tracted with CH_2Cl_2. Drying and evaporating the CH_2Cl_2 left a residue which was filtered through silica gel (1/1 hexanes/EtOAc). Evaporation left 68 mg, 88% yield of a mixture of **41a** and **41b** that was used immediately. To an acetic acid (2 mL) solution of **41a,b** (68 mg, 0.197 mmol) was added NaI (147 mg, 0.985 mmol). This solution was stirred for 2 h at room temperature and then neutralized with saturated $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with saturated $Na_2S_2O_3$, dried, and evaporated. The residue was chromatographed on silica gel (1/1 hexanes/EtOAc) to give 29 mg, 47% yield of a yellow oil which partially decomposed upon standing at room temperature for a few days.

41 (major epimer): IR 2960, 2880, 2855, 1725 cm^{-1}; ^1H NMR δ 9.68 (s, 1 H), 7.37 (d, 1 H, J = 8.23 Hz), 7.24 (d, 1 H, J = 2.26), 6.81 (dd, 1 H, J = 8.23, 2.31), 5.88 (bd, 1 H, J = 10.1), 5.69 (bd, 1 H, J = 10.1), 4.72 (s, 1 H), 3.84 (s, 3 H), 3.56–3.41 (m, 1 H), 3.09–2.85 (m, 3 H), 2.63–1.93 (m, 3 H), 0.81 (t, 3 H, J = 7.54).

42: $[\alpha]^{20}_D$ +29.4° (c 1.0, $CHCl_3$); IR 3460, 2950, 2850, 2830, 2760, 1725, 1635 cm^{-1}; ^1H NMR δ 9.78 (s, 1 H), 8.33 (bs, 1 H), 7.34 (d, 1 H, J = 8.56 Hz), 6.83 (d, 1 H, J = 2.13), 6.75 (dd, 1 H, J = 8.55, 2.24), 6.15 (ddd, 1 H, J = 10.1, 4.83, 1.56), 5.84 (bd, 1 H, J = 10.0), 3.95 (s, 1 H), 3.84 (s, 3 H), 3.41 (ddd, 1 H, J = 17.1, 4.91, 1.52), 3.20–2.85 (m, 3 H), 2.75–2.60 (m, 2 H), 1.74–1.50 (m, 2 H), 0.90 (t, 3 H, J = 7.45); mass spectrum, calcd for $C_{19}H_{22}N_2O_2$, m/e 310.1681, found m/e 310.1679.

(1*R*,12b*R*)-1-Acetyl-1-ethyl-16-methoxy-1,2,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (43). To a solution of **4b** (200 mg, 0.588 mmol) in THF (10 mL) at 0 °C was slowly added methyllithium (1.9 mL of 1.5 M MeLi in Et_2O, 2.82 mmol). The reaction was stirred at 0 °C for 15 min, quenched with pH 6 phosphate buffer, and extracted with EtOAc which was dried and evaporated, and the residue was chromatographed on silica gel (7/3 hexanes/EtOAc) to yield **43**: 150 mg, 79% yield; mp 95 °C; $[\alpha]^{20}_D$ +143° (c 1.1, $CHCl_3$); IR 3460, 2960, 2860, 2830, 2770, 1705, 1635 cm^{-1}; ^1H NMR δ 8.31 (bs, 1 H), 7.33 (d, 1 H, J = 8.54 Hz), 6.83 (d, 1 H, J = 2.15), 6.74 (dd, 1 H, J = 8.53, 2.24), 6.08 (ddd, 1 H, J = 10.2, 5.05, 1.61), 5.81 (bd, 1 H, J = 10.2), 3.92 (s, 1 H), 3.84 (s, 3 H), 3.42 (ddd, 1 H, J = 16.5, 5.06, 1.32), 3.18–2.87 (m, 3 H), 2.72–2.59 (m, 2 H), 2.36 (s, 3 H), 1.90–1.50 (m, 2 H), 0.75 (t, 3 H, J = 7.56); mass spectrum, calcd for $C_{20}H_{24}N_2O_2$ m/e 324.1838, found m/e 324.1843.

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Single-Operation Synthesis of Vinylsilanes from Alkenes and Hydrosilanes with the Aid of $Ru_3(CO)_{12}$

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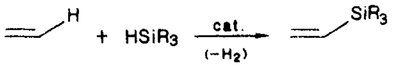
Alkenes ($RCH{=}CH_2$, where R = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, 2-naphthyl, $(CH_3)_3C$, $Me_3SiO(CH_3)_2C$, n-C_4H_9O, and Et_3Si) with $HSiEt_3$ with $Ru_3(CO)_{12}$ as a catalyst gave corresponding vinylsilanes (**1**, **6–13**) without formation of simple addition products. Hydrosilanes such as $HSiMe_3$, $HSiEt_2Me$, $HSiPhMe_2$, and $HSi(OEt)_3$ also yielded vinylsilanes. Alkenes having a hydrogen atom at the allylic position (1-hexene, allylbenzene, 3-phenoxyprop-1-ene, vinylcyclohexane, β-methylstyrene, α-methylstyrene, 2-hexene) formed mixtures of vinylsilanes and allylsilanes. The ratio of vinylsilane **16** to allylsilane **17** decreased with an increase in temperature and with time. Substituted styrenes with a hydrosilane in the presence of 1-hexene gave vinylsilanes **1** and **6–8** in good yields based on the styrenes along with n-hexane.

Vinylsilanes have recently been shown to be versatile intermediates in organic synthesis.[2] Various methods are available for the preparation of vinylsilanes. Most of them utilize alkynes (hydrosilylation of alkynes or hydrogenation of silylacetylene), carbonyl compounds (diazoation/lithiation/thermolysis in the presence of chlorosilanes), or vinyl halides (metalation followed by silylation) as starting materials. The reaction (eq 1) is of a type not easy to achieve, since alkenes with hydrosilanes usually produce corresponding alkylsilanes by hydrosilylation.[3]



(1)

Several diverse examples with a limited degree of success of the reaction of eq 1 can be found in the literature. Nesmeyanov and co-workers reported that the reaction of ethylene with $HSiEt_3$ in the presence of a catalytic amount of $Fe(CO)_5$ gave the corresponding vinylsilane and the similar reaction of propene or 1-decene gave a mixture of an alkylsilane and an alkenylsilane.[4] Some rhodium and osmium complexes have been described to be effective as the catalyst for the reaction of styrene with hydrosilanes, leading to vinylsilanes $RhCl(PPh_3)_3$[5], $Rh(dmg)_2PPh_3$[6], $Rh(acac)_3$,[7] and $H_2OsCl_6{\cdot}2H_2O$.[8] Related reactions have also been known for Pt, Ni, Ir–C, Ru–C, Ru–Al_2O_3, and Re–C catalysts.[8] Maitlis and co-workers reported that the reaction of 1-hexene with $HSiEt_3$ in the presence of $(RhC_5Me_5)_2Cl_4$ gave a mixture of an alkylsilane and an alkenylsilane.[9] Photocatalyzed reaction of alkenes with trialkylsilanes in the presence of metal carbonyls [$Fe(CO)_5$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$] to give a mixture of the corresponding alkyl- and alkenylsilanes has been reported

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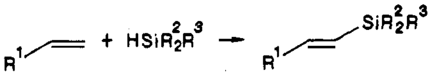
Table I. Preparation of Vinylsilanes from Alkenes Having No Allylic Hydrogen and Hydrosilanes[a]



R^1	R^2	R^3	reactn temp, °C	product	yield,[b] %
C_6H_5	Et	Et	80	**1**	93
	Me	Me	100	**2**	86
	Et	Me	80	**3**	93
	Me	Ph	80	**4**	96
	OEt	OEt	160[c]	**5**	36
p-$CH_3C_6H_4$	Et	Et	80	**6**	100
p-$CH_3OC_6H_4$			80	**7**	83
p-ClC_6H_4			80	**8**	94
2-naphthyl			80	**9**	88
$(CH_3)_3C$			reflux	**10**	88
$Me_3SiO(CH_3)_2C$			60[d]	**11**	42
n-C_4H_9O			60[e]	**12**	58
Et_3Si			80[f]	**13**	94
CO_2Et			80[g]	**14**	39[i]
H			50[h]	**15**	65[j]

[a] Alkene (30 mmol), silane (10 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), benzene (10 mL), 5 h unless otherwise noted. [b] Determined by GLC. [c] In xylene. [d] 48 h. [e] Alkene (50 mmol), 24 h. [f] 20 h. [g] Alkene (50 mmol), 48 h. [h] Ethylene (30 kg/cm²). [i] Accompanied by ethyl propionate (12% yield). [j] Accompanied by Et_4Si (25% yield).

by Wrighton and co-workers.[10]

We have been studying the new catalytic reactions of alkenes or oxygenated compounds with hydrosilanes and carbon monoxide.[11] Examination of various transition-metal complexes indicated that the effective catalysts for the new reaction were those known to be effective for both hydrosilylation and hydroformylation.[11] The apparent exception to this generalization was $Ru_3(CO)_{12}$. The ruthenium carbonyl was found effective for the new reaction of an olefin with a hydrosilane and carbon monoxide.[12] While the ruthenium carbonyl was known also effective for hydroformylation,[13] there seemed to be only a few reports (vide infra) on the catalytic activity of $Ru_3(CO)_{12}$ for hydrosilylation reaction.[3,10] Thus, we initiated the study of the reaction of alkenes with hydrosilanes in the presence of $Ru_3(CO)_{12}$ and soon discovered that $Ru_3(CO)_{12}$ was a particularly effective catalyst to produce vinylsilanes from aromatic alkenes and hydrosilanes.[14] The $Ru_3(CO)_{12}$-catalyzed reaction is unusual in the sense that it does not produce hydrosilylation adducts at all. This paper describes the scope and limitation of the $Ru_3(CO)_{12}$-catalyzed synthesis of vinylsilanes from alkenes and hydrosilanes (eq 1).[15]

Results and Discussion

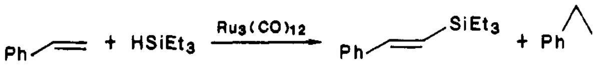
Reaction of Alkenes Having No Allylic Hydrogen. The catalytic activity of ruthenium complexes for hydrosilylation of alkenes has received so far less attention.[3] Speier reported hydrosilylation of 1-pentene using $RuCl_3$ as a catalyst.[16] The following ruthenium complexes are known to have catalytic activity: $RuH_3(PPh_3)Si(OMe)_2Ph$,[17] $RuH_2(PPh_3)_4$,[17b] $RuCl_2(PPh_3)_3$.[17b,18] These ruthenium complexes, however, yield only a corresponding alkylsilane. As mentioned before, photocatalyzed reaction employing $Ru_3(CO)_{12}$ is known to give a mixture of alkyl- and alkenylsilanes.[10]

Table II. $Ru_3(CO)_{12}$-Catalyzed Reaction of 1-Hexene with $HSiEt_3$[a]

reactn temp, °C	reactn time, h	combined yield of 16 and 17,[b] %	ratio of 16 and 17,[b] %	
			16	**17** (Z:E)
64	4	100	29	71 (32:68)
50	7	99	84	16 (31:69)
20	50	47	83	17 (37:63)
64	2	89	36	64 (28:72)
	4	100	29	71 (32:68)
	9	100	17	83 (35:65)
	24	100	16	84 (40:60)

[a] 1-Hexene (50 mmol), $HSiEt_3$ (10 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), in all runs. [b] Determined by GLC.

In contrast to these results, we have found that when $Ru_3(CO)_{12}$ was used as a catalyst for the reaction of styrene and $HSiEt_3$, the product obtained almost quantitatively (93% yield) was (E)-1-phenyl-2-(triethylsilyl)ethylene (1) instead of an addition product (eq 2). The reaction proceeded at 50–160 °C in benzene, or without solvents, under nitrogen. Hydrogen did not evolve, but ethylbenzene was formed in 96% yield based on $HSiEt_3$. Results with various alkenes are summarized in Table I.



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(2)

Trialkylsilanes ($HSiEt_3$, $HSiMe_3$, $HSiEt_2Me$, $HSiMe_2Ph$) smoothly reacted to give the vinylsilanes (**1**–**4**) in high yields. The reaction of $HSi(OEt)_3$ needed higher temperature (160 °C) to give **5**. A vinylsilane was not obtained from $HSiMeCl_2$. p-Methylstyrene, p-methoxystyrene, p-chlorostyrene, and 2-vinylnaphthalene also gave the vinylsilanes (**6**–**9**) in high yields based on hydrosilanes.

Aliphatic alkenes such as 3,3-dimethylbut-1-ene also gave the vinylsilane (**10**) in 88% yield. On the other hand, aliphatic alkenes having hydrogen at the allylic position such as 1-hexene yielded a mixture of vinylsilanes and allylsilanes as will be described later. With alkenes having an alkoxy or siloxy group at the allylic or vinylic position, side reactions involving C–O bond cleavage occurred. For example, the reaction of 3-methyl-3-(trimethylsiloxy)but-1-ene afforded **11** in low yield, and $Et_3SiOSiMe_3$ was obtained as a byproduct. The reaction of n-butoxyethylene gave **12** in 58% (Z:E = 29:71) and butoxytriethylsilane in 23% yields. Interestingly, hydrosilylation did not take place in general for the $Ru_3(CO)_{12}$-catalyzed reaction. Only in the cases of ethyl acrylate and ethylene were the vinylsilanes (**14**, **15**) as well as the simple addition products (alkylsilanes) obtained. (Triethylsilyl)ethylene (**15**) yielded 1,2-bis(triethylsilyl)ethylene (**13**) in 94% yield. The reaction of vinylsilanes with hydrosilanes in the presence of ruthenium[8,19] or osmium[8] complexes has already been re-

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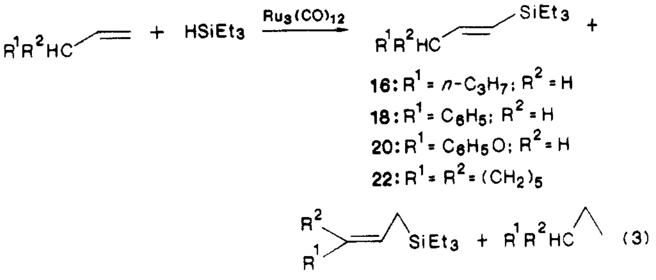
Table III. Formation of Vinylsilanes and Allylsilanes from Alkenes and $HSiEt_3$[a]

alkene	reactn temp, °C	reactn time, h	product	yield,[b] %
1-hexene	50	7	**16**	83
			17	16[c]
allylbenzene	50	12	**18**	77
			19	15
	140	4	**18**	3
			19	86
3-phenoxyprop-1-ene	50	12	**20**	80
			21	3
	140	4	**20**	22
			21	37[d]
vinylcyclohexane	50	12	**22**	79
			23	15
β-methylstyrene	140	5	**19**	58
2-hexene	64	5	**16**	41
			17	22
α-methylstyrene	140	5	**24**	52[e]
			25	15

[a] Alkene (50 mmol), $HSiEt_3$ (10 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), in all runs. [b] Yield determined by GLC. [c] Z:E = 31:69. [d] Z:E = 50:50. [e] Z:E = 79:21.

ported to give 1,2-disilylethylenes but only in low yields. The following alkenes were recovered unchanged: acrylonitrile, vinyl propionate, cyclohexene, 1,1-diphenylethylene.

Reaction of Alkenes Having Hydrogen at the Allylic Position. $Ru_3(CO)_{12}$-catalyzed reaction of alkenes having hydrogen at the allylic position with a hydrosilane gave a mixture of vinylsilanes and allylsilanes in addition to the corresponding alkanes (eq 3). It should be noted that again no hydrosilylation took place. For example, the reaction of 1-hexene with $HSiEt_3$ in the presence of $Ru_3(CO)_{12}$ gave the vinylsilane (**16**) and the allylsilane (**17**) in 83% and 16% yields, respectively, when the reaction was run at 50 °C for 7 h without solvent using a 5-fold excess of 1-hexene. The ratio of **16** to **17** decreased with an increase in the reaction temperature and with the elapse of time as shown in Table II. These results suggest that the initially formed vinylsilane (**16**) isomerized to **17**. Results with several alkenes are shown in Table III. Allylbenzene with $HSiEt_3$ under mild conditions also gave a mixture of the vinylsilane (**18**) and the allylsilane (**19**) in 77% and 15% yields, respectively. Under more forcing conditions, **19** was obtained almost exclusively in 86% yield. The reaction of 3-phenoxyprop-1-ene gave **20** with high selectivity under mild conditions. Vinylcyclohexane yielded the vinylsilane (**22**; 79% yield), along with the allylic isomer (**23**; 15% yield).



16: $R^1 = n\text{-}C_3H_7$; $R^2 = H$
18: $R^1 = C_6H_5$; $R^2 = H$
20: $R^1 = C_6H_5O$; $R^2 = H$
22: $R^1 = R^2 = (CH_2)_5$

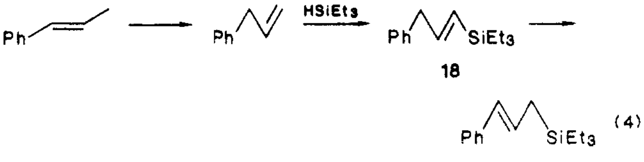
17: $R^1 = n\text{-}C_3H_7$; $R^2 = H$
19: $R^1 = C_6H_5$; $R^2 = H$
21: $R^1 = C_6H_5O$; $R^2 = H$
23: $R^1 = R^2 = (CH_2)_5$

Disubstituted alkenes were generally less reactive than monosubstituted alkenes, and those that could not isomerize to the terminal alkenes gave no reaction product. For example, β-methylstyrene gave selectively **19** under the more forcing conditions than those of allylbenzene, but cyclohexene did not yield any products even at 140 °C. The reaction path of β-methylstyrene is assumed as follows (eq 4). Initially, β-methylstyrene would isomerize to allylbenzene, and then the allylbenzene would react with $HSiEt_3$ to give **18**. The vinylsilane (**18**) may isomerize to **19** at the high reaction temperature. Similarly, the reaction of 2-hexene gave the same products as those of 1 hexene. The reaction of α-methylstyrene also gave a mixture of vinylsilanes (**24**) and an allylsilane (**25**) in 52% and 15% yields, respectively (eq 5).

Table IV. Reaction of Styrene with $HSiEt_3$ in the Presence of Alkenes[a]

coexisting alkene	yield of 1 based on styrene,[b] %	coexisting alkene	yield of 1 based on styrene,[b] %
1-pentene	70	allylbenzene	61
1-hexene	75	β-methylstyrene	49
2-hexene	48	acrylonitrile	0
2-methylhex-1-ene	50	methyl acrylate	0
cyclohexene	46	methyl vinyl ketone	34

[a] Styrene (10 mmol), alkene (10 mmol), $HSiEt_3$ (10 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), benzene (10 mL), 80 °C, 3 h. [b] Determined by GLC.



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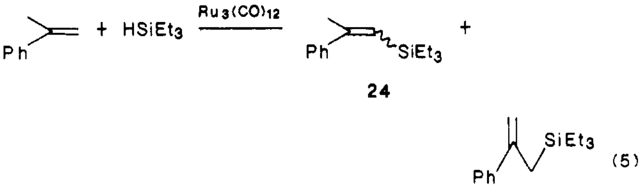

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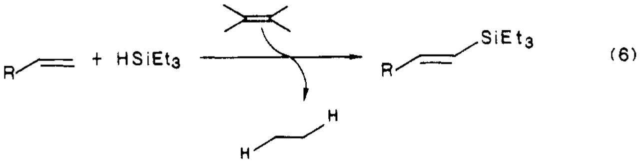
Reaction of Substituted Styrene with $HSiEt_3$ in the Presence of 1-Hexene. It is expected that the yield of vinylsilanes from precious alkenes will increase if a less expensive alkene can act only as the hydrogen acceptor (eq 6).



The $Ru_3(CO)_{12}$-catalyzed reaction of styrene (10 mmol) with $HSiEt_3$ (10 mmol) was carried out in the presence of an equimolar amount of an alkene (10 mmol). If one assumes that the coexisting alkene does not participate in the reaction of styrene with $HSiEt_3$, the possible maximal yield of **1** is 5 mmol or 50%, because a half-amount of styrene should be consumed by hydrogenation.

The results are shown in Table IV. The reaction in the presence of 1-hexene gave **1** in 75% yield, along with a small amount of **16** and **17** (7% and 12% yields, respectively). On the other hand, 2-methylhex-1-ene, 2-hexene, cyclohexene, and β-methylstyrene did not participate in the reaction of styrene. The reaction in the presence of allylbenzene also gave **1** in more than 50% yield. The

Table V. 1-Hexene as a Hydrogen Acceptor in the Reaction of Styrene[a]

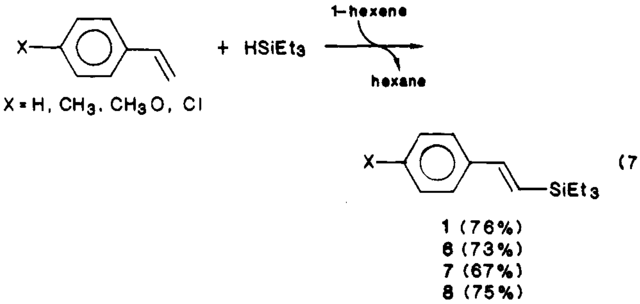
1-hexene, mmol	styrene, mmol	$HSiEt_3$, mmol	yield of 1,[b] %
5	10	10	60
9	10	10	64
10	10	10	75
15	10	10	67
20	10	10	64
30	10	10	31
10	10	15	64
15	10	15	76

[a] $Ru_3(CO)_{12}$ (0.05 mmol), benzene (10 mL), 80 °C, 3 h. [b] Determined by GLC, based on styrene.

alkenes having the ability of the hydrogen acceptor seemed to be monosubstituted alkenes. Strongly coordinating alkenes such as acrylonitrile, methyl acrylate, and methyl vinyl ketone did not behave as a hydrogen acceptor.

The scope of the reaction using 1-hexene was then studied. When the ratio of 1-hexene to styrene was increased from 5:10 to 10:10, the yield of 1 increased as shown in Table V. Further increase in the ratio of 1-hexene to styrene resulted in the decrease in the yield of 1. The reaction in the presence of a 3-fold excess of 1-hexene gave the alkenylsilanes (**16**, **17**) produced from 1-hexene in 69% combined yield, along with **1** (31% yield). Thus, in the presence of a large excess amount of 1-hexene, the reaction of 1-hexene with $HSiEt_3$ became predominant. The yield of **1** was highest (76%) under the reaction conditions employing a 1.5-fold excess of both 1-hexene and $HSiEt_3$.

This reaction was applied to several alkenes under the best reaction conditions. Substituted styrene smoothly reacted to give the corresponding vinylsilane (**6**–**8**) in good yields (eq 7). As the substituted styrenes are usually expensive, this method is useful for the preparation of the (*E*) isomer of the vinylsilanes from the substituted styrene. The similar reactions of allylbenzene in the presence of 1-hexene was not successful, and the combined yield of **18** and **19** was only 29%. Therefore, it seems that a search for a good hydrogen acceptor for a given precious alkene must be undertaken.

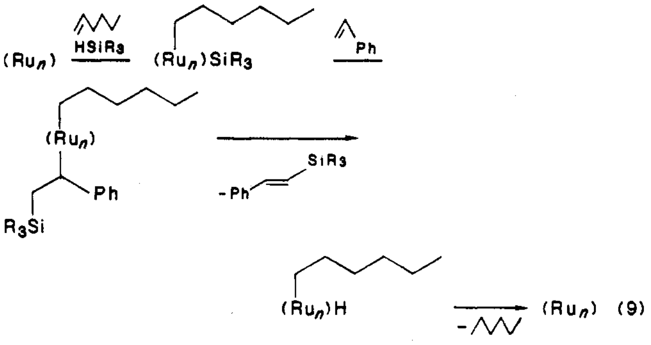


As to the mechanism of the vinylsilane formation from alkenes and hydrosilanes, some related comments are found in the literature. Wrighton and co-workers proposed that the key intermediate would be $(H)(R_3Si)Fe(CO)_3$(alkene) in the $Fe(CO)_5$-photocatalyzed reactions of trialkylsilanes with alkenes and the transfer of the R_3Si moiety to the coordinated alkene would lead to a vinylsilane.[10] The similar mechanism in the $RhCl(PPh_3)_3$-catalyzed reaction of styrene with a hydrosilane has been described by Onopchenko and co-workers.[5b] Maitlis and co-workers proposed a dialkylrhodium intermediate containing a β-silylalkyl group for the rhodium complex catalyzed reaction of 1-hexene with $HSiEt_3$.[9] Ojima and co-workers suggested the formation of a similar dialkyl complex intermediate in the $Ru_3(CO)_{12}$-catalyzed reaction of fluoroalkenes (eq 8).[15]

$$CF_3CH{=}CH_2 + HSiEt_3 \xrightarrow{Ru_3(CO)_{12}} CF_3CH{=}CHSiEt_3 \quad (8)$$

As possible routes to the alkenylsilanes such as **1**, dehydrogenation of an alkylsilane, hydrogenation of an alkynylsilane, or hydrosilylation of an alkene may be envisioned. However, these possibilities can be ruled out as follows. A mixture of styrene and 2-(triethylsilyl)-1-phenylethane was reacted with $HSiEt_2Me$ in the presence of $Ru_3(CO)_{12}$. From the reaction mixture, **3** was obtained in high yield, but 2-(triethylsilyl)-1-phenylethane did not afford the vinylsilane **1** and was recovered unchanged. The fact that the vinylsilane **24** was formed from α-methylstyrene excludes the possibility of any acetylenic intermediates.

For the present reaction using $Ru_3(CO)_{12}$, it is attractive to assume the reaction scheme like eq 9 that also involves



the silylmetalation followed by hydride elimination. However, it should be emphasized that almost no information relating to the mechanism is available at present time. For example, it is not clear whether the active catalyst is monomeric,[20] dinuclear,[21] or trinuclear.[22] It is not known even whether a (β-silylalkyl)ruthenium complex is involved. More experiments are needed to understand the mechanism of the present catalytic reaction.

In conclusion, the present studies have revealed that $Ru_3(CO)_{12}$ is effective catalyst for the one-step synthesis of vinylsilanes from alkenes and hydrosilanes. The new ruthenium chemistry seemed attractive for the synthesis of some silicon monomers of industrial importance. To demonstrate its applicability, the synthesis of a vinyltrialkoxysilane from ethylene was attempted. Although the reaction conditions have not been optimized, vinyltriethoxysilane was obtained from ethylene (eq 10).

$$CH_2{=}CH_2 + HSi(OEt)_3 \xrightarrow{Ru_3(CO)_{12}} \underset{41\%}{CH_2{=}CHSi(OEt)_3} + \underset{19\%}{CH_3CH_2Si(OEt)_3} \quad (10)$$

The results may open a new route to vinyltrialkoxysilanes without using any chlorine containing materials, since trialkoxysilanes are obtainable directly from alcohols and metallic silicon.[23] A conventional route to the vi-

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[20] (a) Wrighton suggested a monomeric ruthenium in the photocatalyed reaction.[10] (b) **Note Added in Proof.** Very recently Randolph and Wrighton have demonstrated photoinduced alkene insertion into the Fe–Si bond of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, an important reaction that is relevant to the mechanism of the present vinylsilane synthesis, see: Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

[21] Stone reported a SiRuRuSi complex: Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2560.

[22] Fink has shown a catalytic reaction involving a triruthenium cluster: Suss-Fink, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73.

[23] Suzuki, T.; Imaki, N.; Yamamura, T. Japan Kokai 55-76891.

nyltrialkoxysilanes involves addition of trichlorosilane to acetylene followed by alcoholysis.

Experimental Section

General Comments. All temperatures are uncorrected. IR spectra were recorded with a Shimazu IR-400 or a Shimazu IR-27G. The ^1H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer or a Varian EM-360 spectrometer with Me_4Si as an internal standard. Mass spectra were recorded on a Hitachi mass spectrometer, Model RMU-6E and M-80. Analytical gas chromatography (GLC) was carried out on a Shimazu GC-3BF with flame ionization detecters. The GLC columns used were as follows: (A) 6 m × 3 mm stainless steel containing 5% Silicon OV-1 supported on 60–80-mesh Uniport KS; (B) 3 m × 3 mm stainless-steel containing 15% DEGS supported on 60–80-mesh Chromosorb W. Preparative GLC was carried out on a Hitachi GC-164. Alkenes were commercially available except for 3-methyl-3-(trimethylsiloxy)but-1-ene, which was prepared by the reaction of 3-hydroxy-3-methylbut-1-ene with trimethylsilyl chloride and triethylamine in DMF. $Ru_3(CO)_{12}$ and $HSi(OEt)_3$ were commercially available. All the hydrosilanes and (triethylsilyl)ethylene (**15**) were prepared from the corresponding chlorosilanes by standard methods.[24]

Reaction of Alkenes with Hydrosilanes in the Presence of $Ru_3(CO)_{12}$. A general procedure is given by the preparation of (*E*)-1-phenyl-2-(triethylsilyl)ethylene (**1**). A 20-mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stir bar was flame dried under a flow of nitrogen and then was charged with 30 mmol of styrene, 10 mmol of $HSiEt_3$, 0.05 mmol of $Ru_3(CO)_{12}$, and 10 mL of benzene. The solution was evacuated and refilled to atmospheric pressure with pure nitrogen. This procedure was repeated three times. The solution was heated at 80 °C with stirring. After about 10 min, $Ru_3(CO)_{12}$ completely dissolved and the solution became clear brown. The brown gradually faded to become clear bright yellow and then gradually changed to dark brown. The reaction temperature was maintained at 80 °C for 5 h. Analysis of the reaction mixture by GLC (column A, 160 °C, *n*-heptadecane as an internal standard) showed it to contain **1** in 93% yield. Analysis by GLC (column B, 100 °C, toluene as an internal standard) showed the formation of ethylbenzene in 96% yield. Distilation [152–154 °C (20 mmHg)] of the reaction mixture and the purification by preparative GLC afforded the analytical sample.

1: IR (neat) 1605 cm^{-1} (C=C); NMR (CCl_4) δ 0.066 (m, 6 H), 1.00 (m, 9 H), 6.28 (d, *J* = 19 Hz, C=CHSi), 6.83 (d, *J* = 19 Hz, HC=CSi), 7.08–7.40 (c, 5 H); mass spectrum, *m*/*e* (relative intensity) 218 (16), 189 (100), 161 (61), 159 (17), 133 (29), 131 (28). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.16. Found: C, 76.72; H, 10.30.

(*E*)-1-Phenyl-2-(trimethylsilyl)ethylene (2). A solution of styrene (30 mmol) and $Ru_3(CO)_{12}$ (0.05 mmol) in 10 mL of benzene was placed in a 100-mL stainless-steel autoclave. The autoclave was cooled to −70 °C. $HSiMe_3$ (10 mmol) was introduced to the autoclave by trap-to-trap distillation under vacuum (30 mmHg), and then the autoclave was heated at 100 °C for 5 h. Analysis of the reaction mixture by GLC with an internal standard (*n*-tetradecane) showed it to contain **2** in 86% yield: bp 125–135 °C (35 mmHg); IR (neat) 1610 cm^{-1} (C=C); NMR (CCl_4) δ 0.15 (s, 9 H), 6.27 (d, *J* = 19 Hz, C=CHSi), 6.80 (d, *J* = 19 Hz, HC=CSi), 7.06–7.43 (c, 5 H); mass spectrum, *m*/*e* (relative intensity) 176 (30), 161 (94), 145 (41), 135 (28). Anal. Calcd for $C_{11}H_{16}Si$: C, 74.92; H, 9.15. Found: C, 74.64; H, 9.24.

(*E*)-1-Phenyl-2-(diethylmethylsilyl)ethylene (3): yield 93%; bp 140–145 °C (28 mmHg); IR (neat) 1605 cm^{-1} (C=C); NMR (CCl_4) δ 0.10 (s, 3 H), 0.63 (m, 4 H), 0.97 (m, 6 H), 6.28 (d, *J* = 19 Hz, C=CHSi), 6.86 (d, *J* = 19 Hz, HC=CSi), 7.10–7.46 (c, 5 H); mass spectrum, *m*/*e* (relative intensity) 204 (13), 189 (3), 175 (100), 147 (53), 145 (39), 131 (10), 121 (11). Anal. Calcd for $C_{13}H_{20}Si$: C, 76.39; H, 9.86. Found: C, 76.43; H, 10.07.

(*E*)-1-Phenyl-2-(dimethylphenylsilyl)ethylene (4): yield 96%; bp 150–160 °C (26 mmHg); IR (neat) 1605 cm^{-1} (C=C); NMR (CCl_4) δ 0.40 (s, 6 H), 6.43 (d, *J* = 19 Hz, C=CHSi), 6.90 (d, *J* = 19 Hz, HC=CSi), 7.07–7.59 (c, 10 H); mass spectrum, *m*/*e* (relative intensity) 238 (48), 223 (83), 145 (100), 135 (10), 121 (36), 105 (4). Anal. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61. Found: C, 80.63; H, 7.71.

(*E*)-1-Phenyl-2-(triethoxysilyl)ethylene (5): yield 36%; bp 130–140 °C (33 mmHg); IR (neat) 1610 cm^{-1} (C=C); NMR (CCl_4) δ 1.23 (t, *J* = 6 Hz, 9 H), 3.77 (q, *J* = 6 Hz, 6 H), 5.97 (d, *J* = 19 Hz, C=CHSi), 7.03 (d, *J* = 19 Hz, HC=CSi), 7.03–7.43 (c, 5 H). Anal. Calcd for $C_{14}H_{23}O_3Si$: C, 63.11; H, 8.32. Found: C, 62.77; H, 8.34.

(*E*)-1-(*p*-Methylphenyl)-2-(triethylsilyl)ethylene (6): yield 100%; bp 175–179 °C (30 mmHg); IR (neat) 1610 cm^{-1} (C=C); NMR (CCl_4) δ 0.63 (m, 6 H), 0.97 (m, 9 H), 2.30 (s, 3 H), 6.20 (d, *J* = 19 Hz, C=CHSi), 6.80 (d, *J* = 19 Hz, HC=CSi), 7.00–7.23 (m, 4 H); mass spectrum, *m*/*e* (relative intensity) 232 (16), 203 (100), 175 (44), 173 (19), 147 (22), 145 (27). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.72; H, 10.60.

(*E*)-1-(*p*-Methoxyphenyl)-2-(triethylsilyl)ethylene (7): yield 83%; bp 115–120 °C (0.03 mmHg); IR (neat) 1610 cm^{-1} (C=C); NMR (CCl_4) δ 0.63 (m, 6 H), 0.98 (m, 9 H), 3.74 (s, 3 H), 6.07 (d, *J* = 19 Hz, C=CHSi), 6.70 (d, *J* = 10 Hz, 2 H), 6.77 (d, *J* = 19 Hz, HC=CSi), 7.25 (d, *J* = 10 Hz, 2 H); mass spectrum, *m*/*e* (relative intensity) 248 (33), 219 (100), 191 (48), 163 (30), 161 (19). Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.44; H, 9.86.

(*E*)-1-(*p*-Chlorophenyl)-2-(triethylsilyl)ethylene (8): yield 94%; bp 180–185 °C (23 mmHg); IR (neat) 1610 cm^{-1} (C=C); NMR (CCl_4) δ 0.63 (m, 6 H), 0.96 (m, 9 H), 6.25 (d, *J* = 19 Hz, C=CHSi), 6.77 (d, *J* = 19 Hz, HC=CSi), 7.21 (s, 4 H); mass spectrum, *m*/*e* (relative intensity) 254 (8), 252 (15), 223 (100), 195 (75), 167 (35), 165 (25), 141 (15), 131 (15). Anal. Calcd for $C_{14}H_{21}ClSi$: C, 66.50; H, 8.37. Found: C, 66.24; H, 8.66.

(*E*)-1-(2-Naphthyl)-2-(triethylsilyl)ethylene (9): yield 88%; bp 140–150 °C (0.05 mmHg); IR (neat) 1620 cm^{-1} (C=C); NMR (CCl_4) δ 0.69 (m, 6 H), 1.00 (m, 9 H), 6.40 (d, *J* = 20 Hz, C=CHSi), 7.02 (d, *J* = 20 Hz, HC=CSi), 7.18–7.43 (c, 2 H), 7.50–7.79 (c, 5 H); mass spectrum, *m*/*e* (relative intensity) 268 (22), 239 (100), 211 (28), 209 (13), 183 (23), 181 (23), 155 (11). Anal. Calcd for $C_{18}H_{24}Si$: C, 80.53; H, 9.01. Found: C, 80.33; H, 9.09.

(*E*)-3,3-Dimethyl-1-(triethylsilyl)but-1-ene (10): yield 88%; bp 93–96 °C (22 mmHg); IR (neat) 1615 cm^{-1} (C=C); NMR (CCl_4) δ 0.40–0.68 (m, 6 H), 0.82–1.08 (m, 9 H) overlapped with 1.0 (s, 9 H), 5.38 (d, *J* = 19 Hz, C=CHSi), 6.02 (d, *J* = 19 Hz, HC=CSi); mass spectrum, *m*/*e* (relative intensity) 198 (5), 169 (100), 141 (56), 113 (21), 99 (18). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.90; H, 13.49.

(*E*)-3-Methyl-3-(trimethylsiloxy)-1-(triethylsilyl)prop-1-ene (11): yield 42%; bp 90–110 °C (20 mmHg); IR (neat) 1620 cm^{-1} (C=C); NMR (CCl_4) δ 0.08 (s, 9 H), 0.44–0.66 (m, 6 H), 0.92 (m, 9 H), 1.23 (s, 6 H), 5.58 (d, *J* = 19 Hz, C=CHSi), 6.10 (d, *J* = 19 Hz, HC=CSi); mass spectrum, *m*/*e* (relative intensity) 272 (11), 257 (37), 199 (26), 175 (37), 157 (58), 131 (100). Anal. Calcd for $C_{14}H_{32}OSi_2$: C, 61.69; H, 11.84. Found: C, 61.76; H, 11.89.

Triethyltrimethylsiloxane: yield 41%; NMR (CCl_4) δ 0.10 (s, 9 H), 0.40–0.80 (m, 6 H), 0.90–1.10 (m, 9 H).

1-Butoxy-2-(triethylsilyl)ethylene (12). *Z* Isomer: yield 17%; bp 130–132 °C (30 mmHg); IR (neat) 1605 cm^{-1} (C=C; NMR (CCl_4) δ 0.40–0.70 (m, 6 H), 0.80–1.10 (m, 12 H), 1.20–1.70 (c, 4 H), 3.70 (t, *J* = 6 Hz, 2 H), 3.98 (d, *J* = 8 Hz, C=CHSi), 6.52 (d, *J* = 8 Hz, HC=CSi).

***E* Isomer**: yield 41%; bp 130–132 °C (30 mmHg); IR (neat) 1620 cm^{-1} (C=C); NMR (CCl_4) δ 0.40–0.68 (m, 6 H), 0.80–1.08 (m, 12 H), 1.20–1.80 (c, 4 H), 3.66 (t, *J* = 6 Hz, 2 H), 4.26 (d, *J* = 16 Hz, C=CHSi), 6.32 (d, *J* = 16 Hz, HC=CSi); mass spectrum, *m*/*e* (relative intensity) 214 (2), 185 (34), 159 (100), 131 (11), 103 (17). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.38; H, 12.33.

***n*-Butoxytriethylsilane**: yield 23%; NMR (CCl_4) δ 0.47–0.77 (m, 6 H), 0.83–1.17 (m, 12 H), 1.33–1.57 (c, 4 H), 3.93 (t, *J* = 6 Hz, 2 H).

(*E*)-1,2-Bis(triethylsilyl)ethylene (13): yield 94%; bp 120–125 °C (15 mmHg); IR (neat) 2950, 2870, 1010, 750, 720 cm^{-1}; NMR (CCl_4) δ 0.56 (m, 12 H), 0.93 (m, 18 H), 6.51 (s, HC=C); mass spectrum, *m*/*e* (relative intensity) 256 (12), 227 (38), 119 (22), 115 (100), 87 (41). Anal. Calcd for $C_{14}H_{32}Si_2$: C, 65.53; H,

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[24] Steward, O. W.; Pierce, O. R. *J. Am. Chem. Soc.* **1961**, *83*, 1916. Gilman, H.; Diehl, J. *J. Org. Chem.* **1961**, *26*, 4817. Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108.

12.57. Found: C, 65.46; H, 12.37.

The chemical shifts of the vinylic proton of 1,1-bis(trimethylsilyl)ethylene and (*E*)-1,2-bis(trimethylsilyl)ethylene were reported to be δ 6.25 and 6.56 in $\mathrm{CCl_4}$ solution, respectively.[25] Furthermore, it is known that the IR spectrum of the (*E*) isomer of 1,2-bis(silyl)ethylene shows a band at 1010 $\mathrm{cm^{-1}}$, while the spectrum of the (*Z*) isomer had no absorption in this region.[26] Therefore, the product (**13**) was assigned to be of the (*E*) configuration.

(*E*)-1-Carboethoxy-2-(triethylsilyl)ethylene (14): yield 39%; bp 138–142 °C (35 mmHg); IR (neat) 1725 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CCl_4}$) δ 0.63 (m, 6 H), 0.98 (m, 9 H), 1.28 (t, *J* = 5 Hz, 3 H), 4.14 (q, *J* = 5 Hz, 2 H), 6.18 (d, *J* = 19 Hz, C=CHSi), 7.11 (d, *J* = 19 Hz, HC=CSi); mass spectrum, *m/e* (relative intensity) 185 (100), 169 (8), 157 (96), 129 (20), 101 (8), 87 (8). Anal. Calcd for $\mathrm{C_{11}H_{22}O_2Si}$: C, 61.63; H, 10.35. Found: C, 61.42; H, 10.49.

The retention time of 1-carobethoxy-2-(triethylsilyl)ethane agreed with that of the authentic sample independently prepared.[27]

Reaction of Ethylene with $\mathbf{HSiEt_3}$. A 100-mL stainless-steel autoclave equipped with a magnetic stirring bar was charged with 10 mmol of $\mathrm{HSiEt_3}$, 0.05 mmol of $\mathrm{Ru_3(CO)_{12}}$, and 10 mL of benzene. The autoclave was flushed with $\mathrm{N_2}$ (30 $\mathrm{kg/cm^2}$) two times and then charged with ethylene to 30 $\mathrm{kg/cm^2}$. The reaction vessel was heated with magnetic stirring in an oil bath. The temperature was maintained at 50 °C for 5 h. Analysis of the reaction mixture by GLC showed it to contain **15** and tetraethylsilane in 65% and 25% yields, respectively.

Reaction of 1-Hexene with $\mathbf{HSiEt_3}$. A solution containing 1-hexene (50 mmol), $\mathrm{HSiEt_3}$ (10 mmol), and $\mathrm{Ru_3(CO)_{12}}$ (0.05 mmol) was stirred at 50 °C for 7 h. Analysis of the reaction mixture by GLC (column A, 140 °C, *n*-tetradecane as an internal standard) showed it to contain **16** and **17** in 83% and 16% (*E*:*Z* = 69:31) yields, respectively. Analytical samples were obtained by distillation [bp 118–122 °C (30 mmHg)] and preparative GLC.

16: RRT 0.44; IR (neat) 1615 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.52 (m, 6 H), 0.92 (m, 9 H), 1.36 (c, 4 H), 2.08 (m, 2 H), 5.46 (d, *J* = 19 Hz, C=CHSi), 5.98 (dt, *J* = 19 and 6 Hz, HC=CSi); mass spectrum, *m/e* (relative intensity) 198 (5), 169 (100), 141 (90), 113 (28). Anal. Calcd for $\mathrm{C_{12}H_{26}Si}$: C, 72.64; H, 13.21. Found: C, 72.72; H, 13.48.

***E* Isomer of 17**: RRT 0.47; IR (neat) 1655 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.40–0.64 (m, 6 H), 0.80–1.08 (m, 9 H), 1.20–1.50 (c, 4 H), 1.82–2.08 (c, 2 H), 5.02–5.40 (c, HC=CH).

***Z* Isomer of 17**: RRT 0.50; IR (neat) 1645 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.40–0.64 (m, 6 H), 0.80–1.08 (m, 9 H), 1.24–1.68 (c, 4 H), 1.84–2.12 (c, 2 H), 5.20–5.44 (c, HC=CH). RRT (relative retention time) is the retention time of the compounds/retention time of the internal standard. The stereochemistry of **17** was decided from the IR spectrum.[28]

(*E*)-3-Phenyl-1-(triethylsilyl)prop-1-ene (18): bp 168–174 °C (30 mmHg); IR (neat) 1620 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.54 (m, 6 H), 0.91 (m, 9 H), 3.43 (d, *J* = 6 Hz, 2 H), 5.54 (d, *J* = 19 Hz, C=CHSi), 6.18 (dt, *J* = 19 and 6 Hz, HC=CSi), 7.15 (m, 5 H); mass spectrum, *m/e* (relative intensity) 232 (4), 203 (100), 175 (83), 147 (40), 145 (14), 141 (11). Anal. Calcd for $\mathrm{C_{15}H_{24}Si}$: C, 77.51; H, 10.41. Found: C, 77.50; H, 10.54.

(*E*)-1-Phenyl-3-(triethylsilyl)prop-1-ene (19):[29] bp 168–174 °C (30 mmHg); IR (neat) 1645 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.56 (m, 6 H), 0.96 (m, 9 H), 1.66 (m, 2 H), 6.14 (m, HC=CH), 7.12 (m, 5 H); mass spectrum, *m/e* (relative intensity) 232 (13), 203 (3), 145 (3), 115 (87), 87 (100). Anal. Calcd for $\mathrm{C_{15}H_{24}Si}$: C, 77.51; H, 10.41. Found: C, 77.29; H, 10.51.

(*E*)-3-Phenoxy-1-(triethylsilyl)prop-1-ene (20): bp 165–170 °C (20 mmHg); RRT 1.68 (*n*-hexadecane as an internal standard); IR (neat) 1600 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.58 (m, 6 H), 0.94 (m, 9 H), 4.50 (d, *J* = 4 Hz, 2 H), 5.88 (d, *J* = 19 Hz, C=CHSi), 6.20 (dt, *J* = 19 and 4 Hz, HC=CSi), 6.82–7.12 (m, 5 H); mass spectrum, *m/e* (relative intensity) 248 (5), 219 (29), 179 (18), 151 (36), 123 (28), 115 (53), 87 (100). Anal. Calcd for $\mathrm{C_{15}H_{24}OSi}$: C, 72.52; H, 9.74. Found: C, 72.26; H, 10.02.

1-Phenoxy-3-(triethylsilyl)prop-1-ene (21). *E* Isomer: RRT 1.81 (*n*-hexadecane as an internal standard); IR (neat) 1665 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.58 (m, 6 H), 0.98 (m, 9 H), 1.40 (d, *J* = 8 Hz, 2 H), 5.28 (dt, *J* = 12 and 8 Hz, 1 H), 6.22 (d, *J* = 12 Hz, 1 H), 6.72–7.32 (m, 5 H).

***Z* Isomer**: RRT 1.54; IR (neat) 1655 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.55 (m, 6 H), 0.96 (m, 9 H), 1.58 (d, *J* = 8 Hz, 2 H), 4.75 (dt, *J* = 6 and 8 Hz, 1 H), 6.25 (d, *J* = 6 Hz, 1 H), 6.80–7.32 (m, 5 H); mass spectrum, *m/e* (relative intensity) 248 (17), 219 (49), 179 (7), 151 (11), 123 (11), 115 (87), 87 (100). Anal. Calcd for $\mathrm{C_{15}H_{24}OSi}$: C, 72.52; H, 9.74. Found: C, 72.28; H, 10.04.

(*E*)-1-Cyclohexyl-2-(triethylsilyl)ethylene (22): bp 145–149 °C (28 mmHg); IR (neat) 1615 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.53 (m, 6 H), 0.89 (m, 9 H), 1.09–1.85 (c, 11 H), 5.36 (d, *J* = 19 Hz, C=CHSi), 5.96 (dt, *J* = 19 and 5 Hz, HC=CSi); mass spectrum, *m/e* (relative intensity) 224 (8), 195 (100), 167 (48), 139 (16), 115 (8), 111 (9); exact mass calcd for $\mathrm{C_{14}H_{28}Si}$ ($\mathrm{M^+}$) 224.1961, found 224.1963.

1-Cyclohexylidene-2-(triethylsilyl)ethane (23): IR (neat) 1610 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.40–0.73 (m, 6 H), 0.73–1.37 (m, 11 H), 1.37–1.83 (c, 6 H), 1.83–2.27 (c, 4 H), 5.00 (t, *J* = 8 Hz, C=CH); mass spectrum, *m/e* (relative intensity) 224 (16), 195 (25), 167 (19), 115 (100), 87 (97). Anal. Calcd for $\mathrm{C_{14}H_{28}Si}$: C, 74.91; H, 12.57. Found: C, 74.72; H, 12.86.

1-Methyl-1-phenyl-2-(triethylsilyl)ethylene (24). *Z* Isomer: bp 142–147 °C (15 mmHg); RRT 2.70 (*n*-tetradecane as an internal standard); IR (neat) 1600 $\mathrm{cm^{-1}}$; NMR ($\mathrm{CCl_4}$) δ 0.60–0.90 (m, 6 H), 1.00 (m, 9 H), 2.20 (s, 3 H), 5.77 (s, 1 H), 7.23 (m, 5 H); mass spectrum, *m/e* (relative intensity) 232 (3), 203 (100), 175 (33), 163 (28), 147 (23), 145 (28), 135 (35), 115 (23). Anal. Calcd for $\mathrm{C_{15}H_{24}Si}$: C, 77.51; H, 10.41. Found: C, 77.20; H, 10.50.

***E* Isomer**: RRT 1.58; IR (neat) 1610 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.12–0.44 (m, 6 H), 0.66–0.96 (m, 9 H), 2.14 (d, *J* = 2 Hz, 3 H), 5.44 (brs, 1 H), 7.00–7.32 (m, 5 H); mass spectrum, *m/e* (relative intensity) 232 (2), 203 (100), 175 (15), 173 (11), 163 (14), 145 (15), 135 (17), 107 (18).

2-Phenyl-3-(triethylsilyl)prop-1-ene (25): RRT 2.16 (*n*-tetradecane as an internal standard); IR (neat) 1610 $\mathrm{cm^{-1}}$ (C=C); NMR ($\mathrm{CCl_4}$) δ 0.30–0.63 (m, 6 H), 0.83 (m, 9 H), 2.00 (s, 2 H), 4.83 (brs, 1 H), 5.03 (d, *J* = 2 Hz, 1 H), 7.23 (m, 5 H); mass spectrum, *m/e* (relative intensity) 232 (5), 203 (28), 175 (23), 163 (15), 147 (15), 145 (21), 135 (23), 115 (62), 87 (100). Anal. Calcd for $\mathrm{C_{15}H_{24}Si}$: C, 77.51; H, 10.41. Found: C, 77.37; H, 10.70.

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Registry No. **1**, 21209-32-5; **2**, 19372-00-0; **3**, 62621-34-5; **4**, 64788-85-8; **5**, 65119-09-7; **6**, 75476-54-9; **7**, 75476-55-0; **8**, 75476-56-1; **9**, 75476-57-2; **10**, 42067-73-2; **11**, 104014-88-2; (*Z*)-**12**, 104014-89-3; (*E*)-**12**, 104014-98-4; **13**, 104014-91-7; **14**, 104014-91-7; **15**, 1112-54-5; **16**, 42067-72-1; (*E*)-**17**, 79643-98-4; (*Z*)-**17**, 90584-20-6; **18**, 104014-92-8; **19**, 63522-98-5; **24**, 75476-58-3; (*E*)-**21**, 104014-93-9; (*Z*)-**21**, 104014-94-0; **22**, 104014-94-0; **23**, 104014-95-1; (*Z*)-**24**, 104014-96-2; (*E*)-**24**, 104015-00-1; **25**, 104014-97-3; $\mathrm{Et_3SiOSiMe_3}$, 2652-41-7; $\mathrm{Et_3SiOBu}$, 2751-87-3; $\mathrm{CH_2{=}CHSi(OEt)_3}$, 78-08-0; $\mathrm{CH_3CH_2Si(OEt)_3}$, 78-07-9; $\mathrm{Ru_3(CO)_{13}}$, 15243-33-1; $\mathrm{HSiEt_3}$, 617-86-7; $\mathrm{HSiMe_3}$, 993-07-7; $\mathrm{HSiEt_2Me}$, 760-32-7; $\mathrm{HSiMe_2Ph}$, 766-77-8; $\mathrm{HSi(OEt)_3}$, 998-30-1; $\mathrm{PhCH{=}CH_2}$, 100-42-5; *p*-$\mathrm{CH_3C_6H_4CH{=}CH_2}$, 622-97-9; *p*-$\mathrm{CH_3OC_6H_4CH{=}CH_2}$, 637-69-4; *p*-$\mathrm{ClC_6H_4CH{=}CH_2}$, 1073-67-2; $\mathrm{R^1CH{=}CH_2}$($\mathrm{R^1}$ = 2-naphthyl), 827-54-3; $\mathrm{(CH_3)_3CCH{=}CH_2}$, 558-37-2; $\mathrm{Me_3SiO(CH_3)_2CCH{=}CH_2}$, 19916-99-5; *n*-$\mathrm{C_4H_9OCH{=}CH_2}$, 111-34-2; $\mathrm{Et_3SiCH{=}CH_2}$, 1112-54-5; $\mathrm{EtO_2CCH{=}CH_2}$, 140-88-5; $\mathrm{H_2C{=}CH_2}$, 74-85-1; 1-hexene, 592-41-6; allylbenzene, 300-57-2; 3-phenoxyprop-1-ene, 1746-13-0; vinylcyclohexane, 25168-07-4; β-methylstyrene, 637-50-3; 2-hexene, 592-43-8; α-methylstyrene, 98-83-9.

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