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# <u>Catalytic Olefin Hydrosilations Mediated by</u> <u>Ruthenium η<sup>3</sup>-H<sub>2</sub>Si σ-Complexes of Primary and</u> <u>Secondary Silanes</u>

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Abstract

Unambiguous examples of  $\eta^3$ -H<sub>2</sub>SiH(R) complexes featuring a terminal Si–H bond have been prepared and examined as possible intermediates in olefin hydrosilation. These species were generated by displacement of the secondary silane ligands in  $[PhBP^{Ph}_{3}]RuH[\eta^{3}-H_{2}SiMePh]$  (1b,  $PhBP^{Ph}_{3} = PhB(CH_2PPh_2)_{3})$  by primary silanes RSiH<sub>3</sub> to generate [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiH(R)] (R = Cy, 1d; CH<sub>2</sub>CH<sub>2</sub>Ph, 1e; Trip = 2,4,6-iPr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 1f). Complexes 1d,e were characterized in solution whereas **1f** was isolated and studied in detail. Complex **1b** is not a competent precatalyst for the hydrosilation of 1-hexene with CySiH<sub>3</sub>, whereas comparable conditions gave reasonable yields for the selective, anti-Markovnikov hydrosilations of Cl<sub>3</sub>SiCH<sub>2</sub>CH=CH<sub>2</sub> (89%), pchlorostyrene (73%), and allyl chloride (70%). The <sup>1</sup>H NMR spectrum of **1f** collected at -30 °C displays a downfield signal ( $\delta$  8.26 ppm) for the terminal Si–H bond that suggests electronic similarities between **1f** and cationic silvlene dihydrides  $[Cp^{*}(^{i}Pr_{3}P)Ru(H)_{2}=SiH(R)]^{+}$  that mediate olefin hydrosilations via the direct insertion of the C=C bond into the terminal Si-H bond. However, further mechanistic considerations, including results on the hydrosilation of pchlorostyrene with the secondary silane Et<sub>2</sub>SiH<sub>2</sub> and [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiEt<sub>2</sub>] (**1a**) as catalyst, indicate that an insertion mechanism involving a Ru—H (rather than a Si—H) group is possible. DFT investigations of the hydrosilation of several olefins with CySiH<sub>3</sub> using 1d as a catalyst reveal a preferred pathway involving olefin insertion into a Ru–H bond followed by migration of the resulting alkyl group to the silicon atom of an  $\eta^3$ -H<sub>2</sub>SiH(Cy) ligand. The latter process occurs *via* an unusual transition state in which a Ru—H—Si linkage acts as a pivot point to facilitate an Si—H bond cleavage / Si—C bond formation step that is otherwise similar to those involving the kite-shaped, four-centered transition states of  $\sigma$ -bond metathesis. Direct insertion into the Si—H bond is the next lowest accessible pathway.

Keywords: hydrosilation, silane,  $\sigma$ -complex, silylene, catalysis, mechanism, DFT

## **Introduction**

The catalytic addition of an Si-H bond across a C=C double bond is an important reaction for the formation of C—Si bonded compounds starting from olefins and hydridosilanes (e.g. H—SiR<sub>3</sub>,  $R_3$  = combinations of alkyl, aryl, H, alkoxy, and/or Cl).<sup>1</sup> For example, platinumcatalyzed olefin hydrosilations are used for cross-linking silicone polymers, and these reactions are among the largest scale applications of homogeneous catalysis.<sup>1</sup> In addition, catalytic C—Si bond forming reactions are important for laboratory scale syntheses owing to the utility of silanes in cross coupling reactions,<sup>2</sup> as precursors to alcohols,<sup>3,4</sup> or as directing groups for C—H functionalizations.<sup>4</sup> Considering the numerous applications of hydrosilation reactions, it is important to develop new catalysts that offer wider substrate scope, better selectivity, and/or lower cost than the commonly employed platinum and rhodium catalysts. In this regard, it may be worthwhile to investigate new catalytic cycles that do not rely on oxidative addition and reductive elimination steps that are the basis for the classic Chalk-Harrod and modified Chalk-Harrod mechanisms for platinum- and rhodium-catalyzed olefin hydrosilations.<sup>5</sup> In particular, the utilization of alternative fundamental reaction steps may be essential for developing catalysts based on abundant first-row transition metals or main-group elements,<sup>6</sup> and for hydrosilations of substrates featuring C—X functional groups (X = halide, e.g. allyl chloride) that can compete with Si—H bonds for activation at a transition metal center.<sup>7</sup>

Relevant studies in this laboratory have identified catalytic olefin hydrosilations that feature a different type of fundamental Si—C bond-forming step: insertion of the olefin directly into the Si—H bond of  $L_nM=SiH(R)$  silylene complexes ( $L_nM = [Cp^*(^iPr_3P)RuH_2]^+$  and  $[(PNP)IrH]^+$ , PNP =  $[(2^{-i}Pr_2P-4-Me-C_6H_3)_2N]^-$ ; Scheme 1).<sup>8</sup> For the ruthenium-catalyzed examples, the intermediate silylene complexes possess a substantial degree of  $\{Cp^*(^iPr_3P)Ru[\eta^3-$ 





 $H_2SiH(R)]$ <sup>+</sup> character.<sup>8b</sup> The Ru(II)  $\eta^3$ - $H_2SiH(R)$  and Ru(IV) dihydride silylene bonding descriptions are related *via* a symmetric double Si—H oxidative addition process, and a continuum appears to exist between these structure types (Scheme 1).<sup>9</sup> These observations raise the question of how much Ru(IV) character is needed to promote these hydrosilations.

Notably, electrophilic  $\eta^3$ -H<sub>2</sub>SiRR' complexes of the type [PhBP<sup>Ph</sup>\_3]RuH[ $\eta^3$ -H<sub>2</sub>SiRR'] (RR' = Et<sub>2</sub>, **1a**; MePh, **1b**; Ph<sub>2</sub>, **1c**) lie towards the Ru(II) end of the continuum<sup>9a</sup> and engage in hydrosilation reactions with ketones and isocyanides *via* mechanisms that involve binding of the unsaturated substrate to the electrophilic silicon center.<sup>10</sup> Since these hydrosilations appear to exclusively involve Ru(II) intermediates, it seemed possible that analogous  $\eta^3$ -H<sub>2</sub>SiH(R) complexes might mediate olefin hydrosilations that do not involve redox changes at the metal center. However, initial efforts to prepare  $\eta^3$ -H<sub>2</sub>SiH(Ar) complexes supported by the [PhBP<sup>Ph</sup>\_3]RuH fragment resulted in formation of unusual diruthenium hydridosilicate complexes such as {[PhBP<sup>Ph</sup>\_3]Ru}<sub>2</sub>[ $\mu$ - $\eta^4$ , $\eta^4$ -H<sub>0</sub>Si] (**2**, Scheme 2).<sup>11</sup> Thus, mechanistic relationships between (H)<sub>2</sub>Ru=SiHR and Ru[ $\eta^3$ -H<sub>2</sub>SiH(R)] complexes have been difficult to establish given the lack of definitive examples of the latter type. This contribution describes the successful *in situ* generation of stable [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiH(R)] (R = Cy, **1d**; (CH<sub>2</sub>CH<sub>2</sub>Ph), **1e**) complexes by displacement of PhMeSiH<sub>2</sub> from **1b** with primary alkyl silanes (e.g. CySiH<sub>3</sub>, (PhCH<sub>2</sub>CH<sub>2</sub>)SiH<sub>3</sub>,

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Scheme 2). Complex **1d** was found to be an effective catalyst for the hydrosilation of several olefin substrates with CySiH<sub>3</sub>, including the challenging substrate allyl chloride. A related  $\eta^3$ -H<sub>2</sub>SiH(Trip) complex (Trip = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, **1f**) was isolated and fully characterized to confirm the identity of **1d-f** as unambiguous examples of primary silane  $\eta^3$ -H<sub>2</sub>SiH(R) complexes.

## **Results and Discussion**

Hydrosilations Mediated by [PhBP<sub>3</sub>]RuH( $\eta^3$ -H<sub>2</sub>SiH(Cy)) (1d). Since previous efforts to prepare  $\eta^3$ -H<sub>2</sub>SiH(Ar) complexes were unsuccessful due to competing redistribution of the primary aryl silane to form 2 and diaryl silanes (*i.e.* Ar<sub>2</sub>SiH<sub>2</sub>),<sup>11</sup> it seemed possible that  $\eta^3$ -H<sub>2</sub>SiH(alkyl) complexes might be more stable, since alkyl silanes are less susceptible to redistribution at silicon.<sup>12</sup> Thus, efforts to prepare  $\eta^3$ -H<sub>2</sub>SiH(R) complexes focused on displacement of PhMeSiH<sub>2</sub> from 1b using an excess of a primary alkyl silane. Note that it has previously been demonstrated that secondary silanes readily undergo ligand exchanges that allow

interconversions of **1a-c**, and there does not appear to be a strong preference for binding of one silane over another (*e.g.*, addition of 1 equiv of PhMeSiH<sub>2</sub> to **1c** results in an approximately equal ratio of **1b** to **1c**).<sup>13</sup>

Treatment of **1b** with CySiH<sub>3</sub> (10 equiv in C<sub>6</sub>D<sub>6</sub>) resulted in displacement of PhMeSiH<sub>2</sub> (by <sup>1</sup>H NMR spectroscopy) and formation of a new [PhBP<sup>Ph</sup><sub>3</sub>]Ru species with a <sup>31</sup>P{<sup>1</sup>H} NMR shift (46 ppm) that is similar to those of  $\eta^3$ -H<sub>2</sub>SiRR' complexes **1a-c**.<sup>9a</sup> The new complex (**1d**) is presumed to be the  $\eta^3$ -H<sub>2</sub>SiH(Cy)  $\sigma$ -complex [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiH(Cy)], but the <sup>1</sup>H NMR spectrum displayed a very broad Ru—H resonance ( $\delta$  -5.5 to -8.5) that was not useful for clearly identifying this new species (see below for further discussion).

Notably, complex **1d** was stable for at least 20 h in solution, and this provided the opportunity to investigate this complex (generated *in situ* from **1b** and CySiH<sub>3</sub>) as a possible catalyst for olefin hydrosilation reactions using CySiH<sub>3</sub> as the silane substrate (eq 1). Initial

$$\stackrel{\mathsf{R}}{|} + \operatorname{CySiH}_{3} \xrightarrow{\mathbf{1b} (2.5 - 5 \text{ mol } \%)}_{\begin{array}{c} C_{6} D_{6} \\ 23 \ ^{\circ} C, \ 20 \ h \end{array}} \xrightarrow{\operatorname{SiH}_{2} Cy}_{\mathsf{R}} (1)$$

experiments revealed that **1d** is not an effective catalyst for the hydrosilation of 1-hexene with CySiH<sub>3</sub> after 20 h at 23 °C or at 60 °C (by <sup>1</sup>H NMR spectroscopy in C<sub>6</sub>D<sub>6</sub>, Table 1, entries 1 and 2). Instead, the <sup>1</sup>H NMR spectra of these reaction mixtures displayed several new Ru—H resonances, and thus it appears that **1d** undergoes decomposition in the presence of 1-hexene. However, complex **1d** is an effective precatalyst for hydrosilations of styrene, *p*-chlorostyrene, allyl trichlorosilane, and allyl chloride, with products formed in moderate to good yield after 20 h at 23 °C (Table 1, entries 3 - 9). For each substrate, selective anti-Markovnikov addition is

	Olefin	1b	Time	Yield
	Substrate	(mol %)	(h)	(%) <sup>b</sup>
1	Bu	2.5	20	< 5
2 <sup>c</sup>	Bu	2.5	20	< 5
3	Cl <sub>3</sub> Si	2.5	20	89
4	CI	2.5	20	73
5		2.5	20	56
			48	56
6 <sup>c</sup>	$\langle$	2.5	20	30
7	$\langle \rangle$	5	20	65
8	CI	2.5	20	47
9 <sup>d</sup>	CI~	2.5	20	70

Table 1. Hydrosilation of olefins with CySiH<sub>3</sub> using 1b as a precatalyst (eq 1).<sup>a</sup>

a) 23 °C in C<sub>6</sub>D<sub>6</sub> using 1.1 equiv CySiH<sub>3</sub> b) Yield of anti-Markovnikov hydrosilation product determined by <sup>1</sup>H NMR using a C<sub>6</sub>Me<sub>6</sub> internal standard. c) Heated to 60 °C. d) 5 equiv of CySiH<sub>3</sub>.

clearly indicated by a pseudo-quartet SiH resonance ( ${}^{3}J_{HH} \approx 3.5 \text{ Hz}$ ) that results from 3-bond *J*coupling of the product Si—H hydrogens to the three nearest hydrogens (one methine and two methylene hydrogens). With a 2.5 mol % loading of **1b**, the hydrosilation was most effective for allyl trichlorosilane (Table 1, entry 3) and *p*-chlorostyrene (entry 4), while the yields were only moderate for the hydrosilation of styrene (entry 5) and allyl chloride (entry 8). Notably, allyl trichlorosilane is an uncommon hydrosilation substrate, and the presence of two dissimilar silyl substituents in the product could make Cl<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiH<sub>2</sub>Cy useful as a synthetic building block.

Effective catalysts for the hydrosilation of allyl chloride are uncommon, and the resulting 1-chloro-3-silylpropane products are potentially useful chemical intermediates.<sup>7</sup> Thus, efforts directed at optimizing these hydrosilation reactions were undertaken. Attempts to improve the yields for the hydrosilations of allyl chloride and styrene employed longer reaction times (48 h, entry 5) or higher temperatures (60 °C, entry 6), but were not effective. The use of a sterically

less hindered primary silane substrate, PhCH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>, was also examined. This silane appeared to react with 1b to give  $[PhBP^{Ph}_3]RuH[\eta^3-H_2SiH(CH_2CH_2Ph)]$  (1e, as indicated by a new <sup>31</sup>P{<sup>1</sup>H} NMR resonance at  $\delta$  46 ppm), but resulted in much lower yields of hydrosilation products (by <sup>1</sup>H NMR spectroscopy).<sup>14</sup> The relatively low yields associated with the hydrosilation of styrene may be due to competing decomposition of the  $\eta^3$ -H<sub>2</sub>SiH(Cy) complex 1d, which is the only major ruthenium species initially observed in these reaction mixtures by  ${}^{1}$ H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Continued monitoring of these reactions reveals that complex 1d is converted to several new ruthenium hydride complexes while catalytic activity decreases until no additional turnover is observed after 20 h (Table 1, entry 5). It is worth noting that 1d decomposes more rapidly during the hydrosilation of styrene (nearly full decomposition after 16 h), while 20 % of 1d remains after 20 h for the hydrosilation of the more effective pchlorostyrene substrate. Thus, the effectiveness of catalysis appears to be correlated to the presence of 1d, which is presumably the resting state of the catalytic cycle. However, doubling the loading of **1d** to 5 mol % provided only a modest increase in the yield for the hydrosilation of styrene to 65 %, while 35 % of this alkene substrate remained unconsumed.

The allyl chloride substrate, in contrast, was almost entirely consumed under hydrosilation conditions (95 % conversion by <sup>1</sup>H NMR spectroscopy), and the low yield of product in this case is due to formation of propene (20 - 25 %), propyl chloride (25 - 30 %), and a small amount of another side product that was not identified. Selectivity for the desired hydrosilation product was improved by using an excess of CySiH<sub>3</sub> (5 equiv relative to the alkene substrate), which increased the yield of 1-chloro-3-(CyH<sub>2</sub>Si)-propane to 70 %. This increase in yield appears to result primarily from suppression of the formation of the hydrogenation product propyl chloride, which was not observed by <sup>1</sup>H NMR spectroscopy. Notably, this is the first

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example of an effective hydrosilation of allyl chloride with a primary silane, and the yield is comparable to the best reported yields for the hydrosilation of allyl chloride with any other silanes.<sup>7</sup>

**Characterization of [PhBP3]RuH**( $\eta^3$ -H<sub>2</sub>SiH(Trip)) (1f). In order to study the mechanism of the olefin hydrosilation reactions, efforts were made to confirm the identity of the  $\eta^3$ -H<sub>2</sub>SiH(Cy) complex 1d, which was observed as the catalyst resting state (by <sup>31</sup>P{<sup>1</sup>H} NMR) prior to its decomposition to several unidentified [PhBP<sup>Ph</sup><sub>3</sub>]Ru species. The <sup>1</sup>H NMR spectra for 1d, collected at temperatures between -70 °C to 20 °C, did not exhibit sharp Ru—H or Si—H resonances that might identify this species. Furthermore, efforts to isolate 1d or grow single crystals for X-ray diffraction failed, and thus attention turned to preparation of an analogue that might be easier to identify. It seemed that the broadness of the Ru—H resonance for 1d might be due to rapid exchange on the <sup>1</sup>H NMR timescale of the terminal Si—H hydrogen with the Ru—H—Si and Ru—H positions, and that use of a bulkier silane might slow these exchange processes. Thus, 1b was treated with excess (Trip)SiH<sub>3</sub> (7 equiv in C<sub>6</sub>D<sub>6</sub>), which resulted in displacement of PhMeSiH<sub>2</sub> and formation of **1f** (by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, eq 2).



Complex **1f** was isolated as a yellow powder after treatment of **1b** with  $(Trip)SiH_3$  (5 equiv in toluene), evaporation of solvent, and recrystallization from a fluorobenzene-pentane solvent mixture. Elemental analysis indicated that samples of **1f** prepared in this manner were

slightly impure (Anal. Calcd for **1f**: C, 70.51; H, 6.71; Found: C, 69.84; H, 6.51), and <sup>1</sup>H NMR spectroscopy revealed that the hexahydridosilicate complex **2** was present as a minor impurity (ca. 5 - 10 %). Thus, even the fairly bulky aryl silane (Trip)SiH<sub>3</sub> appears to undergo redistribution mediated by the [PhBP<sup>Ph</sup><sub>3</sub>]RuH fragment. The low solubility and high crystallinity of complex **2** makes this species difficult to separate from samples of other [PhBP<sup>Ph</sup><sub>3</sub>]Ru complexes,<sup>11</sup> but **2** was found to be inactive as a catalyst for alkene hydrosilation, and it does not react appreciably within 2 - 10 days with unsaturated species (e.g. XylNC, CO)<sup>15</sup> that react rapidly (<1 min) with **1a-c**.<sup>10a</sup> Thus, the presence of **2** as a minor impurity in **1f** is unlikely to interfere with the investigation of the reactivity of **1f** with olefins or other unsaturated substrates.

As with **1d**, the room temperature <sup>1</sup>H NMR spectrum of **1f** displays a broad Ru—H resonance ( $\delta$  -6.50 in benzene- $d_6$ ), but the <sup>1</sup>H NMR spectrum of **1f** at -30 °C contains a much sharper Ru—H resonance ( $\delta$  -6.51 ppm in toluene- $d_8$ , Figure 1b), along with a downfield signal for the terminal Si—H bond that is observed as a pseudo-septet ( $\delta$  8.26 ppm,  $J_{\text{HH}} \approx J_{\text{PH}} \approx 5$  Hz, Figure 1a). The <sup>29</sup>Si-filtered <sup>1</sup>H{<sup>31</sup>P} NMR and <sup>29</sup>Si-<sup>1</sup>H{<sup>31</sup>P} HMBC NMR spectra of **1f** (collected at -70 °C, Figure 1c,d) indicated that both the Si—H and Ru—H resonances are coupled to a downfield <sup>29</sup>Si NMR resonance (<sup>29</sup>Si  $\delta$  123 ppm; <sup>1</sup> $J_{\text{SiH}} = 216$  Hz for Si—H;  $J_{\text{SiH}} = 68$  Hz for Ru—H/Ru—H—Si), and these NMR data are consistent with the presence of the  $\eta^3$ -H<sub>2</sub>SiH(Trip) ligand. The identification of **1f** as [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiH(Trip)] was further supported by the FTIR spectrum of **1f** (Nujol mull on NaCl plates), which exhibits two strong, sharp absorptions that correspond to the terminal Si—H (v = 2091 cm<sup>-1</sup>) and Ru—H bonds (v = 1895 cm<sup>-1</sup>). The FTIR spectrum also displays a weaker, broad absorption characteristic of the Ru—H—Si interactions (v = 1628 cm<sup>-1</sup>).<sup>16</sup> Thus, on the FTIR timescale, the terminal Ru—H, terminal Si—H, and bridging Ru—H—Si hydrides of **1f** are distinguished, while on the slower



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**Figure 1.** NMR spectra of **1f** in toluene- $d_8$ . a) Si—H resonance in the <sup>1</sup>H NMR spectra recorded at -30 °C to + 20 °C. b) Ru—H resonance in the <sup>1</sup>H NMR spectra recorded at -30 °C to + 20 °C. c) <sup>29</sup>Si-filtered <sup>1</sup>H{<sup>31</sup>P} NMR spectrum recorded at -70 °C. d) <sup>29</sup>Si-<sup>1</sup>H{<sup>31</sup>P} HMBC NMR spectrum recorded at -70 °C.

<sup>1</sup>H NMR timescale the Ru—H and Ru—H—Si positions were observed as a single Ru—H resonance, even in spectra collected at -70 C. Interestingly, the observation of a single Ru—H resonance in the <sup>1</sup>H NMR spectra implies that there must be an easily accessible exchange process that interconverts the Ru—H and Ru—H—Si positions, but which does not allow exchange of the terminal Si—H bond into these hydride positions (as suggested by the two

pathways of Scheme 3). Notably, this observation provides experimental support for fluxional processes of the type determined by DFT calculations for the Fe—H and Fe—H—Si positions of closely related [PhBP<sup>iPr</sup><sub>3</sub>]FeH( $\eta^3$ -H<sub>2</sub>SiRR') complexes.<sup>9c</sup>

Scheme 3: Possible Hydride Exchange Pathways in [PhBP<sup>Ph</sup><sub>3</sub>]RuH[η<sup>3</sup>-H<sub>2</sub>SiH(Trip)] (1f)



Mechanistic Investigations. The <sup>1</sup>H NMR resonance for the terminal Si—H bond in **1f** ( $\delta$  8.26 ppm at -70 °C in toluene-*d*<sub>8</sub>) is shifted considerably downfield from those typically observed for Si—H bonds ( $\delta$  4.49 ppm for TripSiH<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>).<sup>17</sup> This observation suggests the possibility that the  $\eta^3$ -H<sub>2</sub>SiH(R) complexes may be activated toward direct addition of its terminal Si—H bond to an olefin (Scheme 4), as is observed for [L<sub>n</sub>M=Si(R)H]<sup>+</sup> complexes (Scheme 1) which also exhibit highly downfield Si—H resonances that are indicative of their activated, electrophilic silicon centers.<sup>8b-d</sup> This possibility is further supported by similarities between the olefin hydrosilations catalyzed by [PhBP<sup>Ph</sup><sub>3</sub>]Ru (*vide supra*) and





 $[Cp*({}^{i}Pr_{3}P)Ru]^{+}$  complexes.<sup>8</sup> In particular, both systems exclusively catalyze formation of the anti-Markovnikov hydrosilation product and are more effective with alkyl- vs. aryl- silanes due to competing catalytic redistribution for the latter silanes.<sup>8b-d</sup> Additionally, when PhMeSiH<sub>2</sub> was examined as a substrate for the hydrosilation of *p*-chlorostyrene using **1b** as a catalyst (2.5 mol %), the hydrosilation product was not formed after 24 h at 23 °C (monitored by <sup>1</sup>H NMR spectroscopy), and heating the reactions to 80 °C resulted in decomposition of **1b**. The lack of catalytic activity with PhMeSiH<sub>2</sub> as the silane substrate suggested that the presence of a terminal Si—H bond in **1d** might be important for the olefin hydrosilation reactions catalyzed by this species, just as the terminal Si—H bond in  $[Cp*({}^{i}Pr_{3}P)Ru(H)_{2}=SiH(R)]^{+}$  is necessary for olefin hydrosilations involving these silylene species.<sup>8</sup>

Some differences in reaction rates of  $\eta^3$ -H<sub>2</sub>SiH(R) complexes **1d-e** and hydridosilylene complexes  $[Cp^*(^iPr_3P)Ru(H)_2=SiH(R)]^+$  were noted (Scheme 5). For the latter catalysts, the key steps of the catalytic cycle involve: 1) insertion of the olefin into the terminal Si—H bond to form  $[Cp^*(^iPr_3P)Ru(H)_2=SiRR']^+$  silylene complexes, 2) the elimination of two Si—H bonds from ruthenium to release the secondary silane product, and 3) the activation of two Si—H bonds



Scheme 5: Relative Rates of Si—H Addition vs. Silane Exchange During Hydrosilation

of the primary silane substrate to regenerate  $[Cp^{*}({}^{i}Pr_{3}P)Ru(H)_{2}=SiH(R)]^{+}$ . The first step (olefin insertion into the Si—H bond) occurs very rapidly (< 1 min at 23 °C), while the exchange of the product silane for an equivalent of the RSiH<sub>3</sub> reactant requires heating to 80 °C for appreciable rates (Scheme 5).<sup>8b</sup> Thus, the product/substrate exchange process is rate limiting for catalysis involving  $[Cp^{*}({}^{i}Pr_{3}P)Ru(H)_{2}=SiH(R)]^{+}$ . In contrast, silane-silane exchange reactions involving the  $\eta^{3}$ -H<sub>2</sub>SiRR' complexes **1a-f** occur rapidly (< 5 minutes, Scheme 5), such that complex **1d** was observed as the catalyst resting state during hydrosilations using CySiH<sub>3</sub> (*vide supra*). Thus, with **1d** as a catalyst, the rate limiting step occurs during the hydrosilation steps (i.e. Si—H activation/C—Si and C—H bond formation) of the catalytic cycle, rather than for the silane/product exchange steps.

The differences between the reactivity of **1d** and  $[Cp^{*(i}Pr_{3}P)(H)_{2}Ru=SiH(R)]^{+}$  with olefins might be due to the greater electrophilicity of the  $[Cp^{*(i}Pr_{3}P)Ru]^{+}$  fragment and the higher degree of Si—H activation in its complexes with secondary silanes (Scheme 5). These features would render the silicon center more accessible to reaction with the olefin substrate, while inhibiting elimination of the secondary silane product. The formally zwitterionic complex **1d** would have a less electrophilic ruthenium center that would be weaker at binding and

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activating the silane Si—H bonds. The electrophilic character of the complexes may be more important than the overall degree of Si—H activation since it is known that neutral  $Cp^{*}(^{i}Pr_{3}P)(H)Ru=SiH(R)$  complexes, which have full silylene character, do not exhibit any hydrosilation reactivity with olefins.<sup>8g</sup>

Further investigation of the mechanism of olefin hydrosilation using [PhBP<sup>Ph</sup><sub>3</sub>]RuH( $\eta^3$ -H<sub>2</sub>SiRR') complexes revealed that steric properties of the silane substrate greatly influence the efficacy of these hydrosilation reactions, and this might be a more important factor than the presence of an uncoordinated Si—H bond for these catalysts. When complex **1f** was treated with *p*-chlorostyrene (10 equiv in benzene-*d*<sub>6</sub>), no reaction was observed after 2 h at 23 °C and after 20 h **1f** had decomposed to form several Ru—H species, but the expected hydrosilation product was not observed by <sup>1</sup>H NMR spectroscopy. Furthermore, the relatively small secondary silane Et<sub>2</sub>SiH<sub>2</sub> was found to be an effective substrate for the hydrosilation of *p*-chlorostyrene using **1a** as a catalyst (eq 3). With 5 mol % of **1a**, the anti-Markovnikov hydrosilation product was

$$(3)$$

formed in 60 % yield after heating to 60 °C in benzene- $d_6$  for 20 h (determined by <sup>1</sup>H NMR spectroscopy). Thus, the presence of an uncoordinated Si—H bond in the [PhBP<sup>Ph</sup><sub>3</sub>]RuH( $\eta^3$ -H<sub>2</sub>SiRR') complexes is not essential for all catalytic olefin hydrosilation reactivity. Additionally, complex **1b** was found to catalyze H/D exchange between PhMeSiD<sub>2</sub> and the vinylic C—H bonds of *p*-chlorostyrene (eq 4, 6 turnovers after 20 h at 23 °C), which indicates that alkenes can undergo reversible insertion with the terminal Ru—H bond of the [PhBP<sup>Ph</sup><sub>3</sub>]RuH moiety.



A possible mechanism for olefin hydrosilation with  $Et_2SiH_2$  involves insertion of the olefin into a terminal Ru—H bond to form an alkyl complex, which then engages in Si—H activation and Si—C bond formation (Scheme 6). A similar mechanism is implicated in the catalytic hydrosilation of benzophenone with  $EtMe_2SiH$ , as catalyzed by  $[PhBP^{Ph}_3]Ru$  complexes.<sup>10b</sup> However, for the hydrosilation of carbonyl compounds with  $EtMe_2SiH$ , it was observed that benzene could not be used as a solvent since it rapidly traps the reactive 14-electron intermediate  $[PhBP^{Ph}_3]Ru$ —H to form  $[PhBP^{Ph}_3]Ru(\eta^5-C_6H_7)$ . Given the efficiency of benzene as a trap for the ruthenium hydride species, it seems that hydrosilations with  $Et_2SiH_2$ , as catalyzed by **1a** must not involve  $[PhBP^{Ph}_3]Ru$ —H as an intermediate (Scheme 6, right). This

## Scheme 6: Comparison of Potential Si—C Bond Forming Steps for Hydrosilations Mediated by [PhBP<sup>Ph</sup><sub>3</sub>]RuH[η<sup>3</sup>-H<sub>2</sub>SiEt<sub>2</sub>] (1c)



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reactive intermediate might be avoided if the Si—C bond forming step of the catalytic cycle involves a  $\sigma$ -bond metathesis process similar to that depicted for degenerate Si—H exchange in path a of Scheme 3. In such a process, an  $\eta^3$ -H<sub>2</sub>SiRR' ligand undergoes a concerted process whereby Si—H bond cleavage and Si—C bond formation occur concurrently, while the second coordinated Si—H bond remains unchanged. As shown in Scheme 6, this would lead to the formation of an  $\eta^2$ -H—SiR<sub>3</sub>  $\sigma$ -complex [PhBP<sup>Ph</sup><sub>3</sub>]RuH( $\eta^2$ -H—SiR<sub>3</sub>), which would protect the new terminal Ru—H bond from reaction with benzene until a new equivalent of the silane displaces the product (in re-formation of **1a**, Scheme 6).<sup>10b</sup> Thus,  $\eta^3$ -H<sub>2</sub>SiRR' ligands may be important in the mechanism for olefin hydrosilation even for [PhBP<sup>Ph</sup><sub>3</sub>]RuH( $\eta^3$ -H<sub>2</sub>SiRR') complexes that do not feature a terminal Si—H bond. The mechanism depicted in Scheme 6 may also be operative with CySiH<sub>3</sub> as a substrate, but the decomposition of **1d** over the course of the reaction prevented more detailed investigations of the kinetics of the hydrosilation reactions.

**Computational Investigations.** Experimental evidence indicates that a number of mechanistic pathways may be viable for hydrosilation reactions involving [PhBP<sup>Ph</sup><sub>3</sub>]RuH( $\eta^3$ -H<sub>2</sub>SiRR') complexes, and these mechanisms include: i) insertion of the alkene into an Ru—H bond followed by Si—C bond forming  $\sigma$ -bond metathesis (Scheme 6), ii) insertion of the alkene into a terminal Si—H bond (Scheme 4), and iii) insertion of the alkene into an Si—H bond that is coordinated to ruthenium (see below, Figure 2, TS<sub>A-D</sub>). DFT calculations were employed to compare the energetic accessibility of these three mechanisms for the hydrosilation of allyl chloride, 1-hexene, styrene, *p*-chlorostyrene, and allyl trichlorosilane by an untruncated model complex **1d-DFT**. The results are presented for the first substrate while those for the other olefins are available in the Supporting Information. Calculations were performed with Gaussian 09<sup>18</sup> using the PBE0 hybrid functional<sup>19</sup> with dispersion corrections,<sup>20</sup> and the Def2-SVP basis

set (BS1)<sup>21</sup> for all atoms, with quasi-relativistic effective core potentials for Ru.<sup>22</sup> Energies were refined by single point calculations using the Def2-TZVPP basis set (BS2)<sup>21</sup> and by accounting for solvent (benzene) effects using the SCM continuum model.<sup>23</sup> Gibbs energies were calculated from harmonic approximation of frequencies. See Supporting Information for additional details.

Geometry optimization of **1d-DFT** located an  $\eta^3$ -H<sub>2</sub>SiH(Cy) structure in which the two bridging hydride ligands have average bond distances (Ru—H = 1.79 Å and Si—H = 1.65 Å) that are longer than those calculated for the terminal Ru—H (1.625 Å) and Si—H (1.486 Å) bonds. The ruthenium coordination geometry is octahedral with bond angles that deviate by < 5° from 90°. Silicon exhibits a tetrahedral geometry with a small compression of the H—Si—H bond angle (102.3°) for the two coordinated Si—H bonds. As expected, this optimized structure for **1d-DFT** is very similar to those of previously characterized for [PhBP<sup>Ph</sup><sub>3</sub>]Ru(H)( $\eta^3$ -H<sub>2</sub>SiRR') complexes.<sup>9a</sup> No ruthenium trihydride structure with a silylene group could be located as a secondary minimum.

The calculations indicated that the lowest energy hydrosilation pathway involves insertion of the alkene into the terminal Ru—H bond of the catalyst (Figure 2) in a mechanistic step similar to a key step in the classic Chalk-Harrod cycle for olefin hydrosilation.<sup>5</sup> The olefin



**Figure 2**. Hydrosilation pathways characterized by DFT calculations. Dotted lines between atoms are used to illustrate weak interactions in intermediates and bonds being formed/broken in transition states.

substrate accesses the ruthenium center *via* the displacement of one of the coordinated Si—H bonds, forming intermediate **A** in a step that is mildly endergonic. The remaining coordinated Si—H bond in **A** is elongated to 1.76 Å from an initial distance of 1.65 Å in **1d-DFT**, indicating that this Ru—H—Si interaction exhibits flexibility to accommodate the conversion between  $\eta^3$ -H<sub>2</sub>Si and  $\eta^2$ -HSi binding modes of the silane. Insertion of the olefin into the Ru—H bond of **A** is predicted to be the rate limiting step, with a Gibbs activation energy ( $\Delta G^{\dagger}_{A-B} = +15.4$  kcal mol<sup>-1</sup>) that is readily accessible at room temperature. The resulting alkyl group, as initially formed (intermediate **B**), features a  $\beta$ -agostic C—H bond that is then displaced from ruthenium by an Si—H bond to provide a new  $\eta^3$ -H<sub>2</sub>SiH(Cy) complex (intermediate **C**). This displacement occurs with essentially no energy cost. Interestingly, the  $\eta^3$ -H<sub>2</sub>SiH(Cy) ligand of **C** facilitates a novel type of  $\sigma$ -bond metathesis that constitutes a low energy ( $\Delta G^{\dagger}_{C-D} = +7.9$  kcal mol<sup>-1</sup>) Si—C bond forming step for this pathway.

At the transition state for the Si—C bond-forming process (**TS**<sub>C-D</sub>, Figure 3), one of the coordinated Si—H bonds is cleaved (1.634 Å at structure **C**, 1.881 Å at **TS**<sub>C-D</sub>, 2.401 Å at **D**) with concomitant formation of the Si—C bond (2.95 Å at **C**, 2.422 Å at **TS**<sub>C-D</sub>, 1.905 Å at **D**), while the other bridging Ru—H—Si interaction is only slightly perturbed. This calculated process is consistent with the Si—C bond forming  $\sigma$ -bond metathesis process proposed in Scheme 6 on the basis of experimental evidence. This unusual transition state is reminiscent of the four-center transitions states that are well known for  $\sigma$ -bond metathesis processes involving Si—H/Si—C interconversions.<sup>24</sup> However, **TS**<sub>C-D</sub> is an interesting example of a transition state in which an additional bridging Ru—H—Si interaction is maintained throughout the Si—H/Si—C interchange.



**Figure 3.** Structure of **TS**<sub>C-D</sub>. Carbon atoms are depicted in dark gray, hydrogen in off-white, ruthenium in turquoise, and silicon in yellow. The Ru, C, Si, and H atoms undergoing bonding changes are depicted as spheres. For clarity, all atoms and bonds that do not participate in the reaction are illustrated as stick (bound to Si) or wireframe (all other atoms) representations.

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In the structure **TS**<sub>C-D</sub> (Figure 3), the silicon center is positioned effectively to interact with the transferring H and C atoms as well as the ruthenium center, but the geometric considerations do not give information on the nature of the various bonds and interactions at this transition state. Further insight into this novel  $\sigma$ -bond metathesis process was provided by an NBO analysis,<sup>25</sup> which revealed that **TS**<sub>C-D</sub> possesses an  $[\eta^2$ -HSiH(Cy)]<sup>+</sup> fragment with a silicon center that engages in highly delocalized Si---H and Si---C interactions. Like all of the intermediates and transition states of this reaction pathway, the ruthenium center of TSc-D possesses three filled 4d orbitals. There is only slight delocalization of one of these lone pairs onto the cationic  $[\eta^2$ -HSiH(Cy)]<sup>+</sup> moiety (92% on Ru and 4.3 % on Si) of **TS**<sub>C-D</sub>, as shown by the NLMO description. Notably, this is the largest delocalization of a ruthenium 4d lone pair that was found for any of the structures on this hydrosilation pathway. Thus, this mechanism facilitates hydrosilation processes using a ruthenium fragment that is reluctant to undergo oxidative addition processes, which might be important for avoiding C-Cl bond activation processes for the allyl chloride substrate. It is worth noting that the  $\eta^3$ -H<sub>2</sub>Si coordination mode of the silane may also contribute to inhibiting side reactions since the two Si—H bonds occupy coordination sites at ruthenium, as in intermediate C, that might otherwise lead to C-Cl bond activation.

Calculations carried out with other olefins (1-hexene, styrene, *p*-chlorostyrene, and allyl trichlorosilane) give similar results with variation in the energies of some transition states by less than 2 kcal mol<sup>-1</sup> relative to the results obtained with the allyl chloride (See Supporting Information). This suggests that the difference in the observed yields does not originate in change of efficiencies in the productive pathway, but in decomposition pathways that depend on the nature of the substrate. These decomposition pathways have not been analyzed by

calculations due to limited experimental information on them. Recent studies on these processes highlight how challenging they can be without experimental guidance.<sup>26</sup>

Both of the other two mechanisms that were examined computationally involve the direct insertion of the substrate C=C bond into an Si—H bond. One of these pathways involves insertion of the olefin into an Si—H bond that is coordinated to ruthenium – a process analogous to the mechanisms implicated for the hydrosilation of isocyanides and ketones by **1a-c**.<sup>10</sup> However, for the hydrosilation of allyl chloride, this type of insertion step was predicted to have a relatively high Gibbs activation energy ( $\Delta G^{\dagger}_{A'\cdot D'} = + 26.3 \text{ kcal mol}^{-1}$ ) that would suggest that it is not on the active pathway. Lastly, the silylene-like mechanism, involving insertion of the substrate into the terminal Si—H bond, has a Gibbs activation energy ( $\Delta G^{\dagger}_{A'\cdot E} = + 20.8 \text{ kcal mol}^{-1}$ ) that would be accessible at 23 °C, but which is still significantly higher than that determined for insertion into the terminal Ru—H bond ( $\Delta G^{\dagger}_{A-B} = + 15.4 \text{ kcal mol}^{-1}$ ). Thus, these calculations favor the mechanism in which the olefin is activated at the ruthenium center, while suggesting that the  $\eta^3$ -H<sub>2</sub>SiH(Cy) ligand would still be reactive enough to promote direct insertion of the olefin into the terminal Si—H bond if a terminal Ru—H bond was unavailable.

An NBO analysis was carried out to understand more deeply why insertion of the olefin into the Ru—H bond is preferable to insertion into the terminal Si-H bond. In **1d-DFT**, the ruthenium-bound terminal hydride carries an NBO charge of -0.09 and the bridged hydrogens have a charge of -0.05. The highest negative charge on hydrogen (-0.15) is carried by that of the terminal Si—H bond. The Ru itself carried a negative charge of -0.96 while the silicon is positively charged (1.19). Since the Si—H bond of the isolated complex **1d-DFT** has the strongest positive charge on Si and the strongest negative charge on the hydrogen, it might be expected that the Si—H bond would be more reactive towards the olefin than the Ru-H group,

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which is not the preference indicated by the relative energies of the transition states  $TS_{A-B}$  and  $TS_{A'-E}$ . Therefore, the charges on the isolated system do not help to understand the preferences indicated by the full energy profiles of possible pathways.

To provide more insight into the reactivity of **1d-DFT** with olefins, the transition states for insertion into the Ru—H and terminal Si—H bonds were analyzed with the second order perturbation and NLMO methods, which quantitatively describe the delocalization of electron density from localized lone pairs and bonds into vacant orbitals of the species involved in the reaction. The values calculated by this analysis, which are very similar for all olefins are given in the Supporting Information (see pages S7-10). The Ru-bonded H is found to be an extremely powerful electron donor to the  $\pi^*_{CC}$  orbital of the olefin, while the corresponding  $\pi$ -bond is a modest donor to the available empty orbitals at Ru. For the insertion into the Si—H bond, Si acts as strong acceptor to the  $\pi$ -bond of the olefin while the Si-bonded-H is a moderate donor. Thus, the insertion into the Ru—H bond is dominated by the electron donating power of the hydride while the insertion into the Si—H bond is more under the control of the electron accepting ability of silicon. The Si—H group is, thus, well suited to react with electron rich olefins if the Ru—H site is not available.

## **Conclusion**

The  $\eta^3$ -H<sub>2</sub>SiH(Ar) complex [PhBP<sup>Ph</sup><sub>3</sub>]RuH[ $\eta^3$ -H<sub>2</sub>SiH(Trip)] (**1f**), the first unambiguous example of a transition metal complex possessing a primary silane bound in the  $\eta^3$ -H<sub>2</sub>SiH(R) coordination mode, has been prepared and characterized. Previously reported, related structures exhibit a bonding pattern that is intermediate between [M]( $\eta^3$ -H<sub>2</sub>SiHR) and (H)<sub>2</sub>[M]=SiH(R) descriptions.<sup>8b</sup> Therefore, the synthesis and characterization of **1f** provides new insight into the

continuum between  $\eta^3$ -silane and silylene dihydride structures, and allows for direct interrogation of the properties of terminal Si–H bonds in the  $\eta^3$ -silane structure type. Notably, the <sup>1</sup>H NMR spectrum of **1f** features a downfield resonance for the terminal Si—H bond, which supports the possibility that this Si—H moiety may be chemically similar to those in M=SiH(R) hydridosilylene complexes with respect to electron deficiency at the silicon center.

Additional examples of  $[PhBP^{Ph}_3]RuH[\eta^3-H_2SiH(R)]$  (R = Cy, 1d; (CH<sub>2</sub>CH<sub>2</sub>Ph), 1e) complexes were prepared *in situ*, and 1d was found to be an effective catalyst for the hydrosilation of olefins, including the challenging substrate allyl chloride. The primary silane CySiH<sub>3</sub> is a significantly more effective substrate than secondary silanes, and this suggests that the terminal Si—H bond of  $\eta^3$ -H<sub>2</sub>SiH(R) complexes may be important for facilitating hydrosilation by a pathway similar to that studied for hydridosilylene complexes.

The  $\eta^3$ -H<sub>2</sub>Si coordination mode may also be important for facilitating a novel type of  $\sigma$ bond metathesis step that is responsible for the key Si—C bond forming step of the catalytic cycle when using Et<sub>2</sub>SiH<sub>2</sub> as a substrate. In particular, the pathway identified by DFT calculations involves a concerted Si—H bond cleavage / Si—C bond formation event that proceeds through a transition state in which a Ru—H—Si interaction serves as a pivot-point for facilitating this exchange. This transition state is similar to the kite-shaped transition state usually described for  $\sigma$ -bond metathesis,<sup>24</sup> except that the  $\eta^3$ -H<sub>2</sub>SiRR' ligand maintains an additional coordinated Si—H bond while the other Ru—H—Si interaction undergoes cleavage at the Si—H bond. The extra Ru—H—Si interaction draws electron density away from silicon, which may facilitate the facile  $\sigma$ -bond metathesis process by stabilizing the five-coordinate geometry around silicon at the transition state. This type of pathway was shown by DFT calculations to be favored for the hydrosilation of allyl chloride, 1-hexene, styrene, *p*-chlorostyrene and allyl trichlorosilane

by **1d**, but these computational investigations suggest that direct insertion of the olefin substrate into the terminal Si—H bond of **1d** is also energetically accessible. An NBO analysis reveals that the preference for insertion in the Ru-H bond is dominated by the electron donating power of the hydride while reaction with the terminal Si-H bond is controlled by the electrophilicity of the Si center. Thus, the unusual  $\eta^3$ -H<sub>2</sub>Si coordination mode of silanes may facilitate catalytic hydrosilation reactions by a variety of pathways that are not possible with more common ligand types such as silyl or  $\eta^2$ -H—SiR<sub>3</sub> ligands.

## **Experimental Details**

**General Considerations**. All manipulations of air sensitive compounds were conducted under a nitrogen atmosphere using standard Schlenk techniques or using a nitrogen atmosphere glovebox. Proteo solvents were dried using a JC Meyer solvent drying system, and  $C_6D_6$  was vacuum transferred from NaK. The secondary silanes  $Et_2SiH_2$  and PhMeSiH<sub>2</sub> were purchased from commercial sources and used as supplied. The primary silanes  $CySiH_3$ , PhCH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>, and (Trip)SiH<sub>3</sub> were prepared by reduction of the corresponding trichlorosilanes with LiAlH<sub>4</sub>.<sup>27</sup> Complexes **1a-c** were prepared as previously reported.<sup>9a</sup>

NMR spectra were recorded on Bruker spectrometers at room temperature unless otherwise noted. Spectra were referenced internally by the residual proton signal relative to tetramethylsilane for <sup>1</sup>H NMR, solvent peaks for <sup>13</sup>C{<sup>1</sup>H} NMR, external 85 % H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P{<sup>1</sup>H} NMR, and tetramethylsilane for <sup>29</sup>Si-<sup>1</sup>H HMBC experiments. Assignments of certain <sup>13</sup>C{<sup>1</sup>H} NMR signals were made on the basis of <sup>1</sup>H-<sup>13</sup>C HSQC NMR data. The  $J_{SiH}$  values for Ru—H—Si resonances were determined by examining satellite signals near the main Ru—H resonance in <sup>1</sup>H{<sup>31</sup>P} NMR spectra or by the Ru—H resonances displayed in <sup>29</sup>Si-filtered

<sup>1</sup>H{<sup>31</sup>P} NMR experiments. Infrared spectra (Nujol mulls, KBr plates) were recorded using a Nicolet 6700 FTIR spectrometer at a resolution of 2 cm<sup>-1</sup>. Hydrosilation products were identified by comparison of multinuclear NMR data (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si-<sup>1</sup>H HMBC NMR) to those previously reported for identical or closely related organosilanes, and by GC-MS. Elemental analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

[**PhBP**<sup>Ph</sup><sub>3</sub>]**RuH**( $\eta^3$ -H<sub>2</sub>SiH(Trip)) (1f). Yellow crystals of 1b (59 mg, 0.064 mmol) were added to a solution of (Trip)SiH<sub>3</sub> (70 mg, 0.33 mmol) in 2 mL of toluene, and the resulting mixture was stirred for 10 min to provide a clear yellow solution. The volatile materials were removed under vacuum and the resulting yellow oil was dissolved in fluorobenzene (2 mL) to give a solution that was stirred for 10 minutes before removal of the volatile components. This latter step was repeated once more, but evaporation was stopped with 0.5 mL of solvent remaining. This solution was layered with pentane and cooled to -35 °C. After 1 day, the yellow crystals that formed were isolated by pipetting away solvent, washing with pentane (3 x 2 mL), and briefly drying under vacuum to provide 54 mg of slightly impure 1f (81 % yield). Anal Calcd for C<sub>58</sub>H<sub>52</sub>OBP<sub>3</sub>Ru (969.853): C, 70.51; H, 6.51. Found: C, 69.84; H, 6.22. <sup>1</sup>H NMR (C-<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 8.37 (vbr, 1 H, Si—H), 8.20 (d, J = 7.3 Hz, 2 H), 7.70 (t, J = 7.3 Hz, 2 H), 7.57 (br m, 12 H), 7.44 (tt, J = 7.3 Hz, 1.1 Hz, 1 H), 7.15 (2 H, trip), 6.86 – 6.74 (m, 18 H), 3.81 (septet, J = 6.7 Hz, 2 H, <sup>*i*</sup>Pr methine), 2.76 (septet, J = 6.8 Hz, 1 H, <sup>*i*</sup>Pr methine), 1.89 (br, 6 H, B-CH<sub>2</sub>-P), 1.30 (d, J = 6.7 Hz, 12 H, 'Pr methyl), 1.18 (d, J = 6.7 Hz, 6 H, 'Pr methyl), -6.50 (br, 3 H, Ru—H).  ${}^{13}C{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>, 150.893 MHz):  $\delta$  153.33, 153.02, 150.89, 142.67 (m), 135.97, 132.78, 132.59 (m), 124.72, 122.15, 121.82, 35.58, 35.31, 24.87, 24.36. <sup>31</sup>P {<sup>1</sup>H} NMR

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(C<sub>6</sub>D<sub>6</sub>, 161.976 MHz): δ 46.4. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, - 70 °C, <sup>1</sup>H-<sup>29</sup>Si HMBC: 600 MHz (<sup>1</sup>H), 119.23 MHz (<sup>29</sup>Si)): δ 121. IR (cm<sup>-1</sup>): 2090 (Si—H), 1895 (Ru—H), 1628 (br, Ru—H—Si).

Representative procedure for catalytic hydrosilation reactions. *p*-Chlorostyrene (15 mg, 0.11 mmol) and CySiH<sub>3</sub> (14 mg, 0.12 mmol) were dissolved in  $C_6D_6$  (0.5 mL) containing  $C_6Me_6$  or ferrocene as an internal standard. A <sup>1</sup>H NMR spectrum of this solution was collected prior to the addition of **1b** (2.5 mg, 0.0027 mmol) in  $C_6D_6$  (0.2 mL) to provide a pale yellow solution. The reaction solution was examined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy within 15 minutes of adding **1b**. After 20 h the solution was again examined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and the yield of cyclohexyl(*p*-chlorophenethyl)SiH<sub>2</sub> was determined by integrating the initial and final <sup>1</sup>H NMR spectra using the internal standard resonance as a reference integral. The product silane was isolated as a colorless oil by diluting the solution with hexanes, filtering through a plug of silica, and evaporating solvent under reduced pressure. The isolated product was characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si-<sup>1</sup>H HMBC, and <sup>29</sup>Si-filtered <sup>1</sup>H NMR spectroscopy and by GC-MS. Characterization data for the hydrosilation products are provided below.

Cy(*p*-chlorophenethyl)SiH<sub>2</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz): δ 7.12 (d, J = 8.1 Hz, 2 H), 6.73 ((d, J = 8.1 Hz, 2 H), 3.73 (q, J = 3.4 Hz,  $J_{SiH} = 185$  Hz, 2 H, Si—H), 2.43 (m, 2 H, Ar-CH<sub>2</sub>-), 1.64 (m, 5 H), 1.23 – 1.08 (m, 5 H), 0.77 (m, 2 H, Si-CH<sub>2</sub>-), 0.72 (m, 1 H, methane C—H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.903 MHz): δ 143.20, 132.21, 129.89, 129.07, 31.64, 29.84, 28.34, 27.31, 21.71, 10.26. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H-<sup>29</sup>Si HMBC: 600 MHz (<sup>1</sup>H), 119.23 MHz (<sup>29</sup>Si)): δ -23. GC-MS m/z 252 (M)<sup>+</sup>, 169, 141, 125, 103.

1-(Cl<sub>3</sub>Si)-3-(CyH<sub>2</sub>Si)-propane. Note that this silane was isolated by air-free microscale distillation rather than filtration through silica. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz):  $\delta$  3.67 (q, *J* = 3.5 Hz, *J*<sub>SiH</sub> = 184 Hz, 2 H, Si—H), 1.63 (m, 5 H), 1.50 (m, 2 H, -CH<sub>2</sub>-), 1.23 – 1.06 (m, 5 H), 1.01 (m, 2

H, Cl<sub>3</sub>Si-CH<sub>2</sub>-), 0.72 (m, 1 H, Si-CR<sub>2</sub>H), 0.47 (m, 2 H, methane C—H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.903 MHz): δ 29.81, 28.28, 27.85, 27.29, 21.59, 19.49, 11.01. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H-<sup>29</sup>Si HMBC: 600 MHz (<sup>1</sup>H), 119.23 MHz (<sup>29</sup>Si)): δ -24 (SiCyH<sub>2</sub> group), 12 (SiCl<sub>3</sub>).

Et<sub>2</sub>(*p*-chlorophenethyl)SiH. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz): δ 7.13 (d, J = 7.9 Hz, 2 H), 6.76 (d, J = 7.9 Hz, 2 H), 3.87 (sep, J = 3.2 Hz,  $J_{SiH} = 179$  Hz, 1 H Si—H), 2.41 (m, 2 H, Ar-CH<sub>2</sub>-), 0.94 (t, J = 7.9 Hz, 6 H, Et<sub>2</sub>), 0.74 (m, 2 H Si-CH<sub>2</sub>-), 0.50 (qd, J = 7.9 Hz, 3.2 Hz, 4 H, Et<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.903 MHz): δ 143.74, 132.09, 129.86, 129.06, 30.73, 13.17, 8.72, 3.36. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H-<sup>29</sup>Si HMBC: 600 MHz (<sup>1</sup>H), 119.23 MHz (<sup>29</sup>Si)): δ –2. GC-MS *m/z* -226 (M)<sup>+</sup>, 197, 169, 141, 125, 114, 103.

**1-chloro-3-(CySiH<sub>2</sub>)-propane.** Note that a small amount of an unidentified side product was not separated from the sample that was isolated from the catalytic reaction mixture. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz):  $\delta$  3.67 (q, *J* = 3.4 Hz, *J*<sub>SiH</sub> = 185 Hz, 2 H, Si—H), 3.08 (t, *J* = 6.8 Hz, 2 H, - CH<sub>2</sub>Cl), 1.63 (m, 5 H), 1.54 (m, 2 H, -CH<sub>2</sub>-), 1.21 – 1.05 (m, 5 H), 0.68 (m, 1 H, cyclohexyl methane), 0.49 (m, 2 H, Si-CH<sub>2</sub>-). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.903 MHz):  $\delta$  47.55 (CH<sub>2</sub>Cl), 29.74, 29.62, 28.30, 21.63, 5.90. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H-<sup>29</sup>Si HMBC: 600 MHz (<sup>1</sup>H), 119.23 MHz (<sup>29</sup>Si)):  $\delta$  –22.5. GC-MS *m*/*z* 107 (M - cyclohexyl)<sup>+</sup>, 79, 65, 55, 41, 28, 18. GC-HRMS (EI) calcd for [(1-chloro-3-(CyH<sub>2</sub>)-propane) – H] [C<sub>9</sub>H<sub>17</sub>SiCl]<sup>+</sup>: 188.0788, and 190.0759, found: 188.0789, and 190.0762.

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The authors declare no competing financial interest

## **Supporting Information**

NMR spectra and full computational details. The coordinates of all calculated species are given as .xyz files. This material is available free of charge at <u>http://pubs.acs.org</u>.

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- 15. The hexahydridosilicate complex **2** did not react with XylNC (1 equiv in CD<sub>2</sub>Cl<sub>2</sub>) after 2 days at 23 °C (determined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). Treatment of **2** (in CD<sub>2</sub>Cl<sub>2</sub>) with CO (1 atm) resulted in 20 % conversion to [PhBP<sup>Ph</sup><sub>3</sub>]Ru(CO)<sub>2</sub>H after 10 days at 23 °C (determined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). Complex **2** was also found to be inactive as a catalyst for the hydrosilation of *p*-chlorostyrene with CySiH<sub>3</sub> under the conditions for which **1d** catalyzes this transformation.
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## **TOC Graphic**

