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"Synergistic Effects of Two Si−H Groups and a Metal Center" in Transition Metal-Catalyzed Hydrosilylation of Unsaturated Molecules: A Mechanistic Study of the RhCl(PPh$_3$)$_3$-Catalyzed Hydrosilylation of Ketones with 1,2-Bis(dimethylsilyl)benzene

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Three rhodadisilacyclopentene complexes are synthesized by the reaction of 1,2-bis(dimethylsilyl)benzene with RhCl(PPh$_3$)$_3$ or Rh(H)(PPh$_3$)$_4$, and their contributions to the catalytic hydrosilylation of acetone are discussed. Treatment of the rhodium precursor RhCl(PPh$_3$)$_3$ or Rh(H)(PPh$_3$)$_4$ with 1,2-bis(dimethylsilyl)benzene affords an unstable Rh(V)-trihydride species having a rhodadisilacyclopentene skeleton, Rh(Me$_2$SiC$_6$H$_4$SiMe$_2$)(H)$_3$(PPh$_3$)$_2$ (**1**), as a primary product, which is formed by double oxidative addition of 1,2-bis(dimethylsilyl)benzene to the rhodium center. The complex **1** eliminates H$_2$ upon concentration to quantitatively form a Rh(III)-monohydride complex, Rh(SiMe$_2$C$_6$H$_4$SiMe$_2$)(H)(PPh$_3$)$_2$ (**2**). Further oxidative addition of 1,2-bis(dimethylsilyl)benzene to **2** gives a Rh(III)-trisilyl complex, Rh(Me$_2$SiC$_6$H$_4$SiMe$_2$)(η^1-HSiMe$_2$C$_6$H$_4$SiMe$_2$)(PPh$_3$) (**3**), in which there is an agostic interaction between the Si−H bond and the Rh(III) center. Elimination of H$_2$ from **1** is reversible, and the most effective method for preparing **1** in solution is found to be treatment of **2** with H$_2$. The catalytic behavior of these three new rhodadisilacyclic complexes, RhCl(PPh$_3$)$_3$, and Rh(H)(PPh$_3$)$_4$, in the hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene was studied. The results suggest the important contribution of the trihydride **1** in the synergistic effect of two proximate Si−H bonds, leading to an unusual rate enhancement in the hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene.

Introduction

The catalytic hydrosilylation of alkenes and alkynes is one of the most important reactions for the preparation of organosilicon compounds in the laboratory as well as on an industrial scale.[1] In general, hydrosilylation is recognized as a useful tool in organic synthesis. Activation of Si−H bonds by certain transition metal complexes provides good methods for the reduction of carbonyl compounds, including the asymmetric synthesis of chiral silyl ethers from prochiral ketones.[2] It is well known that the rate and selectivity of these reactions are controlled by appropriate choice of organosilanes and transition metal catalysts. Thus, various hydrosilanes with a wide variety of substituents have been used in hydrosilylation, where the reactivity of the silanes is actually controlled by tuning the steric and electronic character induced by the substituents of the silicon atom. Various transition metal compounds including Rh, Ir, Ru, Pt, Co, Pd, and Ni act as hydrosilylation catalysts, in which the type of metal, the valency of the metal, and the auxiliary ligands used are important factors in determining the rate and selectivity of the reaction.[3]

Interestingly, there are several unique catalytic reactions of hydrosilanes, which are accomplished only when two Si−H groups are located spatially close together. The first example of such a reaction reported in the literature is the RhCl(PPh$_3$)$_3$-catalyzed reduction of nitriles, which cannot be achieved by conventional hydrosilanes: Corriu and co-workers discovered that 1,2-bis(dimethylsilyl)benzene reacted successfully with benzonitrile to afford the corresponding *N*,*N*-disilylated benzylamine in low yields (Scheme 1, eq 1).[4] The second example

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(1) (a) Ojima, I. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rapport, Z., Eds.; Wiley: New York, 1989. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (d) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon: Oxford, U.K., 1992. (e) Marciniec, B.; Guliński, J. *J. Organomet. Chem.* **1993**, *446*, 15. (f) Marciniec, B. *Silicon Chem.* **2002**, *1*, 155.

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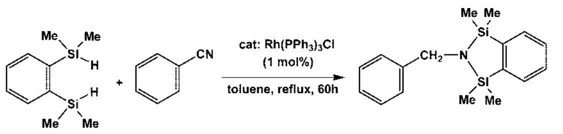
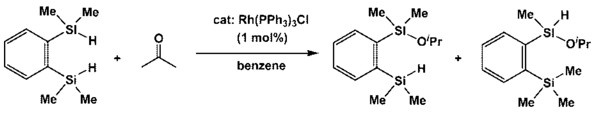
10.1021/om800151w CCC: $40.75

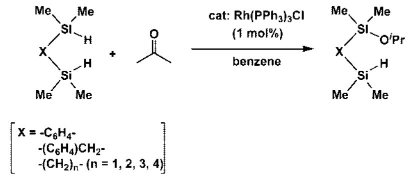
was reported by our research group in 1989: the $RhCl(PPh_3)_3$-catalyzed reduction of ketones with 1,2-bis(dimethylsilyl)benzene showed a significant rate enhancement as compared with the same reaction with phenyldimethylsilane. The reaction was accompanied by a unique methyl group migration between the two silicon atoms (eq 2a).[5] This unusual rate enhancement was generally seen in $Rh(PPh_3)_3Cl$-catalyzed hydrosilylations of ketones with the molecule containing two Si−H groups at a close distance (eq 2b). As a typical example, the hydrosilylation rate of acetone with $Me_2HSi(CH_2)_nSiHMe_2$ (n = 2 or 3) is 50−120 times higher than with $EtMe_2SiH$, whereas there is no difference between the rate of the reaction with $Me_2HSi(CH_2)_nSiHMe_2$ (n = 1 or 4) and that with $EtMe_2SiH$. Our recent work has revealed that the rate enhancement provided by the proximity effect of two Si−H groups is now generally seen in other transition metal-catalyzed reductions of carbonyl compounds as well. Thus, the ruthenium- or platinum-catalyzed silane reductions of carboxamides and other carbonyl compounds (eq 2c) were achieved successfully when using $Me_2HSiOSiHMe_2$ or polymethylhydrosiloxane (PMHS) as the hydrosilane.[6]



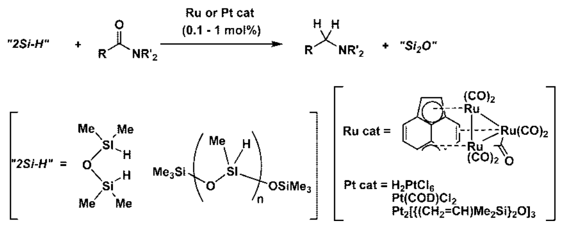
(eq 1)



(eq 2a)

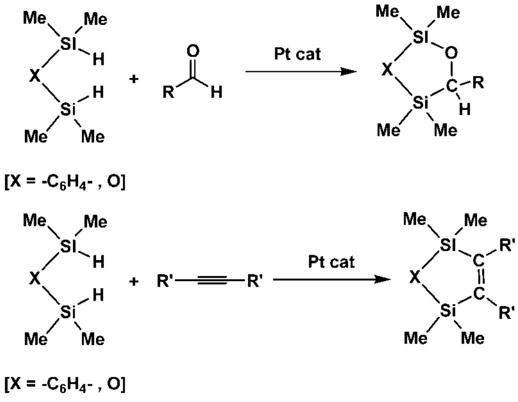


(eq 2b)

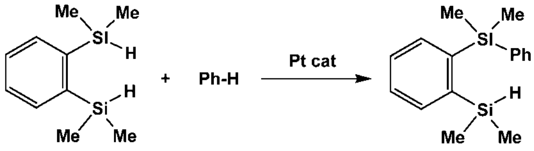


(eq 2c)

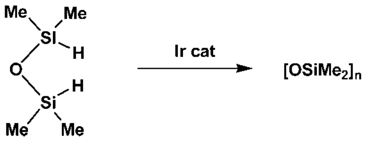
Another example of the proximity effect of silanes is seen in a series of investigations by Tanaka and co-workers, who realized platinum-catalyzed dehydrogenative double silylations of alkynes, alkenes, dienes, and aldehydes with 1,2-bis(dimethylsilyl)benzene (eq 3).[7] They also found that treatment of 1,2-bis(dimethylsilyl)benzene with benzene under platinum catalysis resulted in replacement of a silicon hydride by a phenyl group (eq 4). Such dehydrogenative reactions via C−H bond activation did not occur with phenyldimethylsilane.[8] It is of interest that 1,2-bis(dimethylsilyl)benzene is not the only silane effective for the reaction shown in eq 3. The authors commented briefly that similar dehydrogenative arylation also took place with 1,1,3,3-tetramethyldisiloxane. Iridium-catalyzed oligomerization of 1,1,3,3-tetramethyldisiloxane, reported by Curtis et al., may belong to the same category of reactions, in which redistribution of pentamethyldisiloxane was significantly slow under the same conditions (eq 5).[9]



(eq 3)



(eq 4)



(eq. 5)

The "proximity effect of dual Si−H groups", seen in the above examples, cannot be explained by conventional electronic and steric considerations of hydrosilanes. Metalladisilacyclic complexes, which may give a clue to understand the mechanism and which are shown as **A** and **B** in Chart I, are formed by double oxidative addition of bifunctional silanes to transition metal complexes followed by dehydrogenation. The intermediates **A** and **B** reasonably explain Tanaka's catalytic dehydrogenative double-silylation reactions and Curtis's dehydrogenative oligomerization. However, they cannot be used to explain our $RhCl(PPh_3)_3$-catalyzed hydrosilylation reactions of ketones with silanes, because the hydrosilylation of ketones takes place by way of addition of Si−H across the C=O bond and does not involve dehydrogenation. Although the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of ketones with reactive bifunctional silanes such as $Me_2HSi(CH_2)_nSiHMe_2$ (n = 2) is too rapid to capture possible catalytic intermediates from the reaction of the silane with $RhCl(PPh_3)_3$, the study of the oxidative addition of $RhCl(PPh_3)_3$ with much less reactive $Ph_2HSi(CH_2)_2SiHMe_2$ or $Ph_2HSi(CH_2)_2SiHPh_2$ provided NMR evidence suggesting the

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Scheme 1

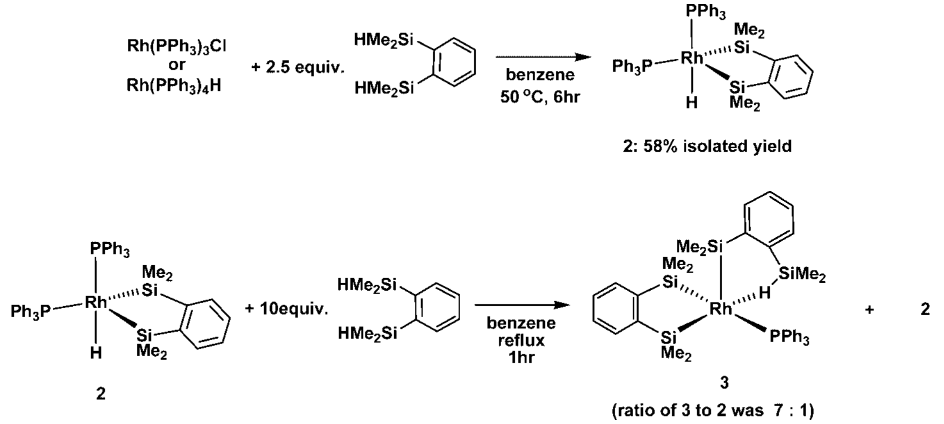
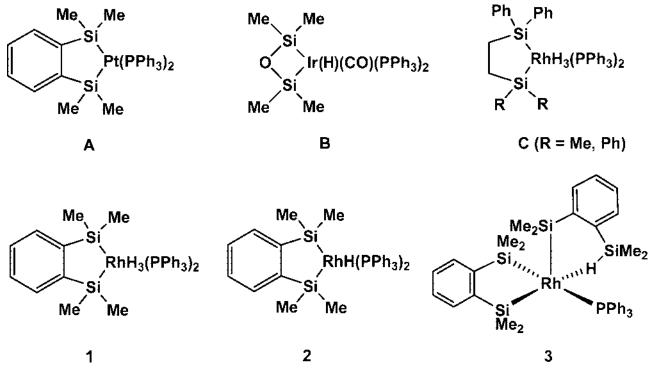


Chart 1



existence of a Rh(V)H_3 metalladisilacyclic species **C**.[5c] However, further mechanistic studies were hampered by the extreme moisture sensitivity of the formed rhodium species. In this paper, we report a solution to this problem, namely, by the characterization of the reaction products of 1,2-bis(dimethylsilyl)benzene with $RhCl(PPh_3)_3$, which can be isolated successfully under conditions where moisture is excluded rigorously. Combination of advanced techniques for the handling of unstable organometallics, their crystallography, and NMR spectroscopy has enabled us to characterize a rhodadisilacyclopentene **1**, similar to **C**, and two novel rhodadisilacyclopentenes, **2** and **3** (Chart 1). Their stoichiometric and catalytic reactions with acetone suggest a role of these intermediates in the catalytic cycle of the hydrosilylation of ketones.

Results and Discussion

NMR Observation of Three Rhodium Species in the Oxidative Addition of 1,2-Bis(dimethylsilyl)benzene to $RhCl(PPh_3)_3$. Catalytic hydrosilylation reactions are believed to be initiated by an oxidative addition of a Si−H moiety to a transition metal species. It is known that the reaction of $RhCl(PPh_3)_3$ with R_3SiH gives the oxidative adduct $(R_3Si)Rh(H)(Cl)(PPh_3)_2$, with a trigonal bipyramidal structure.[10] In contrast to this, we reported earlier[5c] that treatment of $RhCl(PPh_3)_3$ with $Ph_2HSi(CH_2)_2SiHMe_2$ provides a species showing three unresolved Rh−H resonances at −6.7, −7.3, and −10.8 ppm with an integrated ratio of 1:1:1, whereas the reaction with $Ph_2HSi(CH_2)_2SiHPh_2$ gives a species showing two ill-resolved signals at −6.3 and −10.6 ppm in an integral ratio of 2:1. The spectral features of these rhodium species are consistent with those of the Rh-trihydride species **C** in Chart 1, formed by double oxidative addition of bifunctional silanes followed by replacement of the chloro ligand by a hydride. However, at that time, extreme moisture sensitivity of these complexes prevented any further studies, including an X-ray structure determination.

Anticipating the instability of the expected products, we first carried out NMR studies on the products, formed by careful treatment of $RhCl(PPh_3)_3$ with 1,2-bis(dimethylsilyl)benzene (10 equiv) in C_6D_6 at room temperature for 1 h under rigorous exclusion moisture and air. The reaction mixture provided signals due to two different rhodium hydride species, $Rh(Me_2SiC_6H_4SiMe_2)(H)_3(PPh_3)_2$ (**1**) and $Rh(SiMe_2C_6H_4SiMe_2)(H)(PPh_3)_2$ (**2**), in a ratio of 9:1. The rhodium trihydride **1** is unstable and readily liberates H_2 to form **2**. In a typical example, **1** was completely converted to **2**, when the C_6D_6 solution described above was frozen, degassed, and warmed to room temperature. Interestingly, **2** underwent further oxidative addition with 1,2-bis(dimethylsilyl)benzene to form a third rhodium species having three Rh−Si bonds, $Rh(Me_2SiC_6H_4SiMe_2)(\eta^1\text{-}HSiMe_2C_6H_4SiMe_2)(PPh_3)$ (**3**). Thus, treatment of $Rh(PPh_3)_3Cl$ with 10 equiv of 1,2-bis(dimethylsilyl)benzene in C_6H_6 at room temperature for 1 h, followed by concentration of the resulting solution, gave a 1:1 mixture of **2** and **3**. It is likely that **1** was converted to **2** during the concentration process, which subsequently underwent further oxidative addition of 1,2-bis(dimethylsilyl)benzene still present in the reaction mixture to form **3**. In fact, treatment of isolated **2** with 1,2-bis(dimethylsilyl)benzene afforded **3** in ca. 68% yield. Formation of **1** from $RhCl(PPh_3)_3$ involves reduction of Rh−Cl to Rh−H with 1,2-bis(dimethylsilyl)benzene; this is supported by detection of 1-(chlorodimethylsilyl)-2-(dimethylsilyl)benzene in the ^1H NMR spectrum. The hydride precursor $RhH(PPh_3)_4$ is also found to be viable as a precursor of **1**, **2**, and **3**, too.

Isolation and Characterization of Rh(III) Disilacyclic Complexes $Rh(SiMe_2C_6H_4SiMe_2)(H)(PPh_3)_2$ (2) and $Rh(Me_2SiC_6H_4SiMe_2)(\eta^1\text{-}HSiMe_2C_6H_4SiMe_2)(PPh_3)$ (3). Although **1** was detectable in a solution NMR spectrum, facile elimination of H_2 upon workup prevented the isolation of **1**. Attempted isolation of **1** under various conditions led to exclusive formation of a mixture of **2** and **3**, the ratio of which was controlled by both the charged ratio of rhodium precursor and 1,2-bis(dimethylsilyl)benzene and the reaction temperature applied. Treatment of 2.5 equiv of 1,2-bis(dimethylsilyl)benzene with either $Rh(PPh_3)_3Cl$ or $RhH(PPh_3)_4$ at 50 °C for 6 h gave a mixture of **2** and **3**, in which **2** was the major product (**2**:**3** > 9:1). Subsequent recrystallization of the mixture from toluene/hexane

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[10] (a) Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440. (b) de Charentenay, F.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, *787.* (c) Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J. Chem. Soc. A* **1974**, *2311.* (d) Haszeldine, R. N.; Parish, R. V.; Parry, D. *J. Chem. Soc. A* **1969**, 683.

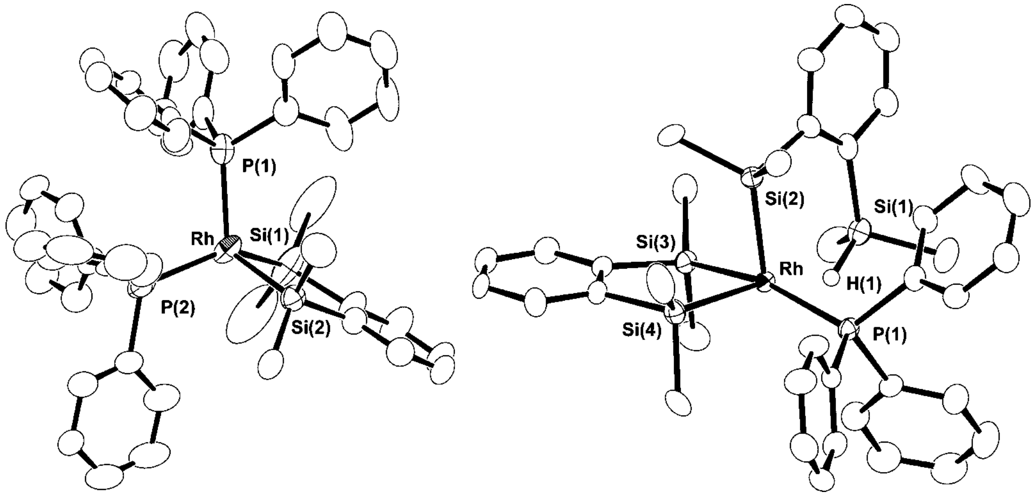

Figure 1. Molecular structures of **2** (left) and **3** (right) with 50% probability ellipsoid. Hydrogen atoms except for the H(1) atom of **3** were omitted for clarity.

gave **2** in a pure form in 58% yield. In contrast, **3** was obtained as the major product, when the reaction was carried out under reflux in benzene for 1 h in the presence of an excess amount of 1,2-bis(dimethylsilyl)benzene. Thus, treatment of 1,2-bis(dimethylsilyl)benzene (10 equiv) with Rh(PPh$_3$)$_3$Cl for 1 h under benzene reflux conditions afforded a mixture of **2** and **3** in a ratio of 2:7, whereas reaction of the silane (10 equiv) with RhH(PPh$_3$)$_4$ gave a mixture of **2** and **3** in a ratio of 2:5. The trisilyl complex **3** was alternatively prepared by the reaction of **2** with 1,2-bis(dimethylsilyl)benzene (10 equiv) under reflux in benzene for 1 h, which afforded a 1:7 mixture of **2** and **3** (Scheme 1).

Isolation of **2** made possible the complete spectroscopic assignments and the determination of the molecular structure by crystallography. In the ^{31}P NMR spectrum of **2**, two doublets appear at 35.7 ($J_{\mathrm{Rh-P}} = 131.5$ Hz) and 26.9 ($J_{\mathrm{Rh-P}} = 92.1$ Hz) ppm, suggesting the existence of two magnetically nonequivalent PPh$_3$ ligands. The ^{1}H NMR spectrum of **2** gave a signal due to a Rh−H at −7.31 ppm as a doublet of doublets. The gNMR simulation[11] of this signal revealed that there is one large trans P−H coupling ($J_{\mathrm{P-H}} = 74$ Hz), together with a small Rh−H and a cis P−H coupling ($J_{\mathrm{P-H}} = 24.4$ Hz, $J_{\mathrm{Rh-H}} = 6.4$ Hz). The T_1 value of this hydride signal was found to be 926 ms at room temperature, which is consistent with that of classical transition metal hydride complexes. The signals due to the SiMe$_2$ groups appeared as two singlets at 0.49 and 0.70 ppm in the ^{1}H NMR spectrum, whereas two carbon resonances were found to be at $\delta = 8.79$, 12.92 in the ^{13}C NMR spectrum. These correspond to the two symmetric organosilyl moieties with two magnetically nonequivalent methyl moieties, as would be observed for the molecular structure described below. The ^{29}Si{^{1}H} NMR spectrum of **2** showed a doublet of doublets at $\delta = 40.4$ ppm (d, $J = 35.7$, 42.5 Hz). The IR spectrum showed one strong absorption band derived from the Rh−H moiety at 1994 cm^{-1}.

These spectroscopic features are fully consistent with the molecular structure of **2**, which was confirmed by X-ray diffraction analysis. ORTEP drawings are shown in Figure 1, and selected bond distances and angles are summarized in Table 1. Complex **2** consists of a five-membered rhodadisilacyclic skeleton with two phosphorus ligands. The rhodium center adopts a distorted trigonal bipyramidal coordination geometry with two silicon atoms and one of two phosphorus atoms (P(2)) at the equatorial plane and the other phosphorus atom (P(1)) at the apical position. The hydride, which should occupy one coordination site of the apical site, was not detected in the Fourier map; however, its existence is reasonable from the space in the molecular structure. The Rh atom is out of the plane defined by Si(1), Si(2), and P(2) by ca. 0.73 Å due to the steric repulsion between the two PPh$_3$ ligands and that between the apical PPh$_3$ and a methyl group of the SiMe$_2$ moieties nearby. The sum of the three angles in the equatorial plane is 324.8°. The Rh−Si bond lengths (2.2918(13), 2.308(2) Å) are comparable to those found in previously reported five-coordinated trigonal bipyramidal rhodium−silyl complexes.[12] The bond distance of Rh−P(1) (2.3919(13) Å) is slightly longer than that of Rh−P(2) (2.3305(14) Å), presumably due to the strong trans influence between the P(1)−Rh−H bonds.

Table 1. Representative Bond Lengths and Angles for 2 and 3

	2	3
	Bond Lengths (Å)	
Rh−Si(1)	2.308(2)	
Rh−Si(2)	2.2918(13)	2.273(2)
Rh−Si(3)		2.356(2)
Rh−Si(4)		2.345(2)
Rh−P(1)	2.3919(13)	2.4610(14)
Rh−P(2)	2.3305(14)	
Rh−H(1)		2.032(8)
Si−H(1)		1.41(10)
	Bond Angles (deg)	
Si(1)−Rh−Si(2)	84.06(6)	
Si(3)−Rh−Si(4)		81.73(6)
P(1)−Rh−P(2)	105.80(4)	
P(1)−Rh−Si(1)	107.27(5)	
P(1)−Rh−Si(2)	117.81(4)	107.58(5)
P(1)−Rh−Si(3)		165.60(6)
P(1)−Rh−Si(4)		98.87(5)
P(2)−Rh−Si(1)	137.37(5)	
P(2)−Rh−Si(2)	103.39(4)	
Rh−H(1)−Si(1)		134.96(5)
H(1)−Si(1)−Rh		27.80(5)

Although **3** was not isolated in pure form, its unequivocal spectroscopic assignment is possible, and recrystallization gave

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(11) *gNMR Ver. 4.0*; Cherwell Scientific Ltd.: Oxford, United Kingdom, 1995.

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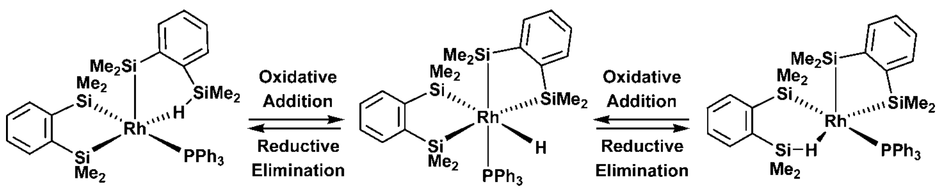
Scheme 2



a single crystal suitable for X-ray structure determination. In contrast to the presence of two doublets of doublets of the Rh−P signals found in **2**, **3** showed a single ^{31}P resonance at 14.2 ppm ($J_{\mathrm{Rh-P}} = 85.5$ Hz). In the ^{1}H NMR spectrum, no peak could be found in the metal−hydride region (−20 to −1 ppm). Instead, a signal accompanied by a satellite appeared at −0.26 ppm. This significant upfield shift compared with that of 1,2-bis(dimethylsilyl)benzene ($\delta = 4.8$ ppm) as well as the coupling constant of the satellite signal ($J_{\mathrm{29Si-1H}} = 112$ Hz) indicates an agostic interaction of the Si−H moiety with the rhodium center. Typical $J_{\mathrm{29Si-1H}}$ values for satellite signals in the presence of an agostic interaction are 20−140 Hz (α-agostic, 20−80 Hz; *β*-, *γ*-, and *δ*-agostic, 80−140 Hz).[13] These values are different from those of H−M−Si species (<20 Hz) and uncoordinated Si−H groups (150−200 Hz; 188 Hz for 1,2-bis(dimethylsilyl)-benzene).[13] As a closely related example with **3**, a *δ*-agostic interaction between the transition metal center and the Si−H moiety was observed in $W(CO)_4\{Ph_2PCH_2CH_2Si(H)R_2\}$ (R = Me, Ph) reported by Schubert and Gilges, in which the $J_{\mathrm{29Si-1H}}$ values are 98.1 Hz for R = Ph and 95.2 Hz for R = Me.[14] Another related complex with a *γ*-agostic Rh−H−Si interaction was reported by Bergman and Brookhart; the $J_{\mathrm{29Si-1H}}$ value of $[Cp^*Rh(PMe_3)\{o\text{-}(HPh_2Si)C_6H_4\}](BAr^F_4)$ ($Ar^F = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$) was reported to be 84 Hz.[15] The crystal structure of **3** (vide infra) indicates that eight inequivalent Me groups should be observed in ^{1}H NMR spectroscopy, in which six ^{1}H resonances are singlets and another two protons are doublets. In the actual ^{1}H NMR spectrum measured at room temperature, only four signals appeared at 0.14, 0.54, 0.58, and 0.63 ppm, and all of them are singlets. Dynamic behavior was observed in the ^{1}H NMR spectra at low temperature, in which these four singlets started to broaden at −70 °C and turned broad at −90 °C. Although ^{13}C NMR measurement at low temperatures was hampered by limited solubility of **3**, it is consistent with ^{1}H NMR that four signals appeared at 1.48, 1.59, 6.15, and 9.66 ppm in the ^{13}C NMR spectrum at room temperature. A plausible explanation of these spectroscopic features is the reversible oxidative addition/reductive elimination process shown in Scheme 2, which could provide the observation of the methyl signal due to the $H-SiMe_2$ group to be a singlet and broadening of the signals at low temperatures. The IR spectrum showed one strong absorption band derived from the Si−H moiety in **3** at 1966 cm^{-1}, ca. 170 cm^{-1} lower than that of free 1,2-bis(dimethylsilyl)benzene (2140 cm^{-1}).

These data are also consistent with the molecular structure of **3**, shown in Figure 1. The coordination geometry around the Rh center in **3** is best described as a square-pyramidal arrangement, formed by one phosphorus, two silicon, and one agostic Si−H moiety in the basal plane, and the remaining silicon (Si(2)) atom is at the apical position. An agostic interaction of the Si−H group in **3** was supported unequivocally by the location of the hydrogen atom in the Fourier map. The Rh···(H−Si) distance (2.032(8) Å) is longer than those of known α-agostic M···(H−Si) complexes (typical values are 1.5−1.8 Å), but close to those in *β*- and *γ*-agostic M···(H−Si) complexes (typical values are 1.8−2.5 Å) reported in the literature.[13a] In several *σ*-Si−H complexes in the literature,[13] strong back-donation from the occupied orbital of the metal to σ^* of the Si−H moiety results in significant elongation of the Si−H bond distances (normally 1.6−1.9 A). The Si(1)−H(1) length (1.41(10) Å) of **3** suggests the weak $\delta_{\mathrm{Rh}} \rightarrow \sigma^*_{\mathrm{Si-H}}$ back-bonding interaction. The Rh−Si(1) distance of 3.082 Å indicates no direct Rh−Si bonding interaction, which is often observed in α-agostic M···(H−Si) complexes.[13] Two of the three Rh−Si bonds (Rh−Si(3) = 2.356(2), Rh−Si(4) = 2.345(2) Å) are longer than that of the third (Rh−Si(2) = 2.273(2) Å), and the Rh−P bond length (2.4610(14) Å) is significantly longer than that found in **2** or those previously reported for trigonal bipyramidal Rh−silyl phosphine complexes. This may indicate a strong trans influence of the silyl, phosphorus, and agostic Si−H moieties. Similar elongation of the Rh−Si and Rh−P bonds in the basal plane have been reported in square-pyramidal $Rh(PMe_3)_2[SiMe_2\text{-}C(Me){=}C(Me)SiMe(SiMe_3)](SiMe_3)$, in which the $Rh-Si_{\mathrm{basal}}$ lengths have been reported to be 2.406(2) and 2.346(2) Å, whereas the shorter $Rh-Si_{\mathrm{apical}}$ bond distance was found to be 2.309(2) Å.[16]

Reversible Reaction of 2 with 1 atm of H_2 to Afford Rh(V) Trihydride Complex 1. As described above, the Rh(V) trihydride complex $Rh(SiMe_2C_6H_4SiMe_2)(H)_3(PPh_3)_2$ (**1**) is unstable and facilely eliminates H_2 to form **2**; this is a problem not only for obtaining a single crystal suitable for X-ray structure determination but also for preparing an NMR sample without contamination of **2**. We have discovered that the elimination of H_2 is reversible and that the best method for preparing a solution containing **1** in pure form is by treatment of **2** with H_2 (1 atm) in C_6D_6 or toluene-d_8 at room temperature. As soon as the solution is exposed to H_2, **1** is quantitatively formed. **1** is stable enough to carry out lengthy NMR experiments as long as the solution is kept under a hydrogen atmosphere. The ^{1}H and ^{31}P NMR resonances show dynamic behavior, typically seen in the seven-coordinated transition metal complexes: the ^{1}H NMR spectrum of **1** in toluene-d_8 at room temperature shows only one broad Rh−H signal at around −8.4 ppm, together with one broad signal at 0.52 ppm due to the $Rh-SiMe_2$ moiety. In contrast, ^{1}H NMR spectra measured in toluene-d_8 at lower than −70 °C afforded two Rh−H signals at −10.42 (br d, $J_{\mathrm{H-P}} = 133$ Hz) and −6.90 (br s) ppm as ill-resolved signals in an integral ratio of 1:2. The T_1 values were estimated to be 2002 ms ($\delta = -6.90$) and 1906 ms ($\delta = -10.42$), respectively, indicating classical hydrides. In the ^{1}H NMR spectrum, the large H−P coupling of the peak at −10.42 ppm suggests that one hydride is located at a position trans to one of the phosphorus ligands. Similarly, the $^{31}P\{^{1}H\}$ NMR spectrum at room temperature shows only one very broad signal at around $\delta = 36$ ppm, whereas two sharp signals appear at 28.4 ($J_{\mathrm{Rh-P}} = 85.5$

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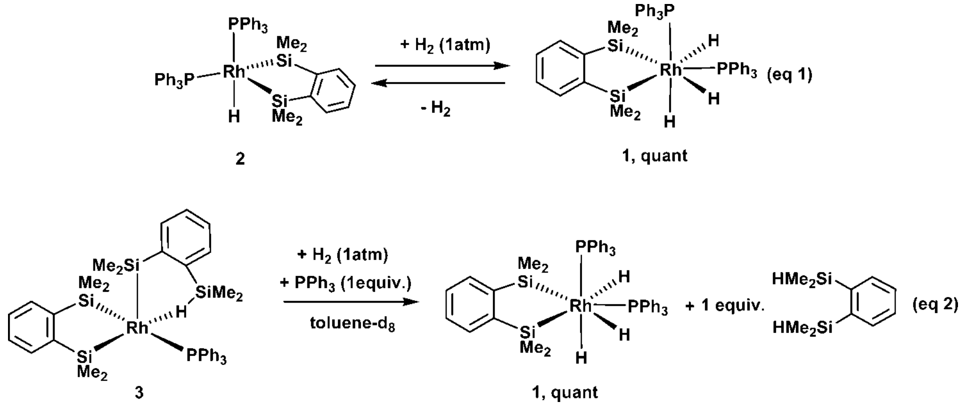
(13) (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (b) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(14) (a) Schubert, U.; Gilges, H. *Organometallics* **1996**, *15*, 2373. (b) Nikolov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217.

(15) Taw, F. L.; Bergman, R. G.; Brookhart, M. *Organometallics* **2004**, *23*, 886.

(16) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477.

Scheme 3



Hz) and 31.7 ($J_{\mathrm{Rh-P}}$ = 98.7 Hz) ppm as doublets due to the coupling with Rh. The ^{1}H$-^{31}$P COSY spectrum shows that the ^{31}P NMR signal at δ = 31.7 ppm correlates to a hydride signal at δ = −10.42 ppm. Two magnetically equivalent hydrides (δ_{1H} = −6.90) and one phosphine ($\delta_{^{31}P}$ = 28.4 ppm) consequently reside in the equatorial plane, as shown in Scheme 3, and the coordination geometry of **1** can best be described as pentagonal bipyramidal. This structure explains the two singlets at 0.52 and 0.91 ppm due to the two magnetically nonequivalent methyl moieties on the two magnetically equivalent SiMe$_2$ groups. Crabtree and co-workers reported an Ir homologue of **1**, Ir(H)$_3$(SiMe$_2$C$_6$H$_4$SiMe$_2$)(PPh$_3$)$_2$, synthesized by the reaction of Ir(H)$_5$(PPh$_3$)$_2$ with 1,2-bis(dimethylsilyl)benzene, of which the molecular structure was determined by X-ray diffraction study to be similar to that of **1** as deduced from our spectroscopic results;[17] the structure has a pentagonal bipyramidal coordination geometry with one PPh$_3$ and one hydride ligand at the apical sites, whereas two Si atoms, two hydrides, and one PPh$_3$ are located in the equatorial plane. The iridium complex also shows the fluxional behavior in ^{1}H and ^{31}P NMR spectroscopy similar to that seen for **1**.

Despite a number of studies on metalladisilacyclic complexes formed by dehydrogenative double oxidative addition of bifunctional hydrosilanes, to the best of our knowledge, there is no report suggesting that elimination of H$_2$ is reversible. We have discovered that the oxidative addition of H$_2$ to **2** is reversible; facile liberation of 1 mol of H$_2$ from **1** to regenerate **2** was accomplished by evacuating the solution (Scheme 3, eq 1). Interestingly, quantitative formation of **1** was also achieved by leaving a toluene-*d*$_8$ solution of **3** stand under a hydrogen atmosphere in the presence of 1 equiv of PPh$_3$ (Scheme 3, eq 2). The reaction involves the oxidative addition of a H$_2$ molecule and is a rare example of the hydrogenolysis of a Rh−Si bond, being accompanied by the dissociation of an equimolar amount of 1,2-bis(dimethylsilyl)benzene.

Studies on the Rhodadisilacyclopentenes 1, 2, and 3 in the Catalytic Hydrosilylation of Acetone with 1,2-Bis(dimethyl)silylbenzene. As described above, the oxidative addition of a Si−H moiety is believed to be an important primary reaction in the catalytic hydrosilylation. The following three experiments were carried out in order to better understand the possible roles of **1**, **2**, and **3** in the catalytic hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene.

(1) Direct Observation of Rhodadisilacyclopentenes in the Catalytic Hydrosilylation. Among the three rhodium species reported in this paper, two of them were observed in solution when running the catalytic hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene. As reported earlier, the hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene proceeds smoothly at room temperature in the presence of 1 mol % of RhCl(PPh$_3$)$_3$.[5] Direct NMR observation of the intermediary Rh species in the catalytic reaction was accomplished when the reaction of acetone with 1,2-bis(dimethylsilyl)benzene was carried out in the presence of larger amounts of RhCl(PPh$_3$)$_3$ (10 mol %) in C$_6$D$_6$ under a nitrogen atmosphere. The results are dependent on the ratios of acetone to 1,2-bis(dimethylsilyl)benzene. With a 1:2 ratio of acetone and 1,2-bis(dimethylsilyl)benzene, two Rh−H signals, due to a 9:1 mixture of **1** and **2**, appeared at the initial stage of the reaction. The ratio did not change even when all of the charged acetone was consumed. In contrast, the experiment with a 1:1 mixture of acetone and 1,2-bis(dimethylsilyl)benzene showed that only the Rh−H signal corresponding to the trihydride **1** was observed when acetone and 1,2-bis(dimethylsilyl)benzene were still present in the reaction mixture. After all of the acetone had been consumed, **1** was converted to **2** within 30 min. In both of the experiments, the trisilyl species **3** was not observed.

(2) Reaction Profiles of the Catalytic Hydrosilylation. Complexes **1**, **2**, **3**, Rh(PPh$_3$)$_3$Cl, and Rh(H)(PPh$_3$)$_4$ were used in the catalytic hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene in C$_6$D$_6$ at 25 °C. The reactions were also performed in the presence of 2 or 10 equiv. (for Rh cat.) of additional PPh$_3$. Reaction profiles following the decrease of 1,2-bis(dimethylsilyl)benzene were determined by the ^{1}H NMR spectrum, as shown in Figure 2. The results are summarized in Table 2. The order of the catalytic activity is **2** > **1**, **3** > Rh(PPh$_3$)$_3$Cl > Rh(H)(PPh$_3$)$_4$. Although **3** was not detected as an intermediate in the above experiment, it has a catalytic activity similar to **1**. In all cases, the reaction rates decreased in the presence of additional PPh$_3$. As described earlier,[5] the reaction gave not only the expected isopropoxysilane **4** but also the product **5** resulting from the methyl group migration shown in Scheme 4. The ratio of **4** to **5** altered within a range of 5:5−8: 2, being dependent on the reaction conditions. It may be worthwhile to point out that **4** was formed in a higher ratio, when an excess of PPh$_3$ was present in the reaction medium.

(3) Stoichiometric Reaction of 2 with Acetone. The highest catalytic activity of **2** prompted us to examine the stoichiometric reaction of **2** with acetone in the presence of 2 equiv of PPh$_3$. Quantitative formation of disilaindane **6** and Rh(H)(PPh$_3$)$_4$ was confirmed (Scheme 5). The characterization of **6** was unequivocally established by ^{1}H, ^{13}C, C−H COSY, ^{29}Si NMR, and FAB-MS spectroscopies. In the ^{1}H NMR spectrum of **6**, one signal appears at 0.05 ppm as a AB quartet, and the ^{13}C NMR spectrum

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[17] Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 2937.

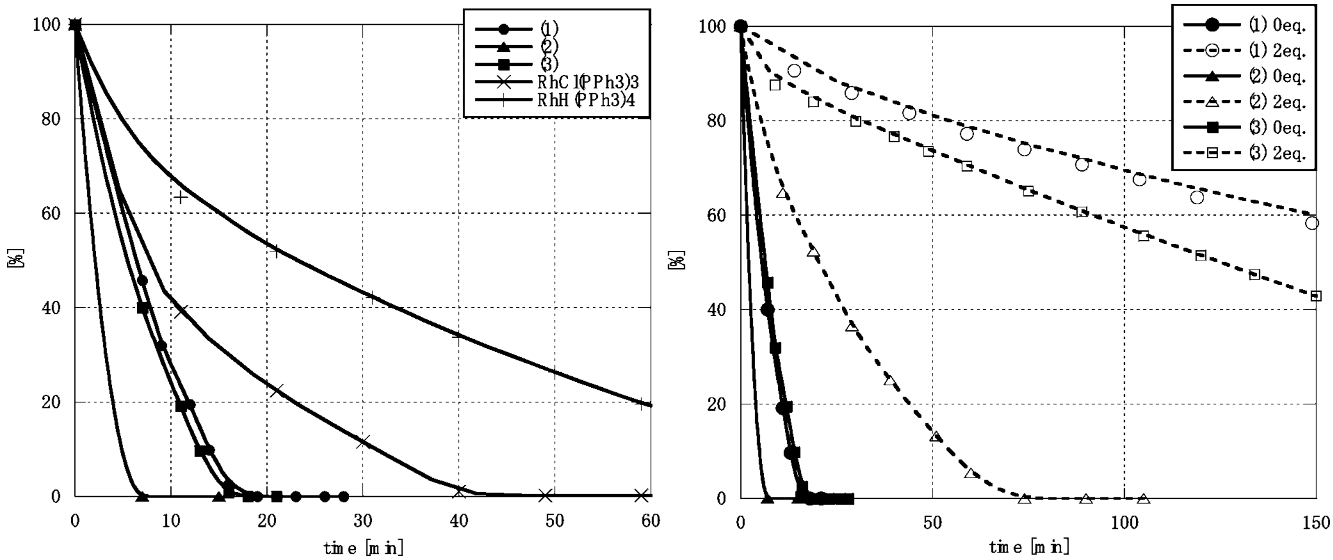

Figure 2. Decrease of 1,2-bis(dimethylsilyl)benzene during the hydrosilylation of acetone catalyzed by Rh catalysts in the absence of additives (left) and in the presence of 2 equiv of additional PPh_3 (right).

Table 2. Hydrosilylation of Acetone Catalyzed by Rh Catalysts

entry	cat.	additive	time (min)	**4**:**5**
1	**1**[a]	none	18	5:5
2	**1**[a]	PPh_3 (2 equiv)	1020	8:2
3	**2**	none	<7	5:5
4	**2**	PPh_3 (2 equiv)	74	7:3
5	**2**	PPh_3 (10 equiv)	300	7:3
6	**3**	none	19	6:4
7	**3**	PPh_3 (2 equiv)	733	8:2
8	**3**	PPh_3 (10 equiv)	1217	7:3
9	$Rh(PPh_3)_3Cl$	none	49	7:3
10	$Rh(PPh_3)_4(H)$	none	104	8:2

[a] Under H_2 (1 atm) atmosphere.

contains a singlet at −1.40 ppm, which is split into a triplet (J_{C-H} = 120 MHz) under off-resonance conditions. The C−H COSY experiment shows a correlation between these two signals, indicating that these signals can be assigned to the $Si-CH_2-Si$ moiety. Three methyl resonances were observed at 0.22 (s, 3H), 0.31 (s, 3H), and 0.41 (s, 3H) ppm, and the signals due to the O*i*Pr group appear at 1.08 (d, 3H, $CHMe_2$), 1.09 (d, 3H, $CHMe_2$), and 3.91 (sept, 1H, $CHMe_2$) ppm in the ^1H NMR spectrum. These spectral features are similar to those of 1,1,3,3-tetramethyldisilaindane reported by Barton and coworkers, which was synthesized by pyrolysis of 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane.[18a] In the ^{29}Si NMR spectrum, two singlets were confirmed at −35.1 and −44.8 ppm.

Mechanistic Considerations

Studies on the oxidative addition resulted in synthesis and characterization of three rhodadisilacyclopentenes, **1**, **2**, and **3**. The coordinatively saturated Rh(V) disilyltrihydride species **1** is apparently a primary product, which is formed by double oxidative addition of 1,2-bis(dimethylsilyl)benzene to the coordinatively unsaturated "$Rh(H)(PPh_3)_3$" species generated from $ClRh(PPh_3)_3$ or $HRh(PPh_3)_4$. Reductive elimination of H_2 from **1** gives the Rh(III) disilyl-monohydride complex **2**. Resulting **2** is coordinatively unsaturated (16 e) and capable of undergoing oxidative addition of another molecule of 1,2-bis(dimethylsilyl)benzene to form **3**. The reaction of **2** with 1,2-bis(dimethylsilyl)benzene would give a coordinatively saturated Rh(V) trisilyldihydride species, which is unstable and readily eliminates H_2. Replacement of a PPh_3 ligand by an agostic Si−H moiety leads to the formation of **3**. This is also coordinatively unsaturated (16 e). An intriguing new aspect obtained from these experiments is the facile oxidative addition and reductive elimination of 1,2-bis(dimethylsilyl)benzene and/or H_2 by way of the redox behavior of Rh(III) and Rh(V), as shown in Scheme 6. Although a number of studies on the dehydrogenative formation of metalladisilacycles have been reported,[19,20] to our knowledge, there has been no report on the regeneration of 1,2-bis(dimethylsilyl)benzene upon contact with H_2, as is seen in the hydrogenation of **3**. Formation of **3** takes place by way of an oxidative addition of three Si−H moieties from two molecules of 1,2-bis(dimethylsilyl)benzene with the dehydrogenation of two molecules of H_2. There have been few reports

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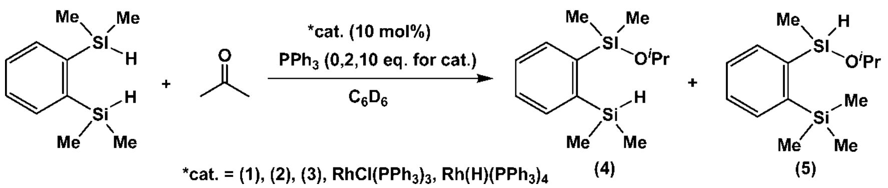
(18) (a) Barton, T. J.; Jacobi, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 7979. (b) Eaborn, C.; Safa, K. D. *J. Organomet. Chem.* **1981**, *2042*, 169. (c) Doszczak, L.; Fey, P.; Tacke, R. *Synlett* **2007**, *5*, 753. (d) Doszczak, L.; Tacke, R. *Organometallics* **2007**, *26*, 5722.

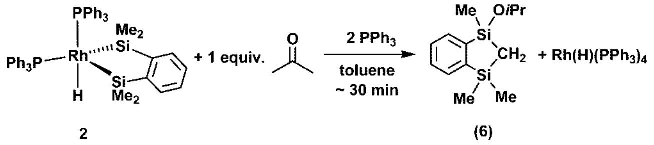
(19) Dehydrogenative double oxidative addition of 1,2-disilylbenzenes and other bifunctional silanes are well-established:(a) Shimada, S.; Tanaka, M. *Coord. Chem. Rev.* **2006**, *250*, 991. (b) Shimada, S.; Tanaka, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1856. (c) Shimada, S.; Rao, M. L. N.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 213. (d) Shimada, S.; Li, Y.-H.; Rao, M. L. N.; Tanaka, M. *Organometallics* **2006**, *25*, 3796. (e) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289. (f) Shimada, S.; Rao, M. L. N.; Li, Y.-H.; Tanaka, M. *Organometallics* **2005**, *24*, 6029. (g) Shimada, S.; Rao, M. L. N.; Tanaka, M. *Organometallics* **1999**, *18*, 291. (h) Chen, W.; Shimada, S.; Tanaka, M. *Science* **2002**, *295*, 308. (i) Bourg, S.; Boury, B.; Carré, F. H.; Corriu, R. J. P. *Organometallics* **1998**, *17*, 167. (j) Lee, Y.-J.; Lee, J. -D.; Kim, S. -J.; Ko, J.; Suh, I. -H.; Cheong, M.; Kang, S. O. *Organometallics* **2004**, *23*, 135. (k) Pfeiffer, J.; Kickelbick, G.; Schubert, U. *Organometallics* **2000**, *19*, 62. (l) Kang, Y.; Kim, K.; Kang, S.-O.; Ko, J.; Heaton, B. T.; Barkley, J. V. *J. Organomet. Chem.* **1997**, *532*, 79. (m) Loza, M. L.; de Gala, S. R.; Crabtree, R. H. *Inorg. Chem.* **1994**, *33*, 5073. (n) Fink, W. *Helv. Chem. Acta* **1976**, *59*, 606. (o) Fink, W. *Helv. Chem. Acta* **1974**, *57*, 1010. (p) Fink, W. *Helv. Chem. Acta* **1975**, *58*, 1464. (q) Corriu, R. J. P.; Moreau, J. J. E.; Pataund-Sat, M. *J. Org. Chem.* **1981**, *46*, 3372. (r) Corriu, R. J. P.; Moreau, J. J. E.; Pataund-Sat, M. J. *Organometallics* **1985**, *4*, 623.

(20) The reaction that may involve the double oxidative addition of two Si−H bonds to the metal center not followed by elimination of H_2 was reported: Dioumaev, V. K.; Yoo, B. R.; Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2003**, *125*, 8936.

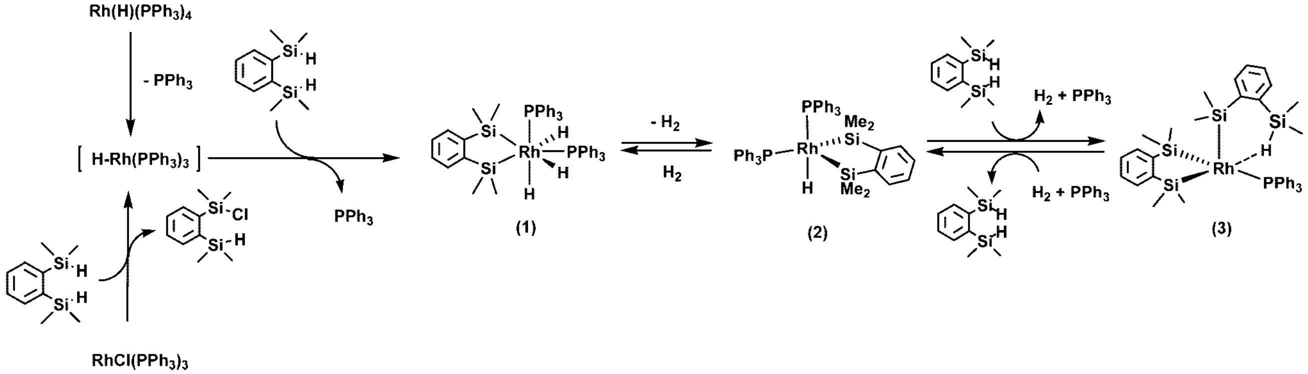
Scheme 4



Scheme 5



Scheme 6



on a "triple oxidative addition" of Si−H to transition metals.[21] The T_1 studies revealed the presence of three "classical hydrides" in the Rh(V) species **1**, whereas NMR and crystallographic evidence showed the "nonclassical" interaction of a Si−H species to the Rh(III) center in **3**,[22] although the Si−H moiety in **3** could undergo an oxidative addition to the 16 e metal center.

Studies on the catalytic hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene showed that the rhodadisilacyclopentenes **1**−**3** catalyzed the reaction much faster than RhCl(PPh$_3$)$_3$ or RhH(PPh$_3$)$_4$. Addition of PPh$_3$ apparently retarded the reaction. A consequence of the above-described oxidative addition studies is that the three rhodadisilacyclopentenes **1**−**3** are in equilibrium when hydrogen exists in the reaction medium. Experiments to characterize **1**−**3** were carried out under strict exclusion of moisture. However, H$_2$ can be present in catalytic reactions when chemists are careful to exclude even trace amounts of water. It is known that hydrosilanes can react with moisture to form H$_2$ under transition metal catalysis.[23] Dehydrogenative silylation of acetone to silyl enol ether is also a potential source of H$_2$ in the reaction medium. Thus, at present, we consider that the three rhodadisilacyclopentenes are interconverted with each other with the aid of trace amounts of H$_2$ in the reaction medium. The net catalytic intermediate should have a minimum number of PPh$_3$ and should be a coordinatively unsaturated species capable of coordinating acetone. Thus, it is worthwhile to assume that a 16 e rhodadisilacycle, formed by dissociation of PPh$_3$ from **1**, could be a probable candidate for the net catalytic species. This may also be in accord with the fact that the trihydride **1** was observed as a major species in the catalytic hydrosilylation of acetone in the presence of larger amounts of RhCl(PPh$_3$)$_3$ (10 mol %) as described above. A possible mechanism is illustrated in Scheme 7.

A detailed mechanism for the catalytic cycle is shown in Scheme 8. The migratory insertion of acetone followed by reductive elimination results in conversion of the 18-electron intermediate **C** to 14-electron species **D**. Double oxidative addition of 1,2-bis(dimethylsilyl)benzene to **D** leads to formation of the product **4** and the rhodacycle **B** through **E** as the intermediate. The rate enhancement by 1,2-bis(dimethylsilyl)benzene, in which two Si−H groups located in a close distance suitable for the formation of rhodacycle, can by explained by two factors. One is the strong trans influence of organosilyl ligands in **A** and **1** in Scheme 7, which facilitates dissociation of PPh$_3$ to generate coordinatively unsaturated species capable of reacting with acetone. Another is the intramolecular oxidative addition of the second Si−H group to the rhodium center, i.e., the reaction from **E** to **B** in Scheme 8, which accelerates the generation of **4** and **B**.

It may be worthwhile to discuss an alternative mechanism as illustrated in Scheme 9, which could explain the rate of the catalytic reaction for **2** being greater than for **1**. In this mechanism, coordination of acetone to **2** is followed by hydrosilylation associated with subsequent oxidative addition of 1,2-bis(dimethylsilyl)benzene. In the absence of the hydrosilane, disilaindane **6** is formed from intermediate **F**. The rate

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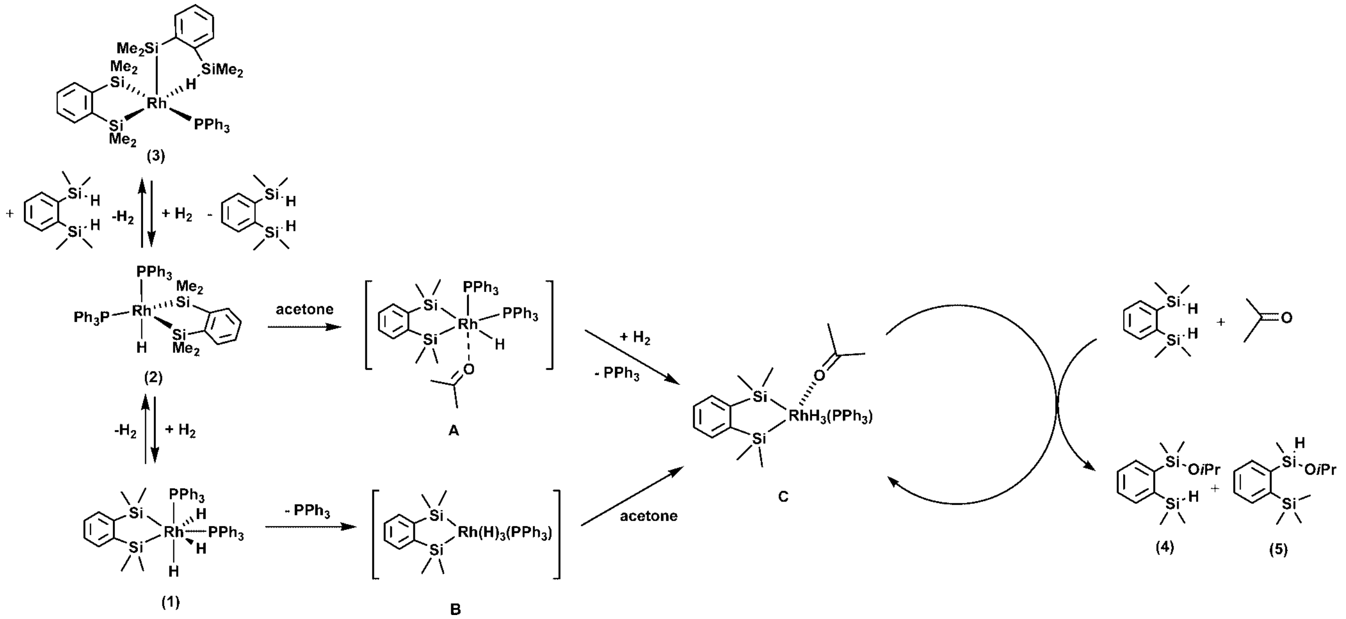
[21] (21) Chelate-assisted triple oxidative addition of three Si−H moieties was reported:(a) Djurovich, P. I.; Safir, A. L.; Keder, N. L.; Watts, R. J. *Inorg. Chem.* **1992**, *31*, 3195. (b) Chen, W.; Shimada, S.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2001**, 1096. (c) Chen, W.; Shimada, S.; Tanaka, M.; Kobayashi, Y.; Saigo, K. *J. Am. Chem. Soc.* **2004**, *126*, 8072.

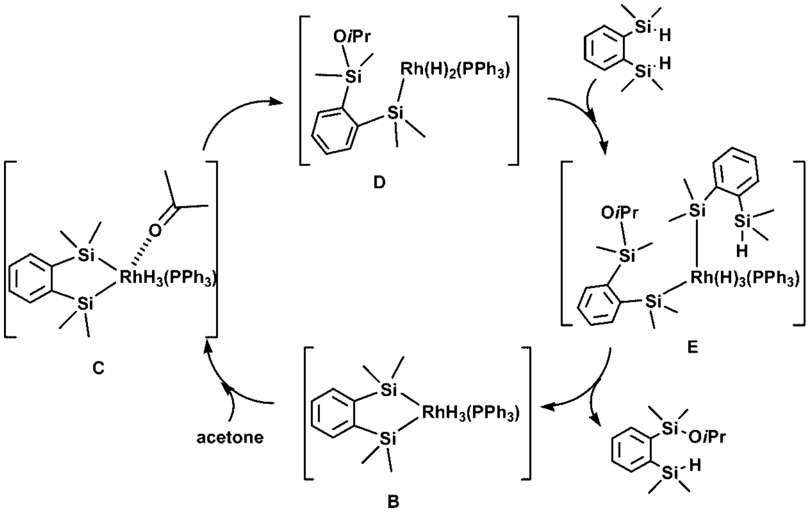
[22] (22) Nonclassical interaction of a Si−H bond of 1,2-bis(dimethylsilyl)benzene was seen in several transition metal complexes bearing a η^2-(H-Si) moiety:(a) Delpech, F.; Sabo-Etienne, S.; Daran, J.-C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J. -C. *J. Am. Chem. Soc.* **1999**, *121*, 6668. (b) Delpech, F.; Sabo-Etienne, S.; Chaudret, B.; Daran, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6668. (c) Schubert, U.; Grubert, S. *Monatsh. Chem.* **1998**, *129*, 437.

[23] (23) (a) Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 11938. (b) Field, L. D.; Messerle, B. A.; Rehr, M.; Soler, L. P.; Hambley, T. W. *Organometallics* **2003**, *22*, 2387.

Scheme 7



Scheme 8



enhancement is explained by the facile intramolecular oxidative addition of a Si−H group in **G**, which forms the product **4** and regenerates the rhodacycle **A**. However, the process is not very reasonable when considering the step forming **G** from **F** (the oxidative addition of another molecule of 1,2-bis(dimethylsilyl)benzene to **F**), a process that is sterically unfavorable.

As described above, the hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene has a special feature in giving two isomers, **4** and **5**. Isomer **5** is formed by metal-catalyzed redistribution of the organosilicon compounds, which is often seen in organosilicon chemistry. The mechanism of the methyl-group migration is not clear, although pathways through M=SiR$_2$ intermediates are often proposed.[7d] In this study, we have not obtained new results suggesting a clear mechanism. However, it is worthwhile to point out that the migration of the methyl group is partly suppressed in the presence of excess PPh$_3$. This implies that the lifetime of coordinatively unsaturated species in the catalytic cycle is important for the methyl group migration. A possible mechanism is shown in Scheme 10, in which the presence of excess PPh$_3$ is unfavorable for the formation of the second intermediate.[24]

Conclusion

A special rate enhancement is often seen in the catalytic hydrosilylation reactions, when bifunctional organosilanes, in which two Si−H groups are located at a close distance, are used as the hydrosilane component. The mechanism of the rate enhancement cannot be explained by conventional electronic and steric effects of the organosilanes, and special interactions of the two Si−H groups and the transition metal should be considered for the interpretation of the phenomena that should be called "synergistic effects of dual Si−H groups". In this paper, we investigated in detail reactions of two rhodium precursors with 1,2-bis(dimethylsilyl)benzene

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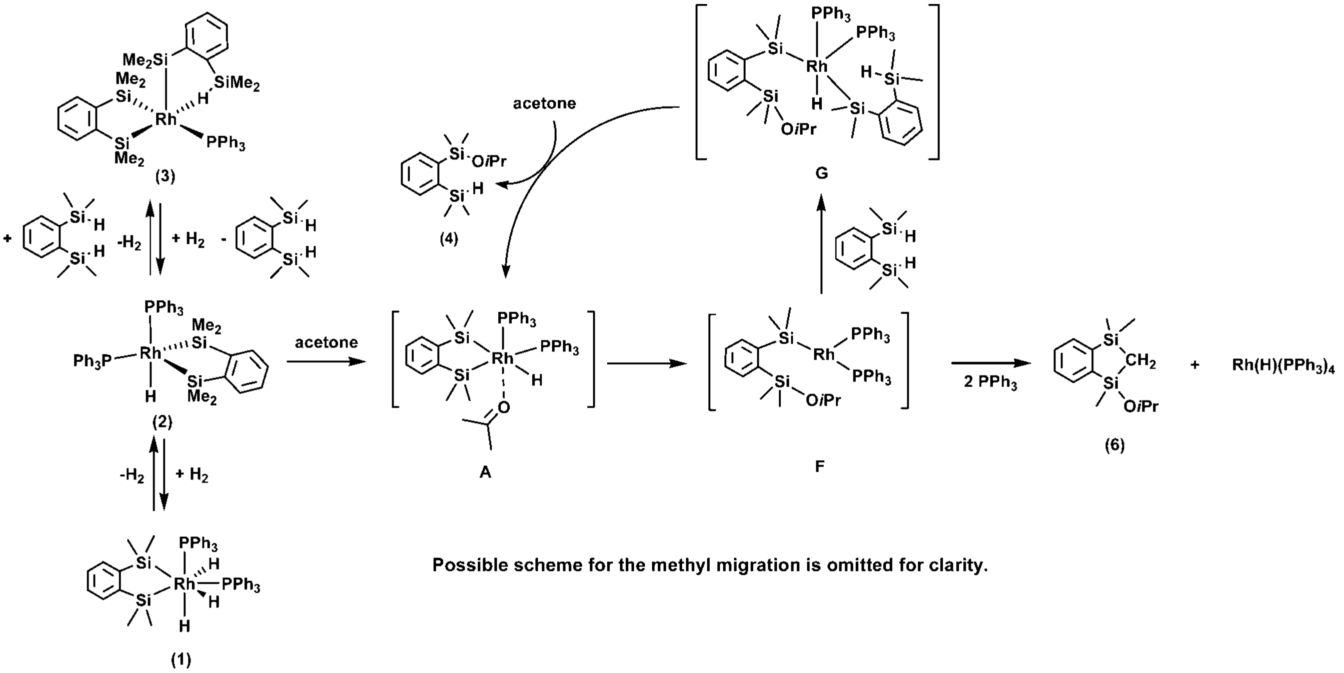
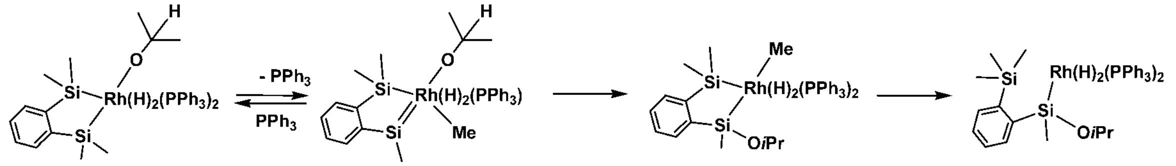
(24) One of the reviewers suggested the possibility of disilaindane **6** as intermediate species to form the methyl migrated product **5**. This is excluded by the RhCl(PPh$_3$)$_3$-catalyzed hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene in the presence of disilaindane **6**, in which **6** was proved to be inert toward the reaction with acetone under the conditions.

Scheme 9



Possible scheme for the methyl migration is omitted for clarity.

Scheme 10



and succeeded in synthesizing and characterizing three new rhodadisilacyclopentenes. In contrast to other metalladisilapentenes so far reported, the rhodacycles reversibly react with H$_2$ by way of a redox reaction between Rh(III) and Rh(V). Possible involvement of these rhodacycles in the catalytic hydrosilylation of acetone with 1,2-bis(dimethylsilyl)benzene is discussed, in which two factors, the strong trans influence of the organosilyl ligand taking part in generation of a catalytically active species and the intramoloecular oxidative addition of the second Si−H group in 1,2-bis(dimethylsilyl)benzene, are proposed to be important, as shown in Schemes 7, 8, and 9. The results provide new and interesting aspects for an explanation of the "synergistic effects of dual Si−H groups" in the unique rate enhancement in rhodium-catalyzed hydrosilylations. This may lead to new ideas in exploring the synergistic effects of dual Si−H groups in other transition metal-catalyzed hydrosilylation reactions.

Experimental Section

General Procedures. The manipulation of air- and moisture-sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (toluene, hexane; Ph$_2$CO/Na, acetone; MS 4A). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR chemical shifts (δ values) are given in ppm relative to the solvent signal (^{1}H, ^{13}C) or standard resonances (^{29}Si, external tetramethylsilane; ^{31}P, external 85% H$_3$PO$_4$). IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Melting points were measured on a Yanaco micro melting point apparatus. The HRMS spectrum was recorded on a JEOL Mstation JMS-70 apparatus. Elemental analyses were performed by a Perkin-Elmer 2400/CHN analyzer. Starting materials, 1,2-bis(dimethylsilyl)benzene,[5c] Rh(PPh$_3$)$_3$Cl,[25] and Rh(PPh$_3$)$_4$(H)[26] were synthesized by the method reported in the literature.

Preparation of Rh(SiMe$_2$C$_6$H$_4$SiMe$_2$)(H)$_3$(PPh$_3$)$_2$ (1). In an NMR tube, complex **2** (16.4 mg, 0.02 mmol) was dissolved in toluene-d_8 (0.4 mL), and the atmosphere was replaced by 1 atm of H$_2$. After mixing this solution for 10 min, complete formation of complex **1** was observed by ^{1}H and ^{31}P NMR spectroscopy. The same compound was alternatively prepared by treatment of **3** with 1 equiv of PPh$_3$ using a similar procedure. ^{1}H NMR (600 MHz toluene-d_8, −70 °C): δ −10.42 (br m, $J_{\text{H-P}}$ = 133 Hz, 1H, Rh−H), −6.90 (br m, 2H, Rh−H), 0.52 (s, 6H, SiMe$_2$), 0.91 (s, 6H, SiMe$_2$), 6.51−6.64 (br m, 2H, Ph), 6.64−6.81 (br m, 5H, Ph), 6.82−6.96 (br m, 10H, Ph), 6.96−7.03 (br m, 2H, Ph), 7.10−7.29 (br m, 6H, Ph), 7.36−7.51 (br m, 7H, Ph), 7.72−7.81 (br m, 2H, Ph). ^{29}Si{^{1}H} NMR (119 MHz, toluene-d_8, −70 °C): δ 20.5 (dd, $J_{\text{Rh-Si}}$ = 71.2, $J_{\text{P-Si}}$ = 20.1 Hz). ^{31}P{^{1}H} NMR (242 MHz, toluene-d_8, −70 °C): δ 28.4 (dd, $J_{\text{Rh-P}}$ = 85.5, $J_{\text{P-P}}$ = 13.2 Hz), 31.7 (dd, $J_{\text{Rh-P}}$ = 98.7, $J_{\text{P-P}}$ = 13.2 Hz).

Preparation of Rh(SiMe$_2$C$_6$H$_4$SiMe$_2$)(H)(PPh$_3$)$_2$ (2). In a 200 mL Schlenk tube were placed Rh(PPh$_3$)$_4$(H) (2.30 g, 2.0 mmol) and a benzene solution (100 mL) of 1,2-bis(dimethylsilyl)benzene (486 mg, 2.50 mmol). The resulting solution was stirred for 6 h at 50 °C, during which the color of the solution turned orange. The solvent was removed in vacuo, and the residue was

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Table 3. Crystallographic Data for 2 and 3

	2	**3**
empirical formula	$C_{46}H_{47}Si_2P_2Rh$	$C_{38}H_{41}Si_4P_1Rh \cdot 1/2C_6H_{14}$
fw	819.89	795.08
cryst syst	monoclinic	monoclinic
lattice type	primitive	primitive
space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a, Å	10.7863(11)	9.532(4)
b, Å	17.538(2)	38.063(15)
c, Å	21.737(2)	12.290(6)
α, deg	90	90
β, deg	101.9792(14)	110.466(5)
γ, deg	90	90
volume, Å^3	4022.4(7)	4177(3)
Z value	4	4
$D_{calc,}$ g/cm^3	1.354	1.259
F(000)	1700.00	1660.00
μ(Mo Kα), cm^{-1}	5.944	5.873
cryst color, habit	orange, platelet	yellow, platelet
cryst dimens, mm	0.20 × 0.15 × 0.05	0.10 × 0.05 × 0.02
no. observns (all reflns)	9096	6218
no. variables	510	480
refln/param ratio	17.84	12.95
R (all reflns)	0.0849	0.1755
R_1 ($I > 2.00\sigma(I)$)[a]	0.0996	0.0690
wR_2 (all reflns)[b]	0.3170	0.1755
GOF	0.863	1.002
max. shift/error in final cycle	0.037	0.000
max. peak in final diff map, e$^-$/Å^3	5.28	1.90
min. peak in final diff map, e$^-$/Å^3	−3.42	−0.89

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

washed twice with hexane (5 mL). The remaining orange solid was dissolved in toluene (30 mL) and layered with hexane (60 mL), from which orange crystals of **2** were obtained in 58% yield (952 mg). Alternatively, the same compound was prepared by treatment of $Rh(PPh_3)_3Cl$ with 1,2-bis(dimethylsilyl)benzene using a similar procedure. Mp: 133 °C (dec). Anal. Calcd for $C_{46}H_{47}P_2Si_2Rh_1$: C, 67.30; H, 5.77. Found: C, 67.15; H, 5.65. ^1H NMR (600 MHz, C_6D_6, rt): δ −7.31 (ddd, J_{H-P} = 6.4, 74 Hz, J_{H-Rh} = 24.4 Hz, 1H, Rh−H), 0.49 (s, 6H, $SiMe_2$), 0.70 (s, 6H, $SiMe_2$), 6.65−7.06 (br m, 14H, Ph), 7.17−7.30 (br m, 8H, Ph), 7.31−7.36 (m, 2H, Ph), 7.36−7.56 (br m, 8H, Ph), 7.65−7.72 (m, 2H, Ph). ^{13}C NMR (150 MHz, C_6D_6, rt): δ 8.79 (s, $SiMe_2$), 12.92 (s, $SiMe_2$), 6.15 (s, $SiMe_2$), 9.66 (s, $SiMe_2$), 129.94 (s, Ph), 131.22 (s, Ph), 134.74 (br s, Ph), 135.26 (br s, Ph), 136.83 (br s, Ph), 137.16 (br s, Ph), 158.88 (s, Ph). $^{29}Si\{^1H\}$ NMR (119 MHz, C_6D_6, rt): δ 40.4 (dd, J = 35.7, 42.5 Hz). $^{31}P\{^1H\}$ NMR (242 MHz, C_6D_6, rt): δ 26.9 (d, J_{Rh-P} = 92.1 Hz), 35.7 (d, J_{Rh-P} = 131.5 Hz). IR (KBr): ν_{Rh-H} (cm^{-1}) = 1994 (s).

Preparation of $Rh(Me_2SiC_6H_4SiMe_2)(\eta^1$-$HSiMe_2C_6H_4SiMe_2)(PPh_3)$ (3). In a 20 mL Schlenk tube were placed complex **2** (410 mg, 0.50 mmol) and a benzene solution (10 mL) of 1,2-bis(dimethylsilyl)benzene (486 mg, 2.50 mmol). The resulting solution was stirred for 1 h under benzene reflux conditions, during which the color of the solution turned dark orange. The solvent was removed in vacuo, and the residue was washed with hexane (4 mL). The remaining yellow solid was dissolved in toluene (4 mL) and layered with hexane (8 mL), from which orange crystals of **3** containing ∼13% of **2** were obtained (305 mg, ca. 68% yield). Alternatively, the same compound was prepared by treatment of $Rh(PPh_3)_4(H)$ or $Rh(PPh_3)_3Cl$ with 1,2-bis(dimethylsilyl)benzene using a similar procedure. ^1H NMR (600 MHz, C_6D_6, rt): δ −0.26 (br s, J_{Si-H} = 112 Hz, 1H, Rh−HSi), 0.14 (s, 6H, $SiMe_2$), 0.54 (s, 6H, $SiMe_2$), 0.58 (s, 6H, $SiMe_2$), 0.63 (s, 6H, $SiMe_2$), 6.84−7.00 (m, 8H, Ph), 7.12−7.15 (m, 4H, Ph), 7.16−7.23 (m, 2H, Ph), 7.26−7.32 (m, 2H, Ph), 7.35−7.46 (m, 5H, Ph), 7.59−7.68 (m, 2H, Ph). ^{13}C NMR (150 MHz, C_6D_6, rt): δ 1.48 (s, $SiMe_2$), 1.59 (s, $SiMe_2$), 6.15 (s, $SiMe_2$), 9.66 (s, $SiMe_2$), 127.57 (s, Ph), 129.28 (s, Ph), 129.33 (s, Ph), 129.75 (s, Ph), 130.85 (s, Ph), 131.12 (s, Ph), 132.81 (s, Ph), 132.92 (s, Ph), 132.94 (s, Ph), 134.97 (s, Ph), 135.09 (s, Ph), 135.94 (s, Ph), 136.08 (s, Ph), 140.80 (s, Ph). $^{29}Si\{^1H\}$ NMR (119 MHz, C_6D_6, rt): δ 11.4 (s, $HSiMe_2$), 37.0 (dd, J = 37.4, 44.7 Hz), 40.5 (d, J = 45.6 Hz), 40.6 (d, J = 45.6 Hz). $^{31}P\{^1H\}$ NMR (242 MHz, C_6D_6, rt): δ 14.2 (d, J_{Rh-P} = 85.5 Hz). IR (KBr): ν_{Si-H} (cm^{-1}) = 1966 (s).

Preparation of Disilaindane (6). In a 20 mL Schlenk tube, **2** (41 mg, 0.05 mmol) and 2 equiv of PPh_3 (26 mg, 0.10 mmol) were dissolved in benzene (0.5 mL), followed by the addition of acetone (7.3 μL, 0.10 mmol) at room temperature. The resulting solution was stirred for 30 min at rt, during which the color of the solution turned orange, and a precipitate of $Rh(H)(PPh_3)_4$ was observed. The solvent was removed in vacuo, and the residue was extracted with hexane (3 mL). The hexane solution was concentrated under vacuum, and a yellow oil of **6** was obtained in 86% yield (11 mg). Anal. Calcd for $C_{13}H_{22}O_1Si_2$: C, 62.33; H, 8.85. Found: C, 62.65; H, 8.96. HRMS: calcd for $^{12}C_{13}{}^1H_{22}{}^{16}O_1{}^{28}Si_2$ 250.1209, found 250.1213. ^1H NMR (600 MHz, C_6D_6, rt): δ 0.05 (AB q, J = 14.3, 101.7 Hz, 2H, Si−CH_2−Si), 0.22 (s, 3H, $SiMe_2$), 0.31 (s, 3H, $SiMe_2$), 0.41 (s, 3H, Si*Me*(O^{i}Pr)), 1.08 (d, J = 5.5 Hz, 3H, CH(C*H*$_3$)$_2$), 1.09 (d, J = 5.5 Hz, 3H, CH(C*H*$_3$)$_2$), 3.91 (sept, J = 5.5 Hz, 1H, C*H*(CH$_3$)$_2$), 7.23−7.28 (m, 2H, Ph), 7.45−7.53 (m, 1H, Ph), 7.67−7.71 (m, 1H, Ph). ^{13}C NMR (150 MHz, C_6D_6, rt): δ −1.40 (s, Si−CH_2−Si), 0.69 (s, $SiMe_2$), 0.88 (s, $SiMe_2$), 1.08 (s, Si*Me*(O^{i}Pr)), 26.40 (s, CH(*C*H$_3$)$_2$), 26.44 (s, CH(*C*H$_3$)$_2$), 30.54 (s, *C*H(CH$_3$)$_2$), 129.06 (s, Ph), 129.44 (s, Ph), 132.79 (s, Ph), 132.99 (s, Ph), 148.86 (s, Ph), 151.22 (s, Ph). $^{29}Si\{^1H\}$ NMR (242 MHz, C_6D_6, rt): δ −35.1 (s, Si(Me)(OiPr)), −44.8 ($SiMe_2$).

Reaction Profiles. A mixture of the rhodium complex **1**, **2**, **3**, $RhCl(PPh_3)_3$, or $RhH(PPh_3)_4$ (0.02 mmol), hexamethylbenzene (internal standard, 33 mg, 0.2 mmol), and C_6D_6 (0.3 mL) was transferred into a flame-dried NMR tube in a glovebox. Addition of a solution of 1,2-bis(dimethylsilyl)benzene (39 mg, 0.2 mmol) in C_6D_6 (0.2 mL) was followed by the addition of a solution of acetone (17.6 μL, 0.24 mmol) in C_6D_6 (0.2 mL). The addition was carried out carefully to make three phases. The solution was quickly frozen and connected to a vacuum line. The tube was evacuated at −78 °C, sealed by flame, quickly warmed, and shaken several times. The NMR measurement was carried out periodically at 25 °C in C_6D_6.

X-ray Data Collection and Reduction. Single crystals of all complexes were grown from toluene/hexane. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71070A). The data were collected at 123(2) K using ω scans in the θ range of 3.0° ≤ θ ≤ 27.5° (**2**) and 3.1° ≤ θ ≤ 27.5° (**3**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[27] and expanded using Fourier techniques.[28] The non-hydrogen atoms were refined anisotropically except for the solvent atoms (hexane for **2**). Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 9096 observed reflections and

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461 variable parameters for **2** and 7328 observed reflections and 476 variable parameters for **3**. Neutral atom scattering factors were taken from Cromer and Waber.[29] All calculations were performed using the CrystalStructure[30,31] crystallographic software package. Details of final refinement as well as the bond lengths and angles are summarized in the Supporting Information, and the numbering scheme employed is also shown in the Supporting Information, which were drawn with ORTEP with 50% probability ellipsoids.

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Supporting Information Available: ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR data (**1**, **2**, **3**, **6**), variable-temperature NMR data (**1**), and details of crystallographic studies (**2** and **3**).This material is available free of charge via the Internet at http://pubs.acs.org.

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