

Exchange Reactions of Primary and Secondary Silanes with Binuclear Rhodium Complexes

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The reaction chemistry between primary and secondary silanes and dppm-bridged binuclear Rh complexes (dppm = bis(diphenylphosphino)methane) has been investigated. The primary silanes studied are RSiH_3 with $\text{R} = \text{Ph}$ and n -hexyl, while secondary silanes include Ph_2SiH_2 , Et_2SiH_2 , and MePhSiH_2 . In one series of reactions, the relative stability of the μ -silylene bridge in the dihydride complex $\text{Rh}_2(\mu\text{-SiRR}')\text{H}_2(\text{CO})_2(\text{dppm})_2$ (2: a, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; b, $\text{R} = n$ -hexyl, $\text{R}' = \text{H}$; c, $\text{R} = \text{R}' = \text{Et}$; d, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; e, $\text{R} = \text{R}' = \text{Ph}$) has been examined. Through exchange reactions between 2 and free alkylsilane, it is found that $\mu\text{-SiRR}'$ bridges with $\text{R}' = \text{H}$ are more stable and that aryl substituents on Si increase the bridge stability. The relative reactivity of the alkyl- and arylsilanes with the dihydride complex $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (1) has been assessed through a series of competition reactions. The primary silanes are more reactive than the secondary silanes, with the order of reactivity correlating with the order of stability. It is probable that these orderings are influenced significantly by steric factors.

Introduction

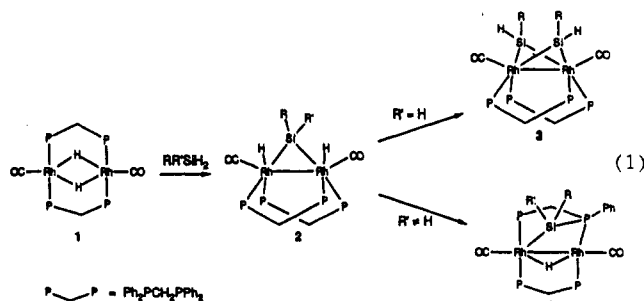
Considerable current interest exists in the reaction chemistry of silanes with platinum group metal complexes, particularly in the context of Si-H oxidative addition,¹ hydrosilation catalysis,² redistribution reactions,³ and dehydrogenative coupling and oligomerization of silanes.⁴⁻⁹ Recently, we reported the reaction of the binuclear complex $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (1) with alkyl- and arylsilanes leading to the formation of bis SiRR' -bridged complexes for primary silanes ($\text{R}' = \text{H}$) and unusual P-Si bond containing products of formula $\text{Rh}_2(\mu\text{-H})(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{SiRR}')(\text{dppm})$ for secondary silanes.¹⁰ For both types of silanes, the reaction proceeds as in eq 1 through the

to be fluxional. Recently, compounds 2 have been observed to promote reaction between silanes and simple amines leading to simple silazane oligomers.¹¹ The present paper focuses on the reaction chemistry of the $\mu\text{-SiRR}'$ dihydrides 2 with regard to silane addition and exchange. The primary silanes examined in this context are PhSiH_3 and n -Hex SiH_3 (n -Hex = C_6H_{13}), while the secondary silanes include Ph_2SiH_2 , Et_2SiH_2 , and MePhSiH_2 .

Results and Discussion

Species of structure 2 (a, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; b, $\text{R} = n$ -Hex, $\text{R}' = \text{H}$; c, $\text{R} = \text{R}' = \text{Et}$; d, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) have previously been observed when eq 1 is carried out at low temperature. While these species can be isolated, repeated efforts to obtain analytically pure samples have been unsuccessful. Compounds 2 are relatively reactive, and even solid samples under inert atmosphere at 290 K give spectroscopic evidence of continued reaction. Previously, the structure of 2 was assigned as shown in eq 1 based on detailed analysis of low-temperature (-70°C) ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, and this assignment is further supported by selective ^{31}P decoupling of the hydride resonance described below. For the $\mu\text{-SiRH}$ and $\mu\text{-SiMePh}$ dihydride complexes 2, the hydride resonance is a distinctive second-order pattern which was simulated as an AA'MM'XX' spin system with a large $J_{\text{HP}(\text{trans})}$ in our previous report. The hydride pattern is shown in Figure 1 for the $\mu\text{-SiH}(\text{Hex})$ derivative 2b. The $^{31}\text{P}\{^1\text{H}\}$ NMR of this species at -65°C exhibits two doublet of doublet resonances at δ 18.78 and 29.92 ppm, indicating the inequivalence of the phosphine donors into two sets (see Figure 1). The coupling of each of these resonances is due to $J_{\text{Rh-P}}$ and $J_{\text{P-P}}$.

When the ^{31}P resonance at δ 29.92 ppm for 2b is selectively irradiated at -65°C , the hydride resonance collapses to a broad signal with unresolved coupling, whereas irradiation at δ 18.77 ppm leads to essentially no change in the hydride signal as shown in Figure 1. These results confirm that the low-temperature hydride resonance has only a single large coupling to one of the dppm phosphine donors, consistent with structure 2 and a large $J_{\text{HP}(\text{trans})}$. Additional support for the structure assignment of 2 is provided by crystal structure studies of the final products $\text{Rh}_2(\mu\text{-SiRH})_2(\text{CO})_2(\text{dppm})_2$ (3a, $\text{R} = \text{Ph}$; 3b, $\text{R} = \text{Et}$) of eq 1 and of the analogous complex $\text{Ir}_2(\mu\text{-SiRR}')_2\text{H}_2(\text{CO})_2(\text{dppm})_2$, which has the same basic structure differing only in the relative orientation of the hydrides.^{12a}



intermediacy of the $\mu\text{-SiRR}'$ dihydrides 2 which were found

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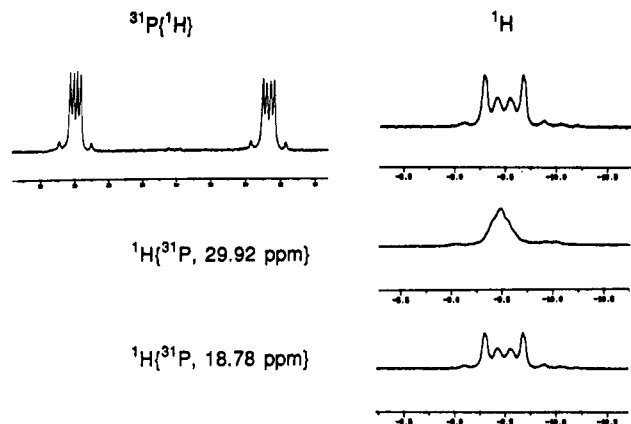
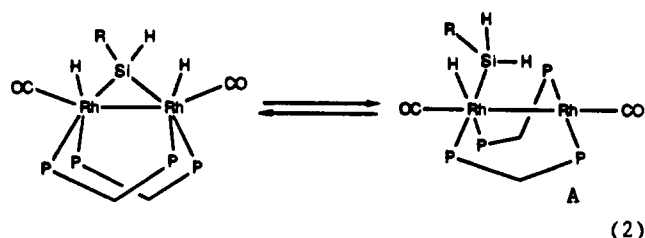


Figure 1. $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of $\text{Rh}_2\text{H}_2(\mu\text{-Si}(n\text{-Hex})\text{H})(\text{CO})_2(\text{dppm})_2$ (**2b**) in CD_2Cl_2 at -65°C .

As noted previously, species **2** is fluxional, and for the $\mu\text{-SiRR}$ derivatives, the Rh hydride and Si-H protons undergo exchange. The mechanism of this fluxionality is thought to involve a reductive elimination/oxidative addition sequence via the intermediacy of unsaturated species **A** in eq 2.



The diphenylsilylene-bridged complex $\text{Rh}_2(\mu\text{-SiPh}_2)\text{H}_2(\text{CO})_2(\text{dppm})_2$ (**2e**) has not been reported previously. It is isolated from the reaction of Ph_2SiH_2 with $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (**1**), and the intensities of its ^1H resonances are in agreement with the formulation for **2** given above. The terminal CO in **2e** is confirmed by ν_{CO} of 1943 cm^{-1} , while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2e** at room temperature exhibits the same second-order pattern as $\text{Rh}_2(\mu\text{-SiEt}_2)\text{H}_2(\text{CO})_2(\text{dppm})_2$ (**2c**). Unlike **2c**, the hydride resonance of **2e** at $\delta -6.68\text{ ppm}$ is broad and unstructured at room temperature. In contrast with other secondary $\mu\text{-SiRR}'$ dihydride species, the hydride resonance of **2e** splits upon cooling into two resonances in a 1:1 ratio at $\delta -1.22$ and -8.91 ppm . However, even at -80°C , the structures of the hydride resonances cannot be resolved. Room-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and low-temperature ^1H NMR spectra of **2e** appear in Figure 2.

Based on the chemical shifts of the hydride resonances at low temperature, the equivalence of the four phosphine donors at room temperature, and a fit of the $^{31}\text{P}\{^1\text{H}\}$ spectrum consistent with an averaged structure similar to **2**, we propose that **2e** possesses structure **B**, which is sim-

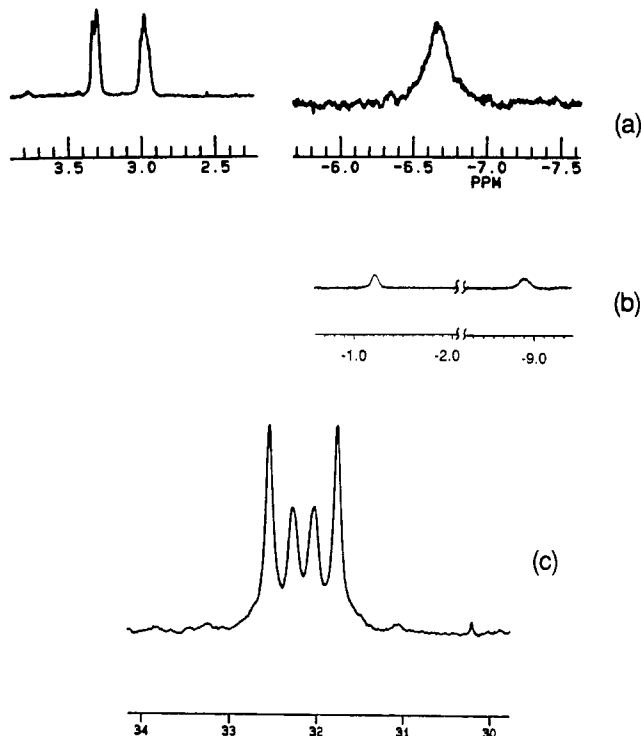
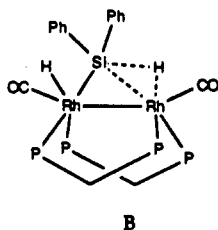
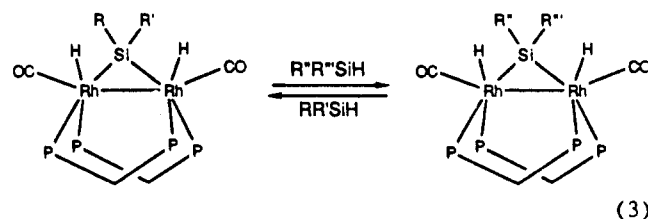


Figure 2. (a) ^1H NMR spectrum of $\text{Rh}_2\text{H}_2(\text{SiPh}_2)(\text{CO})_2(\text{dppm})_2$ (**2e**) in CD_2Cl_2 at room temperature. (b) Hydride region of **2e** in CD_2Cl_2 at -80°C . (c) $^{31}\text{P}\{^1\text{H}\}$ NMR of **2e** in CD_2Cl_2 at room temperature.

ilar to **A** but with an "agostic" interaction between Rh-H-Si. The resonance at $\delta -8.91\text{ ppm}$ is thus assigned as the normal metal hydride, while the unusual $\delta -1.22\text{ ppm}$ resonance corresponds to the hydride involved in the three-center interaction with the Rh and Si atoms. Species containing M-H-Si three-center two-electron bonds are well-known for both mono- and binuclear complexes.¹²

To probe the reactivity of the species $\text{Rh}_2\text{H}_2(\mu\text{-SiRR}')(\text{CO})_2(\text{dppm})_2$ (**2**), two sets of reactions were carried out. One was designed to examine the relative stability of the $\mu\text{-SiRR}'$ dihydride species, while the other addressed the relative reactivity of the silanes with the dihydride complex **1**. In both sets of studies, the reactions were monitored by NMR spectroscopy.

Exchange under Equilibrium Control. The relative stabilities of the $\mu\text{-SiRR}'$ dihydride complexes were studied through a series of exchange reactions illustrated as eq 3.



The use of ^1H NMR spectroscopy for this purpose was possible because of the different chemical shifts and coupling patterns of the Si-H resonance of the different silanes $\text{RR}'\text{SiH}_2$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; $\text{R} = \text{C}_6\text{H}_{13}$, $\text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{Et}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; $\text{R} = \text{R}' = \text{Ph}$). In addition, while the complexes $\text{Rh}_2(\mu\text{-SiRR}')\text{H}_2(\text{CO})_2(\text{dppm})_2$ (**2a**, $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; **2b**, $\text{R} = n\text{-C}_6\text{H}_{13}$, $\text{R}' = \text{H}$; **2c**, $\text{R} = \text{R}' = \text{Et}$; **2d**, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; **2e**, $\text{R} = \text{R}' = \text{Ph}$) are fluxional at room temperature, the alkyl and aryl proton resonances of the $\mu\text{-SiRR}'$ ligands and $\text{dppm}-\text{CH}_2-$ protons are distinguishable for the two $\mu\text{-SiRR}'$ complexes of eq 3, making

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possible direct observation of their relative amounts.

In a typical experiment, 1 equiv of PhSiH_3 was added to a C_6D_6 solution of $\text{Rh}_2(\mu\text{-Si}(n\text{-C}_6\text{H}_{13})\text{H})_2(\text{CO})_2(\text{dppm})_2$ (**2b**) at room temperature and the reaction was monitored immediately by ^1H NMR spectroscopy. Within 4 min, a triplet resonance at δ 3.62 ppm, corresponding to the Si-H proton of free $n\text{-HexSiH}_3$ was observed, as were aliphatic protons at δ 1.20, 0.83, and 0.50 ppm. At the same time, the formation of $\text{Rh}_2(\mu\text{-SiPhH})_2(\text{CO})_2(\text{dppm})_2$ (**2a**) was indicated by the presence of a new doublet at δ 8.78 ppm, which corresponded to the $\mu\text{-SiPhH}$ *o*-phenyl protons of **2a**. The intensity of this resonance and that of the dppm $-\text{CH}_2-$ resonances at δ 4.28 and 3.12 ppm were consistent with there being only *one* metallic species corresponding to **2a** present in solution. On the other hand, the ^1H NMR spectrum of the reaction of 1 μL of $n\text{-HexSiH}_3$ with 5 mg of **2a** in CD_2Cl_2 indicated that neither PhSiH_3 nor the exchange product **2b** was formed. Thus, for the $\text{PhSiH}_3/n\text{-HexSiH}_3$ system, eq 3 lies entirely on the side of free $n\text{-HexSiH}_3$ and the $\mu\text{-SiPhH}$ complex **2a**.

The exchange reactions between the primary $\mu\text{-SiRH}$ dihydride species and free secondary silanes were investigated by following the reaction of either **2a** or **2b** with $\text{RR}'\text{SiH}_2$ ($\text{R} = \text{R}' = \text{Et}$ or Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) by ^1H NMR spectroscopy. In these reactions, the primary $\mu\text{-SiRH}$ moiety of **2a** or **2b** was found not to exchange with the secondary silane leading to the $\mu\text{-SiRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) ligand. In contrast, the corresponding exchange reaction of the $\mu\text{-SiRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) dihydride complexes with primary silanes occurred readily. For instance, when 1 equiv of PhSiH_3 was added to a C_6D_6 solution of $\text{Rh}_2\text{H}_2(\mu\text{-SiEt}_2)(\text{CO})_2(\text{dppm})_2$ (**2c**), the rapid formation of free Et_2SiH_2 was indicated by resonances at δ 3.89 (Si-H), 1.02, and 0.59 ppm ($-\text{CH}_2\text{CH}_3$), while resonances of $\mu\text{-SiPhH}$ phenyl protons at δ 8.78 ppm and dppm $-\text{CH}_2-$ protons at δ 4.28 and 3.12 ppm gave evidence of the generation of **2a**.

The reactions of the $\mu\text{-SiRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) dihydride complexes, $\text{Rh}_2\text{H}_2(\mu\text{-SiRR}')(\text{CO})_2(\text{dppm})_2$ (**2**), with a different secondary silane $\text{R}''\text{R}'''\text{SiH}_2$ were studied in a similar manner. For example, after the addition of 1 equiv of Ph_2SiH_2 to a C_6D_6 solution of $\text{Rh}_2\text{H}_2(\mu\text{-SiMePh})(\text{CO})_2(\text{dppm})_2$ (**2d**), the ^1H NMR spectrum of the solution revealed a quartet resonance at δ 4.48 and a triplet resonance at δ 0.13 ppm, corresponding to the Si-H and Si- CH_3 protons of free MePhSiH_2 , respectively, while formation of $\text{Rh}_2\text{H}_2(\mu\text{-SiPh}_2)(\text{CO})_2(\text{dppm})_2$ (**2e**) was observed by the $\mu\text{-SiPh}_2$ phenyl protons at δ 8.02 ppm and the dppm $-\text{CH}_2-$ proton resonances at δ 3.40 and 3.01 ppm. The formation of **2e** in this exchange reaction was confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which showed a symmetric multiplet at δ 32.14 ppm characteristic of an authentic sample. When a 10-fold excess of MePhSiH_2 was added to a C_6D_6 solution of **2e**, a small amount of **2d** was produced. This observation was based on the growth of the resonance at δ 8.40 ppm of the phenyl protons of the $\mu\text{-SiMePh}$ moiety and a singlet at δ 5.09 ppm for Si-H of free Ph_2SiH_2 . In analogous experiments, ^1H NMR spectra of solutions of **2c** and $\text{RR}'\text{SiH}_2$ ($\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) indicated that the equilibrium corresponding to eq 3 favored the formation of **2d** and **2e** over **2c**.

The equilibrium constants for the exchange reactions involving the $\mu\text{-SiRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) dihydride complexes and free secondary silanes were determined based on the intensities of the four species in eq 3. The values of K_{eq} at 292 K thus obtained are as follows: (1) for the reaction of $\text{Rh}_2\text{H}_2(\mu\text{-SiPh}_2)(\text{CO})_2(\text{dppm})_2$ (**2e**) and Et_2SiH_2 , $(1.3 \pm 0.2) \times 10^{-3}$; (2) for the reaction of $\text{Rh}_2\text{H}_2(\mu\text{-SiMePh})$

$(\text{CO})_2(\text{dppm})_2$ (**2d**) and Et_2SiH_2 , 0.042 ± 0.002 ; (3) for the reaction of **2e** and MePhSiH_2 , 0.046 ± 0.002 . Examination of these equilibria over a 30 °C temperature range revealed no change in K_{eq} , thus showing that the entropy change for these equilibria involving $\mu\text{-SiRR}'$ ($\text{R}, \text{R}' \neq \text{H}$) complexes and secondary silanes is essentially zero.

Equilibrium Considerations. If ΔS of exchange reaction 3 is assumed to be zero, then the free energy change of the reaction is governed solely by the enthalpy change:

$$\Delta G = \Delta H - T\Delta S \approx \Delta H$$

Since the reaction involves neutral molecules in a non-coordinating solvent, the enthalpy change (ΔH) of eq 3 can be approximated by the bond dissociation energies (D) of the bonds broken minus those of the bonds made. That is

$$\Delta H = 2D(\text{Si-Rh})_{\text{react}} + 2D(\text{Si-H})_{\text{react}} - 2D(\text{Si-Rh})_{\text{prod}} - 2D(\text{Si-H})_{\text{prod}}$$

where $D(\text{Si-Rh})$ and $D(\text{Si-H})$ correspond, respectively, to the Si-Rh bond dissociation energy of the $\mu\text{-SiRR}'$ dihydride complexes and the Si-H bond dissociation energy of the free silanes. It has been shown independently that the Si-H bond energies of different silanes are very similar ($(89-91) \pm 2$ kcal/mol),¹³ which means that the enthalpy change and hence the free energy of the exchange reaction simplifies to

$$\Delta G \approx \Delta H \approx 2D(\text{Si-Rh})_{\text{react}} - 2D(\text{Si-Rh})_{\text{prod}}$$

Based on the experimental data and the above analysis, a qualitative order of the stability of the $\mu\text{-SiRR}'$ bridge can be established as $\mu\text{-SiPhH} > \mu\text{-Si}(n\text{-C}_6\text{H}_{13})\text{H} > \mu\text{-SiPh}_2 > \mu\text{-SiMePh} > \mu\text{-SiEt}_2$. Clearly, the primary $\mu\text{-SiRH}$ dihydride complexes are more stable than the secondary $\mu\text{-SiRR}'$ dihydride species. The basis of this order may be the reduced steric interactions which the $\mu\text{-SiRH}$ ligand encounters with dppm phenyl groups. The stability of the $\mu\text{-SiRR}'$ bridge is also influenced in an electronic sense by the substituents on silicon, such that arylsilylene bridges are more stable than the alkylsilylene moieties.

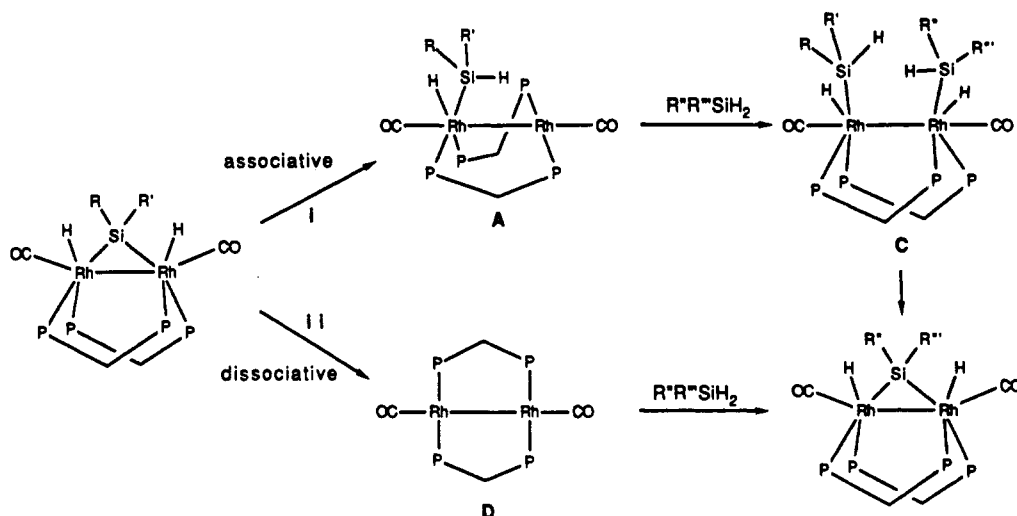
Kinetic Selectivity. To obtain the relative reactivity of various silanes with $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (**1**), a series of low-temperature reactions of **1** with a mixture of two different silanes was carried out.¹⁴ The formation of complex **2** was monitored by the $\mu\text{-SiRR}'$ and dppm methylene resonances in the ^1H NMR spectrum. For example, the reaction of **1** with a 1:1 ratio of PhSiH_3 and $n\text{-HexSiH}_3$ at -60 °C led only to the formation of **2a** as established by integration of resonances of $\mu\text{-SiPhH}$ protons at δ 8.29 and 6.33 ppm, dppm $-\text{CH}_2-$ protons, and a single metal hydride signal. The absence of any alkyl resonances of **2b** supported the notion that only **2a** was formed in this reaction. The fact that PhSiH_3 is the most reactive silane was confirmed by the reaction of **1** with a mixture of PhSiH_3 and the secondary silanes $\text{RR}'\text{SiH}_2$ ($\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; $\text{R} = \text{R}' = \text{Ph}$). Again, **2a** was the sole metal product formed.

When $n\text{-HexSiH}_3$ and $\text{RR}'\text{SiH}_2$ ($\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; $\text{R} = \text{R}' = \text{Ph}$) reacted with **1** at low temperature, **2b** predominated, but was not the sole product. For example, when MePhSiH_2 was used, the resonances at δ 5.89 and -9.32 ppm corresponding to the $\mu\text{-SiRH}$ silyl proton and metal

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(14) These reactions were carried out below -60 °C, and no exchange reactions between free silanes and the $\mu\text{-SiRR}'$ dihydride species occurred at this temperature.

Scheme I. Possible Mechanisms of the Exchange Reaction



hydrides of **2b** were observed, but in addition, a small resonance at δ 8.20 ppm due to the μ -SiMePh phenyl protons of **2d** was noted. The relative amounts of **2b** and **2d** were estimated at 11:1. A $^{31}P\{^1H\}$ NMR spectrum of the solution showed two sets of resonances at δ 29.40 and 18.00 ppm corresponding to **2b** and at δ 29.98 and 20.33 ppm corresponding to **2d** in the same ratio as obtained by 1H NMR spectroscopy. These results suggest a kinetic selectivity of $\approx 10:1$ corresponding to a $\Delta\Delta G^\ddagger$ for the reactions of *n*-HexSiH₃ and MePhSiH₂ with 1 of ~ 1.4 kcal/mol.

The reaction of $Rh_2H_2(CO)_2(dppm)_2$ (**1**) with a mixture of Ph_2SiH_2 and MePhSiH₂ at low temperature was followed by 1H NMR spectroscopy and showed that the kinetically preferred product is not necessarily the most stable product. At $-69^\circ C$, product **2d** clearly predominated as shown by major resonances at δ 8.20 and 0.25 ppm for μ -SiMePh along with the four dppm $-CH_2-$ resonances characteristic of **2d**. As the temperature was increased to $23^\circ C$, the resonances at 3.40 and 3.01 ppm became dominant, confirming that **2e** was the major thermodynamic product. This observation is consistent with the stability studies described above in which the strength of the Rh-Si bond increases with more aryl substituents on the μ -SiRR' moiety.

In another competition experiment, a solution containing a 1:1 ratio of Et_2SiH_2 and MePhSiH₂ was reacted with **1** at $-60^\circ C$, leading to initial formation of both the μ -SiRR' complexes **2c** and **2d** with the latter as the major product. Similarly, the low-temperature reaction of **1** with a mixture of Et_2SiH_2 and Ph_2SiH_2 showed that **2e** was the major kinetic product but that **2c** was also observed to form in the initial 1H NMR spectrum.

On the basis kinetic competition experiments, the reactivity of silanes towards **1** follows the order $PhSiH_3 > n\text{-HexSiH}_3 > MePhSiH_2 > Ph_2SiH_2 > Et_2SiH_2$, which is similar to the stability order given above except for the relative position of MePhSiH₂ and Ph_2SiH_2 . Clearly, primary silanes are more reactive toward **1** than secondary silanes. While the origin of this kinetic preference is uncertain at this time, it may be steric since it is known that primary and secondary silanes have similar Si-H bond dissociation energies.

Mechanism of Exchange. Two possible mechanisms are shown in Scheme I to account for the exchange reactions. Path i involves an associative mechanism in which reductive elimination of one Si-H bond in **2** generates the

unsaturated species A followed by oxidative addition of the incoming silane to form a bis(silyl dihydride) intermediate (C). Support for this path comes from the fact that oxidative addition of two $RSiH_3$ molecules to a closely related binuclear rhodium system has been observed for the dpam (dpam = bis(diphenylarsino)methane) analogue of **1**.¹⁰ Alternatively, a dissociative mechanism (path ii) via the unsaturated species D can be envisioned, but to this point we have no evidence in support of the existence of D.

Experimental Section

All procedures were performed on a high-vacuum line or in a nitrogen-filled glovebox. Solutions for NMR samples were usually prepared in resealable NMR tubes fitted with Teflon valves (J. Youngs or Wilmad Glass Co.) for room-temperature measurement or in NMR tubes which were connected to a high-vacuum line and then flame-sealed for low-temperature measurement. Benzene-*d*₆ and methylene-*d*₂ chloride were dried over CaH_2 for 10 h and then stored under vacuum after vacuum distillation. Liquid silanes were stored in a glovebox and used as received. 1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 400.13 and 161.98 MHz, respectively, on Bruker WH-400 and AMX-400 spectrometers. 1H chemical shifts are measured relative to residual 1H NMR resonances in the deuterated solvents: C_6D_6 , δ 7.150 ppm; CD_2Cl_2 , δ 5.320 ppm. $^{31}P\{^1H\}$ chemical shifts are reported (ppm) downfield from the external reference, 85% H_3PO_4 .

$Rh_2H_2(CO)_2(dppm)_2$ was prepared according to the published method.¹⁵

Preparation of $Rh_2H_2(\mu\text{-SiRR}')(\text{CO})_2(\text{dppm})_2$ ($R = Ph, R' = H; R = n\text{-C}_6\text{H}_{13}, R' = H; R = R' = Et$ or $Ph; R = Me, R' = Ph$). A modification of the previously described procedure¹⁰ was used for the synthesis of these complexes. Solid $Rh_2H_2(CO)_2(dppm)_2$ (**1**; 85 mg, 0.082 mmol) was placed in a 25-mL flask and cooled to $-30^\circ C$. To this was added a CH_2Cl_2 (5 mL) solution of Et_2SiH_2 (16 μL , 0.12 mmol) at ca. $-30^\circ C$. The solution was left for 1 min before the solvent was partially removed under vacuum. Upon addition of cold hexane to the concentrated solution, yellow crystals were formed. The crystals were collected on a frit and washed with hexane. The product was dried by a stream of N_2 and stored in the refrigerator ($-30^\circ C$) of the glovebox; yield 57 mg (62%). The 1H NMR spectrum indicated the product was spectroscopically pure. The same procedure was used for the preparation of **2a-e**.

Spectroscopic data for **2e**: 1H NMR (C_6D_6 ; δ , ppm) 7.92 (d, $J = 8$ Hz, 4 H), 7.48 (s, 8 H), 7.41 (s, 8 H), 7.1-6.7 (m, 30 H), 3.42 (m, 2 H), 3.02 (m, 2 H), -5.70 (br, 2 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 ; δ , ppm) 31.76 (sym mult); IR (CH_2Cl_2 , cm^{-1}) 1943.

Reaction of $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ with $\text{Rh}_2\text{H}_2(\mu\text{-SiPhH})(\text{CO})_2(\text{dppm})_2$ (2a) and Other Exchange Reactions. In a glovebox, 2a (5.0 mg, 4.4 μmol) was placed in a resealable NMR tube. The silane $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ (1.0 μL , 6.2 μmol) was placed in a flask which was sealed with a needle valve. On a high-vacuum line, 0.5 mL of C_6D_6 was transferred into the flask and then the solution was degassed by one freeze-pump-thaw cycle. The solution was transferred to the NMR tube, and the J. Young valve was closed. Upon thawing, the ^1H NMR spectrum of the sample was measured.

The same general procedure was used for all of the other exchange reactions except the reactions involving Ph_2SiH_2 .

Reaction of Ph_2SiH_2 with $\text{Rh}_2\text{H}_2(\mu\text{-SiPhH})(\text{CO})_2(\text{dppm})_2$ (2a) and Related Exchange Reactions. Complex 2a (5.0 mg, 4.4 μmol) was placed in an NMR tube and stored in the refrigerator of the glovebox ($-30\text{ }^\circ\text{C}$). A solution of 0.5 mL of C_6D_6 and Ph_2SiH_2 (1.0 μL , 5.4 μmol) was then added to the NMR tube and the tube sealed with a septum. The reaction was followed by ^1H NMR spectroscopy after the sample was removed from the glovebox and thawed. The above procedure was also used in the preparation of the NMR samples of the reaction of Ph_2SiH_2 and 2b and 2c.

Reaction of $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (1) with a Mixture of PhSiH_3 and $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ and Other Competition Reactions. An NMR tube containing 1 (5.0 mg, 4.8 μmol) and a flask containing a mixture of PhSiH_3 (1.0 μL , 8.0 μmol) and $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ (1.2 μL , 7.4 μmol) were joined by a T-connection and attached to a high-vacuum line. The flask containing the silanes was immersed in liquid nitrogen, and both the NMR tube and the flask were evacuated. The solvent CD_2Cl_2 (0.5 mL) was transferred into the flask containing the silanes, and the solution was degassed by a freeze-pump-thaw cycle. The solution was then transferred into the NMR tube which was subsequently flame-sealed. After the sample was thawed in a dry ice/acetone bath and rapidly shaken, the reaction was monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. All the reactions of 1 with mixtures of different silanes were prepared in the same manner except for the reactions involving Ph_2SiH_2 .

Reaction of $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$ (1) with a Mixture of Ph_2SiH_2 and MePhSiH_2 and Related Competition Experiments. Complex 1 (8.0 mg, 7.7 μmol) was placed in an NMR tube, and Ph_2SiH_2 (1.6 μL , 8.6 μmol) was syringed into the NMR tube

in the glovebox. Meanwhile, MePhSiH_2 (1.2 μL , 8.7 μmol) was put into a flask which was sealed with a needle valve. On a high-vacuum line, both the NMR tube and the flask were immersed in liquid nitrogen and evacuated. After 0.5 mL of CD_2Cl_2 was transferred into the flask, the solution containing CD_2Cl_2 and MePhSiH_2 was degassed via one freeze-pump-thaw cycle. The solution was then transferred into the NMR tube which was flame-sealed. After the sample was thawed in a dry ice/acetone bath and shaken vigorously, the competition reaction was followed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Other samples involving Ph_2SiH_2 were prepared by the same procedure.

K_{eq} Measurements at Different Temperatures. In the glovebox, an NMR tube containing 2e (7.2 mg, 5.9 μmol) and a flask containing Et_2SiH_2 (8.0 μL , 62.0 μmol) were joined by a T-connection and three-way stopcock. Upon removal from the glovebox, the T-valve was attached to a high-vacuum line and the flask was immersed in liquid nitrogen. After the NMR tube and flask were evacuated, 0.5 mL of CD_2Cl_2 was transferred into the flask and the CD_2Cl_2 solution of Et_2SiH_2 was degassed by one freeze-pump-thaw cycle. The solution was then transferred into the NMR tube which was subsequently flame-sealed. The reaction was monitored by ^1H NMR spectroscopy after the sample had been thawed in a dry ice/acetone bath and vigorously shaken. When the ratios of 2c to 2e and Et_2SiH_2 to Ph_2SiH_2 remained the same for three consecutively collected spectra, the reaction was considered at equilibrium. At $-60\text{ }^\circ\text{C}$, no exchange was observed to occur. When the mixtures were warmed to the indicated temperature, the equilibrium constants were determined based on integrations of the resonances of the four species in solution. In this way, K_{eq} of the exchange reaction between 2e and Et_2SiH_2 was measured to be $(1.3 \pm 0.2) \times 10^{-3}$ (265 K), $(1.5 \pm 0.2) \times 10^{-3}$ (275 K), and $(1.3 \pm 0.2) \times 10^{-3}$ (292 K). The reaction of 2d with Et_2SiH_2 was carried out in a similar manner and followed by ^1H NMR spectroscopy at three different temperatures. The corresponding equilibrium constants were found to be 0.046 ± 0.002 (265 K), 0.037 ± 0.002 (275 K), and 0.042 ± 0.002 (292 K).

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