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

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S Supporting Information

ABSTRACT: The rhodium dicarbonyl {PhB(Ox^{Me₂})₂Im^{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 $PhSiD_3$ revealing $k_H/k_D \sim 1$. The reverse reaction, reductive elimination of Si-H from $\{PhB(Ox^{Me_2})_2Im^{Mes}\}RhH(SiH_2R)CO$ (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⁻¹K⁻¹ (for $1 \neq 2$). The rate laws and activation parameters for oxidative addition ($\Delta H^{\ddagger} = 11 \pm 1 \text{ kcal·mol}^{-1}$ and $\Delta S^{\ddagger} = 11 \pm 1 \text{ kcal·mol}^{-1}$ and $\Delta S^{\ddagger} = 11 \pm 1 \text{ kcal}^{-1}$ -26 ± 3 cal·mol⁻¹·K⁻¹) and reductive elimination ($\Delta H^{\ddagger} = 17 \pm 1$ kcal·mol⁻¹ and $\Delta S^{\ddagger} = -10 \pm 3$ 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 $\{PhB(Ox^{Me_2})_2Im^{Mes}\}Rh(CO)_2$ 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) 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.

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 silvl species, are invoked in many catalytic reactions including hydroformylation,^{1,2} 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 metalcarbonyl 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 transformations 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(3,5dimethyl-1-pyrazolyl)borate) with C–H or Si–H bonds.^{33–40} For example, Tp*Rh(CO)₂ and Et₃SiH react under photochemical conditions to give Tp*RhH(SiEt₃)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 timeresolved spectroscopic and computational studies of the mechanism of C-H and Si-H bond activation by CpRh-

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





(CO),^{44–47} Cp*Rh(CO),^{37,38,48} TpRh(CO),⁴⁹ Tp*Rh-(CO),^{46,50–53} and Tp*Rh(CNR),⁴⁰ formed via photolytic ligand dissociation, reveal details and lifetimes of the activation process. Interestingly, bidentate and tridentate coordination modes of pyrazolylborate ligands modulate the electronic structure of rhodium to affect C–H bond oxidative cleavage.

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, counter-intuitively, that a strongly σ -donating ligand could accelerate the dissociation of CO from an electron-rich, nucleophilic rhodium species during a thermal oxidative addition reaction.

The trend in electron-donating ability for tridentate, *fac*coordinating ligands in rhodium dicarbonyl compounds, based on CO stretching frequencies, is $Tp < Tp^* < To^M$ ($To^M =$ tris(4,4-dimethyl-2-oxazolinyl)phenylborate, Figure 1);^{54,55} however, $To^M Rh(CO)_2$ 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 To^M with a N-heterocyclic carbene to give the bis(oxazolinyl)(NHC)borate ligand $Tp*Rh(CO)_2$, $To^MRh(CO)_2$, 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 thermal 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.^{33–36}

RESULTS AND DISCUSSION

Synthesis of Rhodium Silyl Compounds. The reaction of 1 and 3 equiv of PhSiH₃ gives 2a over 18 h in benzene at room temperature in 94% isolated yield.⁵⁷ Similarly, 1 and primary alkylsilanes ($R = C_6H_{13}$, $C_{12}H_{25}$) or arylsilanes (R = p-MeC₆H₄, p-MeOC₆H₄) react to give {PhB(Ox^{Me₂})₂Im^{Mes}}-RhH(SiH₂R)CO ($R = C_6H_{13}$ (2b), $C_{12}H_{25}$ (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 $PhSiH_3$ under equivalent conditions affords **2a** quantitatively after 6 h.

In the solid-state structure of 2d (Figure 2), the Rh1–N1 interatomic distance *trans* to the hydride is shorter by 0.05 Å



Figure 2. Thermal ellipsoid plot of ${PhB(Ox^{Me_2})_2Im^{Me_3}}RhH-(SiH_2C_6H_4Me)CO (2d)$ 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).

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 interatomic distance *trans* to H are consistent across the solid-state structures of $2a^{57}$ and 2b (see Figure S17). In contrast, the reaction of {PhB- $(Ox^{Me_2})_2Im^{Mes}$ }Ir(CO)₂ and benzene, which occurs under photochemical conditions, results in CO *trans* to an oxazoline and the phenyl *trans* to the NHC.⁵⁷ 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*- $MeC_6H_4SiH_3$ or *p*-MeOC₆H₄SiH₃, by performing the reactions at 60 °C, result in organosilane redistribution to give (p- $MeC_6H_4)_2SiH_2$ or $(p-MeOC_6H_4)_2SiH_2$. 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 Ph_2SiH_2 or R_2SiH_2 at 60 °C, instead giving the desired rhodium silyl hydride product selectively.

Kinetic Studies of Oxidative Addition. Initial kinetic studies, in which concentrations of $PhSiH_3$ and 1 were monitored by ¹H 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 influence the rate.

A unimolecular decomposition via reductive elimination of the rhodium silvl 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 PhSiH₃ 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, reproducible kinetic measurements on 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 $PhB(Ox^{Me_2})_2Im^{Mes}H$ as a side product under conditions with higher CO pressures or high temperature (>60 °C). In contrast, the reaction produces only 1 and PhSiH₃ 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 1 and PhSiH₃ 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 2a. Subsequent kinetic experiments monitored the absorption at 385.5 nm. While photolysis of 1 in benzene affords the cyclometalated $\{\kappa^4$ -PhB(Ox^{Me₂})₂Im^{Mes} CH₂}RhH-(CO) resulting from photolytic CO dissociation followed by CH bond oxidative addition of a mesityl methyl,⁵⁷ that process was not observed (from absorption of the UV light) in the spectrophotometer. That is, a series of UV-vis spectra for 1 acquired under otherwise equivalent conditions, but without PhSiH₃, were all identical to the first spectrum.

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 [PhSiH₃], the final concentration of 1 approaches zero (Figure 4). Nonlinear least-squares fits were superior for



Figure 3. Electronic absorption spectra of 1 ($[1]_{ini} = 2.7 \times 10^{-4}$ M) during its reaction with PhSiH₃ (1.1×10^{-3} M) at room temperature in benzene acquired at 15 min intervals. PhSiH₃ does not absorb at >250 nm.



Figure 4. Plots of [1] vs time in its reaction with PhSiH₃ in benzene at 296 K, monitored at 385.5 nm, with [PhSiH₃] = (a) 4.0, (b) 5.8, (c) 10.0, and (d) 25.5 mM. Nonlinear least-squares regression fits to exponential decay curves $[Rh]_t = [Rh]_{ini} e^{-kt}$ confirm first-order dependence.

experiments with higher concentrations of PhSiH₃, while some deviation was observed at longer reaction times with lower [PhSiH₃]_{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 nonzero initial CO concentrations). Thus, the initial portion of the time course approximates the reaction as irreversible under conditions where [CO]_{ini} = 0 M.

Plots of k_{obs} vs [PhSiH₃] provide a forward rate constant k^{app} (given in Figure S21, constrained by the approximation that the rate of reductive elimination is negligible at $[CO]_{ini} = 0$ M). In addition, a plot of log[PhSiH₃] vs log(k_{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 $\Delta H^{\ddagger H-app} = 11 \pm 1$

Table 1. Second-Order Rate Constants k_1^{app} from Pseudo-First-Order Kinetic Studies^{*a*}

temp. (K)	$k_{\rm H}^{\rm app} {\rm M}^{-1} {\rm s}^{-1} (\times 10^{-2})$	$k_{\rm D}^{\rm app} {\rm M}^{-1} {\rm s}^{-1} (\times 10^{-2})$	$k_{ m H}/k_{ m D}$
296.0	1.1 ± 0.1	1.1 ^b	1
297.4	1.2 ^b	1.3 ± 0.1	0.9
308.3	2.0 ± 0.1	2.3 ± 0.1	0.9 ± 0.1
312.3	2.9 ± 0.3	3.0 ± 0.1	1.0 ± 0.1
316.8	3.7 ± 0.1	3.7 ± 0.3	0.99 ± 0.02
322.3	4.2 ± 0.4	5.0 ± 0.1	0.9 ± 0.1
k_1^{app} is t	he rate constant for	the forward, oxidative	addition of

 $\kappa_1^{1/1}$ is the rate constant for the forward, oxidative addition of PhSiH₃ to 1, determined at [CO]_{ini} = 0. ^bCalculated from corresponding Eyring plots.

kcal·mol⁻¹ and $\Delta S^{\pm \text{H-app}} = -30 \pm 3 \text{ cal·mol}^{-1}\text{K}^{-1}$ (Figure S24). For comparison, the ΔS^{\pm} for oxidative addition of Si–H bonds in tertiary silanes to photolytically generated CpMn(CO)₂ range from -6 to -10 cal·mol⁻¹K⁻¹;⁵⁸ however, these values vary considerably with the cyclopentadiene-based ancillary ligand.⁵⁹

The same approach provides the second-order rate constants for the addition of 1 and PhSiD₃. The activation parameters, determined from an Eyring plot, are $\Delta H^{\pm D-app} = 10 \pm 1$ kcal·mol⁻¹ and $\Delta S^{\pm D-app} = -34 \pm 4$ cal·mol⁻¹K⁻¹. These two sets of values are experimentally indistinguishable, thus $k_{\rm H}/k_{\rm D} \sim 1$ for all accessible reaction temperatures.

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).⁶⁰ Under otherwise equivalent conditions, the reaction shows an apparent decrease in rate and a nonzero final concentration of 1 (Figure 5).



Figure 5. Plots of [1] vs time for its reaction with PhSiH₃ (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. $[CO]_{ini} = 7.3 \text{ mM}, [1]_{ini} = 0.2 \text{ mM}, [PhSiH_3]_{ini} = 52.0 \text{ mM}.$

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 $(k_e = k_1 + k_{-1})$.⁶¹ 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).

$$k_{e} = k_{1} [PhSiH_{3}]_{e} [\mathbf{1}]_{e} \left\{ \frac{1}{[PhSiH_{3}]_{e}} + \frac{1}{[\mathbf{1}]_{e}} \right\}$$
$$+ k_{-1} [CO]_{e} \times [\mathbf{2a}]_{e} \left\{ \frac{1}{[CO]_{e}} + \frac{1}{[\mathbf{2a}]_{e}} \right\}$$
(1)

Under high [PhSiH₃] and [CO] (flooding conditions), eq 1 simplifies into eq 2, where the observed rate constant k_e depends on both [PhSiH₃]_e and [CO]_e (which are defined by their initial concentrations). The forward and reverse rate constants are related to the equilibrium constant $K_e = k_1/k_{-1}$.

$$k_{\rm e} = k_1 [{\rm PhSiH}_3]_{\rm e} + k_{-1} [{\rm CO}]_{\rm e} = k_1 [{\rm PhSiH}_3]_{\rm e} + \frac{k_1}{K_{\rm e}} [{\rm CO}]_{\rm e}$$
(2)

To determine K_e , 1 (0.1–0.2 mM) and PhSiH₃ (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 $\Delta H^\circ = -5.5 \pm 0.2$ kcal/mol and $\Delta S^\circ = -16 \pm 1$ cal·mol⁻¹K⁻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 PhSiH₃ and excess CO (7.3 mM). Nonlinear least-squares regression of the data to eq 3 provides $k_{\rm e}$.

$$[\mathbf{1}] = [\mathbf{1}]_{e} + ([\mathbf{1}]_{0} - [\mathbf{1}]_{e})e^{-k_{e}t}$$
(3)

The rate constants k_1 and k_{-1} are determined using eq 2 and k_e , K_{ev} [PhSiH₃]_e and [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 $M^{-1} \text{ s}^{-1}$ (calculated from the Eyring equation and van't Hoff plot for a reaction occurring at 296 K) and the k^{app} (0.012 $M^{-1} \text{ s}^{-1}$, measured experimentally at 296 K) are in good agreement, indicating that the approximate rate constant at [CO]_{ini} = 0 is a reasonable estimate of k_1 .

The activation parameters for oxidative addition of 1 and PhSiH₃ are determined to be $\Delta H^{\ddagger} = 11 \pm 1 \text{ kcal·mol}^{-1}$ 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^{app} in which the reverse direction is neglected at $[CO]_{ini} = 0$. The second-order rate law indicates that 1 and PhSiH₃ 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 ratecontrolling step occurs. The reverse reaction also features a negative entropy of activation ($\Delta H^{\ddagger} = 17 \pm 1 \text{ kcal·mol}^{-1}$ and $\Delta S^{\ddagger} = -10 \pm 3 \text{ cal·mol}^{-1}\text{K}^{-1}$). 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 COfree). 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



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

least on the NMR time scale), and its ¹H 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][CO]). These results, and the principle of microscopic reversibility, indicate that the composition of the transition state for forward and reverse processes is [{PhB(Ox^{Me₂})₂Im^{Mes}}Rh(CO)₂·PhSiH₃]. Thus, the reverse pathway involves coordination of CO to 2a as a first step.

Rates and Equilibrium Constants for Organosilane Addition. The equilibrium constant $K_{e^{j}}$ 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 the corresponding reaction of 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 constant between alkylsilanes and arylsilanes results from the difference in forward rate constant. Note that only two of the three variables $(K_{e}, k_{1}, \text{ and } k_{-1})$ 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.

Comparison of the forward and reverse rate constants between reaction of arylsilanes and alkylsilanes as well as the rate laws and activation parameters for PhSiH₃ oxidative addition and reductive elimination provide considerable insight into the

Table 2. K_{e} , k_{1} , and k_{-}	1 for Reaction	of 1 and RSiH	Measured	at 297 °	°C
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RSiH ₃ / 2	K _e	$k_1 (M^{-1} s^{-1}) (\times 10^{-2})$	$k_{-1} (M^{-1} s^{-1}) (\times 10^{-2})$
<i>n</i> -hexylsilane/ 2b	0.53 ± 0.01	0.23 ± 0.01	0.43 ± 0.01
<i>n</i> -dodecylsilane/ 2 c	0.48 ± 0.01	0.25 ± 0.02	0.53 ± 0.05
phenylsilane ^{<i>a</i>} /2a	2.8 ± 0.3	1.25	0.49
<i>p</i> -methoxyphenylsilane/ 2e	2.1 ± 0.1	1.34 ± 0.02	0.64 ± 0.01
<i>p</i> -tolylsilane/2d	4.5 ± 0.1	1.4 ± 0.1	0.32 ± 0.02
Values for PhSiH ₂ were determined from	Evring and van't Hoff plot	5.	

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

Scheme 2. Proposed Pathway for Oxidative Addition of Si-H Bonds under Thermal Conditions



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, ΔS^{\ddagger} is negative $(-10 \pm 3 \text{ cal})$ $mol^{-1}K^{-1}$), which is consistent with increased order in the transition state. Loss of the H-SiH₂R group during or prior to the rate-limiting step would result in a positive entropy term. Note that ΔS for the overall reductive elimination of PhSiH₃ from 2a is positive, suggesting that PhSiH₃ 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 ratedetermining 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

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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 κ^2 -Tp*RhL or κ^3 -Tp*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 (ΔS^{\ddagger} = -26 ± 3 cal·mol⁻¹·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 $5 \times$ greater with arylsilanes than alkylsilanes, indicating that the relative energy of the starting material vs that of the rate-determining transition 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 energy differences between 2 and the ratelimiting transition for reductive elimination are similar for all the silvl species.

In contrast, we note that $k_{\rm H}/k_{\rm D}$ 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.⁶² 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 canceling 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. We also find that CO dissociation from a low-valent metal complex is not a necessary prerequisite for oxidative addition of nonpolar substrates. The presence of coordinating groups, either as part of polar substrates, ancillary ligands, or as σ -complexes, 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. [Rh(μ -Cl)(CO)₂]₂,⁶³ {PhB(Ox^{Me2})₂Im^{Mes}}-Rh(CO)₂ (1), {PhB(Ox^{Me2})₂Im^{Mes}}RhH(SiH₂Ph)CO,⁵⁷ and *p*methoxyphenylsilane were synthesized according to the literature procedures.⁶⁴ Phenylsilane, *n*-hexylsilane, *n*-dodecylsilane, and *p*tolylsilane were synthesized by reducing corresponding trichlorosilanes with LiAlH₄. PhSiD₃ was synthesized from PhSiCl₃ and LiAlD₄. Potassium benzyl was synthesized by reacting potassium *tert*-butoxide with *n*-BuLi in toluene.⁶⁵

¹H, ¹³C{¹H}, ¹¹B, and ¹⁵N spectra were collected on Bruker Avance III 600 or AVNEO 400 MHz NMR spectrometers. NMR signals (¹H, ¹³C, and ¹⁵N) were assigned based on COSY, HMQC, and HMBC experiments. ¹⁵N chemical shifts were determined by ¹H–¹⁵N HMBC experiments. ¹⁵N chemical shifts were initially referenced to NH₃ and recalibrated to the CH₃NO₂ 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.

 ${PhB(Ox^{Me_2})_2 Im^{Mes}}RhH(SiH_2C_6H_{13})CO$ (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 $\{PhB(Ox^{Me_2})_2Im^{Mes}\}RhH(SiH_2C_6H_{13})CO$ (88 mg, 0.123 mmol, 78%). ¹H NMR (benzene- d_{6} , 600 MHz): δ 8.40 (d, ${}^{3}J_{HH} = 7.8$ Hz, 2 H, o-BC₆H₅), 7.54 (t, ${}^{3}J_{HH} = 7.8$ Hz, 2 H, m-BC₆H₅), 7.39 (t, ${}^{3}J_{HH} = 7.3$ Hz, 1 H, p-BC₆H₅), 6.83 (s, 1 H, m- $C_6H_2Me_3$), 6.78 (s, 1 H, m- $C_6H_2Me_3$), 6.53 (d, ${}^3J_{HH}$ = 1.6 Hz, 1 H, $N_2C_3H_2Mes$), 5.94 (d, ${}^{3}J_{HH}$ = 1.6 Hz, 1 H, $N_2C_3H_2Mes$), 4.91 (t, ${}^{3}J_{HH}$ = 6.8 Hz, ${}^{1}J_{\text{SiH}}$ = 168 Hz, 1 H, SiH), 4.43 (t, ${}^{3}J_{\text{HH}}$ = 6.8 Hz, ${}^{1}J_{\text{SiH}}$ = 180 Hz, 1 H, SiH), 3.60 (m, 3 H, CNCMe₂CH₂O), 3.36 (d, ${}^{2}J_{HH} = 8.3$ Hz, 1 H, CNCMe₂CH₂O), 2.23 (s, 3 H, p-C₆H₂Me₃), 2.09 (s, 3 H, o- $C_6H_2Me_3$), 2.02 (s, 3 H, $o-C_6H_2Me_3$), 1.55 (br, 2 H, SiCH₂CH₂), 1.33-1.40 (br, 6 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), 0.95 (t, ${}^{3}J_{HH} = 7$ Hz, 3 H, CH₂CH₃), 0.41 (m, 1 H, SiH₂CH₂), -0.12 (m, 1 H, SiH₂CH₂), -13.70 (dd, ${}^{1}J_{RhH} = 22.4$ Hz, ${}^{3}J_{HH} = 1.5$ Hz, 1 H, RhH). ¹³C{¹H} NMR (benzene- d_6 , 150 MHz): δ 195.05 (d, ¹ J_{RhC} = 51.9 Hz, 2C-N₂C₃H₂Mes), 179.24 (d, ${}^{1}J_{RhC}$ = 40.5 Hz, CO), 138.49 (br, ipso-BC₆H₅), 137.58 (p-C₆H₂Me₃), 136.70 (o-C₆H₂Me₃), 136.64 $(o-BC_6H_5)$, 136.36 $(o-C_6H_2Me_3)$, 129.58 $(m-C_6H_2Me_3)$, 129.51 $(m-C_6H_2Me_3)$, 129.51 $(m-C_6H_2Me_3)$ C₆H₂Me₃), 127.50 (*m*-BC₆H₅), 127.03 (*p*-BC₆H₅), 124.60 (4,5C- $N_2C_3H_2Mes$), 121.12 (4,5C- $N_2C_3H_2Mes$), 80.40 (CNCMe₂CH₂O), 80.39 (CNCMe₂CH₂O), 68.79 (CNCMe₂CH₂O), 66.64 $(CNCMe_2CH_2O)$, 33.64 (CH_2) , 32.32 (CH_2) , 29.88 (CNCMe₂CH₂O), 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 (CH_3) . $^{15}N{^1H}$ NMR (benzene- d_6 , 61 MHz): δ -160 (CNCMe₂CH₂O trans to Si), -172 (CNCMe₂CH₂O trans to H), -188 ($N_2C_3H_2Mes$). ¹¹B NMR (benzene- d_6 , 192 MHz): δ -9.7. ²⁹Si{¹H} NMR (benzene- d_6 , 119 MHz): δ –19.2. IR (KBr, cm⁻¹): 3135, 3043, 2959, 2923, 2733, 2359, 2279, 2041, 2011, 1652, 1595, 1458, 1275, 967, 820. Anal. calcd for C₃₅H₅₀BN₄O₃RhSi: C, 58.66; H, 7.03; N, 7.82. Found: C, 58.68; H, 7.21; N, 7.61

 ${PhB(Ox^{Me_2})_2 Im^{Me_3}}RhH(SiH_2C_{12}H_{25})CO$ (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 in a white solid which was washed with pentane to give pure { $PhB(Ox^{Me_2})_2Im^{Mes}$ }RhH(SiH₂C₁₂H₂₅)CO(65 mg, 0.08 mmol, 50%). ¹H NMR(benzene- d_{6} , 600 MHz): δ 8.41 (d, ³ J_{HH} = 7.8 Hz, 2 H, o-BC₆H₅), 7.54 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 2 H, m-BC₆H₅), 7.4 (t, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 1 \text{ H}, p\text{-BC}_{6}\text{H}_{5}), 6.84 \text{ (s, 1 H, } m\text{-C}_{6}\text{H}_{2}\text{Me}_{3}), 6.80 \text{ (s, 1 H)}$ H, m-C₆ H_2 Me₃), 6.54 (d, ${}^{3}J_{HH}$ = 1.6 Hz, 1 H, N₂C₃ H_2 Mes), 5.94 (d, ${}^{3}J_{\text{HH}} = 1.8 \text{ Hz}, 1 \text{ H}, \text{ N}_{2}\text{C}_{3}H_{2}\text{Mes}), 4.26 \text{ (t, } {}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, {}^{1}J_{\text{SiH}} = 160$ Hz, 1 H, SiH), 3.81 (t, ${}^{3}J_{HH} = 6.6$ Hz, ${}^{1}J_{SiH} = 180$ Hz, 1 H, SiH), $3.64-3.57(m, 3 H, CNCMe_2CH_2O)$, $3.35 (d, {}^2J_{HH} = 8.4 Hz$, 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, ${}^{3}J_{HH}$ = 7.2 Hz, 3 H, CH₂CH₃), 0.44 (m, 1 H, SiH₂CH₂), -0.07 (m, 1 H, SiH₂CH₂), -13.68 (dd, ${}^{1}J_{RhH} = 22.2$ Hz, ${}^{3}J_{HH} = 1.8$ Hz, 1 H, RhH). ¹³C{¹H} NMR (benzene- d_6 , 150 MHz): δ 195.06 (d, ${}^{1}J_{RhC}$ = 52.8 Hz, 2C-N₂C₃H₂Mes), 185.79 (br, CNCMe₂CH₂O), 179.23 (d, ${}^{1}J_{RhC}$ = 40.7 Hz, CO), 138.49 (*p*-C₆H₂Me₃), 137.60 (*ipso*- $C_6H_2Me_3$), 136.70 ($o-C_6H_2Me_3$), 136.66 ($o-C_6H_2Me_3$), 136.39 ($o-C_6H_2Me_3$), 136.30 ($o-C_6H_2Me_3$)) ($o-C_6H_2Me_3$), 136.30 ($o-C_6H_2Me_3$)) ($o-C_6H_2Me_3$)) ($o-C_6H_2Me_3$) BC_6H_5 , 129.59 (m- $C_6H_2Me_3$), 129.52 (m- $C_6H_2Me_3$) 127.51 (m-BC₆H₅), 127.04 (p-BC₆H₅), 124.61 (4,5-CN₂C₃H₂Mes), 121.12 (4,5- $CN_2C_3H_2Mes$), 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- $C_6H_2Me_3$, 18.02 (CH₂), 18.01 (CH₂), 14.41 (CH₃). ¹⁵N{¹H} NMR (benzene- d_{6} , 61 MHz): δ -160 (CNCMe₂CH₂O trans to Si), -172 (CNCMe₂CH₂O trans to H), -175 (N₂C₃H₁₂Mes), -188 $(N_2C_3H_2Mes)$. ¹¹B NMR (benzene- d_{67} 192 MHz): δ -9.7. ²⁹Si{¹H} NMR (benzene- d_{6} , 119 MHz): δ –18.9. IR (KBr, cm⁻¹): 2957, 2922, 2852, 2149, 2044, 2013, 1595, 1463, 1365, 1316, 1183, 1160, 968.

 ${PhB(Ox^{Me_2})_{2}Im^{Mes}}RhH(SiH_2C_6H_4Me)CO$ (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(Ox^{Me2})₂Im^{Mes}}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- d_{6} , 600 MHz): δ 8.43 (d, ${}^{3}J_{\text{HH}}$ = 7.8 Hz, 2 H, o-BC₆H₅), 7.56 (t, ${}^{3}J_{\text{HH}}$ = 7.2 Hz, 2 H, m-BC₆H₅), 7.52 (d, ${}^{3}J_{\text{HH}}$ = 7.8 Hz, 2 H, o-C₆H₄Me), 7.41 (t, ${}^{3}J_{\rm HH}$ = 7.2 Hz, 1 H, p-BC₆H₅), 6.95 (d, ${}^{3}J_{\rm HH}$ = 7.8 Hz, 2 H, m- C_6H_4Me), 6.55 (d, ${}^{3}J_{HH}$ = 1.8 Hz, 1 H, N₂C₃H₂Mes), 6.54 (s, 1 H, m- $C_6H_2Me_3$), 6.41 (s, 1 H, m- $C_6H_2Me_3$), 5.94 (d, ${}^3J_{HH}$ = 1.8 Hz, 1 H, $N_2C_3H_2Mes$), 4.91 (t, ${}^2J_{HH}$ = 4.8 Hz, ${}^1J_{SiH}$ = 170 Hz, 1 H, SiH), 4.45 $(d, {}^{2}J_{HH} = 4.8 \text{ Hz}, {}^{1}J_{SiH} = 186 \text{ Hz}, 1 \text{ H}, \text{ SiH}), 3.57-3.65 (m, 3 \text{ H}, 3.57)$ $CNCMe_2CH_2O$), 3.37 (d, ${}^2J_{HH}$ = 8.4 Hz, 1 H, $CNCMe_2CH_2O$), 2.18 (s, 3 H, p-C₆H₂Me₃), 2.03 (s, 3 H, o-C₆H₂Me₃), 2.00 (s, 3 H, o- $C_6H_2Me_3$, 1.90 (s, 3 H, p- C_6H_4Me), 1.16 (3 H, CNCM e_2CH_2O), 1.16 (3 H, CNCMe₂CH₂O), 1.08 (3 H, CNCMe₂CH₂O), 1.02 (3 H, $CNCMe_2CH_2O$, -13.22 (dd, ${}^{1}J_{RhH}$ = 21.6 Hz, ${}^{3}J_{HH}$ = 2.4 Hz, 1 H, RhH). ${}^{13}C{}^{1}H$ NMR(benzene- d_6 , 150 MHz): δ 194.48 (d, ${}^{1}J_{RhC}$ = 52.9 Hz, 2C-N₂C₃H₂Mes), 178.40 (d, ${}^{1}J_{RhC}$ = 40.8 Hz, CO), 138.29 $(ipso-SiC_6H_4Me)$, 136.96 $(p-C_6H_2Me_3)$, 136.68 $(ipso-C_6H_2Me_3)$, 136.67 (o-BC₆H₅), 129.34 (o-SiC₆H₄Me), 129.31 (m-SiC₆H₄Me), 127.54 $(m-C_6H_2Me_3)$, 127.07 $(m-C_6H_2Me_3)$, 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- $C_6H_2Me_3$, 21.04 (p-SiC₆H₄Me), 19.49 (o-C₆H₂Me₃), 19.08 (o- $C_6H_2Me_3$). ¹⁵N{¹H} NMR (benzene- d_6 , 61 MHz): δ -161

(CNCMe₂CH₂O *trans* to Si), -172, (CNCMe₂CH₂O *trans* to H), -174 (N₂C₃H₂Mes), -188 (N₂C₃H₂Mes). ¹¹B NMR (benzene-*d_o*, 192 MHz): δ -9.8. IR (KBr, cm⁻¹): 2962, 2923, 2855, 2279, 2104, 2016, 1917, 1652, 1605.

 ${PhB(Ox^{Me_2})_2Im^{Me_3}}RhH(SiH_2C_6H_4OMe)CO$ (**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 $\{PhB(Ox^{Me_2})_2Im^{Mes}\}RhH$ -(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- d_6 , 600 MHz): δ 8.42 (d, ${}^{3}J_{HH}$ = 7.2 Hz, 2 H, o-BC₆H₅), 7.55 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 2 H, m-BC₆H₅), 7.50 (d, ${}^{3}J_{HH} = 8.4$ Hz, 2 H, o-C₆H₅OMe), 7.40 (t, ${}^{3}J_{HH} = 7.2$ Hz, 1 H, p-BC₆H₅), 6.74 (d, ${}^{3}J_{HH} = 8.4$ Hz, 2 H, m- C_6H_5OMe), 6.57–6.54 (2 H, m- $C_6H_2Me_3$ + $N_2C_3H_2Mes$), 6.43 (s, 1 H, m-C₆H₂Me₃), 5.94 (d, ${}^{3}J_{HH}$ = 1.2 Hz, 1 H, N₂C₃H₂Mes), 4.93 (d, ${}^{2}J_{\text{HH}} = 6 \text{ Hz}, {}^{1}J_{\text{SiH}} = 172 \text{ Hz}, 1 \text{ H}, \text{SiH}), 4.45 (t, {}^{2}J_{\text{HH}} = 6 \text{ Hz}, {}^{1}J_{\text{SiH}} =$ 180 Hz, 1 H, SiH), 3.65-3.57 (m, 3 H, CNCMe₂CH₂O), 3.39 (s, 3 H, C₆H₆OMe), 3.38 (d, ${}^{3}J_{HH}$ = 8.4 Hz, 1 H, CNCMe₂CH₂O), 2.02 (s, 3 H, $p-C_6H_2Me_3$), 2.01 (s, 3 H, $o-C_6H_2Me_3$), 1.96 (s, 3 H, o-C_6H_2Me_3), 1.96 (s, 3 H, o-C_6H_2Me_3), 1.96 (s, 3 $C_6H_2Me_3$), 1.17 (s, 3 H, CNC Me_2CH_2O), 1.16 (s, 3 H, CNC Me_2CH_2O), 1.09 (s, 3 H, CNC Me_2CH_2O), 1.09 (s, 3 H, CNC Me_2CH_2O), 1.04 (s, 3 H, $CNCMe_2CH_2O$, -13.24 (dd, ${}^{1}J_{RhH} = 18$ Hz, ${}^{3}J_{HH} = 2$ Hz, 1 H, RhH). ¹³C{¹H} NMR (benzene- d_6 , 150 MHz): δ 194.23 (d, ¹ J_{RhC} = 76.5 Hz, 2C-N₂C₃H₂Mes), 178.12 (d, ${}^{1}J_{RhC}$ = 60 Hz, CO), 80.11 (CNCMe₂CH₂O), 79.95 (CNCMe₂CH₂O), 68.42 (CNCMe₂CH₂O), 66.33 (CNCMe₂CH₂O), 54.50 (p-C₆H₄OMe), 28.01 (CNCMe₂CH₂O), 27.72 (CNCMe₂CH₂O), 27.41 (CNCMe₂CH₂O), 26.65 (CNCM e_2 CH $_2$ O), 20.70 (p-C $_6$ H $_2$ M e_3), 19.12 (o-C $_6$ H $_2$ M e_3), 18.74 (o-C₆H₂Me₃). ¹⁵N NMR (benzene- d_{6y} 61 MHz): δ -161 (CNCMe₂CH₂O trans to Si), -172 (CNCMe₂CH₂O trans to H), -176 (N₂C₃H₂Mes), -188 (N₂C₃H₂Mes). 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 preheated 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] vs time were fit using nonlinear least-squares regression to an exponential decay curve based on the equation $[1] = [1]_{0} e^{-kt}$ for the analysis.

UV–vis Kinetic Experiments. The experiments consisted of the following: pseudo-irreversible conditions, CO-saturated approach to equilibrium, and equilibrium constant measurements.

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 μ L 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] vs time was fit to the equation $[1] = [1]_{e}e^{-kt}$ using nonlinear least-squares regression analysis, to determine pseudo first-order rate constants. Subsequent experiments varied [PhSiH₃], a plot of k_{obs} vs [PhSiH₃] was linear, and the slope provided the second-order rate constant k_1^{app} . This procedure, performed over a range of temperatures from 296 to 322.3 K, provided the temperature-dependent second-order rate constants for an Eyring plot.

CO-Saturated Approach to Equilibrium. Solutions 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 airfree syringe technique. These samples were used for the kinetic study, following the procedure above, to determine k_e by nonlinear 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.

Equilibrium Constant Measurement. Reactions of 1 and PhSiH₃ (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 [PhSiH₃]_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 ΔH and ΔS .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03425.

Spectra for compounds **2b–e** and kinetics data (PDF)

Accession Codes

CCDC 1879286–1879287 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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