaction rate increases with increasing concentrations of the alkyne and catalyst and with the irradiation duration, however, when the catalyst concentration is 5×10^{-4} mol l^{-1} or higher, the exposure duration has no effect [42, 44]. The following dark reaction is slower than the photoactivated one, but repeated exposure increases the rate [44]. Activity of silanes in the reaction with hex-1-yne decreases in the order: $HSiPh_3 > HSiMe_2Cl > HSi(OEt)_3 > HSiEt_3 > H_2SiEt_2$.

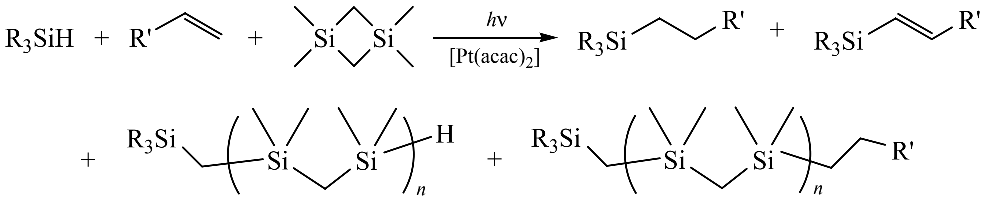
Terminal alkynes react with $HSiEt_3$ faster than internal; aromatic alkynes show high activity (phenylacetylene reacts faster than the hex-1-yne). Alkenes exhibit less activity than alkynes, and, for example, at the competing photocatalytic hydrosilylation with triethylsilane of a mixture of hex-1-yne with styrene the reaction occurs only with hex-1-yne [44].



The β-*trans*-isomer is formed mainly, and its amount relative to the α-isomer increases with the internal alkynes compared with the terminal. Changes in the reactant ratio affect the isomers ratio insignificantly, and the reaction duration and the catalyst concentration do not affect the ratio of the components in the product [44].

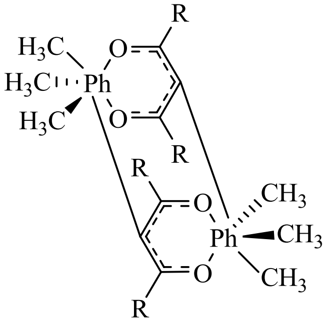
It was noted [44] that the catalytically active species were formed at the joint exposure of alkyne and silane, and separate exposure decreased the reaction system activity, the lowest activity was observed after irradiation with Et_3SiH.

The interaction of the irradiated mixture of a hydrosilane [Et_3SiH, $(EtO)_3SiH$ or (*i*-Pr)$_3$SiH], olefin and 1,1,3,3-tetramethyl-1,3-disilacyclobutane in the presence of [Pt(acac)$_2$] depends on the structure of the reactants used and leads to the products of hydrosilylation, dehydrogenative silylation, telomerization of disilacyclobutane, and the subsequent hydrosilylation of olefin with the formed oligomer [45]. The reaction of $Et_3Si(CH{=}CH_2)$ with $(i\text{-}Pr)_3SiH$ and disilacyclobutane is slower than with $(EtO)_3SiH$, and gives a mixture of products of direct hydrosilylation (19%), dehydrogenative silylation (27%), and hydrosilylation with the telomerized oligomer (54%, $n = 1$), whereas in the case of $(EtO)_3SiH$ the main direction of the reaction is the hydrosilylation (97%). The main process in the case of oct-1-ene is its isomerization (82%), and the maximal yield of the products of hydrosilylation with the telomerized oligomer is observed in the reaction of disilacyclobutane, Et_3SiH, and styrene ($n = 1$, 44%; $n = 2$, 29%) [45].

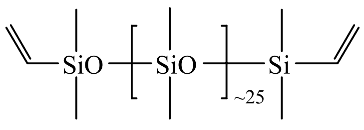


R = Et, EtO, *i*-Pr; R' = Et_3Si, $(EtO)_3Si$, Ph, $COOCH_3$, $(CH_2)_5CH_3$; $n = 1, 2, ...$

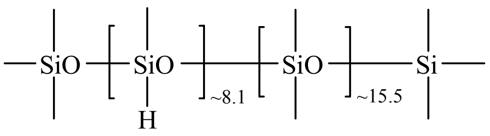
Hydrosilylation of oct-1-ene with pentamethyldisiloxane photoactivated in the presence of trimethyl(β-dicarbony)platinum(IV) proceeds very rapidly [46]. Inverse relationship between the rate of consumption of oct-1-ene and its concentration was observed. The hydrosilylation of industrial oligomers containing siliconvinyl and siliconhydride groups [46–49] proceeds similarly.



R = CH_3, CF_3, Ph, OEt.



PR1



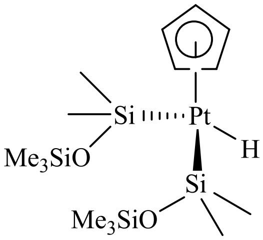
PR2

Trimethyl(β-dicarbonyl)platinum(IV) forms under irradiation a homogeneous catalyst converting gradually into an inactive colloidal platinum (colloidal solution is stable for several hours in acetonitrile), especially under irradiation with a wavelength of 254 nm.

The activity of platinum catalysts depends on the nature of the substituents in β-dicarbonyl ligand. At the hydrosilylation of the oligomers RP1 and RP2 the activity decreases in the series of the substituents: OEt > CH_3 > CF_3 > Ph. The $[Pt(acac)_2]$ is more active only than phenyl-containing β-dicarbonyl complex [46].

Another interesting example of photoactivation of the metal complex is the η^5-cyclopentadienyl platinum catalysts irradiated with UV light, transforming into active colloidal platinum catalyst (particle size 10 nm) [52–54]. Its activity is comparable with that of trimethyl(β-dicarbonyl)complexes of platinum(IV) containing the ethoxy group [46].

Photolysis of $[PtCpMe_3]$ in hydrosilane solution leads to a new complex (the rate depends on the concentration of silane), which contains hydrogen instead of methyl ligands and two organosilicon groups [52].



The quantum yield of photochemical reaction of (η^5-cyclopentadienyl)trimethylplatinum(II) in pentane in the presence of triethylsilane is 0.79–0.83, which is higher than in pure pentane (0.41) or methylcyclohexane (0.34) [56]. The organosilicon group coordinating at the photolysis, in its turn, can be replaced by other silicon hydrides, $(HMe_2SiCH_2)_2$ and $(HMe_2SiO)_2SiMe_2$, under the reaction conditions [52]. The resulting platinum–silyl complexes are active in the thermal hydrosilylation after the induction period of reaction, in contrast to the original $[PtCpMe_3]$, which does not catalyze the reaction in the dark. It suggested [52] that silylmethylhydride derivative $[PtCpMe(SiR_3)H]$ is formed interim between the bis-(silyl)hydride complexes of platinum and the true catalyst, colloidal platinum. The rate of photodegradation of platinum complexes increases in the following series [52]: $[CpPtMe_3] \approx [(C_5H_4Me)PtMe_3] < [C_5H_4(SiMe_2Ph)]PtMe_3 < [(C_5Me_5)\ PtMe_3] < [CpPtMe_2(CH_2CH{=}CH_2)]$. The photoactivated $[CpPt(alkyl)_3]$ complex leads to a very rapid formation of products of hydrosilylation of oct-1-ene with 1,1,3,3,3-pentamethyldisiloxane or 1,1,3,3,5,5-hexamethyltrisiloxane [52] and is more effective compared to other platinum catalysts at the hydrosilylation of hydride and vinyl-containing silicone mixture [55] or aliphatic unsaturated compounds [53].

The irradiation of (η^5-cyclopentadienyl)trialkylplatinum(II) with near UV light in the presence of polycyclic aromatic sensitizers absorbing visible light catalyzes successfully the reaction of hydrosiloxanes $R_nSi[(OSiR_2)_pR]_{4-n}$ [R = H, (cyclo)alkyl, Ph, $\le$ 50% R = H; n = 0–3, p = 1–3000] with vinylsiloxanes $R'_mSi[(OSiR')_tR']_{4-m}$ [R' = halogenated (cyclo)alkyl, Ph, halogenated unsaturated C=C group; t = 1–3000; m = 0–3] [54].

At the irradiation of (methyl-η^5-cyclopentadienyl) trimethylplatinum(II) micron-sized three-dimensional polydimethylsiloxanes are formed [56]. After the absorption of two photons the catalyst remains active in the absence of irradiation. This leads to a decrease in the resolution of the formed net, but it is important for the cross-linking the polysiloxane surfaces together. Use of isopropylthioxanotone (an initiator of radical polymerization) instead of the platinum catalys allows to avoid the dark hydrosilylation, and hence leads to the material with a greater variety of microstructures with high resolution [56].

Other examples of the light action on the catalytic system at hydrosilylation is the irradiation of a mixture of unsaturated cyclic hydrocarbon compounds (e.g., cyclohexene) and a halosilane (for example, $MeSiHCl_2$) in the presence of catalytic amounts of H_2PtCl_6, leading to (cyclohexyl)methyldichlorosilane with 90% yield [57], or irradiation of a mixture of polyorganosiloxanes with the compounds containing a C=C bond and the atoms O, N, P and/or Hlg, in the presence of oxygen and a vinylsiloxane-platinum complex [58], or the creation of a sealant with improved adhesion to plastic, containing silicon fluid, hydrogen- and vinyl-containing polysiloxanes, and a hydrosilylation photocatalyst [59].

Thus, photoactivation of the metal is effective at the hydrosilylation of alkenes, dienes, vinylsilanes and siloxanes, alkynes, aldehydes and ketones, and in the case of prochiral raw material it may proceed with asymmetric induction. The irradiation affects the inner coordination sphere of the metal complex facilitating the first stage of the catalytic cycle consisting in the coordination of the reactants, and consequently increases the reaction rate or reduces its induction period. In most cases, the hydrosilylation selectivity under photoirradiation is comparable to the dark process with the use of alternative catalysts. However, there are exceptions: for example, the flash photolysis of (η^3-2-methyl-2-aza-5,7-octadiene)tetracarbonyltungsten(0) produces the 1,2-addition product selectively, whereas in the dark the hydrosilylation does not occur. High activity in hydrosilylation show photoactivated β-diketonate and η^5-cyclopentadienyl catalysts, while the carbonyl complexes capable of photo-elimination of CO mostly are not promising because of the side processes occurring in the presence of these catalysts.

Anyway, the potential of the photoactivated catalysts for the hydrosilylation has not been fully explored so far, and the most active and selective catalysts can be found among the complexes of precious metals, platinum and rhodium.

ACKNOWLEDGMENTS

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