

# Hydrogen/Deuterium Exchange Reactions and Transfer Hydrogenations Catalyzed by $[C_5Me_5Rh(olefin)_2]$ Complexes: Conversion of Alkoxysilanes to Silyl Enolates<sup>†</sup>

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**Abstract:** A series of  $[C_5Me_5Rh(CH_2=CHR)_2]$  complexes (**1a–e**) have been prepared in which the olefin bears a bulky silyl substituent, R = (**a**)  $SiMe_3$ , (**b**)  $SiMe_2OEt$ , (**c**)  $Si(O^iPr)_3$ , (**d**)  $SiMe(OSiMe_3)_2$ , (**e**)  $SiPh_2O^iPr$ . The solid-state structure of **1c** has been determined by X-ray crystallography. When complex **1a** is heated (50 °C) in deuterated solvents ( $C_6D_6$ ,  $C_6D_5CD_3$ ,  $C_6D_5Cl$ , or  $(CD_3)_2CO$ ), deuterium is incorporated into the olefinic sites. Thermolysis at higher temperatures results in further H/D exchange and deuteration of both the  $SiMe_3$  and  $C_5Me_5$  groups. Heating **1a** in  $C_6D_6$  with added substrates (aniline,  $MeO^iBu$ ,  $MeOSiMe_3$ ,  $Cp_2Fe$ , cyclopentene, or  $EtOAc$ ) results in deuteration of these substrates via shuttling of deuterium from  $C_6D_6$  to the olefinic sites and then into certain sites of the substrates. Thermolysis of **1a** in the presence of vinyltrimethylsilane at higher temperatures results in C–Si bond cleavage and generation of a silacyclopentadiene complex (**6**) whose structure was determined by X-ray analysis. Thermolysis of **1c** in  $C_6D_6$  results in facile H/D exchange and incorporation of deuterium not only into the vinylic positions but also into the methine and methyl groups of the isopropyl substituents. At 90 °C in the presence of  $CH_2=CHSi(O^iPr)_3$  a catalytic transfer hydrogenation is observed which converts the vinylsilane to the silyl enolate,  $Et(^iPrO)_2SiOCMe=CH_2$ . A series of catalytic transfer hydrogenations were carried out in which alkoxysilanes  $CH_2=CHSiMe_2OR$  (R = Et, *n*-Bu, CHMeEt,  $C_2H_4^tBu$ ,  $C_2H_4Ph$ , CHMePh, CHMeCH<sub>2</sub>Ph) were converted to the corresponding silyl enolates. Catalytic conversion of the vinylaminosilane  $CH_2=CHSiMe_2NHC_2H_4Ph$  to the silyl enamine  $EtSiMe_2NHC_2H_4Ph$  is also reported.

## Introduction

Transition metal mediated C–H bond activation combined with the functionalization of the activated substrate has been a topic of increasing interest in recent years.<sup>1,2</sup> Initial efforts were directed toward the actual C–H bond activation reaction mediated by a transition metal.<sup>3–6</sup> The focus of many recent studies has moved toward the application of these findings in catalytic processes. Several systems have been described which generate functionalized products based on catalytic carbon–heteroatom or carbon–carbon bond-forming processes.<sup>7–14</sup>

An example that illustrates a functionalization process is the transfer hydrogenation reaction. Early reports have focused mainly on late metals which will activate hydrocarbons to generate, after  $\beta$ -hydride elimination from the activated substrate, an unsaturated product, in general an olefin.<sup>15–26</sup> The traditional approach utilizes a sacrificial hydrogen acceptor, usually a hindered olefin, to drive the catalytic process. Only recently have examples been reported that allow direct dehydrogenation of alkanes to generate an olefin and dihydrogen;

<sup>†</sup> Dedicated to Joseph L. Templeton on occasion of his 50th birthday.

<sup>‡</sup> Contact this author for further details regarding the X-ray analyses.

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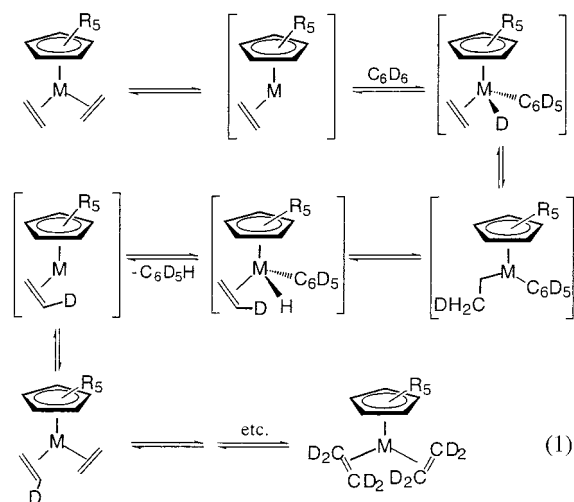
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the most elementary hydrocarbon functionalization process.<sup>27–31</sup> Productivity and selectivity of these catalysts have been generally moderate, but recently promising improvements have been made. Application of catalytic transfer hydrogenation for preparation of functionalized olefins of utility in organic synthesis has received only limited attention.

We have recently investigated C–H bond activations by the first-row metal cobalt and reported the use of  $[\text{C}_5\text{Me}_5\text{Co}(\text{C}_2\text{H}_3\text{-SiMe}_3)_2]$  as a catalyst for H/D exchange in aromatic solvents and for hydroacylation of olefins.<sup>32–34</sup> The key to the increased reactivity of this complex is the bulky trimethylvinylsilane which is lost in a dissociative first step to generate the reactive 16-electron fragment  $[\text{C}_5\text{Me}_5\text{Co}(\text{C}_2\text{H}_3\text{SiMe}_3)]$  capable of C–H bond activations. In this contribution we have applied this strategy to analogous rhodium complexes and have prepared rhodium(I) bis-olefin complexes in which the olefin bears bulky substituents which increases the rate of ligand dissociation and thus finds application in bond activation catalysis. As early as 1974 it was shown that the parent rhodium complex  $[\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2]$  heated in benzene-*d*<sub>6</sub> will activate the solvent to reversibly exchange deuterium for hydrogen in the coordinated olefin following a reversible olefin insertion–deinsertion sequence.<sup>35</sup> A mechanism for this exchange process is shown in Scheme 1 and is supported by our investigations with cobalt and earlier work regarding the rhodium bis-ethylene complexes. The first step, which in part controls the rate of the exchange reaction, is the dissociation of olefin which generates the reactive 16-electron fragment for subsequent bond activation chemistry.

**Scheme 1.** Reversible C–H Bond Activation of Benzene-*d*<sub>6</sub> with  $[\text{C}_5\text{R}_5\text{M}(\text{C}_2\text{H}_4)_2]$  (M = Co, Rh) and H/D Exchange



The low reactivity found in this system stands in clear contrast to the high reactivity of the 16-electron fragment  $[\text{C}_5\text{R}_5\text{Rh}(\text{L})]$  in bond activation reactions. The dissociative loss of 1 equiv

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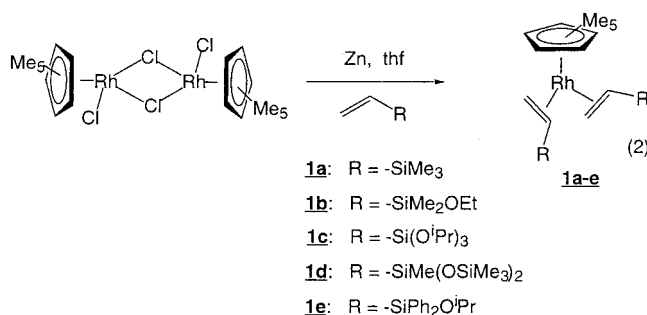
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of olefin and the participation of the second 1 equiv of olefin in insertion reactions are expected to be reversible. In this work we have investigated the reactivity of labile rhodium bis-olefin complexes in bond activation and functionalization reactions. We report here a variety of H/D exchange reactions toward a series of substrates and catalytic transfer hydrogenation of vinyl alkoxy silanes to generate vinyl silyl ethers using complexes of the type  $[\text{C}_5\text{Me}_5\text{Rh}(\text{C}_2\text{H}_3\text{R})_2]$  as catalysts.

## Results and Discussion

**A. Synthesis of Rhodium(I) Olefin Complexes.** A general route into rhodium olefin complexes of the type  $[\text{C}_5\text{Me}_5\text{Rh}(\text{olefin})_2]$  was developed and involves the reduction of the chloro-bridged dimer  $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$  with zinc powder in tetrahydrofuran in the presence of an excess of the desired olefin.<sup>36</sup> A series of new rhodium bis-olefin complexes (**1a–e**) was accessible using this pathway. Extraction into pentane and removal of the solvent allows the isolation of the bis-olefin complexes as yellow-orange crystalline materials or oils which are pure by NMR and elemental analysis (eq 2).



The coordination of two monosubstituted olefins to the  $[\text{C}_5\text{-Me}_5\text{Rh}]$  fragment frequently results in the formation of a mixture of isomers in which the substituent can either face toward or away from the Cp\* ligand as well as being disposed on the same or opposite side as the substituent on the second olefin.<sup>37–39</sup> The NMR analysis of the new rhodium olefin complexes shows that the solids or oils obtained from the pentane filtrates consist of a mixture of isomers with one major isomer accounting for at least 75% (**1d**) and up to 98% (**1a**) of the olefin complexes present. The oil initially obtained in the synthesis of **1a** (which likely contains a mixture of isomers) solidifies during the course of 1 h at room temperature to yield an orange-yellow solid. It was also possible to recrystallize complexes **1a,c** from acetone at -78 °C to obtain yellow crystalline materials which contained the rhodium bis-olefin complex as a single isomer by NMR analysis.

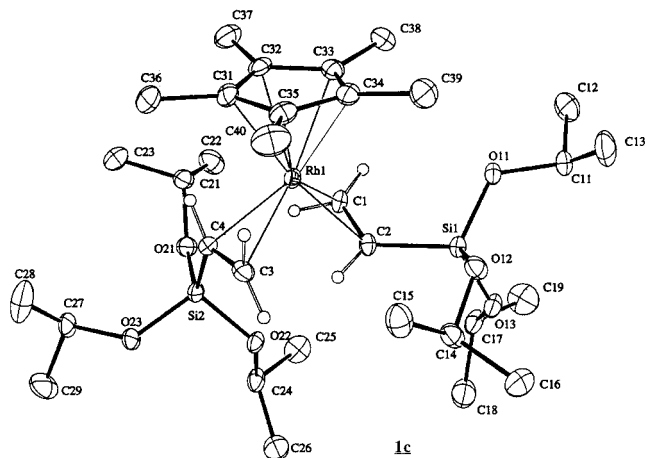
The configuration drawn in eq 2 for the rhodium bis-olefin complexes is based on the structurally characterized cobalt analogue of **1a**<sup>34</sup> and is expected to be the one most favored. NMR data are consistent with this assumption with a single Cp\* resonance at 1.68 ppm and a single SiMe<sub>3</sub> resonance accounting for two SiMe<sub>3</sub> groups at 0.05 ppm along with olefinic

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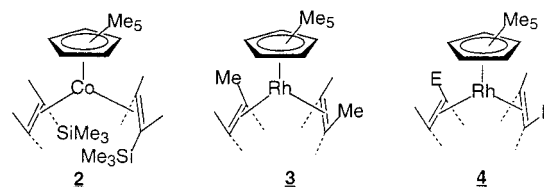
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**Figure 1.** ORTEP view of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>Si(O<sup>i</sup>Pr)<sub>3</sub>)<sub>2</sub>] (**1c**). All atoms are drawn at 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Rh–C(1) 2.135(4), Rh–C(2) 2.167(4), Rh–C(3) 2.138(4), Rh–C(4) 2.172(4), Si(2)–C(4) 1.823(4), Si(1)–C(2) 1.841(4), C(1)–C(2) 1.412(6), C(3)–C(4) 1.422(6), C(1)–Rh–C(2) 38.31(15), C(1)–Rh–C(3) 109.16(16), C(1)–Rh–C(4) 93.84(15), C(2)–Rh–C(3) 86.84(15), C(2)–Rh–C(4) 95.47, C(3)–Rh–C(4) 38.53(15), Rh–C(4)–C(3) 69.43(21), Si(2)–C(4)–C(3) 125.2(3), Rh–C(1)–C(2) 72.07(23), Rh–C(2)–Si(1) 122.08(20), Rh–C(2)–C(1) 69.61(22), Si(1)–C(2)–C(1) 126.6(3), Rh–C(3)–C(4) 72.05(23), Rh–C(4)–Si(2) 128.06(21).

resonances at 2.11 (ddd, 2H) and 1.15 (m, 4H) ppm. The <sup>13</sup>C NMR spectrum shows only five resonances accounting for the Cp\* unit and two equivalent coordinated olefins. Using the same procedure, complex **1b** was isolated as a yellow-brown oil. NMR analysis also showed one dominant rhodium species (>98%), but signs for further reactivity were observed (vide infra). In complex **1c** a significant difference in the coordination of the two bulky olefins to the rhodium center is observed. Again, an orange oil of **1c** was isolated after reduction and pentane extraction; crystalline material in this case was obtained only after cooling an acetone solution of **1c** to –78 °C. NMR analysis of this material showed a single rhodium species with a Cp\* <sup>1</sup>H resonance at 1.72 ppm. In the region of 1.10–1.22 ppm the isopropyl methyl groups are observed as an overlapping series of doublets integrating for 36 protons (see Figure 3 in the Supporting Information). Two separate septet resonances are observed at 4.22 and at 4.32 ppm which integrate together for the six methine protons of the two coordinated triisopropoxyvinylsilane ligands. Most interesting are six different resonances integrating each for one proton which are assigned as the olefinic protons of two inequivalent ligands at 3.23, 2.11, 2.01, 1.88 (dd, 18, 15 Hz), 0.66, and 0.48 (dd, 18, 15 Hz) ppm. The lack of symmetry in this bis-olefin complex is also confirmed by <sup>13</sup>C NMR analysis. Four doublets for the olefinic carbons are observed as well as resonances for inequivalent isopropyl groups and one Cp\* unit. After recrystallization from acetone it was possible to determine the structure of **1c** by X-ray crystallography (Figure 1). The structural analysis confirms the coordination of 2 equiv of triisopropoxyvinylsilane ligands to the Rh(I) center. The bulky substituent on the olefins clearly dominates the structure which results in the observed orientation of the substituents facing away from each other. The bond distances in the coordinated olefin are within the expected range (C1–C2, 1.412 Å; C3–C4, 1.422 Å). The rhodium–olefinic carbon distances reflect the steric effect of the substituent. The Rh–C2 bond distance at 2.167 Å is longer than the Rh–C1 distance at 2.135 Å. Similar bond distances are obtained for the second olefin. Even though the carbon atom bearing the

## Scheme 2. [C<sub>5</sub>Me<sub>5</sub>M] Bis-olefin Complexes (E = –CO<sub>2</sub>Me)



substituent is further removed from rhodium, the C2–Rh–C4 angle (93.8) is considerably smaller than the C3–Rh–C1 angle (109.1). The solid-state structure confirms the observed NMR characteristics for **1c**, in which the coordinated olefins are inequivalent, as opposed to **1a** (or the structurally characterized cobalt analogue of **1a**), in which a local C<sub>2</sub> symmetry is observed.

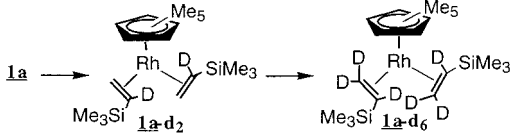
In other structurally characterized rhodium bis-olefin complexes, C<sub>2</sub> symmetry has also been observed. In the methylacrylate complex **4**<sup>40</sup> and the propene complex **3**<sup>41</sup> (Scheme 2), the influence of the substituent is less severe and orientation toward the Cp\* ligand is observed. It is interesting to note that both **3** and **4** in solution show a rapid isomerization to a mixture of three rotational isomers. With an increase in size of the olefin substituent to trimethylsilyl, the olefins are oriented as in complex **2**, facing away both from each other and from the Cp\* ligand. The solution <sup>1</sup>H NMR spectrum shows a single isomer consistent with the simple C<sub>2</sub> symmetry.

The rhodium complex **1a**, analogous to **2**, also shows two equivalent olefinic ligands by NMR spectroscopy. On the other hand, in complex **1c**, the steric bulk of the silyl substituent does not allow the coordination of the two olefins to generate a structure with higher symmetry. The planes generated by the olefinic carbons and the silicon atom of each olefin are nearly perpendicular to each other in **1c**, [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>Si(O<sup>i</sup>Pr)<sub>3</sub>)<sub>2</sub>] (Figure 1). This arrangement is consistent with the observed increased rate of ligand dissociation in this new bis-olefin complex, allowing easier access to the reactive 16-electron fragment (see below).

**B. H/D Isotope Scrambling in 1a by Reversible C–H Bond Activation.** The reactivity of the new rhodium olefin complexes in bond activation reactions is illustrated in a reaction with benzene-*d*<sub>6</sub>. After 3 days at 20 °C the olefin resonances for coordinated vinyltrimethylsilane of **1a** are decreased in intensity along with the partial disappearance of coupling due to deuterium incorporation. Correspondingly, the integration of the residual <sup>1</sup>H solvent resonance (benzene-*d*<sub>5</sub>) is increased in intensity. The resonance of the α-hydrogen atoms integrates at this stage for 55% of its original value whereas the β-hydrogen atoms still show 75% of the initial integrated intensity. No other resonances are changed under these conditions. This reaction of **1a** was investigated in more detail at 78 °C in benzene-*d*<sub>6</sub>. <sup>1</sup>H NMR analysis confirms faster H/D exchange processes; after only 9 min the integral of the resonance for the α-hydrogen has been reduced by 80% due to deuteration whereas the integration for the β-hydrogen signals is reduced by 50%. After 17 min, the resonance for the α-hydrogen has disappeared and the resonances for the β-hydrogens are reduced by 75%. The <sup>13</sup>C NMR spectrum at this stage confirms exchange and shows a 1:1:1 triplet at 45 ppm for C<sub>α</sub> and a pentet at 48 ppm for C<sub>β</sub>. After about 2 h the only resonances observed (besides the now more intense C<sub>6</sub>D<sub>5</sub>H resonance) are the unchanged C<sub>5</sub>Me<sub>5</sub> and the SiMe<sub>3</sub> resonances.

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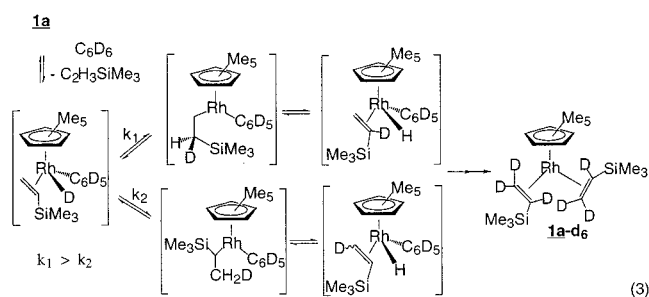
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**Table 1.** H/D Exchange of Vinyl Sites in **1a** in Deuterated Solvents<sup>a</sup>


solvent	temp (°C)	time for 50% reduction in signal intensity (site of deuteration) (min)	
		$\alpha$	$\beta$
C <sub>6</sub> D <sub>6</sub>	50	115	250
C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	50	120	960
C <sub>6</sub> D <sub>5</sub> Cl	50	125	230
(CD <sub>3</sub> ) <sub>2</sub> CO	50	120	210
C <sub>6</sub> D <sub>6</sub>	78	<5	18
C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	78	<5	18

<sup>a</sup> 0.01 g of **1a** ( $2.3 \times 10^{-5}$  mol), 0.6 mL of solvent, capillary insert with ferrocene

The mechanism for this process is similar to that outlined in Scheme 1 with the modification that the regiochemistry of olefin insertion is guided by the trimethylsilyl substituent which explains the observed differences in the rates of deuterium incorporation (eq 3). In the analogous cobalt system (**2**),



comparable deuterium incorporation is observed but with a half-life of 1 h at 20 °C and with highly regioselective incorporation of deuterium into the  $\alpha$ -position of the coordinated olefin.

It is interesting to compare this observation with the thermolysis of the parent bis-ethylene complex [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**5**) in benzene-*d*<sub>6</sub>. Jones and co-workers have reinvestigated this system<sup>42</sup> and found that at 78 °C in benzene-*d*<sub>6</sub> **5** will incorporate deuterium into coordinated ethylene to decrease the <sup>1</sup>H NMR integration after 2 h by 25% of its original value. This indicates that the dissociative lability of the coordinated olefin is significantly increased in **1a** and should therefore allow more effective access to the reactive 16-electron fragment [C<sub>5</sub>Me<sub>5</sub>-RhL] under relatively mild conditions.

This H/D exchange process is also observed in other aromatic solvents. In a series of experiments the intensity of the  $\alpha$ - and  $\beta$ -sites of the coordinated olefin of **1a** was monitored by NMR spectroscopy and half-lives for the deuterium incorporation extracted (Table 1, pseudo-first-order rate constants are given in the Supporting Information). Interesting differences are observed for the deuterium incorporation into the  $\beta$ -sites of coordinated vinyltrimethylsilane. Incorporation of H atoms into toluene is somewhat slower than in benzene and chlorobenzene. The regiochemistry of H incorporation into toluene-*d*<sub>8</sub> indicates that the para site is favored (5 h, 50 °C, the integration of the residual resonance for the para position is increased by 300% in intensity), followed by the meta positions (5 h, 50 °C, 100%

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increase of the original intensity for one site), with the ortho positions being most slowly activated (5 h, 50 °C, 25% increase compared to the original intensity for one site). These results support previous observations that a methyl substituent has considerable impact on reactivity and regioselectivity in the activation reaction.<sup>33,43</sup> The residual <sup>1</sup>H NMR resonance for the methyl group increases only by 20% (50 °C), consistent with the reported lower reactivity of benzylic C–H bonds relative to aromatic C–H bonds in oxidative additions to Rh(I).<sup>43</sup>

Not only solvents containing aromatic sp<sup>2</sup> CH bonds participate in this reversible H/D exchange process. An acetone-*d*<sub>6</sub> solution of **1a** also exhibits H/D exchange by incorporation of deuterium into the coordinated olefin. Exchange rates are comparable to those in aromatic solvents (Table 1). While  $\eta^2$ -arene adducts of [C<sub>5</sub>Me<sub>5</sub>Rh(L)] complexes have been previously observed,<sup>44</sup> we have not spectroscopically observed the likely [C<sub>5</sub>Me<sub>5</sub>Rh(olefin)(acetone)] adduct as an intermediate in any of these exchange reactions. These results clearly demonstrate the ability of these systems, in which olefin dissociation is facile, to activate not only sp<sup>2</sup> C–H bonds but also sp<sup>3</sup> C–H bonds under moderately mild thermal conditions.

Since the olefinic hydrogens are deuterated initially by exchange with solvent, further bond activation reactions followed by reversible insertion and reductive elimination processes can essentially shuttle deuterium from the solvent via the coordinated olefin into other, undeuterated, substrates. The first evidence for this reactivity was observed when a toluene-*d*<sub>8</sub> solution of **1a** was continuously heated at 78 °C. After all resonances for olefinic protons disappeared, a decrease of the SiMe<sub>3</sub> resonance was observed with a half-life of 10 h (pseudo-first-order rate constant:  $7 \times 10^{-6}$  s<sup>-1</sup>). In the <sup>1</sup>H NMR spectrum a 1:1:1 triplet ( $J_{\text{HD}} = 2$  Hz) was observed just upfield of the singlet SiMe<sub>3</sub> resonance. Extended heating for a total of 24 h resulted in the complete disappearance of all <sup>1</sup>H NMR features of the trimethylvinylsilane ligand in this experiment.<sup>45</sup> If additional trimethylvinylsilane is added to a reaction mixture prepared in this fashion, olefin substitution chemistry is observed under these conditions to regenerate protio-**1a** and deuterovinyltrimethylsilane; ongoing H/D exchange will eventually result in complete deuteration of vinyltrimethylsilane (10 equiv) if heating is continued for 1 week at 78 °C.

In the deuteration reactions described thus far, the C<sub>5</sub>Me<sub>5</sub> ligand has not been involved in H/D exchange catalysis; however, thermolysis of **1a** in toluene-*d*<sub>8</sub> at 120 °C for 12 h eventually results in considerable deuteration of the C<sub>5</sub>Me<sub>5</sub> ligand. Referencing to a ferrocene standard in a capillary insert established that the remaining Cp\* resonance decreased while the resonance for benzene-*d*<sub>5</sub>h increased. Throughout this process the reaction mixture is homogeneous (eq 4);<sup>46</sup> continued thermolysis results eventually in decomposition to unassigned products. The integrity of **1a** during this process was confirmed by a ligand exchange reaction. Addition of trimethylvinylsilane resulted in regeneration of the characteristic <sup>1</sup>H NMR features of coordinated protio-olefin in **1a**, while the Cp\* region remained complex due to extensive deuterium incorporation.

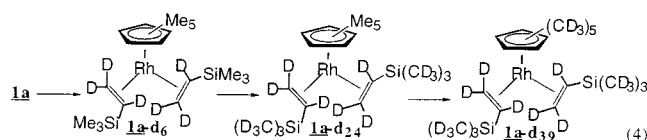
(43) Less than 1% activation of the benzylic position of toluene is observed in the reaction of [C<sub>5</sub>Me<sub>5</sub>Rh(PMe<sub>3</sub>)] with toluene. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(44) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(45) <sup>13</sup>C NMR analysis of these reaction mixtures shows a broad, ill-defined resonance at 0–2 ppm with extensive coupling to deuterium; for the olefin resonances see ref 33.

(46) Besides the residual singlet resonance at 1.57 ppm (toluene-*d*<sub>8</sub>) a triplet (1:1:1) resonance at 1.52 ppm ( $J = 1.8$  Hz) is observed in addition to small amounts of unassigned decomposition products.

Finally, the thermolysis of **1a** in hexane-*d*<sub>14</sub> was investigated. At 78 °C no H/D exchange was observed. However, after 5 h at 120 °C, only two major resonances remain in the <sup>1</sup>H NMR spectrum corresponding to the Cp\* and SiMe<sub>3</sub> groups of **1a** next to a series of broad signals in the Cp\* region assigned as decomposition products. The olefinic sites have been deuterated, and thus, these resonances are absent. In addition, the SiMe<sub>3</sub> resonance clearly shows signs for deuterium incorporation. This was confirmed by <sup>13</sup>C NMR spectroscopy as discussed above. Compared to the other solvent systems, hexane shows the lowest reactivity and solvent activation is not observed without some catalyst decomposition. In contrast, it is significant to point out that no signs for solvent activation and H/D exchange were observed in a series of thermolysis experiments performed in cyclohexane-*d*<sub>12</sub>. This observation is consistent with the marked difference in reactivity previously observed between primary and secondary C–H bonds in bond activation reactions.<sup>3,4,44</sup> Equation 4 summarizes the sequence for deuterium incorporation into complex **1a** in order of site selectivity.



These solvent activation reactions are encouraging for possible applications in catalysis since the general bond activation reactivity of the fragment [C<sub>5</sub>Me<sub>5</sub>RhL] has been well-established and is here incorporated into a reversible sequence of C–H activation steps of sp<sup>2</sup> as well as sp<sup>3</sup> bonds. The use of the more labile olefin trimethylvinylsilane facilitates olefin dissociation to generate the reactive 16-electron intermediate in combination with the second olefin which can participate in an insertion reaction in a possible catalytic cycle. The deuteration of the SiMe<sub>3</sub> group as well as the Cp\* ligand is believed to occur through intermolecular C–H bond activation processes.<sup>47</sup> In addition, vinylic C–H bond activation of the coordinated olefin can contribute to the observed process but no further evidence was observed to support this scenario.

To illustrate the intermolecular reactivity of the olefin complex toward other C–H bonds, a benzene-*d*<sub>6</sub> solution of **1a** was heated in the presence of a variety of substrates. Deuterium incorporation into these substrates was observed via a shuttle process in which deuterium from benzene is exchanged into the olefinic positions of the vinyl silane and then, upon substrate activation, the deuterium is passed on to substrate. Table 2 illustrates several substrates which have been subjected to the shuttle exchange process.

Twenty equivalents of aniline (Table 2, entry 1) react in this process to show after 5 h at 110 °C considerable reduction of the aromatic resonances in the <sup>1</sup>H NMR spectrum. Deuteration of the meta and para positions is fastest, which indicates the steric impact of the amino substituent. It is noteworthy to point out that the NH<sub>2</sub> group does not show deuterium incorporation on the time scale of these experiments.<sup>48</sup> Interesting are also entries 2 and 3 in which two similar substrates show selective H/D exchange at a sp<sup>3</sup> CH bond α to the heteroatom. (For an <sup>1</sup>H NMR spectrum which illustrates deuterium incorporation into MeOSiMe<sub>3</sub> see the Supporting Information.) The presence

(47) (a) An alternative mechanism for deuteration of the Cp\* ligand follows a route via a fulvene rhodium hydride intermediate which operates under different conditions as applied in the reactions of **1a**. Maitlis, P. M.; Moseley, K. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) The activation of the C<sub>5</sub>Me<sub>5</sub> moiety in d<sup>0</sup> transition metal systems has been observed; see refs 1 and 2 for general references.

**Table 2.** H/D Exchange between Benzene-*d*<sub>6</sub> to Other Substrates Catalyzed by **1a**

entry	substrate <sup>a</sup>	product	% deuteration <sup>b</sup>	
			5h	24h
1			<i>ortho</i> : 76	91
			<i>meta</i> : 94	97
			<i>para</i> : 93	97
2	H <sub>3</sub> C–O– <sup>t</sup> Bu	D <sub>3</sub> C–O– <sup>t</sup> Bu	31	44
3	H <sub>3</sub> C–O–SiMe <sub>3</sub>	D <sub>3</sub> C–O–SiMe <sub>3</sub>	46	62
4			93	.
5			49	46
6	H <sub>3</sub> C–C(=O)OCH <sub>2</sub> –CH <sub>3</sub>	D <sub>3</sub> C–C(=O)OCH <sub>2</sub> –CH <sub>3</sub>	61	80

<sup>a</sup> **1a** (0.01 g, 2.3 × 10<sup>−5</sup> mol), substrate (4.6 × 10<sup>−4</sup> mol) in C<sub>6</sub>D<sub>6</sub> at 110 °C. <sup>b</sup> % deuteration estimated from residual <sup>1</sup>H NMR signal intensities.

of the SiMe<sub>3</sub> group in entry 3 in place of the <sup>t</sup>Bu group of entry 2 suggests a slight preference in the exchange process for the substrate with the second-row element which renders the methyl C–H bonds more acidic. In comparison to aromatic substrates, both substrates are ca. 1 order of magnitude less reactive. The rate of deuteration of ferrocene, on the other hand, compares well to the H/D exchange rate of aromatic substrates (Table 2, entry 4), and complete deuteration is observed readily.

Olefins with β-hydrogens are in general isomerized by rhodium systems of type **1**. This is also supported by the observation in entry 5, in which the most likely mechanism involves olefin substitution in **1a** by cyclopentene followed by reversible solvent activation, insertion, and deuterium exchange. Rapid olefin isomerization will incorporate the label with equal rates into all positions of the substrate as is observed. The bis-cyclopentene rhodium complex was not accessible using the synthetic strategies applied here, but the deuteration results indicate that cyclopentene complexes are generated in these reactions<sup>49</sup> and suggests that complex **1a** is a useful general precursor for catalytic reactions with a variety of olefins. The reaction of ethyl acetate with **1a** and benzene-*d*<sub>6</sub> results in selective deuteration of the α-methyl group; deuterium incorporation into other C–H sites is not observed. This compares well with the reversible activation of acetone as discussed above.

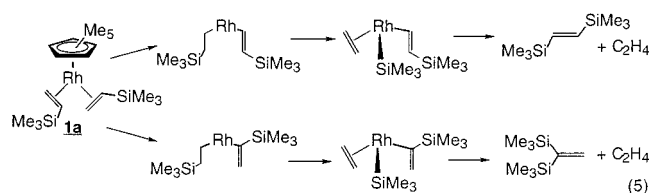
These H/D exchange results indicate that **1a** can effectively activate a variety of C–H bonds and shows selectivity in this process. In addition the presence of a series of functional groups is tolerated. It is noteworthy to point out that some of these reactions were conducted under conditions where compound **1a** was essentially stable (80 °C, > 150 h). However, complete deuteration of certain substrates required longer reaction times.

(48) Reaction mixtures containing aniline and **1a** in benzene-*d*<sub>6</sub> were thermolyzed for 1 week at 110 °C without any signs for deuterium incorporation into the –NH<sub>2</sub> group; complex **1a** decomposes after extensive deuteration to unassigned products. This result also indicates that protic mechanisms for H/D exchange catalyzed by possible decomposition products are not operative.

(49) Addition of cyclopentene to **1a** in cyclohexane-*d*<sub>12</sub> at 50 °C results in the formation of new olefin complexes assigned as mono- and bis-cyclopentene rhodium species. Isolation of these materials was not successful.

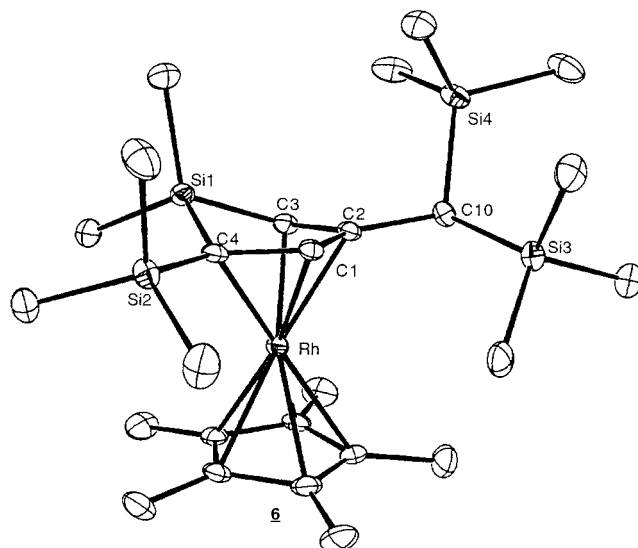
At 110 °C, catalytic H/D exchange is efficient and fast but the catalyst lifetime is reduced depending on the substrate (Table 2).

**C. Thermolysis of **1a** in the Presence of Excess Trimethylvinylsilane.** Complex **1a** is stable for long times at high temperatures but reactive as indicated by the ongoing H/D scrambling processes in solvents such as benzene-*d*<sub>6</sub>. The inert solvent cyclohexane-*d*<sub>12</sub> was investigated to study the reactivity of **1a** under thermolysis conditions. A solution of complex **1a** was heated to 140 °C in cyclohexane-*d*<sub>12</sub> in the presence of 10 equiv of vinyltrimethylsilane. After 4 h new singlet resonances at 6.28 and 6.59 ppm are observed along with a singlet at 5.28 ppm identified as ethylene; in addition, new signals in the SiMe<sub>3</sub> region are observed. After 24 h at 140 °C these resonances account for roughly 30% of all vinyltrimethylsilane present, the major rhodium species (95%) remains complex **1a**. The new singlets in the olefinic region at 6.59 and 6.28 ppm are assigned to (*E*)-1,2-bis(trimethylsilyl)ethene (<sup>13</sup>C: 151.1, d) and 1,1-bis(trimethylsilyl)ethene (<sup>13</sup>C: 140.2, t) and agree well with literature values.<sup>50–52</sup> This result indicates that either vinylic C–H bond can be activated by rhodium. Insertion followed by β-silyl elimination and reductive elimination from a Rh(III) vinylsilyl intermediate generates ethene and the observed bisilylated ethene derivatives (eq 5). The rhodium species is trapped by additional vinyltrimethylsilane to regenerate **1a**.



Continuous heating of this reaction mixture for 1 week at 140 °C results eventually in 80% conversion of vinyltrimethylsilane to 1,2-bis(trimethylsilyl)ethene (72%) and 1,1'-bis(trimethylsilyl)ethene (28%). Significantly, under these conditions, **1a** has been completely converted to new rhodium complexes. Removal of the volatiles by vacuum transfer confirms the observations made during catalysis. Besides vinyltrimethylsilane, ethene, and the two bis(trimethylsilyl)ethene isomers, ethyltrimethylsilane (t, 0.92 and q, 0.42 ppm) is also observed in the volatile fraction. Analysis of the remaining organometallic material indicates a mixture of rhodium complexes incorporating a series of SiMe<sub>3</sub> groups with the dominant thermolysis product accounting for 75% of all organometallic material. Cooling of an acetone solution of this mixture to –30 °C for 1 week results in the formation of orange crystalline material which corresponds to the major decomposition product, **6**, whose <sup>1</sup>H NMR spectrum shows one Cp\* resonance at 1.92 ppm and three 9H singlets accounting for three SiMe<sub>3</sub> groups. Analysis by <sup>13</sup>C NMR spectroscopy also shows three SiMe<sub>3</sub> groups and four resonances which show coupling to rhodium at 45.0 (18 Hz), 43.5 (15 Hz), 87.7 (6 Hz), and 90.0 (9 Hz) ppm.

The structure of **6** was determined by X-ray crystallography. The ORTEP diagram of **6** is shown in Figure 2 and confirms the incorporation of additional SiMe<sub>3</sub> groups to generate a silacyclopentadiene fragment which is coordinated to the [C<sub>5</sub>-



**Figure 2.** ORTEP view of **6**. Selected distances (Å) and angles (deg): Rh–Si(1) 2.8472(2), Rh–C(1) 2.135(4), Rh–C(2) 2.152(5), Rh–C(3) 2.166(5), Rh–C(4) 2.233(5), Si(1)–C(3) 1.849(5), Si(1)–C(4) 1.861(5), Si(2)–C(4) 1.850(5), Si(3)–C(10) 1.908(5), Si(4)–C(10) 1.909(5), C(1)–C(2) 1.434(7), C(1)–C(4) 1.445(7), C(2)–C(3) 1.437(7), C(2)–C(10) 1.528(7); C(1)–Rh–C(2) 39.07(2), C(1)–Rh–C(3) 66.69(2), C(2)–Rh–C(3) 38.88(2), C(3)–Rh–C(4) 71.12(2), C(2)–C(1)–C(4) 115.0(4), C(1)–C(2)–C(3) 110.9(4), C(1)–C(2)–C(10) 124.4(4), Si(1)–C(4)–Si(2) 128.3(3), C(3)–Si(1)–C(4) 87.19(2), Si(1)–C(4)–C(1) 106.9(4), Si(2)–C(4)–C(1) 119.9(4), Si(3)–C(10)–Si(4) 112.99(2); C(4)–Si(1)–C(3)–C(2) 29.7(4), C(4)–C(1)–C(2)–C(3) 2.4(4), C(1)–C(2)–C(3)–Si(1) 24.1(4), C(4)–Si(1)–C(3)–C(2) 29.7(4).

Me<sub>3</sub>Rh] moiety.<sup>53</sup> Two vinyltrimethylsilane molecules and two SiMe<sub>3</sub> groups are utilized to generate this η<sup>4</sup>-silacyclopentadiene complex. The Rh–C1, Rh–C2, and Rh–C3 distances are all very similar and in the range of 2.15 Å. The Rh–C4 distance of 2.23 Å is considerably elongated and reflects the steric impact of the SiMe<sub>3</sub> group at C4. The bond distances in the diene unit also reflect this influence with C1–C4 being notably longer (1.45 Å) and C1–C2 or C2–C3 essentially identical (1.43 Å). The torsion angle of 24° for C1–C2–C3–Si1 is also characteristic for this complex.

The formation of complex **6** during the thermolysis of **1a** in the presence of excess trimethylvinylsilane can be viewed as a stepwise process in which first silylation of vinyltrimethylsilane occurs as observed during the thermolysis. The silacyclopentadiene is then formed from two 1,1-bis(trimethylsilyl)ethene units via dehydrogenative coupling and isomerization. It is significant that in this deactivation process the sp<sup>3</sup> CH bond of a SiMe<sub>3</sub> group must be activated and coupled in a reductive elimination process with a second molecule of olefin. Additional vinyltrimethylsilane functions as the hydrogen acceptor and ethyltrimethylsilane is generated.

**D. Deuteration of Complex **1c**.** The reactivity of complex **1c** follows the general features observed for complex **1a** but with significant differences. A benzene-*d*<sub>6</sub> solution of **1c** shows considerable deuterium incorporation into the α-positions of the coordinated olefin after 3 days at 20 °C.<sup>54</sup> This experiment was repeated at higher temperatures, and a toluene-*d*<sub>8</sub> solution of **1c** was heated to 50 °C while the reaction was monitored by NMR spectroscopy.<sup>55</sup> Deuterium incorporation into multiple

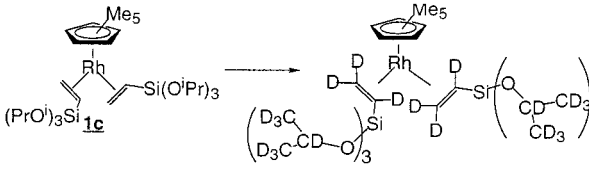
(50) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703.

(51) Birkofer, L.; Kuehn, T. *Chem. Ber.* **1978**, *111*, 3119.

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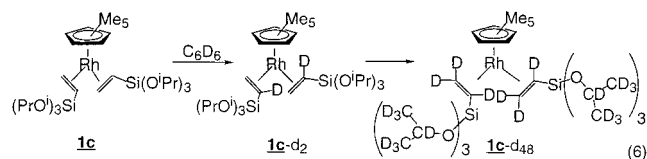
(54) The doublet splitting of the β-protons disappears to generate a singlet for all four inequivalent positions, while the resonances for the α-protons are reduced to 30% in intensity at this stage.

**Table 3.** Selective H/D Exchange of **1c** in Aromatic Solvents


solvent	temp (°C)	time	site of deuteration (% <sup>1</sup> H integral reduction)			
			α	β	OCHMe <sub>2</sub>	OCHMe <sub>2</sub>
C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	50	4 h	>99	15	14	14
C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub>	50	12 h	>99	43	43	44
C <sub>6</sub> D <sub>6</sub>	70	4 min	>99	60	64	64
C <sub>6</sub> D <sub>6</sub>	70	10 h	>99	>99	91	85

sites of the coordinated olefin was observed, and the results of these H/D exchange reactions are summarized in Table 3.

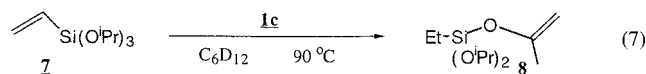
A significant reactivity difference is observed for the exchange of the α-protons compared to the other sites of the olefin. Complete deuteration of the α-protons is observed after 4 min at 70 °C. The rate of deuterium incorporation for all other sites during the exchange process is very similar. The sequence of deuterium incorporation is illustrated in eq 6.



Complex **1c-d<sub>2</sub>** is generated first and functions to shuttle deuterium from the solvent into the C–H bonds of the isopropoxy groups. The deuteration of the β-protons of the vinyltris(isopropoxy)silane is considerably slower than the deuteration of the β-protons in **1a**. This is likely a consequence of the increased steric bulk of the olefin in **1c** which disfavors olefin insertion with opposite regiochemistry (see eq 3). It is also remarkable that the isopropyl groups of the olefinic ligand are deuterated on the time scale of reversible solvent activation (similar H/D exchange results are also observed in acetone-*d*<sub>6</sub>). In these exchange reactions the total <sup>1</sup>H intensity of the methyl groups decreases at the same rate as the isopropyl methine signal. Taking statistical factors into account, this observation suggests that the methyl groups are activated more easily than the less accessible methine protons. In comparison to MeOSiMe<sub>3</sub> (entry 3, Table 2) a significant increase in H/D exchange reactivity is observed for this system, indicating a potential preference for an intramolecular bond activation pathway (vide infra).

**E. Alkoxysilane Isomerization: Transfer Hydrogenation.** Reversible C–H bond activation of triisopropoxyvinylsilane (**7**) in **1c** indicated by the deuterium incorporation experiment is not the only reaction observed with this ligand system. In a reaction of excess silane **7** with **1c** in cyclohexane-*d*<sub>12</sub>, the catalytic formation of a new organic product is observed at 90 °C while excess olefin is depleted. The vinylsilane **7** has undergone intramolecular transfer hydrogenation to generate the bis(isopropoxysilyl)ethyl-protected enol of acetone, compound **8** (eq 7).

(55) In the course of 2 h a second Cp\*–containing species is generated which amounts to 21% of the rhodium complexes present relative to **1c**. Additional olefin resonances suggest that this second species is an isomer of **1c**. A fresh solution of crystallized **1c** shows one isomer as indicated. Monitoring this solution over 1 week at 25 °C shows that a second species with analogous NMR features as the complex indicated here is generated.



Characteristic for **8** are <sup>1</sup>H NMR features which indicate the formation of a Si-bound ethyl group (5H), a singlet resonance at 1.71 ppm (3H), and two isopropoxy groups (septet at 4.18 (2H) and d at 1.13 (12H) ppm) in addition to two singlets at 4.32 and 4.02 ppm (each 1H).

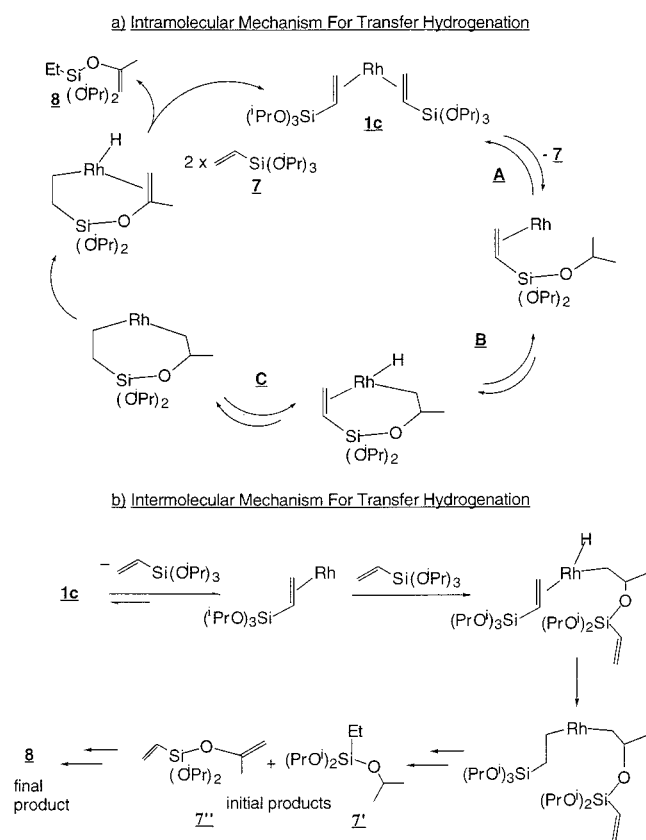
To investigate this catalytic process in more detail, the reaction of 20 equiv of **7** with **1c** in cyclohexane-*d*<sub>12</sub> was followed by <sup>1</sup>H NMR spectroscopy at 90 °C. A plot of turnover number vs time is given in the Supporting Information. In the initial part of catalysis (about 10 h) there is a linear relationship between turnover number (TO) and the time which corresponds to a turnover frequency (TOF) of 0.7 TO/h. However, after 20 h under these conditions, >99% conversion to **8** is observed, which indicates that the TOF increases toward complete conversion of substrate. After 95% conversion of **7** to **8** complex **1c** still amounts to 90% of the initially charged catalyst load. Only after complete conversion of all **7** to **8** does **1c** decay to unassigned products, which indicates that **1c** is the resting state during catalysis. Since reversible olefin dissociation must occur to initiate catalysis, the presence of free vinylsilane will reduce the TOF in this transfer hydrogenation process. Close to complete conversion of **7** the TOF increases on the basis of the reduced binding affinity of the transfer hydrogenation product **8**.

It is efficient to use neat vinylsilane as solvent for the catalytic transfer hydrogenation since the products can be directly used for further applications or freed from rhodium-containing materials by simple vacuum transfer. Catalyst **1a** is also effective in these reactions since fast ligand exchange under reaction conditions will generate the corresponding alkoxyvinylsilane complex in situ. In the case of **7**, addition to **1a** will generate **1c**. Therefore, in a series of experiments, **1a** (0.01 g, 2.3 × 10<sup>−5</sup> mol) was dissolved in neat silane **7** (1 g, 188 equiv) and heated at 140 °C and the reaction mixture sampled at various times. The following time–turnover data were observed: 30 min, 38 TO; 45 min, 61 TO; 65 min, 81 TO; 95 min, 117 TO. This result indicates that the TON is essentially linear with time. Only close to complete conversion is a faster TOF observed. Quantitative conversion (>99%) to **8** is observed after roughly 2 h reaction time. It is possible to achieve very high turnovers with this catalyst system. For example, heating 0.01 g of **1a** and 10 g of **7** for 5 days at 140 °C results in quantitative conversion of **7** to **8**, which corresponds to 1900 turnovers.

During catalytic transfer hydrogenation the only rhodium-containing species observable is **1c**; the formation of a possible rhodium enol complex in which **8** is utilized to stabilize the rhodium fragment is not observed. This was tested by heating **1c** in cyclohexane-*d*<sub>12</sub> at 100 °C. After 8 h 60% of olefin **7** in complex **1c** is converted to enol **8**; however, the only assignable species in the reaction mixture is complex **1c** besides decomposition products.

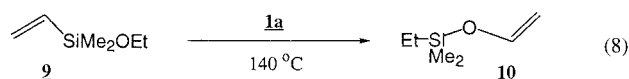
On the basis of the deuterium exchange experiments, the general mechanism of transfer hydrogenation must involve oxidative addition of the C–H bond either α or β to oxygen in **7** to the 16-electron species [C<sub>5</sub>Me<sub>5</sub>Rh(olefin)], migration of the resulting rhodium hydride to the vinyl group, then β-hydride elimination to yield the silyl vinyl ether functionality. This process can occur in an intra- or intermolecular fashion. Scheme 3a illustrates a possible catalytic cycle via an intramolecular mechanism employing the C–H bond β to oxygen (a similar cycle could be written employing the C–H bond α to oxygen). The H/D exchange experiments suggest that at least reactions A, B, and C are reversible.

## Scheme 3



Shown in Scheme 3b is an abbreviated form of the intermolecular mechanism, again employing the  $\beta$ -C-H bond. It is significant to note that the *initial* products of hydrogen transfer are ethyltriisopropoxysilane (**7'**) and a silyl enolate (**7''**) which still possesses a vinyl substituent. While a detailed mechanistic study has not yet been carried out on this hydrogen transfer reaction, we currently favor the intramolecular pathway since (1) spectroscopic evidence ( $^1\text{H}$ ,  $^{13}\text{C}$ ) indicates that **7'** and **7''** are *not* formed at any time during the reaction, (2) the intermolecular transfer hydrogenation using an olefin as hydrogen acceptor and an alkoxy silane was not successful in preliminary experiments using **1a** as a catalyst under these conditions,<sup>56</sup> and (3) the reactivity of the unactivated methyl groups in **7** in the H/D exchange reaction increased compared to methyl groups which require intermolecular activation (see Table 2).

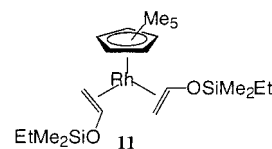
The intramolecular transfer hydrogenation of vinylalkoxysilanes has been extended to other substrates. Reaction of vinyldimethylethoxysilane **9** (2.4 g,  $1.84 \times 10^{-2}$  mol) with **1a** (0.01 g,  $2.3 \times 10^{-5}$  mol) (neat, 140 °C, 72 h) results in quantitative formation of the ethyldimethylsilyl-protected enol of acetaldehyde, **10** (eq 8, 800 total turnovers). Vacuum transfer of **10** away from residual rhodium catalyst results in isolation of analytically pure **10**.



Complex **1b** also can be used to catalyze transfer hydrogenation reactions and, in general, results identical to those obtained

(56) Using *n*-propoxytrimethylsilane as substrate, reactions with norbornene, trimethylvinylsilane, or *tert*-butylethylene using **1a** as a catalyst did not result in the formation of a silyl enolate and hydrogenation products.

with **1a** are observed. When **1b** is treated with **9** (5 equiv) in  $\text{C}_6\text{D}_{12}$  at 90 °C and the reaction is monitored by  $^1\text{H}$  NMR spectroscopy, **10** is formed with an initial turnover frequency of 2 TO/h. In the initial phase of catalysis, **1b** is the only rhodium species present. As catalysis proceeds, a second rhodium complex begins to build up which accounts for 50% of the rhodium complexes after 5% conversion of **9** to **10**. After quantitative conversion of **9** to **10** all rhodium-containing material corresponds to the new species **11**. Isolation of pure samples of this complex has not been possible due to its thermal lability, but spectral data<sup>57</sup> suggest it is the bis-vinyl ether complex, **11**.



The same species is observed when **1b** is thermolyzed in benzene- $d_6$  or acetone- $d_6$  for several hours at 20 °C; however, again the thermal instability of the complex prevents its isolation as a pure compound.

To survey the utility of **1a** as a transfer hydrogenation catalyst, a series of vinylalkoxysilanes was prepared from dimethylvinylchlorosilane and various alcohols and subjected to catalyst **1a**. Results are summarized in Table 4. All reactions were carried out without solvent. Column I describes results using 2 mol % catalyst in 3 h runs at 140 °C, while column II summarizes results of reactions run at 140 °C, 48 h with 0.5 mol % catalyst. Products and isomer ratios were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

Entries 1 and 2 have already been discussed. Using the *n*-butoxy-substituted silane, **12** (entry 3), conversion to the silylvinyl ethers are good (95% in series II) but little selectivity is seen with nearly equal amounts of *E* and *Z* isomers observed. The isobutoxy silane **14** (entry 4) generates not only *E* and *Z* isomers but also regioisomers with little selectivity apparent for activating a methyl vs ethyl group. Yields in series II are 78%; however, under these conditions, all starting material has been consumed. The remainder of the product appears to be derived from C-Si bond cleavage as described above in eq 6.

The comparison of entries 5 and 6 suggests that the  $\beta$ -*tert*-butyl group sterically inhibits C-H bond activation whereas the high yields and quantitative conversion of **18** to **19a,b** (*E*:*Z* of ca. 53:47) indicate that the  $\beta$ -phenyl group activates the  $\beta$ -C-H bond in this case. Conversion of **18** to **19a,b** was followed by  $^1\text{H}$  NMR spectroscopy in cyclohexane- $d_{12}$  at 90 °C with a 20:1 ratio of **18:1a**. After 12 h, 90% conversion to **19** was achieved with an *E*:*Z* ratio for **19a:19b** of 6:1. This result suggests that there is a significant kinetic selectivity for formation of the *E* isomer but that at higher temperatures and longer reaction times *E*/*Z* equilibration occurs (see the Supporting Information). Conversion of substrate **20** bearing an  $\alpha$ -phenyl substituent to the silyl enolate **21** (entry 7) is clean with high conversions (>99% under column II conditions). In the case of **22** (entry 8), yields of transfer hydrogenation products are high (99%, column II) but a mixture of both regio- and stereoisomers are obtained.

The structure of the vinylsilane was varied in a different way with substrate **24**. Catalytic transfer hydrogenation of **24** to **25**

(57) Characteristic for complex **11**:  $^1\text{H}$  NMR 1.65 (s, 15H), 2.57 (dd, 7.2, 2.3 Hz, 2H), 1.55 (dd, 7.2, 2.3 Hz, 2H), 1.22 (ddd, 7.2, 6.0, 2.4 Hz, 2H), -0.04 (s, 3H), 0.28 (s, 3H), -Et resonances obscured;  $^{13}\text{C}$  NMR 101.1 ( $\text{C}_5\text{Me}_5$ ), 52.2 (d, 13.5 Hz,  $\text{H}_2\text{C}=\text{C}$ ), 42.9 (d, 14.1 Hz,  $=\text{CHOSi}$ ), 9.1 ( $\text{C}_5\text{Me}_5$ ), 2.6, 1.8 (-SiMe), 9.85, 6.8 ( $-\text{CH}_2\text{CH}_3$ ).



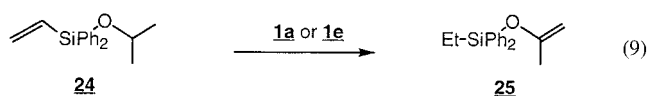
**Table 4.** Catalytic Transfer Hydrogenation of Vinylalkoxysilanes to Vinyl Silyl Ethers<sup>a</sup>

entry	substrate	product	% conversion to vinyl silyl ether product	
			I*	II**
1			> 99	> 99
2			8	95
3			13	41
			17.5	54
4			14, 16	22, 26
			27	30
5			2	0
6			47	47
			53	53
7			69	> 99
8			12, 23	24, 64
			7	11

<sup>a</sup> All reactions run without solvent. \*2% **1a**, 3 h at 140 °C, by NMR. \*\*0.5% **1a**, 48 h at 140 °C, by NMR.

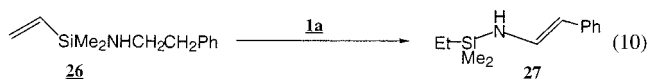
**Table 5.** Experimental Details for X-ray Analyses of **1c** and **6**

	<b>1c</b>	<b>6</b>
mol formula	RhSi <sub>2</sub> C <sub>32</sub> H <sub>63</sub> O <sub>6</sub>	RhC <sub>26</sub> H <sub>51</sub> Si <sub>4</sub>
FW	702.91	578.93
crystal dimensions (mm)	0.40 × 0.20 × 0.15	0.30 × 0.30 × 0.30
no. of reflns for cell	5688	8192
determn		
<i>a</i> (Å)	8.9137(11)	10.9528(5)
<i>b</i> (Å)	13.0204(16)	11.8066(5)
<i>c</i> (Å)	16.9604(21)	12.4378(6)
$\beta$ (deg)	100.845(2)	96.827(1)
<i>V</i> (Å <sup>3</sup> )	1890.2(4)	1565.85(12)
space group	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	2	2
$\mu$ (Mo K $\alpha$ , mm <sup>-1</sup> )	0.55	0.71
<i>F</i> (000)	750.45	614.61
<i>T</i> (°C)	-100	-100
no. of reflns	13301	8855
merging <i>R</i> -value on intens	0.029	0.025
no. of unique reflns	6684	5490
no. of obsns ( <i>I</i> > 3.0 $\sigma$ ( <i>I</i> ))	5212	4347
<i>R</i> <sub>F</sub> <i>R</i> <sub>w</sub>	0.040, 0.046	0.029, 0.054
all reflns: <i>R</i> <sub>F</sub> <i>R</i> <sub>w</sub>	0.051, 0.053	0.034, 0.054
GOF	2.05	1.88



Column I conditions (Table 3) resulted also in >99% conversion to product in both cases. Reactions run at 120 °C for 1 h with 2% catalyst gave with substrate **7** only 5% conversion to **8**, while 10% of **24** was converted to **25**. These preliminary results suggest that the increase in steric bulk at silicon has a small but measurable effect on the rate of the catalytic process.<sup>58</sup>

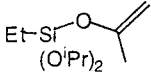
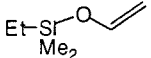
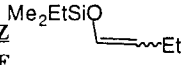
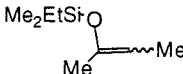
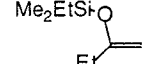
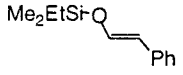
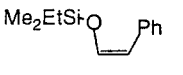
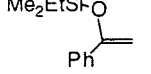
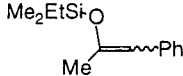
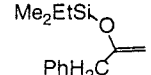
Transfer hydrogenation catalysis of vinyl amino silanes was also briefly examined. Treatment of **26** with **1a** under catalytic conditions (140 °C, 12 h, 0.5 mol % **1a**) results in formation of silyl enamine **27** in 70% yield after 95% conversion of **26** (eq 10). Only a single isomer of **27** is observed, which is assigned



(58) A bis-olefin complex analogous to **1** using triphenylvinylsilyl silane was prepared but not isolated without excess olefin present. This complex is more reactive in catalytic H/D exchange as discussed above due to the increased steric demand.

was observed under standard conditions using either **1a** or **1e** as catalysts (eq 9).

Table 6. NMR Data for Vinyl Silyl Ethers

	<sup>1</sup> H NMR	<sup>13</sup> C NMR
<b>8</b>	 4.04 (s, =CH <sub>2</sub> , 1H); 4.33 (s, =CH <sub>2</sub> , 1H); 4.18 (sep, OCH, 2H); 1.74 (s, -Me, 3H); 1.14 (d, CHMe <sub>2</sub> , 12H); 0.97 (t, -Me, 3H); 0.61 (q, -CH <sub>2</sub> -, 2H).	155.4, 92.4 (OMeC=CH <sub>2</sub> ); 66.2 (OCH); 26.2 (CHMe); 23.1 (Me); 4.62, 7.42 (-Et)
<b>10</b>	 6.65 (dd, 1H); 4.68 (d, 1H); 4.36 (d, 1H); 1.35 (t, 3H); 0.85 (q, 2H); 0.27 (s, 6H);	146.4, 94.8 (OHC=CH <sub>2</sub> ); -2.41 (SiMe <sub>2</sub> ); 6.76, 7.79 (-Et)
<b>13a-Z</b> <b>13b-E</b>	 6.15 (dt, 11 Hz, 1H); 4.97 (dt, 11 Hz, 1H); 1.82 (m, 2H); 0.82 (t, 3H); 0.85 (t, 3H); 0.51 (q, 2H); 0.06 (s, 6H); 6.06 (dt, 7 Hz, 1H); 4.41 (dt, 7 Hz, 1H); 2.10 (m, 2H); 0.89 (t, 3H); 0.82 (t, 3H); 0.50 (q, 2H); 0.05 (s, 6H);	138.3, 137.8, 113.6, 113.2 (E,Z-OHC=CH <sub>2</sub> ); 21.3, 17.6 (E,Z- =HCH <sub>2</sub> -), 15.5, 14.7 (E,Z-CH <sub>3</sub> ); 8.4, 8.3 (E,Z-CH <sub>3</sub> ); 6.8, 6.7 (E,Z-SiCH <sub>2</sub> ); -2.5, -2.7 (E,Z-SiMe <sub>2</sub> );
<b>15a</b> <b>15b</b>	 4.68 (q, 8 Hz, 1H); 4.41 (q, 8 Hz, 1H); 1.68 (d, 3 Hz, 3H); 1.68 (d, 3 Hz, 3H); 1.52 (d, 3H); 1.49 (d, 3H); 0.82, 0.81 (t, 3H); 0.52, 0.51 (q, 2H); 0.11 (s, 6H); 0.11 (s, 6H);	148.7, 147.6, (s, E,Z- =CHMe); 102.6, 101.1 (d, 151 Hz, E,Z-OMeC=); n. a.
<b>15c</b>	 4.04, 4.03 (d, 0.5 Hz, 1H); 1.98 (q, 8 Hz, 2H); 0.95 (t, 3H); 0.83 (t, 3H); 0.50 (q, 2H); 0.05 (s, 6H);	161.3 (s, OEtC=); 88.7 (t, 126 Hz, =CH <sub>2</sub> ); n. a.
<b>19a</b>	 7.02 (d, 16 Hz, 1H); 6.21 (d, 16 Hz, 1H); 7.05 - 7.32 (m, 5H); 0.97 (t, 3H); 0.58 (q, 2H); 0.17 (s, 6H);	142.9 (d, E- OCH=); 113.7 (d, E- =CPhH); 136.8, 129.2, 125.9, 125.6 (-Ph); 8.2 (-Me); 6.7 (Si-CH <sub>2</sub> ); -2.6 (SiMe <sub>2</sub> );
<b>19b</b>	 6.31 (d, 6 Hz, 1H); 5.38 (d, 6 Hz, 1H); 7.18 - 7.25, 7.80 (m, 5H); 1.01 (t, 3H); 0.62 (q, 2H); 0.12 (s, 6H);	140.1 (d, Z- OCH=); 110.1 (d, E- =CPhH); 136.7, 128.4, 125.9, 125.6 (-Ph); 8.1 (-Me); 6.7 (Si-CH <sub>2</sub> ); -2.9 (SiMe <sub>2</sub> );
<b>21</b>	 4.93 (d, 0.5 Hz, 1H); 4.98 (d, 0.5 Hz, 1H); 7.15 - 7.25, 7.70 (m, 5H); 1.11 (t, 3H); 0.71 (q, 2H); 0.22 (s, 6H);	156.4 (s, OCPH=); 91.0 (t, =CH <sub>2</sub> ); 147.0, 128.8, 125.7, 125.6 (-Ph); 8.8 (-Me); 7.0 (Si-CH <sub>2</sub> ); -1.9 (SiMe <sub>2</sub> );
<b>23a</b> <b>23b</b>	 5.44 (s, 1H); 1.88 (s, 3H); 7.10 - 7.30, 7.70 (m, 5H); 0.95 (t, 3H); 0.62 (q, 2H); 0.12 (s, 6H); 5.95 (s, 1H); 1.95 (s, 3H); 7.10 - 7.30, 7.70 (m, 5H); 0.94 (t, 3H); 0.61 (q, 2H); 0.22 (s, 6H);	151.7, 149.3 (s, E,Z-OCMe=); 110.4, 109.3 (d, E,Z- =CHPh); aro. n.a.; 24.3, 19.9 (q, E,Z-Me); 8.8, 9.1 (-Me); 6.9, 7.0 (Si-CH <sub>2</sub> ); -1.7, -1.9 (SiMe <sub>2</sub> );
<b>23c</b>	 4.11 (s, 1H); 4.22 (s, 1H); 3.30 (s, 2H); 7.15 - 7.25, 7.70 (m, 5H); 1.11 (t, 3H); 0.71 (q, 2H); 0.18 (s, 6H);	159.1 (s, OCCH <sub>2</sub> Ph=); 91.3 (t, =CH <sub>2</sub> ); aro. n.a.; 43.8 (t, -CH <sub>2</sub> Ph); 9.4 (-Me); 7.1 (Si-CH <sub>2</sub> ); -1.5 (SiMe <sub>2</sub> );

as the *E* isomer on the basis of the observed 12 Hz coupling between the vicinal olefinic hydrogens ( $\delta$  5.55, 6.72). The remaining 30% of the products are produced from C–Si bond activation as discussed above. Under catalytic conditions analogous to those in series I, Table 3, a 22% yield (42% conversion of **26**) of **27** is obtained.

## Summary

The use of [C<sub>5</sub>Me<sub>5</sub>Rh(olefin)<sub>2</sub>] complexes for catalytic H/D exchange reactions and transfer hydrogenation has been described. Employing bulky olefins that readily dissociate from the Rh(I) center allows facile access to the 16-electron species [C<sub>5</sub>Me<sub>5</sub>Rh(L)] which is capable of C–H bond activation through oxidative addition. Using L = olefin as the ancillary ligand provides a pathway for migratory insertion reactions of the C–H activated substrate and thus catalytic cycles can be closed. The results described here illustrate catalytic H/D exchange reactions in which deuterium can be transferred from deuterated solvents to the bound olefin and, further, can be shuttled to various substrates in solution. Potential utility in synthesis has been demonstrated by constructing a cycle in which, via the C–H bond activation reaction, a catalytic transfer hydrogenation cycle can be established which converts alkyl silyl ethers (readily prepared from alcohols) to silyl vinyl ethers (silyl enolates).

These reactions offer the possibility of synthesis of silyl vinyl ethers under base-free conditions. In addition, since a mild hydrolysis of the vinyl ethers generates ketones or aldehydes, these transformations represent oxidations of alcohols under simple thermal isomerization conditions. The (apparent) intramolecular nature of these reactions has synthetic advantages for selective conversion of alcohols to silyl enolates and selective protection and unmasking of alcohols as the oxidized products.

We are currently exploring more detailed mechanistic aspects of these catalytic transfer hydrogenation reactions and the application of the labile rhodium bis-olefin complexes in other synthetic transformations.

## Experimental Section

**General Considerations.** All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled Vacuum Atmospheres drybox. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to residual <sup>1</sup>H NMR signals and to the <sup>13</sup>C NMR signals of the deuterated solvents, respectively. NMR probe temperatures were measured using an anhydrous ethylene glycol sample. Elemental analyses were performed by Atlantic Microlabs, Inc., of Norcross, GA.

**Materials.** All solvents used for synthesis were deoxygenated and dried via passage over a column of activated alumina.<sup>59</sup> Tetrahydrofuran was distilled from sodium benzophenone–ketyl prior to use. [C<sub>5</sub>Me<sub>5</sub>RhCl<sub>2</sub>]<sub>2</sub> was prepared by following literature procedures.<sup>60</sup> Trimethylvinylsilane, triisopropoxyvinylsilane, dimethylethoxyvinylsilane, bis(trimethylsiloxy)methylvinylsilane, chlorodimethylvinylsilane, and chlorodiphenylvinylsilane are commercially available (Celeste). Benzene-*d*<sub>6</sub>, toluene-*d*<sub>8</sub>, and cyclohexane-*d*<sub>12</sub> were dried over potassium benzophenone–ketyl, chlorobenzene-*d*<sub>5</sub>, and acetone-*d*<sub>6</sub> were dried over CaH<sub>2</sub>, vacuum transferred, and degassed by repeated freeze–pump–thaw cycles.

**Preparation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>SiMe<sub>3</sub>)<sub>2</sub>] (1a).** The precursor [C<sub>5</sub>Me<sub>5</sub>RhCl<sub>2</sub>]<sub>2</sub> (0.4 g, 6.5 × 10<sup>-4</sup> mol) was combined with an excess of zinc powder (~10×, 0.85 g) in a Schlenk flask. To this was added 5–10 mL of tetrahydrofuran and vinyltrimethylsilane (10×, 1.3 g). This reaction mixture was stirred at 20 °C for 12 h. A red-orange homogeneous solution has been generated with only excess zinc powder as the remaining insoluble material. After filtration, the solvent was removed in vacuo and the remaining solids were extracted with pentane until further pentane washings remained colorless. The volatiles of the filtrate were removed, and complex **1a** was obtained as a yellow-orange oil (0.41 g, 72% yield) that solidified in the course of 1 h. This material is pure by NMR and elemental analysis. Recrystallization in acetone at –70 °C results in yellow material which shows only one isomer by NMR spectroscopy: <sup>1</sup>H (400 MHz, 20 °C, acetone-*d*<sub>6</sub>) δ 2.11 (ddd, 10 Hz, 2.4 Hz, 1.6 Hz, 2H), 1.15 (m, 4H), 1.68 (s, 15H), 0.04 (s, 18H); <sup>13</sup>C (100.6 MHz, 20 °C, acetone-*d*<sub>6</sub>) δ 98.2 (C<sub>5</sub>Me<sub>5</sub>), 47.8 (d, 15 Hz, H<sub>2</sub>C=), 45.5 (d, 15 Hz, =CHSi), 9.8 (C<sub>5</sub>Me<sub>5</sub>), 2.2 (–SiMe<sub>3</sub>). Anal. Calcd for C<sub>20</sub>H<sub>39</sub>Si<sub>2</sub>Rh: C, 54.77; H, 8.96. Found: C, 54.88; H, 8.99.

**Preparation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>SiMe<sub>2</sub>OEt)<sub>2</sub>] (1b).** The synthesis follows the general method outlined for the synthesis of **1a**. Complex **1b** was isolated after extraction with pentane and removal of all volatiles as an orange-brown oil. Attempts to crystallize **1b** from pentane or acetone were not successful. Complex **1b** will react at room temperature slowly to generate **11** and deactivation products and its instability precludes elemental analysis: <sup>1</sup>H (300 MHz, 20 °C, C<sub>6</sub>D<sub>12</sub>) δ 2.12 (dd, 11.5 Hz, 2.3 Hz, 2H), 1.05 (m, 4H), 1.66 (s, 15H), 0.16 (s, 6H), 0.10 (s, 6H), 3.61 (q, 15 Hz, 2H), 3.62 (q, 15 Hz, 2H), 1.11 (t, 7.2 Hz, 6H); <sup>13</sup>C (75.5 MHz, 20 °C, C<sub>6</sub>D<sub>12</sub>) δ 97.4 (C<sub>5</sub>Me<sub>5</sub>), 47.9 (d, 13.5 Hz, H<sub>2</sub>C=), 44.2 (d, 13.7 Hz, =CHSi), 9.4 (C<sub>5</sub>Me<sub>5</sub>), 1.00 (–SiMe<sub>3</sub>), 17.9 (–OCH<sub>2</sub>CH<sub>3</sub>), 58.2 (–OCH<sub>2</sub>CH<sub>3</sub>).

**Preparation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>Si(O<sup>i</sup>Pr)<sub>3</sub>)<sub>2</sub>] (1c).** The synthesis follows the general method outlined for the synthesis of **1a**. Complex **1c** was isolated after extraction with pentane and removal of all volatiles as a yellow oil. The material was pure at this stage by elemental analysis; however, NMR spectroscopy showed the presence of one minor isomer. Recrystallization from acetone gave a yellow material which was suitable for X-ray crystallography and showed one isomer by NMR analysis. In the solid form **1c** was stored at 20 °C under argon. Complex **1c** will react in solution at room temperature slowly to generate a mixture of isomers and eventually olefin **8** and decomposition products: <sup>1</sup>H (300 MHz, 20 °C, C<sub>6</sub>D<sub>12</sub>) δ 3.23 (d, 18 Hz, 1H), 2.11 (d, 18 Hz, 1H), 2.01 (d, 15 Hz, 1H), 1.88 (d, 15 Hz, 1H), 0.66 (dd, 18, 15 Hz, 1H), 0.48 (dd, 15, 18 Hz, 1H), 4.22 (spt, 6 Hz, 3H), 4.32 (spt, 6 Hz, 3H), 1.72 (s, 15 H), 1.10–1.21 (–CHMe<sub>2</sub>, d, 6 Hz, 36H); <sup>13</sup>C (75.5 MHz, 20 °C, C<sub>6</sub>D<sub>12</sub>) δ 97.4 (d, 4.2 Hz, C<sub>5</sub>Me<sub>5</sub>), 49.1 (d, 13.6 Hz), 48.6 (d, 13.1 Hz), 39.5 (d, 14.3 Hz), 34.5 (d, 16.6 Hz), 65.0 (s, OCH), 65.2 (s, OCH), 25.9, 26.0, 26.1, 26.2, 26.2 (overlapping –CHMe<sub>2</sub>), 9.8 (C<sub>5</sub>Me<sub>5</sub>). Anal. Calcd for C<sub>32</sub>H<sub>63</sub>O<sub>6</sub>Si<sub>2</sub>Rh: H, 9.03; C, 54.68. Found: H, 8.98; C, 54.87.

**Preparation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>SiMe(OSiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] (1d).** The synthesis follows the general method outlined for the synthesis of **1a**. Complex **1d** was isolated after extraction with pentane and removal of all volatiles as an orange-red oil. Attempts to crystallize **1d** from pentane or acetone were not successful. NMR data for the major isomer: <sup>1</sup>H (300 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 1.96 (dd, 12 Hz, 4 Hz, 2H), 1.35 (d, 15 Hz, 2H), 0.91 (dd, 12 Hz, 15 Hz, 2H), 1.57 (s, 15H), 0.28 (s, 18H), 0.29

(s, 18H), 0.38 (s, 6H); <sup>13</sup>C (75.5 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 97.5 (d, 4 Hz, C<sub>5</sub>Me<sub>5</sub>), 9.5 (C<sub>5</sub>Me<sub>5</sub>), 3.0 (–SiMe), 2.3, 2.3 (–OSiMe<sub>3</sub>), 48.0 (d, 11.6 Hz), 43.4 (d, 13.6 Hz).

**Preparation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>SiPh<sub>2</sub>O<sup>i</sup>Pr)<sub>2</sub>] (1e).** The synthesis follows the general method outlined for the synthesis of **1a**. Complex **1e** was isolated after extraction with pentane and removal of all volatiles as an orange-red oil. Attempts to crystallize **1e** from pentane or acetone were not successful. Complex **1e** contained usually small amounts of additional vinylsilane. Column chromatography at low temperatures was not successful to remove excess olefin; decomposition was observed. Complex **1e** was isolated as an orange-red semisolid. Further reactivity at 20 °C to generate **26** is slow and allowed characterization by NMR spectroscopy: <sup>1</sup>H (300 MHz, 20 °C, acetone-*d*<sub>6</sub>) δ 3.36 (d, 11.2 Hz, 1H), 2.45 (d, 14.8 Hz, 1H), 2.40 (d, 11.5 Hz, 1H), 2.05 (d, 15 Hz, 1H), 1.36 (dd, 11.8, 15 Hz, 1H), 0.66 (dd, 11, 15 Hz, 1H), 1.08 (m, 6H), 0.90 (m, 6H), 1.58 (s, 15H), 4.13 (m, 1H), 4.02 (m, 1H), 7.89 (m, 2H), 7.76 (m, 4H), 7.58 (m, 2H), 7.40 (m, 12H); <sup>13</sup>C (75.5 MHz, 20 °C, acetone-*d*<sub>6</sub>) δ 98.1 (d, 4.5 Hz, C<sub>5</sub>Me<sub>5</sub>), 8.9 (C<sub>5</sub>Me<sub>5</sub>), 66.2, 65.8 (–CHMe<sub>2</sub>), 25.3 (–CHMe<sub>2</sub>), 47.8 (d, 13.3 Hz), 47.0 (d, 17.8 Hz), 42.4 (d, 14.4 Hz), 37.3 (d, 16.2 Hz), 138.9, 138.5, 138.2, 137.6, 135.2, 135.1, 135.0, 134.9, 129.4, 129.3, 129.2, 129.0, 127.6, 127.5, 127.4, 127.3 (s, aromatic). Anal. Calcd for C<sub>44</sub>H<sub>55</sub>O<sub>2</sub>Si<sub>2</sub>Rh: H, 7.15; C, 68.89. Found: H, 7.26; C, 69.05.

**Preparation of 6.** Complex **6** was prepared by heating a solution of **1a** (0.06 g, 1.4 × 10<sup>-4</sup> mol) and 10 equiv of vinyltrimethylsilane in 1 mL of cyclohexane for 2 weeks at 140 °C in a glass tube with Teflon plug. The volatiles were removed in vacuo, and the residue was dissolved in acetone. The reaction mixture was cooled to –20 °C. Orange crystalline material was isolated which was suitable for X-ray analysis: <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 1.92 (s, 15H), 1.22 (s, 1H), 0.18 (s, 3H), 0.37 (s, 3H), 0.19 (s, 9H), 0.21 (s, 9H), 0.23 (s, 9H), 4.69 (d, 16 Hz, 1H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 94.8 (d, 6 Hz, C<sub>5</sub>Me<sub>5</sub>), 11.9 (s, C<sub>5</sub>Me<sub>5</sub>), 11.2, 2.1, 1.3 (s), 3.7, 0.5, –1.1 (s, –SiMe<sub>3</sub>), 45.0 (d, 18 Hz), 43.5 (d, 15 Hz), 87.7 (d, 6 Hz), 90.0 (d, 9 Hz).

**X-ray Structure Determination of 1c and 6.** Data were collected on a Siemens SMART diffractometer, using the ω-scan technique. The structures were solved by direct methods. Refinement was done by full-matrix least squares with weights based on counter statistics. All non-hydrogen atoms were refined anisotropically, while H atoms were refined using a riding model. Crystal data and collection parameters are given in Table 2. All computations were performed using the NRCVAX suite of programs.<sup>61</sup>

**Preparation of Vinylalkoxysilanes.** The substrates triisopropoxyvinylsilane and dimethylethoxyvinylsilane are commercial and were used as received. The general procedure for the synthesis of vinylalkoxysilanes is analogous to the synthesis described below for *n*-butoxydimethylvinylsilane.

*n*-Butanol (5 g, 0.067 mol) was added to 30 mL of tetrahydrofuran and the mixture cooled to 0 °C. To this was added slowly a 2.5 M solution of *n*-butyllithium in hexanes (27 mL). The THF solution was stirred for 1 h while warming to 20 °C. To this was added slowly over the course of 1 h vinyldimethylchlorosilane (8.1 g, 0.067 mol). Close to complete addition a white precipitate formed. The mixture was stirred for 8–12 h and filtered, and the tetrahydrofuran was removed in vacuo to leave a colorless oil that was further purified by distillation. All vinylalkoxysilanes used here were prepared in this manner and were pure by NMR spectroscopy and elemental analysis.

***n*-BuOSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (12):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 5.84, 6.03, 6.20 (dd, –CH=CH<sub>2</sub>, 3H), 3.63 (t, –OCH<sub>2</sub>–, 2H), 1.57 (m, 2H), 1.44 (m, 2H), 0.95 (t, –CH<sub>3</sub>, 3H), 0.26 (s, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 138.6, 132.8 (–CH=CH<sub>2</sub>), 62.5 (–OCH<sub>2</sub>–), 35.2, 19.3, 14.0 (–C<sub>3</sub>H<sub>7</sub>), –2.0 (–SiMe<sub>2</sub>). Anal. Calcd: H, 11.46; C, 60.69. Found: H, 11.64; C, 60.62.

**EtMeCHOSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (14):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 5.60, 5.82, 5.95 (dd, –CH=CH<sub>2</sub>, 3H), 3.58 (m, –OCH, 1H), 1.25 (m, 2H), 0.95 (d, 3H), 0.73 (t, –CH<sub>3</sub>, 3H), 0.15 (s, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 139.6, 133.0 (–CH=CH<sub>2</sub>), 70.5 (–OCH–), 33.1, 24.0, 10.6 (–Me, –Et), –2.9 (–SiMe<sub>2</sub>). Anal. Calcd: H, 11.46; C, 60.69. Found: H, 11.59; C, 60.71.

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***t*-BuCH<sub>2</sub>CH<sub>2</sub>OSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (16):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 5.80, 6.03, 6.20 (dd, -CH=CH<sub>2</sub>, 3H), 3.68 (t, -OCH<sub>2</sub>-, 2H), 1.55 (t, -CH<sub>2</sub>-, 2H), 0.94 (s, 9H), 0.20 (s, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 138.5, 132.7 (-CH=CH<sub>2</sub>), 60.0 (-OCH<sub>2</sub>-), 46.5 (-CH<sub>2</sub>-), 29.8 (-CMe<sub>3</sub>), -2.0 (-SiMe<sub>2</sub>). Anal. Calcd: H, 11.90; C, 64.45. Found: H, 11.87; C, 63.50.

**PhCH<sub>2</sub>CH<sub>2</sub>OSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (18):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 7.15–7.13 (m, -Ph, 5H), 5.80, 6.01, 6.17 (dd, -CH=CH<sub>2</sub>, 3H), 3.81 (t, -OCH<sub>2</sub>-, 2H), 2.86 (t, Ph-CH<sub>2</sub>-, 2H), 0.19 (s, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 139.4, 133.0 (-CH=CH<sub>2</sub>), 137.9, 129.4, 128.5, 126.4 (-Ph), 64.3 (-OCH<sub>2</sub>-), 39.8 (-CH<sub>2</sub>-), -2.0 (-SiMe<sub>2</sub>). Anal. Calcd: H, 8.79; C, 69.84. Found: H, 8.86; C, 70.00.

**PhCHMeOSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (20):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 7.11–7.25, 7.32 (m, -Ph, 5H), 5.84, 6.03, 6.20 (dd, -CH=CH<sub>2</sub>, 3H), 4.88 (q, -OCHMe-, 1H), 1.42 (d, 3H), 0.19 (s, 3H), 0.15 (s, 3H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 138.2, 132.8 (-CH=CH<sub>2</sub>), 137.9, 128.5, 127.3, 125.8 (-Ph), 71.0 (-OCHMe-), 27.5 (-CH<sub>3</sub>), -1.4, -1.6 (-SiMe<sub>2</sub>). Anal. Calcd: H, 8.79; C, 69.84. Found: H, 8.84; C, 69.93.

**PhCH<sub>2</sub>CHMeOSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (22):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 7.08–7.32 (m, Ph, 5H), 5.84, 5.95, 6.15 (dd, -CH=CH<sub>2</sub>, 3H), 3.95 (m, -OCH-, 1H), 2.58–2.77 (m, -CH<sub>2</sub>, 2H), 1.17 (d, -Me, 3H), 0.18 (s, 3H), 0.08 (s, 3H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 139.8, 130.1, 128.5, 126.5 (-Ph), 138.6, 132.7 (-CH=CH<sub>2</sub>), 70.5 (-OCH-), 46.8 (-CH<sub>2</sub>), 24.1 (-CH<sub>3</sub>), -1.6, -1.8 (-SiMe). Anal. Calcd: H, 9.15; C, 70.85. Found: H, 9.26; C, 71.12.

**Me<sub>2</sub>CHOSiPh<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (24):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 7.22 (m, 4H), 6.71 (m, 6H), 5.43, 5.62, 6.05 (dd, -CH=CH<sub>2</sub>, 3H), 3.65 (m, -OCH-, 1H), 0.71 (d, -Me, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 135.5, 135.0, 128.1 (-Ph), 136.6, 130.1 (-CH=CH<sub>2</sub>), 66.3 (-OCH-), 25.9 (-Me). Anal. Calcd: H, 7.51; C, 76.07. Found: H, 7.61; C, 75.92.

**PhCH<sub>2</sub>CH<sub>2</sub>NHSiMe<sub>2</sub>C<sub>2</sub>H<sub>3</sub> (26):** <sup>1</sup>H (400 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 7.28–7.45 (-Ph, 5H), 5.90, 6.12, 6.35 (dd, -CH=CH<sub>2</sub>, 3H), 3.19 (q, -NHCH<sub>2</sub>-, 2H), 2.83 (m, 2H), 0.72 (t, broad, 1H), 0.29 (s, 6H); <sup>13</sup>C (100.6 MHz, 20 °C, C<sub>6</sub>D<sub>6</sub>) δ 140.7, 129.4, 128.7, 126.4 (-Ph), 139.9, 131.8 (-CH=CH<sub>2</sub>), 44.1 (-NHCH<sub>2</sub>-), 41.9 (-CH<sub>2</sub>-), -1.3 (-SiMe<sub>2</sub>). Anal. Calcd: H, 9.32; C, 70.18. Found: H, 9.48; C, 70.37.

**Hydrogen–Deuterium Exchange Reactions.** All H/D exchange reactions were conducted in purified, degassed solvents in either sealed NMR tubes (J-young tubes) or thick-walled Kontes flasks sealed with Teflon screw caps. All conditions are clearly indicated in the text and Tables 1–3. Samples were monitored by both <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies. When necessary, internal sealed capillaries containing ferrocene were used as integration standards.

**Procedure for Catalytic Transfer Hydrogenation.** Complex **1a** (0.01 g, 2.3 × 10<sup>-5</sup> mol) was dissolved in the appropriate amount of neat alkoxyvinylsilane (see Table 4, I and II), which was added by weight in a drybox. The vessel was closed with a Teflon plug and the reaction mixture heated to 140 °C for the indicated time in an oil bath. The solutions remained yellow-orange and homogeneous throughout the reaction. After being cooled to room temperature, the vessel was opened and the product analyzed directly by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In all cases, with the exception of **15** (see text), NMR analysis showed only the presence of starting material and silyl enolate(s) and traces of catalyst. Conversions of 95–99% were observed using column II, Table 4 conditions for **8**, **10**, **13**, **19**, **21**, and **23**. Vacuum transfer allowed easy separation from catalyst and access to rhodium-free silyl enolates.

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**Supporting Information Available:** Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1c** and **6**, kinetic plots for H/D exchange of **1a**, spectra for deuteration of **1c**, and catalytic analysis of transfer hydrogenation (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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