# **ORGANOMETALLICS**



# Mechanistic Study of Alkene Hydrosilylation Catalyzed by a $\beta$ -Dialdiminate Cobalt(I) Complex

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**ABSTRACT:** Alkene hydrosilylation is a large-scale process that typically uses precious-metal catalysts. A new generation of highly selective catalysts is based on inexpensive metals, which may have a high-spin electronic configuration and thus may follow novel mechanistic pathways. Here, we describe mechanistic studies on a high-spin cobalt(I) catalyst that performs rapid and regioselective alkene hydrosilylation. Using 1-hexene and PhSiH<sub>3</sub> as substrates, we elucidate features of the rate law, test for free radical intermediates with radical clock substrates, and use deuterium substitution to provide mechanistic insight. The resting state has PhSiH<sub>3</sub> bound  $\eta^6$  through the phenyl group and evolves over the course of the reaction from a substrate-bound form to a product-bound form. This complicates analysis by variable time normalization analysis (VTNA) because the dependence of the rate on [PhSiH<sub>3</sub>] is not constant throughout the reaction. Despite this challenge, the accumulated results are consistent with



initial oxidative addition of PhSiH<sub>3</sub>, followed by alkene binding, and then insertion through the Chalk–Harrod or modified Chalk– Harrod mechanism to form the hydrosilylation product. Though the catalyst has a paramagnetic metal center, none of the data implicate radicals participating in the mechanism, and a conventional electron-pair mechanism is most consistent.

# INTRODUCTION

Alkene hydrosilylation has received sustained attention from chemists for over 50 years because it leads to many useful products containing C–Si bonds.<sup>1</sup> Early alkene hydrosilylation catalysts used Co as the central metal,<sup>2</sup> though Co catalysts have been supplanted by more robust Pt catalysts that remain the most used catalysts in practice.<sup>1,3</sup> However, growing attention to sustainable chemistry has sparked a renaissance of Co-based hydrosilylation catalysts.<sup>4</sup> Since Deng and co-workers reported an NHC silyl Co catalyst in 2013,<sup>5</sup> numerous Co alkene hydrosilylation catalysts have been reported in the literature in the past few years.<sup>6</sup>

Although many Co catalysts are now known, mechanistic studies on these catalysts are few. Studies on the mechanism of Co-catalyzed alkene hydrosilylation catalysts date back to classic studies by Chalk and Harrod in 1965 (Scheme 1a).7 Later, Wrighton and co-workers' work on Co carbonyl<sup>8</sup> and Cp\*Fe carbonyl catalysts9 along with Brookhart and Grant's work on Cp\*Co(phosphite) catalysts<sup>10</sup> established the modified Chalk-Harrod mechanism (Scheme 1b). The carbonyl, cyclopentadienyl, and phosphite ligands in these systems led to low-spin electronic configurations. Many of the more recent cobalt catalysts,<sup>6</sup> however, have weak-field ligands and low-coordinate environments, and it is possible that a high-spin electronic configuration could alter the mechanism. In particular, given the likelihood of weaker homolytic M-C bond strengths in high-spin complexes, one must consider the metal complex acting as an initiator that generates transient

radicals.<sup>11</sup> Such radical species are known to effect alkene hydrosilylation through a radical chain mechanism (Scheme 1c).<sup>1c,12</sup> Thus, it is important to pursue mechanistic studies on the catalytic reactions catalyzed by the new generation of weak-field, high-spin catalysts, in order to understand the fundamental aspects of their reactivity and selectivity. Such insight will provide the underpinning for the next generation of inexpensive alkene hydrosilylation catalysts by enabling the rational control of catalyst reactivity and selectivity. We are aware of no other base-metal-catalyzed alkene hydrosilylation systems for which the potential radical mechanisms have been queried.<sup>13</sup>

# RESULTS

Identification of the Catalyst Resting State. As we previously reported, compound 1 (Scheme 2) is an active catalyst for the conversion of 1-hexene to hexylphenylsilane (PhSiH<sub>2</sub>hex) with high yield and regioselectivity at room temperature.<sup>6p</sup> Also, addition of 1 drop of Hg does not affect the regioselectivity and conversion, suggesting that the active

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# Scheme 1. Potential Mechanisms for Hydrosilylation

(a) Chalk-Harrod Mechanism



Scheme 2. Catalytic Alkene Hydrosilylation by 1

R<sub>2</sub>S



species is likely to be homogeneous.<sup>14</sup> Compound 1 has been crystallographically characterized, which reveals  $\eta^6$  binding of the benzene to cobalt.<sup>6p</sup> Magnetic susceptibility studies show that it has a high-spin cobalt(I) center (S = 1), and it gives a characteristic set of paramagnetically shifted peaks in its <sup>1</sup>H NMR spectrum from  $\delta$  +20 to -91 ppm that are the same for solutions in  $C_6D_6$  or  $C_6D_{12}$ . A broad peak at  $\delta$  11 ppm integrates as six protons, corresponding to the  $\eta^6$ -benzene ligand, and in C<sub>6</sub>D<sub>6</sub> this peak disappears over the course of several hours due to exchange with C6D6. In an NMR-scale catalytic hydrosilylation of 1-hexene by PhSiH<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> at room temperature, the only paramagnetically shifted peaks observed by <sup>1</sup>H NMR spectroscopy after 5 min (58% conversion) corresponded to those of 1, suggesting that this benzene complex is the resting state in benzene solution. When catalytic hydrosilylation is performed in noncoordinating

 $C_6D_{12}$  using 1 as the catalyst, the Co speciation was again evaluated by looking at the paramagnetically shifted peaks after 5 min (95% conversion). In the  ${}^{1}$ H NMR spectrum, the peaks shift slightly, suggesting the formation of a new paramagnetic species (Figure S1). Because the chemical shifts of paramagnetic compounds are very sensitive to the geometry at the metal,<sup>15</sup> we surmise that the environment of the high-spin cobalt(I) center in the new paramagnetic species is similar to that in 1.

When excess  $PhSiH_2hex$  is added to 1 in  $C_6D_{12}$ , a solution with a spectrum identical with that of the resting state in  $C_6 D_{12}$ is generated within 5 min. This observation indicates that the resting state of the catalytic reaction is the hydrosilylation product bound to cobalt in an  $\eta^6$  mode (2, Chart 1). Addition

#### Chart 1. Possible Catalyst Resting States



of excess PhSiH<sub>3</sub> gave a similar spectrum within 5 min as well, which we attribute to 3. It is interesting that exchange of benzene with benzene- $d_6$  is slower (several hours). This steric dependence is not expected for an associative substitution mechanism, and the rate dependence on the entering group is inconsistent with a dissociative mechanism. The rate of exchange of  $C_6H_6$  for toluene- $d_8$  is slower, like that for  $C_6H_6$ with C<sub>6</sub>D<sub>6</sub>. We infer that the mechanism of arene exchange is influenced by the presence of a Si-H bond. This may be rationalized through an associative mechanism (Scheme 3) in

Scheme 3. Possible C<sub>6</sub>H<sub>6</sub> and Silane Ligand Exchange Mechanism



which the coordinated benzene is rapidly isomerizing between the ground-state  $\eta^6$  binding and other modes such as  $\eta^4$  or  $\eta^2$  $(\eta^2$  binding is shown in Scheme 3), one of which can accommodate binding of the silane Si–H bond.<sup>16</sup> This binding mode is apparently transient, because the NMR chemical shifts indicate a product that has  $\eta^6$  binding. However, in this binding mode the metal would be more exposed toward binding of a second arene, explaining the substrate dependence on the arene exchange rate.

As judged by <sup>1</sup>H NMR spectroscopy, 2 is the only cobalt compound in solutions that results from adding 5 equiv of PhSiH<sub>2</sub>hex to 1, but all crystallization attempts from mixtures containing 2 were unsuccessful. Fortunately, a mixture of 1 and 100 equiv of  $PhSiH_3$  in pentane yielded crystals of 3 (Chart 1). The solid-state structure of 3 (Figure 1) shows PhSiH<sub>3</sub> bound to Co in an  $\eta^6$  binding mode, as expected from the NMR



Figure 1. ORTEP diagram of 3 with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond metrics (bond lengths in Å and angles in deg): Co-N1, 2.008(2); Co-N2, 2.022(2); N1-Co-N2, 90.92(9); C1-Si, 1.867(3); Co-C1, 2.207(3); Co-C2, 2.201(3); Co-C3, 2.203(3); Co-C4, 2.184(3); Co-C5, 2.244(3); Co-C6, 2.251(3).

evidence presented above. The range of Co-C<sub>benzene</sub> distances in 3 (2.184(3)-2.251(3) Å) is comparable to that in 1 (2.200(3)-2.254(3) Å), indicating minimal distortion of the benzene ring. Moreover, the distances between the cobalt and the Si-bound H atoms are all longer than 1.8 Å,  $^{16a}$  indicating that there is no bonding interaction between the Si-H bond and the Co in the solid state. Unfortunately, the solution characterization of 3 was complicated by its instability in solution. When isolated 3 was dissolved in  $C_6D_{12}$ , the <sup>1</sup>H NMR spectrum after 5 min at room temperature showed not only 3 but also a new paramagnetic species along with unidentifiable diamagnetic species. In contrast, in the presence of 100 equiv of PhSiH<sub>3</sub>, 3 decomposes more slowly over the course of 1 day at room temperature in solution, presumably into NMR-silent species. Though we were not able to characterize the nature of these decomposition processes, it is notable that degradation in the presence of PhSiH<sub>3</sub> is much slower than catalytic hydrosilylation, and thus it was not considered further.

Addition of excess benzene (10 equiv) and 1-hexene (70 equiv) to 1 in  $C_6D_{12}$  gave a <sup>1</sup>H NMR spectrum indicative of a second, new paramagnetic species with distinct peaks at 273, 26, 14, and -35 ppm. This new species was assigned as the cobalt(1)  $\eta^2$ -hexene complex 4 (Figure S8). The observation of only four resonances suggests that other peaks of 4 may be masked by the large peaks from the excess 1-hexene. All crystallization attempts yielded crystals of 1, which is explained by the small equilibrium constant for binding hexene (see below).

Despite the inability to isolate 2 and 4, we took advantage of their stability in the presence of excess alkene/arene to measure equilibrium constants for the conversion of 1 to 2/3/4 at 10 °C using <sup>1</sup>H NMR spectroscopy. For these experiments, the equilibrium mixtures were generated by adding an excess mixture of benzene and the target ligand (PhSiH<sub>2</sub>hex, PhSiH<sub>3</sub>, or 1-hexene) to 1 in C<sub>6</sub>D<sub>12</sub> (Figure 2). By using a large excess of the organic ligands, we can safely assume that the final ratio of the free ligands is the same as the initial ratio, and that  $K_{eq} = \left(\frac{[\text{benzene}]}{[\text{ligand}]}\right)_{\text{initial}} \left(\frac{[2,3,4]}{[1]}\right)_{\text{observed}}$ . We used several different ratios of benzene to target ligand, in order to verify the accuracy of the derived values. The

order to verify the accuracy of the derived values. The formation of measurable amounts of 4 required an excess of 1hexene that was larger than the ratio used in the other equilibria, indicating a smaller equilibrium constant for formation of a higher-energy hexene complex. In these



Figure 2.  $K_{eq}$  and  $\Delta G$  values relating the potential intermediates to the benzene complex 1.

experiments, both 1 and the new cobalt(I) complexes were observed as separate peaks, indicating that the cobalt(I) complexes are in slow exchange on the NMR time scale; however, the equilibria are established within 5 min. Exchange on the time scale of seconds to minutes at 10 °C is consistent with this step being kinetically competent during catalysis at room temperature (see kinetics below). The derived  $\Delta G$  values (Figure 2) show that the formation of 2 and 3 from 1 is roughly thermoneutral while the formation of 4 is more uphill.

In order to monitor changes in the catalyst resting state during catalysis, hydrosilylation of 1-hexene with PhSiH<sub>3</sub> was repeated in  $C_6D_{12}$  at 10 °C and was monitored by <sup>1</sup>H NMR spectroscopy with a  $Cp_2Ni$  internal standard. After 5 min, **3** is the catalyst resting state but **2** eventually becomes the resting state over time (Figure 3). Moreover, the sum of the



Figure 3. Catalyst speciation monitored by <sup>1</sup>H NMR spectroscopy.

concentrations of the Co species remains constant throughout the reaction, indicating that there is no significant catalyst decomposition under these catalytic conditions. Thus, the catalyst resting state shifts, depending on the predominant arene in solution. No alkene-bound Co species are observed during catalysis, and this is consistent with the less favorable equilibrium constants leading to 4.

Tests for Radical Intermediates. It was important to consider the potential for radical formation during the mechanism, since one anticipates weak Co-C bonds in this system, and some hydrosilylation reactions proceed through radical mechanisms.<sup>17</sup> Thus, we tested for the intermediacy of

transient radicals using two types of "radical clock" substrates.<sup>18</sup> In order to consider the radicals that could potentially be formed at both internal and terminal positions of the alkene, we used both **5** and **6**, shown in Scheme 4.

Scheme 4. Testing for Radical Intermediates: (a) Ring-Opening Substrate; (b) Ring-Closing Substrate



possible radical rearrangement:





possible radical rearrangement:



Formation of a terminal radical in the hydrosilylation of **5** would lead to the cyclopropylmethyl radical **5R**, which is known to undergo rapid ring opening  $(k_{298} = 1.8 \times 10^{11} \text{ s}^{-1})$ .<sup>19</sup> Formation of an internal radical in the hydrosilylation of **6** would be expected to lead to *exo* cyclization of the pentenylmethyl radical **6R** to form a methylcyclopentane derivative  $(k_{298} = 1.0 \times 10^5 \text{ s}^{-1}$  for the closely related hept-1-ene-6-radical).<sup>20</sup>

Hydrosilylation of each radical clock substrate in  $C_6D_6$  gave the expected hydrosilylation product, which was isolated in greater than 80% yield in each case. The purified products were characterized using NMR spectroscopy (Supporting Information). No ring-opening or ring-closing products were detected.<sup>21</sup> This suggests that the catalytic reactions do not have free radicals as intermediates. We cannot rule out the possibility that the mechanism includes radicals with lifetimes shorter than the rearrangement rates of these clocks, but it is notable that these experiments provided no evidence toward radical mechanisms.

**Deuterium Labeling Studies.** Use of PhSiD<sub>3</sub> in place of PhSiH<sub>3</sub> in the catalytic reaction gave hexylphenylsilane- $d_3$ , in which the product was enriched in deuterium only at the Si and at the  $\beta$ -carbon, as judged by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy (Scheme 5a).

In another experiment, equal amounts of  $PhSiH_3$  and  $PhSiD_3$  were treated with 1 at room temperature for 1 h in  $C_6D_6$  (Scheme 5b). Interestingly, <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy showed that the phenylsilane isotopologues had converted to a mixture of  $PhSiH_3$ ,  $PhSiH_2D$ ,  $PhSiHD_2$ , and  $PhSiD_3$  (Supporting Information). This exchange did not occur in the absence of 1. The most likely mechanism for this isotopic exchange is through reversible oxidative addition of

Scheme 5. (a, b) Labeling Studies Using PhSiD<sub>3</sub> and (c) Mechanism Consistent with These Experiments



Si-H bonds to give the unobserved cobalt(III) silyl hydride 8, which can then exchange Co-H and Si-D groups either through a second reversible oxidative addition (accessing a formally Co<sup>V</sup> intermediate)<sup>22</sup> followed by reductive elimination or through reversible  $\sigma$ -bond metathesis (Scheme 5c). In either case, these experiments suggest that oxidative addition of the silane Si-H bond gives a species that maintains an available coordination site, which could alternatively bind 1-hexene in the productive hydrosilylation reaction. None of these intermediates can be observed, because they are higher in energy than the observed  $\eta^6$ -arene complexes, but their intermediacy is implied by the isotopic scrambling.

**Examining the Rate Law.** The reaction orders in the rate law of the reaction were initially addressed by monitoring the reaction at 10 °C using <sup>1</sup>H NMR spectroscopy (focusing on the disappearance and appearance of Si-H resonances) and analyzing the data graphically using variable time normalization analysis (VTNA).<sup>23</sup> VTNA suggested the rate law rate =  $k[Co][hexene][PhSiH_3]^n$ , where the rate dependence on phenylsilane (n) was less than 1 and could be fit adequately to 0.5-order dependence (Figure 4, as well as additional plots in the Supporting Information). The rate dependences on [Co] and [hexene] were reliably first order. The noninteger order dependence on [PhSiH<sub>3</sub>] is confusing, but the order did not approach 0 or 1 when [PhSiH<sub>3</sub>] was varied over the feasible concentration range from 63 to 380 mM (Figure S30, Supporting Information). Since VTNA is not well adapted to determining complicated rate laws,<sup>23</sup> we surmised that the rate law might not be a simple product of concentrations.

In order to determine whether the apparent noninteger order dependence on  $[PhSiH_3]$  results from catalyst decomposition, we used a method popularized within reaction progress kinetic analysis.<sup>24</sup> Two hydrosilylation reactions were set up in parallel, with the first starting as usual and the second reaction starting with lower concentrations of starting materials and added product (independently prepared), in order to mimic the concentrations of reactants and products in a partially complete reaction, but one in which the catalyst did not have time to undergo decomposition. The two reaction profiles (Figure S32) overlay well, suggesting that the catalyst does not degrade significantly during catalysis and arguing against catalyst decomposition as an explanation for the noninteger order.

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Figure 4. VTNA of the kinetics data: (a) rate order of catalyst; (b) rate order of 1-hexene; (c) rate order of PhSiH<sub>3</sub>.

We considered next the possibility that the arene exchange between 2 and 3 is responsible for the noninteger order. This was tested by flooding the reaction with the product PhSiH<sub>2</sub>hex ([PhSiH<sub>2</sub>hex] = 320 mM) in order to force the resting state toward 2 from the beginning of the reaction (Figure S33). Initial rates (up to 10% conversion) under these conditions had a first-order dependence on [PhSiH<sub>3</sub>] (Figure \$34). Moreover, variation of [PhSiH<sub>3</sub>] from 63 to 380 mM gave initial rates that reached a plateau at higher [PhSiH<sub>3</sub>], where the concentration of PhSiH<sub>3</sub> surpassed that of PhSiH<sub>2</sub>hex (Figure S31). Thus, at high [PhSiH<sub>3</sub>], where 3 is the resting state, there is saturation to a zero-order dependence on [PhSiH<sub>3</sub>] because PhSiH<sub>3</sub> is already bound to Co in the resting state. However, when [PhSiH<sub>3</sub>] is lower than  $[PhSiH_2hex]$  and the resting state is 2, there is a first-order dependence on [PhSiH<sub>3</sub>] because the PhSiH<sub>3</sub> substrate must displace PhSiH<sub>2</sub>hex from 2. In other words, the equilibrium between 2 and 3 changes during catalysis, resulting in a changing rate dependence on [PhSiH<sub>3</sub>] that is poorly fit using VTNA. In support of this idea, when we monitored the catalytic reaction using <sup>1</sup>H NMR spectroscopy (Figure 3), comparable amounts of both 2 and 3 were observed (ratio of 45:55) after 5 min (16% conversion).<sup>25</sup>

**Kinetic Isotope Effect.** The kinetic isotope effect (KIE) was measured through parallel reactions by performing two hydrosilylation reactions with either  $PhSiH_3$  or  $PhSiD_3$  under identical conditions and measuring their initial rates by NMR spectroscopy. The H/D KIE thus obtained at 10 °C is  $1.55 \pm 0.35$  (Supporting Information, section 6E), showing a normal kinetic isotope effect that is large enough to be a primary KIE. This value is difficult to interpret because it can be a composite of the KIE for the turnover-frequency-determining transition state (TDTS) and any equilibrium isotope effect (EIE) between this TS and the resting state.<sup>26</sup> Additionally, it is likely to be influenced by the reversibility of Si-H cleavage.<sup>27</sup>

For example, depending on the magnitude of the EIE for oxidative addition of  $PhSiH_3$  to 3,<sup>28</sup> the KIE value could vary greatly. Therefore, the measured KIE does not illuminate the mechanism in our system.

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# DISCUSSION

In this work, we address the mechanism of hydrosilylation of 1hexene by  $PhSiH_3$  using a cobalt(I) species. The evidence above can be most easily accommodated by the mechanism in Scheme 6. Reversible arene exchange of benzene with  $PhSiH_3$ gives 3, which can then form 8 via reversible oxidative addition of the Si-H bond, which is thermodynamically unfavorable but kinetically facile. The observed isotopic exchange between  $PhSiH_3$  and  $PhSiD_3$  is explained by the interaction of  $PhSiH_3/$  $PhSiD_3$  with 8. When 8 coordinates the alkene, it generates a 16-electron cobalt(III) alkene silyl hydride complex that could undergo C-H bond formation (Chalk-Harrod mechanism, red) or C-Si bond formation (modified Chalk-Harrod mechanism, blue) on the way to the product. Finally, reductive elimination releases the product, and the cycle is closed by arene exchange between 2 and 3.

As indicated above, the experimental rate law is not straightforward to express, because the resting state changes from 3 (when little product has been formed) to 2 (when the phenylsilane has been depleted by hydrosilylation) over the course of the reaction. Despite this difficulty, the rate has a first-order dependence on [Co] and [alkene]. The rate law is inconsistent with the TDTS being step A, since this would give a zero-order dependence on [alkene]. However, our kinetic data do not distinguish among B–D as the TDTS.

Distinguishing between the Chalk–Harrod mechanism (C1/D1) and the modified Chalk–Harrod mechanism (C2/D2) in our system has been not been possible. Brookhart and Grant's mechanistic study on a Cp\*Co(phosphite) catalyst<sup>10</sup> proposed the modified Chalk–Harrod mechanism on the basis

Scheme 6. Proposed Mechanism Consistent with Experimental Data



of their ability to identify the product from Co–Si alkene insertion by NMR spectroscopy. In our system, the only observed Co species are 1–3, and the analogue to their observed intermediate is apparently higher in energy in our system. Second, the lack of deuterium scrambling during hydrosilylation of 1-hexene with PhSiD<sub>3</sub> (Scheme 5b) suggests that step C1 (if followed) is irreversible and there is no competitive  $\beta$ -hydride elimination. Testing the reversibility of the silyl insertion step C2 was not feasible. However, the literature examples of  $\beta$ -silyl elimination<sup>9,29</sup> suggest that it is feasible for step C2 to be reversible.

Ruling out Alternative Mechanisms. An alternative mechanism (Scheme 7a) involving a vinylsilane intermediate, which is a variation of the modified Chalk-Harrod mechanism, can be ruled out on the basis of the exclusive deuteration at the  $\beta$  carbon in the hydrosilylation of 1-hexene with PhSiD<sub>3</sub>. Deuteration at the  $\alpha$  carbon would occur as well if the vinylsilane intermediate had been hydrogenated to give the hydrosilvlation product. Moreover, vinylsilane has not been observed in the current system, although the absence of formation of vinylsilane rules out neither this mechanism nor the modified Chalk-Harrod mechanism. Another possible mechanism is the silylene mechanism (Scheme 7b).<sup>16b,30</sup> In the silvlene mechanism, the cobalt silvlene complex 9 would be formed from 8 followed by insertion of alkene into the terminal Si-H to give 10. Then 1,2-hydride migration would yield 11, and the cycle can be closed by reductive elimination. One key feature of the silylene mechanism is that tertiary silanes cannot give the hydrosilylation product. However, 1 was previously shown to catalyze the hydrosilylation of 1hexene with (EtO)<sub>3</sub>SiH, suggesting that the silvlene mechanism is unlikely.<sup>31</sup> Moreover, all silylene complexes known to catalyze alkene hydrosilylation are cationic, while the cobalt catalyst described here is neutral.<sup>30b</sup>

Scheme 7. Alternative Mechanisms: (a) Mechanism Involving a Vinylsilane Intermediate; (b) Silylene Mechanism



### CONCLUSIONS

A number of mechanistic tests have been applied to the hydrosilylation of hexene and phenylsilane, as catalyzed by a  $\beta$ dialdiminate-supported cobalt(I) arene catalyst. In an initial communication, we showed that this reaction works with a number of alkenes and also with trimethoxysilane.<sup>6p</sup> Because we focus on a single substrate here, it is possible that the mechanistic results described here do not hold for the other substrates (particularly trimethoxysilane, which lacks the phenyl group). In this study, the catalyst resting state in cyclohexane solution or in neat substrate is a cobalt(I) complex with silane bound through the phenyl group of either the substrate or product. Kinetic studies show that the rate is first order in both catalyst and alkene, while the order in silane depends on the speciation of the catalyst moving from substrate-bound to product-bound during the catalytic reaction. Isotopic exchange between PhSiH<sub>3</sub> and PhSiD<sub>3</sub> in the absence of alkene suggests that the cobalt(I) complex can undergo Si-H oxidative addition prior to alkene binding. Oxidative addition of the silane and then alkene binding can then add the hydride and silvl groups to the alkene, and our data do not illuminate the order of these bond formations (distinguishing between the Chalk-Harrod mechanism and the modified Chalk-Harrod mechanism). The use of multiple radical clock substrates showed no evidence for radical intermediates. We conclude that standard two-electron mechanisms are feasible in this system, despite the anticipation that unpaired electrons on the metal ("metalloradicals") might lead to different mechanisms with high-spin catalysts. This is

reminiscent of our earlier mechanistic studies on  $\beta$ -hydride elimination with  $\beta$ -diketiminate complexes of iron and cobalt,<sup>32</sup> where the mechanisms have the same elementary steps that are familiar from low-spin complexes. Thus, high-spin electronic configurations and weak ligand fields are not a hindrance to well-controlled organometallic catalysis.

# EXPERIMENTAL SECTION

General Considerations. All manipulations except the syntheses of alkene substrates and PhSiD<sub>2</sub> were performed in an argon-filled MBraun glovebox maintained below 1 ppm of O<sub>2</sub> and H<sub>2</sub>O. Syntheses of alkene substrates and PhSiD<sub>3</sub> were performed under an N<sub>2</sub> atmosphere using standard Schlenk techniques. Glassware was ovendried at 150 °C for at least 12 h prior to use. Celite and molecular sieves were dried above 200 °C under vacuum for at least 12 h. Pentane, hexane, benzene, toluene, and diethyl ether were purified by passage through activated alumina and Q5 columns from Glass Contour Co., under argon. Cyclohexane was dried over CaH2, vacuum-transferred, and stored over 4 Å molecular sieves. THF was distilled under argon from a potassium benzophenone ketyl still. Benzene- $d_6$  was dried over activated alumina and stored over 4 Å molecular sieves. C<sub>6</sub>D<sub>12</sub> was vacuum-transferred from a solution of potassium benzophenone ketyl and was stored over 4 Å molecular sieves. 1-Hexene and PhSiH<sub>3</sub> were obtained from TCI and used as received after checking their purity by <sup>1</sup>H NMR spectroscopy. 1-Hexene was vacuum-transferred from CaH2, passed through activated alumina, and stored over 4 Å molecular sieves. PhSiH<sub>3</sub> was dried over 4 Å molecular sieves prior to use. The hydrosilylation catalyst 1 and PhSiH<sub>2</sub>hex were prepared by following a previously reported procedure.<sup>6p</sup> PhSiD<sub>3</sub> was synthesized by modifying a known procedure (reduction of PhSiCl<sub>3</sub> was done in tetraglyme instead of THF).<sup>33</sup> Substrates  $5^{34}$  and  $6^{35}$  were synthesized following previously reported procedures. NMR data were collected on Agilent 400 or 500 MHz spectrometers. Chemical shifts in <sup>1</sup>H NMR spectra are referenced to the residual protiated solvent peaks of  $C_6D_5H$  ( $\delta$  7.16 ppm) and  $C_6 D_{11} H$  ( $\delta$  1.38 ppm).

**NMR-Scale Alkene Hydrosilylation.** A 20 mL scintillation vial was charged with the solvent ( $C_6D_6$  or  $C_6D_{12}$ , 0.80 mL), 1 (5.0 mg, 0.011 mmol), PhSiH<sub>3</sub> (0.14 mL, 1.1 mmol), and 1-hexene (0.14 mL, 1.1 mmol). The solution was transferred to a J. Young NMR tube, and a 1,3,5-trimethoxybenzene internal standard capillary was added. The <sup>1</sup>H NMR spectrum was measured periodically, and the product PhSiH<sub>2</sub>hex was identified on the basis of previously reported NMR assignments in  $C_6D_6$ .<sup>6p</sup> PhSiH<sub>2</sub>hex: <sup>1</sup>H NMR (400 MHz,  $C_6D_{12}$ )  $\delta$  7.47–7.51 (m, 2H), 7.19–7.26 (m, 3H), 4.34 (t, 2H, J = 3.6 Hz), 1.42–1.50 (m, 2H), 1.34–1.41 (m, 2H), 1.24–1.32 (m, 4H), 0.86–0.94 (m, 5H) ppm.

Determination of  $K_{eq}$  for Arene/Alkene Exchange. The  $K_{eq}$ measurement of benzene and PhSiH<sub>2</sub>hex exchange is shown as a representative example (other exchange  $K_{eq}$  measurements were performed in the same fashion at a comparable scale). Solid 1 (10.0 mg, 22.6  $\mu$ mol) was suspended in C<sub>6</sub>D<sub>12</sub> (0.53 mL) in a 20 mL scintillation vial. An equimolar solution of benzene (0.32 mL, 3.6 mmol) and PhSiH<sub>2</sub>hex (0.80 mL, 3.6 mmol) was prepared in a separate vial. The benzene/PhSiH<sub>2</sub>hex solution (74 uL, 0.24 mmol of both benzene and PhSiH<sub>2</sub>hex) was added to 1, and the suspension became homogeneous. The resulting solution was transferred to a J. Young NMR tube with a NiCp<sub>2</sub> internal standard capillary, and the <sup>1</sup>H NMR spectrum was recorded at 10 °C. Additional  $C_6H_6$  (7.5  $\mu$ L, 0.084 mmol) was added to the NMR tube, and the <sup>1</sup>H NMR spectrum was recorded at 10 °C. This process was repeated again by adding more benzene (15  $\mu$ L, 0.17 mmol).  $K_{eq}$  was calculated by quantifying the Co species (see the Supporting Information for more details). 2: <sup>1</sup>H NMR (500 MHz,  $C_6D_{12}$ )  $\delta$  21.1 (4H, m-H), -97.8 (1H, dialdiminate ligand backbone) ppm. 4: <sup>1</sup>H NMR (500 MHz,  $C_6D_{12}$ )  $\delta$  273.2 (1H, vinyl H), 25.7. (1H, dialdiminate ligand backbone), 13.7 (4H, m-H), -34.6 (6H, p-H) ppm. Full assignment of 2 was not feasible due to the peaks overlapping with those of 1, and for 4, only the observed paramagnetic peaks were assigned.

**Synthesis of 3.** Solid 1 (34 mg, 0.078 mmol) was suspended in pentane (6.5 mL) in a 20 mL scintillation vial with a stir bar. PhSiH<sub>3</sub> (0.96 mL, 7.8 mmol) was added, and the resulting solution was stirred for 5 min. The solution was filtered through Celite and was stored at -40 °C overnight. Red-orange X-ray diffraction quality crystals (5.5 mg, 15% yield) were obtained. A second crop of crystals (6.1 mg, 17% yield) was grown by leaving the mother liquor for 1 day more at -40 °C to give an overall yield of 32%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub> + drop of PhSiH<sub>3</sub>):  $\delta$  29.3 (3H, Si–H), 20.6 (4H, *m*-H), 16.1 (12H, *o*-H), 15.7 (6H, *p*-H), and -94.6 (1H, dialdiminate ligand backbone) ppm. Peaks corresponding to remaining protons are apparently either broadened or obscured under peaks for free PhSiH<sub>3</sub>. Anal. Calcd for C<sub>27</sub>H<sub>33</sub>N<sub>2</sub>SiCo: C, 68.62; H, 7.04; N, 5.93. Found: C, 68.69; H, 6.91; N, 6.10 (first crop). C, 68.30; H, 6.96; N, 5.78 (second crop).

X-ray Crystallography. Low-temperature diffraction data ( $\omega$ scans) were collected at the Advanced Light Source, Lawrence Berkeley National Laboratory, on a Bruker D8 goniometer coupled to a PHOTON 100 detector with synchrotron radiation ( $\lambda = 0.7749$  Å) for the structure of 3. The data were integrated with the APEX2 software package, and an absorption correction was applied with SADABS.<sup>36</sup> The structure was solved using SHELXT and was refined against  $F^2$  on all data by full-matrix least squares with SHELXL.<sup>37</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exceptions were the Si-bound H14a, H14b, and H14c which were found in the difference map and freely refined. The full numbering scheme of 3 can be found in the full details of the Xray structure determination, which is included as Supporting Information.

Monitoring the Catalyst Resting State. A stock solution of 1 (11 mM) was made by dissolving 1 (20 mg, 0.045 mmol) in  $C_6D_{12}$  (4.0 mL). A J. Young NMR tube was charged with  $C_6D_{12}$  (0.40 mL), PhSiH<sub>3</sub> (28  $\mu$ L, 0.23 mmol), and 1-hexene (28  $\mu$ L, 0.23 mmol), and the resulting solution was frozen in the cold well at -78 °C. Then, an aliquot of the stock solution of 1 (0.10 mL, 1.1  $\mu$ mol of 1) was placed in the J. Young tube, and it was frozen in the cold well as well. The NMR tube was thawed immediately before inserting the sample into the spectrometer. An <sup>1</sup>H NMR spectrum was recorded every 5 min for 8 h. <sup>1</sup>H NMR assignments of the Co species used in the  $K_{eq}$  determination were used.

Hydrosilylation of 2-Phenyl-1-Methylenecyclopropane (5). In a 1 dram vial equipped with a stir bar in an N2 glovebox were placed 1 (200  $\mu$ L of a 12.5 mM C<sub>6</sub>D<sub>6</sub> stock solution, 2.5  $\mu$ mol of 1), PhSiH<sub>3</sub> (125 µL, 1.0 mmol), 5 (63 mg, 0.48 mmol), and C<sub>6</sub>D<sub>6</sub> (175  $\mu$ L). The vial was capped with a resealable valve and then brought out of the glovebox and heated at 80 °C for 8 h. Then, the reaction mixture was exposed to air. Diethyl ether (2.0 mL) was added, and the solution was filtered through a short silica gel pad (1 cm, prewashed with diethyl ether) in a disposable pipet. The filtrate was concentrated under reduced pressure. The hydrosilylation product was isolated via flash chromatography (hexane) as a clear oil (108 mg, 82% yield). Integration of the peaks in the <sup>1</sup>H NMR spectrum, along with COSY, HSQC, and HMBC spectra, identified 5 (see the Supporting Information). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.38 (m, 2H), 7.01–7.14 (m, 8H), 4.42 (m, 2H,  $J_{Si-H}$  = 96.5 Hz), 1.87 (dt, 1H, J = 8, 6 Hz), 0.89–0.97 (m, 1H), 0.69–0.78 (m, 2H), 0.46 (dt, 1H, J = 5, 5 Hz), 0.34–0.42 (m, 1H) ppm. <sup>13</sup>C NMR (125 MHz,  $C_6D_6$ ):  $\delta$ 139.3, 135.6, 132.7, 129.8, 129.6, 128.34, 128.3, 126.1, 22.5, 15.4, 11.4, 9.7 ppm.<sup>2</sup>

**Hydrosilylation of Dimethyl 2,2-Diallylmalonate (6).** The reaction mixture was prepared as above using 1 (200  $\mu$ L of a 25 mM C<sub>6</sub>D<sub>6</sub> stock solution, 5.0  $\mu$ mol of 1), PhSiH<sub>3</sub> (125  $\mu$ L, 1.0 mmol), 6 (106 mg, 0.51 mmol), and C<sub>6</sub>D<sub>6</sub> (75  $\mu$ L). The reaction mixture was brought out of the glovebox and stirred at room temperature for 1 h. Then, the reaction mixture was exposed to air. Diethyl ether (2.0 mL) was added, and the solution was filtered through a short silica gel pad (1 cm, prewashed with diethyl ether) in a disposable pipet. The

filtrate was concentrated under reduced pressure. The hydrosilylation product was isolated via flash chromatography (hexane) as a clear oil (174 mg, 81% yield). Integration of the peaks in the <sup>1</sup>H NMR spectrum was consistent with a symmetric compound with two silane fragments and three sets of methylene protons, clearly indicating no ring closing. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.40–7.45 (m, 4H), 7.12–7.19 (m, 6H), 4.38 (tt, 4H, *J* = 3.5 Hz, *J*<sub>Si-H</sub> = 96 Hz), 3.31 (s, 6H), 2.01–2.06 (m, 4H), 1.35–1.42 (m, 4H), 0.74–0.77 (m, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $C_6D_6$ ):  $\delta$  171.9, 135.6, 132.4, 129.9, 58.1, 51.8, 36.3, 20.3, 10.5 ppm (one aromatic peak overlaps with solvent peaks).

**Hydrosilylation of 1-Hexene with PhSiD<sub>3</sub>.** A 20 mL scintillation vial was charged with 1 (2.7 mg, 6.1 μmol), benzene (0.5 mL), a stir bar, PhSiD<sub>3</sub> (150 μL, 1.2 mmol), and 1-hexene (150 μL, 1.2 mmol). After it was stirred for 2.5 h at room temperature, the reaction mixture was exposed to air and filtered through a short silica gel pad (1 cm) using hexanes (15 mL). The filtrate was concentrated under reduced pressure to give the product as a clear oil (207.6 mg, 87% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.53–7.51 (m, 2H), 7.17 (m, overlapped with NMR solvent), 1.33–1.41 (m, 1H), 1.13–1.28 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.80 (d, *J* = 8.0 Hz, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz,  $C_6D_6$ ):  $\delta$  135.6, 129.8, 128.4 (one peak buried under solvent peak), 32.8, 31.8, 25.0 (t, *J* = 19.3 Hz), 22.9, 14.3, 10.1 ppm. <sup>2</sup>H{<sup>1</sup>H} NMR (500 MHz,  $C_6H_6$ ):  $\delta$  4.51 (2D), 1.34 (1D) ppm.

**Phenylsilane H–D Exchange.** To a solution of PhSiH<sub>3</sub> (62.5  $\mu$ L, 0.50 mmol), PhSiD<sub>3</sub> (62.5  $\mu$ L, 0.50 mmol), and C<sub>6</sub>D<sub>6</sub> (175  $\mu$ L) in a J. Young NMR tube was added 1 (200  $\mu$ L of 12.5 mM C<sub>6</sub>D<sub>6</sub> stock solution, 2.5  $\mu$ mol of 1). The solution was monitored with <sup>1</sup>H NMR spectroscopy for 1 h at room temperature. After 2 days, the <sup>1</sup>H NMR spectrum was recorded, and the volatile materials were vacuum-transferred to another J. Young NMR tube to examine the diamagnetic organic compounds without broadening from Co species. The <sup>1</sup>H NMR and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra showed a mixture of PhSiH<sub>3</sub>, PhSiH<sub>2</sub>D, PhSiHD<sub>2</sub>, and PhSiD<sub>3</sub>. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.36–7.40 (m, 2H), 7.06–7.17 (m, 3H), 4.23 (m, 1.4 H, J<sub>Si-H</sub> = 125 Hz); <sup>29</sup>Si{<sup>1</sup>H} NMR (99.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –59.70 (PhSiH<sub>3</sub>, s), –59.92 (PhSiH<sub>2</sub>D, t, J<sub>Si-D</sub> = 30.6 Hz), –60.13 (PhSiHD<sub>2</sub>, quintet, J<sub>Si-D</sub> = 30.6 Hz), –60.34 (PhSiD<sub>3</sub>, septet, J<sub>Si-D</sub> = 30.5 Hz) ppm.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00241.

Crystallographic details, spectra, and kinetics experiments (PDF)

# Accession Codes

CCDC 1994891 contains 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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#### Notes

The authors declare no competing financial interest.

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