CO Displacement in an Oxidative Addition of Primary Silanes to Rhodium(I)

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CO Displacement in an Oxidative Addition of Primary Silanes to Rhodium(I)

Abstract
The rhodium dicarbonyl \{PhB(Ox(Me2))(2)Im(Mes)}Rh(CO)(2), (1) and primary silanes react by oxidative addition of a nonpolar Si-H bond and, uniquely, a thermal dissociation of CO. These reactions are reversible, and kinetic measurements model the approach to equilibrium. Thus, 1 and RSiH3 react by oxidative addition at room temperature in the dark, even in CO-saturated solutions. The oxidative addition reaction is first-order in both 1 and RSiH3, with rate constants for oxidative addition of PhSiH3 and PhSiD3 revealing \( k(H)/k(D) \) similar to 1. The reverse reaction, reductive elimination of Si-H from \{PhB(Ox(Me2))(2)Im(Mes)}RhH(SiH2R)CO (2), is also first-order in [2] and depends on [CO]. The equilibrium concentrations, determined over a 30 degrees C temperature range, provide \( \Delta H = -5.5 \pm 0.2 \text{ kcal/mol} \) and \( \Delta S = -16 \pm 1 \text{ cal/molK} \) (for 1 < 2). The rate laws and activation parameters for oxidative addition (\( \Delta H^* = 11 \pm 1 \text{ kcal/mol} \) and \( \Delta S^* = -26 \pm 3 \text{ cal/molK} \)) and reductive elimination (\( \Delta H^* = 17 \pm 1 \text{ kcal/mol} \) and \( \Delta S^* = -10 \pm 3 \text{ cal/molK} \)), particularly the negative activation entropy for both forward and reverse reactions, suggest the transition state of the rate-determining step contains \{PhB(Ox(Me2))(2)/mMes}Rh(CO)(2) and RSiH3. Comparison of a series of primary silanes reveals that oxidative addition of arylsilanes is ca. 5x faster than alkylsilanes, whereas reductive elimination of Rh-Si/Rh-H from alkylsilyl and arylsilyl rhodium(III) occurs with similar rate constants. Thus, the equilibrium constant \( K_e \) for oxidative addition of arylsilanes is >1, whereas reductive elimination is favored for alkylsilanes.

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CO Displacement in an Oxidative Addition of Primary Silanes to Rhodium(I)

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ABSTRACT. The rhodium dicarbonyl \{PhB(Ox\textsubscript{Me\textsuperscript{2}})\textsubscript{2}Im\textsuperscript{Mes}\}Rh(CO)\textsubscript{2} (1) and primary silanes react by oxidative addition of a nonpolar Si–H bond and, uniquely, a thermal dissociation of CO. These reactions are reversible, and kinetic measurements model the approach to equilibrium. Thus, 1 and RSiH\textsubscript{3} react by oxidative addition at room temperature in the dark, even in CO-saturated solutions. The oxidative addition reaction is first-order in both 1 and RSiH\textsubscript{3}, with rate constants for oxidative addition of PhSiH\textsubscript{3} and PhSiD\textsubscript{3} revealing \(k\textsubscript{H}/k\textsubscript{D} \sim 1\). The reverse reaction, reductive elimination of Si–H from \{PhB(Ox\textsubscript{Me\textsuperscript{2}})\textsubscript{2}Im\textsuperscript{Mes}\}RhH(SiH\textsubscript{2}R)CO (2), is also first-order in [2] and depends on [CO]. The equilibrium concentrations, determined over a 30 °C temperature range, provide \(\Delta H^\circ = -5.5 \pm 0.2\) kcal/mol and \(\Delta S^\circ = -16 \pm 1\) cal·mol\textsuperscript{-1}·K\textsuperscript{-1} (for 1 \(\rightleftharpoons\) 2). The rate laws and activation parameters for oxidative addition (\(\Delta H^\ddagger = 11 \pm 1\) kcal·mol\textsuperscript{-1} and \(\Delta S^\ddagger = -26 \pm 3\) cal·mol\textsuperscript{-1}·K\textsuperscript{-1}) and reductive elimination (\(\Delta H^\ddagger = 17 \pm 1\) kcal·mol\textsuperscript{-1} and \(\Delta S^\ddagger = -10\) cal·mol\textsuperscript{-1}·K\textsuperscript{-1})
± 3 cal·mol⁻¹K⁻¹), particularly the negative activation entropy for both forward and reverse reactions, suggest the transition state of the rate-determining step contains \{PhB(OxMe₂)₂ImMes\}Rh(CO)₂ and RSiH₃. Comparison of a series of primary silanes reveals that oxidative addition of arylsilanes is ca. 5× faster than alkylsilanes, whereas reductive elimination of Rh–Si/Rh–H from alkylsilyl and arylsilyl rhodium(III) occur with similar rate constants. Thus, the equilibrium constant \(K_e\) for oxidative addition of arylsilanes is greater than 1, whereas reductive elimination is favored for alkylsilanes.

**Introduction**

Oxidative addition of nonpolar bonds (H–H, C–H, Si–H) to low valent rhodium and iridium metal complexes has been widely studied because this elementary step, and the resulting metal hydride, alkyl, or silyl species, are invoked in many catalytic reactions including hydroformylation,⁴⁻¹² hydrosilylation,³⁻⁷ and silane dehydrocoupling.⁸⁻¹⁴ Such transformations often involve carbon monoxide directly or metal carbonyls as catalysts, but catalytic steps involving CO dissociation are notably absent in their proposed mechanistic cycles. Instead, open coordination sites for oxidative addition are generated via product-forming reductive elimination steps, and CO itself is frequently an inhibitor in many catalytic reactions.

The strong coordination of CO must also be overcome to affect catalytic decarbonylation chemistry. Stoichiometric reactions of aldehydes and esters typically provide metal-carbonyl compounds (e.g., Ni–CO or Rh–CO),¹⁵⁻¹⁸ and in fact, oxidative addition of polar C–O bonds of esters to Ni(0) is reversible upon addition of CO.¹⁸ Catalytic processes involving decarbonylation of aldehydes,¹⁹,²⁰ ketones,²¹,²² acyl halides,¹⁷,²³⁻²⁶ esters,²⁷⁻³¹ and amides³² require high
temperatures or photochemical activation. Key intermediates proposed in catalytic cycles for these decarbonylative transformation include oxidized metal carbonyls, resulting from deinsertion of metal acyl species, and low valent, electron-rich metal sites that react with polar substrates by oxidative addition. Likely, low valent metal carbonyl compounds are present, considering that low valent metal species readily bind CO, formed from the decarbonylation process. Ancillary ligand effects in these systems are, as expected, significant, but trends are likely obscured by changing reaction conditions (reagents, temperatures, reactants) and complex, multistep mechanisms.

In contrast, the active species are well defined in photochemically activated oxidative additions of nonpolar bonds. Photolytic dissociation of CO is a prerequisite for reactions of Cp*Rh(CO)$_2$ or Tp*Rh(CO)$_2$ (Cp* = C$_5$Me$_5$; Tp* = tris(3,5-dimethyl-1-pyrazolyl)borate) with C–H or Si–H bonds.$^{33-40}$ For example, Tp*Rh(CO)$_2$ and Et$_3$SiH react under photochemical conditions to give Tp*RhH(SiEt$_3$)CO and CO (Figure 1).$^{41}$ A sequence of photolytic CO dissociation followed by C–H cleavage is invoked here, as well as in rhodium- or iridium-catalyzed carbonylations of benzene, which occur under continuous irradiation.$^{42,43}$ Detailed time-resolved spectroscopic and computational studies of the mechanism of C–H and Si–H bond activation by CpRh(CO)$_2$, TpRh(CO)$_2$, $^{37,38,48}$ Tp*Rh(CO)$_2$, $^{49}$ Tp*Rh(CO)$_2$, $^{46,50-53}$ and Tp*Rh(CNR)$_2$,$^{40}$ formed via photolytic ligand dissociation, reveal details and lifetimes of the activation process. Interestingly, bidentate and tridentate coordination of pyrazolylborate ligands modulate the electronic structure of rhodium to affect C–H bond oxidative cleavage.
Bond activation initiated by photochemical CO dissociation

\[
\begin{align*}
\text{R-B-N} & \quad \text{E-H, hv} \quad -\text{CO} \\
\text{Tp: E-H = R}_3\text{Si-H} \quad \text{Tp*, To}^M,\text{PhB(OxMe}_2\text{)}_2\text{Im}^{\text{Mes}} : \text{E-H = Ph-H}
\end{align*}
\]

Thermal bond activation process

\[
\begin{align*}
\text{E-H = R}_3\text{Si-H}
\end{align*}
\]

Figure 1. Photochemical and thermal pathways for oxidative addition of C–H and Si–H bonds to rhodium(I).

Although these studies elucidate the influence of ancillary ligands on C–H bond oxidative addition steps, new strategies are needed to affect both the bond activation and CO displacement for development of new, thermal conversions. Oxidized or electron-poor metal centers that are poorly π-back-donating disfavor CO binding; however, such species are also less likely to react by oxidative addition. Alternatively, a nucleophilic metal complex could interact with the E–H bond, and σ-coordination might reduce the π-back donating ability to CO and promote its dissociation. This idea implies, perhaps counter-intuitively, that a strongly σ-donating ligand that generates an electron-rich, nucleophilic rhodium species, even when coordinated by CO, could be reactive in thermal oxidative additions and accelerate the dissociation of CO.
The trend in electron-donating ability for tridentate, fac-coordinating ligands in rhodium dicarbonyl compounds, based on CO stretching frequencies, is \( \text{Tp} < \text{Tp}^* < \text{To}^\text{M} \) (\( \text{To}^\text{M} = \text{tris}(4,4\text{-dimethyl-2-oxazolinyl})\text{phenylborate}, \) Figure 1);\textsuperscript{54,55} however \( \text{To}^\text{M}\text{Rh(CO)}_2 \) does not appear to react with hydrocarbons or silanes under thermal conditions, and we concluded that the tris(oxazolinyl)borate ligand was not sufficiently electron donating for the rhodium to undergo the desired oxidative addition. In order to further increase the electron-donating ability of the fac-coordinating ligand system, we replaced one oxazoline in \( \text{To}^\text{M} \) with a \( \text{N} \)-heterocyclic carbene to give the bis(oxazolinyl)(NHC)borate ligand \( \text{PhB(Ox} \text{Me}_2)_2\text{Im}^\text{Mes} \) (Figure 1, Ox\text{Me}_2 = 4,4-dimethyl-2-oxazolinyl, Im\text{Mes} = 1-(2,4,6-trimethylphenyl)imidazole).\textsuperscript{56} In fact, PhSiH\textsubscript{3} and \{PhB(Ox\text{Me}_2)_2Im\text{Mes}\}Rh(CO)\textsubscript{2} (1) react in the dark to give \{PhB(Ox\text{Me}_2)_2Im\text{Mes}\}RhH(SiH\textsubscript{2}Ph)CO (2a) and CO.\textsuperscript{57}

\( \text{Tp}^*\text{Rh(CO)}_2, \text{To}^\text{M}\text{Rh(CO)}_2, \) and 1 all contain monoanionic, multidentate ligands, which coordinate either in fluxional bidentate or tridentate modes. The carbonyls are photochemically labile, and all undergo C–H bond oxidative addition upon photolysis. Both four- and five-coordinate ground state structures contain photolabile carbonyl ligands and access the low coordinate states needed for C–H bond activation.

Here we study the kinetic and thermodynamic features of Si–H bond oxidative addition to 1 and Rh–Si/Rh–H bond reductive elimination from 2a. These investigations of the thermal processes provide contrast with photochemical-promoted Si–H and C–H bond oxidative additions.\textsuperscript{33-36}

**Results and discussion**

**Synthesis of rhodium silyl compounds.** The reaction of 1 and 3 equiv. of PhSiH\textsubscript{3} gives 2a over 18 h in benzene at room temperature in 94% isolated yield.\textsuperscript{57} Similarly, 1 and primary
alkylsilanes (R = C₆H₁₃, C₁₂H₂₅) or arylsilanes (R = p-MeC₆H₄, p-MeOC₆H₄) react to give {PhB(OxMe₂)₂ImMes}RhH(SiH₂R)CO (R = C₆H₁₃ (2b), C₁₂H₂₅ (2c), p-MeC₆H₄ (2d), p-MeOC₆H₄ (2e); Scheme 1). The reactions of alkylsilanes and 1 are slower than the corresponding reactions of arylsilanes under equivalent reaction conditions. For example, the reaction of 1 and hexylsilane (10 equiv) in benzene requires 1 d at room temperature to form 2b quantitatively, whereas the reaction of PhSiH₃ under equivalent conditions affords 2a quantitatively after 6 h.

**Scheme 1.** Thermal reactions of {PhB(OxMe₂)₂ImMes}Rh(CO)₂ (1) and primary silanes.

![Reaction Scheme](image)

In the solid-state structure of 2d (Figure 2), the Rh1–N1 interatomic distance *trans* to the hydride is shorter by 0.05 Å than the Rh1–N2 distance of the oxazoline *trans* to the silyl group. The CO ligand and the NHC group are *trans*. This configuration and the shorter Rh–N *trans* to H are consistent across the solid-state structures of 2a and 2b (see Figure S17). In contrast, the reaction of {PhB(OxMe₂)₂ImMes}Ir(CO)₂ and benzene, which occurs under photochemical conditions, results in CO *trans* to an oxazoline and the phenyl *trans* to the NHC. These distinct configurations of the two products suggest distinct mechanisms for thermal and photochemical processes.

Contamination by residual arylsilane hinders reproducible isolation of 2d and 2e as pure species. These compounds are instead spectroscopically characterized in the presence of RSiH₃. Attempts to increase the rate of oxidative addition of p-MeC₆H₄SiH₃ or p-MeOC₆H₄SiH₃, by
performing the reactions at 60 °C, result in organosilane rearrangement to give (p-MeC₆H₄)₂SiH₂
or (p-MeOC₆H₄)₂SiH₂. Neither triarylsilanes nor the SiH₄ product expected from redistribution
were detected by NMR spectroscopy or GC-MS; however, additional SiH and RhH signals
suggest that these species, if formed, might have undergone further reaction. The majority of
redistribution products appear in the latter stages of the reaction after almost all of 1 is
consumed, suggesting that 2d and 2e are involved in redistribution. This process is faster for p-
MeOC₆H₄SiH₃ than for p-MeC₆H₄SiH₃, and only the oxidative addition pathway is observed at
room temperature. Interestingly, neither PhSiH₃ nor the alkylsilanes appear to undergo
rearrangement to Ph₂SiH₂ or R₂SiH₂ at 60 °C, instead giving the desired rhodium silyl hydride
product selectively.
Figure 2. Thermal ellipsoid plot of \( \{\text{PhB(OxMe}_2\text{)}_2\text{Im}^{\text{Mes}}\}\text{RhH(SiH}_2\text{C}_6\text{H}_4\text{Me})\text{CO} \) (2d) at 35% probability. One of two positions of the disordered tolyl group is shown. H atoms bonded to Rh1 and Si1 were located objectively in the difference Fourier map, refined isotropically, and were included in the representation. Selected interatomic distances (Å): Rh1–Si1, 2.336(1); Rh1–C11, 2.070(4); Rh1–C36, 1.888(3); Rh1–H1r, 1.58(4); Rh1–N1, 2.197(3); Rh1–N2, 2.242(3).

Kinetic studies of oxidative addition. Initial kinetic studies, in which concentrations of PhSiH\(_3\) and 1 were monitored by \(^1\text{H} \) NMR spectroscopy, suggested first order dependence of reaction rate on [PhSiH\(_3\)] and [1]. Unfortunately, reactions in sealed NMR tubes do not result in
complete conversion, even with excess PhSiH$_3$. For example, 15 equiv. of PhSiH$_3$ (140 mM) vs 1 (9 mM) gives 92% yield of 2a after 70 min. (1:2a = 0.085:1). Although the concentration of 1 follows an exponential decay over the first few half-lives, the composition of the reaction mixture changes more slowly in the later stages of the reaction than expected for a pseudo-first order reaction that should proceed to completion. Moreover, a plot of pseudo-first order rate constants vs [PhSiH$_3$] provides only a rough trend, and considerable scatter suggests additional factors influenced the rate.

A unimolecular decomposition via reductive elimination of the rhodium silyl hydride is ruled out because compound 2a is isolable and persistent in pure form. In contrast, the reaction of 2a and CO (1 atm) results in ca. 30% conversion to 1 and PhSiH$_3$ at room temperature after 1 d. This observation indicates that oxidative addition of Si–H to 1 is reversible in the presence of CO. Thus, the reproducible kinetics for reactions of 1 might be complicated by slow and variable loss of CO into the NMR tube headspace. An additional complication to studying the CO-promoted reductive elimination from 2a involves the formation of PhB(OxMe$_2$)$_2$ImMesH as a side product under conditions with higher CO pressures or high temperature (>60 °C). In contrast, the reaction produces only 1 and PhSiH$_3$ under ambient conditions. Apparently, the number of CO ligands coordinated to Rh increases at higher pressure, leading to reductive elimination of C–H rather than Si–H. Note that the harsher conditions required for C–H reductive elimination indicate that the Si–H reductive elimination is kinetically preferred.

Solution-phase IR and UV-vis spectroscopies were tested as alternative methods to study the reactions, with the latter method appearing to be most promising. UV-vis spectroscopy provides the advantage that the disappearance of 1 could be monitored in sealed cuvettes with negligible headspaces, eliminating one of the issues associated with the NMR kinetic studies. In a first
experiment, spectra (250 – 700 nm) of a reaction mixture of \( \mathbf{1} \) and \( \text{PhSiH}_3 \) were acquired at 15 min. intervals over the reaction (Figure 3). The signal at 385.5 nm systematically decreased, while the center of the band at 301 nm blue-shifted and appeared non-Gaussian in the final spectrum of \( \mathbf{2a} \). Subsequent kinetic experiments monitored the absorption at 385.5 nm. While photolysis of \( \mathbf{1} \) in benzene affords the cyclometalated \( \{\kappa^4\text{-PhB(OxMe}_2\}\text{ImMe}_2\text{CH}_2\}\text{RhH(CO)} \) resulting from photolytic CO dissociation followed by CH bond oxidative addition of a mesityl methyl,\textsuperscript{57} that process was not observed (from absorption of the UV light) in the spectrophotometer. That is, a series of UV-vis spectra for \( \mathbf{1} \) acquired under otherwise equivalent conditions, but without \( \text{PhSiH}_3 \), were all identical to the first spectrum.

![Figure 3](image_url)

**Figure 3.** Electronic absorption spectra of \( \mathbf{1} \) ([\( \mathbf{1} \)\textsubscript{ini} = 2.7 × 10\textsuperscript{-4} M) during its reaction with \( \text{PhSiH}_3 \) (1.1 × 10\textsuperscript{-3} M) at room temperature in benzene acquired at 15 min. intervals. \( \text{PhSiH}_3 \) does not absorb at >250 nm.
Under conditions employing large excesses of PhSiH$_3$ (ranging from 25 to 140 equiv vs 1) for reactions monitored at 296 K, plots of [1] vs time followed an exponential decay for 3 half-lives, indicating first-order dependence on [1]. Under the conditions of these experiments, particularly with dilute [1] and high [PhSiH$_3$], the final concentration of 1 approaches zero (Figure 4). Non-linear least-squares fits were superior for experiments with higher concentrations of PhSiH$_3$, while some deviation was observed at longer reaction times with lower [PhSiH$_3$]$_{ini}$. This observation suggests that at longer reaction times, [CO] increases and the reverse reaction contributes to the observed rate constant (see below for studies with non-zero initial CO concentrations). Thus, the initial portion of the time course approximates the reaction as irreversible under conditions where [CO]$_{ini} = 0$ M.

**Figure 4.** Plots of [1] vs time in its reaction with PhSiH$_3$ in benzene at 296 K, monitored at 385.5 nm, with [PhSiH$_3$] = (a) 4.0, (b) 5.8, (c) 10.0, and (d) 25.5 mM. Non-linear least-squares regression fits to exponential decay curves [Rh]$_t$ = [Rh]$_{ini}$ e$^{-kt}$ confirm first-order dependence.
Plots of $k_{\text{obs}}$ vs [PhSiH$_3$] provide a forward rate constant $k_{\text{app}}$ (given in Figure S21, constrained by the approximation that the rate of reductive elimination is negligible at [CO]$_{\text{ini}}$ = 0 M). In addition, a plot of log[PhSiH$_3$] vs. log($k_{\text{obs}}$) is linear with a slope of 1 (Figure S23), indicating first-order dependence on phenylsilane concentration. The rate constants were measured over five temperatures (up to 322 K, Table 1) to determine the activation parameters of $\Delta H^{\text{H-app}} = 11 \pm 1$ kcal·mol$^{-1}$ and $\Delta S^{\text{H-app}} = -30 \pm 3$ cal·mol$^{-1}$K$^{-1}$ (Figure S24). For comparison, the $\Delta S^\ddag$ for oxidative addition of Si–H bonds in tertiary silanes to photolytically-generated CpMn(CO)$_2$ range from –6 to –10 cal·mol$^{-1}$K$^{-1}$; however, these values vary considerably with the cyclopentadiene-based ancillary ligand.

The same approach provides the second-order rate constants for the addition of 1 and PhSiD$_3$. The activation parameters, determined from an Eyring plot, are $\Delta H^{\text{D-app}} = 10 \pm 1$ kcal·mol$^{-1}$ and $\Delta S^{\text{D-app}} = -34 \pm 4$ cal·mol$^{-1}$K$^{-1}$. These two sets of values are experimentally indistinguishable, thus $k_H/k_D \sim 1$ for all accessible reaction temperatures.

**Table 1.** Second-order rate constants $k_{1\text{app}}$ from pseudo-first order kinetic studies

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<th>Temp. (K)</th>
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<th>$k_{\text{D-app}}$ M$^{-1}$s$^{-1}$ ($\times 10^{-2}$)</th>
<th>$k_{\text{H}}/k_{\text{D}}$</th>
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<td>322.3</td>
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<td>5.0 $\pm$ 0.1</td>
<td>0.9 $\pm$ 0.1</td>
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$^a$ $k_{1\text{app}}$ is the rate constant for the forward, oxidative addition of PhSiH$_3$ to 1, determined at [CO]$_{\text{ini}}$ = 0. $^b$ Calculated from corresponding Eyring plots.
Equilibrium kinetic studies. Additional evidence that oxidative addition of phenylsilane is reversible in the presence of CO comes from the reaction with PhSiH$_3$ in a CO-saturated benzene solution (7.3 mM). Under otherwise equivalent conditions, the reaction shows an apparent decrease in rate and final concentration (Figure 5).

Figure 5. Plots of [1] vs time for its reaction with PhSiH$_3$ (260 equiv.) in benzene saturated with (a) ca. 35 equiv. of CO and (b) without CO at 296 K, measured by UV-Vis spectroscopy at 385.5 nm. [CO]$_{ini}$ = 7.3 mM, [1]$_{ini}$ = 0.2 mM, [PhSiH$_3$]$_{ini}$ = 52.0 mM.

Clearly, mechanisms of both forward and reverse reactions are of interest. Note that for a first-order reaction that approaches equilibrium, the observed rate constant (i.e., the coefficient of the
exponential describing time-dependence of the reactant’s concentration) is the sum of forward and reverse rate constants ($k_e = k_1 + k_{-1}$). In the present case, the observed pseudo-first order rate constant ($k_e$) is equal to the sum of the oxidative addition and reduction elimination rate constants, multiplied by concentrations of flooded reagents, respectively (eq. 1).

$$k_e = k_1[\text{PhSiH}_3]^e_1 + \frac{1}{[\text{PhSiH}_3]^e_1} + k_{-1}[\text{CO}]^e_2a + \frac{1}{[\text{CO}]^e_2a}$$

(1)

Under high [PhSiH$_3$] and [CO] (flooding conditions), eq. 1 simplifies into eq. 2, where the observed rate constant $k_e$ depends on both [PhSiH$_3$]$_e$ and [CO]$_e$ (which are defined by their initial concentrations). The forward and reverse rate constants are related to the equilibrium constant $K_e = k_1/k_{-1}$.

$$k_e = k_1[\text{PhSiH}_3]^e_1 + k_{-1}[\text{CO}]^e_2a = k_1[\text{PhSiH}_3]^e_1 + \frac{k_1}{K_e}[\text{CO}]^e_2a$$

(2)

To determine $K_e$, 1 (0.1 – 0.2 mM) and PhSiH$_3$ (4.8 – 8 mM) are allowed to react in CO-saturated benzene solution (7.3 mM) over 1 – 2 days, until the absorbance of 1 becomes static and corresponds to [1]$_e$. [2a]$_e$ is determined from the relationship [1]$_{ini} - [1]_e$. At 297 K, $K_e$ is 2.8 ± 0.2 (from four independent measurements). The equilibrium constants were measured from 297 to 328 K, and a van’t Hoff plot provides $\Delta H^o = -5.5 \pm 0.2$ kcal/mol and $\Delta S^o = -16 \pm 1$ cal·mol$^{-1}$K$^{-1}$ (Figure S25). The van’t Hoff plot also allows the prediction of equilibrium constants for other temperatures.

The concentration of 1 vs. time was measured under conditions of excess PhSiH$_3$ and excess CO (7.3 mM). Non-linear least-squares regression of the data to eq. 3 provides $k_e$.

$$[1] = [1]_e + ([1]_0 - [1]_e)e^{-k_et}$$

(3)
The rate constants $k_1$ and $k_{-1}$ are determined using eq. 2 and $k_e, K_e, [\text{PhSiH}_3]_e$ and $[\text{CO}]_e$ values. Measurements of [1] vs time from 297 to 328 K (four measurements at each temperature) provide temperature-dependent $k_e$ (Table S1). These rate constants, combined with the $K_e$ from the van’t Hoff analysis, provide $k_1$ and $k_{-1}$ over a 30 K range. Here, we note that the rate constant $k_1^{296 \text{ K}}$ of 0.01 M$^{-1}$s$^{-1}$ (calculated from the Eyring equation and van’t Hoff plot for a reaction occurring at 296 K) and the $k_{\text{app}}$ (0.012 M$^{-1}$s$^{-1}$, measured experimentally at 296 K) are in good agreement, indicating that the approximate rate constant at $[\text{CO}]_{\text{ini}} = 0$ is a reasonable estimate of $k_1$.

The activation parameters for oxidative addition of 1 and PhSiH$_3$ are determined to be $\Delta H^\ddagger = 11 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -26 \pm 3 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (Figure 6). These values are also equivalent to those determined above from rate constants $k_{\text{app}}$ in which the reverse direction is neglected at $[\text{CO}]_{\text{ini}} = 0$. The second-order rate law indicates that 1 and PhSiH$_3$ are present in that transition state, while this negative entropy of activation suggests (but does not prove) that CO (which ultimately dissociates) is also present in the transition state as the rate-controlling step occurs. The reverse reaction also features a negative entropy of activation ($\Delta H^\dagger = 17 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\dagger = -10 \pm 3 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). In addition, the rhodium tolylsilyl (2d, see below) is not detected in NMR spectra of a mixture of 2a and p-tolylsilane (as long as the solution is CO-free). Thus, the reductive Si–H coupling and silane formation from 2 requires a molecule of CO to interact with the rhodium center. Moreover, compound 2a is stereochemically rigid (at least on the NMR timescale), and its $^1\text{H}$ NMR spectrum contains distinct resonances for the oxazoline trans to hydride and silyl, as noted above, suggesting that five-coordinate fluxional intermediates, possibly from reductive coupling of Si–H or dissociation of an oxazoline, are not involved. From these data, a probable rate law for reductive elimination is second-order ($\propto [2a][\text{CO}]$).
results, and the principle of microscopic reversibility, indicate that the composition of the transition state for forward and reverse processes is \([\{\text{PhB(OxMe}^2\text{)}_2\text{Im}^\text{Mes}\}\text{Rh(CO)}_2\cdot\text{PhSiH}_3]\). Thus, the reverse pathway involves coordination of CO to \(2a\) as a first step.

![Eyring plots](image)

**Figure 6.** Eyring plots (\(\ln(k/T)\) vs \(1/T\)) for (a) \(k_1\) representing oxidative addition and (b) \(k_{-1}\) representing reductive elimination.

**Rates and equilibrium constants for organosilane addition.** The equilibrium constant \(K_e\), forward rate constant \(k_1\), and reverse rate constant \(k_{-1}\) are determined for the reaction of \(1\) with four primary silanes (Table 2). Comparison of \(K_e\) values reveals that oxidative addition of
arylsilanes is more favorable than alkylsilanes. The forward rate constant ($k_1$) is nearly five times faster for arylsilanes than for alkylsilanes, whereas the rate constants for the reverse reaction are similar across all silanes. Because the reverse rate constants are relatively similar, the difference in equilibrium constant between alkylsilanes and arylsilanes results from the difference in forward rate constant. Note that only two of the three variables ($K_e$, $k_1$ and $k_{-1}$) are independent.

The rate constant for oxidative addition of alkylsilanes is smaller than that for reductive elimination, whereas reductive elimination of arylsilanes occurs with a lower rate constant than the oxidative addition. Even though this thermodynamic assessment indicates that compounds 2d and 2e are favored while 2b and 2c are unfavored with respect to 1 (without excess reagent to perturb the equilibrium), somewhat ironically, the latter compounds are the isolable species. Clearly, the unfavorable thermodynamic bias may be overcome under synthetic conditions by removing CO from the system.

**Table 2.** $K_e$, $k_1$, $k_{-1}$ for reaction of 1 and RSiH$_3$ measured at 297 °C.

<table>
<thead>
<tr>
<th>RSiH$_3$ / 2</th>
<th>$K_e$</th>
<th>$k_1$ (M$^{-1}$s$^{-1}$) ($\times 10^{-2}$)</th>
<th>$k_{-1}$ (M$^{-1}$s$^{-1}$) ($\times 10^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexylsilane / 2b</td>
<td>0.53 ± 0.01</td>
<td>0.23 ± 0.01</td>
<td>0.43 ± 0.01</td>
</tr>
<tr>
<td>n-dodecylsilane / 2c</td>
<td>0.48 ± 0.01</td>
<td>0.25 ± 0.02</td>
<td>0.53 ± 0.05</td>
</tr>
<tr>
<td>phenylsilane / 2a</td>
<td>2.8 ± 0.3</td>
<td>1.25</td>
<td>0.49</td>
</tr>
<tr>
<td>p-methoxyphenylsilane / 2e</td>
<td>2.1 ± 0.1</td>
<td>1.34 ± 0.02</td>
<td>0.64 ± 0.01</td>
</tr>
<tr>
<td>p-tolylsilane / 2d</td>
<td>4.5 ± 0.1</td>
<td>1.4 ± 0.1</td>
<td>0.32 ± 0.02</td>
</tr>
</tbody>
</table>

**Conclusion**

Comparison of the forward and reverse rate constants between reaction of arylsilanes and alkylsilanes, as well as the rate laws and activation parameters for PhSiH$_3$ oxidative addition and
reductive elimination, provide considerable insight into the pathway and mechanisms. First, reductive elimination (the back reaction) likely follows a second-order rate law. The dissociation of silane from rhodium does not occur in the absence of free CO, the rhodium center in 2 is stereochemically rigid, and silyl/silane exchange is not observed. Thus, two CO groups are present in the transition state of the rate-limiting step on the pathway for reductive elimination (eq. 6 of Scheme 2, in reverse). Alternative mechanisms, in which one oxazoline dissociates from 2 to give a high energy 16-electron rhodium(III) species that is trapped by CO or undergoes Si–H bond reductive elimination, are ruled out by the dependence on CO.

Two additional observations suggest that coordination of CO to 2 is the rate-limiting step of the reductive elimination process. In this reaction, $\Delta S^\ddagger$ is negative ($-10 \pm 3 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), which is consistent with increased order in the transition state. Loss of the H–SiH$_2$R group during or prior to the rate-limiting step would result in a positive entropy term. Note that $\Delta S$ for the overall reductive elimination of PhSiH$_3$ from 2a is positive, suggesting that PhSiH$_3$ dissociation from 2a occurs after the rate-controlling step. In addition, the rate constants are similar for the reductive elimination reactions of 2a-e, where the alkylsilyl and arylsilyl ligand is varied. A rate-determining step involving either Rh–Si bond cleavage, and especially Si–H bond formation, would be expected to vary significantly with the silyl substituent. On the basis of these ideas, we conclude that the rate-limiting step for the reductive elimination pathway involves substitution of a coordinated oxazoline by the incoming CO. This step is the first step in the overall pathway from 2 back to 1.

This interpretation limits the possible mechanisms of the oxidative addition (forward) pathway (Scheme 2). In oxidative addition of Si–H to 1, two CO ligands are present up to the transition state of the rate-limiting step, at which point CO dissociates from rhodium, as required by the
principle of microscopic reversibility. Thus, low coordinate species, analogous to 
photochemically generated \( \kappa^2\text{-Tp}^*\text{RhL} \) or \( \kappa^3\text{-Tp}^*\text{RhL} \) (L = CO, CNR), are never accessed in this 
transformation. In addition, the Si–H bond is cleaved during or prior to the rate-limiting step in 
the reaction of 1 and silanes. The evidence for this aspect of the mechanism includes the second-
order rate law which contains first-order dependence on silane concentration. The activation 
entropy \( (\Delta S^\ddagger = -26 \pm 3 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \) is more negative than for the reverse direction, which is 
consistent with the loss of entropy resulting from creation of the rhodium-silane interaction.
Finally, the rate constants for oxidative addition to 1 are 5× greater with arylsilanes than 
alkylsilanes, indicating that the relative energy of the starting material vs. that of the rate-
determining transitions state is affected by the nature of the silane. Thus, we attribute the change 
in rate of oxidative addition for 1 and silanes to large changes in the energy of the silane
(variation in the ground state). This interpretation is consistent with the similar rates for 
reductive elimination over the series \( 2a-e \), which indicates the energies difference between 2 and 
the rate-limiting transition for reductive elimination are similar.

**Scheme 2.** Proposed pathway for oxidative addition of Si–H bonds under thermal conditions.
In contrast, we note that $k_{H}/k_{D}$ is ~1. The most straightforward interpretation of these data is that the Si–H is broken prior to the rate-determining step. A second possibility is that Si–H bond cleavage occurs during the rate-determining step, and an inverse equilibrium isotope effect from the formation of a silane-rhodium σ-complex balances a normal kinetic isotope effect for Si–H oxidative cleavage. The data cannot unambiguously distinguish these alternatives, but we favor the former pathway of Scheme 2 because the observed kinetic isotope effect is unity over a range of temperatures, such that coincidental cancelling of equilibrium and kinetic isotope effects is less likely, and this scheme provides the simplest kinetically consistent mechanism.

The thermodynamic and kinetic data are entirely inconsistent with a mechanism resembling the photochemical activation and E–H bond oxidative addition chemistry of the classical
cyclopentadienyl and tris(pyrazolyl)borato rhodium and iridium species. The newly proposed mechanism invokes associative steps to access the trivalent rhodium intermediate, which is then susceptible to displacement of CO by a chelating oxazoline. This work shows that thermal pathways for catalytic functionalization are plausible, even in the presence of CO, but such reactions still face considerable challenges due to kinetic and thermodynamic constraints on bond activation. Moreover, CO dissociation from a low valent metal complex is not a necessary pre-requisite for oxidative addition. The presence of coordinating groups, either as part of polar substrates, may also facilitate coordination, oxidative addition, and CO dissociation during catalytic conversions.

**Experimental Section**

**General.** All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox. Benzene, toluene, methylene chloride, pentane, and tetrahydrofuran were dried and deoxygenated using an IT PureSolv system. Benzene-$d_6$ was heated to reflux over Na/K alloy and vacuum transferred. $[\text{Rh}(\mu-\text{Cl})(\text{CO})_2]_2$, $\{\text{PhB(OxMe}_2)\text{ImMes}\}_\text{Rh(CO)}_2$ (1), $\{\text{PhB(OxMe}_2)\text{ImMes}\}_\text{RhH(SiH}_2\text{Ph)CO}$, and $p$-methoxyphenylsilane were synthesized according to the literature procedure. Phenylsilane, $n$-hexylsilane, $n$-dodecylsilane and $p$-tolylsilane were synthesized by reducing corresponding trichlorosilanes with LiAlH$_4$. PhSiD$_3$ was synthesized from PhSiCl$_3$ and LiAlD$_4$. Potassium benzyl was synthesized by reacting potassium tert-butoxide with $n$-BuLi in toluene.

$^1$H, $^{13}$C{$^1$H}, $^{11}$B and $^{15}$N spectra were collected on Bruker Avance III 600 or AVNEO 400 MHz NMR spectrometers. NMR signals ($^1$H, $^{13}$C, and $^{15}$N) were assigned based on COSY, HMQC, and HMBC experiments. $^{15}$N chemical shifts were determined by $^1$H–$^{15}$N HMBC
experiments. $^{15}$N chemical shifts were initially referenced to NH$_3$ and recalibrated to the CH$_3$NO$_2$ chemical shift scale by adding $-381.9$ ppm. Infrared spectra were recorded on a Bruker Vertex spectrometer. Elemental analyses were performed using a PerkinElmer 2400 Series II CHN/S in the Iowa State Chemical Instrumentation Facility.

{PhB(OxMe$_2$)$_2$Im$^{Mes}$}RhH(SiH$_2$C$_6$H$_{13}$)CO (2b). n-Hexylsilane (185 mg, 1.6 mmol) was added to a solution of 1 (100 mg, 0.158 mmol) in benzene to give a pale yellow solution. The resulting solution was allowed to stir for 24 h. The volatile materials were evaporated in vacuo giving {PhB(OxMe$_2$)$_2$Im$^{Mes}$}RhH(SiH$_2$C$_6$H$_{13}$)CO (88 mg, 0.123 mmol, 78%). $^1$H NMR (benzene-$d_6$, 600 MHz): $\delta$ 8.40 (d, $^3$J$_{HH}$ = 7.8 Hz, 2 H, $\sigma$-BC$_6$H$_5$), 7.54 (t, $^3$J$_{HH}$ = 7.8 Hz, 2 H, $m$-BC$_6$H$_5$), 7.39 (t, $^3$J$_{HH}$ = 7.3 Hz, 1 H, $p$-BC$_6$H$_5$), 6.83 (s, 1 H, $m$-C$_6$H$_2$Me$_3$), 6.78 (s, 1 H, $m$-C$_6$H$_2$Me$_3$), 6.53 (d, $^3$J$_{HH}$ = 1.6 Hz, 1 H, N$_2$C$_3$H$_2$Mes), 5.94 (d, $^3$J$_{HH}$ = 1.6 Hz, 1 H, N$_2$C$_3$H$_2$Mes), 4.91 (t, $^2$J$_{HH}$ = 6.8 Hz, $^1$J$_{SiH}$ = 168 Hz, 1 H, SiH), 4.43 (t, $^2$J$_{HH}$ = 6.8 Hz, $^1$J$_{SiH}$ = 180 Hz, 1 H, SiH), 3.60 (m, 3 H, CNCMe$_2$CH$_2$O), 3.36 (d, $^2$J$_{HH}$ = 8.3 Hz, 1 H, CNCMe$_2$CH$_2$O), 2.23 (s, 3 H, $p$-C$_6$H$_2$Me$_3$), 2.09 (s, 3 H, $o$-C$_6$H$_2$Me$_3$), 2.02 (s, 3 H, $o$-C$_6$H$_2$Me$_3$), 1.55 (br, 2 H, SiCH$_2$CH$_2$), 1.33-1.40 (br, 6 H, CH$_2$CH$_2$CH$_2$), 1.23 (s, 3 H, CNCMe$_2$CH$_2$O trans to H), 1.16 (s, 3 H, CNCMe$_2$CH$_2$O trans to H), 1.10 (s, 3 H, CNCMe$_2$CH$_2$O trans to Si), 0.99 (s, 3 H, CNCMe$_2$CH$_2$O trans to Si), 0.95 (t, $^3$J$_{HH}$ = 7 Hz, 3 H, CH$_2$CH$_3$), 0.41 (m, 1 H, SiH$_2$CH$_2$), $-0.12$ (m, 1 H, SiH$_2$CH$_2$), $-13.70$ (dd, $^1$J$_{RhH}$ = 22.4 Hz, $^3$J$_{HH}$ = 1.5 Hz, 1 H, RhH). $^{13}$C {$^1$H} NMR (benzene-$d_6$, 150 MHz): $\delta$ 195.05 (d, $^1$J$_{RhC}$ = 51.9 Hz, 2C-N$_2$C$_3$H$_2$Mes), 179.24 (d, $^1$J$_{RhC}$ = 40.5 Hz, CO), 138.49 (br, $ipso$-BC$_6$H$_5$), 137.58 ($p$-C$_6$H$_2$Me$_3$), 136.70 ($o$-C$_6$H$_2$Me$_3$), 136.64 ($o$-BC$_6$H$_5$), 136.36 ($o$-C$_6$H$_2$Me$_3$), 129.58 ($m$-C$_6$H$_2$Me$_3$), 129.51 ($m$-C$_6$H$_2$Me$_3$), 127.50 ($m$-BC$_6$H$_5$), 127.03 ($p$-BC$_6$H$_5$), 124.60 (4,5-C$_6$N$_2$C$_3$H$_2$Mes), 121.12 (4,5-C$_6$N$_2$C$_3$H$_2$Mes), 80.40 (CNCMe$_2$CH$_2$O), 80.39 (CNCMe$_2$CH$_2$O), 68.79 (CNCMe$_2$CH$_2$O), 66.64 (CNCMe$_2$CH$_2$O), 33.64 (CH$_2$), 32.32 (CH$_2$), 29.88 (CNCMe$_2$CH$_2$O), 28.37
(CNCMe₂CH₂O), 28.08 (CNCMe₂CH₂O), 27.03 (CNCMe₂CH₂O), 23.29 (CH₂), 21.16 (p-C₆H₂Me₃), 19.52 (o-C₆H₂Me₃), 19.37(o-C₆H₂Me₃), 18.01 (CH₂), 17.99 (CH₂), 14.50 (CH₃).

¹³N {¹H} NMR (benzene-d₆, 61 MHz): δ −160 (CNCMe₂CH₂O trans to Si), −172 (CNCMe₂CH₂O trans to H), −188 (N₂C₃H₂Mes). ¹¹B NMR (benzene-d₆, 192 MHz): δ −9.7. IR (KBr, cm⁻¹): 3135, 3043, 2959, 2923, 2733, 2359, 2279, 2041, 2011, 1652, 1595, 1458, 1275, 967, 820. Anal. Calcd for C₅₀H₅₀BN₄O₃RhSi: C, 58.66; H, 7.03; N, 7.82. Found: C, 58.68; H, 7.21; N, 7.61

{PhB(OxMe₂)₂ImMes}RhH(SiH₂C₁₂H₂₃)CO (2c). n-dodecylsilane (318 mg, 1.59 mmol) was added to a solution of 1 (100 mg, 0.159 mmol) in benzene to give a pale yellow solution. The resulting solution was allowed to stir for 24 h. The volatile materials were evaporated in vacuo resulting a white solid which was washed with pentane to give pure {PhB(OxMe₂)₂ImMes}RhH(SiH₂C₁₂H₂₃)CO (65 mg, 0.08 mmol, 50%). ¹H NMR (benzene-d₆, 600 MHz): δ 8.41 (d, ³J_HH = 7.8 Hz, 2 H, o-BC₆H₃), 7.54 (t, ³J_HH = 7.2 Hz, 2 H, m-BC₆H₃), 7.4 (t, ³J_HH = 7.2 Hz, 1 H, p-BC₆H₃), 6.84 (s, 1 H, m-C₆H₂Me₃), 6.80 (s, 1 H, m-C₆H₂Me₃), 6.54 (d, ³J_HH = 1.6 Hz, 1 H, N₂C₃H₂Mes), 5.94 (d, ³J_HH = 1.8 Hz, 1 H, N₂C₃H₂Mes), 4.26 (t, ²J_HH = 7.2 Hz, 1 J_SiH = 160 Hz, 1 H, SiH), 3.81 (t, ²J_HH = 6.6 Hz, 1 J_SiH = 180 Hz, 1 H, SiH), 3.64-3.57 (m, 3 H, CNCMe₂CH₂O), 3.35 (d, ²J_HH = 8.4 Hz, 1 H, CNCMe₂CH₂O), 2.26 (s, 3 H, p-C₆H₂Me₃), 2.09 (s, 3 H, o-C₆H₂Me₃), 2.03 (s, 3 H, o-C₆H₂Me₃), 1.58 (br, 2 H, SiCH₂CH₂), 1.33-1.29 (br, 21 H, CH₂CH₂CH₂), 1.23 (s, 3 H, CNCMe₂CH₂O trans to H), 1.16 (s, 3 H, CNCMe₂CH₂O trans to H), 1.10 (s, 3 H, CNCMe₂CH₂O trans to Si), 0.99 (s, 3 H, CNCMe₂CH₂O trans to Si), 0.93 (t, ³J_HH = 7.2 Hz, 3 H, CH₂CH₃), 0.44 (m, 1 H, SiH₂CH₂), −0.07 (m, 1 H, SiH₂CH₂), −13.68 (dd, ¹J_RH = 22.2 Hz, ³J_HH = 1.8 Hz, 1 H, RhH). ¹³C {¹H} NMR (benzene-d₆, 150 MHz): δ 195.06 (d, ¹J_RH = 52.8 Hz, 2C-N₂C₃H₂Mes), 185.79 (br, CNCMe₂CH₂O), 179.23 (d, ¹J_RH = 40.7 Hz, CO), 138.49
(p-C₆H₄Me₃), 137.60 (ipso-C₆H₂Me₃), 136.70 (o-C₆H₂Me₃), 136.66 (o-C₆H₂Me₃), 136.39 (o-
BC₆H₅), 129.59 (m-C₆H₂Me₃), 129.52 (m-C₆H₂Me₃) 127.51 (m-BC₆H₅), 127.04 (p-BC₆H₅),
124.61 (4,5-CN₂C₃H₂Mes), 121.12 (4,5-CN₂C₃H₂Mes), 80.40 (CNCMe₂CH₂O), 80.39
(CNCMe₂CH₂O), 68.79 (CNCMe₂CH₂O), 66.64 (CNCMe₂CH₂O), 34.00 (CH₂), 32.38 (CH₂),
30.37 (CH₂), 30.31 (CH₂), 30.26 (CH₂), 30.19 (CH₂), 29.94 (CH₂), 29.87 (CH₂), 28.37
(CNCMe₂CH₂O), 28.08 (CNCMe₂CH₂O), 28.02 (CNCMe₂CH₂O), 27.03 (CNCMe₂CH₂O), 23.16
(CH₂), 21.18 (p-C₆H₂Me₃), 19.53 (o-C₆H₂Me₃), 19.38 (o-C₆H₂Me₃), 18.02 (CH₂), 18.01 (CH₂),
14.41 (CH₃). ¹³N{¹H} NMR (benzene-d₆, 61 MHz): δ –160 (CNCMe₂CH₂O trans to Si), –172
(CNCMe₂CH₂O trans to H), –175 (N₂C₆H₁₂Mes), –188 (N₂C₆H₂Mes). ¹¹B NMR (benzene-d₆,
192 MHz): δ –9.9. IR (KBr, cm⁻¹): 2957, 2922, 2852, 2149, 2044, 2013, 1595, 1463, 1365,
1316, 1183, 1160, 968.

{PhB(OxMe₂)₂ImMes}RhH(SiH₂C₆H₄Me)CO (2d). p-tolylsilane (195 mg, 1.6 mmol) was
added to a solution of 1 (100 mg, 0.158 mmol) in benzene to give a pale yellow solution. The
resulting solution was allowed to stir for 24 h. The volatile materials were evaporated in vacuo
giving {PhB(OxMe₂)₂ImMes}RhH(SiH₂C₆H₄Me)CO with some residual p-tolylsilane. This
mixture was characterized by NMR and IR spectroscopy; the residual silane hindered ¹³C{¹H}
NMR assignments in the aryl region. An X-ray quality crystal was obtained from a pentane
solution; however, this approach was not reliable for purification from residual p-tolylsilane. ¹H
NMR (benzene-d₆, 600 MHz): δ 8.43 (d, ³J_HH = 7.8 Hz, 2 H, o-BC₆H₅), 7.56 (t, ³J_HH = 7.2 Hz, 2
H, m-BC₆H₅), 7.52 (d, ³J_HH = 7.8 Hz, 2 H, o-BC₆H₄Me), 7.41 (t, ³J_HH = 7.2 Hz, 1 H, p-BC₆H₅),
6.95 (d, ³J_HH = 7.8 Hz, 2 H, m-BC₆H₄Me), 6.55 (d, ³J_HH = 1.8 Hz, 1 H, N₂C₆H₂Mes), 6.54 (s, 1 H,
m-BC₆H₂Me₃), 6.41 (s, 1 H, m-BC₆H₂Me₃), 5.94 (d, ³J_HH = 1.8 Hz, 1 H, N₂C₆H₂Mes), 4.91 (t, ²J_HH
= 4.8 Hz, ¹J_SiH = 170 Hz, 1 H, SiH), 4.45 (t, ²J_HH = 4.8 Hz, ¹J_SiH = 186 Hz, 1 H, SiH), 3.57-3.65
(m, 3 H, CNCMe₂CH₂O), 3.37 (d, ²JHH = 8.4 Hz, 1 H, CNCMe₂CH₂O), 2.18 (s, 3 H, p-C₆H₂Me₃), 2.03 (s, 3 H, o-C₆H₂Me₃), 2.00 (s, 3 H, o-C₆H₂Me₃), 1.90 (s, 3 H, p-C₆H₄Me), 1.16 (3 H, CNCMe₂CH₂O), 1.16 (3 H, CNCMe₂CH₂O), 1.08 (3 H, CNCMe₂CH₂O), 1.02 (3 H, CNCMe₂CH₂O), -13.22 (dd, ¹JRhH = 21.6 Hz, ³JHH = 2.4 Hz, 1 H, RhH). ¹³C {¹H} NMR (benzene-d₆, 150 MHz): δ 194.48 (d, ¹JRBC = 52.9 Hz, 2C-N₂C₃H₂Mes), 178.40 (d, ¹JRBC = 40.8 Hz, CO), 138.29 (ipsø-SiC₆H₄Me), 136.96 (p-C₆H₂Me₃), 136.68 (ipsø-SiC₆H₂Me₃), 136.67 (o-BC₆H₃), 129.34 (o-SiC₆H₄Me), 129.31 (m-SiC₆H₄Me), 127.54 (m-C₆H₂Me₃), 127.07 (m-C₆H₂Me₃), 124.60 (4,5C-N₂C₃H₂Mes), 121.50 (4,5C-N₂C₃H₂Mes), 80.49 (CNCMe₂CH₂O), 80.31 (CNCMe₂CH₂O), 68.80 (CNCMe₂CH₂O), 66.70 (CNCMe₂CH₂O), 28.38 (CNCMe₂CH₂O), 28.07 (CNCMe₂CH₂O), 27.78 (CNCMe₂CH₂O), 27.03 (CNCMe₂CH₂O), 21.48 (p-C₆H₂Me₃), 21.04 (p-SiC₆H₄Me), 19.49 (o-C₆H₂Me₃), 19.08 (o-C₆H₂Me₃). ¹⁵N {¹H} NMR (benzene-d₆, 61 MHz): δ -161 (CNCMe₂CH₂O trans to Si), -172, (CNCMe₂CH₂O trans to H), -174 (N₂C₃H₂Mes), -188 (N₂C₃H₂Mes). ¹¹B NMR (benzene-d₆, 192 MHz): δ -9.8. IR (KBr, cm⁻¹): 2962, 2923, 2855, 2279, 2104, 2016, 1917, 1652, 1605.

{PhB(OxMe₂)₂ImMes}RhH(SiH₂C₆H₄OMe)CO (2e). p-methoxyphenylsilane (220 mg, 1.6 mmol) was added to a solution of 1 (100 mg, 0.158 mmol) in benzene to give a pale yellow solution. The resulting solution was allowed to stir for 24 h. The volatile materials were evaporated in vacuo giving {PhB(OxMe₂)₂ImMes}RhH(SiH₂C₆H₄OMe)CO with some residual p-methoxyphenylsilane. This mixture was characterized by NMR and IR spectroscopy; the residual silane and its slow catalyzed redistribution hindered ¹³C {¹H} NMR assignments in the aryl region. ¹H NMR (benzene-d₆, 600 MHz): δ 8.42 (d, ³JHH = 7.2 Hz, 2 H, o-BC₆H₃), 7.55 (t, ³JHH = 7.2 Hz, 2 H, m-BC₆H₃), 7.50 (d, ³JHH = 8.4 Hz, 2 H, o-C₆H₅OMe), 7.40 (t, ³JHH = 7.2 Hz, 1 H, p-BC₆H₃), 6.74 (d, ³JHH = 8.4 Hz, 2 H, m-C₆H₅OMe), 6.57-6.54 (2 H, m-C₆H₂Me₃ + N₂C₃H₂Mes),
6.43 (s, 1 H, m-C₆H₄Me₃), 5.94 (d, 3 J_HH = 1.2 Hz, 1 H, N₂C₂H₂Mes), 4.93 (t, 2 J_HH = 6 Hz, 1 J_SiH = 172 Hz, 1 H, SiH), 4.45 (t, 2 J_HH = 6 Hz, 1 J_SiH = 180 Hz, 1 H, SiH), 3.65-3.57 (m, 3 H, CNCMe₂CH₂O), 3.39 (s, 3 H, C₆H₆O Me), 3.38 (d, 3 J_HH = 8.4 Hz, 1 H, CNCMe₂CH₂O), 2.02 (s, 3 H, p-C₆H₄Me₃), 2.01 (s, 3 H, o-C₆H₄Me₃), 1.96 (s, 3 H, o-C₆H₄Me₃), 1.17 (s, 3 H, CNCMe₂CH₂O), 1.16 (s, 3 H, CNCMe₂CH₂O), 1.15 (s, 3 H, CNCMe₂CH₂O), 1.09 (s, 3 H, CNCMe₂CH₂O), 1.04 (s, 3 H, CNCMe₂CH₂O), −13.24 (dd, 1 J_RhH = 18 Hz, 3 J_HH = 2 Hz, 1 H, RhH).

13C{¹H} NMR (benzene-d₆, 150 MHz): δ 194.23 (d, 1 J_RhC = 76.5 Hz, 2 C-N₂C₂H₂Mes), 178.12 (d, 1 J_RhC = 60 Hz, CO), 80.11 (CNCMe₂CH₂O), 79.95 (CNCMe₂CH₂O), 68.42 (CNCMe₂CH₂O), 66.33 (CNCMe₂CH₂O), 54.50 (p-C₆H₄O Me), 28.01 (CNCMe₂CH₂O), 27.72 (CNCMe₂CH₂O), 27.41 (CNCMe₂CH₂O), 26.65 (CNCMe₂CH₂O), 20.70 (p-C₆H₂Me₃), 19.12 (o-C₆H₂Me₃), 18.74 (o-C₆H₂Me₃).

15N NMR (benzene-d₆, 61 MHz): δ –161 (CNCMe₂CH₂O trans to Si), –172 (CNCMe₂CH₂O trans to H), –176 (N₂C₂H₂Mes), –188 (N₂C₂H₂Mes).

11B NMR (benzene-d₆, 192 MHz): δ –9.9. IR (KBr, cm⁻¹): 2961, 2933, 2836, 2562, 2531, 2170, 2016, 1903.

**NMR kinetic study.** A stock solution of 1 (0.011 M) and Si(SiMe₃)₄ (0.097 M) as an internal standard in benzene was prepared. Portions of this solution were placed in an NMR tube, and the initial concentration of [1] was verified by the integrated spectrum. Excess PhSiH₃ (to give concentrations greater than 0.1 M) was added by syringe through the septum of the NMR tube. The NMR tube was placed in the NMR probe, which had been pre-heated and calibrated to the desired temperature for the reaction. ¹H NMR spectra were acquired at regular programmed intervals, and concentrations were determined by integrating appropriate signals in each spectrum. Plots of [1] versus time were fit using non-linear least-squares regression to an exponential decay curve based on the equation [1] = [1]₀ e⁻ᵏᵗ for the analysis.
UV-vis kinetic experiments: (a) Pseudo-irreversible conditions, (b) CO-saturated approach to equilibrium, and (c) equilibrium constant measurements.

(a) Pseudo-irreversible conditions. Four UV-Vis cuvettes, completely filled with phenylsilane dissolved in benzene at four concentrations (0.0192, 0.0238, 0.0291, 0.0348 M), were capped in the glovebox. The temperature of the UV-Vis chamber was set to 308.3 K, and the sample was placed in the cavity and allowed to reach the preset temperature. Approximately 20 μL of a solution of 1 (40 mM) was added to the cuvette through a syringe. The absorption of the reaction mixture was measured at 385.5 nm at programmed time intervals, and [1] was calculated using Beer’s law. A plot of [1] versus time was fit to the equation $[1] = [1]_0 e^{-kt}$ using non-linear least-squares regression analysis, to determine pseudo first-order rate constants. Subsequent experiments varied [PhSiH$_3$], a plot of $k_{obs}$ versus [PhSiH$_3$] was linear, and the slope provided the second-order rate constant $k_{1\text{app}}$. This procedure, performed over a range of temperatures from 296 K to 322.3 K, provided the temperature-dependent second-order rate constants for an Eyring plot.

(b) CO-saturated approach to equilibrium. Solution of PhSiH$_3$ (14 mM, 15 mM, 18 mM, 19 mM) in benzene were degassed by three freeze-pump-thaw cycles, and then saturated with CO by stirring under a CO atmosphere (298 K, 1 atm). The solutions were transferred to nitrogen-flushed and dried UV-Vis cuvettes using air-free syringe technique. These samples were used for the kinetic study, following the procedure above, to determine $k_e$ by non-linear least-squares analysis. The series of experiments, combined with $K_e$ (determined below) provide forward ($k_1$) and reverse ($k_{-1}$) rate constants. This procedure was repeated for the three other temperatures (308.4, 318.4, 328.4 K). For the silane p-tolylsilane, p-methoxysilane, hexylsilane, and
dodecylsilane, this procedure was applied at room temperature to determine forward and reverse rate constants.

(c) Equilibrium constant measurement. Reactions of 1 and PhSiH$_3$ (3.2 mM, 3.8 mM, 4 mM, 11.9 mM), in CO-saturated benzene solution, were monitored by UV-Vis, as described above, until the reaction mixture reached equilibrium. [1] was determined from Beer’s law, [2a]$_e$ was determined from difference between [Rh]$_{total}$ and [1]$_e$, and [PhSiH$_3$]$_e$ and [CO]$_e$ were approximated to be equal to their initial concentration (in large excess of [Rh]$_{total}$). This procedure was repeated for other temperatures (296, 301.5, 318.4, 328.4 K) to provide data for a van’t Hoff plot to determine $\Delta H$ and $\Delta S$.

ASSOCIATED CONTENT

Supporting Information. Spectra for compounds 2b-e and kinetics data (PDF)

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Notes

The authors declare no competing financial interest.

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Synopsis: Oxidative addition of silanes to a rhodium dicarbonyl occurs under thermal conditions. Reversible oxidative addition of primary silane to Rh(I) displaces coordinated CO, with thermodynamic and kinetic parameters dictated by the organosilane. Oxidative addition of Si–H bonds for arylsilanes is faster than for alkylsilanes. Kinetic data characterizing oxidative addition and reductive elimination steps implicate an associative interaction of rhodium and silane or CO, respectively, rather than CO-dissociation limited mechanisms.
Figure 1. Photochemical and thermal pathways for oxidative addition of C–H and Si–H bonds to rhodium(I).

167x102mm (600 x 600 DPI)
Scheme 1. Thermal reactions of $\{\text{PhB(OxMe$_2$)2ImMes}\}\text{Rh(CO)$_2$ (1)}$ and primary silanes.

1. R = C$_8$H$_5$ (94%) (2a)
2. n-C$_6$H$_{13}$ (78%) (2b)
3. n-C$_{12}$H$_{25}$ (50%) (2c)
4. p-MeC$_6$H$_4$ (2d)
5. p-MeOC$_6$H$_4$ (2e)

(Reactions in benzene, r.t. - CO, R = alkyl (1 d) or aryl (6 h))
Figure 2. Thermal ellipsoid plot of \((\text{PhB(OxMe}_2\text{)2ImMes})\text{RhH(SiH}_2\text{C}_6\text{H}_4\text{Me})\text{CO}\) (2d) at 35% probability. One of two positions of the disordered tolyl group is shown. H atoms bonded to Rh1 and Si1 were located objectively in the difference Fourier map, refined isotropically, and were included in the representation. Selected interatomic distances (Å): Rh1–Si1, 2.336(1); Rh1–C11, 2.070(4); Rh1–C36, 1.888(3); Rh1–H1r, 1.58(4); Rh1–N1, 2.197(3); Rh1–N2, 2.242(3).
(a) $k_{obs} = 4.9 \times 10^{-5}$ s$^{-1}$
(b) $k_{obs} = 7.0 \times 10^{-5}$ s$^{-1}$
(c) $k_{obs} = 1.1 \times 10^{-4}$ s$^{-1}$
(d) $k_{obs} = 3.1 \times 10^{-4}$ s$^{-1}$
\[ \ln \left( \frac{k}{T} \right) \] vs. \[ \frac{1}{T} \text{ (K}^{-1}) \] for (a) and (b)
Scheme 2. Proposed pathway for oxidative addition of Si–H bonds under thermal conditions.

128x119mm (600 x 600 DPI)