Kinetic Study of the Hydrosilylation of Acetophenone by [Rh(cod)Cl]$_2$/(*R*)-BINAP

Clementina Reyes, Alfred Prock,* and Warren P. Giering*

Department of Chemistry, Metcalf Science and Engineering Center, Boston University, Boston, Massachusetts 02215

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The [Rh(cod)Cl]$_2$/(*R*)-BINAP catalyzed hydrosilylation reaction between acetophenone and H_2SiPh_2, H_2SiEt_2, H_2SiBu_2, $HSiBu_3$, $HSiPh_3$, and $HSi(p\text{-}F_3CC_6H_4)_3$ in benzene-d_6 at 63 °C has been studied by ^{1}H NMR spectroscopy, GC/MS, and H/D exchange experiments with acetophenone-d_6. The reactions afford varying amounts of $PhCH(OSiZ_3)Me$ (**3**), $PhC(OSiZ_3)=CH_2$ (**4**), and PhCH(OH)Me (**5**). The product distribution of the reaction is dependent on the order of mixing for the secondary silanes but independent of the order of mixing for tertiary silanes. The product distributions and initial rates of reaction of the tertiary silanes, which react more slowly than the secondary silanes, are dependent on the stereoelectronic properties of the silane, with $HSi(p\text{-}F_3CC_6H_4)_3$ being 10 times more reactive than $HSiPh_3$. The reaction involving $HSiBu_3$ is first order in the initial concentration of [Rh(cod)Cl]$_2$/(*R*)-BINAP as well as the concentration of $HSiBu_3$ but shows a saturation effect at high concentrations of acetophenone. In the earliest phases of the reaction, the coordinated cyclooctadiene is liberated and converted to cyclooctane and cyclooctene. The requisite hydrogens for the hydrogenation process come mainly from $HSiBu_3$. The products **4** and **5** appear to be formed independently of the formation of **3**. The catalysts for the formation of **4** and **5** appeared to decay, thereby abruptly terminating the formation of these materials after about 40% of the acetophenone had been consumed. Simulation of the kinetic results, based on the Ojima mechanism, qualitatively fits the production of **3**.

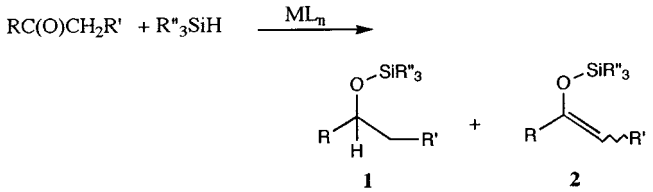
Introduction

The catalytic hydrosilylation of ketones and aldehydes, which leads directly to silylated (protected) alcohols, is a useful synthetic alternative to the reduction of the carbonyl group by main-group hydrides and catalytic hydrogenation.[1,2] Although the reaction normally gives the saturated silyl ether **1** as the major product, it often gives variable amounts of the silyl enol ether **2** (Scheme 1).[1] The asymmetric version of the catalytic hydrosilylation of prochiral ketones can give poor to excellent stereoselectivity, depending on the nature of the metal, chiral ligand, silane, and carbonyl compound.[2]

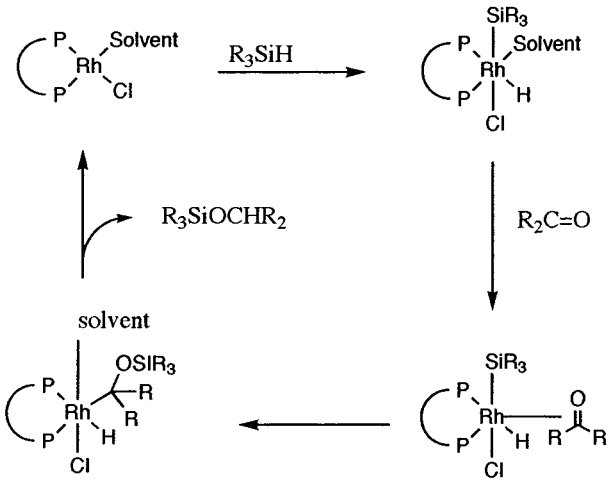
This is a technically attractive reaction, since it does not require high pressure or temperature. It is chemically attractive because many aspects of the reaction may be probed by systematically varying the components (metal, chiral ligand, silane, and ketone) of the reaction.

Although this reaction has been around for decades, there have been few investigations of its mechanism. The most commonly accepted mechanism was proposed by Ojima nearly 30 years ago (Scheme 2).[3] Kolb and

Scheme 1



Scheme 2



Hetflejs'[4] kinetic study of the hydrosilylation of *tert*-butyl phenyl ketone by diphenylsilane using [{Rh((−)-diop)}]$^+ClO_4^-$ largely supports the Ojima mechanism.

(1) Ojima, I. *The Hydrosilylation Reaction: The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1479.
(2) Ojima, I.; Li, Z.; Zhu, J. *Recent Advances in the Hydrosilylation and Related Reactions: Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 1687.
(3) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, Y. *J. Organomet. Chem.* **1976**, *122*, 83.

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Table 1. Effect of the Order of Addition of Reactants on the Initial Rates of Formation of PhCH(OSiZ$_3$)Me (3), PhC(OSiZ$_3$)=CH$_2$ (4), and PhCH(OH)Me (5) and Their Respective Product Distributions for the Hydrosilylation of Acetophenone Using Secondary and Tertiary Silanes at 63 °C[a]

				yield (%)				init rate of formation[e]		
no.	silane[b]	SiZ$_3$	order of addition	PhC(O)Me (residual)	**3**	**4**	**5**	**3**	**4**	**5**
1	H_2SiPh_2	$HSiPh_2$	*c*	0	90	10	0			
2	H_2SiEt_2	$HSiEt_2$	*c*	0	85	15	0			
3	H_2SiBu_2	$HSiBu_2$	*c*	0	89	11	0			
4	H_2SiPh_2	$HSiPh_2$	*d*	0	19	81	0			
5	H_2SiEt_2	$HSiEt_2$	*d*	0	52	48	0			
6	H_2SiBu_2	$HSiBu_2$	*d*							
7	$HSiBu_3$	$SiBu_3$	*c*	4	86	7	3	0.162	0.113	0.099
8	$HSiPh_3$	SiPh3	*c*	2.7	93	4.4	0	0.59		0
9	HSi(*p*-$F_3CC_6H_4)_3$	Si(*p*-$F_3CC_6H_4)_3$	*c*	1	98	<1	0	3.513	0.019	0
10	$HSiBu_3$	$SiBu_3$	*d*	7	82	7	4	0.182	0.197	0.166
11	$HSiPh_3$	$SiPh_3$	*d*	8.8	90	1.2	0	0.35		0
12	HSi(*p*-$F_3CC_6H_4)_3$	Si(*p*-$F_3CC_6H_4)_3$	*d*	2	97	<1	0	3.631	0.023	0

[a] The solvent was benzene-d_6. [b] For all these experiments the initial concentration of (*R*)-BINAP, silane, acetophenone, and [Rh(cod)Cl]$_2$ were 0.0041, 0.820, 0.410, and 0.0041 M, respectively. [c] The order of addition was (*R*)-BINAP, silane, acetophenone, and then [Rh(cod)Cl]$_2$. [d] The order of addition was (*R*)-BINAP, silane, [Rh(cod)Cl]$_2$, and then acetophenone. [e] In units of M d^{-1}.

Significantly, they observed a saturation effect as the concentration of the ketone was increased. In their view, this observation suggested that prior to the oxidative addition of the silane (Scheme 2) there is reversible complexation of the ketone that deactivates the rhodium. Waldman et al. also observed that the rate of hydrosilylation of 2,2-dimethylcyclopentanone with Rh(diphos)(PPh$_3)_2^+$(PF$_6^-$ or BF$_4^-$) is first order in both silane and catalyst but is independent of ketone concentration for [ketone] > 0.5 M.[5] They suggested that the ketone adds to the rhodium before the oxidative addition of the silane. Zheng and Chan studied the rhodium-catalyzed hydrosilylation of α,β-unsaturated carbonyl compounds. They concluded that the Ojima mechanism could not account for their observation that tertiary silanes give 1,2-addition, whereas primary and secondary silanes give 1,4-addition.[6] They also observed a small kinetic isotope effect, suggesting that the rate-determining step is the coordination of the ketone with a silylhydridorhodium species.

We became interested in this reaction as a model for testing our idea that asymmetric catalytic reactions can be tuned in terms of rate, product distribution, and stereoselectivity by rational manipulation of the structure of the spectator ligands and the silanes in the hydrosilylation reaction. Furthermore, we desire ultimately to test the idea that the results of these experiments can be analyzed by means of the QALE model[7,8] (quantitative analysis of ligand effects). We began our studies by examining the factors that influence the product distribution and rates of the hydrosilylation of acetophenone by various silanes in the presence of [Rh(cod)Cl]$_2$/(*R*)-BINAP. Herein, we report the results of this study. In later papers, we will describe our studies on how the enantioselectivity of the hydrosilylation of acetophenone is influenced by variations in the chiral ligand, the stereoelectronic properties of the silanes, and the role of additives.

Experimental Section

Kinetic Studies. Hydrosilylation studies were carried out at 63 °C on benzene-d_6 samples of mixtures of [Rh(cod)Cl]$_2$,[9] (*R*)-BINAP (Aldrich, used as purchased), freshly distilled $HSiBu_3$ (Aldrich), and freshly distilled acetophenone (Aldrich). Acetophenone-d_3 (Aldrich) was used as purchased. The orders of addition and the concentrations of the reactants for the various experiments are presented in Table 1. Samples were prepared by adding the reactants sequentially and freeze−thaw degassing the samples after each addition. Finally, the samples were transferred to an NMR tube, which was freeze−thaw degassed and sealed under vacuum. Dry ice/acetone was used in the freeze−thaw process. In all cases, the sample was allowed to stand at room temperature for 1 h before adding final reactant. The progress of the reactions was monitored by observing the disappearance of the starting materials and appearance of products by ^{1}H NMR spectroscopy. Integrations were measured relative to 7 μL of trichloroethylene in a sealed 10 μL pipet capillary (Drummond Scientific). When $HSiBu_3$ (or acetophenone) was in excess, we monitored the disappearance of acetophenone (or $HSiBu_3$). The reaction was monitored every 1 h for the first 10 h of the reaction and then every 12 h until there was no observable change. The initial rates of the various reactions are presented in Table 1.

The time dependencies of the concentrations of the reactants and products of the various reactions are displayed in the tables in the Supporting Information. GC/MS experiments were performed on a GCD series gas chromatograph equipped with a Supelco column (2-4205-u) and an electron ionization detector.

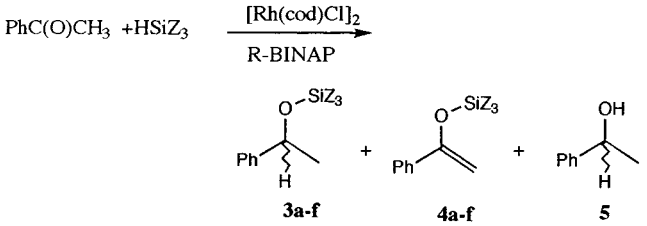
Simulations. Computer simulations are based on Scheme 5. The rate constants that gave the best fit are shown in the text. The code is presented in the Supporting Information.

Results

We have studied the [Rh(cod)Cl]$_2$/(*R*)-BINAP catalyzed hydrosilylation of acetophenone with various secondary and tertiary silanes (Scheme 3). The reactions were run in benzene-d_6 at 63 °C and were followed by ^{1}H NMR spectroscopy. The reactions with the secondary silanes were too fast to obtain kinetic data under these conditions. The reactions with the tertiary silanes were considerably slower and were followed for up to 30 days. The reactions afford varying amounts of PhCH(OSiZ$_3$)Me (**3**), PhC(OSiZ$_3$)=CH$_2$ (**4**), and PhCH(OH)Me (**5**). The

(4) Kolb, I.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2808.
(5) Waldman, T. E.; Schaefer, G.; Riley, D. P. *ACS Symp. Ser.* **1993**, *No. 517*, 58.
(6) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70.
(7) See www.bu.edu/qale for a detailed discussion of the QALE model.
(8) Woska, D.; Prock, A.; Giering, W. P. *Organometallics* **2000**, *19*, 4629.
(9) Crabtree, R. H.; Giordano, G. *Inorg. Synth.* **1976**, *19*, 218.

Scheme 3[a]



[a] Legend: (a) $SiZ_3 = SiHPh_2$; (b) $SiZ_3 = SiHEt_2$; (c) $SiZ_3 = SiHBu_2$; (d) $SiZ_3 = SiBu_3$; (e) $SiZ_3 = SiPh_3$; (f) $SiZ_3 = Si(p\text{-}F_3CC_6H_4)_3$.

Scheme 4

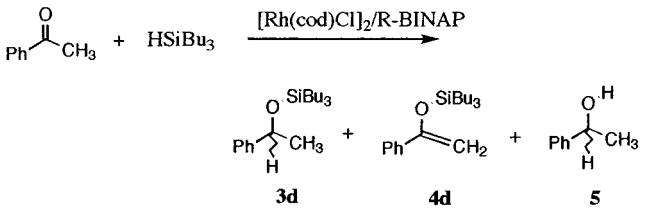


Table 2. Initial Concentrations[a] of (*R*)-BINAP, $HSiBu_3$, Acetophenone, and Rh (from $[Rh(cod)Cl]_2$) Used to Examine the Factors that Influence the Rates of Hydrosilylation of Acetophenone

no.	10^3[(*R*)-BINAP]	10[$HSiBu_3$]	10[acetophenone]	10^3[Rh]
	Variation of [(*R*)-BINAP]			
1	0.00	8.20	4.10	4.10
2	4.10	8.20	4.10	4.10
3	5.00	8.20	4.10	4.10
4	5.80	8.20	4.10	4.10
5	6.60	8.20	4.10	4.10
	Variation of [Rh]			
6	4.10	8.20	4.10	4.10
7	4.10	8.20	4.10	9.02
8	4.10	8.20	4.10	12.3
	Variation of [Rh] and [(*R*)-BINAP]			
9	4.10	8.20	4.10	4.10
10	7.30	8.20	4.10	7.30
11	8.90	8.20	4.10	8.90
12	20.5	8.20	4.10	20.5
	Variation of $HSiBu_3$			
13	4.10	4.10	4.10	4.10
14	4.10	6.15	4.10	4.10
15	4.10	8.20	4.10	4.10
16	4.10	12.30	4.10	4.10
	Variation of [acetophenone]			
17	4.10	4.10e−1	4.10	4.10
18	4.10	4.10e−1	6.15	4.10
19	4.10	4.10e−1	8.20	4.10
20	4.10	4.10e−1	20.5	4.10

[a] In units of mol L^{-1}. [b] All solutions were prepared by mixing the reactants in the following order: (*R*)-BINAP, $HSiBu_3$, and acetophenone, and then after 1 h $[Rh(cod)Cl]_2$ was added.

reactions with secondary silanes afford distributions of products that are dependent on the order of mixing of the reagents and the structure of the secondary silane. For example, H_2SiPh_2 gave an 81% yield of $PhC(OSiHPh_2)=CH_2$ (**4a**; see Scheme 3 for the numbering system) when acetophenone was added last and a 90% yield of $PhCH(OSiHPh_2)Me$ (**3a**) when $[Rh(cod)Cl]_2$ was added last. In contrast, H_2SiEt_2 gave a 48% yield of $PhC(OSiHEt_2)=CH_2$ (**4b**) when acetophenone was added last and a 85% yield of $PhCH(OSiHEt_2)Me$ (**3b**) when $[Rh(cod)Cl]_2$ was added last. Similar results were reported by Waldman et al.[5]

Table 3. Effect of the Initial Concentration of Reactants on Product Distributions and Initial Rates of the $[Rh(cod)Cl]_2$/(*R*)-BINAP Catalyzed Reaction between Acetophenone and $HSiBu_3$[a]

	PhC(O)Me	yield[b]			init rate of formation[c]		
no.[d]	(residual)	**3d**	**4d**	**5**	**3d**	**4d**	**5**
	Variation of [(*R*)-BINAP]						
1	37	62	<1	<1	0.037	0.035	0.035
2	4	86	7	3	0.162	0.113	0.099
3	3	92	3	2	0.176	0.092	0.132
4	19	75	3	3	0.203	0.054	0.152
5	27	69	<1	4	0.200	0.026	0.160
	Variation of [Rh]						
6	4	86	7	3	0.162	0.113	0.099
7	6	79	14	1	0.149	0.129	0.053
8	6	76	18	<1	0.127	0.132	0.032
	Variation of [Rh] and [(*R*)-BINAP]						
9	4	86	7	3	0.309	0.113	0.099
10	6	83	9	2	0.923	0.338	0.189
11	5	85	9	1	1.294	0.393	0.274
12	2	88	10	<1	2.433	0.611	0.355
	Variation of [$HSiBu_3$]						
13	19	73	4	4	0.069	0.043	0.055
14	16	73	8	3	0.119	0.097	0.083
15	4	86	7	3	0.162	0.113	0.099
16	5	81	8	6	0.261	0.204	0.196
	Variation of [acetophenone]						
17	19	73	4	4	0.069	0.043	0.055
18	21	68	7	4	0.087	0.094	0.100
19	16	71	9	4	0.100	0.105	0.127
20	6	79	8	7	0.141	0.070	0.143

[a] Reactants were added as follows: R−BINAP, Bu_3SiH, and ketone, and then after 1 h $[Rh(cod)Cl]_2$ was added. [b] Percentages are based on the initial concentration of acetophenone. [c] In units of mol L^{-1} d^{-1}. [d] Entry numbers correspond to those in Table 2.

On the other hand, the initial rates of reaction and distributions of products are independent of the order of mixing of the reactants when tertiary silanes are used. The product distributions and initial rates are dependent on the stereoelectronic properties of the tertiary silanes. For example, $HSi(p\text{-}F_3CC_6H_4)_3$ is 10 times more reactive than $HSiPh_3$. In terms of product distribution, both triarylsilanes give almost exclusively **3e** and **3f**, whereas $HSiBu_3$ gives a mixture of **3d**, **4d**, and **5**.

Kinetic and H/D Exchange Studies Involving $HSiBu_3$. For the remainder of the study, we focused on the hydrosilylation of acetophenone with $HSiBu_3$ (Scheme 4). The reactions with $HSiBu_3$ were run in benzene-d_6 at 63 °C in the presence or absence of the chiral diphosphine ligand (*R*)-BINAP and with varying initial concentrations of $[Rh(cod)Cl]_2$, (*R*)-BINAP, $HSiBu_3$, and acetophenone. The progress of each reaction was monitored by ^1H NMR spectroscopy. When the silane was in excess, we followed the consumption of the ketone, whereas when the ketone was in excess, we followed the consumption of the silane. In all of the reactions we observed the formation of $PhCH(OSiBu_3)Me$ (**3d**) and $PhC(OSiBu_3)=CH_2$ (**4d**) as well as of PhCH(OH)Me (**5**) (Scheme 4). The sequence of loading the reactants and catalyst made no difference in the initial rate of reaction or the product distribution. The reactions with $HSiBu_3$ were followed for 20−30 days. The results of a typical experiment (entry 2, Tables 2 and 3) are displayed in Figure 1, where we show the time dependence of the concentrations of the products and the reactant. After a short induction period, we observed the consumption of acetophenone and $HSiBu_3$ and the concomitant

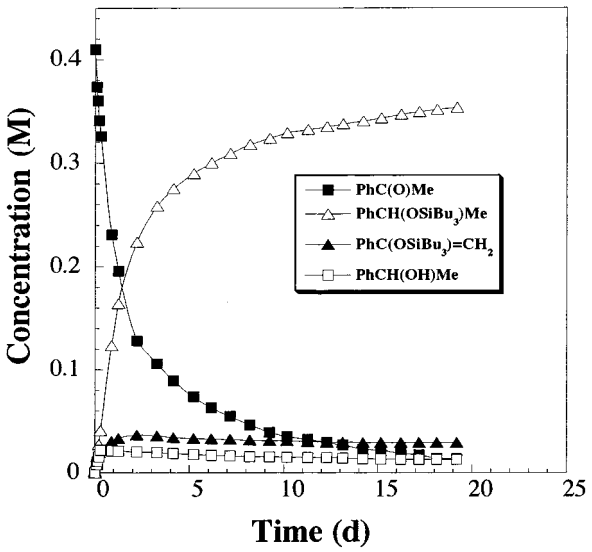


Figure 1. Plots of the concentrations of acetophenone, **3d**, **4d**, and **5** versus time for the experiment described in entry 2 of Tables 2 and 3. Data are taken from the data in the Supporting Information.

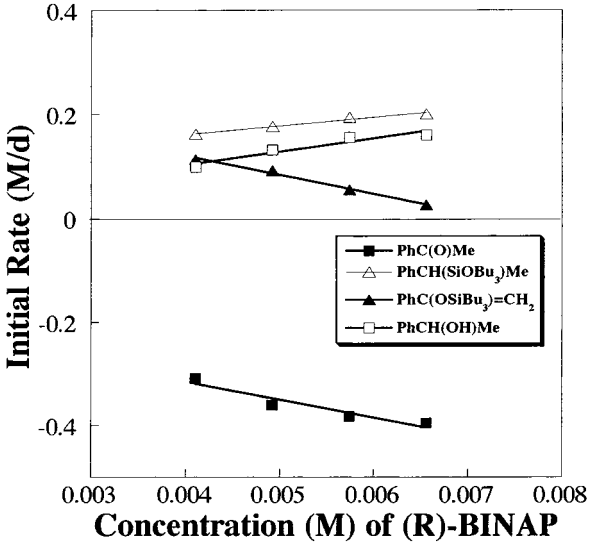


Figure 2. Plot of the initial rates of reaction versus the initial concentration of (*R*)-BINAP. The initial concentrations of other reactants were constant.

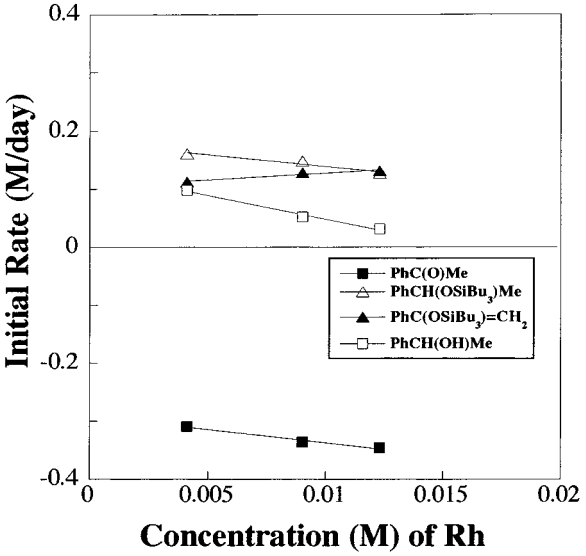


Figure 3. Plot of the initial rates of reaction versus the initial concentration of rhodium. The initial concentrations of other reactants were constant.

formation of **3d**, **4d**, and **5**. Surprisingly, **4d** and **5** were formed almost as rapidly as **3d** during the initial phase of the reaction, but after the consumption of about 40% of the ketone the concentrations of **4d** and **5** reached a maximum and then remained almost constant over the duration of the experiment. After several days a small amount of particulate matter was observed. At the end of about 20 days an 86% yield of **3d** was realized along with 7% and 3% yields of **4d** and **5**, respectively. In addition, we found that approximately 50% of the cyclooctadiene (from $[Rh(cod)Cl]_2$) was converted to cyclooctane. This result is confirmed by GC/MS analysis, which also revealed that about 25% of the cyclooctadiene was converted to cyclooctene. The fate of the remainder of the cyclooctadiene is unknown. Examination of the NMR spectrum, consideration of the mass balance, and GC/MS analysis also revealed that there was no H/D exchange between the solvent, benzene-d_6, and any of the reactants or products.

We examined the effect of varying the concentrations of the various reactants on the product distributions and initial rates of reaction. These data are presented in Tables 2 and 3.

Hydrosilylation in the Absence and Presence of (*R*)-BINAP. In the first experiment, we looked at the reaction in the absence and presence of (*R*)-BINAP while keeping the initial concentrations of the other reactants constant (entries 1 and 2 in Tables 2 and 3). In the absence of (*R*)-BINAP (entry 1, Tables 1 and 2), the reaction with $HSiBu_3$ was very slow, forming in 62 days a 62% yield of **3d** and less than 1% yields of **4d** and **5**. In contrast, in the presence of (*R*)-BINAP (entry 2, Tables 2 and 3) the reaction gave, in 19 days, yields of 86%, 7%, and 3% for **3d**, **4d**, and **5**, respectively.

Variation of the Initial Concentration of (*R*)-BINAP. In the second experiment, we varied the initial concentration of (*R*)-BINAP from 0.0041 to 0.006 06 M while the concentrations of the other components were held constant (entries 2−5, Tables 2 and 3). As the concentration of (*R*)-BINAP increased, the rates of formation of **3d** and **5** increased, whereas the rate of formation of **4d** was diminished (Figure 2). In fact, the rate of formation of **4d** was sufficiently diminished that only a trace of **4d** was formed at the highest concentration of (*R*)-BINAP employed.

Variation of the Initial Concentration of Rhodium. In the third experiment, we varied the initial concentration of rhodium (from $[Rh(cod)Cl]_2$) from 0.0041 to 0.0123 M, while keeping the concentrations of the other reactants constant (entries 6−8, Tables 2 and 3). As the concentration of rhodium increased, we observed an increase in the initial rate of formation of **4d** and an attenuation of the initial rates of formation of **3d** and **5** (Figure 3). In fact, only a trace of **5** was formed at the highest concentration of rhodium used.

Variation of the Initial Concentrations of Rhodium and (*R*)-BINAP. In the fourth experiment, we increased the concentrations of both the rhodium and the (*R*)-BINAP from their standard values of 0.0041 M to 0.0205 M (entries 9−12 in Tables 2 and 3). Under

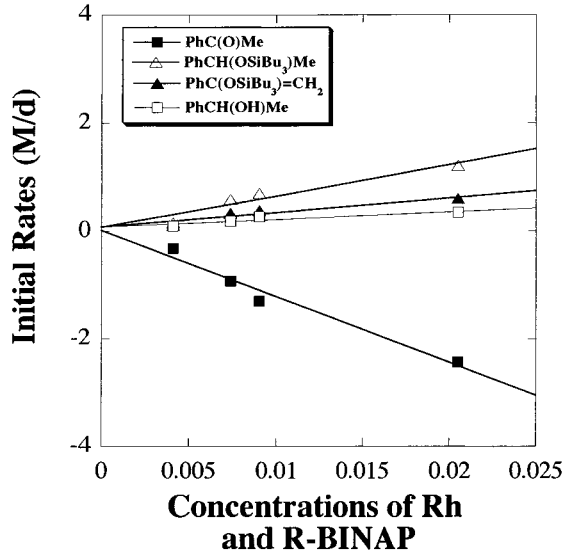


Figure 4. Plot of the initial rates of reaction versus the initial concentration of rhodium and (*R*)-BINAP. The initial concentrations of other reactants were constant.

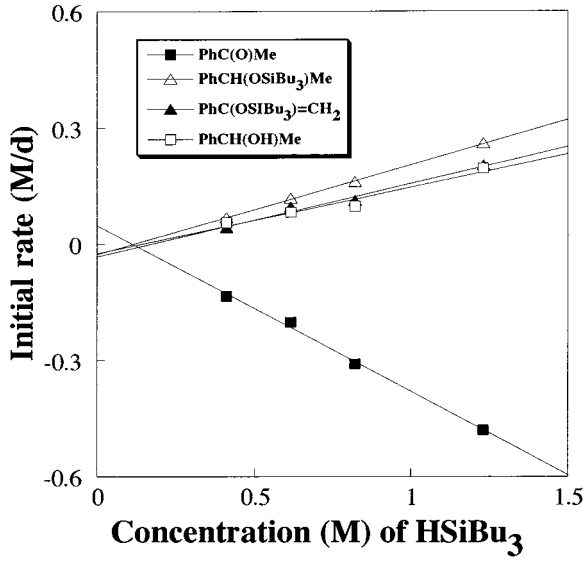


Figure 5. Plot of the initial rates of reaction versus the initial concentration of $HSiBu_3$. The initial concentrations of other reactants were constant.

these conditions, we observed linear increases in the initial rates of consumption and formation of the all the reactants and products (Figure 4).

Variation of the Initial Concentration of $HSiBu_3$. In the fifth experiment, we varied the concentration of $HSiBu_3$ from 0.41 to 1.23 M while keeping the concentrations of the other reactants constant (entries 13−16, Tables 2 and 3). The rates of consumption and formation of the reactants and products increased linearly (Figure 5).

Variation of the Initial Concentration of Acetophenone. In the sixth experiment, the concentration of acetophenone was varied from 0.41 to 2.05 M while the concentrations of the remaining reactants were held constant (entries 17−20 in Tables 2 and 3). Although the rate of formation of **3d** increases as the concentration of acetophenone increases, the slope of the plot is less at higher concentrations of acetophenone. The rates of formation of **4d** and **5** also increase

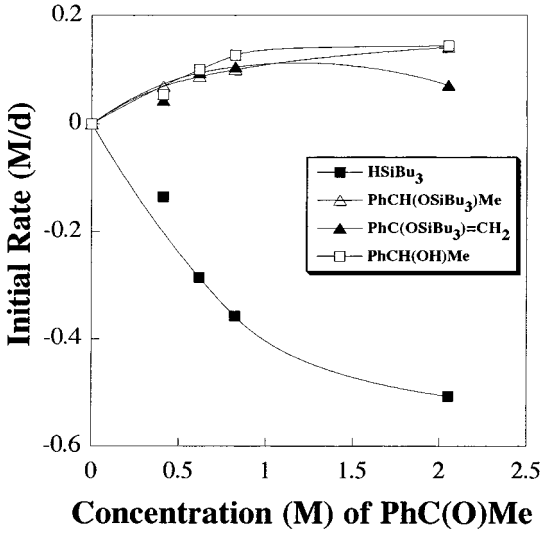


Figure 6. Plot of the initial rates of reaction versus the initial concentration of acetophenone. The initial concentrations of other reactants were constant.

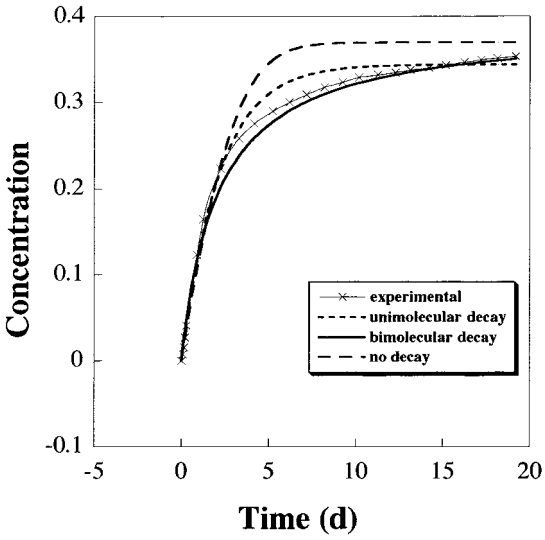
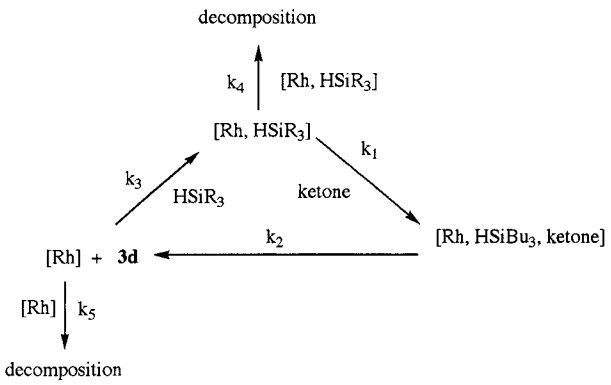


Figure 7. Simulation of the time dependence of the concentration of **3d** for a nominally 2:1 $HSiBu_3$ to acetophenone mixture as a function of the decay of the catalyst, as shown in Scheme 5.

Scheme 5



and then appear to level off as the concentration of acetophenone was increased (Figure 6).

Simulation of Experimental Kinetic Data. We simulated the formation of **3d** as functions of the

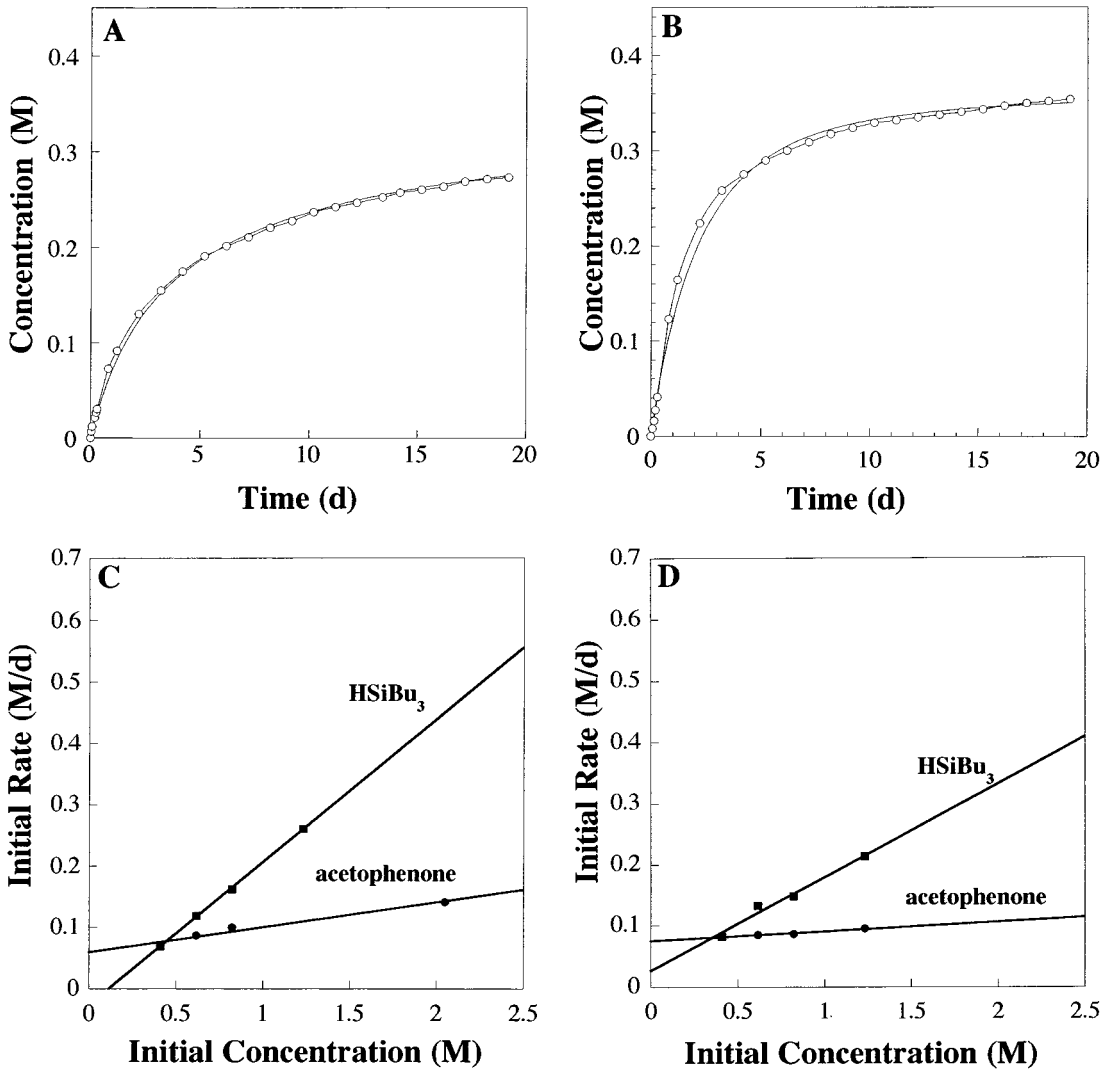


Figure 8. (A) Simulation of the time dependence of the concentration of **3d** for a nominal 2:1 mixture of acetophenone and $HSiBu_3$. (B) Simulation of the time dependence of the concentration of **3d** for a nominal 1:2 mixture of acetophenone and $HSiBu_3$. In parts A and B, the experimental points are shown as filled squares. (C) Experimental initial rates of formation of **3d** as a function of acetophenone and $HSiBu_3$ concentrations. (D) Simulation of the data shown in Figure C.

concentrations of $HSiBu_3$ and acetophenone according to Scheme 5. The code is provided in the Supporting Information. We simulated the experiments described in entries 13−20 in Tables 2 and 3. The concentrations of acetophenone and $HSiBu_3$ were adjusted in order to account for the formation of the small amount of **4d** and **5**. The inclusion of back reactions did not improve the quality of the fit. In addition, to reproduce the observed experimental results, we found it necessary to introduce decay pathways for the catalyst as shown in Scheme 5. Furthermore, only bimolecular decay pathways reproduced the observed concentration versus time curves (Figure 7). In the simulations we used the following rate constants: $k_1 = 70\ M^{-1}\ d^{-1}$, $k_2 = 2400\ M^{-1}\ d^{-1}$, $k_3 = 780\ M^{-1}\ d^{-1}$, $k_4 = 400\ d^{-1}$, $k_5 = 123\ M^{-1}\ d^{-1}$. In parts A and B of Figure 8, we compare the simulated and experimental concentration versus time curves for 2:1 and 1:2 $HSiBu_3$ to acetophenone mixtures (entries 15 and 19 in Tables 2 and 3). In parts C and D of Figure 8, we compare the simulated initial rates and experimental initial rates.

Product Distribution. The GC-MS examination of the reaction mixture showed, in addition to the presence of starting materials and major products (**3d, 4d**, and **5**), trace amounts of cyclooctane, cyclooctene, and $ClSiBu_3$. We did not observe any cyclooctadiene, silylated cyclooctanes, or silylated cyclooctenes. Although we did not observe any $Bu_3Si-SiBu_3$ either via NMR spectroscopy or by GC/MS, we did observe in a similar experiment $EtMe_2Si-SiMe_2Et$ when $HSiBu_3$ was replaced by $HSiEt_2Me$.

H/D Exchange Experiments. We used GC/MS to study H/D exchange in the hydrosilylation reactions involving $HSiBu_3$. We followed the protocol described in refs 10 and 11. We found no evidence of H/D exchange between benzene-d_6 and any of the reactants or products (**3d, 4d**, and **5**). This conclusion was based on the fact that the ^1H NMR spectra of the reaction mixture always showed a mass balance for reactants and products, and there was no indication of incorporation of ^1H into the benzene-d_6 solvent. GC/MS analysis of the reactants and

(10) Sorokin, A.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1993**, *115*, 7293.
(11) Kiani, S.; Tapper, A.; Staples, R. J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7503.

Table 4. GC/MS Analysis of the Reactants and Products Involved in the Hydrosilylation of Acetophenone-d_3 Using [Rh(cod)Cl]$_2$/(*R*)-BINAP as a Catalyst

compd	% of each species present	% H substitution
Acetophenone-d_3 (As Purchased)		
C_8H_8O	0.7	
C_8H_7DO	0.7	
$C_8H_6D_2O$	6.2	
$C_8H_5D_3O$	92.4	3.2[a]
Acetophenone (Residual)		
C_8H_8O	2	
C_8H_7DO	3	
$C_8H_6D_2O$	16	
$C_8H_5D_3O$	79	9.5[a]
$HSiBu_3$		
unable to determine because of fragmentation		
$PhCH(OH)CD_3$		
$C_8H_{10}O$	1	
C_8H_9DO	4	
$C_8H_8D_2O$	23	
$C_8H_7D_3O$	78	11.3[a]
$PhC(OSiBu_3)=CD_2$		
$C_{20}H_{34}OSi$	40	
$C_{20}H_{33}DOSi$	42	
$C_{20}H_{32}D_2OSi$	18	61[b]
Cyclooctane		
C_8H_{16}	68	
$C_8H_{15}D$	19	
$C_8H_{14}D_2$	9	
$C_8H_{13}D_3$	3	
$C_8H_{12}D_4$	1	88[c]
$PhCH(OSiBu_3)CD_3$		
unable to analyze because of fragmentation		
Other Substances Present		
$ClSiBu_3$		
cyclooctene		
cyclooctadiene		

[a] The percentage of methyl hydrogens that are ^{1}H. [b] The percentage of methylene hydrogens that are ^{1}H. [c] The percentage of the four hydrogens that transform cyclooctadiene into cyclooctane that are ^{1}H.

products also failed to reveal any evidence for H/D exchange.

We performed the experiment described in entry 2 of Table 2 using acetophenone-d_3 in place of acetophenone. We followed the course of the reaction via ^{1}H NMR spectroscopy and then analyzed the final reaction mixture by GC/MS. During the first 24 h of the reaction we observed only the formation of **3d**-d_3 and **5**-d_3. (Presumably, **4d**-d_2 is also formed, but we could not observe it by ^{1}H NMR spectroscopy because of overlapping peaks.) After 4 days we began to observe the formation of **4d**-d and **4d**-d_0, which continued for the duration of the experiment. We interrupted the reaction after 14 days and analyzed the reaction mixture by GC/MS. The results are displayed in Table 4.

We observed only a small (6%) incorporation of hydrogen into the residual acetophenone-d_3 and a somewhat larger (8%) incorporation of hydrogen into **5**. (Both of these values are corrected for the fact that the methyl group of the acetophenone was not fully deuterated.) Of the four hydrogens used to hydrogenate the cyclooctadiene to cyclooctane, 88% are ^{1}H. We were unable to determine the degree of incorporation of ^{1}H into **3d** or the degree of incorporation of ^{2}H into $HSiBu_3$. The silyl enol ether **4d**-d_2 had 61% of its deuterium replaced by hydrogen by the end of the experiment.

Discussion

In part, our results agree with what has been reported in the literature.[1,2,4,5] We observed the predominant formation of the silyl ether **3d,** accompanied by a small amount of **4d** and **5**. Furthermore, the reaction is first order in silane and rhodium and appears to show a saturation effect in acetophenone, in agreement with results of Waldman[5] and of Kolb and Hetflejs.[4]

The reactions with secondary silanes are quite fast; the slower reactions with the tertiary silanes allowed us to follow the reactions by ^{1}H NMR spectroscopy. We focused on the hydrosilylation reaction with $HSiBu_3$. In doing so, we were able to observe the appearance and disappearance of the various components of the reaction. We observed that the displacement of cyclooctadiene from [Rh(cod)Cl]$_2$ occurred within minutes after the mixing of the reactants. During the first few hours of the reaction, the uncomplexed cyclooctadiene was transformed into cyclooctane and cyclooctene as observed by ^{1}H NMR spectroscopy, with most of the requisite hydrogens coming from $HSiBu_3$. We found no evidence for the formation of silylated cyclooctanes, silylated cyclooctenes, chlorinated cyclooctanes, or chlorinated cyclooctenes.

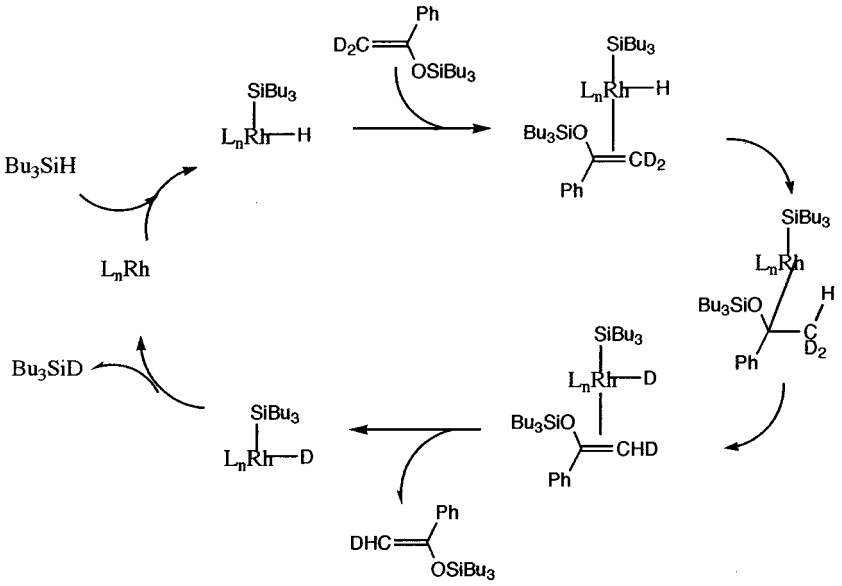
The observation that the hydrogens used to transform cyclooctadiene into cyclooctane are mainly ^{1}H suggests that we are observing transfer hydrogenation involving $HSiBu_3$. It is likely then that $Bu_3Si-SiBu_3$ is also formed. Although we could not detect $Bu_3Si-SiBu_3$, in an analogous experiment with $HSiEtMe_2$, we easily detected $Me_2EtSi-SiEtMe_2$ by GC/MS. Lappert has also reported the formation of a disilane during the rhodium-catalyzed hydrosilylation of ketones.[12] The formation of the small amounts of $ClSiBu_3$ observed by GC/MS finds precedent in the work of Osakada et al.,[13] who reported that $RhCl(H)(SiAr_3)(PMe_3)_3$ eliminated $ClSiAr_3$. Thus, certainly the cyclooctadiene is removed from the coordination sphere of the rhodium as well as some of the chloride ligand. Since we were unable to quantify the amount of $ClSiBu_3$ formed or, for that matter, when during the reaction it was formed, we do not know if the active catalysts contain chlorine.

The formation of the silyl enol ether **4d** was not unexpected, since it has been reported to be a common byproduct of the hydrosilylation of ketones and aldehydes. The formation of 1-phenylethanol (**5**) was surprising, since we are not aware that it has previously been reported as a byproduct of this reaction. It is curious that, although **4d** and **5** were only formed in low yields overall, they were formed initially at rates that were comparable to the rate of formation of **3d**. The low yields of **4d** and **5** are directly attributable to the abrupt termination of their formation when about 40% of the acetophenone is consumed.

The formation of **5** is somewhat problematic. The amount of **5** formed and its rate of formation are

(12) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217.
(13) Osakada, K.; Koizumi, T.; Sarai, S.; Yamamoto, T. *Organometallics* **1998**, *17*, 1868.

Scheme 6



dependent on a number of factors. Generally, the factors that enhance or diminish the rates of formation of **3d** have a parallel effect on **5** (see Figures 2−6). It is possible that **5** is the result of hydrolysis of **3d** by adventitious water. We do not believe that this is case because the results are reproducible, which we would not expect if adventitious water were playing an important role. Another possibility is that if **5** is formed by catalytic hydrogenation of acetophenone, **5** might then be an intermediate on the way to **3d**, displaying an induction period followed by a steady-state concentration of **5**. We think that this is not the case, because if **5** were a steady-state intermediate, then **5** would need to be formed from the ketone in a turnover-limiting step, to be followed by rapid reaction with $HSiBu_3$ to give the final product, **3d**. Then the reaction would be first order in the concentration of acetophenone and rather insensitive to the concentration of silane. We see the opposite behavior.

The silyl enol ether **4d** appears to be formed independently of **3d**, i.e., by a different form of rhodium catalyst which is less stable than the catalyst that is responsible for the formation of **3d**. There are two cases where the factors that influence the rate of formation of **4d** have the opposite effect on the rate of formation of **3d**. In one of the cases, as the concentration of (*R*)-BINAP increases, the rate of formation of **3d** increases but the rate of formation of **4d** decreases. In fact, the amount of **4d** formed can be reduced to virtually zero if enough (*R*)-BINAP is added to the reaction mixture. In the other case, when the concentration of $[Rh(cod)Cl]_2$ increases the rate of formation of **3d** decreases while the rate of formation of **4d** increases.

Two routes to the silyl enol ethers have been suggested. One, proposed by Brunner,[14] is the alcoholysis of the enol by the silane, and the second is the catalytic dehydrogenative silylation of the ketone. We do not believe that the alcoholysis pathway is valid for the following reason. If our hypothesis that **5** is not an intermediate is true, then the conversion of **5** to **3d** via alcoholysis of $HSiBu_3$ must be slow, since the concentration of **5** decays only slightly over a period of many days after it reaches its peak. Since the relative equilibrium concentration of the enol isomer of acetophenone is very small, its conversion to **3d** would be expected to be even slower than the conversion of **5** to **3d**.

On the basis of the evidence in hand, we believe that **4d** is produced by catalytic dehydrogenative silylation of the acetophenone. This process, which has been proposed by others,[15] requires β-hydride elimination from the siloxyalkyl ligand. To accomplish this, there must be an open coordination site on the rhodium. At a higher concentration of (*R*)-BINAP one of the phosphino groups could compete for this coordination site, thus inhibiting the elimination of the β-hydride. This is in accord with our observation that increasing the concentration of (*R*)-BINAP diminishes the rate of formation of **4d**.

The behavior of the silyl enol ether **4d** in the hydrosilylation of acetophenone-d_3 sheds more light on what is going on in this reaction. In the experiments with acetophenone we follow the formation of **4d** by monitoring vinylic hydrogens of **4d** via ^1H NMR spectroscopy. In this manner we know that the concentration of **4d** reaches its peak in less than 2 days. Of course with acetophenone-d_3 we do not see the vinyl hydrogens, at least initially. After 4 days, however, we begin to see H/D exchange, as evidenced by the growing in of the vinyl resonances. This process continued for the duration of the experiment (14 days). We interpret these results as shown in Scheme 6, which is in essence an arrested hydrosilylation of **4d**.

Origin of the Nonlinear Dependence of the Rates of Formation of 3d, 4d, and 5 on the Concentration of Acetophenone. The rates of formation of **3d**, **4d**, and **5** increase linearly with the concentration of $HSiBu_3$, whereas the rates of formation all show a saturation effect as the concentration of acetophenone increases. Waldman et al.[5] and Kolb and Hetfleis[4] also observed this saturation effect. They attributed it to the formation of inactive rhodium species formed by revers-

(14) Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499.

(15) Haag, D.; Runsink, J.; Scharf, H. D. *Organometallics* **1998**, *17*, 398.

ible complexation by the ketone. However, our simulations of the production of **3d**, based on the Ojima mechanism, shows that this particular model can give a saturation effect without the need to include a deactivating complexation of the ketone. All is that is needed is the turnover-limiting oxidative addition of $HSiBu_3$. The saturation behaviors of each initial rate at high concentrations of acetophenone as well as the linear dependencies on the concentration of $HSiBu_3$ suggest that similar turnover-limiting steps occur for the formation of **3d**, **4d**, and **5** (i.e., the oxidative addition of $HSiBu_3$ to a rhodium complex).

Conclusions

The hydrosilylation of acetophenone by $[Rh(cod)Cl]_2$/(*R*)-BINAP/$HSiBu_3$ in benzene-d_6 is clearly a complex process that gives multiple products. The reaction probably involves multiple catalysts. The initial phase of the reaction involves displacement of cyclooctadiene followed by its hydrogenation to cyclooctene and cyclooctane. The products **4d** and **5** appear to be formed independently of the formation of **3d**. The catalysts for the formation of **4d** and **5** decay quickly, thereby abruptly terminating the formation of these materials. Simulation, based on the Ojima mechanism, qualitatively fits the formation of **3d**. Thus, we find that the saturation effect observed at high concentrations of ketone is attributable to the oxidative addition of silane to rhodium being the turnover-limiting step.

Supporting Information Available: Code for the computer simulations used in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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