Reactivity of Rhodium–Triflate Complexes with Diphenylsilane: Evidence for Silylene Intermediacy in Stoichiometric and Catalytic Reactions

Roman Goikhman and David Milstein*[a]

Abstract: Addition of Ph_2SiH_2 to [Rh(iPr$_3$P)$_2$(OTf)] (**1**) yielded the thermally unstable Rh^{III} adduct [Rh(iPr$_3$P)$_2$(OTf)(H)(SiPh$_2$H)] (**2**), which decomposed to [Rh(iPr$_3$P)$_2$(H)$_2$(OTf)] (**3**), liberating (unobserved) silylene. The silylene was trapped by **1**, resulting in the Rh^I–silyl complex [Rh(iPr$_3$P)$_2$(SiPh$_2$OTf)]. Complex **3** was converted to **2** by addition of diphenylsilane, providing a basis for a possible catalytic cycle. The last reaction did not involve a Rh^I intermediate, as shown by a labeling study. Complex **1** catalyzed the dehydrogenative coupling of Ph_2SiH_2 to $Ph_2HSi{-}SiHPh_2$. A mechanism involving a silylene intermediate in this catalytic cycle is proposed. The mechanism is supported by complete lack of catalysis in the case of the tertiary silanes Ph_2MeSiH and $PhMe_2SiH$, and by a study of individual steps of the catalytic cycle. The outcome of the reaction of Ph_2SiH_2 with styrene in the presence of **1** depends on the complex/substrate ratio; under stoichiometric conditions olefin hydrogenation prevailed over hydrosilylation, whereas with excess of substrates hydrosilylation prevailed. Catalytic hydrosilylation resulted in double addition giving $Ph_2Si(CH_2CH_2Ph)_2$. Mechanistic aspects of the reported processes are discussed, and a new hydrosilylation mechanism based on silylene intermediacy is proposed.

Keywords: dehydrogenative coupling · diphenylsilane · elimination · hydrosilylation · silylene

Introduction

Transition metals catalyze various synthetically important reactions involving silanes, such as hydrosilylation of olefins and other unsaturated substrates, dehydrogenative coupling of silanes, and various polymerization and polycondensation reactions.[1] The mechanisms of these processes have been extensively studied, but the operating mechanism in each case is still under discussion. For example, several mechanisms describing dehydrocoupling of silanes[1f–j] and hydrosilylation of olefins[1a,b,m] have been proposed. They include an oxidative addition/reductive elimination sequence, σ-bond metathesis, and transition-metal–silylene intermediate complexes. The reported evidence of intermediate silylene complexes in catalytic reactions is mostly indirect. However, a number of stable metallo–silylene complexes have been synthesized and investigated, as summarized in several reviews.[1b,d,2] We report here new findings in the silylene chemistry of unsaturated rhodium complexes, including intermolecular silylene transfer, and propose silylene-based mechanisms for dehydrogenative coupling of silanes and for the industrially important hydrosilylation of alkenes.

Results and Discussion

Reaction of the Rh^I complex [Rh(iPr$_3$P)$_2$(OTf)] (**1**)[3] with Ph_2SiH_2 in toluene at −30 °C quantitatively yielded the oxidative addition Rh^{III} product [Rh(iPr$_3$P)$_2$(OTf)(H)(SiPh$_2$H)] (**2**).[4] Two-dimensional ^{29}Si NMR spectroscopy at −30 °C showed a clear doublet of triplets at $\delta = 19$ ppm. This compound was unstable above 0 °C and decomposed to yield the dihydride [Rh(iPr$_3$P)$_2$(H)$_2$(OTf)] (**3**)[3a] in addition to several minor complexes and a small amount of tetraphenyldisilane (see detailed discussion below).

When two equivalents of **1** were treated with Ph_2SiH_2 at −30 °C, and the reaction mixture allowed to warm up to 0 °C and left at this temperature overnight, formation of complex **3** and a new Rh^I compound (**4**) were detected by NMR spectroscopy. Following the reaction by ^{31}P NMR spectroscopy, we observed the slow simultaneous disappearance of signals assigned to **1** and **2**, and generation of signals assigned to **3** and **4** in the exact proportions: **1**+**2**=**3**+**4**.

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[a] Dr. R. Goikhman, Prof. D. Milstein
Department of Organic Chemistry
The Weizmann Institute of Science, Rehovot 76100 (Israel)
Fax: (+972) 8-934-4142
E-mail: david.milstein@weizmann.ac.il

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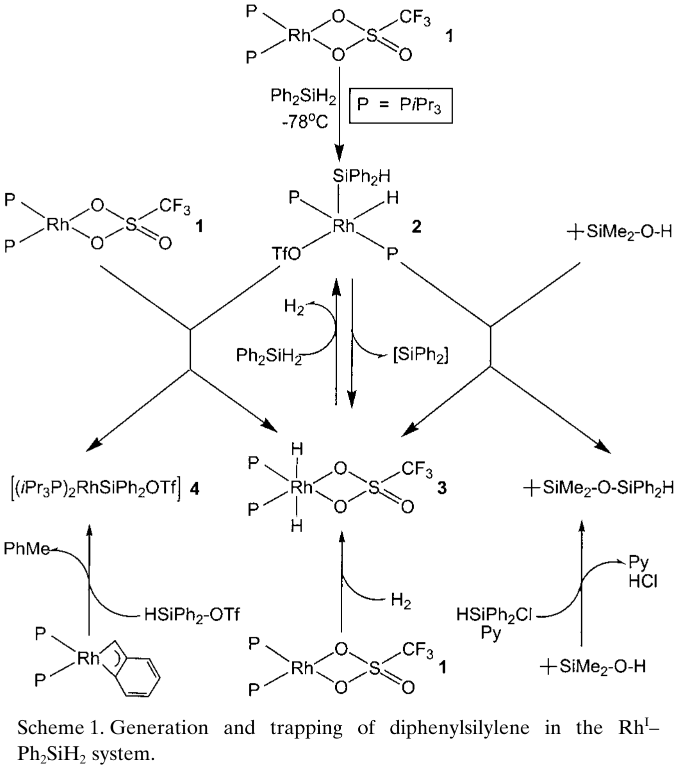
The new compound **4** was identified as [Rh(iPr$_3$P)$_2$(SiPh$_2$OTf)] by ^{1}H, ^{31}P, and two-dimensional ^{29}Si,^{1}H NMR measurements. The spectral data of **2** and **4** clearly reflect the difference in Rh oxidation state. The ^1J(Rh,P) coupling constants are 112 and 150 Hz, respectively. Similar ^1J(Rh,P) coupling constants of 110–117 Hz were reported for [Rh(iPr$_3$P)$_2$(SiAr$_3$)(H)(Cl)] complexes,[4] whereas values for ^1J(Rh,P) higher than 130 Hz usually indicate Rh$^{\text{I}}$ structures.[5]

A doublet of triplets is observed in the ^{29}Si NMR spectrum of **2** at $\delta = 19$ ppm (^1J(Rh,Si) = 62 Hz, ^2J(P,Si) = 14 Hz) and in that of **4** at $\delta = 71.3$ ppm (^1J(Rh,Si) = 106 Hz, ^2J(P,Si) = 19 Hz). ^{29}Si NMR spectroscopy of a Rh$^{\text{III}}$–SiHPh$_2$ complex was reported to give rise to a signal at $\delta = 15$ ppm (^1J(Rh,Si) = 43 Hz).[6] The considerable downfield shift ($\delta =$ 52 ppm) of the ^{29}Si NMR signal of the SiPh$_2$OTf ligand relative to that of SiPh$_2$H has been reported for organic compounds: ^{29}Si NMR signals for HSiPh$_2$OTf and H$_2$SiPhOTf[7a] appear at 27 and 52 ppm downfield from those of H$_2$SiPh$_2$ and H$_3$SiPh,[7b] respectively.

Complex **4** was also generated independently from reaction of [Rh(iPr$_3$P)$_2$(η^3-CH$_2$Ph)][8] with HSiPh$_2$OTf[7a] (see Scheme 1). This last reaction resulted in several other products due to side reactions, such as both Si–H and Si–OTf addition followed by Si–C coupling, and compound **4** was formed in about 15 % yield (by NMR spectroscopy). Preparation of a Rh$^{\text{I}}$–silyl complex from a diphosphine–Rh–benzyl precursor and hydridosilane was reported previously.[5d]

Although the NMR data and the independent generation of **4** clearly indicate that **4** is a Rh$^{\text{I}}$–silyl complex, and that there is no Rh-Si-Rh bridge according to the ^{29}Si NMR spectrum, the exact structure of compound **4** is still ambiguous. A partial silylene character of a SiPh$_2$OTf ligand was observed with a Ru complex based on NMR data, although the triflate group was found to be covalently bound to the silicon in nonpolar solvents.[9] Some resonance contribution of a Rh=Si double bond might make a tricoordinated structure of **4** more stable. The broad ^{31}P NMR signal probably indicates a dynamic process. Due to the bulk of the ligands, a dimeric structure seems to be unlikely. It is possible that the triflate ligand is involved in (reversible) intramolecular coordination to the unsaturated rhodium center. Rhodium(I) 14e complexes, stabilized by weak interactions, have been isolated.[10] A tri-coordinate Rh$^{\text{I}}$ complex was characterized spectroscopically at low temperature,[11a] and such a complex, lacking stabilizing interactions, was also isolated very recently.[11b] Unfortunately, complex **4** is not stable and cannot be isolated.



Scheme 1. Generation and trapping of diphenylsilylene in the Rh$^{\text{I}}$–Ph$_2$SiH$_2$ system.

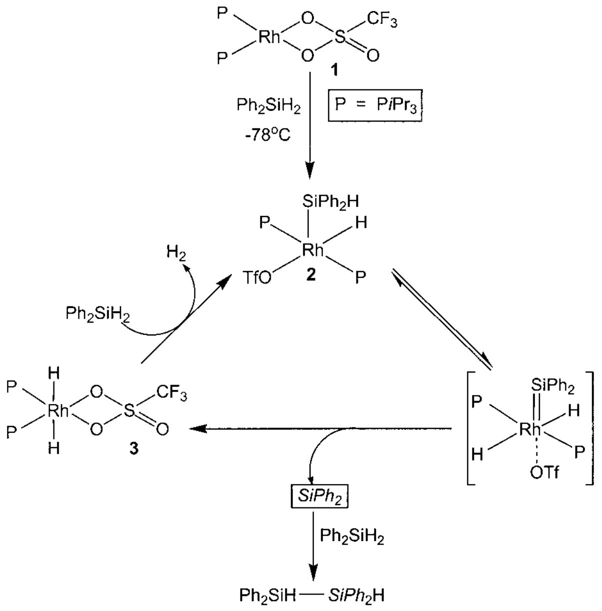
Apparently, the decomposition of **2** involves α-hydrogen elimination from a Rh–SiPh$_2$H moiety, followed by elimination of the silylene SiPh$_2$ from the Rh center. α-Hydrogen transfer from silicon to a metal center in M–SiR$_2$H systems has been reported with other metal complexes.[2d,12] When two equivalents of **1** react with one equivalent of the silane, excess of the Rh$^{\text{I}}$ starting complex can serve as a silylene trapping agent. An alternative mechanism involving dihydrogen elimination from **2** followed by H$_2$ trapping with **1** is unlikely, based on the following experiment. When a solution of **2** in mesitylene was decomposed under vacuum and, in parallel, under atmospheric pressure, no differences were detected in the ratio of the products after completion of the reactions. The reactions resulted in the formation of the expected dihydride complex **3** as a major product rather than the Rh$^{\text{I}}$–silyl **4**. The experiment was carried out with two different concentrations, and no difference whatsoever in the ^{31}P and ^{1}H NMR patterns of the final products was observed. This tends to rule out H$_2$ elimination from **2**, since the liberated H$_2$ would be expected (at least partially) to be removed under vacuum, decreasing the amount of the dihydride **3** formed.

Other experiments aimed at trapping the silylene product were carried out with tBuMe$_2$SiOH, since OH bonds are known to be good trapping agents for silylenes.[13a–d] The silanol was chosen due to its bulk which can minimize side reactions, and also due to the easy characterization and high stability of the desired siloxane product.

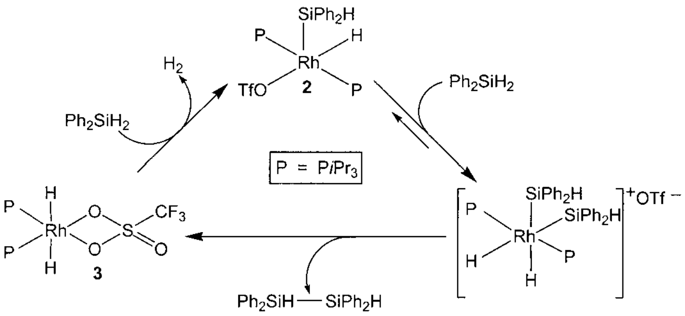
Decomposition of complex **2** in the presence of two equivalents of the silanol resulted in formation of the dihydride **3** and the expected unsymmetrical siloxane tBuMe$_2$Si–O–SiPh$_2$H (over 90 % by NMR spectroscopy based on **2**). Following the slow decomposition of **2** in the presence of the silanol at $-30\,^\circ$C by ^{31}P NMR spectroscopy revealed first-order kinetics in complex **2** ($k_{\text{obs}} = 1.3 \times 10^{-4}$ s^{-1}). The siloxane product was also synthesized independently by reaction of tBuMe$_2$Si–O–H with Cl–SiPh$_2$H in the presence of pyridine. These transformations are summarized in Scheme 1.[14]

Remarkably, the Rh$^{\text{III}}$–dihydride **3** reacted with Ph$_2$SiH$_2$ at 0 °C to yield compound **2**, which in turn decomposed back to **3**, liberating the unobserved silylene intermediate. This reaction sequence forms a basis for catalytic generation of silylenes under very mild conditions.[15] Again, no Rh^I intermediate was involved in the reaction of **3** with the silane, as was confirmed by the following labeling experiment. The deuterio analogue of **3** was prepared from **1** and D_2, and treated with diphenylsilane. At the beginning of the reaction only $[Rh(iPr_3P)_2(OTf)(D)(SiPh_2H)]$ was detected by NMR spectroscopy, and D–H scrambling took place only at later stages of the reaction. Thus the silane seems to react with the Rh^{III}–dihydride complex rather than with a Rh^I intermediate formed by H_2 reductive elimination.

When a 50-fold excess of the diphenylsilane was added to complex **1** at room temperature (or at 0 °C), catalytic dehydrogenative coupling to give $(Ph_2SiH)_2$ took place (92 % yield based on starting Ph_2SiH_2, at 0 °C, 24 h). Since decomposition of **2** very likely proceeds via a silylene intermediate, the mechanism of catalysis may involve silylene insertion into the Si–H bond of a free silane (Scheme 2).[16] A similar mechanism including silane addition to the $M{=}SiR_2$ bond of an intermediate complex resulting in formation of $H{-}M{-}SiR_2{-}SiR_2H$, followed by reductive elimination of the disilane was proposed by Ojima et al. 30 years ago,[17a] but there was no direct evidence for the silylene intermediate, and this mechanism could not explain formation of higher polysilanes. The more accepted Curtis and Epstein mechanism[17b] includes silane double addition followed by Si–Si elimination from the metal center (Scheme 3). To clarify the mechanism we checked the reaction of tertiary silanes that are similar both sterically and electronically to Ph_2SiH_2, namely Ph_2MeSiH and $PhMe_2SiH$. In both cases no catalytic reaction was observed with complex **1** under the same conditions. To ascertain that the methyl substituent does not play a crucial role in reactivity, we performed the reaction with the secondary silane $PhMeSiH_2$, resulting in the expected catalytic formation of disilane $(PhMeSiH)_2$ under the same conditions that were used in the case of Ph_2SiH_2.



Scheme 2. Proposed mechanism for catalytic dehydrogenative coupling of Ph_2SiH_2.



Scheme 3. Curtis–Epstein mechanism for dehydrogenative coupling of Ph_2SiH_2 catalyzed by a Rh^I complex.

The difference in the reactivity of Ph_2SiH_2 (and $PhMeSiH_2$) in comparison with that of the tertiary silanes is striking: no catalysis at all in case of tertiary silanes was detected, whereas the secondary silane was rapidly converted catalytically to the disilane. Steric reasons can be ruled out by comparison of cone angles of the silanes. The available cone angles of phosphines[18] are reported to be identical to those of analogous silyl ligands.[19] Thus, the cone angles of the $SiHPh_2$ and $SiMe_2Ph$ groups are 128° and 122°, respectively, that is, $HSiMe_2Ph$ is sterically less demanding than Ph_2SiH_2. In addition, since $HSiMe_2Ph$ and $H_2SiMePh$ are very similar electronically, major influence of electronic factors on reactivity can be excluded as well.

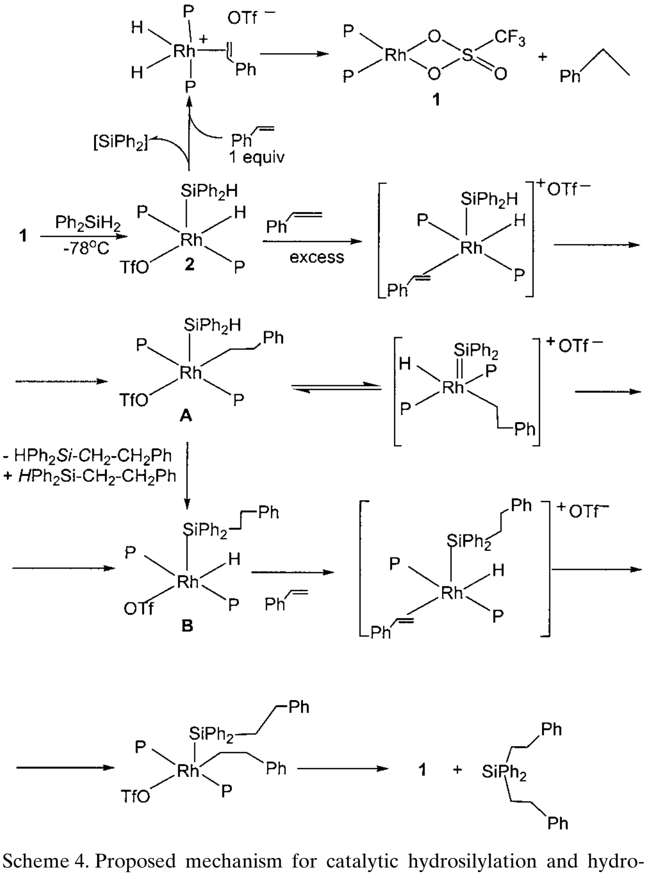
Thus, since the tertiary silanes we studied are very similar sterically and electronically to diphenylsilane, we have to attribute the strikingly different reactivity to the number of Si–H bonds in the silane.

These results demonstrate that a SiH_2 group is essential, and strongly support the suggested mechanism involving activation of *both* hydrogen atoms at *one* silicon center, apparently generating silylene (free or bound) intermediates. Our mechanism is supported not only by the silylene trapping in a single step by using two different trapping agents, but also by extensive previous reports that demonstrated α-elimination from $M{-}SiR_2H$ fragments[12] and insertion of silylenes into Si–H bonds.[13,16] Moreover, a very similar mechanism was recently proposed and investigated for catalytic dehydrocoupling of stannanes.[20] Our proposed mechanism includes a silylene elimination step from a hydrido silyl complex, rather than H_2 elimination, which was suggested by Ojima. The mechanism we propose can lead to formation of higher silanes as a result of silylene insertion into a Si–H bond of the primary disilane product, although it has not been observed in our case. Nevertheless, at this stage Ojima's mechanism cannot be ruled out completely for our system.

Coming back to the decomposition of **2** above 0 °C, we can now identify and explain the resulting mixture. Oxidative addition of silanes to Rh^I complexes is reversible,[21] and hence small amounts of complex **1** and free diphenylsilane are present in the reaction mixture. Conversion of **2** to **3** is accompanied by the generation of diphenylsilylene, which is trapped by small amounts of **1** and Ph_2SiH_2, giving complex **4** and $HSiPh_2SiPh_2H$, respectively (detected by multinuclear NMR spectroscopy).

Another potential silylene trapping agent used was styrene. Interestingly, when a 1:1 mixture of styrene and diphenylsilane was added to a stoichiometric amount of **1**, formation of compound **2** was initially observed. Compound **2** decomposed in the presence of styrene, and the final products of this reaction sequence were complexes **1** and **4**, along with a small amount of **3**. The main organic products were ethylbenzene and bis(2-phenylethyl)diphenylsilane, formed in a ratio of 5:1.

The proposed mechanism is depicted in Scheme 4. The first step (oxidative addition of the silane) was discussed above. The next expected steps (reversible coordination of the olefin and formation of intermediate **A**) are well-defined processes in a catalytic hydrosilylation.[1c] Intermediate **A** is similar to complex **2**, and it most probably decomposes in a similar manner through α-hydrogen elimination (compare with Scheme 2) due to the presence of α-SiH and a labile triflate ligand. However, the resulting silylene intermediate in this case can be intramolecularly trapped by the alkyl ligand to form irreversibly intermediate **B**, as was suggested by Tilley et al.[22] Alternatively, intermediate **B** can be formed from **A** also by Si–C reductive elimination followed by Si–H oxidative addition,[1c] as shown in Scheme 4. Intermediate **B** can easily react with styrene by means of the traditional hydrosilylation mechanism, resulting in the final products depicted in Scheme 4.



Scheme 4. Proposed mechanism for catalytic hydrosilylation and hydrogenation of styrene with Ph_2SiH_2.

Apparently, under *stoichiometric* conditions, coordination of styrene to the intermediate complex **2** is much slower than the α-hydrogen elimination process leading to complex **3**. Following this step, styrene dehydrogenates the dihydride complex **3**, resulting in **1** and ethylbenzene (Scheme 4 top). When ten equivalents of each silane and styrene were added to one equivalent of complex **1**, a *catalytic* reaction took place, resulting in the formation of ethylbenzene and bis(2-phenylethyl)diphenylsilane as the main products in a ratio of 2:5 (as opposed to 5:1 under stoichiometric conditions). This result is likely to be due to reversible coordination of styrene to intermediate **2**, with excess styrene directing the process to hydrosilylation.

Interestingly, formation of the product of addition of two styrene molecules to one molecule of silane is preferred to the mono-addition product, which was not observed in the reactions. A possible explanation for this unusual finding is that intermediate **A** (Scheme 4) undergoes fast rearrangement to intermediate **B**, which adds a second olefin molecule at a much faster rate than Si–H reductive elimination, followed by irreversible Si–C elimination. A similar process was reported with diphenylsilane and ethylene with another Rh system, in which the mono-addition product was not detected;[23] however, it was detected when ethylene was replaced with the less reactive 1-butene. The proposed intermediate step included a bridging silylene complex.[23] Another mechanism involving a silylene intermediate complex in the hydrosilylation reaction as a result of α-hydrogen elimination from a M–Si–H moiety has been proposed recently[24] and studied computationally.[25]

Conclusion

A rare example of α-hydrogen elimination in a Rh–silyl complex was detected, leading to a (unobserved) silylene intermediate, which was trapped with a cationic Rh^I complex[26] or with an organic silanol. Based on our results, a mechanism for dehydrogenative coupling of silanes involving a silylene intermediate was proposed. An interesting competition between hydrosilylation and hydrogenation in a reaction of an olefin with a silane was reported and discussed. A new mechanism for catalytic hydrosilylation resulting in olefin double addition to a silane substrate was proposed.

Experimental Section

General: All the manipulations of air- and moisture-sensitive compounds were carried out by using a nitrogen-filled Vacuum Atmospheres glove box. Solvents were purified by standard procedures, degassed, and stored over molecular sieves in the glove box. All the reagents were of reagent grade. Commercially available silanes were used without further purification. Rhodium complexes were synthesized according to or similarly to literature procedures, as referenced in the paper. NMR spectra were obtained with a Bruker AMX 400 spectrometer at ambient probe temperature in [D$_8$]toluene unless otherwise specified.

Reactions of [Rh(*i*Pr$_3$P)$_2$OTf] (1) with Ph$_2$SiH$_2$

Ratio of reagents 1/Ph$_2$SiH$_2$ 1:1: A solution of **1** (57 mg, 0.1 mmol) in [D$_8$]toluene (0.6 mL) was treated with Ph$_2$SiH$_2$ (18 mg, 0.1 mmol) at −30 °C. The color of the solution changed immediately from deep violet to brown. Complex **2** was formed quantitatively (by NMR spectroscopy). It slowly decomposed at 0 °C to the dihydride complex **3** in approximately 80 % yield and small amounts of **4** and tetraphenyldisilane. NMR data of **2**: ^{31}P{^{1}H}: $\delta = 43.6$ ppm (d, ^1J(Rh,P) = 112 Hz, 2P); ^{1}H NMR: $\delta = 7.87$ (m, 4H; Si-Ph), 7.20 (m, 4H; Si-Ph), 7.10 (m, 2H; Si-Ph), 5.44 (ddt, ^3J(P,H) = 12.3 Hz, ^2J(Rh,H) = 2.3 Hz, ^3J(H,H) = 2.0 Hz, 1H; Si-H), 2.22 (m, 6H; P-C*H*(CH$_3$)$_2$), 1.04 (m, 36H; P-CH(C*H*$_3$)$_2$), −21.85 ppm (ddt, ^2J(Rh,H) = 29.6 Hz, ^3J(P,H) = 13.7 Hz, ^3J(H,H) = 2.0 Hz, 1H; Rh-H); ^{29}Si: $\delta = 19$ ppm (dt, ^1J(Rh,Si) = 62 Hz, ^2J(P,Si) = 14 Hz).

Ratio of reagents 1/Ph$_2$SiH$_2$ 2:1: A solution of **1** (57 mg, 0.1 mmol) in [D$_8$]toluene (0.6 mL) was treated with Ph$_2$SiH$_2$ (9 mg, 0.05 mmol) at −30 °C. The color of the solution changed from deep violet to dark brown and a mixture of complexes **1** and **2** in approximately 1:1 ratio was observed by NMR spectroscopy. The reaction mixture was warmed up to 0 °C and was followed by NMR spectroscopy overnight. Slow decomposition of complex **2** was accompanied by an equivalent consumption of complex **1** and simultaneous appearance of complexes **3** and a new Rh$^{\mathrm{I}}$ complex in 1:1 ratio. The latter compound was assigned as [Rh(*i*Pr$_3$P)$_2$(SiPh$_2$OTf)] (**4**). NMR of **4**: ^{31}P{^{1}H}: $\delta = 45.2$ ppm (d, ^1J(Rh,P) = 150 Hz, 2P); ^{1}H NMR: $\delta = 8.40$ (m, 4H; Si-Ph), 7.23 (m, 4H; Si-Ph), 7.13 (m, 2H; Si-Ph), 2.08 (m, 6H; P-C*H*(CH$_3$)$_2$), 1.02 ppm (m, 36H; P-CH(C*H*$_3$)$_2$); ^{29}Si: $\delta = 71.3$ ppm (dt, ^1J(Rh,Si) = 106 Hz, ^2J(P,Si) = 19 Hz).

Catalytic experiment with a ratio of reagents 1/Ph$_2$SiH$_2$ 1:50: Ph$_2$SiH$_2$ (92 mg, 0.5 mmol) was added to a solution of **1** (6 mg, 0.01 mmol) in [D$_8$]toluene (0.6 mL), and the reaction was stirred overnight at 0 °C. Quantitative conversion of the silane was detected, and (Ph$_2$SiH)$_2$ was formed in 92 % yield (based on starting Ph$_2$SiH$_2$), along with a small amount of Ph$_3$SiH and traces of other silicon species.

Ratio of reagents 1/Ph$_2$SiH$_2$ 1:1 under vacuum: A solution of **1** (80 mg, 0.14 mmol) in mesitylene (2 mL) was treated with Ph$_2$SiH$_2$ (26 mg, 0.14 mmol) at −30 °C. The color of the solution changed immediately from deep violet to brown, indicating the formation of adduct **2**. The reaction mixture was separated into two equal portions at −30 °C. One of the portions was kept under vacuum for 4 h at room temperature, whereas another portion was allowed to stand for the same period of time at normal conditions. ^{31}P NMR spectroscopy of the final mixture was identical in the two experiments.

When the experiment was carried out with 5 mL of mesitylene (instead of 2 mL) almost no difference in the final product ratio was observed. Complex **3** was the major product, along with some starting adduct **2** and a small amount of **4**.

Reaction of [Rh(*i*Pr$_3$P)$_2$OTf] (1) with PhMeSiH$_2$: PhMeSiH$_2$ (12 mg, 0.1 mmol) was added to a solution of **1** (6 mg, 0.01 mmol) in [D$_8$]toluene (0.6 mL), and the reaction was stirred overnignt. Over 90 % conversion of the silane was detected, and (PhMeSiH)$_2$ was formed in 92 % yield (based on starting PhMeSiH$_2$), along with a small amount of other silicon species.

Reactions of [Rh(*i*Pr$_3$P)$_2$OTf] (1) with excess of Ph$_2$MeSiH and PhMe$_2$SiH: The silane (0.5 mmol; 68 mg of PhMe$_2$SiH or 99 mg of Ph$_2$MeSiH) was added to a solution of **1** (6 mg, 0.01 mmol) in [D$_8$]toluene (0.6 mL), and the reaction was stirred overnignt at 0 °C. No catalytic reaction was detected by ^{1}H NMR spectroscopy. Stoichiometric products were not analyzed.

Reaction of [Rh(*i*Pr$_3$P)$_2$OTf] (1) with a mixture of Ph$_2$SiH$_2$ and *t*BuSiMe$_2$OH: A solution of **1** (34 mg, 0.06 mmol) in [D$_8$]toluene (0.5 mL) was treated with a mixture of Ph$_2$SiH$_2$ (11 mg, 0.06 mmol) and *t*BuSiMe$_2$OH (16 mg, 0.12 mmol) in [D$_8$]toluene (0.3 mL) of at −30 °C. Complex **2** was formed quantitatively (by NMR spectroscopy). The reaction mixture was followed by NMR spectroscopy overnight, resulting in slow decomposition of complex **2** to the dihydride **3**. The major organic product was *t*BuSiMe$_2$-O-SiHPh$_2$ (90 % based on the initial Ph$_2$SiH$_2$ amount). ^{1}H NMR of *t*BuSiMe$_2$-O-SiHPh$_2$: $\delta = 7.63$ (m, 4H; Ph), 7.16 (m, 6H; Ph), 5.80 (s, 1H; Si-H, ^1J(Si,H) = 214 Hz), 0.93 (s, 9H; *t*Bu), 0.08 ppm (s, 6H; Me).

Independent synthesis of *t*BuSiMe$_2$-O-SiHPh$_2$: A solution of *t*BuSiMe$_2$OH (13 mg, 0.1 mmol) and pyridine (8 mg, 0.1 mmol) in C$_6$H$_6$ (0.5 mL) was added dropwise to a solution of Ph$_2$SiHCl (22 mg, 0.1 mmol) in C$_6$H$_6$ (0.5 mL) at room temperature. The reaction mixture was stirred for half hour, the pyridinium salt was filtered off, and the solution was evaporated to give the desired siloxane in 80 % yield (25 mg). The ^{1}H NMR data were identical to that reported above.

Reaction of [Rh(*i*Pr$_3$P)$_2$(H)$_2$OTf] (3) with Ph$_2$SiH$_2$

Method 1: A solution of complex **3** (17 mg, 0.03 mmol) in [D$_8$]toluene (0.6 mL) was treated with Ph$_2$SiH$_2$ (5.5 mg, 0.03 mmol) at 0 °C, producing complex **2** as a major product within minutes. Compound **2** decomposed overnight to the starting complex **3** and a mixture of unidentified silicon-containing products.

Method 2: A solution of [Rh(*i*Pr$_3$P)$_2$(D)$_2$OTf] (prepared analogously to **3**[3] from **1** using deuterium bubbling) (17 mg, 0.03 mmol) in [D$_8$]toluene (0.6 mL) was treated with Ph$_2$SiH$_2$ (5.5 mg, 0.03 mmol) at −10 °C. Only [Rh(*i*Pr$_3$P)$_2$(D)(SiPh$_2$H)OTf] was detected by ^{1}H and ^{2}H NMR spectroscopy at early stages of the reaction. After 15 min a scrambling between Rh−D and Si−H was observed.

Reactions of 1 with a mixture of Ph$_2$SiH$_2$ and styrene

Ratio of reagents 1/Ph$_2$SiH$_2$/styrene 1:1:1: A solution of **1** (17 mg, 0.03 mmol) in [D$_8$]toluene (0.5 mL) was treated with a mixture of Ph$_2$SiH$_2$ (5.5 mg, 0.03 mmol) and styrene (3 mg, 0.03 mmol) at −30 °C. The color of the solution immediately changed from deep violet to brown. Complex **2** was formed quantitatively (by NMR spectroscopy). The reaction mixture was warmed up to 0 °C and followed by NMR spectroscopy overnight. Slow decomposition of complex **2** was observed, accompanied by initial appearance of the dihydride **3**, which transformed to complex **1** towards the end of the reaction. The major organic products were ethylbenzene (60 % NMR yield, based on the initial amount of styrene) and bis(phenethyl)diphenylsilane (12 % NMR yield, based on the initial amount of diphenylsilane), along with some unidentified silicon-containing products. ^{1}H NMR data of bis(phenethyl)diphenylsilane: $\delta = 7.0$–7.5 (overl. m, 20H; Ph), 2.58 (m, 4H; Ph-C*H*$_2$), 1.33 ppm (t, 4H; Si-C*H*$_2$). The NMR spectrum was identical to that of the commercially purchased compound (Aldrich).

Ratio of reagents 1/Ph$_2$SiH$_2$/styrene 1:10:10: A solution of **1** (17 mg, 0.03 mmol) in [D$_8$]toluene (0.5 mL) was treated with a mixture of Ph$_2$SiH$_2$ (55 mg, 0.3 mmol) and styrene (30 mg, 0.3 mmol) at −30 °C. The color of the solution immediately changed from deep violet to brown, and complex **2** was formed quantitatively (by NMR spectroscopy). The reaction mixture was warmed up to 0 °C and followed by NMR spectroscopy overnight. Decomposition of complex **2** to **1** was observed, and the major organic products were ethylbenzene (15 % NMR yield) and bis(phenethyl)diphenylsilane (37 % NMR yield), along with some unidentified silicon-containing products.

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