2.1 (m, 1 H, H_{2a}), 1.70 (dt, J = 14.5, 1.7 Hz, 1 H, H_{2e}), 1.15 (d, J = 6.0 Hz, 3 H, H_6); ^{13}C NMR (D_2O) β anomer δ 88.0, 78.0, 73.1, 67.6, 57.8, 35.4, 18.3; α anomer δ 92.1, 81.7, 80.9, 68.2, 57.0, 39.0, 18.7.

***ribo*-4-(Benzylamino)hept-1-ene-5,6-diol (21).** A resealable Carius tube was charged with 490 mg (3.83 mmol) of (+)-18, 0.42 mL (3.85 mmol) of benzylamine, 32 mg (0.34 mmol) of phenol, and 0.9 mg (0.04 mmol) of BHT. The tube was purged with argon and heated to 145 °C for 86 h. The crude product was dissolved in CH_2Cl_2 and concentrated in vacuo to give 971 mg of crude product. Recrystallization of this sample from Et_2O–CCl_4 afforded 366 mg (mp 62–64 °C) of pure **21** as bulky plates. The mother liquors were chromatographed on 90 g of silica gel (4% MeOH in CH_2Cl_2) to afford an additional 448 mg (814 mg total, 91% yield) of crystalline **21**: $[\alpha]^{20}_D$ +27° (c 1.2, EtOH); ^1H NMR ($CDCl_3$) δ 7.3 (s, 5 H, aromatic), 5.76 (m, 1 H, H_2), 5.13 (m, 2 H, H_1), 3.83, 3.75 (AB, J = 12.6 Hz, 2 H, benzylic), 3.76 (m, 1 H, H_6), 3.28 (t, J = 6.8 Hz, 1 H, H_5), 2.89 (dt, J = 4.1, 6.8 Hz, 1 H, H_4), 2.3–2.6 (m, 2 H, H_3), 1.24 (d, J = 6.2 Hz, 3 H, H_7); IR (CH_2Cl_2) 3100–3700 (br NH and OH), 3070, 3030, 2920, 1640, 1607, 1500, 1455, 1070, 995, 920 cm^{-1}; mass spectrum, m/e 236 (M^+ + 1). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.58; H, 8.80; N, 5.95.

***ribo*-4-Azidohept-1-ene-5,6-diol (22).** A solution of 97 mg (0.76 mmol) of (+)-18, 275 mg (4.2 mmol) of NaN_3, and 90 mg (1.7 mmol) of NH_4Cl in 8 mL of 8:1 methoxyethanol–H_2O was heated to reflux for 6 h. The dark solution was then cooled, diluted with 3 mL of MeOH, and neutralized with saturated aqueous $NaHCO_3$ solution. Solvents were removed in vacuo, and the residue was dissolved in EtOAc and filtered through 20 g of silica gel. This procedure afforded 120 mg of crude **22** which was used directly in the next experiment. Pure **22** was obtained in 78% yield from a similar experiment following silica gel chromatography: mp 66–67 °C; $[\alpha]^{23}_D$ −62.5° (c 0.28, CH_2Cl_2); ^1H NMR ($CDCl_3$, D_2O exchange) δ 5.8 (m, 1 H, H_2), 5.19 (br d, J = 18 Hz, 1 H, H_{1Z}), 5.13 (br d, J = 10 Hz, 1 H, H_{1E}), 3.90 (dq, J = 4.1, 6.3 Hz, 1 H, H_6), 3.50 (dd, J = 4.1, 7.5 Hz, 1 H, H_5), 3.3 (m, 1 H, H_4), 2.5–2.7 (d with fine splitting, J = 14.6 Hz, H_3), 2.35 (dt, J = 14.6, 7.5 Hz, 1 H, $H_{3'}$), 1.15 (d, J = 6.3 Hz, 3 H, H_7); IR (CH_2Cl_2) 3100–3700 (br OH), 3080, 2980, 2920, 2100, 1640, 1380, 1065, 990, 920 cm^{-1}; mass spectrum, m/e 171 (parent ion). Anal. Calcd for $C_7H_{13}N_3O_2$: C, 49.11; H, 7.65; N, 24.54. Found: C, 49.10; H, 7.51; N, 24.42.

The crude azide from the preceding experiment was dissolved in 15 mL of CH_2Cl_2 and treated with 0.4 mL of pyridine and 1.6 mL of Ac_2O at room temperature for 16 h. Analysis of the crude product by 250-MHz ^1H NMR revealed that only one isomer was present. The crude product was purified by preparative TLC (0.5-mm silica gel plate, 2:1 hexane–Et_2O, two developments, R_f 0.7) to yield 105 mg (54% from 18) of the azido diacetate: $[\alpha]^{19}_D$ +36.5° (c 3.52, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 5.72 (m, 1 H, H_2), 5.0–5.2 (m, 4 H, H_1, H_5, H_6), 3.43 (ddd, J = 4.3, 6.1, 9.2 Hz, H_4), 2.0–2.4 (m, 2 H, H_3), 2.04 (s, 3 H, acetate), 1.94 (s, 3 H, acetate), 1.19 (d, J = 6.2 Hz, 3 H, H_7); IR (CH_2Cl_2) 3080, 2940, 2110, 1740, 1640, 1370, 1225, 1020, 920 cm^{-1}; mass spectrum, m/e 256 (M^+ + 1).

Acknowledgment. This research was supported by grants from the National Cancer Institute (Grant No. CA-29847 and Training Grant No. T32-CA-09258). We are grateful to Professor K. B. Sharpless for helpful discussions and to Dr. C. Costello for measurement of high-resolution mass spectra.

Rhodium(I)-Catalyzed Hydrosilylation of Styrene

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The investigation of Rh(I)-catalyzed hydrosilylation of styrene with trisubstituted silanes (R_3SiH, R = Et, *i*-Pr, Ph, OEt, and Cl) uncovered an unusual product dependence on the rhodium-to-silane ratio, a reflection of Rh concentration, and a novel, selective route to β-silyl-substituted *trans*-styrenes. At a ratio of 10^{-4}, the expected 1-silyl- and 2-silyl-substituted 1-phenylethanes were formed. At a ratio of 10^{-3}, however, a novel β-silyl-substituted *trans*-styrene was formed as a major product. In the intermediate range, both product types were formed. The results are rationalized on the basis of predominant intermediacy of monomeric Rh(III) complexes in the former and dimeric Rh complexes in the latter. The novel *trans*-styrenes are believed to be formed via a dihydridorhodium elimination process in which the dihydridorhodium hydrogenates styrene to give ethylbenzene as the coproduct.

Introduction

The chloroplatinic acid catalyzed addition of various chlorosilanes to styrene is well documented.[1] More recently, the reaction of trimethyl-, triethoxy-, and trichlorosilanes with styrene, catalyzed by Rh(I) complexes, was reported.[2] In both cases, a mixture of 1-silyl- and 2-silyl-substituted-1-phenylethanes was obtained. A recent review of the hydrosilylation reaction is available.[3]

In the present study, we investigated the rhodium-catalyzed hydrosilylation of styrene with trisubstituted silanes. The nature of the products was found to depend on the rhodium-to-silane ratio; under appropriate reaction conditions, β-silyl-substituted *trans*-styrenes were actually the major products of reaction.[4] While compounds of this type are known and can easily be prepared via hydrosilylation of phenylacetylene,[3,5] previous researchers failed to recognize the new reaction pathway that occurs during hydrosilylation of styrene.

Results

In the Rh(I)-catalyzed reaction of triethylsilane with styrene, under the reported conditions,[2] three silyl-containing products were obtained: 1-(triethylsilyl)-1-

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[1] Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1964**, *29*, 2519.

[2] Rejhon, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3680.

[3] Speier, J. L. In "Advances in Organometallic Chemistry", Academic Press: 1979; Vol. 17, p 407.

[4] A similar product has been reported by using a ruthenium carbonyl cluster as catalyst: Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 928.

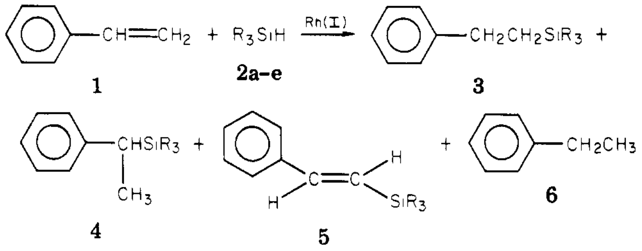
[5] Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91.

Table I. Hydrosilylation of Styrene with Triethylsilane[a]

$RhH(CO)(PPh_3)_3/Et_3SiH$, mmol/mmol	reaction time,[f] h	% yield[b] $PhCH_2CH_3$ (6)	$PhCH_2CH_2SiEt_3$ (3)	*trans*-$PhCH=CHSiEt_3$ (5)	$PhCH(CH_3)SiEt_3$ (4)	Et_3SiH, % conv[c]
3.9×10^{-3} (43.3)[e]	6.5	43	8	44	trace	53
6.3×10^{-4} (7.0) $^{-4}$	5.5	35	15	38	9	62
1.9×10^{-4} (2.1)	16	8	23	8	49	80
0.9×10^{-4} (1.0)	4.5[d]	2	27	1	51	79
6.3×10^{-4} (7.0)[g]	7.5	2	4	3	8	16

[a] Reactants: 19.2 mmol of styrene and 17.2 mmol of Et_3SiH in benzene (15 mL); 50 °C, under N_2. [b] Based on Et_3SiH, values rounded off to the nearest whole number. [c] Based on isolated silyl-containing products. [d] 65 °C. [e] Relative ratio. [f] Arbitrary reaction times. [g] Repeat of standard run in benzene (200 mL); 65 °C, under N_2. Product also contained 1% of 7.

Scheme I[a]



[a] a, R = Et; b, R = Ph; c, R = *i*-Pr; d, R = OEt; e, R = Cl.

phenylethane (9%), 2-(triethylsilyl)-1-phenylethane (15%), and β-(triethylsilyl)-*trans*-styrene (38%). Additionally, a 35% yield of ethylbenzene was coproduced, which corresponded to the amount of β-(triethylsilyl)-*trans*-styrene formed (Scheme I). The only difference between our work and that of Rejhon and Heflejs[2] is the higher $Rh(I)/Et_3SiH$ molar ratio employed by us (6.3×10^{-4}). Indeed, when the ratio was lowered to that reported (0.9×10^{-4}),[2] the silyl-containing *trans*-styrene had virtually disappeared and 1-(triethylsilyl)- and 2-(triethylsilyl)-1-phenylethanes were formed instead. In this case less than 1% of ethylbenzene was formed. Similar results were obtained with styrene and trisubstituted silanes in which the silane was substituted with phenyl, isopropyl, ethoxy, and chloro substituents, respectively. A lower yield of the *trans*-styrene product was formed from the reaction of styrene with triethoxysilane and virtually none from the reaction of styrene with trichlorosilane, in spite of the high $Rh(I)/R_3SiH$ ratio used.

Thus, a new reaction was discovered, which affords high selectivity of β-silyl-substituted *trans*-styrenes, and which occurs at the expense of styrene, which is hydrogenated to ethylbenzene. This reaction depends on the $Rh(I)/Et_3SiH$ molar ratio, a reflection of rhodium concentration. Results are shown in Tables I and II. The reactions were carried out by employing an excess of styrene, and the yields were based on silane, the limiting reagent. The ethylbenzene yield was based on silane converted, assuming that hydrogen was donated by the silane. The data in Tables I and II show that both $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ are effective catalysts for hydrosilylation of styrene, with the former being more active and the latter more selective. Selectivity to the *trans*-styrene product may be due to the more bulky nature of the latter Rh(I) complex.[6] Selectivity could also be increased by placing more bulky substituents on the silane (Table III).

The hydrosilylation reaction to prepare several silyl-substituted styrenes for characterization work was carried out with phenylacetylene, using chloroplatinic acid or Wilkinson's catalyst as reported[3,5] (Table IV).

Discussion

A systematic study of the effect of the $Rh(I)/R_3SiH$ ratio on the type of product was carried out. We found that at the low ratio, the catalyst functions as hydrosilylation catalyst, but at the high ratio, a competitive hydrogenation of substrate occurs and the composition of the silyl products changes. A low molar ratio of $Rh(I)/R_3SiH$ is defined as being $\sim 10^{-4}$ or lower, and a high ratio as $\sim 10^{-3}$ or higher. As expected, when the ratio of catalyst-to-silane is between the above two ranges, products from both reaction paths are formed.

A plot of the percent of silyl-containing product accumulated in the reaction mixture vs. time showed that both the low and high catalyst-to-silane runs exhibited induction times of ~0.5 h, during which time the active catalyst species were formed. Both runs showed a typical concentration–time-dependence curve. The products in the low catalyst run were mainly 1-(triethylsilyl)- and 2-(triethylsilyl)-1-phenylethanes, which were formed about twice as fast as the β-(triethylsilyl)-*trans*-styrene in the high catalyst run. Since the products are different, the mechanisms could also be expected to differ.

Addition of 1 equiv of triphenylphosphine to the low catalyst run completely inhibited the reaction, and only by raising the temperature from 50 to 65 °C to shift the equilibrium did the reaction proceed. This suggests the existence of the equilibrium $RhClL_3 \rightleftharpoons RhClL_2 + L$, where L is a triphenylphosphine. Addition of triphenylphosphine to the high catalyst run also led to initial retardation, but not suppression, of the reaction rate at 50 °C. After a while, however, the rate increased. It could be that excess triphenylphosphine in this case prevented the catalyst from precipitating out.

For determination of whether 1-(triethylsilyl)- and 2-(triethylsilyl)-1-phenylethanes were precursors to the β-silyl-substituted *trans*-styrene, their mixture was reacted under the usual reaction conditions in the presence of styrene and a high ratio of Rh(I). After reacting for 4 h at 60 °C, not even a trace of β-(triethylsilyl)-*trans*-styrene or ethylbenzene was formed. Therefore, the above two silanes are not precursors to the *trans*-styrene product.

Measurements of the competitive reaction rate at both

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(6) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 789.

Table II. Hydrosilylation of Styrene[a]

$RhCl(PPh_3)_3/R_3SiH$, mmol/mmol	R_3SiH	reaction time,[f] h	% yield[b] $PhCH_2CH_3$ (6)	$PhCH_2CH_2SiR_3$ (3)	*trans*-$PhCH{=}CHSiR_3$ (5)	$PhCH(CH_3)SiR_3$ (4)	R_3SiH, % conv[c]
3.1×10^{-3} (25.8)[e]	Et_3SiH	4.7	39	34	43	3	80
1.6×10^{-3} (13.3)	Et_3SiH	5	37	35	42	2	79
6.3×10^{-4} (5.2)	Et_3SiH	3	35	25	34	18	77
1.2×10^{-4} (1.0)	Et_3SiH	17	3	25	2	47	74
2.2×10^{-3}	$(Ph)_3SiH$[g]	6.5[d]	78	12	75	1	88
1.4×10^{-3}	$(i\text{-}Pr)_3SiH$[h]	6[d]	31	1	30	1	32
1.2×10^{-3}	$(EtO)_3SiH$	4[i]	5	30	7	11	48
1.2×10^{-3}	Cl_3SiH	3.5[j]	0	20	trace	6	26

[a] Reactants: 19.2 mmol of styrene and 17.2 mmol of R_3SiH in benzene (15 mL); 50 °C, N_2. [b] Based on R_3SiH, values rounded off to the nearest whole number. [c] Based on isolated silyl-containing products. [d] 65 °C. [e] Relative ratio. [f] Arbitrary reaction time. [g] Styrene:silane molar ratio, 6:1. [h] Styrene:silane molar ratio, 3.6:1. [i] Parr shaker, 28.8 mmol of styrene, 12.8 mmol of $(EtO)_3SiH$, $RhHCO(PPh_3)_3$ catalyst, in toluene (20 mL), 100 °C, N_2. [j] Parr shaker, 28.8 mmol of styrene, 13.3 mmol of Cl_3SiH, in toluene (20 mL), 100 °C, N_2.

Table III. Effect of R_3SiH Structure on Hydrosilylation of Styrene

catalyst	R_3SiH	Rh(I)/ R_3SiH, mmol/mmol	% selectivity to *trans*-$PhCH{=}CHSiR_3$ (GLC)[a]
$RhCl(PPh_3)_3$	Et_3SiH	3.2×10^{-3}	54
$RhCl(PPh_3)_3$	Et_3SiH	1.6×10^{-3}	53
$RhCl(PPh_3)_3$	$(Ph)_3SiH$	2.2×10^{-3}	85
$RhCl(PPh_3)_3$	$(i\text{-}Pr)_3SiH$	1.4×10^{-3}	94
$RhH(CO)(PPh_3)_3$	Et_3SiH	3.9×10^{-3}	85

[a] Remainder consisted of 1-silyl- and 2-silyl-substituted 1-phenylethanes.

the low and high catalyst loading (50 °C) showed that 1-alkenes (1-decene and 1-dodecene) were of about the same order of reactivity as styrene (1 ± 0.2), while α-methylstyrene, β-methylstyrene, and 2-ethyl-1-hexene were essentially unreactive. This order of reactivity is not the one expected for a typical free-radical or ionic addition but is consistent with a cis covalent type addition. The low reactivity of α- and β-methylstyrenes and of vinylidene olefin in this system is attributed to steric factors that apparently prevent contact between the double bond and the catalyst. *p*-Methylstyrene showed similar reactivity as styrene toward reaction with triethylsilane and afforded similar products.

The formation of exclusively *trans*-styrene products under conditions of high rhodium concentration can be rationalized on the basis of a favored transition state in which the bulky phenyl group of styrene and the trialkylsilyl group are located as far apart as possible. The metal hydride eliminated would be capable of reducing olefins present in the mixture. Since the reactant alkene is present in excess and would be generally more reactive than the product alkene, it would be the one reduced preferentially.

For convenience, most experiments were run at a fixed volume of solvents and reagents, and the results were expressed in terms of a $Rh(I)/R_3SiH$ ratio. If the dimer formation equilibrium $2RhCl(PPh_3)_2 \rightleftharpoons [RhCl(PPh_3)_2]_2$ was involved in the high rhodium system, the concentration of Rh was expected to be important. Indeed, changing the concentration of Rh(I) from a typical 5.3×10^{-4} to 5.3×10^{-5} M, while maintaining the same $Rh(I)/R_3SiH$ ratio, had a significant effect on the hydrosilylation. First, the reaction rate was reduced considerably, and an increased temperature had to be used to effect hydrosilylation. Secondly, the nature of product changed drastically; i.e., the molar selectivity to the *trans*-styrene product had decreased from 61% to 19%. Wilkinson et al.[7] discussed properties of $RhCl(PPh_3)_3$ and concluded that such halides in solution exist as a concentration-dependent equilibrium between monomer and halogen-bridged dimer.

The formation of 1-silyl- and 2-silyl-1-phenylethanes can be rationalized on the basis of the mechanism depicted in eq. 1–8. Thus, chlorotris(triphenylphosphine)rhodium(I) undergoes an oxidative addition with a trisubstituted silane to give Rh(III) adduct I. Complexes of this type have been isolated and their reactivity in hydrosilylation investigated.[8-10] Following the loss of a triphenylphosphine ligand, a pentacoordinate complex II is formed, which then

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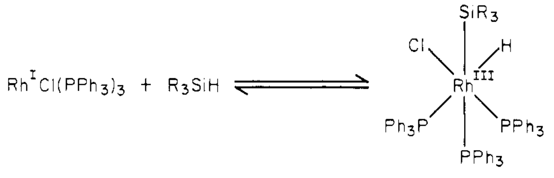
(7) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(8) Haszeldine, R. N.; Parish, R. V.; Parry, D. J. *J. Chem. Soc. A* **1969**, 683.

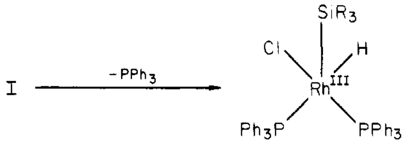
(9) Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J. Chem. Soc. Dalton Trans.* **1974**, 2311.

(10) de Charentenay, F.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 787.



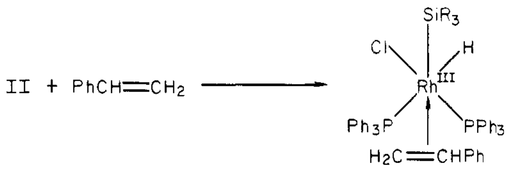
(1)

I



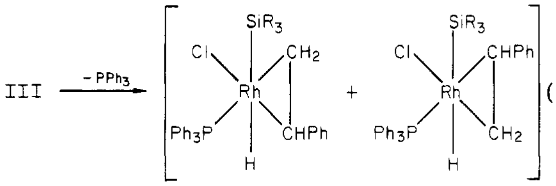
(2)

II



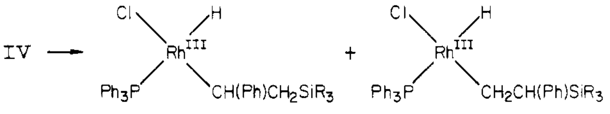
(3)

III



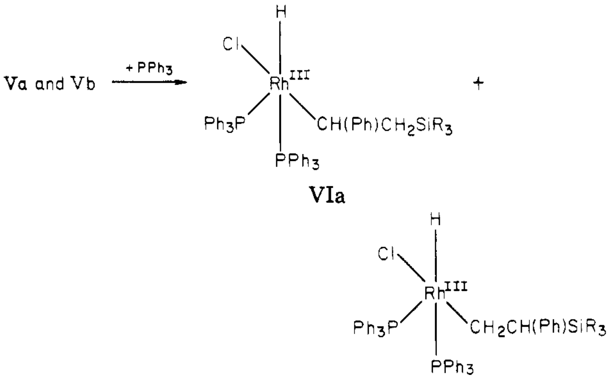
(4)

IVa IVb



(5)

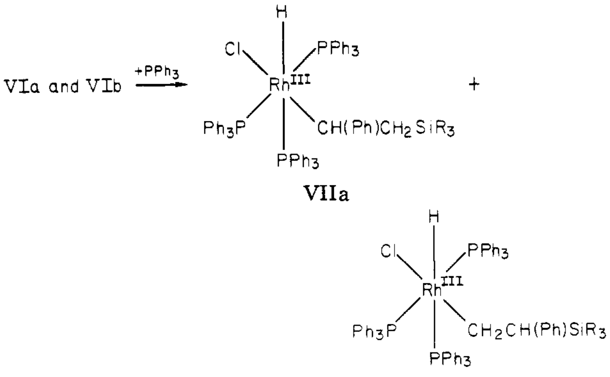
Va Vb



VIa

VIb

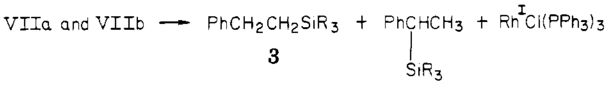
(6)



VIIa

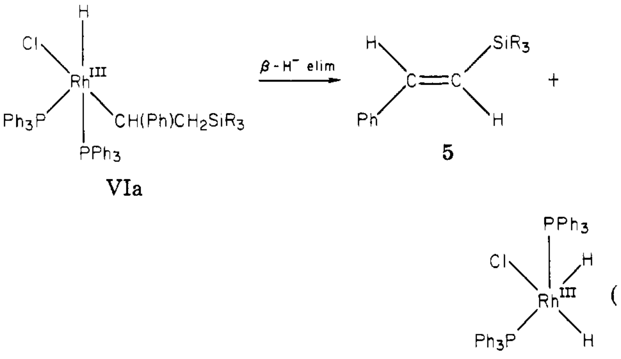
VIIb

(7)



$$\text{VIIa and VIIb} \longrightarrow \underset{\mathbf{3}}{PhCH_2CH_2SiR_3} + \underset{\mathbf{4}}{\underset{SiR_3}{PhCHCH_3}} + Rh^{I}Cl(PPh_3)_3 \qquad (8)$$

is capable of coordinating with styrene to give III. Following the loss of a second ligand, a formal bonding such as that shown by IV (a and b) can occur, resulting in intermediates Va and Vb. Intermediates V (a and b) can pick up the lost ligands and eventually undergo reductive elimination to form 1-silyl- and 2-silyl-1-phenylethanes and the starting Rh(I) catalyst for recycle. The formation of a β-silyl-*trans*-styrene product could result from the β-hydride elimination from intermediate VIa (eq 9), and the dihydridorhodium(III) complex coproduced (VIII), a well-known hydrogenation catalyst,[6] can be expected to hydrogenate styrene to ethylbenzene (eq 11).

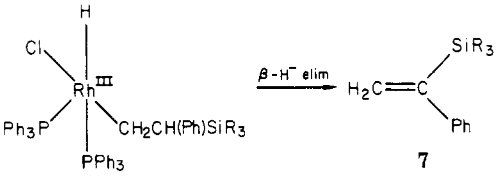


VIa

5

VIII

(9)



VIb

7

+ VIII (10)

$$\text{VIII} + \underset{\mathbf{1}}{PhCH{=}CH_2} \longrightarrow \underset{\mathbf{6}}{PhCH_2CH_3} + Rh^{I}Cl(PPh_3)_2 \qquad (11)$$

That VI (a and b) are reasonable intermediates is based on the fact that large amounts of the β-silyl-*trans*-styrene is formed in the high Rh system. Intermediate VIb, following β-hydride elimination, was expected to give α-silyl-substituted styrene, which in some runs could be detected by GLC (<0.3%). Of the intermediates VIa and VIb, VIa appears to be of lower thermodynamic stability and hence greater reactivity than VIb (Rh–CH_2R bond is more stable than Rh–CHR_2),[6] since steric repulsion in the latter could drive the reaction to preferential dissociation. The hydride elimination reaction from VIa can also be expected to be favored over that from VIb on a statistical basis. Most recently, Milstein[11] isolated stable *cis*-hydridoalkylrhodium(III) complexes and studied their reductive elimination. It was demonstrated that before any elimination occurred, a pentacoordinated complex of the type proposed by us (VIa) must be present. There is a precedent for the proposed mechanism in the organopalladium chemistry,[12] where the most stable *trans*-styrene was formed by elimination of hydridopalladium. While the mechanism formulated in eq 1–11 used monomeric Rh complexes, an equal set of equations could be drawn using dimeric Rh species. The extent of 2Rh $\rightleftharpoons$ Rh_2 equilibrium and its effect on product distribution is beyond the scope of the present investigation.

Finally, a lower percentage of *trans*-styrene product was formed with styrene and triethyoxysilane, and virtually none from styrene and trichlorosilane, in spite of the high

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[11] Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.
[12] Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707.

Table IV. Hydrosilylation of Phenylacetylene

		% selectivity (GLC)[a]				
catalyst	silane	$PhC{\equiv}CSiR_3$ (9)	*cis*-$PhCH{=}CHSiR_3$ (8)	*trans*-$PhCH{=}CHSiR_3$ (5)	$Ph(SiR_3)C{=}CH_2$ (7)	R_3SiH,[f] % conv
$RhCl(PPh_3)_3$	Et_3SiH[b]	4	31	57	8	18
$RhCl(PPh_3)_3$	Et_3SiH[c]	3	55	35	7	50
$H_2PtCl_6{\cdot}6H_2O$	Et_3SiH[d]			79	21	46
$RhCl(PPh_3)_3$	$(Ph)_3SiH$[e]	1	26	67	6	28

[a] Values rounded off to the nearest whole number. [b] Conditions: 19.6 mmol of $PhC{\equiv}CH$, 17.2 mmol of Et_3SiH, 1×10^{-2} mmol of $PhCl(PPh_3)_3$, in benzene (20 mL); 65 °C, 22 h, N_2. [c] 80 °C, 65 h. [d] 2.8×10^{-3} mmol of $H_2PtCl_6{\cdot}6H_2O$, 65 °C, 6.5 h, N_2. [e] 58.7 mmol of $PhC{\equiv}CH$, 11.5 mmol of $(Ph)_3SiH$, 1×10^{-2} mmol of $RhCl(PPh_3)_3$, in toluene (20 mL); 80 °C, 23 h, N_2. [f] Based on isolated products. % yield = selectivity × conversion.

Rh(I)/R_3SiH ratio used. This result can be explained by considering intermediate VIa (eq 9). The presence of electron-withdrawing substituents on the silicon (EtO, Cl) makes the carbon atom bearing a β-hydrogen more positive, and this makes the hydride ion transfer more difficult.

Experimental Section

Hydrosilylation reactions at atmospheric pressure were performed in standard laboratory glassware under nitrogen. Reactions under pressure were performed in a 500-mL Parr shaker. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FI detector) chromatograph, employing a 10-m, 2% OV-101, fused silica capillary column, programmed from 50 to 300 °C at 8°/min, or a 50-m, Carbowax 20M fused silica capillary column, programmed from 70 to 220 °C at 4°/min. The ^1H NMR spectra were obtained on a Varian T-60 spectrometer, usually in carbon tetrachloride or acetone-d_6. The ^{13}C and ^{29}Si NMR spectra were obtained on a Varian FT-80A spectrometer, usually in $CDCl_3$. The chemical shifts are in δ units (ppm) relative to Me_4Si (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. GC/MS data were obtained on a Finnigan 4510 system. The precise mass measurements were obtained on a Kratos MS-50 spectrometer (70 eV). Melting points (uncorrected) were obtained between glass plates on a Fisher-Johns apparatus. The following procedure is representative of the reaction of styrene with silanes.

Reaction of Triethylsilane with Styrene. A 100-mL, three-necked, round-bottomed flask, fitted with a condenser connected to a nitrogen source, a thermometer, and a serum cap, was charged with styrene (19.2 mmol), triethylsilane (17.2 mmol), and hydrido(carbonyl)tris(triphenylphosphine)rhodium(I) (1.5 mg, 1.63×10^{-3} mmol) in benzene (15 mL). After the system was purged with nitrogen for 15 min, the mixture was heated to 65 °C and the reaction was allowed to proceed for 4.5 h, monitoring the course of reaction by periodic withdrawal of samples for GLC analysis. When the reaction was terminated, the solution was cooled, and then passed over short alumina (80–100 mesh) column to remove the catalyst. The filtrate was concentrated on a rotary evaporator, and the residue was dried under high vacuum to give 3.0 g of product. Analysis by GLC showed three components, 64.9%, 34.0%, and 1.1%, respectively, in order of their emergence from the GLC column, corresponding to a silane conversion of 79%. The most diagnostic peak in the ^1H NMR spectrum of the mixture was a methyl group doublet centered at 1.35 ppm (J = 7 Hz) for **4a**. Integration of the peaks in the spectrum indicated that **4a** and **3a** were formed in a ratio of 66 to 34: GC/MS (**4a**), m/e (relative intensity) 220 (7) M^+, 191 (2) $(M - Et)^+$, 115 (100) $(Et_3Si)^+$, 87 (93), 59 (25) $(EtSiH_2)^+$; GC/MS (**3a**), no parent M^+, 191 (82) $(M - Et)^+$, 163 (51), 135 (24), 107 (15) $(M - Et_3Si)^+$, 87 (100) $(Et_2SiH)^+$, 59 (51) $(EtSiH_2)^+$; ^{29}Si NMR δ 7.48 (**4a**, 64%), 6.9 (**3a**, 35%), 0.1 (impurity, 1%), later identified as **5a**. When the above reaction was repeated with a Rh(I)/Et_3SiH ratio of 6.3×10^{-4}, the products consisted of **3a** (15% yield), **4a** (9%), **5a** (38%), and **6** (35%) at a silane conversion of 62%. Increasing the Rh(I)/Et_3SiH ratio to 3.9×10^{-3} led to formation of **3a** (8%), **5a** (44%), and **6** (43%) at a silane conversion of 53%. The last two runs were carried out at 50 °C. **5a**: ^1H NMR (CCl_4) AB pattern δ 6.15 (d, 1 H_a, J = 19 Hz), 6.72 (d, 1 H_b, J = 19 Hz), identical with that reported.[4,13] NMR of **3a** has also been reported.[14]

Reaction of Triethylsilane with Phenylacetylene. The exact procedure was used as in the case of styrene above. Experimental details are given as footnotes in Table IV. The total product mixture was characterized by ^1H NMR spectroscopy and GC/MS. The order of products emerging off the GLC column followed the sequence **7a**, **8a**, **9a**, and **5a**. **5a**: GC/MS, m/e (relative intensity) 218 (12) M^+, 189 (100), 161 (92), 131 (52), 105 (26), 59 (26); ^1H NMR (CCl_4) δ 6.15 (d, 1 H_a, J = 19 Hz), 6.72 (d, 1 H_b, J = 19 Hz), similar to that reported;[13] IR (neat) 1605 cm^{-1} (s) (C=C). **7a**: GC/MS, m/e (relative intensity) 218 (3), M^+, 190 (54), 161 (100), 133 (56), 107 (51), 87 (25), 59 (19); ^1H NMR δ 5.46 (m, 1 H_a), 5.77 (m, 1 H_b), showing a complex geminal proton–proton coupling. **8a**: GC/MS, m/e (relative intensity) 218 (6) M^+, 189 (100), 161 (67), 133 (47), 131 (67), 105 (32), 87 (5), 59 (18); ^1H NMR δ 7.43 (d, 1 H_a, J = 14 Hz), 5.72 (d, 1 H_b, J = 14 Hz). **9a**: GC/MS, m/e (relative intensity) 216 (4) M^+, 187 (80), 159 (90), 131 (100), 105 (30), 79 (8). Other compounds characterized included the following: **3b**: GC/MS, m/e (relative intensity) no parent ion, 286 (32), 259 (100), 181 (27), 155 (10), 105 (24). **4b**: m/e no parent ion, 259 (100), 181 (19), 155 (6), 105 (12). **5b**: GC/MS, m/e (relative intensity) 362 (22) M^+, 284 (60), 259 (17), 207 (34), 183 (40), 182 (70), 181 (100), 105 (60); ^1H NMR δ 7.37 (m, 20 H, ring), 6.94 (s, 2 H, olefin); IR (Nujol) 1600 cm^{-1} (s) (C=C); mp 148–149.5 °C (lit.[15] mp 148.5 °C). **7b**: GC/MS, m/e (relative intensity) no parent ion, 288 (69), 259 (27), 211 (33), 210 (39), 199 (19), 183 (22), 167 (13), 105 (18), 91 (100). **8b**: ^1H NMR δ 6.28 (d, 1 H_b, J = 14 Hz); H_a is obscured by ring protons. **5c**: GC/MS, m/e (relative intensity) 260 (10) M^+, 217 (91), 175 (100), 145 (59), 133 (32), 105 (34), 73 (33), 59 (43), 45 (11). Anal. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83; m/e 260.1960. Found: C, 78.38; H, 10.92; m/e 260.1964; ^1H NMR (CCl_4) δ 1.0 (s, 21 H, CH_3 and CH), 6.14 (d, 1 H_a, J = 19 Hz), 6.80 (d, 1 H_b, J = 19 Hz), 7.0–7.3 (m, 5 H, ring). **3d**: GC/MS, m/e (relative intensity) 268 (10) M^+, 195 (10), 177 (15), 163 (100), 149 (15), 135 (50), 119 (53), 107 (20), 91 (22), 79 (27), 63 (13). **4d**: GC/MS, m/e (relative intensity) 268 (3) M^+, 163 (100), 135 (17), 119 (51), 107 (13), 91 (14), 79 (22). **5d**: GC/MS, m/e (relative intensity) 266 (5) M^+, 251 (24), 222 (70), 193 (42), 176 (70), 149 (93), 147 (100), 131 (56), 119 (40), 118 (46), 103 (58), 91 (30), 83 (37), 79 (42), 63 (32), 45 (22). **3e** and **4e**: GLC 76% and 24%, respectively; ^1H NMR spectrum of the mixture was similar to that reported for **3e**,[14] with several overlapping peaks for **4e**. Integration gave values similar to GLC values. No evidence for the unsaturated product was found. **3e**: GC/MS, m/e (relative intensity) 238 (3) M^+, 105 (22), 91 (100), 78 (14), 65 (10), 51 (16), 39 (15). **4e**: GC/MS, m/e (relative intensity) 238 (2) M^+, 105 (100), 77 (19), 63 (8), 51 (14), 39 (13). **5e**: GC/MS, m/e (relative intensity) 236 (2) M^+, 145 (4), 105 (25), 91 (100), 78 (15), 65 (10), 51 (14), 39 (14).

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