

**Insertion of Ethyne into the Ru–Si Bonds of
Coordinatively Unsaturated Ruthenium Silyl Complexes.
X-ray Crystal Structures of
Ru(CH=CHSiMe₂OEt)Cl(CO)₂(PPh₃)₂ and
[Ru(CH=CHSiMe₂OH)(CN-*p*-tolyl)(CO)(PPh₃)₂]ClO₄**

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The five-coordinate silyl complexes Ru(SiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**1a**), Et₃ (**1b**), Ph₃ (**1c**), Me₂Cl (**1f**)) are conveniently prepared through reaction of Ru(Ph)Cl(CO)(PPh₃)₂ with the appropriate silane, HSiR₃. Reaction of the Si–Cl bond in **1f** with ethanol or hydroxide gives the corresponding ethoxysilyl or hydroxysilyl products Ru(SiMe₂X)Cl(CO)(PPh₃)₂ (X = OEt (**1d**), OH (**1e**)). Ethyne readily inserts into the Ru–Si bond of **1a–d**, and the corresponding five-coordinate, silylalkenyl complexes Ru(CH=CHSiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**2a**), Et₃ (**2b**), Ph₃ (**2c**), Me₂OEt (**2d**)) can be isolated in good yield. The complexes Ru(CH=CHSiR₃)Cl(CO)₂(PPh₃)₂ (SiR₃ = SiMe₃ (**3a**), SiEt₃ (**3b**), SiMe₂OEt (**3d**)) result from carbonylation of **2a,b,d**. An X-ray crystal structure determination of Ru(CH=CHSiMe₂OEt)Cl(CO)₂(PPh₃)₂ (**3d**) has been obtained. Reaction of Ru(CH=CHSiMe₃)Cl(CO)(PPh₃)₂ (**2a**) with CN-*p*-tolyl or sodium acetate gives Ru(CH=CHSiMe₃)Cl(CO)(CN-*p*-tolyl)(PPh₃)₂ (**4a**) or Ru(CH=CHSiMe₃)(η^2 -O₂CCH₃)(CO)(PPh₃)₂ (**5a**), respectively. Insertion of ethyne into the Ru–Si bond of **1e** results in the formation of the metallacyclic ring-containing complex, Ru(CH=CHSiMe₂OH)Cl(CO)(PPh₃)₂ (**6e**), in which the hydroxysilyl oxygen atom is coordinated to ruthenium. Reaction of **6e** with AgClO₄ gives [Ru(CH=CHSiMe₂OH)(CO)(NCMe)(PPh₃)₂]ClO₄ (**7e**) and substitution of the labile acetonitrile in this compound with CO or CN-*p*-tolyl generates [Ru(CH=CHSiMe₂OH)(CO)₂(PPh₃)₂]ClO₄ (**8e**) or [Ru(CH=CHSiMe₂OH)(CO)(CN-*p*-tolyl)(PPh₃)₂]ClO₄ (**9e**), respectively. The crystal structure of **9e** has been determined. Deprotonation of **8e** or **9e** with KOH gives the neutral complexes Ru(CH=CHSiMe₂O)(CO)₂(PPh₃)₂ (**10e**) or Ru(CH=CHSiMe₂O)(CO)(CN-*p*-tolyl)(PPh₃)₂ (**11e**), respectively. Complex **1b** has been shown to catalyze the hydrosilylation of both ethyne and phenylethyne by HSiEt₃.

Introduction

The hydrosilylation of alkynes to give vinylsilanes is a reaction of considerable importance in both laboratory and industrial applications.¹ The number of studies pertaining to this reaction have been modest in comparison to those reported for the closely related alkene hydrosilylation reaction. Nevertheless, in a number of cases a reasonably clear picture has now emerged of the mechanism by which alkyne hydrosilylation proceeds.^{2,3} The essential features of the catalytic cycle involve insertion of the alkyne into the metal–silicon bond followed by addition of silane and cleavage of silylalkene from the silylalkenyl intermediate. This last step

regenerates the starting silyl complex. The distributions of the (*E*)- and (*Z*)-isomers observed for the silylalkene products arise from the varying degrees to which the silylalkenyl intermediates isomerize before cleavage and the silylalkene products isomerize after cleavage from the metal (see Scheme 1).

One of the key steps in the catalytic hydrosilylation mechanism depicted in Scheme 1 involves the insertion of an alkyne into a transition metal–silicon bond. Examples of this reaction in which well-characterized, silylalkenyl complexes have been isolated are very rare,⁴ and almost all involve substituted alkynes rather than ethyne itself.⁵

As part of our ongoing research interest in the reaction chemistry of coordinatively unsaturated silyl complexes of ruthenium and osmium,⁶ we have inves-

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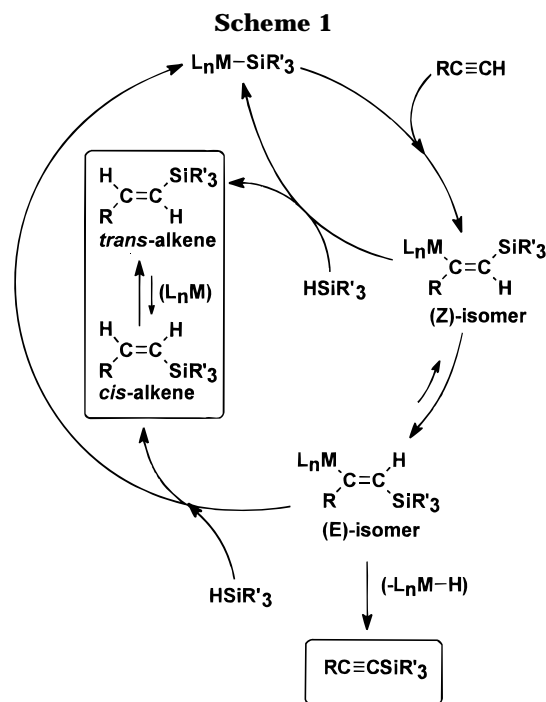
(1) (a) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21 and references cited therein. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 25, pp 1479–1526 and references cited therein.

(2) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

(3) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(4) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1993**, *12*, 988.

(5) Takao, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1994**, *13*, 2554.



tigated the ethyne insertion reactions of the complexes Ru(SiR₃)Cl(CO)(PPh₃)₂. We report in this paper the isolation and characterization of the silylalkenyl products that are formed in these reactions and also show that Ru(SiEt₃)Cl(CO)(PPh₃)₂ is an alkyne hydrosilylation catalyst.

Results and Discussion

Synthesis of the Five-Coordinate Silyl Complexes Ru(SiR₃)Cl(CO)(PPh₃)₂. A simple and efficient route to the five-coordinate silyl complexes Ru(SiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**1a**), Et₃ (**1b**), Ph₃ (**1c**), Me₂Cl (**1f**)) is provided through reaction of the phenyl complex Ru(Ph)Cl(CO)(PPh₃)₂ with the appropriate silane HSiR₃. The ethoxysilyl and hydroxysilyl derivatives Ru(SiMe₂X)Cl(CO)(PPh₃)₂ (X = OEt (**1d**), OH (**1e**)) can be conveniently prepared through reaction of **1f** with ethanol or hydroxide, respectively (see Scheme 2). We have reported previously the synthesis of other closely related five-coordinate silyl complexes of ruthenium and osmium using similar procedures.⁶

Ethyne Insertion Reactions. The five-coordinate silyl complexes Ru(SiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**1a**), Et₃ (**1b**), Ph₃ (**1c**), Me₂OEt (**1d**)) all react with ethyne under mild conditions to give the corresponding five-coordinate silylalkenyl insertion products Ru(CH=CH-SiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**2a**), Et₃ (**2b**), Ph₃ (**2c**), Me₂OEt (**2d**)) in good yield (see Scheme 2). The derivatives **2a–d** all display similar spectral features,⁷ and the pertinent data for one representative example, namely **2b**, are discussed below.

In the IR spectrum of solid samples of Ru(CH=CH-SiEt₃)Cl(CO)(PPh₃)₂ (**2b**) the ν(CO) band appears at

1931 cm⁻¹ (see Table 1). This is significantly higher than the value of 1904 cm⁻¹ observed for the ν(CO) band of **1b** and illustrates the reduced electron-releasing properties of the alkenyl group compared to the triethylsilyl group. A band at 1512 cm⁻¹ is assigned to ν(C=C) of the alkenyl group.

In the ¹H NMR spectrum of **2b** the two alkenyl protons are observed as doublets of triplets of δ 8.32 (³J_{HH} = 12.9, ³J_{HP} = 1.5) and 5.22 (³J_{HH} = 12.9, ⁴J_{HP} = 2.0 Hz) ppm. The value of ³J_{HH} falls within the normally encountered limits for both *cis*- and *trans*-alkenes, and thus unambiguous assignment of structure on this basis is not possible.⁸ However, the results of a preliminary X-ray structure determination of **2b** clearly indicate a *trans*-geometry about the double bond in the solid state.⁹ The other five-coordinate, silylalkenyl complexes (**2a,c,d**) are expected to have a similar geometry. The resonance at 8.32 ppm is assigned to the proton bound to the α-carbon of the alkenyl group on the basis of the chemical shift value and the results of a 2D-NMR CH correlation experiment (see below). The value of ³J_{HP} for this proton appears to be anomalous in that it is smaller than ⁴J_{HP} for the proton on the alkenyl β-carbon atom. One possible explanation might be that in solution there is either some zwitterionic carbene character or η²-character to the metal-alkenyl bond. It has been proposed that intermediate (*Z*)-silylalkenyl metal complexes (see Scheme 1) rearrange to the corresponding (*E*)-isomers via intermediates such as these.^{2,3}

In the ¹³C NMR spectrum of **2b** a triplet resonance at 163.7 ppm (²J_{CP} = 9.7 Hz) is assigned to the alkenyl carbon that is directly bound to the metal on the basis of the chemical shift position and the relatively large value of the coupling constant to phosphorus. The other alkenyl carbon resonance was obscured by the PPh₃ phenyl resonances centered at 134 ppm (see below). However, both alkenyl carbon resonances were observed for all the other five-coordinate alkenyl complexes

(6) (a) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682. (b) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, *11*, 3931. (c) Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Pure Appl. Chem.* **1990**, *62*, 1039.

(7) See Table 1 and the Experimental Section for complete IR and NMR data.

(8) A very similar value for ³J_{HH} (13 Hz) has been reported for the alkenyl protons in the complex Ru(*trans*-CH=CHPh)Cl(CO)(PPh₃)₂: Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. J. *Organomet. Chem.* **1986**, *309*, 169.

(9) A single-crystal X-ray structure determination of Ru(CH=CH-SiEt₃)Cl(CO)(PPh₃)₂ (**2b**) has been obtained. However, the crystal quality was such that after refinement an *R* factor of 12% was obtained. While this structure determination is not suitable for publication in its present form, the data do clearly show a *trans* arrangement about the alkenyl double bond.

Table 1. Infrared Data^a for New Compounds

	$\nu(\text{CO})^b$	other bands
1a	1919, 1900, (1911 ^c)	830 m
1b	1904	999 w
1c	1923	
1d	1925, 1910, (1923 ^c)	1063 m, 924 m, 831 m, 804 m
1e	1921	3618 m, 902 w, 833 m, 810 m
1f	1944, 1929, 1917, (1933 ^c)	836 m, 801 m
2a	1913	1524 m, 1242 m, 852 m, 833 m
2b	1931	1512 m, 1244 m, 1001 w, 771 m
2c	1927	1541 m, 1535 w, 1508 m, 768 m, 727 m
2d	1929	1523 m, 1247 m, 1078 m, 831 m, 791 m
2e	1929	1274 m, 847 m, 837 m, 789 m
3a	2031, 1971	1520 m, 1242 m, 862 m, 835 m
3b	2037, 1979	1507 w, 1015 m, 772 m
3d	2039, 1981	1516 m, 1246 m, 1072 m, 935 m, 843 m, 833 m, 791 m
4a	1969	2124 s, 1506 m, 1240 m, 862 m, 833 m, 818 m
5a	1912	1504 w, 1532 m, 1240 m, 861 m, 835 m
6e	1929	1274 m, 847 m, 837 m, 789 m
7e	1954	1109 s, 843 m, 791 m
8e	2050, 1970	1091 s, 922 m, 849 m, 837 m, 795 m
9e	1960	2155 s, 1503 w, 1093 s, 926 w, 844 m, 820 w, 790 m
10e	2014, 1950	930 s, 828 m
11e	1923	2143 s, 1506 m, 1238 w, 914 m, 833 m, 816 m, 762 m

^a Spectra recorded as Nujol mulls between KBr plates; values in cm^{-1} ; intensities of IR bands are described as s, strong, m, medium, and w, weak. ^b All bands strong in intensity. ^c Spectra recorded as dichloromethane solutions between KBr plates.

studied (**2a,c,d**). Values for C- α and C- β appeared in the ranges 162.9–168.7 ($^2J_{\text{CP}} = 9.8\text{--}10\text{ Hz}$) and 135.8–137.9 ($^3J_{\text{CP}} = 0\text{--}3.1\text{ Hz}$), respectively, for these compounds. Examination of the cross-peaks obtained in a 2D-NMR CH correlation experiment on **2b** indicates that the proton giving rise to the doublet of triplets at 8.32 ppm is bonded to the carbon atom with the signal at 163.7 ppm. Similarly, the proton giving rise to the doublet of triplets at 5.22 ppm is bonded to a carbon atom with a resonance at ca. 134 ppm, although this latter signal is obscured by the PPh_3 phenyl resonances in this region. These data allow confident assignments to be made for the H- α and H- β resonances in **2b** and, by extension, to the other five-coordinate alkenyl compounds.

The formation of isolable, silylalkenyl complexes arising from the insertion of unactivated alkynes into metal–silicon bonds is rare.^{4,5} The ethyne insertion reactions described above could serve as models for one of the two key steps in the catalytic cycle for the hydrosilylation of alkynes depicted in Scheme 1.

One of the characteristic reactions that five-coordinate organoruthenium complexes of formula $\text{RuRCl}(\text{CO})(\text{PPh}_3)_2$ undergo is reaction with small Lewis bases such as CO and CNR to form the corresponding coordinatively saturated derivatives $\text{RuRCl}(\text{CO})\text{L}(\text{PPh}_3)_2$.¹⁰ The silylalkenyl complexes **2a,b,d** also show this reactivity, and the corresponding colorless, dicarbonyl complexes, $\text{Ru}(\text{CH}=\text{CHSiR}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ ($\text{R}_3 = \text{Me}_3$ (**3a**), Et_3 (**3b**), Me_2OEt (**3d**)), are rapidly formed on exposure to CO (see Scheme 2). It is noteworthy that the H- α , H- β , C- α , and C- β resonances for the alkenyl carbon atoms of these compounds appear in positions similar to those observed for the precursor five-coordinate compounds. The values of $^2J_{\text{CP}}$, $^3J_{\text{CP}}$, and $^4J_{\text{HP}}$ for the alkenyl group change only slightly on carbonylation, but $^3J_{\text{HH}}$ and $^3J_{\text{HP}}$ change considerably. $^3J_{\text{HH}}$ is close to 20 Hz in **3a,b,d**, and this is now clearly in the range associated with a

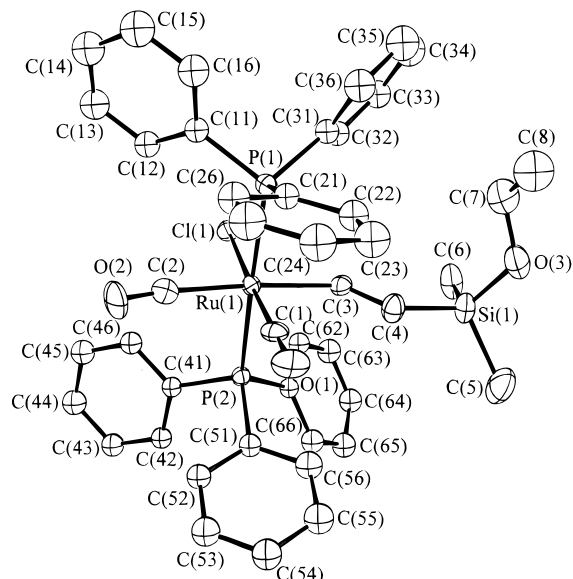


Figure 1. ORTEP view of $\text{Ru}(\text{CH}=\text{CHSiMe}_2\text{OEt})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**3d**) with thermal ellipsoids at the 50% probability level.

trans-geometry for the carbon–carbon double bond. The values of $^3J_{\text{HP}}$ are close to 4 Hz, and in each case are now larger than the $^4J_{\text{HP}}$ values.

A single-crystal X-ray structure determination of $\text{Ru}(\text{CH}=\text{CHSiMe}_2\text{OEt})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (**3d**) has been obtained and the *trans*-arrangement of the alkenyl double bond confirmed. The molecular geometry is depicted in Figure 1, and important bond lengths and angles are collected in Tables 3 and 4. The crystal data and refinement data for compounds **3d** and **9e** are collected in Table 2. The geometry about ruthenium is octahedral; the two PPh_3 ligands are mutually *trans*, and the two carbonyls, mutually *cis*. The Ru–C(3) distance (2.108(7) Å) is very close to the mean value for reported Ru–C(sp²) single bonds.¹¹ The bond lengths and angles

(10) (a) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. (b) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27. (c) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46.

(11) A search of the Cambridge Structural Database revealed a mean value of 2.109 Å for reported Ru–C(sp²) single-bonded distances (N_{obs} , 1606; $\text{SD}_{\text{sample}}$, 0.178; SD_{mean} , 0.004).

Table 2. Crystal and Refinement Data for 3d and 9e

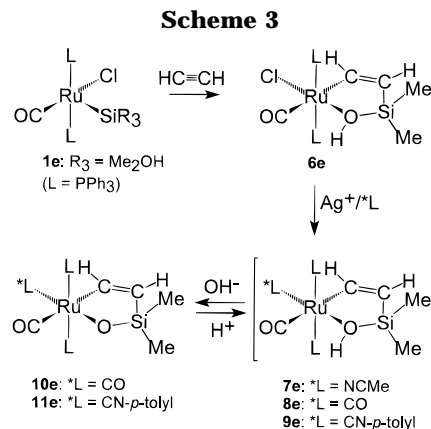
	compound	
	3d	9e
formula	C ₄₄ H ₄₈ ClO ₃ P ₂ RuSi	C ₅₀ H ₄₄ Cl ₃ NO ₆ P ₂ RuSi
M _r	851.37	1054.33
cryst system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
a, Å	10.247(5)	12.974(3)
b, Å	12.904(3)	23.427(3)
c, Å	16.587(4)	15.924(4)
α, deg	105.68(2)	
β, deg	93.39(3)	92.09(2)
γ, deg	98.80(3)	
V, Å ³	2075.1(12)	4837(2)
Z	2	4
d(calc), g cm ⁻³	1.363	1.448
F(000)	882	2160
μ, mm ⁻¹	0.58	0.63
radiation, Mo Kα (monochromatic) λ, Å	0.710 69	0.710 69
T, K	193	193
diffractometer	Nonius CAD4	Nonius CAD4
scan technique	ω/2θ	ω/2θ
2θ(min–max), deg	1–26	1–25
h,k,l range	–12 ≤ h ≤ 12 –15 ≤ k ≤ 15 0 ≤ l ≤ 20	–15 ≤ h ≤ 15 0 ≤ k ≤ 27 0 ≤ l ≤ 17
no. of unique reflns	8144	7125
no. of obsd reflns (I > 2σ(I))	5059	4474
cryst size, mm	0.32 × 0.20 × 0.20	0.35 × 0.18 × 0.12
A(min–max)	1.00–0.92	1.00–0.94
least-squares weights, a, b	0.113, 0.00	0.138, 44.4
no. of variables in LS	476	621
goodness of fit on F ²	0.970	1.016
function minimized	Σw[F _o ² – F _c ²] ²	Σw[F _o ² – F _c ²] ²
R and wR2 (obsd data) ^a	0.061, 0.151	0.059, 0.142
max–min peak heights in final electron density map, e Å ⁻³	1.22–1.26	0.98–1.08

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|; wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^3] \}^{1/2}; w = 1.0 / [\sigma^2(F_o^2) + aP^2 + bP], \text{ where } P = (F_o^2 + 2F_c^2) / 3.$$

associated with the alkenyl group compare favorably with those reported in related compounds.⁸ Importantly, the structure clearly shows that the geometry about the double bond is *trans*.

The coordinatively unsaturated compounds **2a,b,d** also react with CN-*p*-tolyl or acetate to form the corresponding coordinatively saturated derivatives. Thus, on addition of CN-*p*-tolyl to **2a**, Ru(CH=CHSiMe₃)Cl(CO)(CN-*p*-tolyl)(PPh₃)₂ (**4a**) is formed and addition of sodium acetate to **2a** results in the formation of Ru(CH=CHSiMe₃)(η²-O₂CCH₃)(CO)(PPh₃)₂ (**5a**). The ¹H and ¹³C NMR spectra are consistent with a *trans* geometry about the carbon–carbon double bond for these compounds.

Insertion of ethyne into the Ru–Si bond of the hydroxysilyl complex, Ru(SiMe₂OH)Cl(CO)(PPh₃)₂ (**1e**), also occurs. However, in this instance a colorless product formulated as Ru(CH=CHSiMe₂OH)Cl(CO)(PPh₃)₂ (**6e**) is formed. In this compound the oxygen of the hydroxysilyl group coordinates to the ruthenium, forming a metallacyclic ring (see Scheme 3). The alkenyl protons appear in the ¹H NMR spectrum at 7.60 (dt, ³J_{H(a)H(b)}} = 12.6 Hz, ³J_{H(a)P}} = 1.6 Hz) and 5.55 (ddt, ³J_{H(b)H(a)}} = 12.6 Hz, ⁴J_{H(b)H(c)}} = 2.2 Hz, ⁴J_{H(b)P}} = 2.3 Hz) ppm (where H_a is the proton on the alkenyl carbon bonded to ruthenium, H_b is the remote alkenyl proton, and H_c is the silanol proton). The hydroxyl proton appears as a sharp doublet signal at 2.61 (⁴J_{H(c)H(b)}} = 2.3 Hz) ppm, and the methyl signals appear as a singlet at –0.75 ppm. This compound is only sparingly soluble in all common NMR solvents, and so a satisfactory ¹³C NMR spectrum could not be obtained. Confirmation of



the metallacyclic ring formulation was made possible through study of simple derivatives of **6e**.

Surprisingly, when a solution of **6e** is exposed to CO under mild conditions (1 atm of CO pressure, 20 °C, 15 min), the hydroxyl group is not displaced from the metal center to give the corresponding dicarbonyl product. Only unreacted starting material is recovered under these conditions. Upon increase of the time of the reaction to 16 h, the alkenyl group is lost from the metal and Ru(CO)₃(PPh₃)₂ is formed. In contrast, the chloride ligand of **6e** can be easily removed by reaction with AgClO₄ in the presence of NCCH₃ to give the soluble, cationic complex [Ru(CH=CHSiMe₂OH)(NCCH₃)(CO)(PPh₃)₂]ClO₄ (**7e**). The acetonitrile ligand in this complex can, in turn, be easily displaced by CN-*p*-tolyl or CO to form the new cationic complexes [Ru(CH=CH-

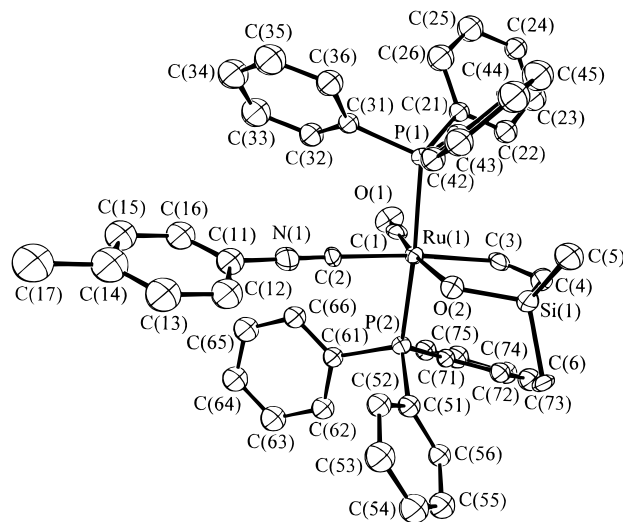
Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3d**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Ru(1)	2179(1)	3196(1)	3202(1)	19(1)
P(1)	1690(2)	4780(1)	2851(1)	22(1)
P(2)	2742(2)	1602(1)	3501(1)	20(1)
Cl(1)	4489(2)	4128(1)	3659(1)	26(1)
Si(1)	2677(2)	1410(2)	255(1)	35(1)
O(1)	-593(5)	2017(4)	2563(4)	42(1)
O(2)	953(6)	3863(5)	4884(4)	57(2)
O(3)	2126(6)	1965(5)	-463(3)	51(2)
C(1)	468(7)	2474(5)	2806(4)	29(2)
C(2)	1535(7)	3673(6)	4304(5)	31(2)
C(3)	2726(7)	2578(5)	1981(4)	25(1)
C(4)	2001(7)	1952(6)	1265(4)	34(2)
C(5)	2046(11)	-90(7)	-188(6)	65(3)
C(6)	4527(8)	1713(8)	388(5)	52(2)
C(7)	2295(12)	3139(9)	-301(7)	65(3)
C(8)	1055(24)	3473(19)	-634(15)	70(6)
C(8')	1626(23)	3495(18)	-973(14)	67(6)
C(11)	1932(6)	6042(5)	3723(4)	27(1)
C(12)	2651(7)	6120(6)	4476(4)	31(2)
C(13)	2805(8)	7075(6)	5138(5)	42(2)
C(14)	2280(9)	7929(6)	5064(6)	50(2)
C(15)	1574(9)	7874(6)	4308(6)	54(2)
C(16)	1427(8)	6934(6)	3642(5)	42(2)
C(21)	-77(6)	4553(5)	2488(4)	26(1)
C(22)	-539(7)	3922(6)	1667(4)	35(2)
C(23)	-1903(8)	3594(7)	1434(5)	47(2)
C(24)	-2783(8)	3891(7)	2017(6)	46(2)
C(25)	-2323(8)	4513(7)	2816(6)	49(2)
C(26)	-978(7)	4839(6)	3063(5)	40(2)
C(31)	2535(7)	5240(5)	2034(4)	27(1)
C(32)	3834(7)	5127(6)	1939(4)	30(2)
C(33)	4525(8)	5530(6)	1356(5)	39(2)
C(34)	3894(9)	6064(7)	875(5)	54(2)
C(35)	2625(9)	6188(7)	968(5)	55(2)
C(36)	1943(8)	5771(7)	1549(5)	47(2)
C(41)	3407(6)	1763(5)	4586(4)	23(1)
C(42)	3587(6)	858(5)	4842(4)	25(1)
C(43)	4108(7)	966(6)	5659(4)	31(2)
C(44)	4453(7)	1997(6)	6218(4)	35(2)
C(45)	4301(7)	2898(6)	5968(4)	34(2)
C(46)	3768(7)	2799(5)	5155(4)	28(2)
C(51)	1249(6)	574(5)	3323(4)	26(1)
C(52)	486(6)	496(5)	3977(4)	28(1)
C(53)	-734(7)	-213(6)	3819(5)	37(2)
C(54)	-1196(7)	-825(6)	3013(5)	40(2)
C(55)	-478(7)	-718(6)	2355(5)	42(2)
C(56)	745(7)	-24(6)	2504(5)	37(2)
C(61)	3936(6)	884(5)	2897(4)	23(1)
C(62)	5102(6)	1493(6)	2766(4)	27(1)
C(63)	6067(7)	994(7)	2355(5)	38(2)
C(64)	5881(7)	-135(6)	2054(4)	37(2)
C(65)	4720(8)	-755(6)	2161(4)	38(2)
C(66)	3747(7)	-256(6)	2594(4)	31(2)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

SiMe₂OH)L(CO)(PPh₃)₂]ClO₄ (L = CN-*p*-tolyl (**9e**), CO (**8e**)) as illustrated in Scheme 3.

In the IR spectrum of [Ru(CH=CHSiMe₂OH)(CN-*p*-tolyl)(CO)(PPh₃)₂]ClO₄ (**9e**) the relatively high values for $\nu(\text{CN})$ (2155 cm⁻¹) and $\nu(\text{CO})$ (1960 cm⁻¹) are consistent with a cationic formulation for this complex. The strong, broad band at 1093 cm⁻¹ is assigned to the perchlorate anion. In the ¹H NMR spectrum the chemical shift positions and coupling constant values observed for the alkenyl protons, i.e. 8.06 (dt, ³*J*_{H(a)H(b)} = 14.1 Hz, ³*J*_{H(a)P} = 2.1 Hz) and 6.15 (ddt, ³*J*_{H(b)H(a)} = 14.1 Hz, ⁴*J*_{H(b)H(c)} = 2.1 Hz, ⁴*J*_{H(b)P} = 2.2 Hz) ppm (where H_a is the proton on the alkenyl carbon bonded to ruthenium, H_b is the remote alkenyl proton, and H_c is the silanol

**Figure 2.** ORTEP view of [Ru(CH=CHSiMe₂OH)(CN-*p*-tolyl)(CO)(PPh₃)₂]ClO₄ (**9e**) with thermal ellipsoids at the 50% probability level.**Table 4. Selected Bond Lengths (\AA) and Angles (deg) for **3d****

Ru(1)–C(1)	1.846(7)	Ru(1)–Cl(1)	2.460(2)
Ru(1)–C(2)	1.954(7)	Si(1)–O(3)	1.660(6)
Ru(1)–C(3)	2.109(6)	Si(1)–C(4)	1.851(7)
Ru(1)–P(2)	2.386(2)	Si(1)–C(6)	1.863(8)
Ru(1)–P(1)	2.385(2)	Si(1)–C(5)	1.870(9)
C(1)–Ru(1)–C(2)	87.0(3)	C(3)–Ru(1)–P(1)	90.2(2)
C(1)–Ru(1)–C(3)	88.3(3)	P(2)–Ru(1)–P(1)	177.21(6)
C(2)–Ru(1)–C(3)	175.1(3)	C(1)–Ru(1)–Cl(1)	177.2(2)
C(1)–Ru(1)–P(2)	90.7(2)	C(2)–Ru(1)–Cl(1)	95.8(2)
C(2)–Ru(1)–P(2)	91.3(2)	C(3)–Ru(1)–Cl(1)	88.9(2)
C(3)–Ru(1)–P(2)	87.3(2)	P(2)–Ru(1)–Cl(1)	89.29(6)
C(1)–Ru(1)–P(1)	90.4(2)	P(1)–Ru(1)–Cl(1)	89.46(6)
C(2)–Ru(1)–P(1)	91.3(2)		

proton), are very similar to those found for **6e**. The hydroxyl proton appears considerably downfield (5.24 ppm, d, ⁴*J*_{H(c)H(b)} = 2.1 Hz) from the corresponding signal in **6e** (2.61 ppm) suggesting that it has increased acidic character in the cationic complex (see later). The increased solubility of **9e** enabled a satisfactory ¹³C NMR spectrum of this compound to be obtained. The alkenyl carbon resonances were observed as a triplet at 177.9 (²*J*_{CP} = 10.8 Hz) and a singlet at 139.9 ppm. Very similar resonances are observed for the metallacyclic ring atoms in the ¹H and ¹³C NMR spectra of the related cationic complexes **7e** and **8e**.

A crystal structure determination of **9e** has been performed, and the molecular geometry is depicted in Figure 2. Important bond lengths and angles are collected in Tables 5 and 6. The geometry about ruthenium can be described in terms of a distorted octahedron with the two PPh₃ ligands mutually *trans*. A metallacyclic ring is formed by coordination of the hydroxysilyl oxygen atom of the alkenyl group to ruthenium. CO (*trans* to oxygen) and CN-*p*-tolyl (*trans* to the alkenyl carbon) complete the coordination sphere. The five-membered ring is planar,¹² and two of the internal angles of the ring are considerably smaller than the others ($\angle\text{C}(3)\text{--Ru--O}(2) = 81.3^\circ$ and $\angle\text{C}(4)\text{--Si--O}(2) = 99.0^\circ$). The Ru–C(3) bond length of 2.085(10) Å is normal¹¹ and is also very similar to the corresponding

(12) Deviations are only of the order of 0.003 Å from the mean plane through the atoms Ru(1)C(3)C(4)Si(1)O(2).

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **9e**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Ru(1)	1621(1)	1031(1)	2872(1)	20(1)
P(1)	2968(1)	543(1)	3677(1)	22(1)
P(2)	380(2)	1480(1)	1946(1)	22(1)
Si(1)	27(2)	1123(1)	4476(1)	30(1)
O(1)	2166(5)	319(3)	1401(4)	47(2)
O(2)	1008(4)	1442(2)	3986(3)	24(1)
N(1)	3110(5)	2113(3)	2832(4)	36(2)
C(1)	1980(6)	604(3)	1974(6)	32(2)
C(2)	2596(5)	1719(3)	2790(5)	23(2)
C(3)	490(5)	440(3)	3145(5)	28(2)
C(4)	-130(6)	496(4)	3802(5)	35(2)
C(5)	399(7)	994(4)	5580(5)	41(2)
C(6)	-1120(6)	1595(4)	4457(5)	40(2)
C(11)	3738(6)	2604(4)	2887(5)	36(2)
C(12)	3446(7)	3033(4)	3457(6)	46(2)
C(13)	4094(8)	3509(4)	3536(6)	52(3)
C(14)	4967(8)	3569(4)	3094(6)	54(3)
C(15)	5207(8)	3127(4)	2543(6)	49(2)
C(16)	4592(7)	2644(4)	2427(6)	43(2)
C(17)	5706(8)	4056(5)	3203(8)	71(3)
C(21)	3096(6)	-233(3)	3561(5)	26(2)
C(22)	2231(6)	-570(3)	3481(5)	34(2)
C(23)	2309(7)	-1156(4)	3457(6)	43(2)
C(24)	3256(6)	-1417(4)	3494(5)	34(2)
C(25)	4121(7)	-1086(4)	3552(6)	48(2)
C(26)	4054(6)	-492(4)	3585(6)	41(2)
C(31)	4249(5)	803(3)	3410(5)	25(2)
C(32)	4494(6)	855(3)	2577(6)	35(2)
C(33)	5440(6)	1076(4)	2357(6)	48(3)
C(34)	6155(7)	1240(4)	2977(8)	56(3)
C(35)	5939(7)	1179(4)	3800(7)	45(2)
C(36)	4996(6)	966(3)	4007(6)	37(2)
C(41)	2974(6)	636(3)	4812(5)	27(2)
C(42)	3008(6)	1192(3)	5140(5)	30(2)
C(43)	3060(6)	1280(4)	5993(5)	37(2)
C(44)	3078(7)	826(4)	6534(6)	44(2)
C(45)	3012(7)	274(4)	6232(6)	4(2)
C(46)	2957(6)	180(4)	5363(5)	30(2)
C(51)	-375(6)	2057(3)	2393(4)	26(2)
C(52)	167(7)	2466(3)	2881(5)	33(2)
C(53)	-333(8)	2927(4)	3211(6)	43(2)
C(54)	-1384(7)	2979(4)	3083(5)	43(2)
C(55)	-1922(7)	2594(4)	2601(5)	39(2)
C(56)	-1418(6)	2132(4)	2248(5)	31(2)
C(61)	919(6)	1845(3)	1038(5)	27(2)
C(62)	258(7)	2180(4)	535(5)	35(2)
C(63)	639(8)	2457(4)	-157(5)	45(2)
C(64)	1664(7)	2413(4)	-351(6)	41(2)
C(65)	2304(7)	2077(4)	138(6)	41(2)
C(66)	1949(6)	1799(4)	824(5)	32(2)
C(71)	-564(5)	993(3)	1453(5)	24(2)
C(72)	-414(7)	793(3)	647(5)	33(2)
C(73)	-1107(7)	399(4)	282(6)	43(2)
C(74)	-1938(6)	220(4)	696(6)	37(2)
C(75)	-2074(6)	407(4)	1510(6)	37(2)
C(76)	-1396(6)	783(3)	1889(5)	29(2)
Cl(1)	1383(2)	2773(1)	5338(2)	59(1)
O(3)	1650(6)	2464(3)	4630(5)	75(2)
O(4)	297(7)	2902(6)	5243(6)	127(4)
O(5)	1490(8)	2449(5)	6070(5)	118(4)
O(6)	1971(8)	3271(4)	5412(7)	113(4)
Cl(2)	9125(4)	4154(2)	5069(4)	106(2)
Cl(3)	10041(7)	4542(3)	3639(5)	163(3)
C(7)	10419(13)	4280(7)	4635(10)	111(5)
Cl(2')	6441(17)	829(9)	8636(13)	33(5)
Cl(3')	9366(21)	4478(12)	4002(20)	65(7)
Cl(2'')	10861(19)	4385(10)	3674(14)	36(5)
Cl(3'')	9306(21)	4264(13)	4458(21)	57(7)

^a See footnote *a* of Table 3.

distance found in **3d** (2.108(7) Å). The C(3)–C(4) distance of 1.358(16) Å is consistent with a double bond between these atoms. The Ru–O(2) bond length is 2.192(7) Å. Although this is at the longer end of

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **9e**

Ru(1)–C(1)	1.821(9)	Si(1)–O(2)	1.691(5)
Ru(1)–C(2)	2.055(8)	Si(1)–C(4)	1.826(9)
Ru(1)–C(3)	2.075(7)	Si(1)–C(5)	1.831(8)
Ru(1)–O(2)	2.193(5)	Si(1)–C(6)	1.852(8)
Ru(1)–P(2)	2.387(2)	C(3)–C(4)	1.350(11)
Ru(1)–P(1)	2.417(2)		
C(1)–Ru(1)–C(2)	101.8(3)	C(3)–Ru(1)–P(1)	94.4(2)
C(1)–Ru(1)–C(3)	90.0(3)	O(2)–Ru(1)–P(1)	93.15(13)
C(2)–Ru(1)–C(3)	168.0(3)	P(2)–Ru(1)–P(1)	173.89(7)
C(1)–Ru(1)–O(2)	171.0(3)	O(2)–Si(1)–C(4)	98.8(3)
C(2)–Ru(1)–O(2)	87.1(3)	O(2)–Si(1)–C(5)	109.8(3)
C(3)–Ru(1)–O(2)	81.0(3)	C(4)–Si(1)–C(5)	116.8(4)
C(1)–Ru(1)–P(2)	86.7(2)	O(2)–Si(1)–C(6)	110.3(3)
C(2)–Ru(1)–P(2)	91.1(2)	C(4)–Si(1)–C(6)	113.5(4)
C(3)–Ru(1)–P(2)	87.6(2)	C(5)–Si(1)–C(6)	107.3(4)
O(2)–Ru(1)–P(2)	92.88(13)	Si(1)–O(2)–Ru(1)	118.8(3)
C(1)–Ru(1)–P(1)	87.5(2)	C(4)–C(3)–Ru(1)	122.9(6)
C(2)–Ru(1)–P(1)	88.2(2)	C(3)–C(4)–Si(1)	118.5(6)

reported Ru–OSiR₃ distances, it is identical to the Ru–O(silanol) bond length in Ru(PPh₂CH₂SiMe₂OH)(CO)₂(CO₂CF₃)₂.Et₂O.¹³ This latter complex is related to **9e** in that it also contains a five-membered chelate ring formed by coordination of a silanol oxygen atom to the metal center. The hydroxyl proton was not located in the structure of **9e**, but its presence can be inferred by the close approach made to the hydroxyl oxygen atom by one of the perchlorate oxygens (2.724(9) Å). This distance is slightly shorter than twice the van der Waals' radius for oxygen and falls near the middle of the range normally observed for O–H...O hydrogen-bonding interactions.¹⁴ The value of ⁴J_{H(c)(H(b))} (2.1 Hz) for this compound is not markedly different from the corresponding value observed for the neutral precursor, **6e** (2.2 Hz). This suggests that in **9e** a significant interaction is still retained between the hydroxyl proton and O(2).

An important feature of the structure of **9e** is that the geometry about the carbon–carbon double bond is *cis*. Insertion of ethyne into the Ru–Si bond of **1e** is expected to give a *cis*-alkenyl complex as the initial product.^{2–4} It appears that this *cis*-alkenyl complex is then trapped through coordination of the hydroxysilyl oxygen to the metal to give complex **6e** before rearrangement to the *trans* isomer can occur. Complex **6e** therefore serves as a model for the product initially formed when alkyne inserts into a metal–silicon bond during catalytic alkyne hydrosilylation. No metallacyclic ring formation of this type is observed for **2d**, which is the ethoxysilyl analogue of **6e**. In this case the much larger steric bulk of the ethyl group is probably responsible for the failure of the oxygen atom to coordinate to ruthenium.

The cationic complex [Ru(CH=CHSiMe₂OH)(CN-*p*-tolyl)(CO)(PPh₃)₂]ClO₄ (**9e**) can be deprotonated in solution by treatment with KOH and the resulting neutral complex, Ru(CH=CHSiMe₂O)(CN-*p*-tolyl)(CO)(PPh₃)₂ (**11e**), isolated in good yield (see Scheme 3). The ν(CN) and ν(CO) bands in the IR spectrum of **11e** appear

(13) Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R.; Zaworotko, M. J.; Cameron, T. S.; Kumari, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1523. A search of the Cambridge Structural Database revealed a mean value of 2.091 Å for Ru–OSi distances (*N*_{obs}, 15; *SD*_{sample}, 0.051; *SD*_{mean}, 0.013 Å).

(14) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1989; p 65.

Table 7. Silicon-Containing Products Formed in the Hydrosilylation of Ethyne and Phenylethyne Catalyzed by 1b^a

alkyne	products	yield, ^b %
HC≡CH	H ₂ C=CHSiEt ₃	83
	SiEt ₃ OSiEt ₃ ^c	<1
	HSiEt ₃	17
PhC≡CH	<i>trans</i> -PhHC=CHSiEt ₃	41
	<i>cis</i> -PhHC=CHSiEt ₃	11
	PhC≡CSiEt ₃	22
	SiEt ₃ OSiEt ₃ ^c	5
	HSiEt ₃	15

^a Conditions: 65 °C, 24 h, 10 mol % Ru(SiEt₃)Cl(CO)(PPh₃)₂ vs added HSiEt₃ (alkyne present in excess). ^b Mol % of silicon-containing products formed vs HSiEt₃ added at the beginning of the reaction. ^c Hexaethyldisiloxane is probably formed by reaction with traces of oxygen remaining in the reaction vessel after purging.

at the lower values of 2143 and 1923 cm⁻¹, respectively, and there are no bands that can be assigned to the perchlorate anion. The alkenyl protons are observed in the ¹H NMR spectrum at 8.08 (dt, ³J_{HH} = 12.8 Hz, ³J_{HP} = 2.3 Hz) and 6.13 (dt, ³J_{HH} = 12.8 Hz, ⁴J_{HP} = 1.8 Hz). The coupling between the β-hydrogen and the hydroxyl proton that is evident in each of the complexes **6–9e** is necessarily absent in this compound. The related

neutral compound, Ru(CH=CHSiMe₂O)(CO)₂(PPh₃)₂ (**10e**), is formed in a similar manner on deprotonation of **8e**. These deprotonation reactions are reversible, and upon exposure of **10e** or **11e** to perchloric acid, **8e** or **9e**, respectively, are regenerated.

Catalytic Hydrosilylation of Ethyne and Phenylethyne. The observation that the five-coordinate phenyl complex RuPhCl(CO)(PPh₃)₂ reacts with HSiEt₃ to give benzene and the five-coordinate silyl complex Ru(SiEt₃)Cl(CO)(PPh₃)₂ (**1b**) (see above) indicated that the alkenyl complex Ru(CH=CHSiEt₃)Cl(CO)(PPh₃)₂ (**2b**) might react with HSiEt₃ in a similar way. Preliminary investigations showed this to be so, and both CH₂=CHSiEt₃ and **1b** are formed in good yield from this reaction. These observations, together with the results of the ethyne insertion reactions that form **2a–d**, demonstrate that the five-coordinate silyl complex Ru(SiEt₃)Cl(CO)(PPh₃)₂ (**1b**) can undergo both of the key reactions depicted in the catalytic cycle in Scheme 1 for the hydrosilylation of ethyne by HSiEt₃, viz. insertion of ethyne into the Ru–Si bond and cleavage of the resulting alkenyl complex with triethylsilane to release vinylsilane and regenerate the catalyst. The potential of complex **1b** to catalyze the hydrosilylation of alkynes was therefore investigated, and the results of our preliminary investigations are described below.

In a typical experiment a benzene solution of triethylsilane, **1b** (1 mol %), and ethyne (pressure maintained at 0.8 atm) was heated in a pressure vessel at 65 °C for 24 h. The organic products in the resulting solution were then separated from the metal-containing species by chromatography on silica gel. Analysis of the organic fraction was achieved by ¹H NMR and GC-MS. No attempts were made to optimize the hydrosilylation conditions.

The silicon-containing products obtained, with yields, are given in Table 7 for the reactions with ethyne and phenylethyne (see below). Perhaps the most striking feature is the high selectivity of the hydrosilylation of ethyne. Vinyltriethylsilane is the only major product

formed under these conditions. The yield of this product (based on HSiEt₃) is 83%, and this corresponds to an average catalyst turnover rate of 3.5/h. Very similar turnover rates have been reported for the hydrosilylation of higher alkynes catalyzed by [IrH(7,8-benzoquinolino)(H₂O)(PPh₃)₂]SbF₆.²

Compound **1b** also catalyzes the addition of HSiEt₃ to phenylethyne under conditions similar to those described above. Three major silyl-containing products are formed in this case, *cis*-CHPh=CHSiEt₃, *trans*-CHPh=CHSiEt₃, and PhC≡CSiEt₃ (see Table 7). The combined yield of these products is 74% (based on HSiEt₃), and this corresponds to an average catalyst turnover rate of 3.1/h. The only other silicon-containing product formed is a trace amount of hexaethyldisiloxane. This may arise from reaction with small amounts of oxygen remaining in the reaction vessel after purging. No α-(triethylsilyl)styrene (SiEt₃[Ph]C=CH₂) was detected in the products.

Metal-catalyzed hydrosilylation of alkynes usually gives a mixture of *trans*- and *cis*-silylalkenes.^{2–4} In two systems that have been studied in depth recently^{2,3} the *cis/trans* ratio was found to depend on a number of factors including the temperature, the nature of the silane, and the size of the substituents on the alkyne. It was proposed that the *cis/trans* ratio of alkenes produced depends on the relative amount of reductive elimination that occurs from the (*Z*)-silylalkenyl intermediate before isomerization to the (*E*)-isomer takes place (Scheme 1). The *trans/cis* ratio of the alkenes formed by the [IrH(7,8-benzoquinolino)(H₂O)(PPh₃)₂]SbF₆-catalyzed hydrosilylation of phenylethyne is 0.2.² This is considerably smaller than the value of 3.7 that was obtained in the same reaction catalyzed by **1b**. However, this large difference does not necessarily mean that a higher proportion of cleavage occurs from the (*Z*)-alkenyl isomer in the reaction catalyzed by **1b**. It could simply reflect the much greater efficiency of **1b** as an alkene isomerization catalyst. Support for this contention comes from the observation that, under the hydrosilylation conditions used, **1b** efficiently catalyzes the conversion of *cis*-CHPh=CHSiEt₃ to the *trans*-isomer.¹⁵ Therefore, during the catalytic hydrosilylation reaction, significant amounts of *trans*-CHPh=CHSiEt₃ could be formed via isomerization of the corresponding *cis*-isomer.

Formation of phenylalkynylsilanes from metal-catalyzed hydrosilylation of phenylethyne has also been reported before.² It was proposed that these products arise through β-hydrogen elimination from the (*E*)-(silylalkenyl)metal intermediate that is formed by insertion of phenylethyne into the metal–silicon bond (Scheme 1). The resulting metal hydride may then react with further phenylethyne and silane to form styrene and regenerate the silyl metal catalyst.² It is reasonable to expect that a similar mechanism might also be involved for the formation of PhC≡CSiEt₃ in the Ru(SiEt₃)Cl(CO)(PPh₃)₂-catalyzed reactions above. Indeed, styrene was identified as the only major, silicon-free product formed and the observed PhC≡CSiEt₃/styrene ratio of 1.37 is similar to the silylalkyne/styrene ratios reported for alkyne hydrosilylation reactions catalyzed by [IrH-

(15) No *cis*-CHPh=CHSiEt₃ could be detected by ¹H NMR after an equimolar mixture of the *cis*- and *trans*-isomers of this compound was heated with 1% Ru(SiEt₃)Cl(CO)(PPh₃)₂ at 65 °C for 24 h.

(7,8-benzoquinolinato)(H₂O)(PPh₃)₂]SbF₆.² The observation that no significant amounts of HC≡CSiEt₃ are formed in the hydrosilylation of ethyne catalyzed by **1b** is also consistent with a previous report² which notes that as the steric bulk of the alkyne substituents decrease so does the amount of silylalkyne formed in the products. The reduced steric pressures in the (*E*)-silylalkenyl intermediate (Scheme 1) presumably lower the propensity for β-hydrogen elimination.

Summary and Conclusions

The five-coordinate silyl complexes Ru(SiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**1a**), Et₃ (**1b**), Ph₃ (**1c**), Me₂OEt (**1d**)) all react with ethyne under mild conditions to give the corresponding five-coordinate silylalkenyl insertion products Ru(CH=CHSiR₃)Cl(CO)(PPh₃)₂ (R₃ = Me₃ (**2a**), Et₃ (**2b**), Ph₃ (**2c**), Me₂OEt (**2d**)) in good isolated yield. Structural evidence clearly shows a *trans* arrangement about the double bond for **2b** in the solid state, and a similar arrangement is found for the six-coordinate dicarbonyl derivative, **3d**. The five-coordinate complexes are expected to retain this *trans* geometry in solution. In contrast to these results, the insertion of ethyne into the Ru–Si bond of Ru(SiMe₂OH)Cl(CO)(PPh₃)₂ results in the formation of Ru(CH=CHSiMe₂OH)Cl(CO)(PPh₃)₂ (**6e**), which has a metallacyclic ring with a *cis* arrangement about the double bond. The formation of this product may proceed via insertion of alkyne to give a *cis*-alkenyl product, which is then trapped through coordination of the hydroxysilyl oxygen to the metal before rearrangement to the *trans* isomer can occur.

The stoichiometric reactions of complex **1b** that involve alkyne insertion into a ruthenium–silicon bond and cleavage of the resulting alkenyl complex by reaction with added silane model the two key steps in the proposed catalytic cycle depicted in Scheme 1. In addition, the five-coordinate alkenyl compounds **2a–d** and **6e** that have been isolated serve as models for the key intermediates that are proposed to be formed during the transition metal catalyzed hydrosilylation of alkynes.^{2,3}

The complex **1b** has been shown to catalyze the hydrosilylation of ethyne and phenylethyne. Vinyltriethylsilane is formed with high selectivity and in good yield from ethyne and HSiEt₃. The major products formed in the related reaction with phenylethyne are *trans*-CHPh=CHSiEt₃, *cis*-CHPh=CHSiEt₃, and PhC≡CSiEt₃. The formation of these compounds can be rationalized in terms of the proposed catalytic scheme depicted in Scheme 1. However, we have no proof concerning the actual mechanism of the alkyne hydrosilylation reactions catalyzed by **1b**, and we also cannot rule out the possibility that **1b** acts as a precatalyst rather than the true catalytic species for these reactions.

Experimental Section

General Data. Preparation of the silyl complexes was carried out in an inert atmosphere using standard vacuum-line and Schlenk techniques. Where necessary, solvents were dried over sodium/benzophenone ketyl prior to use. Reactions involving ethyne were carried out in a Fisher-Porter bottle. Ru(Ph)Cl(CO)(PPh₃)₂^{16,17} and HSiMe₃¹⁸ were prepared according to literature procedures. HSiEt₃, HSiMe₂Cl (Aldrich), and HSiPh₃ (Merck) were used as received.

Analytical data were obtained by the Microanalytical Laboratory, University of Otago. IR spectra (4000–400 cm⁻¹) were recorded on a Digilab FTS-7 spectrophotometer as Nujol mulls between KBr plates. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC 200 or a Bruker DRX 400 spectrometer. ²⁹Si NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 79.5 MHz. Chemical shifts are reported in ppm. In the ¹³C NMR spectra of the complexes below which contain mutually *trans* PPh₃ ligands, the PPh₃ carbon atoms couple to both phosphorus atoms and therefore form part of a second-order AXX' spin system. In principle, each carbon nucleus should therefore give rise to a five-line, second-order spectrum. In practice the *ipso*, *ortho*, and *meta* signals were observed as apparent triplets and the *para* signal as a broad singlet. For the *ipso*, *ortho*, and *meta* signals, the sum of the two coupling constants, ^mJ_{CP} and ⁿJ_{CP}, was obtained by measuring the separation in Hz between the two outermost lines of the apparent triplet and is denoted below as ^{m,n}J_{CP} (*m* = 1, 2, 3; *n* = 3, 4, 5). The multiplicity of each of these signals is given as *t'*. The assignments of the *ortho* and *meta* signals were made by comparing the chemical shift positions with those for the corresponding carbon atoms in closely related monophosphine complexes where simple first-order coupling to phosphorus is observed. The assignments in these latter complexes were made using the assumption that ³J_{CP} > ²J_{CP}.²³ Gas chromatography/mass spectroscopy was performed on a Hewlett Packard 5890 Series II gas chromatograph with a 5971 Series mass selective detector. Melting points (uncorrected) were recorded on a Reichert hot-stage microscope.

Ru(SiMe₃)Cl(CO)(PPh₃)₂ (1a**).** HSiMe₃ was vigorously bubbled through a solution of Ru(Ph)Cl(CO)(PPh₃)₂ (0.200 g, 0.263 mmol) in dry toluene (10 mL) for approximately 10 s, ensuring an atmosphere of HSiMe₃ was present before the Schlenk tube was sealed. This solution was heated for 15 min at 55 °C, affording a clear, yellow solution. The solvent was removed *in vacuo*, and recrystallization of the residue from dichloromethane/ethanol yielded yellow crystals of **1a** (0.141 g, 71%), mp 160–161 °C. Anal. Calcd for C₄₀H₃₉ClO₂RuSi: C, 63.02, H, 5.16. Found: C, 63.04, H, 5.16. ¹H NMR (CDCl₃; δ): 7.64–7.33 (m, 30H, PPh₃); 0.22 (s, 9H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 200.3 (t, CO, ²J_{CP} = 13.9 Hz); 134.6 (*t'*, PPh₃ *meta*, ^{3,5}J_{CP} = 11.0 Hz); 132.7 (*t'*, PPh₃ *ipso*, ^{1,3}J_{CP} = 42.0 Hz); 130.0 (s, PPh₃ *para*); 128.1 (*t'*, PPh₃ *ortho*, ^{2,4}J_{CP} = 9.0 Hz); 10.9 (s, Si(CH₃)). ²⁹Si NMR (CH₂Cl₂/CDCl₃ 30%; δ): 55.74 (t, ²J_{SiP} = 10.9 Hz).

Ru(SiEt₃)Cl(CO)(PPh₃)₂ (1b**).** A solution of Ru(Ph)Cl(CO)(PPh₃)₂ (0.25 g, 0.33 mmol) and HSiEt₃ (0.30 g, 2.6 mmol) in toluene (15 mL) was heated for 3 h at 62 °C. The solvent was removed *in vacuo* from the resulting dark red solution, affording a dark red solid. This solid was dissolved in dichloromethane (3 mL) and placed on a silica gel column (12 × 2.5 cm). Elution with dichloromethane gave an intense yellow band as the first band eluted from the column. This was collected and evaporated to a low volume under reduced pressure, and ethanol was added slowly to effect crystallization. The yellow product was recrystallized from dichloromethane/ethanol to give pure **1b** (0.16 g, 63%), mp 146–148 °C. Anal. Calcd for C₄₃H₄₅ClO₂RuSi·0.5CH₂Cl₂: C, 61.70; H, 5.48. Found: C, 62.05; H, 6.04. ¹H NMR (CDCl₃; δ): 7.62–7.31 (m, 30H, PPh₃); 0.85 (q, 6H, Si(CH₂CH₃), ³J_{HH} = 7.5 Hz); 0.71 (t, 9H, Si(CH₂CH₃), ³J_{HH} = 7.5). ¹³C NMR (CDCl₃; δ): 200.9 (t, CO, ²J_{CP} = 13.9 Hz); 134.8 (*t'*, PPh₃ *meta*, ^{3,5}J_{CP} = 11.0 Hz); 132.9 (*t'*, PPh₃ *ipso*, ^{1,3}J_{CP} = 41.6 Hz); 129.9 (s, PPh₃ *para*); 128.0 (*t'*, PPh₃ *ortho*, ^{2,4}J_{CP} = 8.8 Hz); 14.8 (s, Si(CH₂CH₃)); 9.5 (s, Si(CH₂CH₃)). ²⁹Si NMR (CH₂Cl₂/CDCl₃ 30% δ): 71.70 (t, ²J_{SiP} = 11.7 Hz).

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Ru(SiPh₃)Cl(CO)(PPh₃)₂ (1c). Benzene (16 mL) was deoxygenated in a Schlenk tube, and to this were added Ru(SiMe₃)Cl(CO)(PPh₃)₂ (0.500 g, 0.656 mmol) in HSiPh₃ (1.67 g, 6.41 mmol). The Schlenk tube was evacuated, sealed, and then heated in an oil bath at 90 °C for 4 h. The yellow solution gradually turned red. The reaction vessel was evacuated several times during the course of the reaction to remove HSiMe₃ that had been formed. The volume of the solvent was reduced to approximately 2 mL *in vacuo*, and hexane (20 mL) was added to precipitate the product. Recrystallization from dichloromethane/ethanol gave pure **1c** (0.525 g, 84%), mp 149–152 °C. Anal. Calcd for C₅₅H₄₅ClO₂P₂RuSi-CH₂Cl₂: C, 65.08; H, 4.58. Found: C, 65.16; H, 4.79. ¹H NMR (CDCl₃; δ): 7.30–7.03 (m, 39H, PPh₃, SiPh₃); 6.84 (t, 6H, SiPh₃ *meta*). ¹³C NMR (CDCl₃; δ): 201.7 (t, CO, ²J_{CP} = 13.3 Hz); 141.1 (t, SiPh₃ *ipso*, ³J_{CP} = 1.5 Hz); 137.2 (s, SiPh₃); 134.8 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.4 Hz); 132.3 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.4 Hz); 129.7 (s, PPh₃ *para*); 127.8 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.8 Hz); 126.6 (s, SiPh₃). ²⁹Si NMR (CH₂Cl₂/CDCl₃ 30%; δ): 40.3 (t, ²J_{SiP} = 13.1 Hz).

Ru(SiMe₂OEt)Cl(CO)(PPh₃)₂ (1d). Ru(SiMe₂Cl)Cl(CO)(PPh₃)₂ (0.100 g, 0.128 mmol) was dissolved in dichloromethane (20 mL), ethanol (10 mL) was added, and the resulting solution was stirred at room temperature for 2 min. Reduction of the solvent volume under reduced pressure afforded large, yellow crystals of pure **1d** (0.076 g, 75%), mp 190–192 °C. Anal. Calcd for C₄₁H₄₁ClO₂P₂RuSi: C, 62.15; H, 5.22. Found: C, 61.65; H, 5.39. ¹H NMR (CDCl₃; δ): 7.68–7.25 (m, 30H, PPh₃); 3.28 (q, 2H, OCH₂CH₃), ³J_{HH} = 7.0 Hz); 0.77 (t, 3H, OCH₂CH₃, ³J_{HH} = 7.0 Hz); 0.27 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 200.2 (t, CO, ²J_{CP} = 13.7 Hz); 134.6 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.2 Hz); 132.8 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 42.8 Hz); 129.9 (s, PPh₃ *para*); 127.9 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.2 Hz); 58.5 (s, OCH₂CH₃); 17.9 (s, OCH₂CH₃); 8.7 (s, Si(CH₃)).

Ru(SiMe₂OH)Cl(CO)(PPh₃)₂ (1e). Ru(SiMe₂Cl)Cl(CO)(PPh₃)₂ (0.100 g, 0.128 mmol) was dissolved in tetrahydrofuran containing aqueous sodium hydroxide (0.2 M, 0.70 mL, 0.14 mmol), and the solution was stirred for 5 min at room temperature. The tetrahydrofuran was removed under reduced pressure, and dichloromethane (10 mL) was then added to extract the compound. The dichloromethane solution was dried (magnesium sulfate) and filtered. Hexane (10 mL) was added to effect crystallization of the product, which was recrystallized from dichloromethane/hexane to give pure **1e** (0.081 g, 83%), mp 160–162 °C. Anal. Calcd for C₃₉H₃₇ClO₂P₂RuSi: C, 61.29; H, 4.88. Found: C, 61.14; H, 5.05. ¹H NMR (CDCl₃; δ): 7.64–7.34 (m, 30H, PPh₃); 2.09 (s, 1H, SiOH); 0.30 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 199.8 (t, CO, ²J_{CP} = 13.4 Hz); 134.4 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.2 Hz); 132.4 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 42.8 Hz); 130.2 (s, PPh₃ *para*); 128.3 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.2 Hz); 11.2 (s, Si(CH₃)).

Ru(SiMe₂Cl)Cl(CO)(PPh₃)₂ (1f). HSiMe₂Cl (0.40 g, 4.0 mmol) was introduced to a solution of Ru(Ph)Cl(CO)(PPh₃)₂ (0.20 g, 0.26 mmol) in dry toluene (10 mL) in a Schlenk tube, which was then evacuated and sealed. The solution was heated at 55 °C for 30 min. The resulting yellow solution was evaporated to a small volume *in vacuo*, and then dry hexane (ca. 40 mL) was added to effect crystallization of pure yellow **1f** (0.19 g, 95%), mp 185–187 °C. Anal. Calcd for C₃₉H₃₆Cl₂O₂P₂RuSi: C, 59.85; H, 4.64. Found: C, 60.03; H, 4.76. ¹H NMR (CDCl₃; δ): 7.67–7.30 (m, 30H, PPh₃); 0.60 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 199.2 (t, CO, ²J_{CP} = 13.4 Hz); 134.6 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.0 Hz); 131.9 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.8 Hz); 130.2 (s, PPh₃ *para*); 128.2 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.4 Hz); 15.0 (s, Si(CH₃)).

Ru(CH=CHSiMe₃)Cl(CO)(PPh₃)₂ (2a).¹⁹ Ru(SiMe₃)Cl(CO)(PPh₃)₂ (0.500 g, 0.656 mmol) was dissolved in benzene (12 mL) in a Fisher-Porter bottle. The solution was stirred under ethyne pressure (0.8 atm) for 3½ h during which time

the solution turned brown. The solvent volume was reduced under reduced pressure and then chromatographed on a silica gel column (5 × 2 cm) using dichloromethane as eluent. The orange fraction was collected, ethanol was added, and the solvent volume was reduced to afford the orange product. Recrystallization from dichloromethane/ethanol gave pure **2a** (0.284 g, 55%), mp 163.5–164.5 °C. Anal. Calcd for C₄₂H₄₁ClO₂P₂RuSi: C, 63.99; H, 5.24. Found: C, 63.84; H, 5.30. ¹H NMR (CDCl₃; δ): 8.23 (dt, 1H, CH=CH, ³J_{HH} = 13.2 Hz, ³J_{HP} = 1.6 Hz); 7.62–7.31 (m, 30H, PPh₃); 5.13 (dt, 1H, CH=CH, ³J_{HH} = 13.1 Hz, ⁴J_{HP} = 2.0 Hz); –0.28 (s, 9H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 202.0 (t, CO, ²J_{CP} = 14.3 Hz); 162.9 (t, CH=CH, ²J_{CP} = 10.0 Hz); 137.9 (t, CH=CH, ³J_{CP} = 3.1 Hz); 134.1 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 12.0 Hz); 132.1 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.6 Hz); 130.0 (s, PPh₃ *para*); 128.1 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.6 Hz); –0.9 (s, Si(CH₃)).

Ru(CH=CHSiEt₃)Cl(CO)(PPh₃)₂ (2b). Ru(SiEt₃)Cl(CO)(PPh₃)₂ (0.195 g, 0.243 mmol) was dissolved in benzene (7 mL) in a Fisher-Porter bottle. The solution was stirred under ethyne pressure (0.8 atm) for 50 min during which time the solution became deep orange. The volume was reduced *in vacuo* and ethanol added to effect crystallization. Recrystallization from dichloromethane/ethanol gave pure **2b** (0.165 g, 82%), mp 161–163.5 °C. Anal. Calcd for C₄₅H₄₇ClO₂P₂RuSi: C, 65.09; H, 5.70. Found: C, 64.92; H, 5.74. ¹H NMR (CDCl₃; δ): 8.32 (dt, 1H, CH=CH, ³J_{HH} = 12.9 Hz, ³J_{HP} = 1.5 Hz); 7.61–7.30 (m, 30H, PPh₃); 5.22 (dt, 1H, CH=CH, ³J_{HH} = 12.9 Hz, ⁴J_{HP} = 2.0 Hz); 0.64 (t, 9H, Si(CH₂CH₃), ³J_{HH} = 7.8 Hz); 0.28 (q, 6H, Si(CH₂CH₃), ³J_{HH} = 7.8 Hz). ¹³C NMR (CDCl₃; δ): 202.1 (t, CO, ²J_{CP} = 14.4 Hz); 163.7 (t, CH=CH, ²J_{CP} = 9.7 Hz); 134.1 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.4 Hz); 132.2 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.4 Hz); 130.0 (s, PPh₃ *para*); 128.2 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.6 Hz); 7.2 (s, Si(CH₂CH₃)); 3.9 (s, Si(CH₂CH₃)). ²⁹Si NMR (CH₂Cl₂/CDCl₃ 30%; δ): –6.1 (s).

Ru(CH=CHSiPh₃)Cl(CO)(PPh₃)₂ (2c). Ru(SiPh₃)Cl(CO)(PPh₃)₂ (0.250 g, 0.264 mmol) was dissolved in benzene (5 mL) in a Fisher-Porter bottle. The bottle was pressurized with ethyne (0.8 atm) and the solution stirred for 1½ h during which time it turned brown. The volume was reduced to approximately 1 mL and placed on a silica gel column (1.5 × 4 cm). Dichloromethane was used as eluent. The yellow orange band was collected, the solvent volume reduced, and ethanol added to effect crystallization. Recrystallization from dichloromethane/ethanol gave pure **2c** (0.175 g, 68%), mp 194.5–196 °C. Anal. Calcd for C₅₇H₄₇ClO₂P₂RuSi: C, 70.25; H, 4.86. Found: C, 70.10; H, 5.10. ¹H NMR (CDCl₃; δ): 8.79 (d, 1H, CH=CH, ³J_{HH} = 13.2 Hz); 7.62–7.25 (m, 45H, PPh₃, SiPh₃); 5.90 (dt, 1H, CH=CH, ³J_{HH} = 13.2 Hz, ⁴J_{HP} = 2.1 Hz). ¹³C NMR (CDCl₃; δ): 202.3 (t, CO, ²J_{CP} = 14.5 Hz); 171.3 (t, CH=CH, ²J_{CP} = 10.0 Hz); 135.8 (s, SiPh₃); 135.6 (s, SiPh₃); 134.1 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 12.0 Hz); 131.9 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 44.2 Hz); 130.1 (s, PPh₃ *para*); 128.8 (s, SiPh₃); 128.2 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.8 Hz); 127.5 (s, SiPh₃).

Ru(CH=CHSiMe₂OEt)Cl(CO)(PPh₃)₂ (2d). Ru(SiMe₂OEt)Cl(CO)(PPh₃)₂ (0.370 g, 0.467 mmol) was dissolved in benzene (10 mL) in a Fisher-Porter bottle. The solution was stirred under ethyne pressure (0.8 atm) for 3¼ h, during which time the orange solution turned red. The volume was reduced *in vacuo*, and ethanol was added to precipitate the product. Recrystallization from dichloromethane/ethanol to give orange crystals of **2d** (0.198 g, 52%). Anal. Calcd for C₄₃H₄₃ClO₂P₂RuSi: C, 63.11; H, 5.30. Found: C, 63.00; H, 5.06. ¹H NMR (CDCl₃; δ): 8.58 (dt, 1H, CH=CH, ³J_{HH} = 13.4 Hz, ³J_{HP} = 1.6 Hz); 7.60–7.32 (m, 30H, PPh₃); 5.32 (dt, 1H, CH=CH, ³J_{HH} = 13.4 Hz, ⁴J_{HP} = 2.0 Hz); 3.21 (q, 2H, OCH₂CH₃, ³J_{HH} = 7.0 Hz); 0.95 (t, 3H, OCH₂CH₃, ³J_{HH} = 7.0 Hz); –0.15 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 202.0 (t, CO, ²J_{CP} = 14.2 Hz); 168.7 (t, CH=CH, ²J_{CP} = 9.8 Hz); 135.9 (s, CH=CH); 134.1 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.4 Hz); 132.0 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.8 Hz); 130.1 (s, PPh₃ *para*); 128.2 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.2 Hz); 57.7 (s, OCH₂CH₃); 18.4 (s, OCH₂CH₃); –1.8 (s, Si(CH₃)).

(19) Ru(CH=CHSiMe₃)Cl(CO)(PPh₃)₂ can be synthesized by insertion of (trimethylsilyl)ethyne into the Ru–H bond of RuHCl(CO)(PPh₃)₃; see: Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1987**, *326*, 413.

Ru(CH=CHSiMe₃)Cl(CO)₂(PPh₃)₂ (3a). Ru(CH=CHSiMe₃)Cl(CO)(PPh₃)₂ (0.130 g, 0.165 mmol) was dissolved in dichloromethane (5 mL), and CO was bubbled through the solution until it decolorized. The solvent volume was reduced under reduced pressure and ethanol was added to precipitate the white product. Recrystallization from dichloromethane/ethanol gave pure **3a** (0.082 g, 61%), mp 163–164 °C. Anal. Calcd for C₄₃H₄₁ClO₂P₂RuSi: C, 63.27; H, 5.06. Found: C, 63.10; H, 4.87. ¹H NMR (CDCl₃; δ): 8.00 (dt, 1H, CH=CH, ³J_{HH} = 19.8 Hz, ³J_{HP} = 4.0 Hz); 7.81–7.31 (m, 30H, PPh₃); 5.73 (dt, 1H, CH=CH, ³J_{HH} = 19.9 Hz, ⁴J_{HP} = 1.6 Hz); –0.32 (s, 9H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 197.6 (t, CO, ²J_{CP} = 11.4 Hz); 193.6 (t, CO, ²J_{CP} = 8.1 Hz); 175.0 (t, CH=CH, ²J_{CP} = 13.7 Hz); 143.9 (t, CH=CH, ³J_{CP} = 3.7 Hz); 134.1 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 10.2 Hz); 133.2 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 46.2 Hz); 129.9 (s, PPh₃ *para*); 127.9 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.6 Hz); –1.6 (s, Si(CH₃)).

Ru(CH=CHSiEt₃)Cl(CO)₂(PPh₃)₂ (3b). Ru(CH=CHSiEt₃)Cl(CO)(PPh₃)₂ (0.105 g, 0.126 mmol) was dissolved in dichloromethane (5 mL). CO was bubbled through the solution until the orange color was discharged. The volume was reduced under low pressure and ethanol added to effect crystallization of the colorless product. Recrystallization from dichloromethane/ethanol gave pure **3b** (0.100 g, 92%), mp 161.5–163 °C. Anal. Calcd for C₄₆H₄₇ClO₂P₂RuSi: C, 64.36; H, 5.52. Found: C, 64.23; H, 5.48. ¹H NMR (CDCl₃; δ): 8.23 (dt, 1H, CH=CH, ³J_{HH} = 20.1 Hz, ³J_{HP} = 4.0 Hz); 7.86–7.30 (m, 30H, PPh₃); 5.86 (dt, 1H, CH=CH, ³J_{HH} = 20.1 Hz, ⁴J_{HP} = 1.6 Hz); 0.68 (t, 9H, Si(CH₂CH₃), ³J_{HH} = 7.9 Hz); 0.18 (q, 6H, Si(CH₂CH₃), ³J_{HH} = 7.8 Hz). ¹³C NMR (CDCl₃; δ): 197.5 (t, CO, ²J_{CP} = 11.4 Hz); 193.4 (t, CO, ²J_{CP} = 8.4 Hz); 176.0 (t, CH=CH, ²J_{CP} = 13.6 Hz); 141.5 (t, CH=CH, ³J_{CP} = 3.7 Hz); 134.0 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 10.6 Hz); 133.4 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 45.8 Hz); 130.0 (s, PPh₃ *para*); 128.0 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.8 Hz); 7.5 (s, Si(CH₂CH₃)); 3.4 (s, Si(CH₂CH₃)). ²⁹Si NMR (CH₂Cl₂/CDCl₃ 30%; δ): –6.1 (s).

Ru(CH=CHSiMe₂OEt)Cl(CO)₂(PPh₃)₂ (3d). Ru(CH=CHSiMe₂OEt)Cl(CO)(PPh₃)₂ (0.066 g, 0.081 mmol) was dissolved in dichloromethane (5 mL). CO was bubbled through the solution until the orange color was discharged. On reduction of the volume and addition of ethanol the white product precipitated. Recrystallization from dichloromethane/ethanol gave pure **3d** (0.061 g, 89%), mp 120–122 °C. Anal. Calcd for C₄₄H₄₃ClO₃P₂RuSi: C, 62.44; H, 5.12. Found: C, 62.26; H, 5.03. ¹H NMR (CDCl₃; δ): 8.30 (dt, 1H, CH=CH, ³J_{HH} = 20.3 Hz, ³J_{HP} = 3.6 Hz); 7.84–7.30 (m, 30H, PPh₃); 5.92 (dt, 1H, CH=CH, ³J_{HH} = 20.2 Hz, ⁴J_{HP} = 1.6 Hz); 3.12 (q, 2H, OCH₂CH₃, ³J_{HH} = 7.0 Hz); 0.97 (t, 3H, OCH₂CH₃, ³J_{HH} = 7.0 Hz); –0.27 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 197.2 (t, CO, ²J_{CP} = 11.3 Hz); 193.6 (t, CO, ²J_{CP} = 8.5 Hz); 180.9 (t, CH=CH, ²J_{CP} = 13.6 Hz); 141.7 (t, CH=CH, ³J_{CP} = 3.7 Hz); 134.0 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 10.0 Hz); 133.3 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 46.6 Hz); 130.1 (s, PPh₃ *para*); 128.1 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.8 Hz); 57.7 (s, OCH₂CH₃); 18.6 (s, OCH₂CH₃); –2.6 (s, Si(CH₃)).

Ru(CH=SHSiMe₃)Cl(CO)CN-*p*-tolyl)(PPh₃)₂ (4a). Ru(CH=SHSiMe₃)Cl(CO)(PPh₃)₂ (0.100 g, 0.127 mmol) was dissolved in dichloromethane (5 mL), and to this was added a solution of *p*-tolyl isocyanide (0.016 g, 0.140 mmol) in dichloromethane (3 mL). The orange solution decolorized, and on addition of ethanol and reduction of the solvent volume a white product precipitated. Recrystallization from dichloromethane/ethanol gave pure **4a** (0.061 g, 52%), mp 159–163 °C. Anal. Calcd for C₅₀H₄₈ClN₂O₂P₂RuSi: C, 66.32; H, 5.34; N, 1.55. Found: C, 66.35; H, 5.24; N, 1.50. ¹H NMR (CDCl₃; δ): 8.30 (dt, 1H, CH=CH, ³J_{HH} = 20.1 Hz, ³J_{HP} = 3.4 Hz); 7.88–7.30 (m, 30H, PPh₃); 6.98 (d, 2H, CNC₆H₄CH₃, ³J_{HH} = 8.3 Hz); 6.40 (d, 2H, CNC₆H₄CH₃, ³J_{HH} = 8.4 Hz); 5.69 (dt, 1H, CH=CH, ³J_{HH} = 20.2 Hz, ⁴J_{HP} = 1.6 Hz); 2.31 (s, 3H, CNC₆H₄CH₃); –0.32 (s, 9H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 200.3 (t, CO, ²J_{CP} = 12.7 Hz); 178.7 (t, CH=CH, ²J_{CP} = 13.6 Hz); 142.2 (t, CH=CH, ³J_{CP} = 3.8 Hz); 138.8 (s, CNC₆H₄CH₃); 134.3 (t', PPh₃

meta, ^{3,5}J_{CP} = 10.6 Hz); 134.2 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.4 Hz); 129.5 (s, CNC₆H₄CH₃); 129.3 (s, PPh₃ *para*); 127.6 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.6 Hz); 125.5 (s, CNC₆H₄CH₃); 21.3 (s, CNC₆H₄CH₃); –1.4 (s, Si(CH₃)).

Ru(CH=CHSiMe₃)(η²-O₂CCH₃)(CO)(PPh₃)₂ (5a). Ru(CH=CHSiMe₃)Cl(CO)(PPh₃)₂ (0.100 g, 0.127 mmol) was dissolved in dichloromethane (5 mL). A solution of sodium acetate (0.050 g, 0.61 mmol) in water (1 mL) and ethanol (10 mL) was added, and the red solution turned colorless. On reduction of the solvent volume the white product precipitated. Recrystallization from dichloromethane/ethanol gave pure **5a** (0.090 g, 87%), mp 188–192 °C. Anal. Calcd for C₄₄H₄₄O₃P₂RuSi: C, 65.09; H, 5.46. Found: C, 64.76; H, 5.30. ¹H NMR (CDCl₃; δ): 7.73 (dt, 1H, CH=CH, ³J_{HH} = 16.8 Hz, ³J_{HP} = 2.2 Hz); 7.55–7.38 (m, 30H, PPh₃); 5.59 (dt, 1H, CH=CH, ³J_{HH} = 16.9 Hz, ⁴J_{HP} = 1.6 Hz); 0.61 (s, 3H, O₂CCH₃); –0.52 (s, 9H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 206.2 (t, CO, ²J_{CP} = 15.7 Hz); 182.4 (s, O₂CCH₃); 170.4 (t, CH=CH, ²J_{CP} = 10.3 Hz); 134.3 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.4 Hz); 131.5 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.0 Hz); 129.7 (s, PPh₃ *para*); 128.0 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 10.0 Hz); 22.1 (s, O₂CCH₃); –1.1 (s, Si(CH₃)).

Ru(CH=CHSiMe₂OH)Cl(CO)(PPh₃)₂ (6e). Ru(SiMe₂OH)Cl(CO)(PPh₃)₂ (0.600 g, 0.785 mmol) was dissolved in benzene (10 mL) in a Fisher-Porter bottle. The solution was stirred under ethyne pressure (0.8 atm) for 5 h. The yellow color of the starting material was gradually lost, and a white precipitate appeared. The volume of benzene was reduced *in vacuo* to approximately 5 mL, and ethanol (10 mL) was added to precipitate the remaining product (0.550 g, 89%), mp 172–174 °C. Anal. Calcd for C₄₁H₃₉ClO₂P₂RuSi: C, 62.31; H, 4.97. Found: C, 62.45; H, 4.98. ¹H NMR (CDCl₃; δ): 7.70–7.67 (m, 10H, PPh₃); 7.60 (dt, 1H, CH=CH, ³J_{HH} = 12.6 Hz, ³J_{HP} = 1.6 Hz); 7.51–7.33 (m, 20H, PPh₃); 5.55 (oddt, 1H, CH=CH, ³J_{HH} = 12.6 Hz, ⁴J_{HP} = 2.3 Hz); 2.61 (d, 1H, SiOH, ⁴J_{HH} = 2.3 Hz); –0.75 (s, 6H, Si(CH₃)).

[Ru(CH=CHSiMe₂OH)(CO)(NCMe)(PPh₃)₂]ClO₄ (7e).

Ru(CH=CHSiMe₂OH)Cl(CO)(PPh₃)₂ (0.555 g, 0.702 mmol) was suspended in dichloromethane (20 mL) and acetonitrile (0.180 g, 4.39 mmol). A solution of AgClO₄ (0.153 g, 0.738 mmol) in ethanol (10 mL) was added. The solution was stirred for 15 min during which time the initial suspension of starting material was replaced by a precipitate of AgCl. After filtration through Celite twice, the volume was reduced under reduced pressure and ethanol added to effect crystallization of the product (0.545 g, 91%), mp 154–155.5 °C. Anal. Calcd for C₄₃H₄₂ClNO₆P₂RuSi: C, 57.68; H, 4.73; N, 1.56. Found: C, 57.44; H, 4.87; N, 1.67. ¹H NMR (CDCl₃; δ): 7.95 (dt, 1H, CH=CH, ³J_{HH} = 13.0 Hz, ³J_{HP} = 2.0 Hz); 7.56–7.44 (m, 30H, PPh₃); 5.87 (oddt, 1H, CH=CH, ³J_{HH} = 13.0 Hz, ⁴J_{HP} = 2.2 Hz); 4.99 (d, 1H, SiOH, ⁴J_{HH} = 2.4 Hz); 1.70 (s, 3H, NCCH₃); –0.86 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃; δ): 202.9 (t, CO, ²J_{CP} = 17.5 Hz); 177.9 (t, CH=CH, ²J_{CP} = 9.9 Hz); 134.3 (t', PPh₃ *meta*, ^{3,5}J_{CP} = 11.2 Hz); 130.7 (t', PPh₃ *ipso*, ^{1,3}J_{CP} = 43.0 Hz); 130.5 (s, PPh₃ *para*); 128.6 (t', PPh₃ *ortho*, ^{2,4}J_{CP} = 9.4 Hz); 2.8 (s, NCCH₃); –0.4 (s, Si(CH₃)).

[Ru(CH=CHSiMe₂OH)(CO)₂(PPh₃)₂]ClO₄ (8e).

[Ru(CH=CHSiMe₂OH)(CO)(NCMe)(PPh₃)₂]ClO₄ (0.410 g, 0.458 mmol) was dissolved in dichloromethane (20 mL) in a Fisher-Porter bottle. The solution was placed under CO pressure (2 atm) and stirred for 30 min. The solvent volume was reduced, and ethanol was added to effect precipitation. Recrystallization from dichloromethane/ethanol gave pure **8e** (0.315 g, 78%), mp 138–140 °C. Anal. Calcd for C₄₂H₃₉ClO₇P₂RuSi·0.25CH₂Cl₂: C, 56.16; H, 4.41. Found: C, 56.09; H, 4.67. ¹H NMR (CDCl₃; δ): 7.69 (dt, 1H, CH=CH, ³J_{HH} = 13.6 Hz, ³J_{HP} = 2.3 Hz); 7.51–7.40 (m, 30H, PPh₃); 6.19 (d, 1H, CH=CH, ³J_{HH} = 13.6 Hz); 5.60 (s, 1H, SiOH); 0.84 (s, 6H, Si(CH₃)).

[Ru(CH=CHSiMe₂OH)(CO)(CN-*p*-tolyl)(PPh₃)₂]ClO₄

(9e). $[\text{Ru}(\text{CH}=\text{CHSiMe}_2\text{OH})(\text{CO})(\text{NCMe})(\text{PPh}_3)_2]\text{ClO}_4$ (0.400 g, 0.447 mmol) was dissolved in dichloromethane (30 mL). A solution of *p*-tolyl isocyanide (0.065 g, 0.554 mmol) in dichloromethane (5 mL) was added, and the reaction mixture was stirred for 5 min. Ethanol was added and the solvent volume reduced under low pressure to effect crystallization and washed well with ethanol, water, and then ethanol again. Recrystallization from dichloromethane/ethanol gave pure **9e** (0.296 g, 68%), mp 168–170 °C. Anal. Calcd for $\text{C}_{49}\text{H}_{46}\text{ClNO}_6\text{P}_2\text{RuSi}\cdot 0.25\text{CH}_2\text{Cl}_2$: C, 58.64; H, 4.67; N, 1.38. Found: C, 58.60; H, 4.60; N, 1.32. ^1H NMR (CDCl_3 ; δ): 8.06 (dt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 14.1$ Hz, $^3J_{\text{HP}} = 2.1$ Hz); 7.69–7.16 (m, 30H, PPh_3); 7.00 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^3J_{\text{HH}} = 8.2$ Hz); 6.72 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^3J_{\text{HH}} = 8.4$ Hz); 6.15 (ddt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 14.1$ Hz, $^4J_{\text{HH}} = 2.1$ Hz, $^4J_{\text{HP}} = 2.2$ Hz); 5.24 (d, 1H, SiOH , $^4J_{\text{HH}} = 2.1$ Hz); 2.28 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); –0.83 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 ; δ): 203.0 (t, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^2J_{\text{CP}} = 15.7$ Hz); 181.3 (t, CO , $^2J_{\text{CP}} = 11.5$ Hz); 177.9 (t, $\text{CH}=\text{CH}$, $^2J_{\text{CP}} = 10.8$ Hz); 139.9 (s, $\text{CH}=\text{CH}$); 134.3 (t', PPh_3 meta, $^3.5J_{\text{CP}} = 11.0$ Hz); 131.1 (t', PPh_3 ipso, $^1.3J_{\text{CP}} = 45.0$ Hz); 130.6 (s, PPh_3 para); 130.3 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 129.6 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 128.7 (t', PPh_3 ortho, $^2.4J_{\text{CP}} = 9.0$ Hz); 125.9 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 21.4 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); –0.4 (s, $\text{Si}(\text{CH}_3)_2$).

Ru(CH=CHSiMe₂O)(CO)₂(PPh₃)₂ (10e). $[\text{Ru}(\text{CH}=\text{CHSiMe}_2\text{OH})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ (0.200 g, 0.227 mmol) was dissolved in dichloromethane (20 mL). KOH (0.050 g, 0.909 mmol) in ethanol (5 mL) was added. The solution turned very pale yellow and went slightly cloudy. The volume was reduced under low pressure, and further ethanol was added to effect crystallization. Recrystallization from dichloromethane/ethanol gave pure **10e** (0.145 g, 82%), mp 161–162 °C. Anal. Calcd for $\text{C}_{42}\text{H}_{38}\text{O}_3\text{P}_2\text{RuSi}\cdot 0.25\text{CH}_2\text{Cl}_2$: C, 63.19; H, 4.83. Found: C, 63.11; H, 4.88. ^1H NMR (CDCl_3 ; δ): 7.93 (dt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 12.0$ Hz, $^3J_{\text{HP}} = 2.6$ Hz); 7.60–7.34 (m, 30H, PPh_3); 6.03 (dt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 12.4$ Hz, $^4J_{\text{HP}} = 1.6$ Hz); –0.86 (s, 6H, $\text{Si}(\text{CH}_3)_2$).

Ru(CH=CHSiMe₂O)(CO)(CN-*p*-tolyl)(PPh₃)₂ (11e). $[\text{Ru}(\text{CH}=\text{CHSiMe}_2\text{OH})(\text{CO})(\text{CN-}i\text{-}p\text{-tolyl})(\text{PPh}_3)_2]\text{ClO}_4$ (0.163 g, 0.168 mmol) was dissolved in dichloromethane (20 mL). To this was added a solution of KOH (0.017 g, 0.304 mmol) in ethanol (5 mL). There was immediate formation of a small amount of fine white precipitate. The solvent volume was reduced under low pressure and further ethanol added to effect crystallization. The product was collected by filtration and washed well with water. Recrystallization from dichloromethane/ethanol gave pure **11e** (0.120 g, 82%), mp 163–165 °C. Anal. Calcd for $\text{C}_{49}\text{H}_{45}\text{NO}_2\text{P}_2\text{RuSi}$: C, 67.57; H, 5.21; N, 1.61. Found: C, 67.09; H, 5.06; N, 1.56. ^1H NMR (CDCl_3 ; δ): 8.08 (dt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 12.8$ Hz, $^3J_{\text{HP}} = 2.3$ Hz); 7.67–7.33 (m, 30H, PPh_3); 6.93 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^3J_{\text{HH}} = 8.2$ Hz); 6.33 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^3J_{\text{HH}} = 8.2$ Hz); 6.13 (dt, 1H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 12.8$ Hz, $^4J_{\text{HP}} = 1.8$ Hz); 2.28 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); –0.85 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3 ; δ): 202.0 (t, $\text{CNC}_6\text{H}_4\text{CH}_3$, $^2J_{\text{CP}} = 15.6$ Hz); 178.9 (t, CO , $^2J_{\text{CP}} = 11.5$ Hz); 161.6 (s, $\text{CH}=\text{CH}$); 140.1 (s, $\text{CH}=\text{CH}$); 138.7 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 134.9 (s, PPh_3 meta); 133.5 (t', PPh_3 ipso, $^1.3J_{\text{CP}} = 41.2$ Hz); 129.5 (s, PPh_3 para); 127.6 (s, PPh_3 ortho); 125.4 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 21.2 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 2.73 (s, $\text{Si}(\text{CH}_3)_2$).

Hydrosilylation of Ethyne. $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (0.030 g, 0.037 mmol), HSiEt_3 (0.434 g, 3.73 mmol), and benzene (0.5 mL) were placed in a Fisher-Porter bottle. The solution was deoxygenated by several cycles of freeze–evacuate–thaw. The bottle was pressurized with ethyne to 0.8 atm and heated in an oil bath at 65 °C for 24 h. The bottle was repressurized several times during the course of the reaction to maintain the pressure of ethyne. The solution was cooled and separated from the catalyst by chromatography on a silica gel column (1 × 4 cm) using hexane as eluent. The identities of the products

were determined by ^1H NMR and GC/MS.² In calculation of the product yields, assumptions were that no losses occurred during isolation and that all the products formed were detected.

Vinyltriethylsilane. ^1H NMR (ppm): 6.06 (m, 2H, $\text{H}_2\text{C}=\text{C}$); 5.70 (dd, 1H, $\text{SiCH}=\text{C}$, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HH}} = 1.2$ Hz); 0.99 (m, 9H); 0.62 (m, 6H). MS: m/z 113 (79), 85 (100), 57 (32).

Triethylsilane. MS: m/z 116 (M^+ , 7), 87 (100), 59 (97).

Hexaethyldisiloxane. MS: m/z 217 (100), 189 (85), 161 (48), 105 (20), 80 (24), 66 (25).

Hydrosilylation of Phenylethyne. $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (0.030 g, 0.037 mmol), HSiEt_3 (0.433 g, 3.72 mmol), and phenylethyne (0.456 g, 4.46 mmol) were placed in a carbonylation tube. The solution was deoxygenated by several cycles of freeze–evacuate–thaw. The solution was heated in an oil bath at 65 °C for 24 h during which time it turned red/brown. The solution was cooled and separated from the catalyst on a silica gel column (1 × 5 cm) using hexane as eluent. The identities of the products were determined by ^1H NMR and GC/MS.² In the calculation of the product yields, assumptions were that no losses occurred during isolation and that all the products formed were detected.

cis-1-Phenyl-2-(triethylsilyl)ethene. ^1H NMR (vinyl region, ppm): δ 5.80 (d, $\text{SiCH}=\text{C}$, $^3J_{\text{HH}} = 15.2$ Hz). MS: m/z 218 (M^+ , 13), 189 (100), 161 (65), 133 (38), 131 (49), 105 (25), 59 (33).

trans-1-Phenyl-2-(triethylsilyl)ethene. ^1H NMR (vinyl region, ppm): δ 6.96 (d, 1H, $\text{PhCH}=\text{C}$, $^3J_{\text{HH}} = 19.2$ Hz); 6.46 (d, 1H, $\text{SiCH}=\text{C}$, $^3J_{\text{HH}} = 19.2$ Hz). MS: m/z 218 (M^+ , 6), 189 (100), 161 (44), 133 (30), 131 (45), 105 (24), 59 (24).

(Phenylethynyl)triethylsilane. MS: m/z 216 (M^+ , 7), 187 (100), 159 (82), 131 (94), 105 (27).

Hexaethyldisiloxane. MS: m/z 217 (100), 189 (85), 161 (48), 105 (20), 80 (24), 66 (25).

Triethylsilane. MS: m/z 116 (M^+ , 7), 87 (100), 59 (97).

X-ray Diffraction Study of 3d and 9e. Suitable crystals of both compounds were grown from dichloromethane/ethanol solutions. Crystal data and data collection parameters are given in Table 2. Unit cell dimensions were derived from least-squares fits of the four-circle coordinates of 25 reflections. The data were corrected for Lorentz, polarization, and absorption²⁰ using locally written programs.

The structures were solved by Patterson and difference Fourier techniques. Programs used were SHELXS²¹ and SHELXL-93.²² Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached. The terminal carbon of the ethoxy group in **3d** is disordered and has been modeled by two half-weighted atoms. There is a disordered molecule of dichloromethane in **9e**, and this has been modeled by partially weighted chlorine atoms bonded to a common carbon atom. Atomic coordinates for **3d** and **9e** are given in Tables 3 and 5 and selected bond lengths and angles for **3d** and **9e** in Tables 4 and 6, respectively.

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Supporting Information Available: Tables of bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and *U* values for **3d** and **9e** (16 pages). Ordering information is given on any current masthead page. OM9509711

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