Non-classical hydrosilane mediated reductions promoted by transition metal complexes

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Abstract

This article reviews the most recent advances on the study of non-classical mechanisms for the reduction of organic substrates with hydrosilanes catalyzed by transition metals. A wide variety of catalytic cycles that go beyond the classical steps described for Ojima, Chalk-Harrod and modified Chalk-Harrod mechanisms, as representative examples, have been proposed in recent years. In this review, these alternative mechanistic proposals have been analyzed and classified according to the type of substrate, focusing on the reduction / hydrosilylation of carbonyl compounds (ketones and aldehydes), carbon dioxide, silylesters, amides, *N*-heterocycles, alkyl halides, nitriles, alkenes and alkynes. In spite of the broad diversity of non-classical reaction mechanisms hitherto reported, the catalytic cycles described for each substrate have been arranged in different categories according to their characteristics. The epigraph dedicated to the first type of substrate (carbonyl compounds) comprises most of the mechanisms described in this review for the reduction of polar bonds, which, to some extent, show a relationship to those proposed for non-polar bonds (alkenes and alkynes). Remarkable types of reaction mechanisms that will be dealt with in this work are: ionic mechanisms, ligand-assisted mechanisms, nonhydride mechanisms, NHC-Cu-H mediated mechanisms, and silylene-mediated mechanisms.

List of abbreviations

POCOP, 1,3-bis((diphenylphosphino)oxy)benzene and related ligands; NHC, N-heterocyclic carbene; Cp, cyclopentadienyl; Cp*, 1,2,3,4,5-Pentamethylcyclopentadienyl; py, Pyridine; Mes, mesityl; DFT, Density Functional Theory; saldach, N,N'-cyclohexanediylbis(salicylideneimine); Ar, Generic aromatic substituent; Tp = tris(pyrazolyl); KIE, Kinetic Isotope Effect; Me, methyl; Et, Ethyl;

Ph, phenyl; Bn, benzyl; Pr, propyl; PNN, 6-(di-tert-butylphosphinomethylene)-2-(N,N-diethylamino-methyl)-1,6-dihydropyridine; FLP, frustrated Lewis pairs; Tf, Trifluoromethanesulfonyl; Ac, acetyl; coe, cyclooctene; phen = phenanthroline.

Keywords

Homogeneous catalysis; Hydrosilylation; Silane; Reduction; Transition metal.

Dedication

Dedicated to Professor Armando J.L. Pombeiro for his outstanding achievements in Coordination Chemistry and Catalysis

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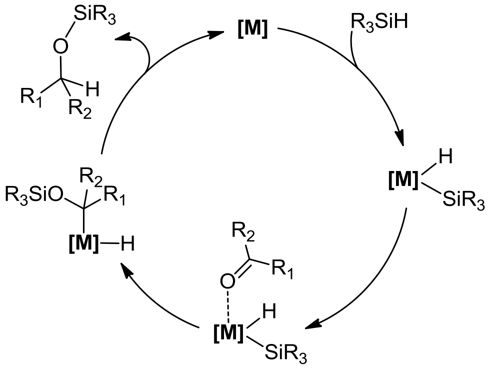
References

1. Introduction

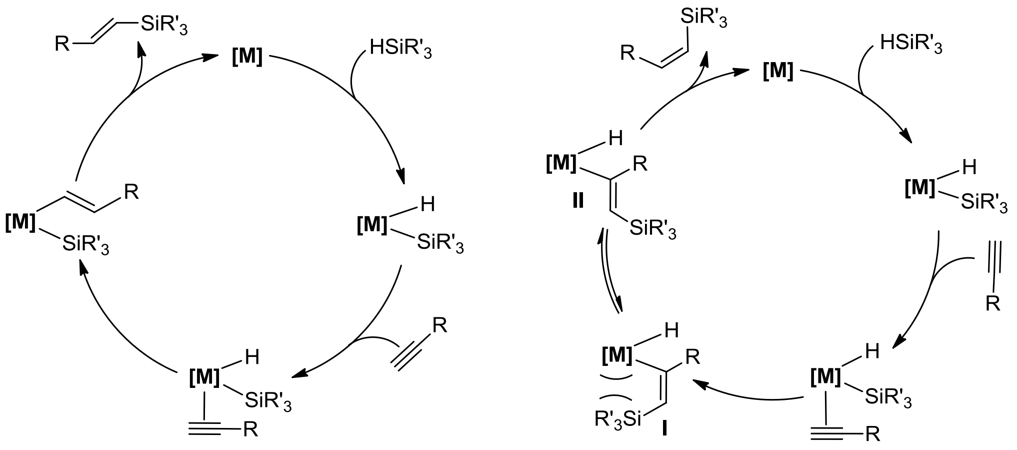
The catalytic reduction of organic molecules with hydrosilanes is of great importance in modern synthetic chemistry. These silicon reagents are easily available, non-toxic and liquid (or solid) at room temperature. The organosilanes obtained from the reduction of organic compounds are often valuable intermediates for the preparation of complex molecular architectures, or even intrinsically interesting materials [1]. Moreover, the use of silanes as reducing agents circumvents the use of stoichiometric amounts of metallic hydrides or reactions under elevated pressure with molecular hydrogen. A wide variety of substrates can be reduced by hydrosilanes under mild conditions (e.g. aldehydes, ketones, alkynes, alkenes, imines, nitriles, amides, ethers, esters or CO_2) using homogeneous catalysts (transition metal complexes, Lewis acids or bases). The synthetic versatility shown by hydrosilane mediated reductions led to a thorough study of the reaction mechanisms involved in these transformations. This review will focus on reactions catalyzed by transition metal complexes that take place by means of non-classical mechanisms. For that purpose, we will consider classical reaction mechanisms those consisting of conventional elemental steps (oxidative addition, reductive elimination, migratory insertion, β-hydride elimination); in this case, reaction pathways related to the Ojima and Chalk-Harrod mechanisms [2]. The common ground for all these mechanisms is that all of them entail the oxidative addition of the Si–H bond followed by migratory insertion of the substrate into the M–Si or M–H bond. Reductive elimination of the silylated product restarts the catalytic cycle.

The Ojima mechanism for the hydrosilylation of carbonyl compounds (polar bonds) involves initially the oxidative addition of the Si–H bond, followed by coordination of the substrate (a ketone in Scheme 1). Subsequently, the ketone undergoes migratory insertion into the M–Si bond. Finally, reductive elimination of the silylether regenerates the active species [3].



Scheme 1. Ojima mechanism for the hydrosilylation of ketones.

The Chalk-Harrod and modified Chalk-Harrod mechanisms (Scheme 2) have been proposed for the hydrosilylation of alkenes and alkynes (non-polar bonds). In the case of alkynes, the Chalk-Harrod mechanism was initially proposed to explain the formation of β-(E)-vinylsilanes. The first step is the oxidative addition of the Si–H bond, analogous to Ojima's mechanism. Successively, alkyne coordination followed by 1,2-migratory insertion into the M–H bond takes place. The β-(E)-vinylsilane is generated by reductive elimination together with the active catalyst. The modified Chalk-Harrod mechanism, on the other hand, was postulated to explain the formation of the β-(Z)-vinylsilane. The main difference with the Chalk-Harrod mechanism is the migratory insertion step, which is a 2,1-migratory insertion into the M–Si bond. The resulting alkenyl intermediate **I** isomerizes to **II** due to steric interactions between the ancillary ligands and the SiR_3 moiety. Then, reductive elimination from **II** would explain the formation of the β-(Z)-vinylsilane. The isomerization of **I** to **II** has been proposed to occur by two different reaction intermediates, the metallacyclopropene or the zwitterionic carbene proposed by Crabtree [4] and Ojima [5], respectively.



Scheme 2. Chalk-Harrod (left) and modified Chalk-Harrod (right) mechanisms for the hydrosilylation of terminal alkynes.

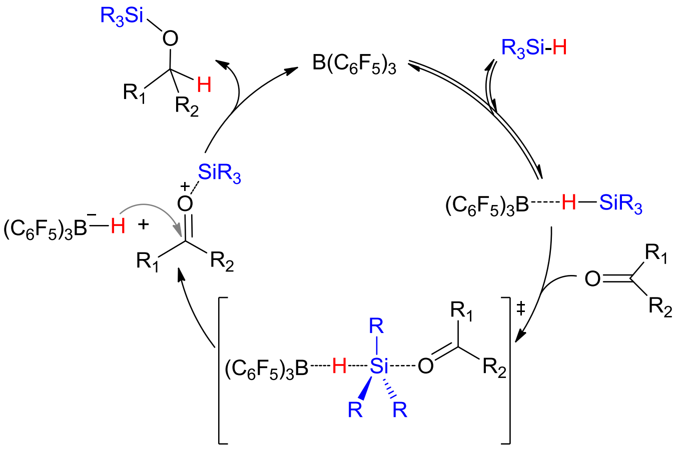
A great wealth of new reaction mechanisms for the reduction of organic molecules with hydrosilanes has been so far reported. The type of mechanism that operates depends on the substrate, silane and nature of the catalyst (ligand system, metal center and oxidation state). This review aims to gather and discuss the most relevant non-classical mechanisms proposed for the reduction of organic substrates with hydrosilanes.

2. Hydrosilylation of carbonyl compounds

The hydrosilylation of carbonyl compounds has been extensively investigated from a mechanistic viewpoint. In recent years, a wide variety of new mechanisms has been disclosed, including ionic, ligand assisted, NHC–Cu–H-mediated mechanisms, silylene-mediated or σ-bond metathesis mechanisms.

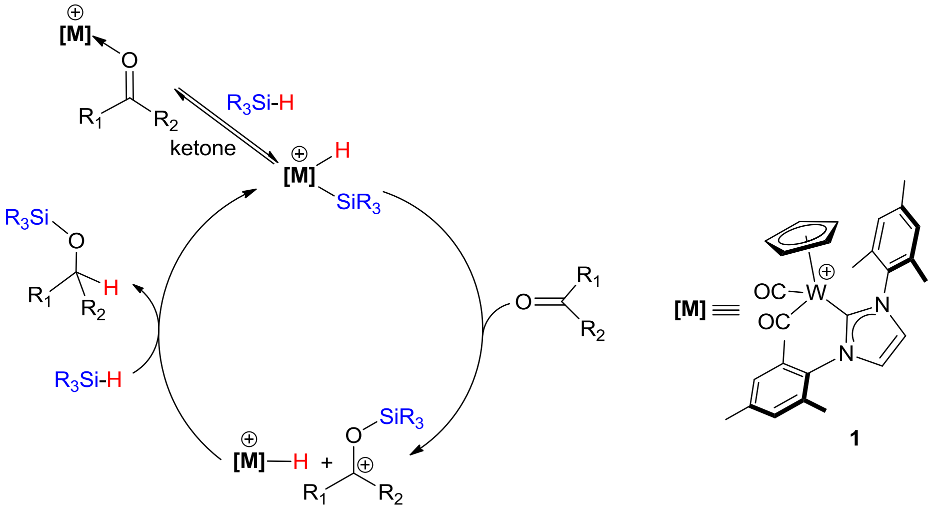
2.1. Ionic mechanisms

Initial studies by Piers on the hydrosilylation of carbonyl compounds catalyzed by Lewis acid boranes, e.g. tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) [6], later revisited by Oestreich [7], resulted in the postulation of the first ionic mechanism for this type of reaction (Scheme 3). The first step implies the activation of the Si–H bond of the silane by the borane, which then undergoes the nucleophilic attack of the carbonyl compound by an S_N2 mechanism. This results in the heterolytic cleavage of the Si–H bond, with concomitant formation of the oxocarbenium (silylcarboxonium) cation. The last step consists of the nucleophilic attack of the hydride on the carbonyl carbon to afford the silylether.



Scheme 3. Catalytic cycle proposed by Piers and Oestreich for the hydrosilylation of carbonyl compounds catalyzed by $B(C_6F_5)_3$.

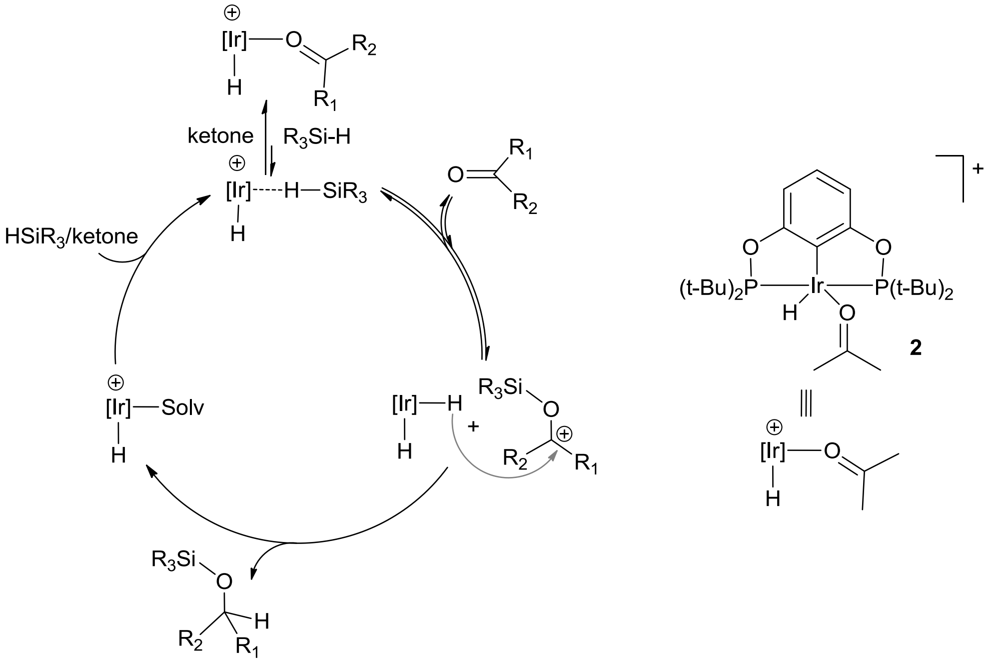
A related mechanism was proposed later by Bullock et al. for the hydrosilylation of ketones catalyzed by organometallic tungsten complex **1**, $[W(CO)_2(Cp)(IMes)][B(C_6F_5)_4]$ (Cp = cyclopentadienyl, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [8]. The first stage of the mechanism encompasses the oxidative addition of the silane to the metal center, analogous to a classical mechanism. However, the next step involves the transfer of the silylenium ion to the carbonyl compound to give the corresponding carbocation (oxocarbenium cation), probably by an ionic mechanism, although the authors did not discard a certain concerted character. Abstraction of the hydride ligand by the carbocation yields the silylether closing the catalytic cycle (Scheme 4). Therefore, the first part of the cycle resembles a classic mechanism, while the last stages are reminiscent of an outer-sphere ionic mechanism.



Scheme 4. Bullock's mechanism for the hydrosilylation of ketones with $[W(CO)_2(Cp)(IMes)][B(C_6F_5)_4]$ (**1**).

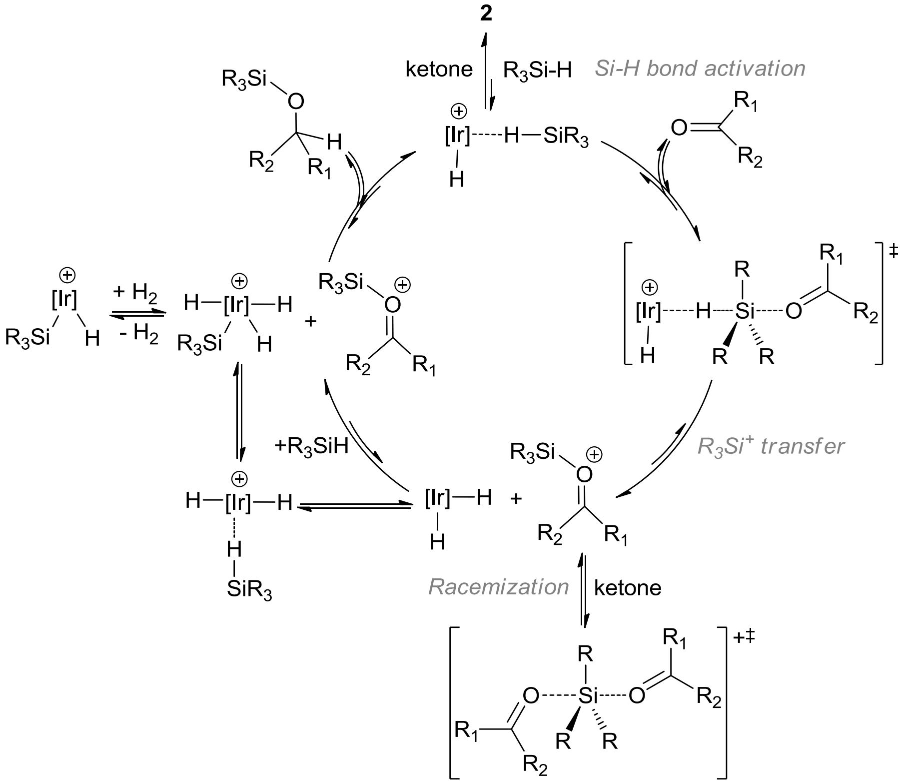
Remarkably, this complex catalyzes the hydrosilylation of a variety of aromatic and aliphatic ketones under solvent-free conditions at 296 K, showing excellent selectivities for carbonyl versus alkene functionalities. Furthermore, the catalyst self-separates at the end of the reaction due to a change of polarity in the reaction media as the reaction proceeds (a polar ketone is transformed into a non-polar silylether), which allows the straightforward recovery and recycling of the catalyst.

An analogous mechanism to that proposed for the borane-catalyzed ionic hydrosilylation of ketones was proposed by Brookhart and co-workers employing POCOP-Ir complex (**2**) as catalyst (Scheme 5) [9]. Based on NMR experiments, the authors propose an equilibrium between the catalyst (acetone complex) and an end-on hydrosilane (η^1-H(Si) species), which is sharply displaced to the formation of the acetone complex. The strongly electrophilic Ir center in **2** is able to abstract a hydride form R_3SiH to generate a dihydride species and R_3Si^+, which reacts with the ketone to afford the oxocarbenium ion. Hydride transfer from the metal center to the carbonyl carbon affords the hydrosilylated product. The vacant site thus generated is occupied by a solvent molecule, and subsequent silane or ketone coordination restarts the catalytic cycle. This mechanistic proposal has been substantiated by the DFT studies performed by Wei and co-workers [10].



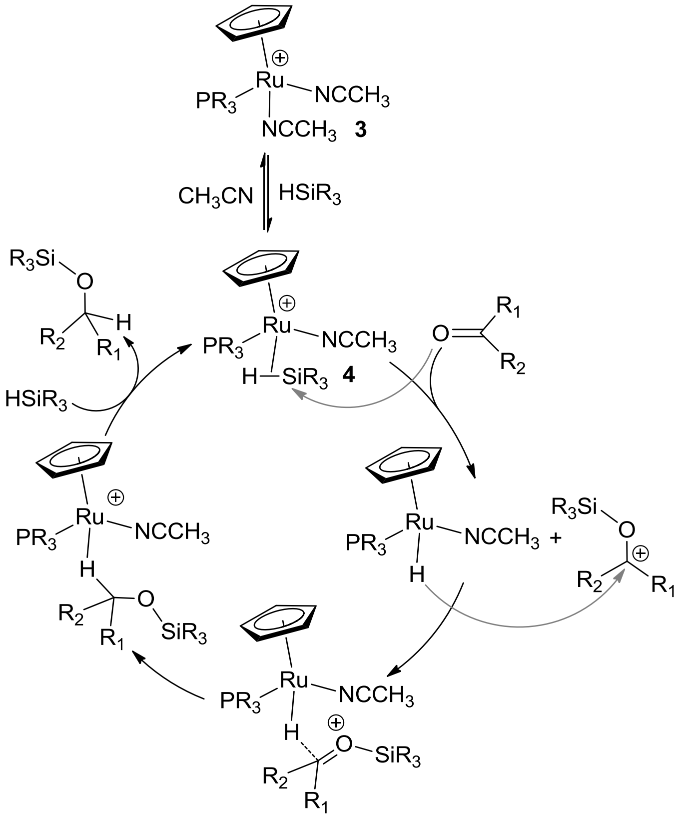
Scheme 5. Ir-based ionic mechanism proposed by Brookhart's group for the hydrosilylation of ketones.

Further investigations on this system performed by Oestreich's group shed light into the intimate reaction mechanism (Scheme 6). The first part of the mechanism is analogous to that proposed for the $B(C_6F_5)_3$ catalyzed reaction [7] and the postulation of Brookhart [9] and Wei [10], i.e. the catalytic cycle starts with the η^1-H(Si) coordination of the silane followed by formation of the oxocarbenium ion via an S_N2 mechanism (Si–H bond activation and R_3Si^+ transfer). The thus formed dihydride complex, however, does not undergo the hydride transfer to the oxocarbenium ion based on experimental data and theoretical calculations. Instead, the Ir(V)-trihydride complex resulting from reaction of the dihydride with a molecule of silane seems to be the most plausible hydride donor. Although, it must be mentioned that the Ir(V)-trihydride and the parent Ir(III)-dihydride (featuring an η^1-H(Si) silane) show similar computed hydricities and ionic M–H bond character; therefore, the latter should not be totally discarded as hydride donor. The racemization of silicon stereogenic silanes observed experimentally was proposed to occur by reaction of a second ketone molecule with the oxocarbenium ion via an oxocarbenium transition state.



Scheme 6. Ir(V)-trihydride hydride donor mechanism proposed by Oestreich´s group.

Nikonov et al. reported on the hydrosilylation of a variety of carbonyl compounds with hydrosilanes employing a Ru(II) catalyst (**3**) [11]. Based on NMR studies, the authors proposed complex **4** as the active species. Theoretical calculations suggest that the catalyst operates by an ionic outer-sphere mechanism instead of the classical Ojima type mechanism. In this case, nucleophilic attack of the ketone on the η^2-σ-hydrosilane, i.e. R_3Si^+ transfer, was found to be the rate-limiting step. Subsequently, hydride transfer to the oxocarbenium ion furnishes the σ-complex $[Ru(CH_3CN)(Cp)(PR_3)(\eta^1\text{-}H–CR_2–O–SiR_3)]^+$, which upon coordination of a new molecule of silane restarts the catalytic cycle (Scheme 7).



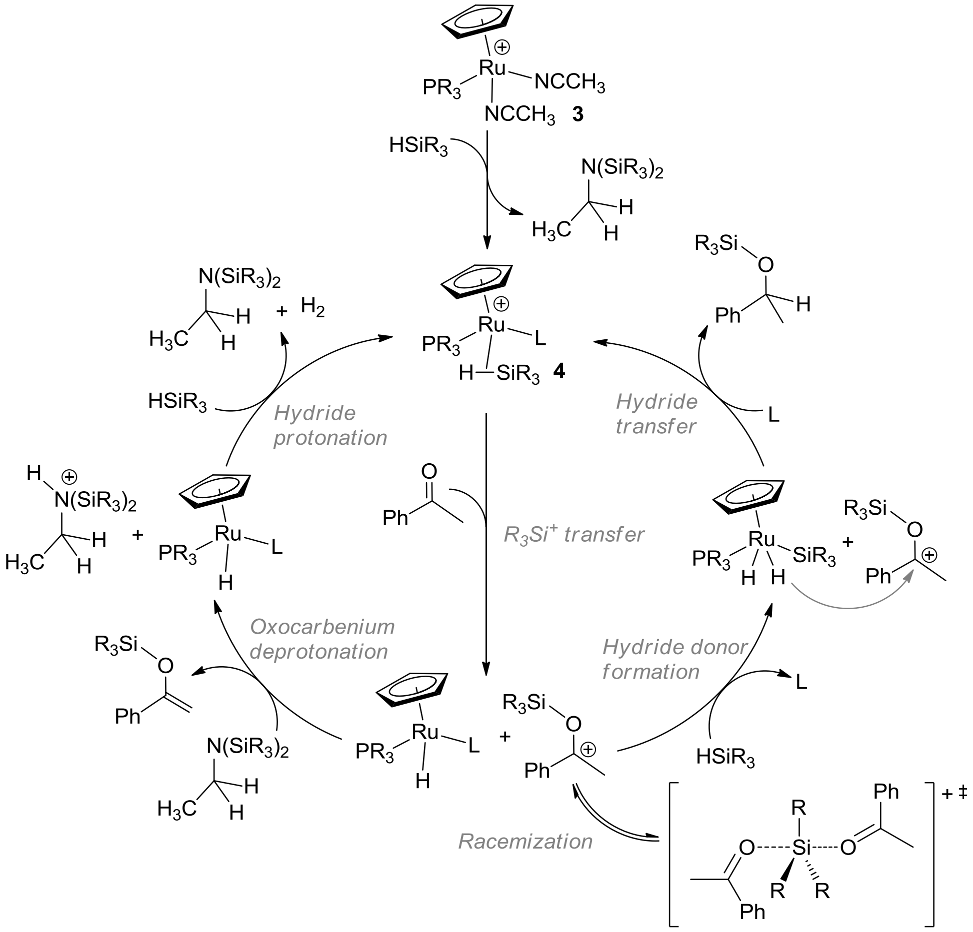
Scheme 7. Ionic mechanism proposed by Nikonov and co-workers.

This mechanism was revised later by Oestreich's group, showing that a second molecule of silane is required to activate the monohydride species that undergoes the hydride transfer to the oxocarbenium ion (Scheme 8)—analogous to the revision of Brookhart's mechanism performed by the same authors (Scheme 6) [12]. Stoichiometric experiments showed that formation of $[Ru(CH_3CN)(Cp)(PR_3)(\eta^1\text{-}H–CR_2–O–SiR_3)]^+$ was accompanied by a double hydrosilylation of one of the acetonitrile ligands to give $CH_3CH_2N(SiR_3)_2$. Analogous to Brookhart's catalyst, the stereochemical analysis showed racemization of the silylether because of the competition between formation of a silylenium ion and the hydride transfer to the oxocarbenium ion. However, the major product of this reaction was a silyl enol ether. Under catalytic conditions, the formation of silylether improves when increasing amounts of hydrosilane are added. This suggests that higher silane/ketone ratios boost the activation of the Ru(II) monohydride complex to give a Ru(IV) dihydride species that acts as hydride donor. This favors the counterclockwise cycle in Scheme 8, which renders the silylether. On the other hand, the doubly silylated acetonitrile ligand ($CH_3CH_2N(SiR_3)_2$) may deprotonate the methyl group of the oxocarbenium ion to give the silyl enol ether and $[CH_3CH_2NH(SiR_3)_2]^+$. Finally, protonation of the hydride ligand at $[Ru(Cp)(L)(PR_3)]$ (L = CH_3CN or acetophenone) generates a molecule of H_2 and restarts the catalytic cycle.

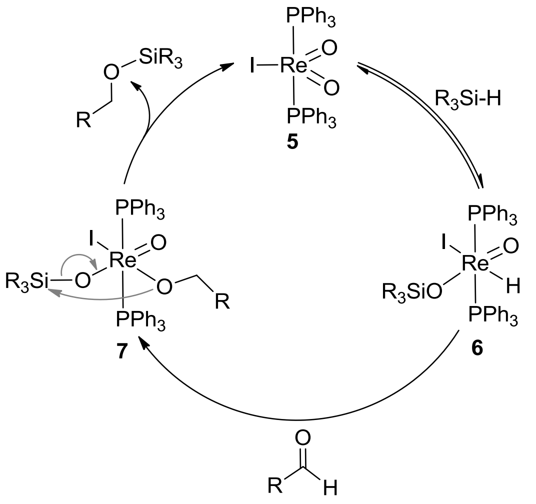
Scheme 8. Revised mechanism proposed by Oestreich and co-workers for Nikonov's catalyst (**3**); L = CH_3CN or acetophenone.

2.2. Ligand-assisted mechanisms

The activation of the Si–H bond has also been reported to occur by a ligand assisted mechanism, where a heteroatom in the proximity of the metal center aids the heterolytic splitting of the hydrosilane by means of a [2+2]-addition. This activation mechanism requires the silicon atom to interact with an available lone electron pair at the heteroatom while the metal center attacks the hydrogen atom.

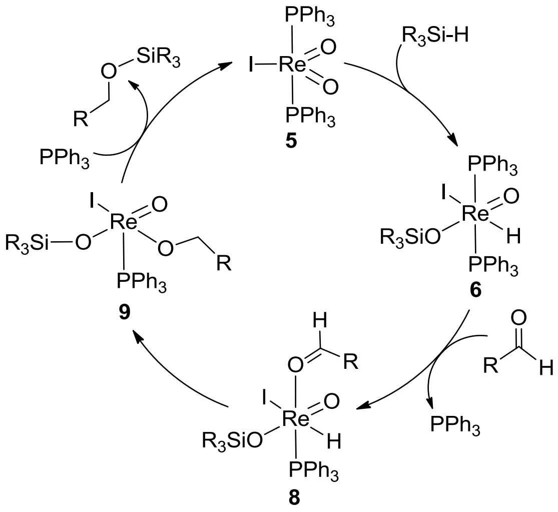


Based on previous reports by Bergman and Anderson on the heterolytic activation of hydrogen by [Ti(Cp*)$_2$(py)(S)] complexes [13], Toste et al. developed the hydrosilylation of ketones and aldehydes catalyzed by a dioxo Re complex, namely [Re(I)(O)$_2$(PPh$_3$)$_2$] (**5**) [14]. Stoichiometric experiments suggest that the first step involves the heterolytic splitting of the Si–H bond assisted by the oxo ligand. The reaction takes place according to a [2+2]-addition mechanism that results in the formation **6**, which features a Re–H and a Re–OSiR$_3$ bond. Remarkably, **6** can be isolated by addition of the hydrosilane to **5**. The authors were unable to isolate **7** since addition of the aldehyde to **6** leads directly to silylether formation. However, *in operando* ^{1}H NMR experiments hint at the formation of a Re–OCH$_2$Ph moiety that was attributed to the presence of alkoxy-metal intermediate **7** under catalytic conditions. Formation of **7** would take place by insertion of the aldehyde into de Re–H bond and, finally, a *retro*-[2+2] reaction would furnish the silylether and regenerate the dioxo complex **5** (Scheme 9). It is noteworthy that this catalyst shows excellent chemoselectivities towards ketones and aldhehydes, as esters, halides and nitrocompounds cannot be reduced.



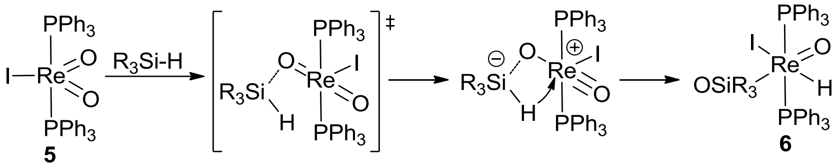
Scheme 9. Initial proposal for the dioxo-rhenium (**5**) catalyzed hydrosilylation of aldehydes.

Subsequent mechanistic studies on this system by the same authors [14] and Lin, Wu and co-workers [15] further support the initial proposal and provide additional information (Scheme 10).



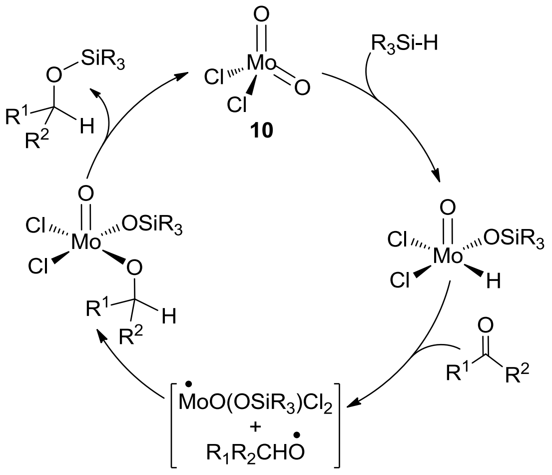
Scheme 10. Revised proposal for the dioxo-rhenium (**5**) catalyzed hydrosilylation of aldehydes.

The [2+2]-addition of the hydrosilane across the Re=O bond to give the silyloxyrhenium hydride **6** was proposed to occur by a non-dissociative mechanism based on kinetic experiments. Moreover, a concerted pathway for this step was discarded due to the lack of a primary isotope exchange for this reaction when deuterated silanes were employed. In fact, the inverse secondary isotope exchange observed for this reaction suggests initial interaction of the oxo ligand with the silicon atom followed by hydride abstraction from the activated silane by the Re center (Scheme 11). The presence of the second oxo ligand has been proposed to be crucial for the stability of the silyloxorhenium intermediate due to two factors. First, because the reduction of one of the oxo ligands decreases the π-electron density that both ligands donate to the metal center and, second, the ancillary oxo ligand increases the nucleophilicity of the reacting oxo ligand. Subsequently, dissociation of one of the phosphine ligands allows aldehyde coordination followed by migratory insertion into the Re–H bond. Finally, coordination of the dissociated phosphine regenerates **5** and produces a molecule of silylether. Kinetic analysis of the catalytic reaction proved that the rate-limiting step depends on the type of silane employed for the reduction.



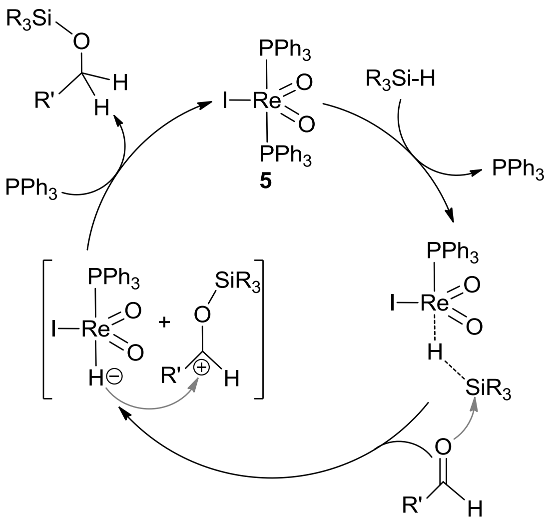
Scheme 11. Stepwise mechanism proposed for the formation of **6**.

Similar mechanisms have been proposed for the hydrosilylation of ketones and aldehydes catalyzed by dioxo-Mo complexes [16]. Several molybdenum catalysts have shown activity for this reaction, e.g. [Mo(Cl)$_2$(CH$_3$CN)$_2$(O)$_2$], [Mo(acac)$_2$(O)$_2$] (acac = acetylacetonate), [Mo(Mes)$_2$(O)$_2$] (Mes = mesityl), [Mo(O)$_2$(S$_2$CNEt$_2$)$_2$] (S$_2$CNEt$_2$ = diethylthiocarbamate), [Mo(Cl)(Cp*)(O)$_2$] (Cp* = pentamethylcyclopentadienyl) and [Mo(Cl)$_2$(O)$_2$] (**10**), the latter being the most efficient. Experimental evidence and theoretical calculations strongly point to the heterolytic splitting of the Si–H bond assisted by the oxo-ligand according to a [2+2] addition pathway, analogous to the mechanism previously described for dioxo-rhenium catalysts. Conversely, in this case, Mo–H bond undergoes homolytic cleavage in the presence of the carbonyl compound obeying an oxygen-centered radical mechanism. This results in H-transfer to the carbonyl compound and subsequent formation of a silyloxy-alkoxy-intermediate, which, by reductive elimination, affords the corresponding silylether and regenerates the active species (Scheme 12).



Scheme 12. Catalytic cycle proposed for the hydrosilylation of carbonyl compounds with **10**.

In contrast to the mechanistic studies by Toste et al., which indicate an oxo ligand-assisted mechanism for catalyst **5**, recent DFT studies have postulated that an ionic outer-sphere pathway (Scheme 13) may compete with the [2+2] addition mechanism in the case of carbonyl compounds. Furthermore, in the case of imines, the outer-sphere pathway would prevail [17].

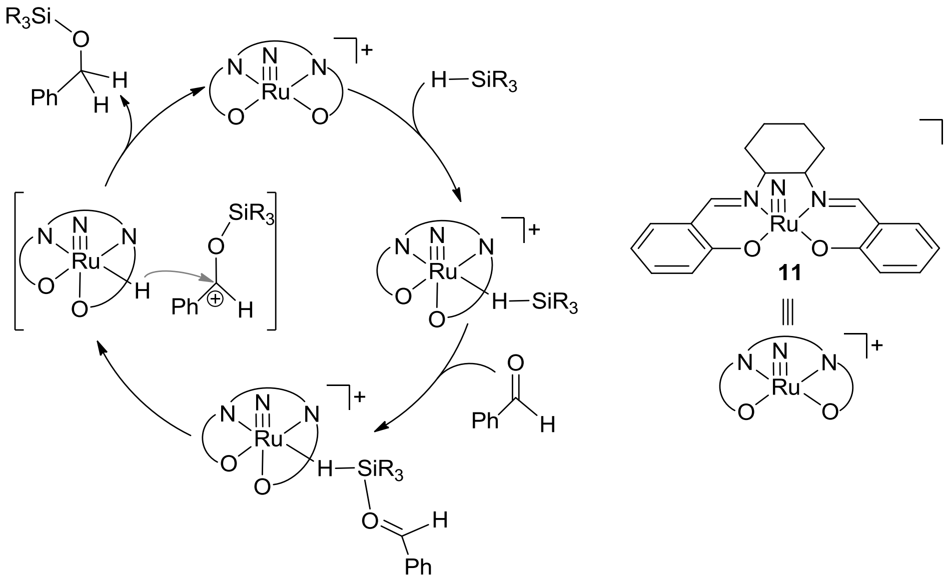


Scheme 13. Ionic outer-sphere mechanism proposed by Wei's group for **5**.

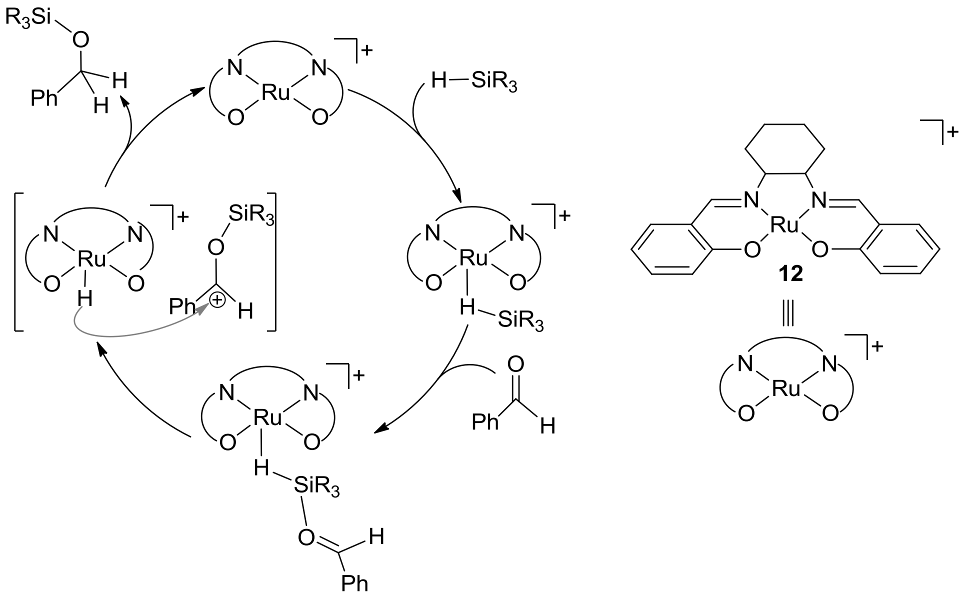
DFT calculations by Wei's group also support an analogous ionic outer-sphere mechanism for the hydrosilylation of carbonyl compounds catalyzed by [$Mo(Cl)_2(O)_2$] (**10**), which was found to be more favorable than the [2+2]-addition pathway [18]. Recent mechanistic investigation by Nikonov's group cast doubt on the nature of the mechanisms previously described for catalysts **5** and **10**. In fact, these elegant deuteration experiments strongly suggest that the reaction proceeds by a nonhydride pathway [19]. These types of mechanisms will be more thoroughly discussed in section 2.3.

The high valent Ru^{VI} complex [$Ru(CH_3OH)(N)(saldach)$][ClO_4] (**11**) has shown good activities for the hydrosilylation of ketones and aldehydes (saldach = N,N'-cyclohexanediylbis(salicylideneimine)) [20]. The mechanism of this reaction was studied by theoretical calculations by Wei and co-workers [21]. Three possible pathways were considered: (i) a [2+2]-addition at the Ru≡N bond, (ii) a nitrido ligand-centered mechanism and (iii) an ionic outer-sphere mechanism. The first possibility was discarded based on the high activation energy resulting from the addition of the Si–H bond across the Ru≡N bond and the endergonic nature of the process. Pathway (ii) was deemed unlikely owing to the high stability of the silyl amido complex resulting from the addition of the Si–H bond at the nitride ligand. Moreover, subsequent steps of the suggested catalytic cycle lead to high energy transition states. The most plausible pathway according to this theoretical study would be an ionic outer-sphere mechanism catalyzed by **11** (Scheme 14). The first stage of the mechanism entails the end-on coordination of the silane in the equatorial position and concomitant reorganization of the saldach ligand, which now presents one of the oxygen atoms situated in *trans* position to the nitride ligand. Subsequently, heterolytic cleavage of the Si–H bond takes place by nucleophilic attack of the aldehyde. The catalytic cycle is closed by reaction of the Ru-hydride with the oxocarbenium ion, which regenerates **11** while affording the corresponding silylether.

Ru^{VI}-nitrido species **11** can straightforwardly give Ru^{III} complex **12** by an N-N coupling reaction, this low-valent complex (**12**) being able to trigger a similar reaction mechanism to that described for **11** (Scheme 15).

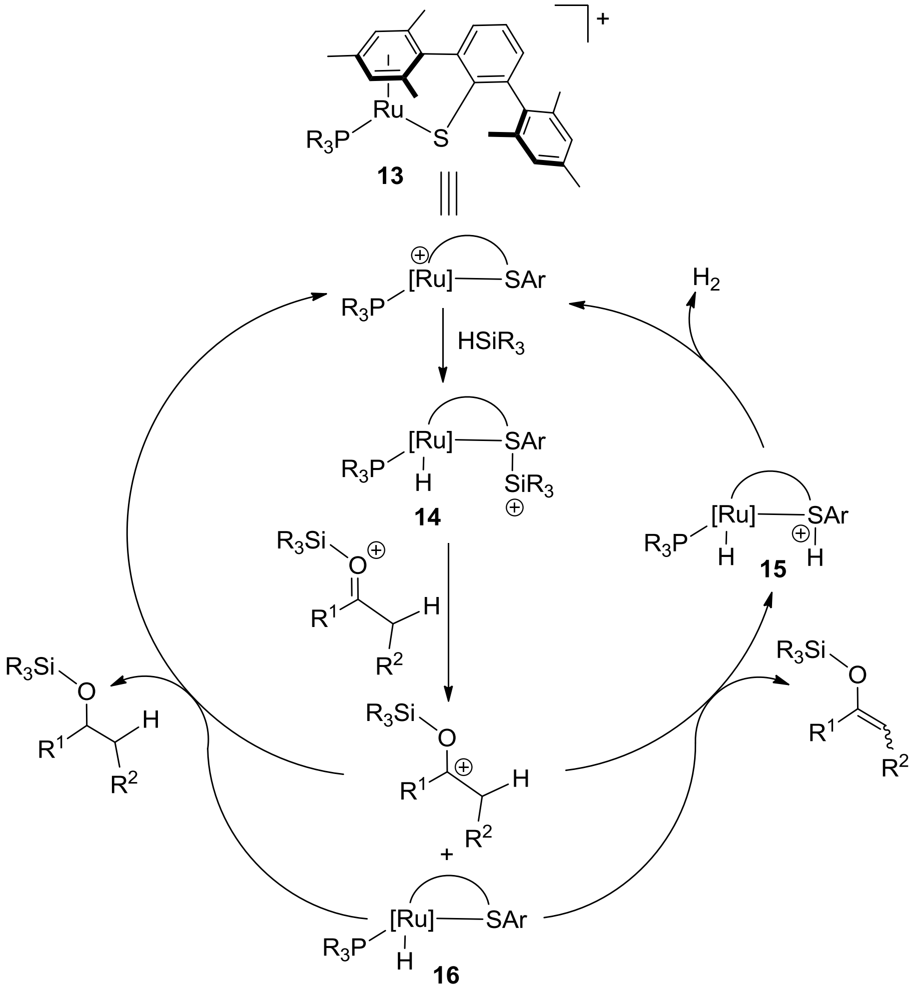


Scheme 14. Ionic outer-sphere mechanism proposed by Wei's group for **11**.



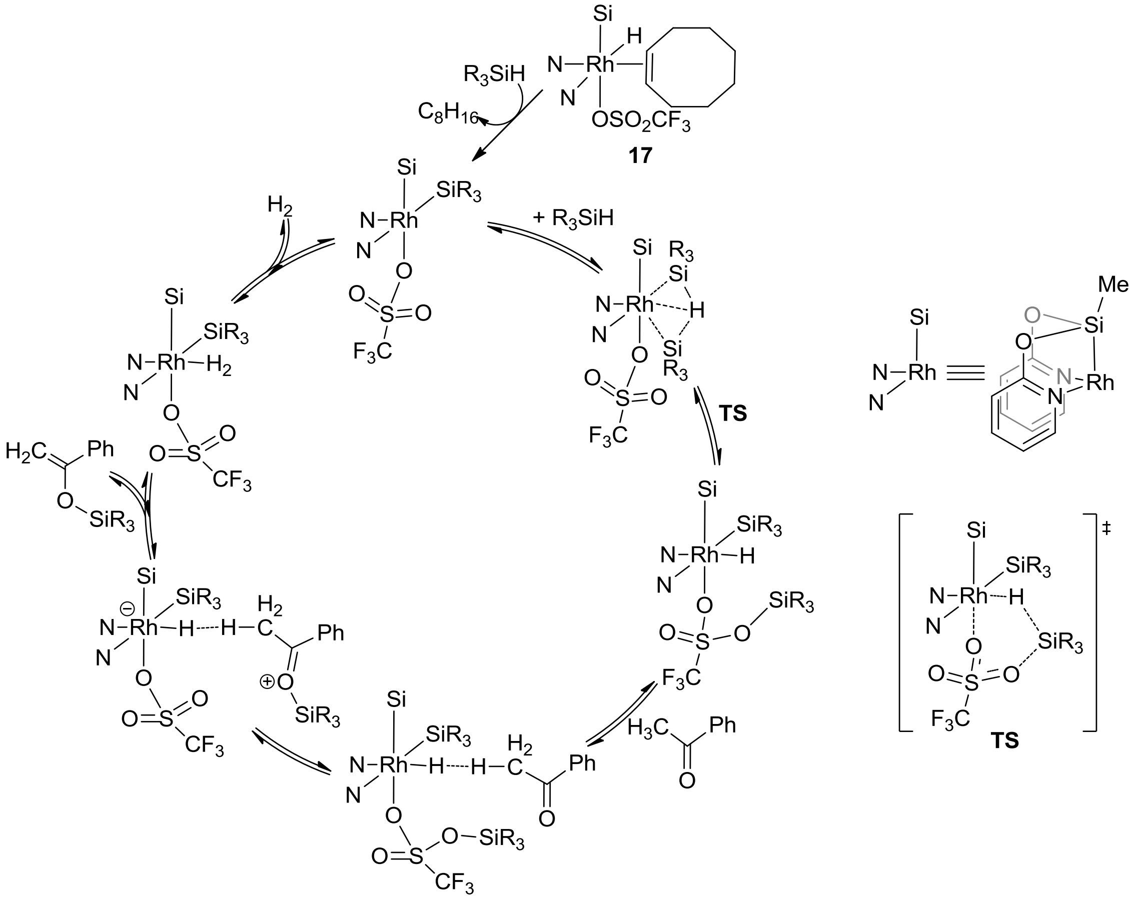
Scheme 15. Ionic outer-sphere mechanism proposed by Wei's group for **12**.

Complex **13** has shown good activities for the reduction of a variety of substrates with hydrosilanes by means of a ligand-assisted mechanism that allows the heterolytic cleavage of the Si–H bond [22]. The hydrosilylation of carbonyl compounds catalyzed by **13** was found to give the expected silylether, together with the related silyl enol ether as the major reaction product in the case of enolizable ketones [23]. This reactivity was explained by Oestreich et al. by way of two competing catalytic cycles (Scheme 16). The first step for both catalytic cycles is the cooperative Si–H bond splitting by the Ru center and the thiolate ligand, which affords intermediate **14**. Subsequent silyl transfer to the carbonyl moiety renders an oxocarbenium cation, which may undergo a nucleophilic attack of the hydride ligand in **15** to yield the silylether. Alternatively, deprotonation of the α-proton by **15** renders the silyl enol ether and intermediate **16**, which releases a hydrogen molecule to regenerate **13**.



Scheme 16. Competing catalytic cycles for the formation of silylethers and silyl enol ethers catalyzed by **13**.

The selective dehydrogenative silylation of ketones by means of a rhodium catalyzed process has been recently reported [24]. The catalytic cycle operates by a ligand-assisted outer-sphere mechanism. Remarkably, the silylether generated as a by-product was not obtained by a classic hydrosilylation process. Instead, it was found to be produced by hydrogenation of the silyl enol ether with the Rh-H$_2$ complex generated by the dehydrogenative silylation reaction. The dehydrogenative silylation cycle depicted in Scheme 17 requires a pre-activation step, namely, the hydrogenation of the cyclooctene ligand to give an unsaturated silyl species. Subsequently, hydrosilane coordination results in the heterolytic splitting of the Si–H bond aided by the trifluoromethanesulfonate ligand. The calculated transition state involves the concerted interaction of the silicon atom with one of the oxygen atoms of the trifluoromethanesulfonate ligand, and the hydrogen of the silane with the rhodium center. This leads to formation of a hydride intermediate with an *O*-silylated trifluoromethanesulfonate. This hydride ligand interacts with one of the hydrogen atoms at the ketone's methyl group, which allows the silyl moiety to be transferred to the carbonyl group. Finally, dehydrogenation of the methyl group affords the silyl enol ether and a Rh-H_2 intermediate. This complex may dissociate a molecule of hydrogen to regenerate the active species or, alternatively, it can coordinate a new molecule of silane to start the hydrogenation cycle that would lead to silylether formation.



Scheme 17. Proposed catalytic cycle for the dehydrogenation of acetophenone with catalyst **17**.

2.3. Nonhydride mechanisms

The mechanism of the hydrosilylation of carbonyl compounds by dioxorhenium catalyst **5** was studied by means of the 1:1:1 reaction of the hydride complex **6** (resulting from the addition of silane across one of the Re=O bond in **5**), with $DSiMe_2Ph$ and benzaldehyde. At 50% conversion the Re-hydride showed no deuterium scrambling, and incorporation of one deuterium atom was observed at the methylene moiety of the thus formed silylether. Besides, the 1:1:1 reaction was finished in 1h, while the 1:1 reaction of **6** with benzaldehyde had to be left overnight to reach full conversion [19]. These data suggest that the most favorable pathway does not require aldehyde insertion into the Re–H bond. Furthermore, these experiments would also discard the ionic outer-sphere mechanism proposed by Wei's group (Scheme 13) [17]. Therefore, the [2+2]-addition reaction of the hydrosilane to complex **5** would afford the active species **6**, thus triggering a nonhydride mechanism for the hydrosilylation of carbonyl compounds.

Abu-Omar and co-workers reported on a series of complexes (Figure 1) that feature a Re≡X bond (X = O, N, NAr). Complexes **18-21** are efficient catalysts for the hydrosilylation of carbonyl compounds that seem to operate by similar mechanisms [25]. The catalytic cycles proposed for complexes **18-20** consist of nonhydride pathways, according to which the hydrosilane is activated at the Re center via formation of a η^2-R_3SiH complex. Subsequently, formation of the silylether takes place by addition of the carbonyl moiety across de activated Si–H bond (Scheme 18) [25a,b].

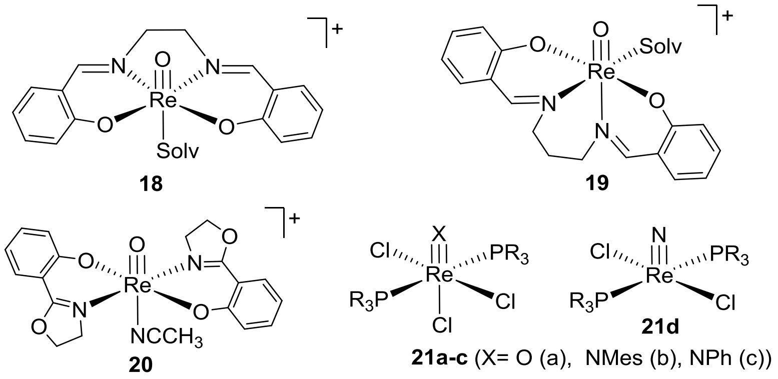
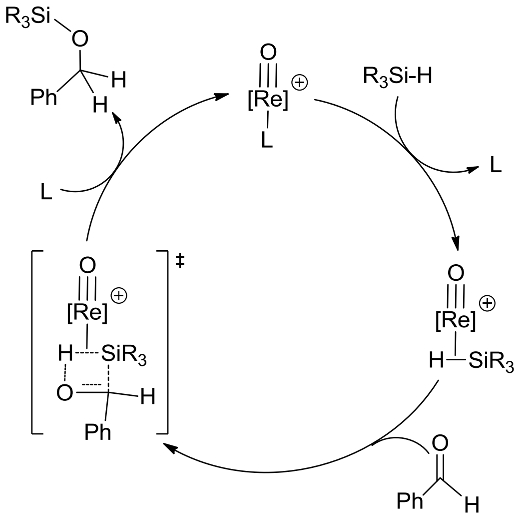
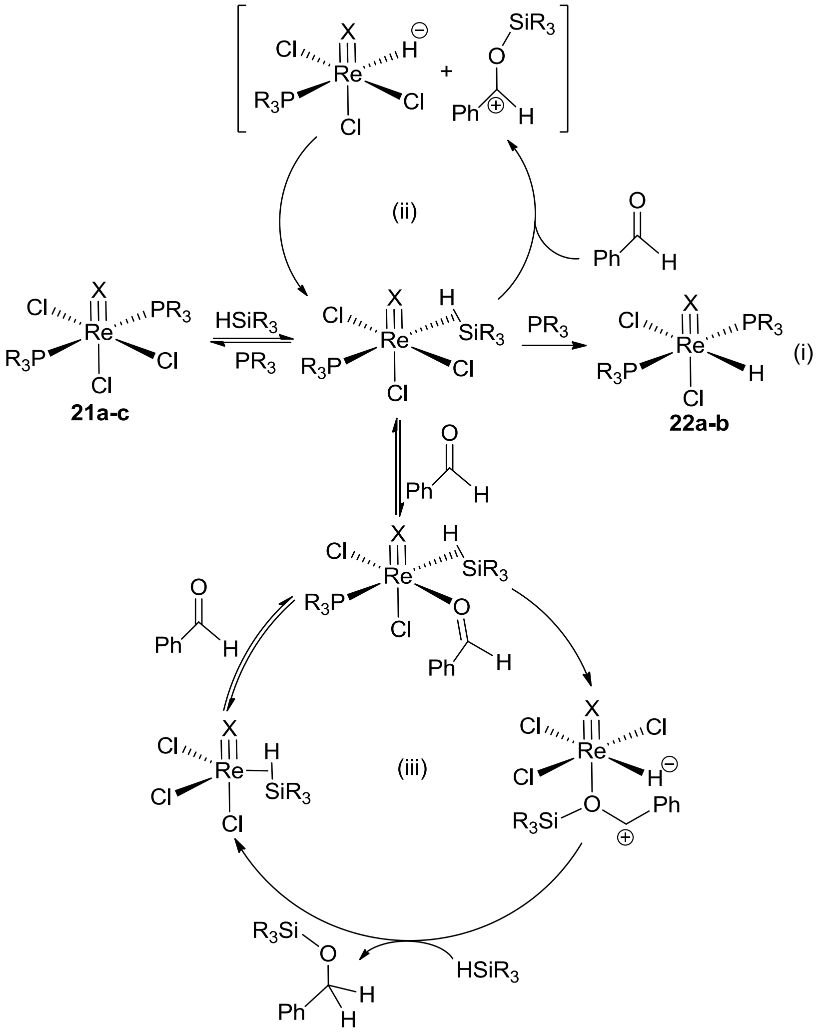


Figure 1. Re≡X hydrosilylation catalysts reported by the group of Abu-Omar (PR_3 = PPh_3, PCy_3).



Scheme 18. Catalytic cycle proposed for the hydrosilylation of benzaldehyde by catalysts **18**-**20**.

A thorough mechanistic study on the hydrosilylation of benzaldehyde by catalysts **21a-d** postulates two viable reaction pathways that require the formation of a σ-complex [25c]. The [2+2]-addition mechanism was discarded based on kinetic experiments; moreover, the imido derivatives are more active than the related oxorhenium complexes and show no activity dependence on the steric bulk. Since oxidative addition of the Si–H bond at a Re(V) center is highly unlikely, a heterolytic cleavage of the silane by means of a σ-complex was postulated. The heterolytic cleavage may happen by three different mechanisms. (i) The first possibility would entail a silane-chloride (or alkoxide) metathesis to give a Re^V-hydride complex. Two of these complexes, **22a-b**, were isolated and characterized; however, this possibility was ruled out on the grounds of the low activity showed when these complexes were used as catalyst. (ii) An ionic outer-sphere mechanism, i.e. formation of a Re^V-hydride and R_3Si^+, with the latter being transferred to the carbonyl moiety and subsequent nucleophilic attack of the hydride on the carbonyl carbon to furnish the silylether. The authors also proposed a concerted mechanism, analogous to that depicted in Scheme 18 as a plausible alternative. (iii) Coordination of the carbonyl moiety to the Re center (by substitution of a phosphine ligand), followed by attack of the R_3Si^+ from the η^2-silane to generate a cationic silylether *O*-bound to rhenium that affords the hydrosilylation product by recombination with the hydride ligand. This mechanism was deemed unlikely owing to the fact that to strongly coordinating phosphine ligands must be displaced by two labile ligands (silane and carbonyl compound). Consequently, the two possibilities described in point (ii) were seen by the authors as the most probable reaction pathways (Scheme 19). This mechanism was revised by Nikonov postulating that **22a** is, as a matter of fact, the active species, thus discarding an ionic mechanism and postulating a nonhydride pathway [19].



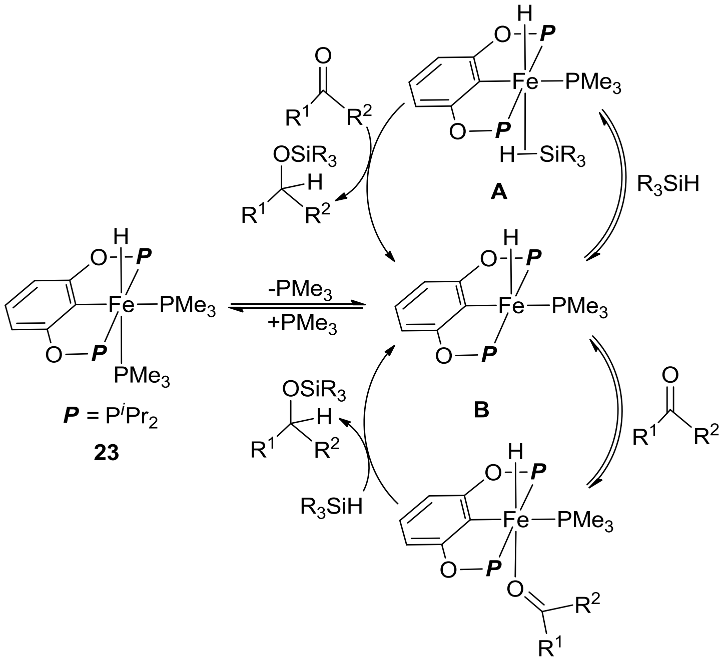
Scheme 19. Reaction mechanisms proposed Abu-Omar et al. for catalysts **21a-c**.

The hydrosilylation of carbonyl compounds with PR_3Cu–H catalysts had been proposed to take place by a catalytic cycle that involves insertion of the carbonyl moiety into the Cu–H bond. The Cu-alkoxyde undergoes addition with the silane across the Cu–O bond to give the silylether, thus regenerating the hydride species [26]. However, Nikonov's experiment for the detection of nonhydride mechanisms suggests that Stryker's reagent, $(Ph_3PCu–H)_6$, prompts a nonhydride pathway [19].

Nikonov's experiment also points to nonhydride mechanisms for the hydrosilylation of carbonyl compounds for a variety of catalysts, namely, $[Mo(H)(NAr)(PMe_3)(Tp)]$

(Tp = tris(pyrazolyl) borate; Ar = diisopropylphenyl) [19], [Ni(Cp*-NHC)(Cl)] [27], [Fe(H)(POCOP)(PMe$_3$)$_2$] (**23**) [28], and [Mo(Cl)(H)(NAr)(PMe$_3$)$_3$] (**24**) [29].

Two possible catalytic cycles were proposed for catalyst **23** (Scheme 20), both requiring the dissociation of a phosphine ligand as initial step. Subsequently, either the hydrosilane (**A**) or the ketone (**B**) may coordinate to the metal center. Reaction of the σ-silane complex with the ketone would generate the silylether in the case of **A**. In pathway **B**, activation of the ketone would take place by formation of a η^1- or η^2-(C=O) adduct, which could react with the silane to give the silylation product.



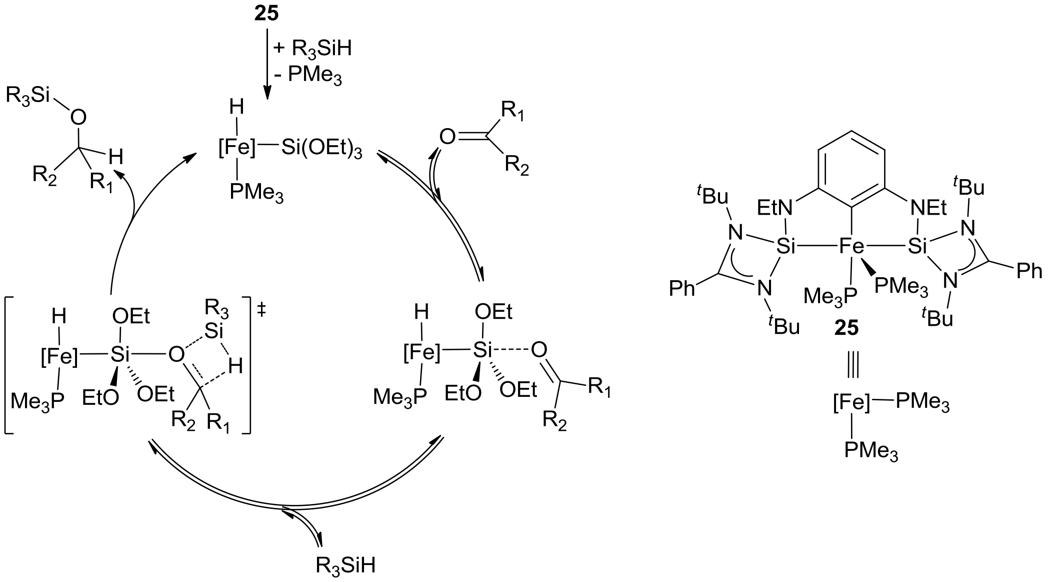
Scheme 20. Plausible mechanistic pathways proposed for catalyst **23**.

In the case of molybdenum-based catalyst **24**, the main reaction mechanism for the hydrosilylation of aldehydes was proposed to occur by a hydride mechanism that entails: (i) phosphine dissociation, (ii) aldehyde coordination, (iii) dissociation of a second phosphine, (iv) coordination of a second molecule of aldehyde, (v) migratory insertion of the carbonyl into the Mo–H bond and, finally, (vi) reaction of the silane

($PhSiH_3$) with the resulting silylalkoxide to give the silylether under an unknown reaction pathway. However, ketones seem to follow an alternative reaction mechanism based on experimental evidence: (i) cyclohexanone reacts faster than benzaldehyde, (ii) no η^2-ketone species was observed, and (iii) Nikonov's test for a nonhydride mechanism indicates that Mo–H insertion of the ketone is not the main reaction pathway. Tentatively, the authors propose a Lewis acid activation of the substrate, likely the silane.

The group of Oestreich has recently disclosed a new type of reaction mechanism for the hydrosilylation of ketones for which the term *peripheral mechanism* has been coined [30]. The proposed mechanism (Scheme 21) may be considered a nonhydride mechanism since the Fe–H bond in the active species —generated by oxidative addition of triethoxysilane to the pre-catalyst (**25**), upon phosphine dissociation— remains untouched throughout the catalytic cycle. Instead, the activation of the substrates takes place at the silyl ligand, which acts as a Lewis acid. Therefore, the activation of the substrates occurs outside the coordination sphere of the catalyst, without the hydride ligand at the Fe center getting directly involved in the reaction mechanism.

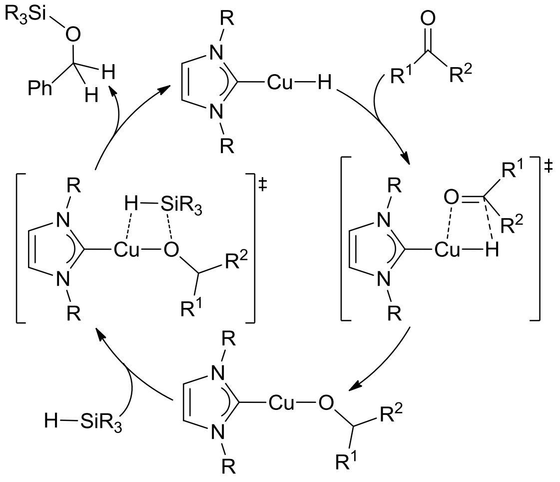
Inner and ionic outer-sphere mechanisms were discarded because of their high energy barriers calculated by DFT, and due to de fact that they were not in good agreement with the experimental data. The proposed peripheral mechanism entails as first step the activation of the pre-catalyst **25** by reaction with a molecule of hydrosilane. This affords the silyl hydride active species, which activates the ketone by means of the Lewis acidic silicon center. Subsequently, hydosilylation of the activated ketone takes place by reaction with the hydrosilane. This happens via a transition state that entails the concerted transfer of the R_3Si^+ moiety to the oxygen atom and concomitant hydride transfer from the silane to the carbonyl carbon.



Scheme 21. Peripheral mechanism proposed for catalyst **25**.

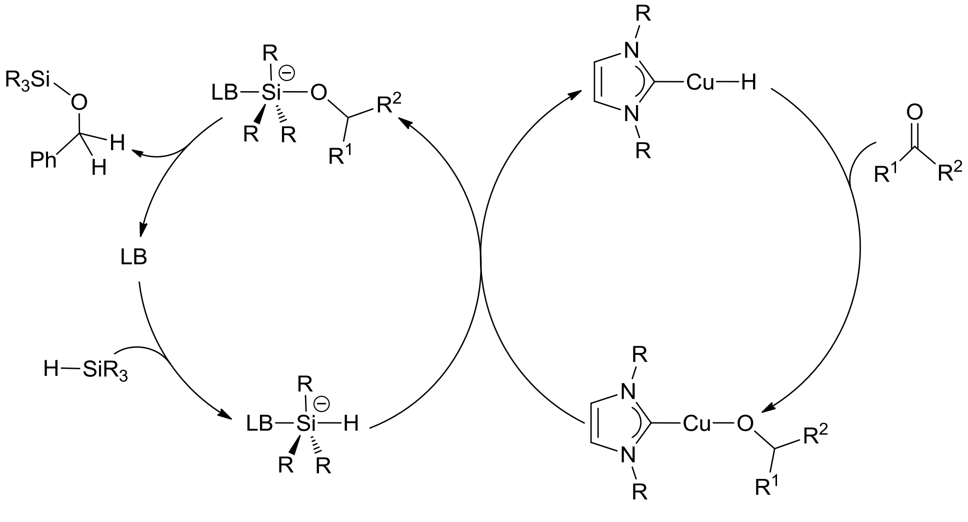
2.4. NHC-Cu-H mediated mechanisms

The most commonly proposed catalytic cycle for the hydrosilylation of carbonyl complexes by NHC-Cu(I) (NHC = N-heterocyclic carbene) entails as first step the formation of the active species NHC-Cu-H, usually by reaction of a NHC-Cu(I) halide complex with an alkoxide and subsequent reaction with a silane molecule. NHC-Cu(I)-F complexes could also be used as catalyst precursors, these species react with the silane to afford the active species NHC-Cu(I)-H and the corresponding fluorosilane. It has been demonstrated that the presence of the fluorosilane formed during the catalyst activation process exerts a positive effect on the catalytic activity of NHC-Cu(I)-H [31]. Subsequently, insertion of carbonyl into the Cu–H bond takes place by a four-center transition state. The resulting copper alkoxide reacts with the silane by σ-bond metathesis reaction to afford the silylated product with concomitant regeneration of the active species (Scheme 22) [32].



Scheme 22. Catalytic cycle proposed for the NHC-Cu-H catalyzed hydrosilylation of carbonyls.

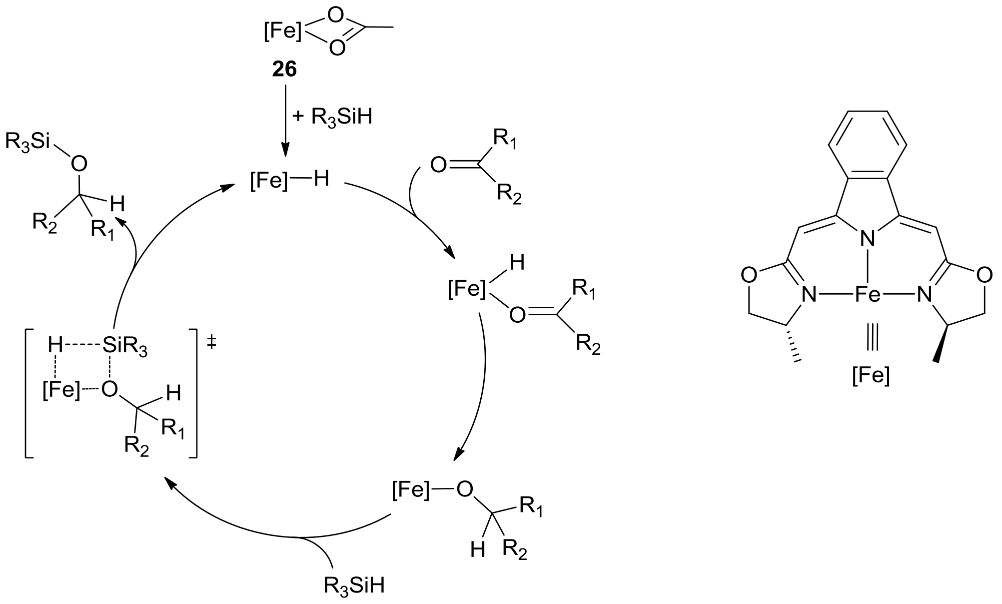
Interestingly, the use of Lewis base additives has been described to improve the activity of the catalyst, especially in the case of trialkylsilanes. Experimental and theoretical studies by Leyssens et al. suggest that the formation of a pentavalent hydrosilicate activates the hydrosilane, thus facilitating the σ-bond metathesis step (Scheme 23) [32f].



Scheme 23. Mechanism proposed by Leyssens and co-workers the Lewis base (LB) assisted hydrosilylation of carbonyls by NHC-Cu-H catalysts.

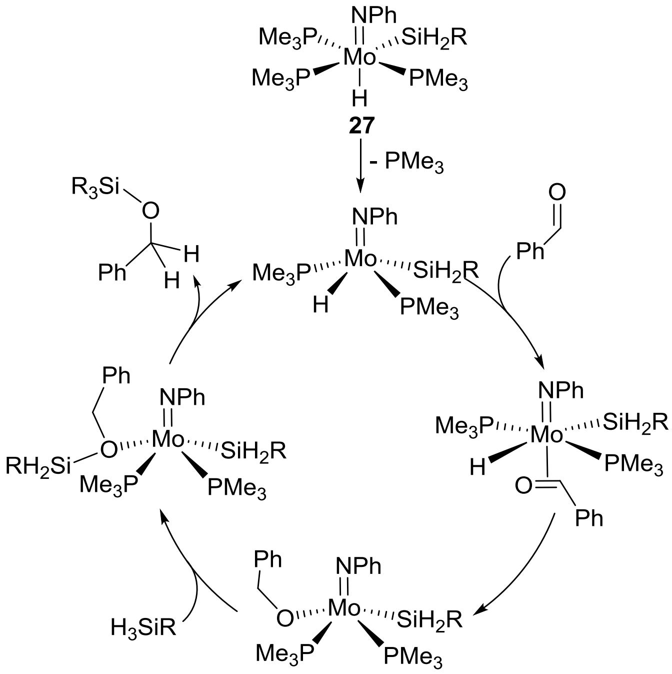
2.5. Miscellaneous

An alternative to a classic oxidative addition / reductive elimination sequence for the transfer of the silyl moiety from the hydrosilane to the final silylether is the presence of a σ-bond metathesis step in the catalytic cycle. In contrast to Ojima-type mechanisms, σ-bond metathesis pathways circumvent the oxidative addition of the Si–H bond into the metal center. Recently, theoretical calculations and experimental evidence presented by Gade's group suggest that iron complex **26** operates via a catalytic cycle that involves a σ-bond metathesis step for the transfer of the silyl moiety from the hydrosilane to the alkoxide ligand, the latter being formed by migratory insertion of the carbonyl into the Fe–H bond (Scheme 24) [33]. In summary, the proposed mechanism entails three steps: (i) coordination of the ketone, (ii) insertion into the Fe–H bond, and (iii) the rate limiting σ-bond metathesis of the hydrosilane and the alkoxide intermediate.



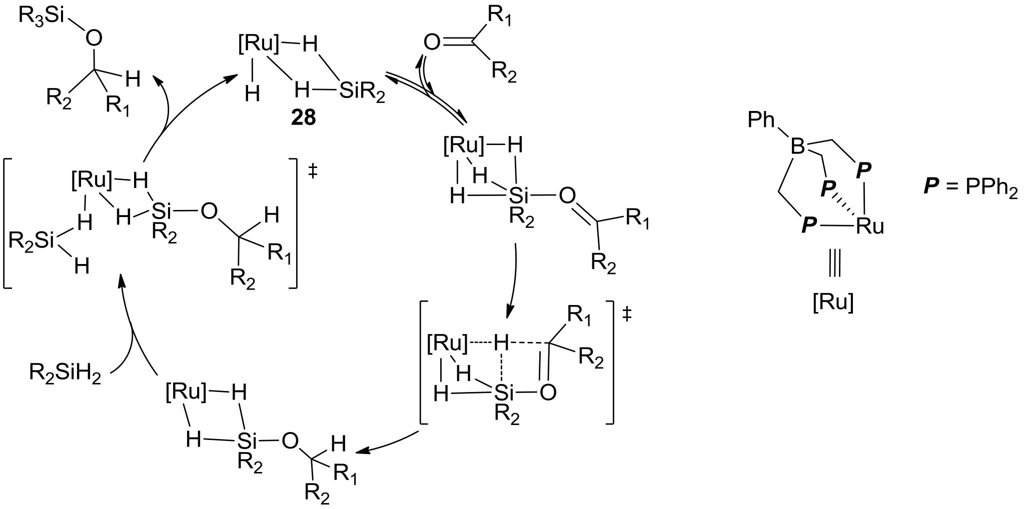
Scheme 24. σ-Bond metathesis pathway proposed by Gade and co-workers.

The imido molybdenum complex **27** catalyzes the hydrosilylation of aldehydes with primary, secondary and tertiary silanes, showing noticeably higher rates with the former [34]. Remarkably, the reaction mechanism does not entail a [2+2]-addition across the Mo=N bond. Instead, migratory insertion of the aldehyde into the Mo–H bond takes place, followed by heterolytic splitting of the silane by the resulting Mo-alkoxide intermediate (at the Mo–O bond). Upon addition of a new molecule of silane the thus formed silylether is released and the active species regenerated (Scheme 25).



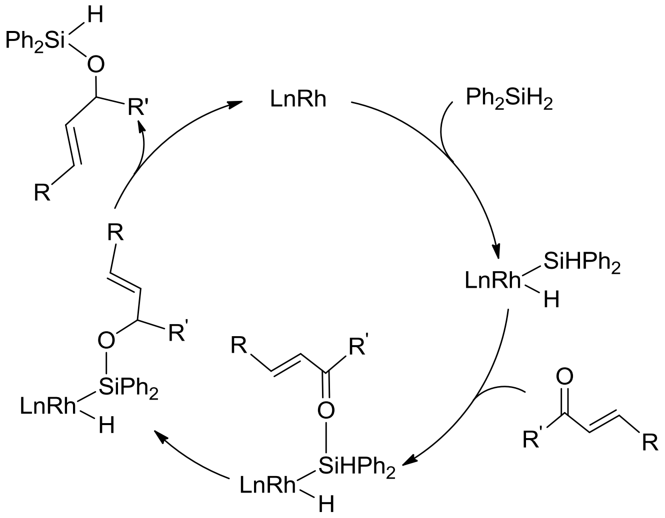
Scheme 25. Catalytic cycle proposed by Nikonov for Mo-imido complex **27**.

Tilley and co-workers disclosed a new mechanism for the hydrosilylation of carbonyl compounds with secondary silanes triggered by ruthenium σ-silane catalyst **28** [35]. The electrophilic silicon center at **28** prompts the formation of a Si–O bond with the carbonyl moiety. Subsequently, hydride transfer to the carbonyl carbon affords a η^2-$H_2SiR_2OCHR^1R^2$ σ-complex, which, upon reaction with a new molecule of H_2SiR_2, affords the corresponding silylether and regenerates the active species (Scheme 26). In summary, the proposed catalytic cycle does not require the coordination of the carbonyl compound to the metal center, which is reminiscent of nonhydride mechanisms. However, in this case the metal participates in the transfer of the hydride to the carbonyl moiety. Remarkably, the use of tertiary silanes brings about a classic mechanism, conceivably due to the fact that the resulting σ-silane complex does not render a silicon center electrophilic enough to allow the attack of the ketone, thus rendering oxidative addition as the most favorable pathway.



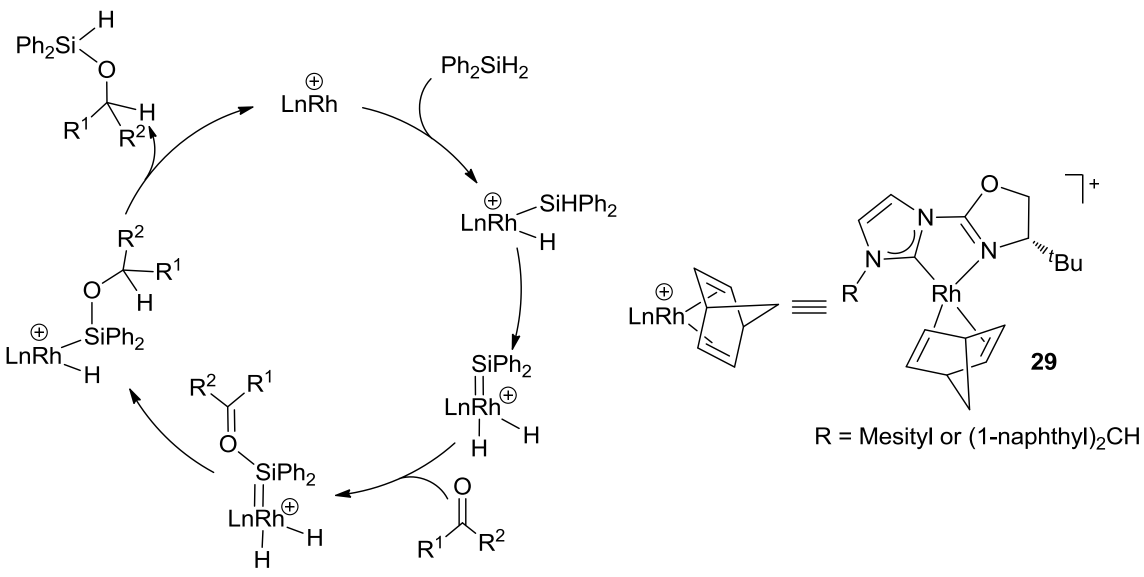
Scheme 26. σ-Bond metathesis pathway proposed by Tilley and co-workers.

The higher activity observed when dihydrosilanes are employed instead of monohydrosilanes cannot be explained by invoking the Ojima mechanism. Zheng and Chan proposed an alternative pathway that clarifies the different activity and selectivity observed for the hydrosilylation of α,β-unsaturated carbonyl compounds with dihydrosilanes [36]. Catalyst $[RhH(PPh_3)_3]$ selectively undergoes the 1,2-hydrosilylation of α,β-unsaturated carbonyl compounds with Ph_2SiH_2, while monohydrosilanes bring about the 1,4-hydrosilylation. The behavior of dihydrosilanes was explained on the grounds of an alternative to Ojima’s mechanism, with the latter operating in the case of monohydrosilanes (Scheme 27). The postulated catalytic cycle requires the oxidative addition of the Si–H bond, analogous to Ojima's mechanism. In contrast to Ojima´s mechanism, the next step entails the interaction of the carbonyl moiety with the silicon center at the silyl ligand. Subsequent insertion into the Si–H bond affords the alkoxysilylrhodium intermediate, which, by reductive elimination affords the silylether and the active species.



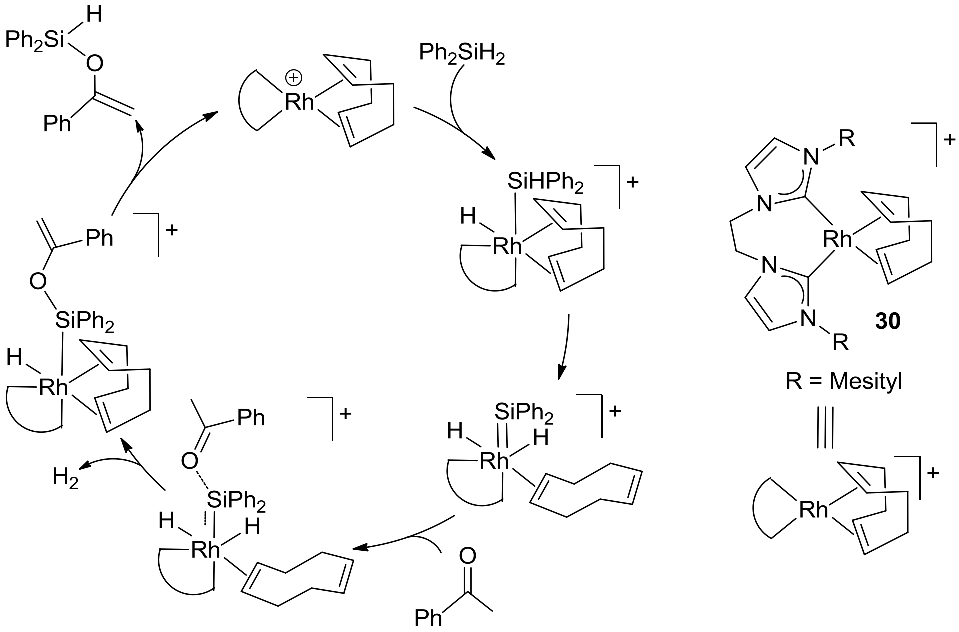
Scheme 27. Chan's mechanism for the hydrosilylation of carbonyl compounds with dihydrosilanes. (LnRh = $RhH(PPh_3)_3$).

More recently, Gade et al. reported a new mechanism based on the formation of silylene intermediates that explain the higher activity observed for dihydrosilanes when compared to monohydrosilanes [37]. The formation of silylene intermediates is inaccessible for monohydrosilanes, consequently, the different activity described for both types of silanes can be explained in terms of the diverse reaction pathways that operate in this reaction. The first stage of the catalytic cycle includes two consecutive Si–H oxidative addition reactions to afford the silylene intermediate from Rh catalyst **29**. Subsequently, the substrate (ketone) interacts with the silicon center at the silylene ligand. Then, one of the hydride ligands at the Rh center is transferred to the carbonyl carbon of the activated ketone. Finally, reductive elimination restarts the catalytic cycle yielding the hydrosilylated product (Scheme 28). Remarkably, this mechanism agrees well with experimental data—the inverse KIE (kinetic isotope effect) especially being noteworthy— and theoretical calculations. In the case of the latter, the Ojima mechanism applied to mono- and di-hydrosilanes results in similar activation barriers that fail to explain the noticeably higher activity observed for dihydrosilanes. On the contrary, the calculated silylene mechanism gives rise to a considerably less energetic pathway —a value of 55 kJ·mol^{-1} was calculated for the silylene mechanism and 120 kJ·mol^{-1} for Ojima's mechanism.



Scheme 28. Gade mechanism for the hydrosilylation of carbonyl compounds with dihydrosilanes.

Kühn et al. observed the formation of silyl enol ethers employing dihydrosilanes with enolizable ketones employing Rh catalyst **30** [38]. The proposed catalytic cycle is similar to that proposed by Gade for the hydrosilylation of ketones, except that once the ketone is bound to the silicon center a deprotonation of the methyl group and concomitant H_2 release takes place. The catalytic cycle is restarted upon reductive elimination, which affords the silyl enol ether and regenerates the active species (Scheme 29).



Scheme 29. Kühn mechanism for the dehydrogenative silylation of enolizable carbonyl compounds with Ph_2SiH_2.

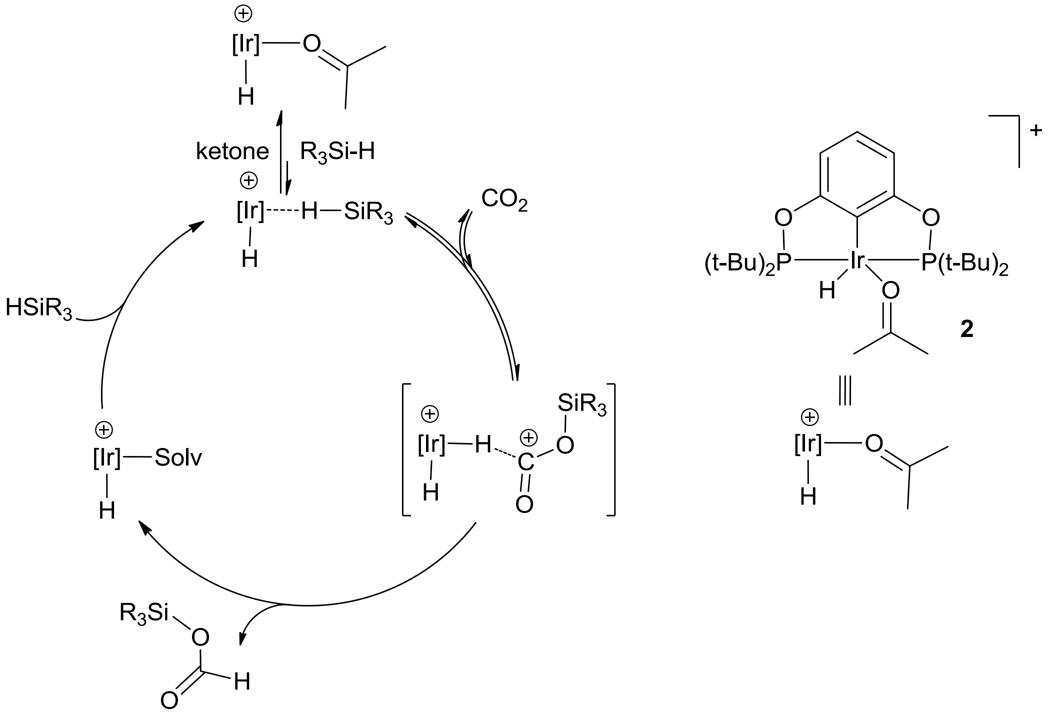
3. Hydrosilylation of carbon dioxide

During this decade, the catalytic reduction of CO_2 with silicon-hydrides has risen up as a thermodynamically favored methodology for CO_2 reduction. Thus, several homogeneous catalytic systems based on transition metal complexes, organocatalysts and acid/base Lewis catalysts have been reported [39]. However, the highest catalytic performances have been achieved using transition-metal based catalytic systems [40]. Considering the relevance of these catalytic transformations, the lack of mechanistic information on this type of reaction stands out. Indeed, only a few mechanistic studies including stoichiometric and/or kinetic studies and theoretical calculations have been reported. Some of them involve classical hydrosilylation mechanisms [41-46]; however, examples of mechanisms based on the activation and subsequent hydrosilylation of CO_2 without the need for the coordination of the CO_2 molecule to the metal center have also been reported. Therefore, the transition-metal hydride catalyzed CO_2 hydrosilylation processes could take place via two different pathways: (i) direct transfer of the hydrogen atom to CO_2 by nucleophilic attack of the hydride on the carbon atom of the CO_2 molecule, or (ii) coordination of the CO_2 molecule to the transition metal and its subsequent insertion into metal–H bond. Other non-classical mechanisms involve the intra or intermolecular Lewis acid-based assisted heterolytic cleavage of the Si-H bond and transfer of the silylenium cation followed by nucleophilic attack of the hydride. This section summarizes some of the most outstanding mechanistic aspects of the so called non-classic CO_2-hydrosilylation processes.

3.1. Metal-hydride catalysts

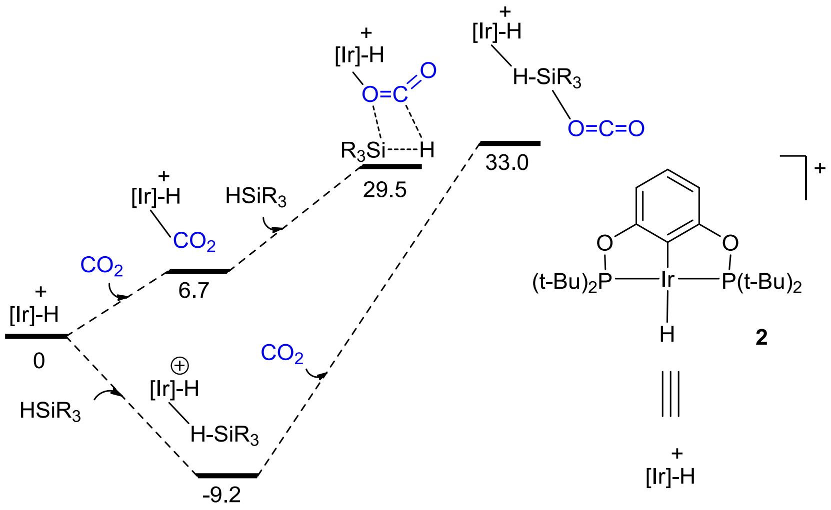
In 2012, Brookhart et al reported one of the first examples of catalytic reduction of CO_2 to methane with hydrosilanes [47]. They found that the Ir(III) cationic complex $[Ir(H)(POCOP)(O{=}CMe_2)]^+$ (**2**) catalyzed the reaction of CO_2 (1 atm) with $HSiMe_2R$ (R = Et, Ph) to quantitatively give the corresponding siloxane $O(SiMe_2R)_2$ and CH_4. The performance of these reactions strongly depends on the steric bulk of the hydrosilanes. Thus, when $HSiEt_3$ and $HSiPh_3$ were used as reductants, instead of $HSiMe_2R$ (R = Et, Ph), a decrease of the activity was observed.

The authors proposed that the Ir(III) complex **2** behaves as a Lewis acid when it reacts with the hydrosilane, leading to a η^1-H(Si) species (Scheme 30). The heterolytic Si-H bond cleavage generates the cation $SiMe_2R^+$, which is transferred to the CO_2 molecule yielding the corresponding siloxycarbenium ion, which reacts with the Ir–H bond to produce the active species and the corresponding silylformate [47]. It is worth mentioning that experimental and theoretical support on the higher electrophilic character of the silicon atom of hydrosilanes η^1-H(Si) coordinated to iridium in comparison with the corresponding free silane was previously reported by Brookhart et al [48].



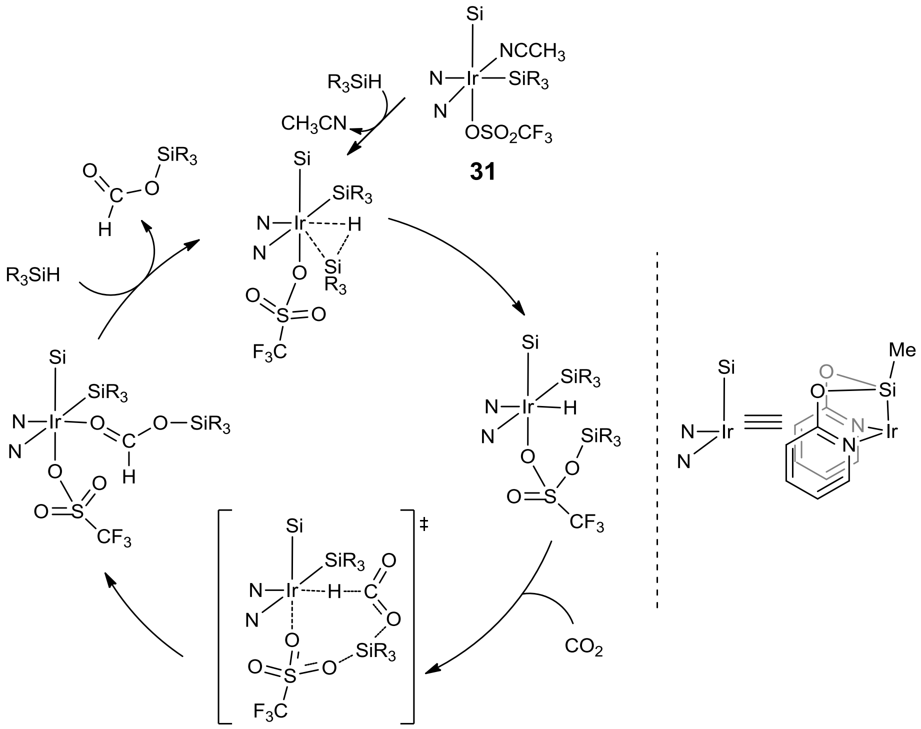
Scheme 30. Mechanism proposal the **2**-catalyzed reduction of CO_2 with $HSiMe_2R$.

In this regard, Wei et al. have recently reported a theoretical study on the catalytic CO_2 reduction with hydrosilanes promoted by Brookhart´s catalyst [49]. The outcomes from these studies revealed that the activation of the CO_2 molecule by κ^1-O=CO coordination to the iridium atom and subsequent reaction of this intermediate with the Si–H bond of the silane is preferred by 3.5 kcal mol^{-1} to the iridium mediated SiR_3^+ transfer to the CO_2 molecule. Moreover, the direct insertion of CO_2 molecules into the Ir–H bond was found to be not energetically affordable (Scheme 31) [49]. Therefore, the coordination of CO_2 to the iridium atom along these catalytic processes could not excluded.



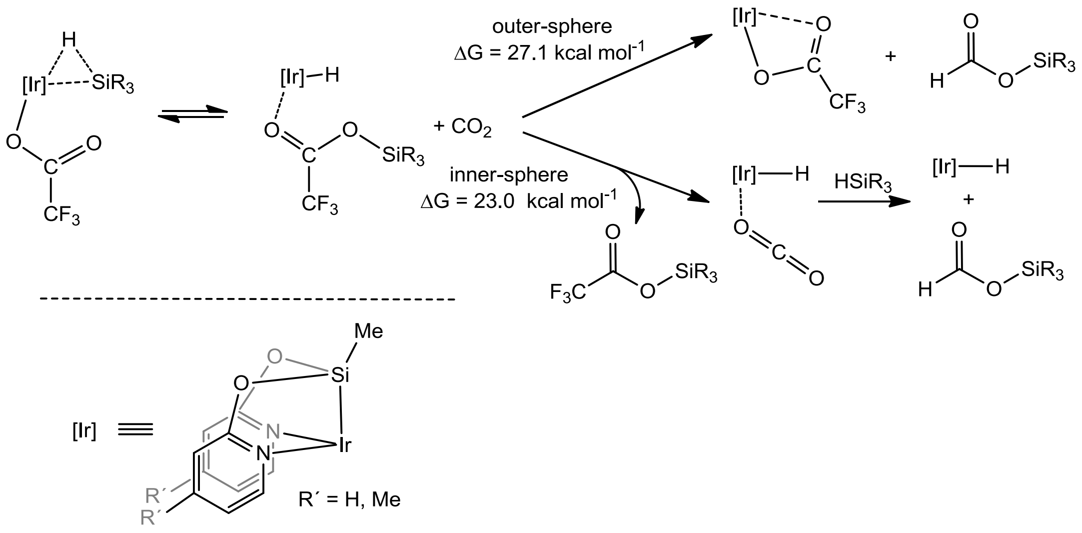
Scheme 31. Energy profile (Kcal mol^{-1}) for the outer-sphere CO_2 activation *versus* outer-sphere $HSiR_3$ activation in the catalytic CO_2 hydrosilylation promoted by Brookhart´s catalyst.

Neutral iridium(III) complexes were also found to be active for the catalytic hydrosilylation of CO_2 [50]. Indeed, we have reported that complex $[Ir(SiR_3)(CF_3SO_3)(NSiN)(NCMe)]$ (**31**) (NSiN = bis(pyridine-2-yloxy)methylsilyl) catalyzed the solvent-free reduction of CO_2 with $HSiMe(OSiMe_3)_2$ to the corresponding silylformate, $HCO_2SiMe(OSiMe_3)_2$. Theoretical calculations at the DFT level show a two steps process, which involves (i) triflate assisted Si–H bond activation, and (ii) outer-sphere CO_2 activation via an eight-membered concerted transition structure (Scheme 32). The highest energetic barrier of the overall hydrosilylation process corresponds to the CO_2 activation step (22.6 kcal mol^{-1}) [50].



Scheme 32. Triflate assisted Si–H bond activation and outer-sphere CO_2 activation in the catalytic CO_2 hydrosilylation promoted by $[Ir(SiR_3)(CF_3SO_3)(NSiN)(NCMe)]$ (**31**).

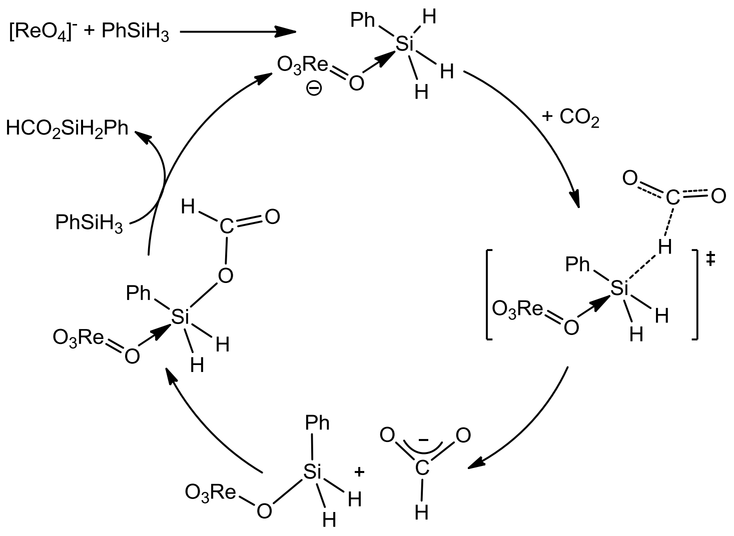
It has been found that the nature of the ancillary ligand strongly influences the catalytic performance of these Ir(NSiN)-based catalytic systems. Thus, Ir-NSiN catalyst precursors with trifluoroacetate ancillary ligands were found to be more active and selective catalysts for CO_2 hydrosilylation than those with triflate ligands [42]. Mechanistic studies showed that a possible reason behind this different catalytic performance could be that while those catalysts that used triflate as ancillary ligand prefer to follow outer-sphere mechanisms, while in the case of catalytic systems based on Ir-NSiN-trifluoroacetate species the inner-sphere CO_2 activation mechanism was found to be preferred by 4.1 kcal mol^{-1} (Scheme 33) [42].



Scheme 33. CO_2 hydrosilylation catalyzed by Ir-(NSiN)(CF_3CO_2) species.

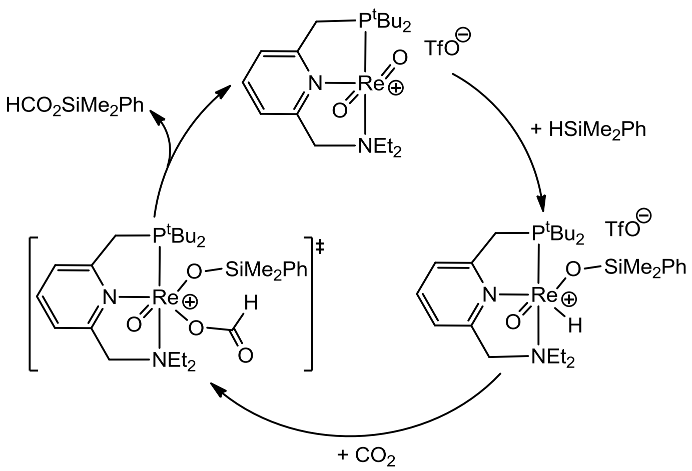
3.2. Metal-oxo catalysts

Recent studies reported by Love et al. have shown that the perrhenate salt [N(hexyl)$_4$][ReO_4] catalyzes the reduction of CO_2 (1 bar) with hydrosilanes to give mixtures of the corresponding silylformate, bis-silylacetal and methoxysilane [51]. The best outcomes were achieved at 353 K in CD_3CN and using Ph_2SiH_2 as reductant. ^{13}C NMR studies evidenced that in the absence of silane $^{13}CO_2$ did not react with [N(hexyl)$_4$][ReO_4], which suggests that the first step of the catalytic reaction could be the $[ReO_4]^–$ mediated Si–H bond activation. Accordingly, DFT studies of the system $[ReO_4]^–$, H_3SiPh and CO_2 allow to conclude that the catalytic process could be understood as a three step mechanism including: (i) activation of one of the Si–H bonds by coordination of one oxygen atom of the $[ReO_4]^-$ to silicon, (ii) nucleophilic attack of one of the activated Si-H bonds on the carbon atom of CO_2 to form $HCO_2^–$ and $H_2PhSiOReO_3$, and (iii) addition of the $HCO_2^–$ to the silicon atom to give the corresponding silylformate as a $[ReO_4]^–$ adduct (Scheme 34) [51].



Scheme 34. $[ReO_4]^-$ catalyzed CO_2 hydrosilylation.

In this regard, it should be mentioned that Abu-Omar et al. reported that the cationic oxorhenium pincer complex $[Re(O)_2(PNN)][CF_3SO_3]$ (PNN = 6-(di-tert-butylphosphinomethylene)-2-(N,N-diethylamino-methyl)-1,6-dihydropyridine) catalyzed the reduction of CO_2 with $HSiMe_2Ph$ to give the corresponding silylformate [52]. In agreement with the above described $[ReO_4]^-$ catalyzed processes, the first step of the catalytic cycle is the Si–H bond activation to give the intermediate $[Re(O)(OSiMe_2Ph)(H)][CF_3SO_3]$, which could be obtained by stoichiometric reaction of $[Re(O)_2(PNN)][CF_3SO_3]$ with one equivalent of $HSiMe_2Ph$ and characterized by means of NMR spectroscopy [52]. The stoichiometric reaction of $[Re(O)(OSiMe_2Ph)(H)][CF_3SO_3]$ with CO_2 produces the corresponding silylformate (Scheme 35).



Scheme 35. $[Re(O)_2(PNN)][CF_3SO_3]$ catalyzed CO_2 hydrosilylation.

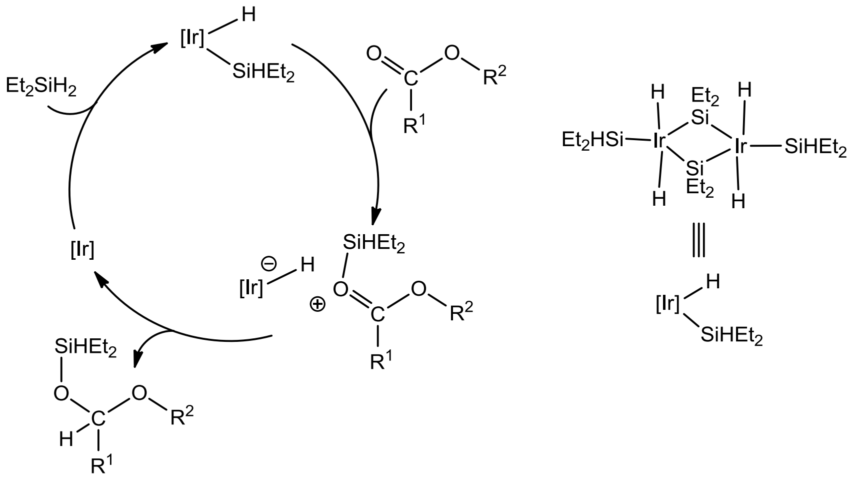
3.3. Ru–S complexes

Metsänen and Oestreich demonstrated that tethered Ru−S complexes (**13**) are active catalysts for carbon dioxide hydrosilylation. Indeed, they have achieved reduction of CO_2 to bis(silyl)acetal with a variety of hydrosilanes. Moreover, at long reaction time (more than 7 days) and high temperatures (423 K), a 65% conversion to methoxysilane was observed [53].

The authors proposed that, similarly to the Ru-S catalyzed ketone hydrosilylation processes (see section 2.2) [22,23], the Ru–S bond at the catalyst promotes the heterolytic Si–H bond cleavage. Thus, the silylenium group binds to the ruthenium atom and the hydride to the sulfur. The subsequent silylenium transfer from ruthenium to a molecule of CO_2 followed by the nucleophilic attack of the hydride on the carbon atom explains the formation of the silylformate, which is reduced to bis(silyl)acetal and this to methoxysilane in a similar fashion.

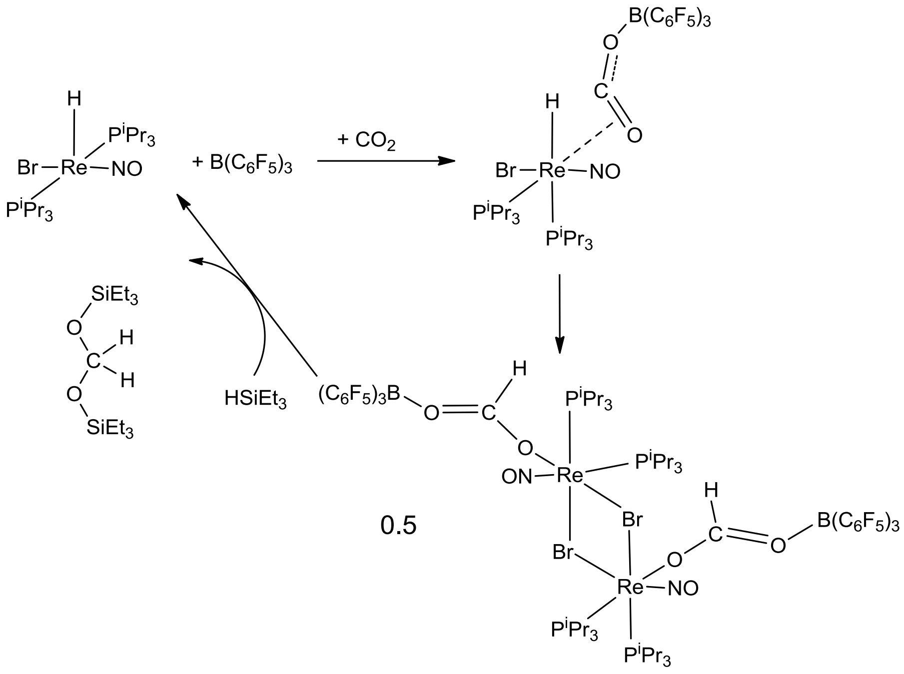
4. Reduction of esters and silylesters with hydrosilanes

The catalytic reduction of esters with hydrosilanes remains a challenge [54]. Indeed, few examples of transition metal-based catalysts effective for the reduction of esters and their derivatives (silylesters) have been reported. Brookhart and Cheng published in 2012 that the commercially available iridium complex [IrCl(coe)$_2$]$_2$ catalyzed the reduction of a broad scope of esters to aldehydes using H_2SiEt_2 as reductant [55]. The authors proposed that the rate-determining step of this catalytic process corresponds to the heterolytic cleavage of a Ir-SiEt$_2$H bond and subsequent transfer of the silylenium cation $[SiEt_2H]^+$ to the oxygen atom of the carboxylic group of the corresponding ester (Scheme 36) [55].



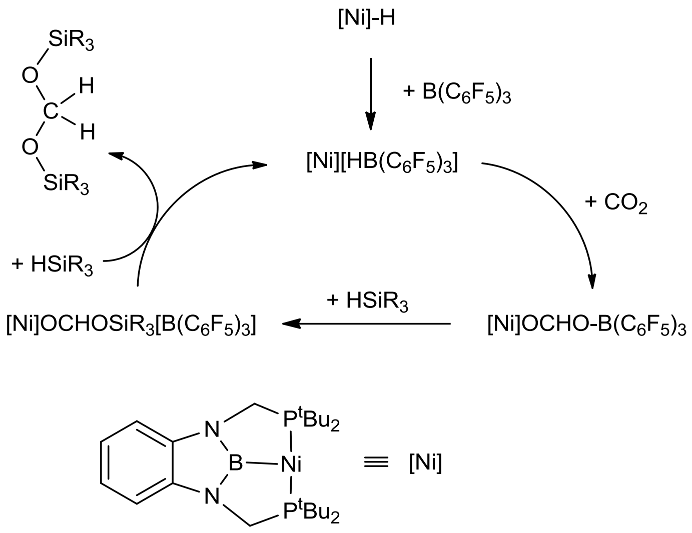
Scheme 36. Ir-catalyzed hydrosilylation of silylesters (R_1 = aryl or alkyl; R_2 = Et, Me, Bn).

The *in situ* reduction of silylformates to afford the corresponding bis(silyl)acetal have been achieved using Re [56] and Ni [57] based homogeneous catalysts. In this regard, Berke et al. reported that the catalytic system formed by [Re(H)(Br)(NO)(P^{i}Pr$_3$)$_2$] and $B(C_6F_5)_3$ catalyzed the reduction of CO_2 with $HSiEt_3$ to give $CH_2(OSiEt_3)_2$ [56]. The authors proposed, based on stoichiometric studies as well as on theoretical calculations, that the CO_2 activation could take place by insertion of the CO_2 molecule into the Lewis pair Re-H···B(C_6F_5)$_3$ in a similar fashion to that reported for frustrated Lewis pairs (FLPs) (Scheme 37) [58].



Scheme 37. Re-catalyzed reduction of silylformates to bis(silyl)acetals.

Rodriguez at al. have also reported the Ni-H/B(C_6F_5)$_3$ pair catalyzed reduction of CO_2 to the bis(silyl)acetal level with hydrosilanes [57]. The authors found that, analogous to that previously reported by Berke et al. [56], a FLP-like heterolytic Si–H bond activation could explain the formation and transfer of the silylenium group [SiR_3]$^+$ to the oxygen atom of the carboxylic group at the Ni-OC(O)H moiety to afford a [Ni←OCHOSiR_3][HB(C_6F_5)$_3$] species, which evolves via nucleophilic attack of the borohydride to the carboxylic carbon atom of the silylformate to give the corresponding [Ni-OCH_2OSiR_3]. This intermediate reacts with [R_3Si-H-B(C_6F_5)$_3$] to lead to the formation of the bis(silyl)acetal, $CH_2(OSiR_3)_2$ and to regenerate the active Ni-H/B(C_6F_5)$_3$ system (Scheme 38) [57].



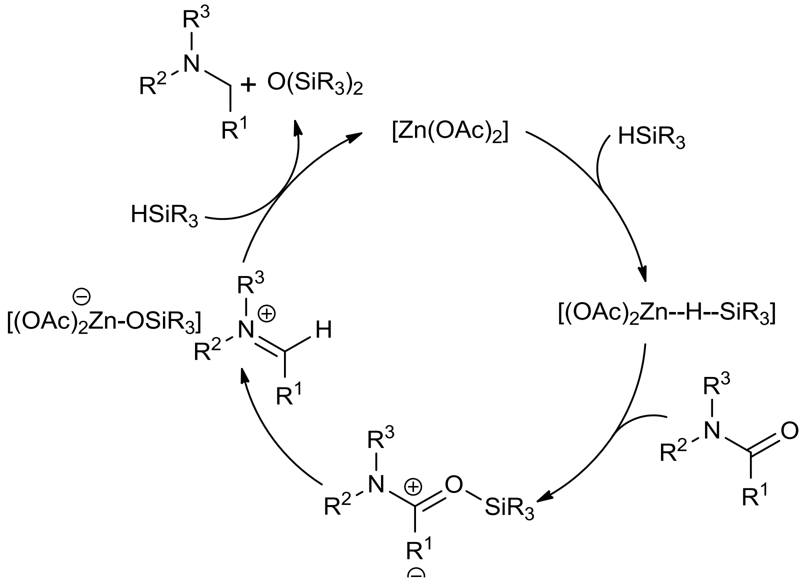
Scheme 38. Ni-catalyzed reduction of silylformates to bis(silyl)acetals.

Therefore, the above described Re-H/B and Ni-H/B FLP mechanisms proposed for CO_2 reduction with hydrosilanes are very similar. In both cases, the role of the metal-hydride is to trap the CO_2 molecule by formation of a metal-formate intermediate, which is stabilized by coordination of $B(C_6F_5)_3$ to the carboxylic oxygen atom. In addition, the borane reacts with the hydrosilane to afford a $[R_3Si\text{-}H\text{-}B(C_6F_5)_3]$ species, which transfers the silylenium group to the corresponding oxygen atom and generates the borohydride that, in a subsequent step, is transferred to the electrophilic carbon atom.

5. Reduction of amides with hydrosilanes

The development of catalytic systems for the reduction of amides to amines under mild reaction conditions using innocuous chemical reagents constitutes a research field of great relevance, mainly due to the multiple applications of amines in organic synthesis and the pharmaceutical and agrochemical industries. During the last decade some examples of transition metal based homogeneous catalysts, effective for the reduction of amides to amines using hydrosilanes as reductants, have been reported.

Beller at al. reported in 2010 the efficient reduction of tertiary amides using $Zn(AcO)_2$ as catalyst and $HSi(OEt)_3$ as reducing agent [59]. This system operated with excellent chemoselectivity and functional group tolerance. They proposed that the first step of the catalytic process could be the reaction of zinc-acetate with the hydrosilanes to afford an activated $[Zn\text{-}H\cdots SiR_3]$ species, which undergoes heterolytic cleavage of the Si–H bond and subsequent transfer of the silylenium group to the oxygen atom of the amide to give a *N,O*-acetal species. This species successively evolves to give the amines and regenerates the $Zn(AcO)_2$ active species. It should be mentioned that these reactions did not work with other ZnX_2 salts (X = F, Cl, Br, TfO) which suggests a non-innocent role of the acetate ligand (Scheme 39) [59].



Scheme 39. Zn-catalyzed reduction of amides to amines.

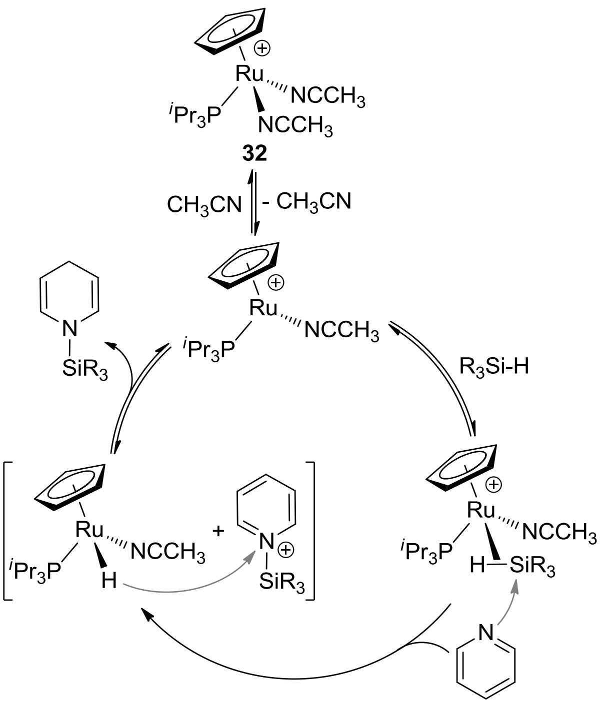
Shortly after, in 2012, Cheng and Brookhart reported that the easily available iridium complex $[IrCl(coe)_2]_2$ is an effective catalyst for the stepwise reduction of secondary amides through imine intermediates [60]. A mechanism based on the electrophilic addition of the silylenium $[HSiEt_2]^+$ ion to the oxygen followed by hydride attack on the carboxylic carbon atom has been proposed [60]. The formation of the imine intermediate was explained by iridium-promoted reaction of the corresponding hemiacetal derivative R^1-NH-CR^2H-$OSiEt_2H$ with H_2SiEt_2 to afford the corresponding imine, $O(SiHEt_2)_2$ and H_2.

The same year, Park and Brookhart published a mechanistic study of the **2**-catalyzed reduction of tertiary amides with H_2SiEt_2 to give the corresponding amines [61]. These studies show that the neutral Ir(V) intermediate $[IrH_3(SiHEt_2)(POCOP)]$ could act as the active species of the catalytic process. In this regard, it is worth mentioning that, although the authors did not isolate this intermediate, examples of Ir(V) derivatives, containing the $IrH_3(SiR_3)$ moiety have been reported [62]. The reaction of the *in situ* generated complex $[IrH_3(SiHEt_2)(POCOP)]$ with the amide gives the hemiaminal silylether and the Ir(III) complex $[IrH_2(POCOP)]$. In the presence of $[Et_3NH][B(C_6F_5)_4]$ the hemiaminal molecule is ionized to give the iminium ion, which is then reduced to the amine by reaction with H_2SiEt_2.

Nakatani et al. have recently reported a theoretical study on platinum catalyzed reduction of amides with hydrosilanes [63]. They have found that the formation of a pentacoordinate Pt(IV) dihydride disilyl intermediate by double oxidative addition of the Si–H bond of 1,2-bis(dimethylsilyl)benzene is a key step for these reduction processes. Once the Pt(IV) species is formed, the reaction follows a classical Chalk-Harrod mechanism [63].

6. Hydrosilylation of *N*-heterocycles

The reduction of *N*-heterocycles is crucial for the synthesis and development of new drugs due to their ubiquitous presence in bioactive molecules. The reduction of heteroaromatic compounds with hydrosilanes is an attractive synthetic route to the preparation of saturated heterocycles, e. g. piperidine and hydropyridine derivatives, owing to the difficulties associated with the hydrogenation of aromatic compounds. The ruthenium complex $[Ru(Cp)(NCCH_3)_2(P^iPr_3)]^+$ (**32**) is able to reduce a variety of substituted pyridines to *N*-silyl 4-hydropyridines, quinoline to *N*-silyl 2- and 4-hydroquinoline, and *N*,*N*-disilyl 1,3,5-triazine to dihydrotriazine. The more sterically hindered catalyst $[Ru(CH_3CN)(Cp^*)(\kappa^2\text{-phen})]^+$ (phen = phenanthroline) (**33**) works remarkably well for the reduction of polycyclic substrates, namely, phenanthroline to *N*-silyl 4-hydrophenantroline, acridine to *N*-silyl, and isoquinoline to *N*-silyl 8-hydroquinoline [64]. The proposed ionic outer-sphere reaction mechanism proposed by Nikonov is analogous to those reported for the hydrosilylation of carbonyl compounds (see section 2.1), and somewhat related to the stepwise outer-sphere pathway proposed by Crabtree and Eisenstein for the hydrogenation of quinolines [65]. Complex **32** dissociates one of the acetonitrile ligands to afford an unsaturated species that reacts with the hydrosilane to give a η^2-(Si–H) σ-complex. Subsequently, the substrate (pyridine in Scheme 40) abstracts the silylenium ion to give an *N*-silyl pyridinium salt and a Ru hydride intermediate. Finally, the hydride is transferred from the Ru complex to the 4-position of the *N*-silyl pyridinium salt to give *N*-silyl 4-hydropyridine, with concomitant regeneration of the active species.



Scheme 40. Ionic outer-sphere catalytic cycle proposed by Nikonov and co-workers for catalyst **32**.

The selectivity of the reaction may be explained in terms of the electronic and steric properties of the carbon atom of the pyridine ring. The 2- and 4-positions are the most susceptible to experiencing a nucleophilic attack, which can be easily visualized by invoking the most likely resonance structures for the *N*-silyl pyridinium salt (Figure 2). Between these two possible attacks, the 4-position is the less hindered and, consequently, the one that accepts the hydride transfer.

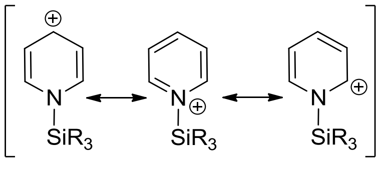
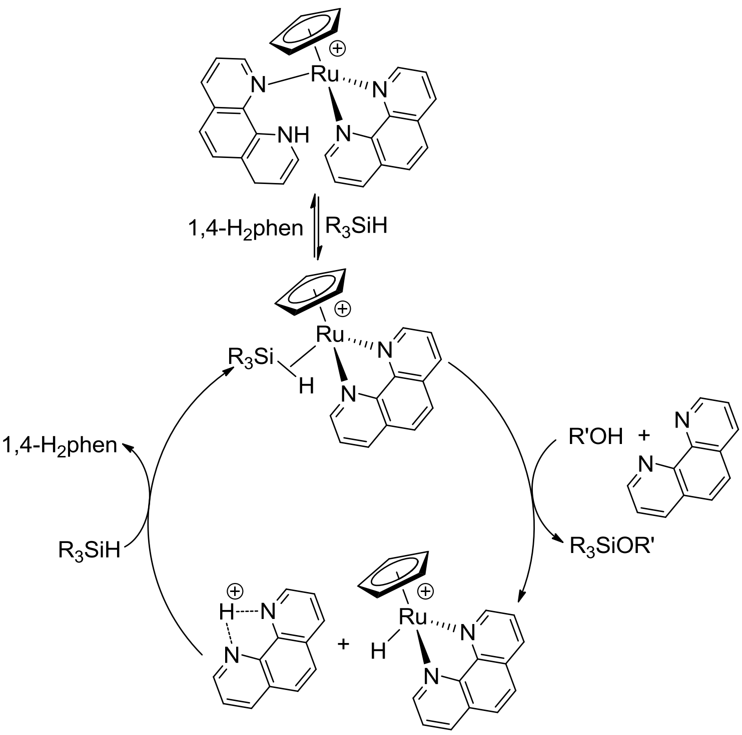


Figure 2. Resonance structures of the *N*-silyl pyridinium salt.

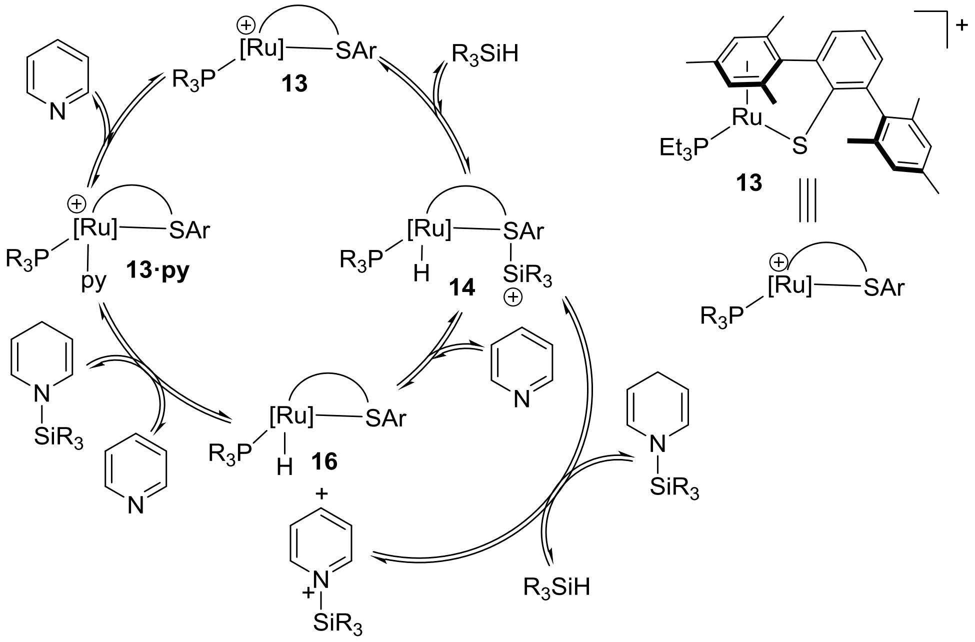
Significant experimental data that the authors present to support this mechanism are (i) the reaction of the Ru hydride complex [Ru(Cp)(H)(NCCH$_3$)(P^{i}Pr$_3$)] with an *N*-silyl pyridinium salt, namely, $[py\text{-}SiEt_3]^+$, renders the corresponding *N*-silyl 4-hydropyridine (reduced product); (ii) the use of a deuterosilane affords selectively the 4-deuterated *N*-silyl hydropyridine; (iii) a Lewis base such as $B(C_6F_5)_3$ abstracts the hydride from the 4-position; (v) furthermore, kinetic experiments are fully consistent with the proposed catalytic cycle.

It is noteworthy that complex **32** is inactive towards the hydrosilylation of phenanthroline due to the formation of the very stable complex $[Ru(Cp)(\kappa^2\text{-}phen)(P^iPr_3)]^+$, but the related complex $[Ru(CH_3CN)(Cp)(\kappa^2\text{-}phen)^+$ (**33**) is able to hydrogenate phenanthroline to 1,4-dihydrophenantroline in the presence of alcohols. Copious amounts of hydrogen are generated concomitantly as a result of silane alcoholysis; however, H_2 was experimentally discarded as hydrogen source. The proposed mechanism is depicted in Scheme 41 [65]. The pre-catalyst **33** is able to generate an unsaturated species able to form a η^2-(Si–H) σ-complex, which reacts with the alcohol to generate a Ru-hydride intermediate and a protonated silylether. The latter is deprotonated by phenanthroline to give the corresponding silylether and the protonated phenanthroline. Subsequently, hydride transfer to the 4-position of the protonated phenanthroline takes place to furnish the 1,4-hydrogenated product. Finally, coordination of the hydrosilane regenerates the active species.



Scheme 41. Proposed catalytic cycle for the reduction of phenanthroline with **33**.

The bifunctional catalysts **13** proved to be selective for the 1,4-hydrosilylation of a broad variety of *N*-heterocycles without the formation of overreduction by-products [66]. The reaction mechanism was studied in detail to conclude that an ionic one-step hydride transfer was the most likely pathway, discarding the possibility of two-step radical pathway by EPR experiments [67]. The postulated catalytic cycle starts from the unsaturated complex **13**, which reversibly coordinates the substrate, in this case pyridine (py), to give **13·py** (the resting state). The unsaturated complex **13** is capable of activating the silane by a ligand-assisted process, which brings about the formation of intermediate **14**. Subsequent formation of the *N*-silyl pyridinium cation takes place upon transfer of the silyl moiety to the Lewis basic pyridine substrate. Hydride transfer from the resulting Ru^{II}-hydride complex **16** to the *N*-silyl pyridinium cation furnishes the 1,4-hydrosilylation product (Scheme 42). Remarkably, the opposite reaction is also possible, with this giving rise to an uncommon case of retro-hydrosilylation reaction [66b].



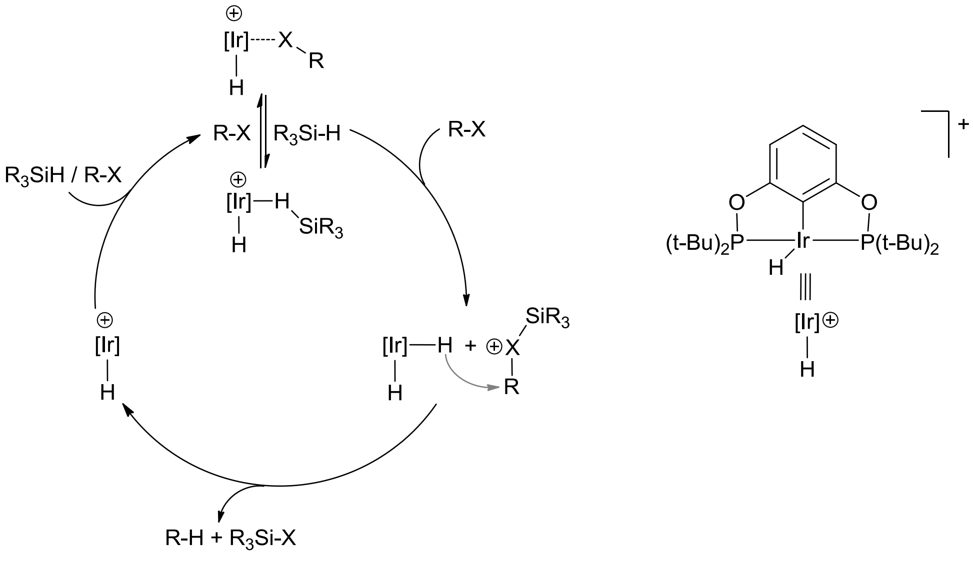
Scheme 42. Proposed catalytic cycle for the reduction of pyridine with **13**.

Inner-sphere mechanisms that require a C=N insertion into the M–H bond have also been proposed [68], especially noteworthy being the 1,2-hydrosilylation of *N*-heteroarenes with dihydrosilanes catalyzed by $[IrCl(coe)_2]_2$ [69] and the Ca-catalyzed 1,2-hydrosilylation of pyridines with Ph_3SiH [70].

7. Reduction of alkyl halides with hydrosilanes

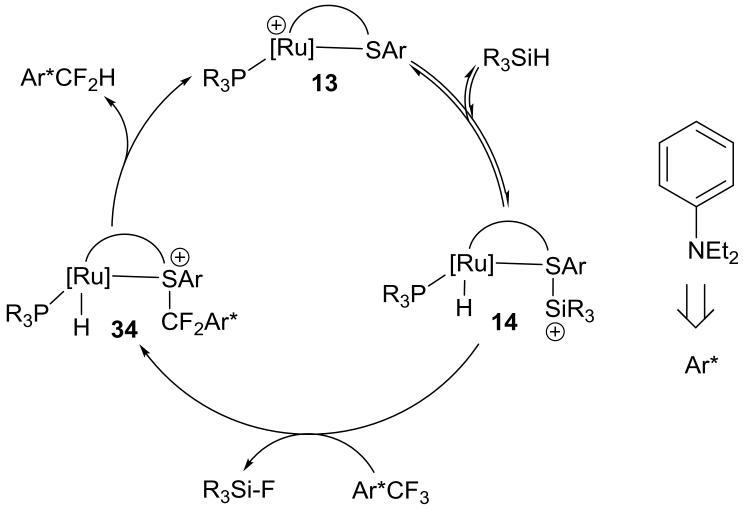
The reduction of organic halides by stoichiometric reagents is a recurrent transformation in synthetic organic chemistry. However, the catalytic version of this reaction, employing readily available hydrosilanes, is less widespread [71].

Brookhart's catalyst (complex **2**) proved to efficiently hydrodehalogenate iodo-, bromo- and chloro- alkyl halides under mild reaction conditions using Et_3SiH as hydride source [72]. NMR experiments showed that addition of Et_3SiH to **2** leads to the formation of $(CH_3)_2CHOSiEt_3$ and a very reactive solvate able to afford σ-complexes with the alkyl halide substrate. In the case of chloro- and bromo-pentane these complexes are in equilibrium with the σ-silane complexes. A radical mechanism was discarded based on the reactivity order in separate flasks (RI < RCl < RBr), which is different to that in a competitive experiment (RCl < RBr < RI). Besides, the fact that CD_2HCl is reduced significantly faster than CD_2Cl_2 seems to rule out a radical mechanism. Similarly to other reductions with hydrosilanes catalyzed by **2** (*vide supra*), the electrophilic active species (an unsaturated species formed by hydrosilylation of the acetone ligand) is able to coordinate the silane in an end-on fashion. This intermediate is in fast equilibrium with the alkyl halide σ-complex, with the position of equilibrium depending upon the binding affinities and relative concentrations of both substrates. Then, the σ-silane complex transfers the R_3Si^+ cation to the halide to furnish a silyl halonium cation and the Ir-dihydride intermediate. The former was proposed to be reduced by the latter via nucleophilic attack of one of the hydride ligands. This yields the reduced organic compound (R-H), the halosilane by-product (R_3Si-X), and the active species (Scheme 43).



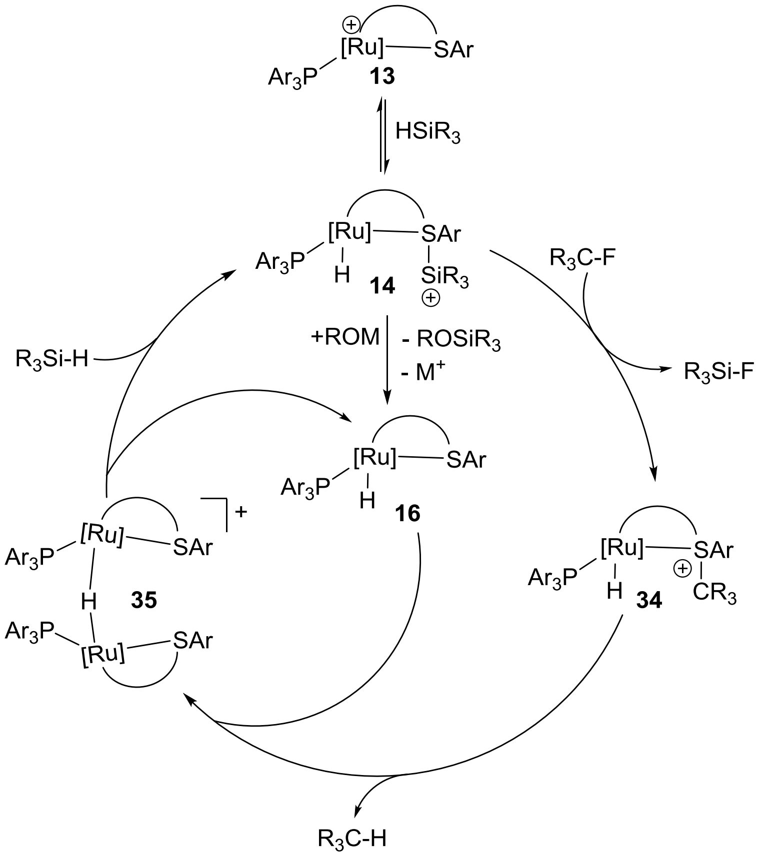
Scheme 43. Proposed catalytic cycle for the reduction of alkyl halides (RX; X = F, Cl, Br, I) with hydrosilanes catalyzed by **2**.

The hydrodefluorination of the -CF_3 moiety of various anilines to the corresponding CH_3-derivatives has been achieved employing **13** as catalyst [73]. The reaction needs 3 cycles of the catalyst to render the RCH_3 molecule, going through $RCHF_2$ and RCH_2F intermediates. Based on previous mechanistic studies (*vide supra*) the authors proposed the catalytic cycle depicted in Scheme 44. The first step is the heterolytic cleavage of the Si–H bond by the Ru complex **13**. The resulting hydride silyl intermediate **14** transfers the R_3Si^+ cation to the fluoride to form a fluorosilane and the cationic thioether complex **34**. Finally, intramolecular transfer of the hydride furnishes the hydrodefluorinated product and regenerates **13** (Scheme 44). The fluoride abstraction was proposed to be the rate limiting step for the hydrodefluorination of RCF_3 to $RCHF_2$ based on the fact that no $RCHF_2$ or RCH_2F formation was detected.



Scheme 44. Proposed catalytic cycle for the hydrodefluorination of CF_3-substituted anilines with hydrosilanes catalyzed by **13**.

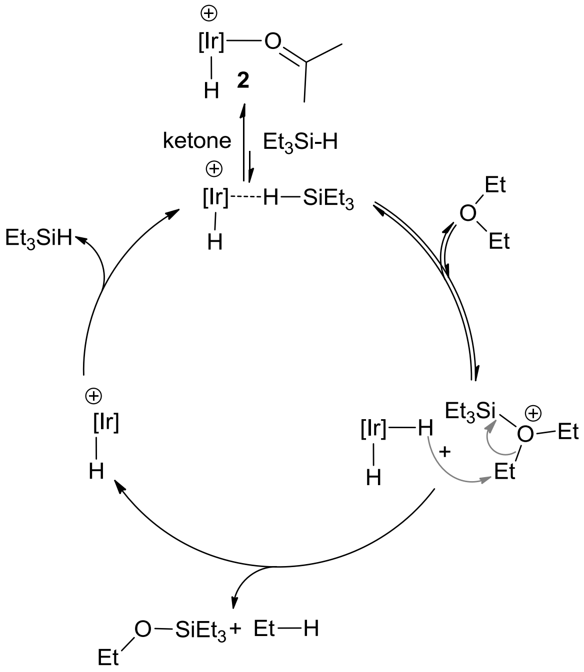
The use of alkoxides as additives and phosphine ligands that feature electron withdrawing groups at **13** trigger an alternative reaction mechanism (Scheme 45). The use of electron-poor phosphines, e.g. P(*p*-F-C_6H_4)$_3$, decreases the electron density at the Ru center and, consequently, increases the Lewis acidity of R_3Si^+ in **14**. This enhances the catalytic activity, allowing full conversion of the CF_3-subtituted aniline into the corresponding CH_3 derivative after 18 hours in the presence of an alkoxide as additive [73]. The generation of the unsaturated complex **13** is hampered when electron-poor phosphines are employed. Therefore, the use of an alkoxide that acts as R_3Si^+ scavenger is required to enhance the concentration of the hydride species **16**, which eases the intramolecular hydride transfer to the sulfur-stabilized carbocation in **34** owing to the formation of hydride-bridged dinuclear species **35**. It is worth noting that the hydride transfer becomes the rate-determining step in the presence of electron-poor phosphines due to the lower hydricity of these species. Finally, **35** activates a new molecule of hydrosilane regenerating **14** and the hydride intermediate **16** [73].



Scheme 45. Proposed catalytic cycle for the reduction of CF_3-substituted anilines with hydrosilanes catalyzed by **13** using an alkoxide additive (ROM) and PAr_3 (Ar = p-FC_6H_4).

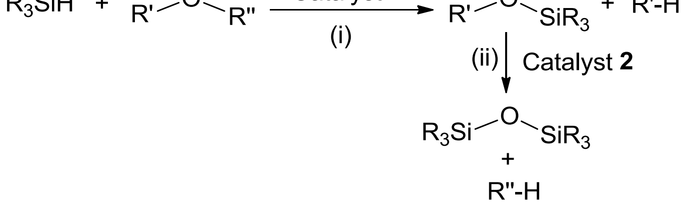
8. Reduction of ethers with hydrosilanes

The cleavage and reduction of the C–O bond of alkyl ethers can also be achieved employing Brookhart's catalyst, by means of an outer-sphere mechanism (complex **2**) similar to those described above (Scheme 46) [74]. An equilibrium between the σ-silane complex and the iridium dihydride / diethyl(triethylsilyl) oxonium ion couple was proposed to occur throughout the catalytic process based on NMR experiments. The reduction of the oxonium species by the dihydride intermediate would be the rate limiting step according to experimental observations. Upon the hydride transfer required for the reduction to take place a monohydride intermediate is formed. Subsequently, coordination of Et_3SiH regenerates the σ-silane complex.



Scheme 46. Proposed catalytic cycle for the reduction of diethyl ether with triethylsilane catalyzed by **2**.

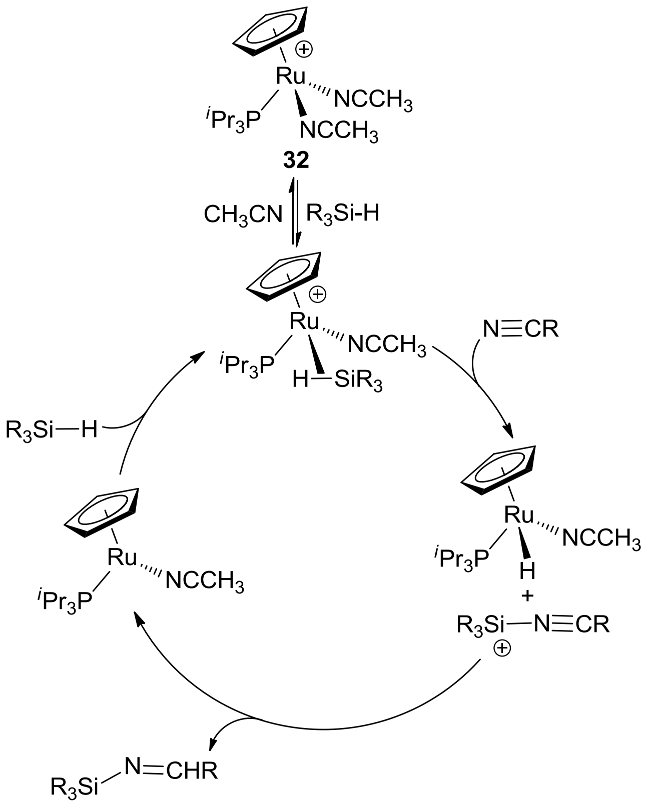
This catalyst proved active for the reduction of a variety of ethers to the corresponding silylether (Scheme 47(i)) [74a], including epoxides [75] and protected sugars [76]. Remarkably, the latter can be reduced to a mixture of *n*-hexane, 2- and 3-methylpentane and traces of 2,3-dimethylbutane by further reduction of the intermediate silylethers (Scheme 47(ii)).



Scheme 47. Reduction of alkyl ethers with hydrosilanes.

9. Hydrosilylation of nitriles

The hydrosilylation of a wide variety of unsaturated bonds has been disclosed; however, scarce examples using nitriles as substrates are present in the literature. Moreover, the selective reduction to *N*-silylaldimines (R_3Si-N=CHR) is challenging due to the fact that the monohydrosilylated product is usually more reactive than the starting nitrile, thus the hydrosilylation of nitriles is more likely to afford *N*,*N*'-disilylamines ($(R_3Si)_2NCH_2R$) [77]. Remarkably, catalyst **32** is able to hydrosilylate a broad diversity of nitriles selectively to *N*-silylaldimines under mild reaction conditions. The corresponding *N,N*'-disilylamine (bis(hydrosilylated) product) may also be obtained by addition of two equivalents of silane. Nikonov and co-workers tentatively postulated a mechanism analogous to that previously proposed for ketones with the same catalyst (Scheme 48) [78]. This mechanism was later substantiated by theoretical calculations, confirming the initially proposed catalytic cycle [79].



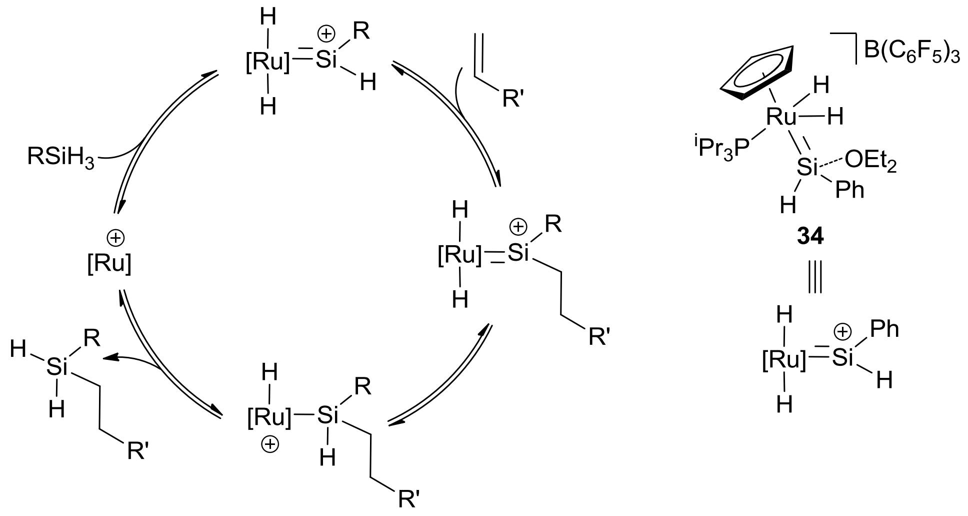
Scheme 48. Proposed catalytic cycle for the hydrosilylation of nitriles with catalyst **32**.

The hydrosilylation of nitriles with catalyst **13** may afford the *N*-silylaldimines or disilylamines, mono- and bis- hydrosilylated products, respectively, depending on the hydrosilane. The use of Et_3SiH permits the selective formation of *N*-silylaldimines while $PhMe_2SiH$ leads to formation of disilylamines, these chemoselectivities being independent of the stoichiometry of the reaction [80]. Although no mechanism was proposed by the authors, the selectivity of the reactions, together with previous mechanistic studies on this catalyst, strongly suggest an outer-sphere catalytic cycle analogous to those described above for **13**.

10. Hydrosilylation of alkenes and alkynes

The hydrosilylation of non-polar C-C multiple bonds diverges from the substrates described above from a mechanistic viewpoint due to the intrinsic electronic differences between them. The lack of an available lone pair at alkenes and alkynes that allows them to act as Lewis bases limits their reactivity compared to C-heteroatom multiple bonds. Therefore, the myriad of organometallic catalysts hitherto reported for the hydrosilylation of C-C multiple bonds mostly operate by Chalk-Harrod-type mechanisms—usually being catalyzed by organometallic complexes featuring transition metal centers in low oxidation states [81].

Glaser and Tilley reported detailed mechanistic studies that support the first silylene-mediated mechanism (Scheme 49) [82]. This reaction permits the hydrosilylation of aromatic and aliphatic alkenes with $PhSiH_3$, catalyzed by a Ru(IV)-silylene catalyst (**34**).



Scheme 49. Glaser-Tilley mechanism for the hydrosilylation of alkenes with catalyst **34**.

The first step of this mechanism involves the insertion of the alkene into the Si–H bond of the silylene complex, which has been proposed to occur in a concerted manner according to the transition state depicted in Figure 3. Subsequently, 1,2-hydride migration from the ruthenium to the silicon center followed by reductive elimination render the hydrosilylated product. The active species is regenerated upon activation of $RSiH_3$ by two consecutive Si–H oxidative addition reactions.

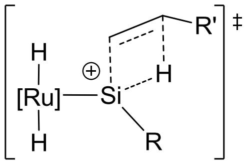
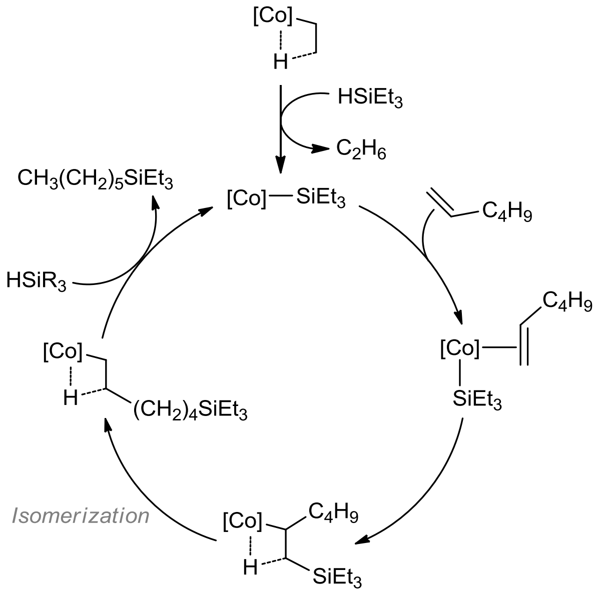


Figure 3. Transition state proposed for the concerted insertion of the alkyne into the Si–H bond.

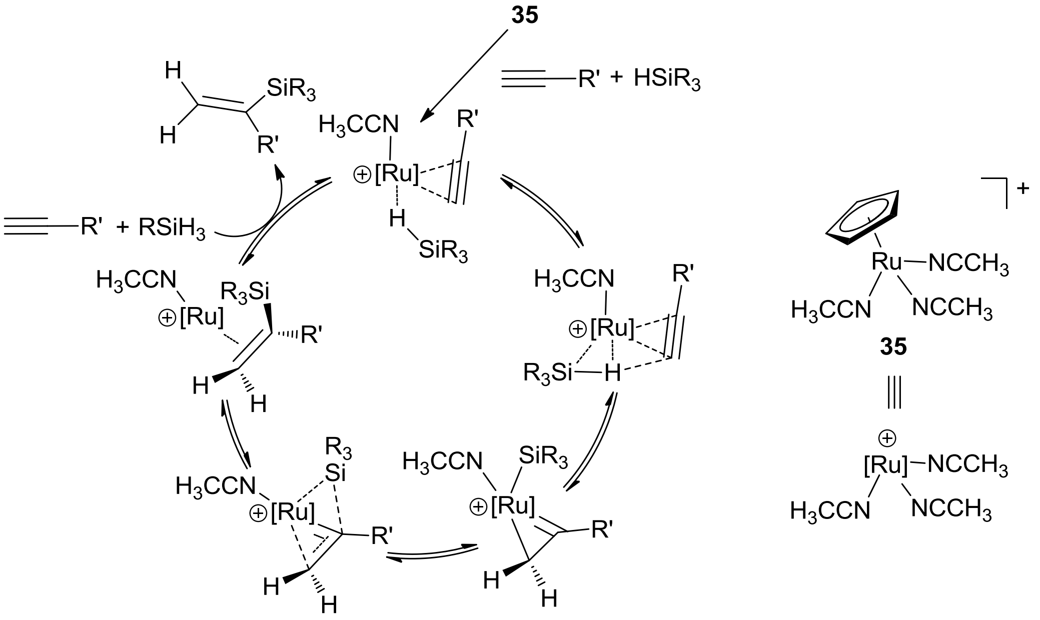
This mechanism has been further studied by theoretical calculations [83] and experimentally by means of stoichiometric experiments that support the key insertion step of the alkene into the Si–H bond [84]. It is noteworthy that this mechanism accounts for the selectivity for trihydrosilanes, which are needed for the formation of a hydrogen substituted silylene, an also for the anti-Markovnikov regioselectivity and the *cis*-stereochemistry of the addition.

Brookhart et al. described a silyl migration pathway for the hydrosilation of olefins by means of a cobalt(III) catalyst $[Co(Cp^*)(P(OMe)_3(CH_2CH_2\text{-}\mu\text{-}H)]^+$. The proposed catalytic cycle, based on deuterium labeling experiments, kinetic studies and NMR identification of intermediates, discards the presence of Co(V) intermediates, in contrast to what would be expected for a Chalk-Harrod-type mechanism. Instead, the authors propose a σ-bond metathesis process for the last step of the catalytic cycle, which circumvents the formation of a cationic Co(V) species [85].



Scheme 50. Catalytic cycle proposed for the hydrosilylation of 1-hexene catalyzed by $[Co(Cp^*)(P(OMe)_3(CH_2CH_2\text{-}\mu\text{-}H)]^+$.

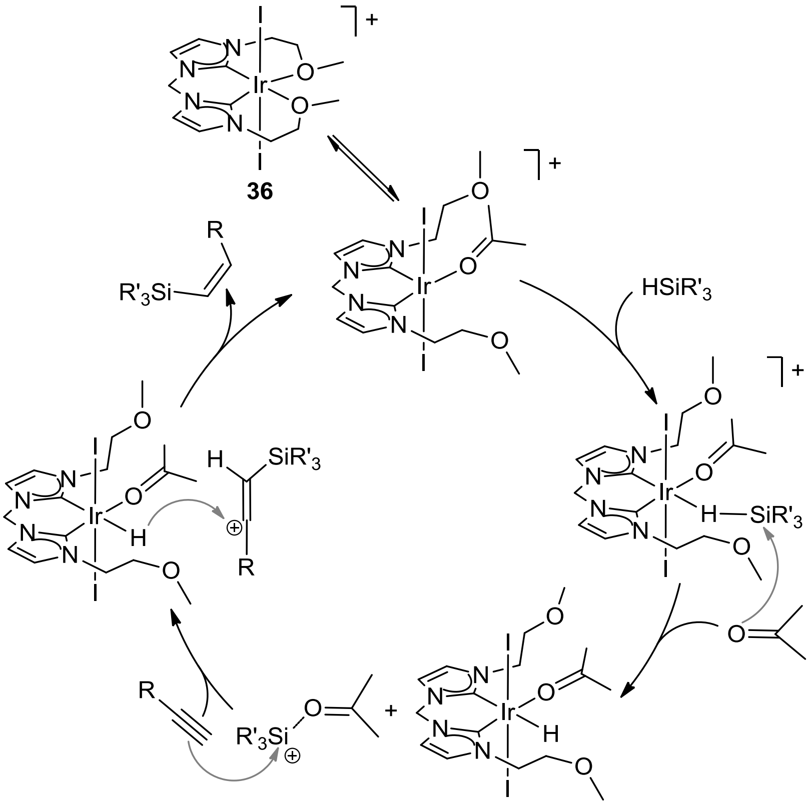
The reaction of terminal alkynes with hydrosilanes may give rise to three different hydrosilylation products, namely β-(Z)-, β-(E)- and α-vinylsilanes, with the latter being rarely obtained selectively [86]. The use of $[Ru(Cp)(NCCH_3)_3]^+$ (**35**) as catalyst for the hydrosilylation of terminal alkynes affords selectively α-vinylsilanes [87]. Wu and Trost proposed an inner sphere mechanism that proceeds via formation of a metallocyclopropene intermediate, which, by means of reductive silyl migration to the carbene, justifies the uncommon regioselectivity of the reaction (Scheme 51). Based on theoretical calculations, the oxidative addition reaction to give a Ru(IV) intermediate are unlikely. Instead, the concerted oxidative addition and hydride-insertion step occurs to afford a metallocyclopropene, which explain the *trans* stereochemistry of the addition. Regarding the regioselectivity of this reaction, the Markovnikov hydride insertion is the lowest energy possibility (favored over Markovnikov or anti-Markovnikov silyl insertion). Subsequently, a counterclockwise rotation of the C_α-C_β bond takes place, followed by silyl migration to the C_α atom. This affords the α-vinylsilane and regenerates the active species.



Scheme 51. Mechanism proposed by Wu and Trost for the Markovnikov hydrosilylation of terminal alkynes with catalyst **35**.

Further theoretical calculations by Wu and Chung on the hydrosilylation of terminal alkynes by complex **32** support the mechanism postulated in Scheme 50 [88]. However, in this case, the silyl Markovnikov addition is the most stable pathway. Subsequently, C_α-C_β bond rotation takes places followed by hydride migration to the C_α atom. This mechanism accounts for the formation of β-(Z)- and β-(E)-vinylsilanes as the major reaction products.

An ionic outer-sphere mechanism that explains the selective formation of β-(Z)-vinylsilanes with Ir-bisNHC complex **36** has been proposed. The first stage of the mechanism entails the dissociation of the ether groups of the k-*C*,*C*,*O*,*O*-(bis-NHC) ligand and concomitant coordination of a solvent molecule (acetone), thus leaving a vacant coordination site for the end-on coordination of the hydrosilane. Subsequently, nucleophilic attack of an acetone molecule (solvent) leads to heterolytic splitting of the Si–H bond. This results in the formation of an oxocarbenium ion and a hydride complex. The latter transfers the silyl moiety to the alkyne to yield the most thermodynamically stable carbocation—the one that results from the anti-Markovnikov addition. Finally, the least hindered nucleophilic attack of the hydride on the carbocation—that with the silyl moiety pointing away from the metal center—furnishes the β-(Z)-vinylsilanes and regenerates the active species (Scheme 52) [89].



Scheme 52. Proposed outer-sphere ionic mechanism for the hydrosilylation of terminal alkynes with catalyst **36**.

Conclusions

In recent years the number of examples of transition metal catalyzed hydrosilylation processes that follow non-classical mechanisms has grown dramatically. The wide diversity of mechanisms that respond to alternative proposals to Ojima-, Chalk-Harrod- and modified Chalk-Harrod-related mechanisms makes it difficult to establish a general pattern that encompasses all of them. However, the great majority of these types of processes share the fact that the electrophilic nature of the silicon species formed thereby plays a key role in the reaction mechanism. This type of interaction is crucial for the heterolytic activation of the Si–H bond and the concomitant formation of silylenium ions, which is common ground for many of the mechanisms discussed in this review. The heterolytic splitting of the Si–H bond usually requires the participation of the metal center as Lewis acid and a heteroatom as Lewis base. The latter may be at the substrate or at a ligand that subsequently transfers the thus formed silylenium ion to the substrate. Nonetheless, this is not always the case, with prominent exceptions being: (i) Oestreich's peripheral mechanism—according to which the substrate (ketone) is activated by a triethoxysilane ligand and then the Si–H bond of a "free" hydrosilane molecule adds across the C=O bond to give the corresponding silylether; and (ii) the Glaser-Tilley's and Gade's mechanisms, which occur via a silylene intermediate; therefore, the activation of the silane is homolytic (Si–H oxidative addition at the metal center). In sharp contrast with classical mechanisms, in the case of the latter, the silicon center interacts by an outer-sphere mechanism with the oxygen of the ketone (substrate) and the thus activated carbonyl carbon becomes susceptible to nucleophilic attack of a hydride ligand. In the case of the former, the olefin (substrate) is inserted into the Si–H bond of the silane ligand without participation of the metal center.

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Graphical Abstract

Text for the Graphical Abstract

This work compiles and discusses the great variety of non-classical transition-metal-catalyzed mechanisms hitherto reported for the reduction of organic molecules with hydrosilanes.