Tunable Stereoselective Hydrosilylation of PhC≡CH Catalyzed by Cp*Rh Complexes

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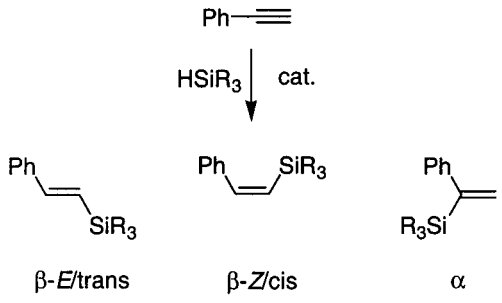
*Summary: The catalysts [Cp*RhCl$_2$]$_2$ and [Cp*Rh(BINAP)](SbF$_6$)$_2$ (Cp* = pentamethylcyclopentadienyl; BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) are effective for the hydrosilylation of phenylacetylene with triethylsilane, triethoxysilane, and triphenylsilane under mild conditions. [Cp*RhCl$_2$]$_2$ promotes the atypical anti addition to yield the β-Z isomer, whereas [Cp*Rh(BINAP)](SbF$_6$)$_2$ gives syn addition to form the β-E isomer. Extraordinarily high regioselectivity and stereoselectivity were observed for reactions involving triphenylsilane. Thus, tuning of the ligand set of Cp*Rh allows preparation of either the β-Z or β-E product.*

The hydrosilylation of alkynes offers a simple and direct means of producing vinylsilanes.[1,2] The main products formed are the α, β-*E*/trans, and β-*Z*/cis isomers (Scheme 1). Regio- and stereoselective syntheses of these products are desirable, since vinylsilanes are important intermediates in organic synthesis.[3] Selective formation of the β-*Z* product would be especially useful, inasmuch as it is the thermodynamically less stable isomer.[4−6]

In early work, transition-metal hydrosilylation catalysts tended to give the β-*E* isomer.[7−9] This formation of the trans isomer was consistent with syn addition. Cationic rhodium complexes were later found to catalyze the hydrosilylation of 1-alkynes to give β-(*E*)-vinylsilanes as the major product, whereas neutral rhodium compounds catalyzed the reaction to give predominantly β-(*Z*)-vinylsilanes.[10,11] This was exceptional, in that it suggested an abnormal anti addition. The original studies were with monocationic complexes of rhodium; hence, we sought to examine a dicationic system and a different neutral system for the potential of greater selectivity. Dicationic [Cp*Rh(BINAP)](SbF$_6$)$_2$, where BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, and neutral [Cp*RhCl$_2$]$_2$ were applied as catalysts in the hydrosilylation of phenylacetylene by triethylsilane, triethoxysilane, and triphenylsilane. Commercially available [Cp*RhCl$_2$]$_2$ is easily prepared by heating pentamethylcyclopentadiene and rhodium trichloride under reflux.[12] [Cp*Rh(BINAP)](SbF$_6$)$_2$ is also easily prepared from [Cp*RhCl$_2$]$_2$, BINAP, and silver hexafluoroantimonate. The procedure for hydrosilylation catalysis involves stirring the appropriate silane with the catalyst for 15 min at room temperature or 45 °C, prior to addition of phenylacetylene. Reaction with the trialkylsilane can be confirmed by the appearance of rhodium hydride resonances in the upfield region of the ^{1}H NMR spectrum. The observed hydride resonances appear where expected, on the basis of published values for analogous compounds.[13−15] In particular, for the complex derived from [Cp*Rh(BINAP)](SbF$_6$)$_2$, the hydride appears as a doublet of triplets owing to coupling to one ^{103}Rh and two ^{31}P nuclei. Furthermore, the Cp* methyls appear as a triplet from coupling to phosphorus. These resonances persist after the catalytic reaction is complete, but this observation does not, of course, indicate that this complex lies directly in the catalytic loop. In fact, the same resonances are observed when the dication is treated with H$_2$, suggesting that the complex observed in the NMR is [Cp*Rh(BINAP)H]$^+$. After the addition of phenylacetylene most of the reactions are complete within a few hours. Overall, reactions performed at 45 °C gave better results. [Cp*Rh(BINAP)](SbF$_6$)$_2$, which probably exists as the solvento or water complex,[16−18] is the first dicationic rhodium complex

Scheme 1. Hydrosilylation of Phenylacetylene



R = Et, **1**; EtO, **2**; Ph, **3**

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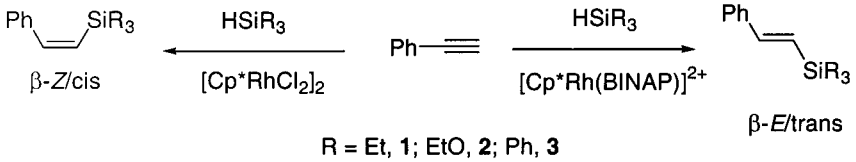
Table 1. Hydrosilylation of Phenylacetylene[a]

catalyst	silane	reacn time (h)	conversion of PhCCH[b] (%)	β-*Z* [b,c] (%)	β-*E* [b,c] (%)	α[b,c] (%)
[Cp*Rh(BINAP)]$(SbF_6)_2$	Ph_3SiH	2.5[d]	100	<1	>99	0
[Cp*Rh(BINAP)]$(SbF_6)_2$	$(EtO)_3SiH$	2.5	100	0	81.2	18.8
[Cp*Rh(BINAP)]$(SbF_6)_2$	Et_3SiH	21	99.5	0	97.4	2.6
[Cp*$RhCl_2]_2$	Ph_3SiH	6[d]	100	>97	<3	0
[Cp*$RhCl_2]_2$	$(EtO)_3SiH$	2.5	100	96.5	3.5	0
[Cp*$RhCl_2]_2$	Et_3SiH	2.5[e]	9.5	92.9	5.5	1.5

[a] Catalyst (5 mol %) and silane (1.1 equiv) were stirred in CH_2Cl_2 at 45 °C, unless otherwise noted, for 15 min before addition of PhCCH (1 equiv). The reaction was continued at the same temperature until 100% conversion or 21 h. [b] Determined by ^1H and ^{13}C NMR. Comparison of minor isomer ^1H resonance to ^{13}C satellites of the major isomer can provide intensity calibration for weak resonances. [c] The percentages of *Z*, *E*, and α are in relation to each other only. [d] Same result for reaction performed at room temperature and 45 °C. [e] Reaction at room temperature.

Scheme 2. Selectivity for Neutral and Dicationic Catalysts



R = Et, **1**; EtO, **2**; Ph, **3**

reported as a hydrosilylation catalyst precursor. As expected, either *rac*- or (*S*)-BINAP can be used without a change in results. [Cp*Rh(BINAP)]$(SbF_6)_2$ produces predominantly β-*E* isomers, and [Cp*$RhCl_2]_2$ produces a greater proportion of β-*Z* isomers, in accord with expectations. The isomers were identified by their ^1H and ^{13}C NMR resonances.[6,19,20] Particularly characteristic are the olefinic proton couplings for the β-*E* isomer, the β-*Z* isomer, and the α isomer, which are 18−20 Hz (trans), 12−16 Hz (cis), and 2−3 Hz (gem), respectively.

The product ratios obtained in the triphenylsilane and triethoxysilane hydrosilylations of phenylacetylene are most significant, since other transition-metal catalysts which give high selectivity for this hydrosilylation most often involve triethylsilane.[4,6,10,11,21,22] Commonly used platinum catalysts, $H_2PtCl_6 \cdot 6H_2O$[23] and $[Bu_4N]_2[PtCl_6]$,[24] give **3**-β-*E* stereoselectively, but, at best, the **3**-β-*E* to **3**-α ratio is 95:5 after reaction at 140 °C for 3 h.[24] The most commonly used rhodium catalyst, $RhCl(PPh_3)_3$,[25] gives a mixture of the isomers, although **3**-β-*E* is preferred. Another rhodium catalyst, [(nbd)(dppe)Rh]-PF_6 (nbd = norbornadiene, dppe = 1,2-bis(diphenylphosphino)ethane),[22] gives no **3**-β-*Z* but there is some α isomer formed. The best catalyst to date, [cymene-$RuCl_2]_2$, exhibited high selectivity for **3**-β-*Z* (β-*Z*:β-*E*:α = 96:4:0).[6] In this work very high regioselectivity and stereoselectivity were obtained for the hydrosilylation of phenylacetylene by triphenylsilane catalyzed by the Cp*Rh catalysts. [Cp*$RhCl_2]_2$ produced >97% **3**-β-*Z*, while [Cp*Rh(BINAP)]$(SbF_6)_2$ produced >99% **3**-β-*E* (Table 1). This high selectivity was also observed in room-temperature reactions.

The selectivities obtained from the Cp*Rh-catalyzed reaction of triethoxysilane with phenylacetylene are not as high as with triphenylsilane, but to our knowledge, they are the highest thus far reported. Karstedt's platinum catalyst yields 0% **2**-β-*Z*, 70% **2**-β-*E*, and 30% **2**-α,[19] whereas the distribution of products resulting from the [Cp*Rh(BINAP)]$(SbF_6)_2$ catalyst, 0% **2**-β-*Z*, 81% **2**-β-*E*, and 18% **2**-α (Table 1), shows some improvement in regioselectivity. In addition, the **2**-β-*Z* isomer is formed in only 50, 60, and 74% yield by $[(C_4H_6)$-$RhCl]_2$,[20] $RhCl(PPh_3)_3$/NaI,[11] and [(1,5-COD)RhCl-(p-$MeC_6H_4NCMe_2$)] (COD = cyclooctadiene),[26] respectively, as compared to 90−96% achieved by [Cp*$RhCl_2]_2$ (Table 1).

The results in Table 1 exhibit how changing the catalyst can affect the product distribution. In particular, a very high stereoselectivity is achieved, producing the β-*E* isomer and no observable β-*Z* isomer, with [Cp*Rh(BINAP)]$(SbF_6)_2$. Since, as mentioned, cationic rhodium complexes do tend to give β-*E* products, the double positive charge appears to enhance the selectivity in this case. There regioselectivity is not >99% in all cases. The varying yields of the α-isomer by this catalyst depend on the nature of the silane, with more being produced from triethoxysilane. [Cp*$RhCl_2]_2$ overall gives better regioselectivity, but, except for the triphenylsilane reaction, it is not 97% stereoselective for β-*Z* products. In summary, the primary products are those shown in Scheme 2.

Styrene is only produced as a byproduct in less than 1% yield with triethoxysilane or triphenylsilane. More of the phenylacetylene, ~25%, is converted to styrene in the reaction involving triethylsilane, particularly in reactions catalyzed by [Cp*Rh(BINAP)]$(SbF_6)_2$. The conversion of phenylacetylene to products is also slower

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when triethylsilane is involved rather than triethoxysilane or triphenylsilane. As the $[Cp^*RhCl_2]_2$-catalyzed triethylsilane reaction is allowed to proceed in order to increase phenylacetylene conversion, isomerization of the initially predominant product, **1**-*β*-*Z*, to the more stable thermodynamic product, **1**-*β*-*E*, occurs. Higher temperature speeds up this isomerization. Others have reported product isomerization when there is either excess silane in solution or prolonged contact with the catalyst.[9,27,28] To evaluate this, the catalysis involving $[Cp^*RhCl_2]_2$ was performed with excess alkyne. The same *Z* to *E* isomerization was observed from the NMR spectra, indicating that the contact with the catalyst and not excess silane is largely inducing the isomerization. In addition, no significant changes in product ratios were observed when phenylacetylene was added to the solution prior to addition of silane.

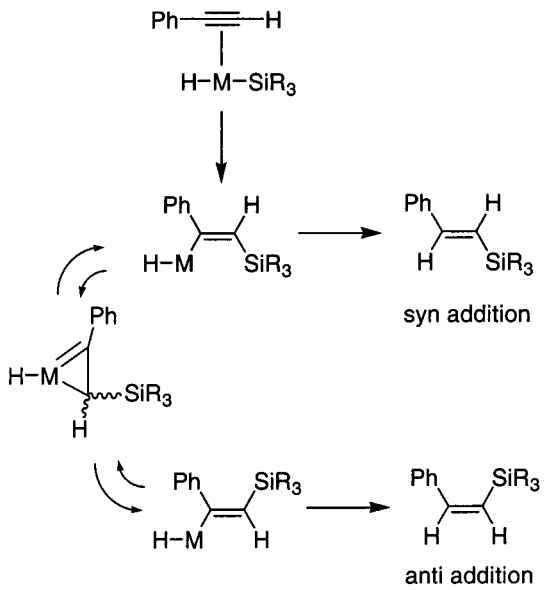
The active catalyst from the neutral complex presumably arises from $Cp^*Rh(H)_2(SiR_3)_2$, which should form upon addition of R_3SiH, removal of chloride from $[Cp^*RhCl_2]_2$ as R_3SiCl, and loss of H_2, followed by oxidative addition of two molecules of R_3SiH.[15,29] A reactive 16-electron intermediate capable of interaction with acetylene would then be available by loss of $HSiR_3$ to yield $[Cp^*Rh(H)(SiR_3)]$.

The nature of the active catalyst with the dicationic system is less clear. Oxidative addition of $HSiR_3$ to the 16-electron $[Cp^*Rh(BINAP)]^{2+}$ should initially produce $[Cp^*Rh(BINAP)(H)(SiR_3)]^{2+}$ or $[Cp^*Rh(BINAP)(HSiR_3)]^{2+}$, which are 18-electron species. It is clear from the product ratios that a different path is involved with the dicationic complex precursor. Following generally accepted mechanisms, one would expect that after oxidative addition of the silane to the metal, acetylene insertion into the metal−hydride bond would occur and subsequent reductive elimination would yield the olefin. A normal syn addition, however, would yield the *β*-*E* isomer. The formation of the *β*-*Z* isomer can be accounted for by acetylene insertion into the metal−silicon bond, isomerization to place the metal trans to the silicon, which is more favorable sterically, and reductive elimination.[4,5,30] Crabtree et al.[4,30] suggest that the isomerization occurs via an η^2-vinyl group, and thus a mechanism as shown in Scheme 3 may be operative.

If the primary process is insertion into the metal−silicon bond, then the *E*/*Z* stereoselectivity is determined by the relative rates of reductive elimination and isomerization. Regardless, after interaction of the dication with the silane, there is no site available for interaction with the acetylene. Thus, the detachment of at least one donor would be anticipated in order to produce the real catalytically active species. Without further evidence it would appear unwarranted to speculate further on the nature of this species.

One should also note that the additions might be reversible,[31] although this is less likely for a vinyl silane. The *β*-*E* isomer could also be produced as a secondary catalytic process which involved isomerization of the *β*-*Z*-olefin. If the *β*-*Z* product of the Cp^*RhCl_2 catalyst is allowed to stand in the presence of the catalyst for an extended time, it gradually isomerizes to the *β*-*E* isomer. This is more likely to be the result of a background catalysis of reversible *β*-hydride addition/elimination to the olefin, but it is an alternative isomerization path which is available. This much slower process might not involve the same catalyst as that responsible for the production of the *β*-*Z* product.

Scheme 3. Mechanism for the Observation of Anti Addition



The α-olefin presumably results from insertion of the acetylene into the Rh−Si bond with the opposite regiochemistry. Insertion into the Rh−Si bond was generally regarded as improbable in the past,[32,33] but there is now ample evidence to the contrary.[4,5,30,34−39] This suggests that the observed "selectivity" of some of the catalysts may not actually reflect the initial selectivity in the formation of the metal silane silyl olefin intermediate but the relative rates of subsequent isomerization processes.

In brief, the tunable selectivity afforded by the readily prepared Cp*Rh compounds $[Cp^*RhCl_2]_2$ and $[Cp^*Rh(BINAP)](SbF_6)_2$ make them attractive catalysts for the hydrosilylation of phenylacetylene under mild conditions. The *β*-*E* products are also available via silylative coupling or metathesis of styrene with vinylsilanes;[40,41] however, higher temperatures are often required.

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Experimental Section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Dichloromethane was dried and distilled over CaH_2. $AgSbF_6$, (*S*)-BINAP, phenylacetylene, triphenylsilane, triethylsilane, triethoxysilane (Aldrich), and *rac*-BINAP (Strem) were used as received. $[Cp^*RhCl_2]_2$[12] was prepared according to literature methods. $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a GE Omega 300 MHz (operating at 121 MHz for ^{31}P) or Bruker 400 MHz (operating at 161 MHz for ^{31}P) spectrometer. ^1H NMR spectra were recorded at room temperature on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm relative to residual solvent peaks (^1H), an 85% H_3PO_4 external standard (^{31}P), or TMS external standard (^{29}Si). Elemental analyses were carried out by Atlantic Microlabs.

Preparation of [Cp*RhCl(η^2-BINAP)]Cl. $[Cp^*RhCl_2]_2$ (385 mg, 0.62 mmol) and BINAP (773 mg, 1.24 mmol) were stirred in CH_2Cl_2 (40 mL) at room temperature for 40 min. Solvents were removed under reduced pressure, and the product was dried in vacuo. The yield of the red-orange product was 1.067 g (92%). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.98−5.96 (32 H, m, aromatic); 1.21 (15 H, pseudo-t, $J_{PH} = 3.6$ Hz, Cp*). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, δ): 34.09 (dd, $J_{RhP} = 137$ Hz, $J_{PP} = 64$ Hz); 20.58 (dd, $J_{RhP} = 133$ Hz, $J_{PP} = 64$ Hz).

Preparation of [Cp*RhCl(η^2-BINAP)]SbF_6. To [Cp*RhCl(η^2-BINAP)]Cl (97.4 mg, 0.10 mmol) in CH_2Cl_2 (6 mL) was added $AgSbF_6$ (36 mg, 0.10 mmol). The mixture was stirred for 1 h, filtered through Celite, and recrystallized from dichloromethane/ether. The yield of the red-orange product was 103 mg (91%). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.94−5.95 (32 H, m, aromatic); 1.14 (15 H, pseudo-t, $J_{PH} = 3.6$ Hz, Cp*). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, δ): 34.15 (dd, $J_{RhP} = 137$ Hz, $J_{PP} = 64$ Hz); 20.69 (dd, $J_{RhP} = 134$ Hz, $J_{PP} = 64$ Hz). Anal. Calcd for $C_{54}H_{47}P_2RhClSbF_6$: C, 57.30; H, 4.18. Found: C, 57.57; H, 4.34.

In Situ Preparation of [Cp*Rh(η^2-BINAP)]$(SbF_6)_2$. Method A. [Cp*Rh(η^2-BINAP)Cl]Cl (21.0 mg, 0.023 mmol) and $AgSbF_6$ (16 mg, 0.046 mmol) were stirred in CH_2Cl_2 (2.0 mL) for 20 min and then centrifuged to remove the AgCl precipitate.

Method B. [Cp*Rh(η^2-BINAP)Cl]SbF_6 (26.0 mg, 0.023 mmol) and $AgSbF_6$ (8 mg, 0.023 mmol) were stirred in CH_2Cl_2 (2.0 mL) for 20 min and then centrifuged to remove the AgCl precipitate.

The NMR spectra were identical from either A or B. ^1H NMR (400 MHz, CD_2Cl_2, δ): 8.09−6.42 (32 H, m, aromatic); 1.35 (15 H, pseudo-t, $J_{PH} = 3.3$ Hz, Cp*). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, δ): 33.81 (d, $J_{RhP} = 148$ Hz). *Note that only one ^{31}P doublet is observed at room temperature.*

Interaction of $HSiPh_3$ with [Cp*Rh(η^2-BINAP)]$(SbF_6)_2$. Treatment of [Cp*Rh(η^2-BINAP)]$(SbF_6)_2$ with $HSiPh_3$ in CD_2Cl_2 apparently ultimately yields the hydride [Cp*Rh(η^2-BINAP)H](Sb_2F_{11}) and $FSiPh_3$. ^1H NMR (400 MHz, CD_2Cl_2, δ): 8.09−6.42 (32H, m, aromatic); 1.44 (15 H, pseudo-t, $J_{PH} = 2.6$ Hz, Cp*), −10.39 (1H, ddd, $J_{Rh-H} = 20.7$, $J_{P-H} = 28.6$, $J_{P-H} = 28.7$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 49.75 (dd, $J_{RhP} = 141$, $J_{PP} = 37$ Hz); 49.29, 49.75 (dd, $J_{RhP} = 141$, $J_{PP} = 37$ Hz). $^{29}Si\{^1H\}$ HMQC NMR: δ −3.70 (d, $J_{SiF} = 238$ Hz). Identical ^1H and ^{31}P NMR parameters were obtained upon treatment of the dication with H_2. Eluting the mixture through silica gel with CH_2Cl_2 yields [Cp*Rh(η^2-BINAP)H](SbF_6). Anal. Calcd for $C_{54}H_{48}P_2RhSbF_6$: C, 59.09; H, 4.41. Found: C, 59.33; H, 4.53.

Hydrosilylation of Phenylacetylene: General Procedure. Addition of Silane to Catalyst. (A) A purple solution of [Cp*Rh(η^2-BINAP)]$(SbF_6)_2$ (0.023 mmol, prepared in situ) in CH_2Cl_2 (2 mL) was stirred with Ph_3SiH (126 mg, 0.48 mmol), $(EtO)_3SiH$ (0.09 mL, 0.49 mmol), or Et_3SiH (0.08 mL, 0.50 mmol) for 15 min at 45 °C or room temperature (see Table 1).

(B) $[Cp^*RhCl_2]_2$ (13.6 mg, 0.022 mmol) in CH_2Cl_2 (2.0 mL) was stirred with Ph_3SiH (120.6 mg, 0.46 mmol), $(EtO)_3SiH$ (0.087 mL, 0.47 mmol), or Et_3SiH (0.074 mL, 0.46 mmol) for 15 min at 45 °C or room temperature (see Table 1).

Hydrosilylation. Phenylacetylene (0.049 mL, 0.45 mmol) was added, and stirring at the appropriate temperature was continued until 100% conversion of PhCCH was determined from the ^1H NMR spectrum or until 21 h passed. The solvent was removed under reduced pressure. NMR (^1H and ^{13}C) spectra were recorded of the residue in $CDCl_3$, and chemical shifts and couplings were compared to published values.[6,19,20,30,39]

Preparative-Scale Reactions. (β-*E*)-Ph(H)C=C($SiPh_3$)H. [Cp*Rh(η^2-BINAP)Cl]Cl (22.3 mg, 0.024 mmol) and $AgSbF_6$ (16 mg, 0.047 mmol) were stirred in CH_2Cl_2 (2.0 mL) for 20 min, and the mixture was then centrifuged to remove the AgCl precipitate. The purple supernatant was stirred with Ph_3SiH (131 mg, 0.50 mmol) for 15 min at 45 °C, during which time it turned orange. Phenylacetylene (0.053 mL, 0.48 mmol) was added and stirring at 45 °C was continued until 100% conversion of PhCCH was determined from the ^1H NMR spectrum or until 21 h passed. The solvent was removed under reduced pressure. Products were separated from leftover catalyst by column chromatography, and 164 mg of the *E* isomer was collected in a 94% isolated yield as clear, colorless needles upon recrystallization from CH_2Cl_2/MeOH. Comparison of its vinylic ^1H NMR resonances to those reported in the literature[19] showed it to be (β-*E*)-Ph(H)C=C($SiPh_3$)H. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.05, 7.00 (2 H, AB quartet, $J = 19.2$ Hz). $^{29}Si\{^1H\}$ HMQC NMR (99 MHz, $CDCl_3$, δ): −16.25 (s).

(β-*Z*)-Ph(H)C=C($SiPh_3$)H. $[Cp^*RhCl_2]_2$ (15.0 mg, 0.024 mmol) in CH_2Cl_2 (2.0 mL) was stirred with Ph_3SiH (133.9 mg, 0.51 mmol) for 15 min at 45 °C, turning it orange. Phenylacetylene (0.053 mL, 0.48 mmol) was added, and stirring at 45 °C was continued until 100% conversion of PhCCH was determined from the ^1H NMR spectrum or until 21 h passed. The solvent was removed under reduced pressure. Products were separated from residual catalyst by column chromatography, and 161 mg of the *Z* isomer was collected in a 92% isolated yield as clear, colorless needles upon recrystallization from CH_2Cl_2/MeOH. Comparison of its vinylic ^1H NMR resonances to those reported in the literature[6,19] showed it to be (β-*Z*)-Ph(H)C=C($SiPh_3$)H. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.77 (1 H, d, $J = 15.6$ Hz); 6.38 (1 H, d, $J = 15.6$ Hz). $^{29}Si\{^1H\}$ HMQC NMR (99 MHz, $CDCl_3$, δ): −20.70 (s).

β-(*E*)-Ph(H)C=C($SiEt_3$)H.[19,30,39] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.90 (1 H, d, $J = 19.2$ Hz); 6.43 (1 H, d, $J = 19.2$ Hz).

β-(*Z*)-Ph(H)C=C($SiEt_3$)H.[6,30,39] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.45 (1 H, d, $J = 15.2$ Hz); 5.77 (1 H, d, $J = 15.2$ Hz).

α-Ph($SiEt_3$)C=CH_2.[19,30,39] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 5.87 (1 H, d, $J = 3.2$ Hz); 5.58 (1 H, d, $J = 3.2$ Hz).

β-(*E*)-Ph(H)C=C($Si(EtO)_3$)H.[19,20] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.20 (1 H, d, $J = 19.2$ Hz); 6.17 (1 H, d, $J = 19.2$ Hz).

β-(*Z*)-Ph(H)C=C($Si(EtO)_3$)H.[20] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.41 (1 H, d, $J = 15.6$ Hz); 5.57 (1 H, d, $J = 15.6$ Hz).

α-Ph($Si(EtO)_3$)C=CH_2.[19,20] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.13 (1 H, d, $J = 2.8$ Hz); 5.95 (1 H, d, $J = 2.8$ Hz).

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Supporting Information Available: A summary table of all hydrosilylation experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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