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$Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$ as Effective Catalysts for Hydrosilylation of Isoprene, Cyclohexanone, and Cyclohexenone

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Hydrosilylation of isoprene, cyclohexanone, and cyclohexenone catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$ is studied. Their catalytic activities are compared with those of $RhCl(PPh_3)_3$ and $Co_2(CO)_8$, and it is found that these Rh and Co–Rh carbonyl clusters are excellent new catalysts for the reactions. The reaction of isoprene catalyzed by those carbonyl clusters is highly regioselective and extremely stereoselective to give (*Z*)-(2-methylbut-2-en-1-yl)dimethylphenylsilane as the predominant product (88–94%). The reactions of cyclohexanone with $HSiEt_3$ catalyzed by $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$ give (cyclohexyloxy)triethylsilane exclusively, while the reactions with $HSiMe_2Et$ and H_2SiPh_2 afford a mixture of (cyclohexyloxy)silane (major) and (cyclohex-1-en-1-yloxy)silane (minor). The reaction of cyclohexenone with $HSiMe_2Ph$ catalyzed by these Rh and Co–Rh carbonyl clusters proceeds smoothly at ambient temperature to give the 1,4-addition product (cyclohex-1-en-1-yloxy)dimethylphenylsilane exclusively. On the other hand, the reaction with H_2SiPh_2 proceeds at −35 °C to give the 1,2-addition product (cyclohex-2-en-1-yloxy)diphenylsilane exclusively, which upon desilylation affords cyclohex-2-en-1-ol in quantitative yield. Kinetic study shows that (i) the reaction is first order to cyclohexenone and $HSiMe_2Ph$ and (ii) $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$ possess more than 1 order of magnitude higher catalytic activity than that of $RhCl(PPh_3)_3$, while $Co_3Rh(CO)_{12}$ is a 1 order of magnitude less active catalyst than $RhCl(PPh_3)_3$.

Introduction

Hydrosilylation of carbon–carbon and carbon–heteroatom multiple bonds has been extensively studied and many transition-metal catalysts have been shown to promote the reaction effectively.[2] Especially, Speier's catalyst, chloroplatinic acid–2-propanol, and Wilkinson's catalyst, $RhCl(PPh_3)_3$, have been used widely and their catalysis has been thoroughly studied.[2] However, little attention has been paid to the catalytic activity of group VIII transition-metal carbonyl clusters.[3] Therefore, we started the study on the catalysis of Rh and Co–Rh carbonyl clusters in hydrosilylation. We describe here the first examples of the hydrosilylation of isoprene, cyclohexanone, and 2-cyclohexenone catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$, which are excellent substrates to examine the characteristics, e.g., regioselectivity as well as chemoselectivity, of these metal carbonyl cluster catalysts.

For example, the hydrosilylation of isoprene has been studied with a wide variety of catalysts, e.g., platinum, palladium, and rhodium complexes.[2] The mode of the reaction depends on the nature of hydrosilane as well as catalyst employed, and in general, 1,4-addition is the preferred mode, with the exception of the reaction catalyzed by chloroplatinic acid, which promotes 1,2- and 1,4-additions with random regioselectivity.[2] It has been shown that phosphine complexes of palladium and rhodium give the 1,4-addition product almost exclusively, but with opposite regioselectivity:[4] Phosphine–palladium catalysts give exclusively (*Z*)-(2-methylbut-2-enyl)silane, while $RhCl(PPh_3)_3$ gives (3-methylbut-2-enyl)silane as the major product. Thus, it is of interest to look at the mode of the hydrosilylation of isoprene catalyzed by Rh and Co–Rh mixed carbonyl clusters.

Hydrosilylation of carbon–oxygen double bonds is known to be promoted by transition-metal catalysts, especially phosphine–rhodium complexes.[2] This reaction provides a useful reduction method, since the resultant silicon–oxygen bond of the product can easily be hydrolyzed to give the corresponding alcohols. It has also been shown that the $Co_2(CO)_8$/amine catalyst system promotes dehydrogenative silylation of nonconjugated ketones to give the corresponding silyl enol ethers,[5] which are useful reagents/intermediates in organic syntheses. Since Co–Rh mixed cluster catalysts have both Rh and Co sites in their molecules, it is curious which metal center acts as the active site for the reaction.

It has been shown that the hydrosilylation of α,β-unsaturated carbonyl compounds followed by hydrolysis provides a unique and effective reduction method, giving the corresponding saturated carbonyl compounds or allylic alcohols.[2] A variety of transition-metal complexes of rhodium, platinum, and ruthenium have been used as catalysts for these reactions; especially, $RhCl(PPh_3)_3$ has proven to be an excellent catalyst for two types of selective hydrosilylations:[6] viz., the hydrosilylation of α,β-enones using monohydrosilanes proceeds exclusively via 1,4-addition, giving the silyl enol ether, while with dihydrosilanes or trihydrosilanes the reaction gives the 1,2-addition product, an allylic silyl ether, with excellent selectivity. Accordingly, it is interesting to compare the selectivity and

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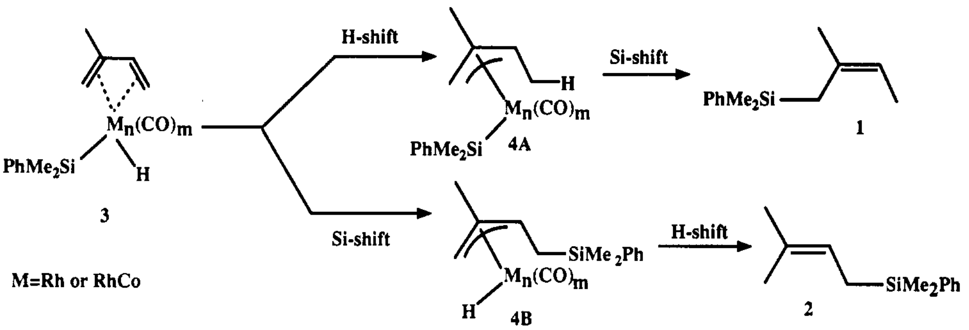
Table I. Hydrosilylation of Isoprene with $HSiMe_2Ph$^{a}

entry	catalyst	substrate/catalyst	conditions, °C/h	solvent	conversion,^{b} %	selectivity,^{b} %	product ratio^b 1	product ratio^b 2
1	$Rh_4(CO)_{12}$	10000	30/11	toluene	100	100	92	8
2		10000	50/9	toluene	100	100	91	9
3		1000	20/16	toluene	100	100	90	10
4		10000	20/16	none^c	100	100	88	12
5	$Co_2Rh_2(CO)_{12}$	10000	30/48	toluene	80	100	89	11
6		10000	50/48	toluene	85	100	89	11
7		1000	20/16	toluene	100	100	91	9
8		10000	20/48	none^d	65	100	94	6
9	$Co_3Rh(CO)_{12}$	1000	20/24	toluene	100	100	92	8
10		5000	20/48	none^d	40	94	94	6
11	$Co_2(CO)_8$	250	25/48	toluene	<1			
12		500	50/12	none^d	81	100	18	82

^{a} Reactions were run with 2.00 mmol of isoprene, 3.00 mmol of $HSiMe_2Ph$ and 15 mL of toluene unless otherwise noted. ^{b} Determined by GLC. ^{c} Reaction was run with 10.0 mmol of isoprene and 10.5 mmol of $HSiMe_2Ph$ without solvent. ^{d} Reaction was run with 2.00 mmol of isoprene and 3.00 mmol of $HSiMe_2Ph$ without solvent.

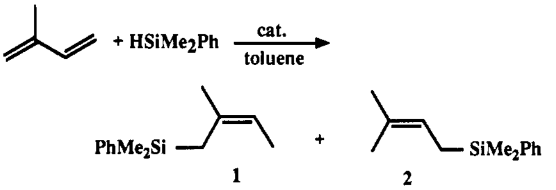
Scheme I



the catalytic activity of Rh and Co–Rh carbonyl clusters with those of $RhCl(PPh_3)_3$.

Results and Discussion

Hydrosilylation of Isoprene. Hydrosilylation of isoprene was carried out with $HSiMe_2Ph$ by using $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $Co_2(CO)_8$ as catalysts (eq 1). Wilkinson's catalyst, $RhCl(PPh_3)_3$, was used as a reference. The reactions were run with or without toluene as the solvent, and it was found that the solvent had little effect on the selectivity of the reaction. The identification of the products, including stereochemical assignment, was easily performed by means of ^1H NMR analyses (see experimental section). Results are summarized in Table I.

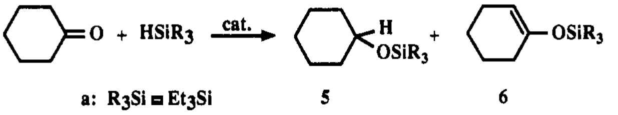


(1)

As Table I shows, the reactions give (*Z*)-(2-methylbut-2-en-1-yl)dimethylphenylsilane (1) as the predominant products (88–94%) accompanied by small amounts (6–12%) of (3-methylbut-2-en-1-yl)dimethylphenylsilane (2); vis, the reactions catalyzed by these Rh and Co–Rh carbonyl clusters are highly regioselective. When $Co_2(CO)_8$ is used as the catalyst, the reversal of the regioselectivity is observed; i.e., 2 is the major product (entry 13). It has been reported that the reaction catalyzed by $RhCl(PPh_3)_3$ also gives 2 as the major product (2/1 = 72/28).[4] These results clearly indicate that (i) Rh carbonyl clusters are totally different from $RhCl(PPh_3)_3$ in their catalytic behavior, (ii) Rh is the active catalyst site in the Co–Rh carbonyl clusters, and (iii) there is no particular synergistic effects in the Co–Rh mixed systems for this reaction.

As for the mechanism of the hydrosilylation of isoprene catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$, it seems that the catalytic cycle is similar to the one proposed for phosphine–palladium complexes[4] on the basis of the observed regioselectivity. A proposed mechanism is depicted in Scheme I, which includes two types of Π-allylic complexes, **4A** and **4B**, giving 1 and 2, respectively. The fact that no *E* isomer for 1 is observed indicates the short lifetime of the intermediate Π-allylic complex (**4A**), i.e., the cisoid complexation of isoprene followed by conjugate addition of hydrosilane.

Hydrosilylation of Cyclohexanone. Hydrosilylation of cyclohexanone was carried out with $HSiEt_3$, $HSiMe_2Et$, and H_2SiPh_2 by using $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$ as the catalysts (eq 2). The reaction catalyzed by $Co_2(CO)_8$ was also performed for comparison. Results are listed in Table II.



(2)

a: $R_3Si = Et_3Si$
b: $R_3Si = EtMe_2Si$
c: $Ph_2(H)Si$

As Table II shows, the reaction catalyzed by $Rh_4(CO)_{12}$ or $Co_2Rh_2(CO)_{12}$ gives (cyclohexyloxy)silane (**5**) and (cyclohex-1-en-1-yloxy)silane (**6**). The selectivity of the reaction depends on the nature of the hydrosilane used; e.g., $HSiEt_3$ gave **5** exclusively, while $HSiMe_2Et$ or H_2SiPh_2 affords a mixture of **5** and **6**. The reaction catalyzed by $Co_2(CO)_8$, with $HSiEt_3$ gives a mixture of **5** and **6** (entry 7), in which **6** is the major product, making a contrast with those catalyzed by $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$. In this

Table II. Hydrosilylation of Cyclohexanone[a]

entry	catalyst	substrate/ catalyst	hydrosilane	conditions, °C/h	solvent	conversion,[b] %	selectivity,[b] %	product ratio[b] 5	6
1	$Rh_4(CO)_{12}$	1000	$HSiEt_3$	25/12	toluene	100	100	100	
2	$Rh_4(CO)_{12}$	1000	$HSiMe_2Et$	25/12	toluene	100	100	84	16
3	$Rh_4(CO)_{12}$	10000	H_2SiPh_2	25/12	toluene	92	100	57	43
4	$Co_2Rh_2(CO)_{12}$	500	$HSiEt_3$	25/12	toluene	100	100	100	
5	$Co_2Rh_2(CO)_{12}$	500	$HSiMe_2Et$	25/12	toluene	100	100	63	37
6	$Co_2Rh_2(CO)_{12}$	5000	H_2SiPh_2	25/12	toluene	100	100	63	37
7	$Co_2(CO)_8$	100	$HSiEt_3$	25/18	none	84	100	38	62
8	$Co_2(CO)_8$	100	$HSiMe_2Et$	25/18	none	96	100	60	40
9	$Co_2(CO)_8$	500	$HSiMe_2Et$	50/16	toluene	100	100	77	23

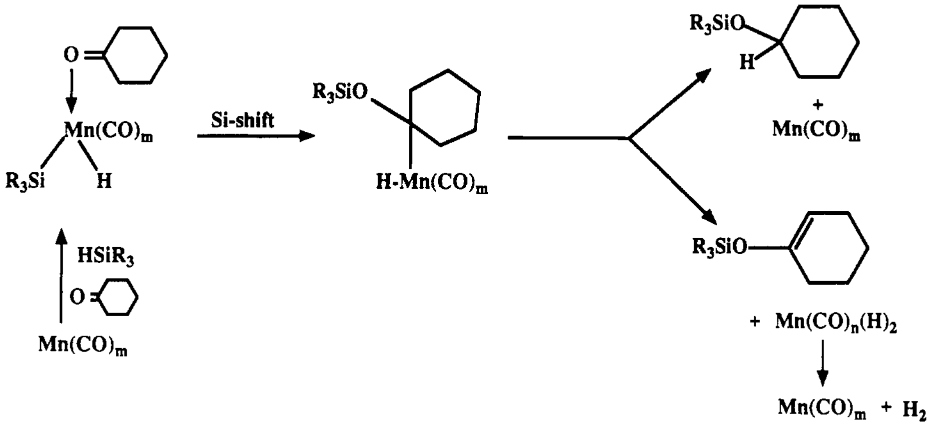
[a] Reactions were run with 2.00 mmol of cyclohexanone and 2.50 mmol of a hydrosilane in 5 mL of toluene unless otherwise noted. [b] Determined by GLC analysis.

Table III. Hydrosilylation of 2-Cyclohexenone with $HSiMe_2Ph$[a] and H_2SiPh_2[b]

entry	catalyst	hydrosilane	substrate/ catalyst	conditions, °C/h	conversion,[c] %	selectivity,[c] %	product ratio[c] 6d	5d	7c
1	$Rh_4(CO)_{12}$	$HSiMe_2Ph$	10000	20/2.5	100	100	100		
2	$Rh_4(CO)_{12}$	H_2SiPh_2	1000	-35/12	100	100			100
3	$Co_2Rh_2(CO)_{12}$	$HSiMe_2Ph$	5000	20/2.5	100	100	100		
4	$Co_2Rh_2(CO)_{12}$	H_2SiPh_2	1000	-35/12	100	100			100
5	$Co_3Rh(CO)_{12}$	$HSiMe_2Ph$	1000	20/12	100	100	100		
6	$Co_3Rh(CO)_{12}$	H_2SiPh_2	1000	-35/12	100	100			100
7	$RhCl(PPh_3)_3$	$HSiMe_2Ph$	2500	20/30	100	100	99.9	0.1	
8	$Co_2(CO)_8$	$HSiMe_2Ph$	100	65/4	98	100	96.0	4.0	

[a] The reactions were run with 2.00 mmol of 2-cyclohexenone and 3.00 mmol of $HSiMe_2Ph$ in 15 mL of toluene. [b] The reactions were run with 2.00 mmol of 2-cyclohexenone and 2.50 mmol of H_2SiPh_2 without solvent. [c] Determined by GLC analysis.

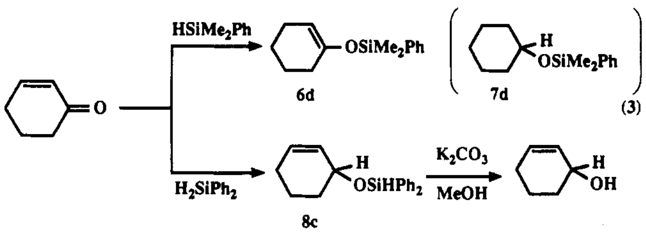
Scheme II



reaction, $Co_2Rh_2(CO)_{12}$ seems to exhibit a catalytic behavior in between $Rh_4(CO)_{12}$ and $Co_2(CO)_8$. A simplified mechanism for the hydrosilylation and the dehydrogenative silylation is shown in Scheme II.

It should be noted that the reaction of cyclohexanone with $HSiMe_2Ph$ has a complication; e.g., an exothermic reaction took place within 60–120 s with evolution of gas when a mixture of 2.00 mmol of the ketone and 3.00 mmol of the silane was mixed with 2 × 10^{-3} mmol of $Rh_4(CO)_{12}$ or $Co_2Rh_2(CO)_{12}$ without solvent at 25 °C, to give bis(dimethylphenyl)disiloxane as the predominant product (>95%) accompanied by a small amount (<5%) of (cyclohexyloxy)dimethylphenylsilane (**5d**), and the capillary GC–MS analysis of the reaction mixture revealed the formation of cyclohexene (5–10%) (cyclohexane was not detected). When the reaction was carried out at −35 °C (12 h)/ambient temperature (2h), **5d** was formed in 40% yield. No further improvement in the yield of **5d** was achieved in spite of extensive efforts on optimization. Curiously, the reaction of acetophenone with $HSiMe_2Ph$ catalyzed by $Rh_4(CO)_{12}$ or $Co_2Rh_2(CO)_{12}$ without solvent proceeded smoothly at 0 °C for 3 h to give the hydrosilylation product (1-phenylethoxy)dimethylphenylsilane (**8**) in 92% yield. It is not clear at present why the combination of cyclohexanone and $HSiMe_2Ph$ causes such a complication.

Hydrosilylation of Cyclohexenone. Hydrosilylation of 2-cyclohexenone was carried out with $HSiMe_2Ph$ by using $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $Co_2(CO)_8$ as the catalysts (eq 3). The reaction catalyzed by $RhCl(PPh_3)_3$ was also carried out as a reference. Results are summarized in Table III.



As Table III shows, the 1,4-addition product (cyclohex-1-en-1-yloxy)dimethylphenylsilane (**6d**) is obtained as

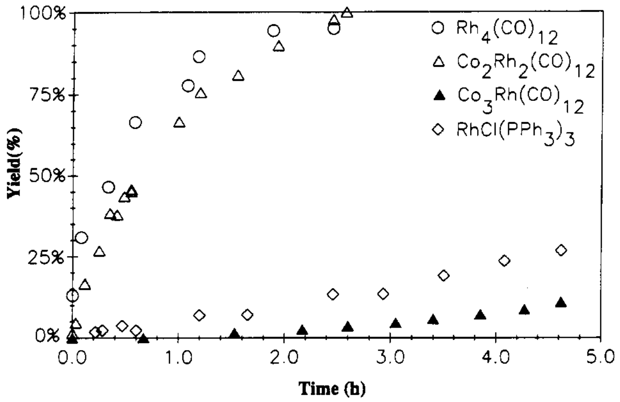


Figure 1. Reaction profiles for the hydrosilylation of 2-cyclohexenone catalyzed by $Rh_4(CO)_{12}$ (○). $Co_2Rh_2(CO)_{12}$ (△), $Co_3Rh(CO)_{12}$ (▲), and $RhCl(PPh_3)_3$ (◇). All reactions were run with 2.00 mmol of 2-cyclohexenone and 3.00 mmol of dimethylphenylsilane in the presence of 2.00×10^{-4} mmol of $Rh_4(CO)_{12}$, 4.00×10^{-4} mmol of $Co_2Rh_2(CO)_{12}$, 8.00×10^{-4} mmol of $Co_3Rh(CO)_{12}$, and 8.00×10^{-4} mmol of $RhCl(PPh_3)_3$, respectively, in 15 mL of toluene at 20 °C.

the exclusive or the predominant product in all cases when $HSiMe_2Ph$ is used. In the reactions catalyzed by $RhCl(PPh_3)_3$ and $Co_2(CO)_8$, a very small amount (0.1–4.1%) of the hydrosilylation–hydrogenation product (cyclohexyloxy)dimethylphenylsilane (**5d**) is formed. Tetrarhodium dodecacarbonyl and $Co_2Rh_2(CO)_{12}$ exhibit very similar catalytic activity, while $Co_3Rh(CO)_{12}$ shows somewhat lower activity compared with these two catalysts. The first two carbonyl clusters are much more active than $RhCl(PPh_3)_3$, and $Co_2(CO)_8$ is the least active catalyst among the catalysts examined. In sharp contrast with this, the 1,2-addition product (cyclohex-2-en-1-yloxy)diphenylsilane (**7c**) is formed exclusively when diphenylsilane is used (entries 2, 4, and 6), which is desilylated by K_2CO_3–MeOH to give cyclohex-2-en-1-ol in quantitative yield. Such marked dependence of regioselectivity in the hydrosilylation of α,β-enones is known for phosphine–Rh complex catalyzed reactions,[2,6] but these Rh and Rh–Co carbonyl clusters exhibit even better selectivities.

We found an interesting effect of the order of the addition of reactants to the catalyst on the selectivity as well as on the reaction rate. For example, when 2-cyclohexenone was added to a solution of $Rh_4(CO)_{12}$ in toluene at 20 °C and stirred for 1 h followed by the addition of $HSiMe_2Ph$, the reaction turned out to be very slow and **5d** was formed (ca. 10%) as the side product; viz., the reaction was at least 1 order of magnitude slower than that following the standard procedure in which the hydrosilane was added to the catalyst first. The result clearly indicates that two different catalyst species are formed just by changing the order of the addition of the reactants to the catalyst.

Comparison of Catalytic Activities of Rh, Co, and Co–Rh Carbonyl Clusters in the Hydrosilylation of 2-Cyclohexenone. In order to obtain quantitative data for the relative catalytic activity of $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $RhCl(PPh_3)_3$, and $Co_2(CO)_8$ in the hydrosilylation of 2-cyclohexenone, a kinetic study was carried out. Figure 1 shows the reaction profiles for the hydrosilylation of cyclohexenone with $HSiMe_2Ph$ catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$, which clearly indicate the difference in the activity of these catalysts. The kinetic study was performed in the presence of excess hydrosilane, and it was found that all four cases were consistent with the first-order plots; viz., the reaction is the first order to the substrate concentration. Thus, the pseudo-first-order rate constants (k_{obs}) were calculated, and turnover frequencies were also evaluated. Results are summarized in Table IV.

Table IV. Comparison of Catalytic Activity of $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$ in the Hydrosilylation of 2-Cyclohexenone with $HSiMe_2Ph$ at 20 °C

catalyst	k_{obs}, s^{-1}	turnover frequency mol^{-1} s^{-1}	 Rh^{-1} s^{-1}
$Rh_4(CO)_{12}$	2.79×10^{-4}	1396	349
$Co_2Rh_2(CO)_{12}$	4.08×10^{-4}	1019	510
$Co_3Rh(CO)_{12}$	1.74×10^{-6}	2	2
$RhCl(PPh_3)_3$	2.55×10^{-5}	32	32

As Table IV shows, the reactions catalyzed by $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$ are more than 1 order of magnitude faster than the one catalyzed by $RhCl(PPh_3)_3$, even per rhodium metal. Thus, it is apparent that those Rh and Co–Rh carbonyl clusters are excellent catalysts for the hydrosilylation of α,β-unsaturated carbonyl compounds. In order to determine the order of the reaction toward hydrosilane, another kinetic measurement was performed in the presence of excess 2-cyclohexenone with $Rh_4(CO)_{12}$ as the catalyst, which revealed that the reaction is first order to the hydrosilane concentration as well. It is very likely that the reactions promoted by other catalysts are consistent with that by $Rh_4(CO)_{12}$.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, and chloroform-d_1 was used as the solvent. Mass spectra (GC–MS) data were obtained on a Spectros MS 30 spectrometer or a Hewlett-Packard HP5980A mass spectrometer equipped with a HP 5710A gas chromatograph and a HP 5933A data system or a Hewlett-Packard HP5971A mass spectrometer with a HP 5890 gas chromatograph and a HP Vecta QS/20 workstation at 70 eV. High-resolution mass spectra (HRMS) were measured with a Kratos MS-80RFA mass spectrometer with a Chrompack Carlo Erba/Kratos gas chromatograph and Data General Eclipse S/120 data station. Analytical gas chromatography (GLC) was performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a HP3396A integrator or a Perkin-Elmer 3920 gas chromatograph equipped with a glass column (3 m) packed with either 3% OV-17, 3% Dexsil-300 on chromosorb WHP, or a 3% OV-17 capillary column (25 ft).

Materials. Toluene was dried over and distilled from sodium/benzophenone ketal before use. The complexes $RhCl_3 \cdot 3H_2O$ and $Co_2(CO)_8$ were obtained from Engelhard Industries KK and Strem Chemicals, Inc., respectively, and used as received. The rhodium complexes $Co_2Rh_2(CO)_{12}$,[7] $Co_3Rh(CO)_{12}$,[7] and $Rh_4(CO)_{12}$[8] were prepared according to literature methods. Isoprene, cyclohexanone, 2-cyclohexenone, cyclohex-2-en-1-ol, acetophenone, and all hydrosilanes were purchased from Aldrich Chemical Co., Inc., and Fluka Chemical Co., Inc., distilled under nitrogen, and stored over molecular sieves. Wilkinson's catalyst $RhCl(PPh_3)_3$, was obtained from Aldrich Chemical Co. and used as received.

Hydrosilylation Procedure A (for Reactions Performed under Neat Conditions). To a dry Schlenk-type reaction vessel charged with the catalyst, evacuated, and thoroughly flushed with nitrogen is added a hydrosilane via a syringe. The mixture is stirred until the solution becomes homogeneous; a substrate is added dropwise via a syringe, while the reaction flask is kept at the required reaction temperature. The progress of the reaction is monitored by GLC, and when the substrate is totally consumed, the quantitative GLC analysis of the products is performed by using *n*-hexadecane, *n*-pentadecane, or *n*-decane as the internal

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standard. The products are identified either by comparison with authentic samples in GLC and/or by ^{1}H NMR analyses. The products are isolated by bulb-to-bulb distillation under reduced pressure. The scale and specific conditions for each experiment are indicated in Tables I and II as footnotes.

Hydrosilylation Procedure B (for Reactions Performed in Toluene). A stock solution of the catalyst is freshly prepared, and the required amount is transferred via a syringe to a dry Schlenk-type reaction vessel that was thoroughly flushed with nitrogen and the required amount of toluene added. A hydrosilane is added via a syringe, and the mixture is stirred until the solution becomes homogeneous; the substrate is added dropwise via a syringe, while the reaction flask is kept at the required reaction temperature. The mixture is stirred under appropriate reaction conditions. Subsequent steps are carried out in the same manner as those described in the procedure A. The scale and specific conditions for each experiment are indicated in Tables I–III as footnotes.

Hydrosilylation of Cyclohexanone and 2-Cyclohexenone with H_2SiPh_2. The reaction of cyclohexanone was carried out by following procedure B using cyclohexanone (196 mg, 2.00 mmol), H_2SiPh_2 (461 mg, 2.50 mmol), and $Co_2Rh_2(CO)_{12}$ (4.00×10^{-4} mmol) in toluene (5 mL) at 25 °C for 12 h. The GLC analysis of the reaction mixture indicated 100% conversion of cyclohexanone, and the ^{1}H NMR analysis of the reaction mixture revealed the clean formation of a mixture of (cyclohexyloxy)diphenylsilane (**5c**) and (cyclohex-1-en-1-yloxy)diphenylsilane (**6c**) in quantitative yield [**5c**: δ 3.90 (m, 1 H, =CH—OSi), 5.55 (s, 1 H, =SiH—O). **6c**:[12] δ 5.09 (m, 1 H, C=CH–), 5.65 (s, 1 H, =SiH—O)]. The hydrosilylation products were treated with K_2CO_3 in methanol (5 mg/5 mL) at ambient temperature for 1 h with stirring. The quantitative GLC analysis of the reaction mixture using *n*-decane as the internal standard showed the formation of cyclohexanol (63% yield) and cyclohexanone (37% yield): This product ratio should reflect the **5c**/**6c** ratio.

In a similar manner, the reaction of 2-cyclohexenone was carried out by following procedure A using 2-cyclohexenone (194 mg, 2.00 mmol), H_2SiPh_2 (461 mg, 2.50 mmol), and $Rh_4(CO)_{12}$ (2.00×10^{-3} mmol) without solvent. The mixture was stirred at −35 °C for 12 h and then warmed to ambient temperature. The GLC analysis of the reaction mixture showed 100% conversion of 2-cyclohexenone, and the ^{1}H NMR analysis revealed a clean formation of (cyclohex-2-en-1-yloxy)diphenylsilane (**8c**). The product **8c** was submitted to desilylation with K_2CO_3 in methanol in the same manner as that described above. The GLC analysis of the reaction mixture showed the formation of cyclohex-2-en-1-ol in quantitative yield.

Hydrosilylation of Acetophenone with $HSiMe_2Ph$. The reaction was carried out in a similar manner to that described for 2-cyclohexenone. A mixture of acetophenone (240 mg, 2.00 mmol), $HSiMe_2Ph$ (354 mg, 2.50 mmol), and $Rh_4(CO)_{12}$ (1.49 mg, 2.00×10^{-3} mmol) was stirred at 0 °C for 4 h and warmed to ambient temperature. The GLC analysis of the reaction mixture using *n*-pentadecane as the internal standard revealed the clean formation of (1-phenylethyloxy)dimethylphenylsilane (**9**) in 92% yield. The desilylation of **9** with K_2CO_3 in methanol gave 1-phenylethanol in quantitative yield.

Identification of Products. The following data were used for the identification of the hydrosilylation products.

(*Z*)-(2-Methylbut-2-en-1-yl)dimethylphenylsilane (1):[4,9] ^{1}H NMR δ 0.31 (s, 6 H), 1.44 (d, J = 7.0 Hz, 3 H), 1.59 (t, J = 1.3 Hz, 3 H), 1.75 (s, 2 H), 5.12 (q, J = 7.0 Hz, 1 H), 7.34–7.56 (m, 5 H).

(3-Methylbut-2-en-1-yl)dimethylphenylsilane (2):[4] ^{1}H NMR δ 0.26 (s, 6 H), 1.50 (s, 3 H), 1.63 (d, J = 8.4 Hz, 2 H), 1.69 (s, 3 H), 5.16 (t, J = 8.4 Hz, 1 H), 7.34–7.56 (m, 5 H).

(Cyclohexyloxy)triethylsilane (5a):[10] ^{1}H NMR δ 0.58 (q, J = 8.0 Hz, 6 H), 0.95 (t, J = 8.0 Hz, 9 H), 1.25 (m, 6 H), 1.76 (m, 4 H), 3.56 (m, 1 H); MS (ion, %) *m/e* 214 (M^+, 0.6), 185 (100), 103 (95), 75 (44).

(Cyclohexyloxy)dimethylethylsilane (5b): NMR δ 0.08 (s, 6 H), 0.56 (q, J = 7.9 Hz, 2 H), 0.94 (t, J = 7.9 Hz, 3 H), 1.27 (m, 6 H), 1.77 (m, 4 H), 3.54 (m, 1 H). HRMS (*m/e*) calcd for $C_{10}H_{22}OSi$: 186.1385. Found: 186.1390.

(Cyclohexyloxy)dimethylphenylsilane (5c):[5] ^{1}H NMR δ 0.38 (s, 6 H), 1.23 (m, 6 H), 1.75 (m, 4 H), 3.60 (m, 1 H); MS (ion, %) *m/e* 234 (M^+, 0.5), 219 (34), 156 (27), 137 (100), 135 (35). HRMS (*m/e*) calcd for $C_{14}H_{22}OSi$: 234.1504. Found: 234.1504.

(Cyclohex-1-en-1-yloxy)triethylsilane (6a):[11] ^{1}H NMR δ 0.65 (q, J = 7.9 Hz, 6 H), 0.97 (t, J = 7.9 Hz, 9 H), 1.51 (m, 2 H), 1.64 (m, 2 H), 2.00 (m, 4 H), 4.87 (m, 1 H).

(Cyclohex-1-en-1-yloxy)dimethylethylsilane (6b): ^{1}H NMR δ 0.09 (s, 6 H), 0.58 (q, J = 7.9 Hz, 2 H), 0.97 (t, J = 7.9 Hz, 3 H), 1.51 (m, 2 H), 1.64 (m, 2 H), 2.00 (m, 4 H), 4.84 (m, 1 H). HRMS (*m/e*) calcd for $C_{10}H_{20}OSi$: 184.1348. Found: 184.1352.

(Cyclohex-1-en-1-yloxy)dimethylphenylsilane (6d):[5] ^{1}H NMR δ 0.44 (s, 6 H), 1.48 (m, 2 H), 1.61 (m, 2 H), 1.96 (m, 4 H), 4.85 (m, 1 H), 7.4–7.6 (m, 5 H); MS (ion, %) *m/e* 232 (M^+, 11), 156 (47), 137 (66), 135 (100), 75 (70). HRMS (*m/e*) calcd for $C_{14}H_{20}OSi$: 232.1301. Found: 232.1287.

(Cyclohex-2-en-1-yloxy)diphenylsilane (7c):[12] ^{1}H NMR δ 1.70–2.10 (m, 6 H), 4.47 (bm, 1 H), 5.55 (s, 1 H), 5.82 (m, 1 H), 7.10–7.70 (m, 10 H).

(1-Phenylethoxy)dimethylphenylsilane (8):[6] ^{1}H NMR δ 0.40 (s, 3 H), 0.45 (s, 3 H), 1.53 (d, 3 H), 4.96 (d, J = 6.4 Hz, 1 H), 7.5 (m, 8 H), 7.75 (m, 2 H); MS (ion, %) *m/e* 256 (2), 241 (30), 178 (66), 167 (30), 137 (100), 135 (66), 105 (15), 91 (8), 77 (10).

Kinetic Study. Kinetic measurements were carried out with 2.00 mmol of 2-cyclohexenone and 3.00 mmol of $HSiMe_2Ph$ in 15 mL of toluene at 25 °C. The substrate/catalyst ratios are adjusted to 2500/1 *per rhodium metal*. The catalyst concentrations for $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$ are 1.33×10^{-5}, 2.67×10^{-5}, 5.33×10^{-5}, and 5.33×10^{-5} M, respectively. The progress of the reactions was monitored by GLC analysis on a column packed with 3% OV-17 using *n*-pentadecane as the internal standard. All cases fitted with the pseudo-first-order plots. Thus, the reaction is first order to the substrate concentration regardless of the catalyst species. Results are summarized in Table IV. In order to determine the order of the hydrosilane, another set of conditions was employed for the $Rh_4(CO)_{12}$-catalyzed reaction: 3.0 mmol of cyclohexenone and 2.0 mmol of $HSiMe_2Ph$ in 15 mL of toluene at 25 °C. The reaction was in accord with the pseudo-first-order plot. Consequently, the hydrosilylation of cyclohexenone is found to be first order to the hydrosilane as well as to the substrate.

In order to calculate the turnover frequencies, the $-\ln[S]$ (S = substrate) was plotted against time, and the slope was obtained by the least-squares methods, which corresponds to k_{obs}. The k_{obs} thus obtained was divided by the moles of catalyst to give the turnover frequency ($mol^{-1}\ s^{-1}$).

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