Mechanistic Study of Ruthenium-Catalyzed Hydrosilation of 1-(Trimethylsilyl)-1-buten-3-yne

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Abstract: Catalytic hydrosilation of 1-(trimethylsilyl)-1-buten-3-yne (**1**) with three kinds of hydrosilanes ($HSiMePh_2$, $HSiMe_2Ph$, and $HSiEt_3$) in $CDCl_3$ at 30 °C in the presence of a catalytic amount of $RuHCl(CO)(PPh_3)_3$ (**2**) gave five types of reaction products: (*1E*,*3E*)-$CH(SiR_3)$═$CHCH$═$CHSiMe_3$ (**3**), R_3SiCH_2-CH═$CHCH_2SiMe_3$ (**4**), R_3SiCH═C═$CHCH_2SiMe_3$ (**5**), (*1Z*,*3E*)-$CH(SiR_3)$═$CHCH$═$CHSiMe_3$ (**6**), and R_3SiC≡CCH═$CHSiMe_3$ (**7**). Detailed investigations on the stoichiometric reactions of intermediate ruthenium species provided definitive evidence for the catalytic mechanism comprised of two catalytic cycles, the Chalk−Harrod cycle **A** and the modified Chalk−Harrod cycle **C**, and their interconnecting processes **B** and **D**. Product **3** is formed by the insertion of **1** into the Ru−H bond of **2** followed by the reaction of the resulting terminal dienyl complex $Ru(CH$═$CHCH$═$CHSiMe_3)Cl(CO)(PPh_3)_2$ (**8**) with hydrosilane. The latter process regenerates **2** and the sequence of reactions proceeds catalytically (cycle **A**). The reaction of **8** with hydrosilane is accompanied by a side reaction giving $Ru(SiR_3)Cl(CO)(PPh_3)_2$ (**9**) and CH_2═$CHCH$═$CHSiMe_3$ (**10**), and the latter is further converted to **4** by hydrosilation (process **B**). Silyl complex **9** thus generated in the system is the key intermediate for catalytic cycle **C**. Thus the insertion of **1** into the Ru−SiR_3 bond of **9** via a formal *trans*-addition process forms an internal dienylruthenium complex $Ru[C(=CHSiR_3)CH$═$CHSiMe_3]Cl(CO)(PPh_3)_2$ (**11**), which reacts with hydrosilane to give **5** and **6** and to regenerate **9**. A part of **11** also undergoes β-hydrogen elimination to give a dehydrogenative silation product **8** and hydride complex **2**. Complex **2** thus formed resumes catalytic cycle **A** (process **D**). The catalytic intermediates **8**, **9**, and **11** were identified by NMR spectroscopy and/or elemental analysis. Factors controlling the catalytic cycles are discussed on the basis of the experimental observations.

Introduction

Transition metal-catalyzed hydrosilation of unsaturated hydrocarbons such as alkenes and alkynes is a versatile synthetic means of organosilicon compounds.[1] One of the most widely accepted mechanisms for this catalysis was first proposed by Chalk and Harrod in 1965 for the platinum-catalyzed hydrosilation of alkenes.[2] The key feature of the Chalk−Harrod mechanism is the insertion of a coordinated alkene (or alkyne) into a metal−hydrogen bond followed by reductive elimination of alkyl (or alkenyl) and silyl ligands. Subsequently, the other type of catalytic process, the so-called modified Chalk−Harrod mechanism, was proposed.[3] In this mechanism, a coordinated alkene (or alkyne) inserts into a metal−silicon bond instead of a metal−hydrogen bond, and the successive reductive elimination of the resulting β-silylalkyl (or β-silylalkenyl) ligand and a hydrido ligand leads to the hydrosilation product. A basis of the modified Chalk−Harrod mechanism is the formation of alkenylsilanes in addition to alkylsilanes in the catalytic hydrosilation of alkenes. That is, the formation of alkenylsilane is best accounted for by β-hydrogen elimination of a β-silylalkyl metal species formed by the insertion of alkene into a metal−silicon bond. Recently, the modified Chalk−Harrod mechanism was confirmed for several reaction systems with ruthenium, rhodium, iridium, and palladium catalysts by the studies of intermediate silylmetal complexes.[4,5]

An interesting question related to the mechanisms of catalytic hydrosilation is how to select one of the two possible mechanisms described above. There are evidences for the insertion into a metal−hydrogen bond to be faster than the insertion into a metal−silicon bond. However, even in such situations,

(1) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1479.

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(4) (a) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906. (b) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793. (c) Hofmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, *490*, 51. (d) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (e) Duckett, S. B.; Pertsz, R. N. *Organometallics* **1992**, *11*, 90. (f) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415.

(5) For other studies on the mechanism of catalytic hydrosilation, see: (a) Brunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21. (b) Recatto, C. A. *Aldrichim. Acta* **1995**, *28*, 85. (c) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377. (d) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (e) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1415.

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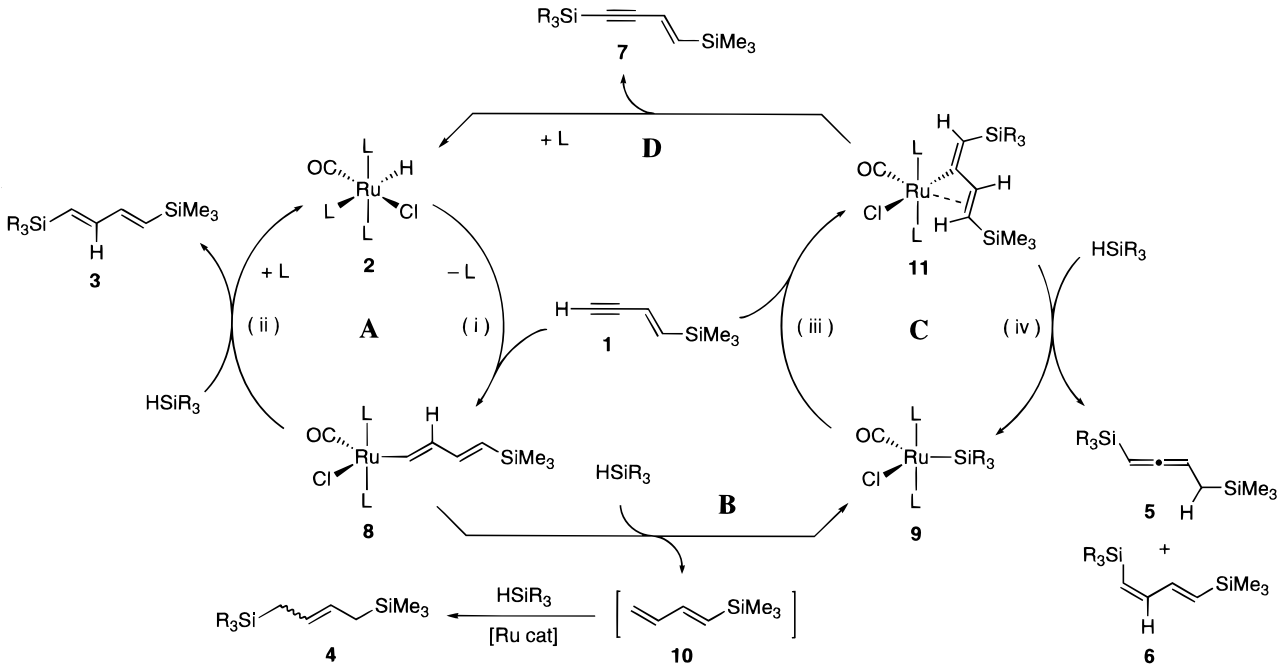
Scheme 1

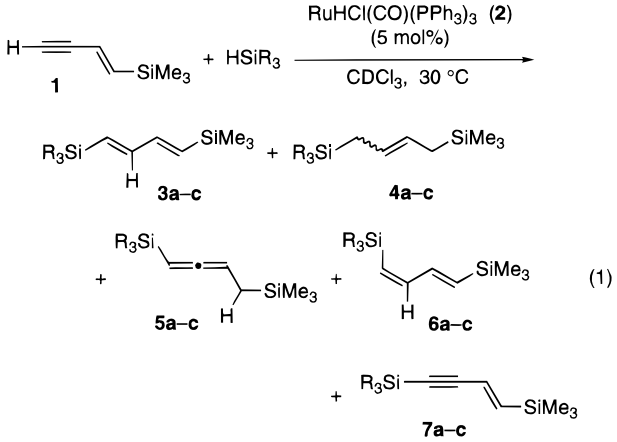


catalytic reactions frequently proceed via the modified Chalk−Harrod mechanism.[4d] The other possibility to control the catalytic mechanism may be found in the product forming steps. Thus the C−H reductive elimination that is assumed at the final stage of the modified Chalk−Harrod mechanism is nowadays a very common and facile process,[6] while definitive examples of the C−Si reductive elimination as the product forming step of the Chalk−Harrod mechanism are still limited.[7] Although it has been recently shown that the C−Si reductive elimination can compete with the C−H reductive elimination in $Ir(CH_3)(H)(SiR_3)(PMe_3)_3$ type complexes, its relevance to actual catalytic reactions has not been investigated.[7e]

This paper reports our mechanistic study of hydrosilation of 1-(trimethylsilyl)-1-buten-3-yne (**1**) catalyzed by $RuHCl(CO)(PPh_3)_3$ (**2**).[8] We found that this catalytic reaction is a rare example where the ruthenium species responsible for most of the catalysis can be identified. Furthermore, as can be seen from Scheme 1, which is the summary of the present study, the catalytic reaction was found to include an almost complete array of the catalytic processes that are expected in the catalytic hydrosilation: the Chalk−Harrod and modified Chalk−Harrod cycles (**A** and **C**, respectively) and the processes connecting these two cycles (**B** and **D**). We describe below the evidence for the mechanisms in Scheme 1 and discuss the factors controlling the hydrosilation processes.

Results and Discussion

1. Hydrosilation of 1 Catalyzed by 2. Reactions of 1-(trimethylsilyl)-1-buten-3-yne (**1**) with three kinds of hydrosilanes ($HSiR_3$ = $HSiMePh_2$, $HSiMe_2Ph$, $HSiEt_3$) were examined in $CDCl_3$ in the presence of a catalytic amount of $RuHCl(CO)(PPh_3)_3$ (**2**; 5 mol %) at 30 °C (eq 1). The reactions gave five



SiR_3 = $SiMePh_2$ (**a**), $SiMe_2Ph$ (**b**), $SiEt_3$ (**c**)

kinds of products **3**−**7**. Dienylsilanes **3** and **6** are the *cis*- and *trans*-addition products of hydrosilane across the triple bond of **1**, respectively. Allylsilane **4** is the product formed by hydrogenation followed by hydrosilation of **1**. Allenylsilane **5** is the 1,4-adduct of hydrosilane across the enyne skeleton of **1**. Bis(silyl)butenyne **7** is the dehydrogenative silation product of **1**. All compounds thus obtained were not isolated, but their structures were successfully confirmed by NMR spectroscopy and GC-mass spectrometry except for **4**, for which the geometry

(6) (a) Yamamoto, A. *Organotransition Metal Chemistry, Fundamental Concepts and Applications;* Wiley-Interscience: New York, 1986. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987.

(7) (a) Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246. (b) Akita, M.; Hua, R.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1996**, *15*, 4162. (c) Okazaki, M.; Tobita, H.; Ogino, H. *Organometallics* **1996**, *15*, 2790. (d) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477. (e) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456. (f) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844. (g) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419. (h) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 2309. (i) Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165. (j) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

(8) For examples of hydrosilation of conjugated enynes, see: (a) Maruyama, Y.; Yoshiuchi, K.; Ozawa, F.; Wakatsuki, Y. *Chem. Lett.* **1997**, 623. (b) Kusumoto, T.; Ando, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1280. (c) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1992**, *11*, 3004. (d) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277. (e) Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1985**, 1405. (f) Licchelli, M.; Greco, A. *Tetrahedron Lett.* **1987**, *28*, 3719. (g) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1968**, *90*, 5694.

Table 1. Catalytic Hydrosilation of 1-(Trimethylsilyl)-1-buten-3-yne (**1**) with $HSiR_3$ in the Presence of 5 mol % of $RuHCl(CO)(PPh_3)_3$ (**2**)[a]

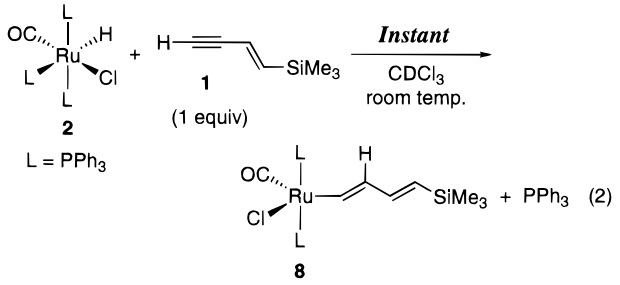
entry	$HSiR_3$	reaction time[b] (h)	product ratio[c] **3**	**4**	**5**	**6**	**7**	(**5** + **6**)
1	$HSiMePh_2$	64	6	4	81	6	3	87
2	$HSiMe_2Ph$	22	14	8	72	4	2	76
3	$HSiEt_3$	73	28	15	29	3	25	32

[a] All reactions were run at 30 °C in $CDCl_3$ with **1** and $HSiR_3$ in a 1:1 ratio. [b] The time required for 100% conversion of **1**. [c] Determined by ^1H NMR spectroscopy and GLC.

around the C=C bond could not be determined (see Experimental Section).

Table 1 summarizes the results. The reaction rate and the product distribution varied with the sort of hydrosilane employed. $HSiMe_2Ph$ exhibited the highest reactivity. $HSiMePh_2$ and $HSiMe_2Ph$ provided allenylsilanes **5a** and **5b** in good selectivities (entries 1 and 2). On the other hand, the reaction with $HSiEt_3$ showed almost no selectivity (entry 3). In the following sections, we examine the formation processes of **3**−**7** in stoichiometric systems.

2. Formation of 3 and 4. Hydride complex **2** was inactive toward hydrosilanes but readily reacted with **1** (1 equiv) in $CDCl_3$ at room temperature (eq 2). When the reaction was

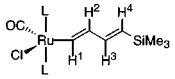
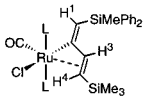
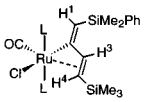
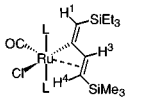
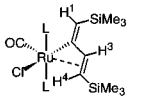


(2)

examined by $^{31}P\{^1H\}$ NMR spectroscopy, the signals of **2** [δ 39.6 (br, 2P), 13.5 (br, 1P)] instantly disappeared and two new singlets appeared at δ 31.2 and −4.7 in a 2:1 ratio. The latter singlet was assigned to free PPh_3 on the basis of its chemical shift. On the other hand, the former singlet was assigned to dienyl complex **8** based on the following NMR evidence.

Table 2 lists the characteristic NMR data of **8**, together with the data of the other dienylruthenium complexes prepared in this study. The ^1H NMR signal of H^1 bound to the C^1-carbon of the dienyl ligand was observed at δ 7.99 as a doublet of triplets due to the relatively large coupling to H^2 on the C^2-carbon ($^3J_{H-H}$ = 12.4 Hz) and to the small couplings to two phosphorus nuclei on ruthenium ($^3J_{H-P}$ = 2.1 Hz). The appearance of only one singlet in the $^{31}P\{^1H\}$ NMR spectrum as well as the small $^3J_{H-P}$ value on H^1 suggested the trigonal bipyramidal structure of **8** having two PPh_3 ligands at the apical positions and the dienyl ligand on the trigonal plane.[9] The geometry around the C^1=C^2 bond was assigned as trans on the basis of the H^1−H^2 coupling constant (12.4 Hz).[10] The other features in the ^1H NMR spectrum were fully consistent with the structure depicted in Table 2. Complex **8** was stable in the reaction solution of eq 2, which contains 1 equiv of free PPh_3,

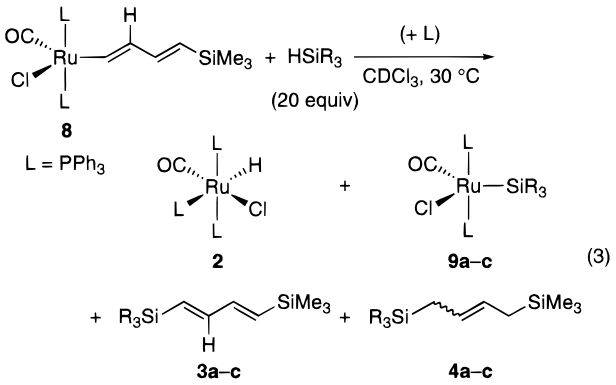
Table 2. Characteristic NMR Data for **8**, **11a**, **11b**, and **11c**

complex[a]	^1H NMR δ	*J* (Hz)	assignments	$^{31}P\{^1H\}$ NMR δ
 **8** (in $CDCl_3$, at room temp)	7.99 (dt)	12.4, 2.1	H^1	31.2 (s)
	6.19 (dd)	18.1, 10.0	H^3	
	5.39 (dd)	12.4, 10.0	H^2	
	4.81 (d)	18.1	H^4	
	−0.02 (s)		$Si(CH_3)_3$	
 **11a** (in C_6D_6, at room temp)	6.19 (d, br)	17.7	H^3	33.0 (br)
	5.43 (s)		H^1	
	5.38 (d, br)	17.7	H^4	(32.8 (br), in $CDCl_3$)
	0.44 (s)		$Si(CH_3)Ph_2$	
	0.01 (s)		$Si(CH_3)_3$	
 **11b** (in C_6D_6, at room temp)	6.24 (d, br)	17.6	H^3	33.1 (br)
	5.34 (d, br)	17.6	H^4	
	5.04 (s)		H^1	(32.9 (br), in $CDCl_3$)
	0.18 (s)		$Si(CH_3)_2Ph$	
	0.10 (s)		$Si(CH_3)_3$	
 **11c** (in C_6D_6, at room temp)	6.31 (d, br)	17.8	H^3	32.4 (br)
	5.29 (br)[b]		H^4	
	5.10 (s)		H^1	(32.2 (br), in $CDCl_3$)
	0.93 (t)	8.1	$Si(CH_2CH_3)_3$	
	0.55 (q)	8.1	$Si(CH_2CH_3)_3$	
	0.13 (s)		$Si(CH_3)_3$	
 **11d** (in C_6D_6, at room temp)	6.36 (d)	18.0	H^3	—[c]
	5.39 (d)	18.0	H^4	
	4.85 (d)	1.2	H^1	
	0.16 (s)		$Si(CH_3)_3$	
	−0.02 (s)		$Si(CH_3)_3$	

[a] L = PPh_3. The data of **11d** were taken from ref 16. [b] The H^c proton was observed as a doublet (δ 4.97, J = 17.7 Hz) at −20 °C in $CDCl_3$. Complete ^1H NMR data for **11c** in $CDCl_3$ at −20 °C are reported in Experimental Section. [c] Not reported.

but readily decomposed during isolation. Therefore, further experiments on the reactions of **8** were carried out without its isolation.

Addition of an excess amount of hydrosilane (20 equiv) to the solution of **8** led to two types of hydrosilation products **3** and **4** (eq 3). The reaction also gave ruthenium hydride **2** and



(3)

SiR_3 = $SiMePh_2$ (**a**), $SiMe_2Ph$ (**b**), $SiEt_3$ (**c**)

silylruthenium **9**. As shown in Table 3, the reaction with $HSiMe_2Ph$ took place instantly at 30 °C (entry 2). In contrast, the reactions with $HSiMePh_2$ and $HSiEt_3$ were rather slow and

(9) Trigonal bipyramidal structures of closely related complexes have been confirmed by X-ray diffraction studies: Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169. Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

(10) The $^3J_{H-H}$ constant of **8** is in a typical range of the values for ruthenium complexes having *trans*-dienyl ligands: Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919.

Table 3. Reactions of Dienyl Complex **8** with $HSiR_3$ (20 equiv)[a]

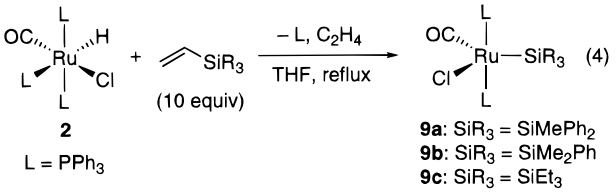
entry	$HSiR_3$	reaction time[b] (h)	product ratio[c] **2**:**9**	**3**:**4**
1	$HSiMePh_2$	3	52:48	55:45
2	$HSiMe_2Ph$	instant	69:31	68:32
3	$HSiEt_3$	3	65:35	66:34

[a] All reactions were run at 30 °C with a $CDCl_3$ solution of **8** prepared according to eq 2. The reaction solution contains 1 equiv of free PPh_3. [b] The time required for 100% conversion of **8**, confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. [c] The ratio of **2**/**9** was determined by $^{31}P\{^1H\}$ NMR spectroscopy. The ratio of **3**/**4** was determined by ^1H NMR spectroscopy with anisole as an internal standard.

they took 3 h for their completion under the same reaction conditions (entries 1 and 3).

It can be seen from the table that for each run the amounts of **2** and **9** are in good agreement with the amounts of **3** and **4**, respectively. This fact strongly indicates the presence of two reaction pathways which correspond to process **ii** in cycle **A** and process **B**, respectively (Scheme 1). In the former process the reaction of **8** with hydrosilane affords **2** and **3** via C−Si and Ru−H bond formation. On the other hand, the latter process leads to C−H and Ru−Si bond formation and provides 1-(trimethylsilyl)-1,3-butadiene (**10**) and silyl complex **9**.[11] The subsequent hydrosilation of **10** affords **4**.[13]

3. Formation of 5, 6, and 7. We next examined the reactions of silylruthenium complexes **9a**−**c** formed in the reactions of eq 3. The pure complexes were independently prepared according to the Wakatsuki's method reported for the syntheses of $SiMe_3$ and $Si(OEt)_3$ analogues (eq 4).[14,15] Treatment of hydride complex **2** with excess amounts of vinylsilanes (10 equiv) in THF under reflux gave **9a**−**c**, which were isolated as orange crystalline solids and characterized by NMR spectroscopy and elemental analysis.



(4)

Complex **9b** was treated with 20 equiv of **1** in $CDCl_3$ at 30 °C (eq 5). The reaction proceeded obeying the first-order kinetics with respect to the concentration of **9b** up to 90% conversion ($k_{obsd} = 8.1 \times 10^{-4}$ s^{-1}), giving the insertion product **11b** in quantitative yield. The reaction progress became slower when benzene-d_6 was used as the solvent in place of $CDCl_3$ ($k_{obsd} = 6.3 \times 10^{-4}$ s^{-1}) and was retarded by addition of free PPh_3 (0.33 equiv) to the benzene solution ($k_{obsd} = 4.2 \times 10^{-4}$ s^{-1}). Similarly, **9a** reacted with **1** to afford the insertion product **11a** in quantitative yield. Complexes **11a** and **11b** thus prepared were isolated as yellow crystalline solids and characterized by NMR and IR spectroscopy and elemental analysis. An interesting feature of **11** is the trans arrangement of the ruthenium moiety and the SiR_3 group around the double bond of the dienyl ligand, indicating the occurrence of formal *trans*-addition of a Ru−SiR_3 bond to **1**. Details of the structural assignments will be described in Section 4.

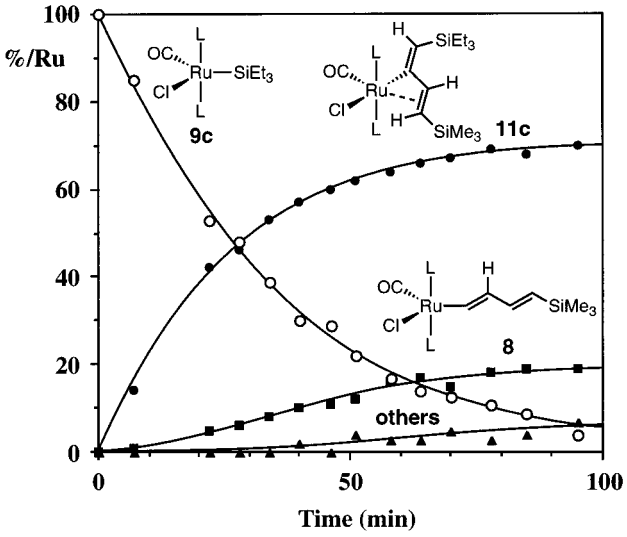
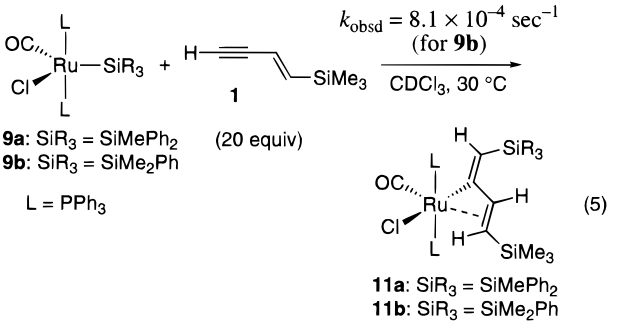


Figure 1. Time-course of ruthenium complexes in the reaction of **9c** and **1** (5 equiv) in $CDCl_3$ at 30 °C.



(5)

Unlike the reactions of **9a** and **9b**, reaction of the $SiEt_3$ analogue **9c** with **1** (5 equiv) provided dienyl complex **8** in addition to insertion product **11c**. Also observed in the reaction system by GLC analysis was the formation of 1-(trimethylsilyl)-4-(triethylsilyl)-1-buten-3-yne (**7c**). As seen from the time-course of ruthenium complexes in Figure 1, the formation of **8** proceeded following the conversion of **9c** to **11c**. After 70% of **9c** was consumed, complex **8** was further converted to some unidentified ruthenium species: δ 31.6 (br), 31.3 (s), and 30.8 (s) in $^{31}P\{^1H\}$ NMR.

These experimental data indicate the sequence of reactions shown in Scheme 2. Initially, the insertion of **1** into the Ru−$SiEt_3$ bond of **9c** takes place. The subsequent β-hydrogen elimination of **11c** gives **7c** and a coordinatively unsaturated ruthenium hydride, the latter undergoes the insertion of **1** to give **8** as already confirmed in eq 2. However, different from eq 2, the reaction system of Figure 1 does not contain free PPh_3, which is essential to stabilize **8** in solution, and thereby complex **8** thus formed further undergoes decomposition to give unidentified ruthenium species (vide supra).

(11) The reactions of dienylruthenium complexes (**8** and **11**) with hydrosilanes may proceed via a conventional mechanism comprised of oxidative addition and reductive elimination processes or σ-bond metathesis. The latter process has been documented for early transition metal complexes,[12] while definitive examples of σ-bond metathesis are still lacking for late transition metals.

(12) (a) Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041. (b) Radu, N. S.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5863. (c) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (d) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047.

(13) There is another possibility that **4** and **9** are formed by hydrogenation of **3** by the aid of **2** and hydrosilane. However, this possibility can be excluded because the reaction of **3** with $HSiMe_2Ph$ in the presence of **2** does not proceed at 30 °C.[8a]

(14) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703.

(15) (a) Complex **9c** is a known complex.[4b] (b) The synthesis of **9b** was reported just prior to submission of this paper: Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320.

Scheme 2

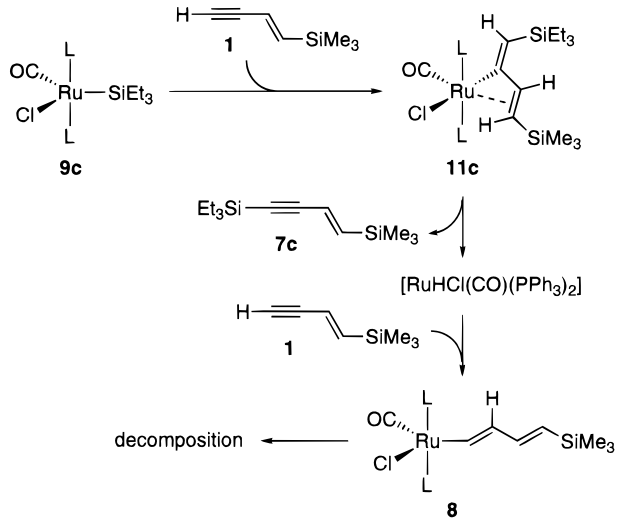


Table 4. Reactions of Dienyl Complexes **11a** and **11b** with $HSiR_3$ in the Presence (entries 1, 3) or Absence (entries 2, 4) of Added PPh_3[a]

entry	complex	$HSiR_3$	reaction time[b] (h)	product ratio[c] **9**:**2**	product ratio[c] **5**:**6**:**7**
1	**11a**	$HSiMePh_2$	instant	>99:<1	96:4:0
2	**11a**	$HSiMePh_2$	5	87:13	83:5:12
3	**11b**	$HSiMe_2Ph$	instant	>99:<1	90:10:0
4	**11b**	$HSiMe_2Ph$	3	96:4	87:9:4

[a] All reactions were run in $CDCl_3$ at 30 °C with **11** and 20 equiv of $HSiR_3$. Entries 2 and 3 were conducted in the presence of free PPh_3 (1 equiv). [b] The time required for 100% conversion of **11**, confirmed by NMR spectroscopy. [c] The ratio of **9**/**2** was determined by $^{31}P\{^1H\}$ NMR spectroscopy. The ratio of **5**/**6**/**7** was determined by ^1H NMR spectroscopy with anisole as an internal standard.

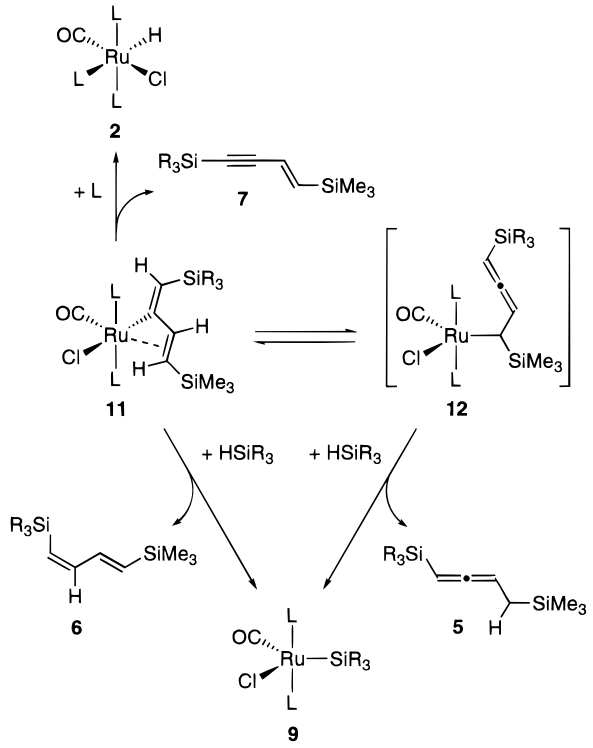
We next examined the reactions of isolated **11a** and **11b** with hydrosilanes, $HSiMePh_2$ and $HSiMe_2Ph$, respectively (Table 4). These reactions instantly took place in $CDCl_3$ at 30 °C to give two kinds of hydrosilation products **5** and **6**, together with the corresponding silyl complex **9a** or **9b**, respectively (entries 1 and 3). In the presence of free PPh_3 (1 equiv), on the other hand, the reaction progress became significantly slow and a considerable amount of dehydrogenative silation product **7** was formed in addition to **5** and **6** (entries 2 and 4). Also formed in the reaction systems was hydridoruthenium complex **2**, the amount of which was in fair agreement with the amount of **7** produced.

The formation of **5**, **6**, **7**, **9**, and **2** is reasonably accounted for by the processes in Scheme 3. Reaction of **11** with hydrosilane with retention of the 2-rutheno-1,3-butadiene structure gives **6** and **9**. On the other hand, 1,3-shift of the RuCl(CO)L_2 moiety in **11** provides an allenylmethylruthenium species **12**, which reacts with hydrosilane to give **5** and **9**. Furthermore, β-hydrogen elimination of **11** gives 1,4-bis(silyl)-butenyne **7** and a 16-electron hydridoruthenium complex, which combines with PPh_3 added to the system to give **2**.

In Schemes 2 and 3, we assumed the β-hydrogen elimination of **11**. This reaction has already been reported for the bis(trimethylsilyl) analogue of **11** (SiR_3=$SiMe_3$, **11d**).[16] As seen from the data in Table 4, in the absence of free PPh_3, this reaction is much slower than the reaction with hydrosilane and thereby no β-hydrogen elimination products (**2** and **7**) are

(16) Wakatsuki, Y.; Yamazaki, H.; Maruyama Y.; Shimizu, I. *J. Organomet. Chem.* **1992**, *430*, C60.

Scheme 3



formed. However, in the presence of free PPh_3, the β-hydrogen elimination competes with the reaction of **11** with hydrosilane. This is probably because the reaction with hydrosilane requires prior dissociation of PPh_3 ligand from **11**, as supported by the following kinetic data. Thus the reaction of **11b** with $HSiMe_2$-Ph (20 equiv) at 30 °C in benzene-d_6 proceeded at a convenient rate for kinetic experiments. The first-order rate constant (k_{obsd}) observed was 5.4×10^{-3} s^{-1}. In contrast, in the presence of a small amount of free PPh_3 (0.33 equiv), the rate constant was reduced to 1/16 ($k_{obsd} = 3.4 \times 10^{-4}$ s^{-1}).

4. Characterization of 11. The NMR data of **11a**−**c** are listed in Table 2, together with the data of $SiMe_3$ analogue **11d**, which was previously prepared by Wakatsuki and co-workers by the insertion of $Me_3SiC{\equiv}CCH{=}CHSiMe_3$ to hydride complex **2**.[16] As a representative example, the ^1H NMR spectrum of **11b** bearing a $SiMe_2Ph$ group exhibited the three signals arising from olefinic protons H^1, H^3, and H^4 at δ 5.04, 6.24, and 5.34, respectively. Among them, H^3 and H^4 were coupled to each other and the coupling constant (17.6 Hz) was typical of *trans*-alkenes. On the other hand, the signal of H^1 at δ 5.04 was observed as a singlet. These NMR data are very similar to those of **11d**, suggesting the closely related structures of **11b** and **11d**. However, there is an important point that should be clarified. Thus **11d** has a trans arrangement of the Ru atom and the $SiMe_3$ group around the $C^1{=}C^2$ bond: the structure is consistent with the *cis*-addition process common to alkyne insertion. On the other hand, in the case of **11b**, *cis*-addition of the Ru−$SiMe_2Ph$ bond to **1** should provide a cis geometry around the $C^1{=}C^2$ double bond. Therefore, we compared the NMR data of **11b** with the data of the complex independently prepared by the insertion of $PhMe_2SiC{\equiv}CCH{=}CHSiMe_3$ to **2** according to Wakatsuki's method.[16] Both data were in fair agreement with each other. Consequently, the insertion of **1** to **9b** was concluded to proceed via a formal *trans*-addition process. The trans arrangement in **11b** was also supported by the formation of *trans*-addition product **6** in the reaction of **11b** with $HSiMe_2Ph$ (Table 4). The formal *trans*-addition of a

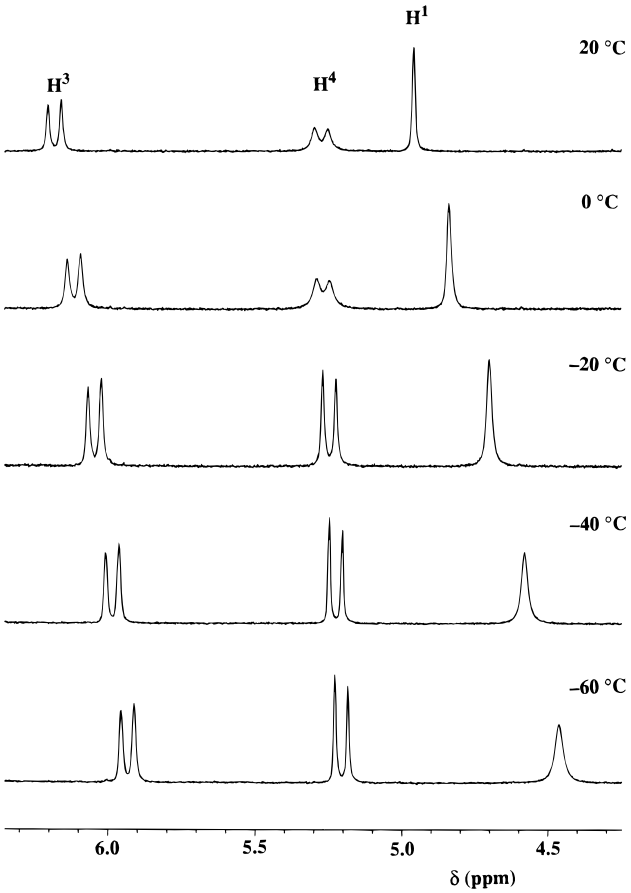
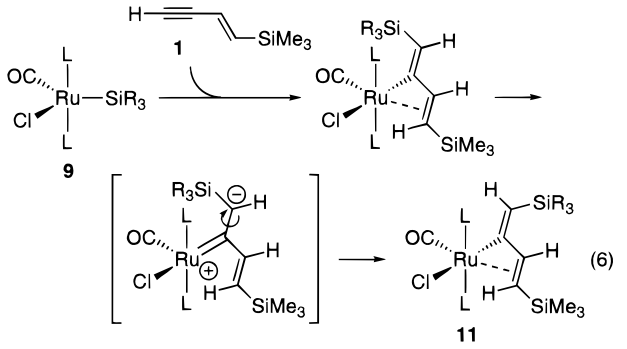


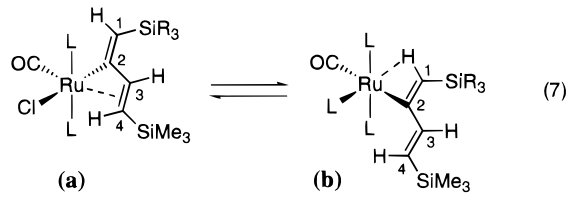
Figure 2. Temperature dependence of the ^{1}H NMR singals of olefinic protons of **11b** in toluene-d_8.

metal−silicon bond to a C≡C bond has some precedents in catalytic[17] as well as stoichiometric[18] systems. The most probable mechanism is the one, originally proposed by Ojima et al.[17] Thus the insertion does proceed via the common *cis*-addition process, but the subsequent cis to trans isomerization via a zwitterionic carbene-like intermediate leads to the formal *trans*-addition product, which is sterically less demanding and more stable than the *cis*-adduct (eq 6). Great stabilization of α-carbanion by a silyl group facilitates the isomerization.



The ^{1}H NMR signals of olefinic protons of **11b** showed significant temperature dependence (Figure 2). At 20 °C, H^3 and H^4 were observed as broad doublets and H^1 as a sharp singlet. With a drop in temperature, the H^3 and H^4 signals broadened further and then sharpened. On the other hand, the H^1 signal broadened and significantly shifted toward the higher magnetic field along with a lowering of temperature.

It has been previously confirmed by X-ray diffraction study[16] that complex **11d** has a 2-butadienyl ligand bound to ruthenium by a σ-bonding of the C^2 carbon and by a weak π-coordination of the C^3═C^4 bond (structure **a** in eq 7). Therefore, the



spectroscopic changes observed for H^3 and H^4 can be attributed to the occurrence of reversible coordination of the C^3═C^4 bond to ruthenium at the NMR time scale. On the other hand, the spectroscopic change observed for H^1 indicates the presence of agostic interaction between H^1 and ruthenium (structure **b** in eq 7). The C^3═C^4 coordination is essential for the interconversion of the dienyl structure **11** to the allenylmethyl structure **12** in Scheme 3, while the agostic interaction of H^1 is required for the β-hydrogen elimination of **11** to give **7** and **2**.

5. Hydrosilation of 1 Catalyzed by 9. In Section 3, we showed that silyl complexes **9a** and **9b** undergo the insertion of **1** to give the corresponding dienyl complexes **11a** and **11b**, respectively. Furthermore, **11a** and **11b** thus formed reacted with hydrosilane to give hydrosilation products **5** and **6** along with the regeneration of silyl complexes **9a** and **9b**, respectively. In the absence of free PPh_3, these reactions selectively proceeded without formation of any other hydrosilation products and ruthenium complexes. Therefore, by using **9** as the catalyst, we may expect a highly selective catalytic cycle that involves **9** and **11** as the ruthenium intermediates and provides **5** and **6** as the hydrosilation products.

Table 5 summarizes the results of catalytic hydrosilation of **1** with **9a**−**c** as the catalysts. The reactions in this table were examined under the same reaction conditions as Table 1 except for catalysts. It is seen that **9** is much more reactive than **2** as the catalyst. Furthermore, **9** leads to higher selectivity than **2** for the formation of **5** and **6**. This tendency is most obvious for the reactions with $HSiEt_3$. Thus the reaction with **2** forms **5c** and **6c** in totally 32% selectivity (Table 1, entry 3), while the reaction with **9c** provides **5c** and **6c** in totally 95% selectivity (Table 5, entry 3). On the other hand, by addition of free PPh_3, the catalytic reaction with **9c** is markedly suppressed and the selectivity is significantly lowered (Table 5, entry 4). The reaction time and the product ratio observed are comparable to those in the reaction with **2** as the catalyst (Table 1, entry 3).

Table 5. Catalytic Hydrosilation of 1-(Trimethylsilyl)-1-buten-3-yne (**1**) with $HSiR_3$ in the Presence of 5 mol % of $Ru(SiR_3)Cl(CO)(PPh_3)_2$ (**9a**−**c**)[a]

entry	catalyst	$HSiR_3$	reaction time[b] (h)	product ratio[c] **3**	**4**	**5**	**6**	**7**	(**5** + **6**)
1	**9a**	$HSiMePh_2$	3	1	2	92	4	1	96
2	**9b**	$HSiMe_2Ph$	3	4	3	86	5	2	91
3	**9c**	$HSiEt_3$	7	2	2	86	9	1	95
4[d]	**9c**	$HSiEt_3$	61	21	12	35	4	28	39

[a] All reactions were run at 30 °C in $CDCl_3$ with **1** and $HSiR_3$ in a 1:1 ratio. [b] The time required for 100% conversion of **1**. [c] Determined by ^{1}H NMR spectroscopy and GLC. [d] The reaction was examined in the presence of added PPh_3 (1 equiv/Ru).

(17) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127 and references therein.

(18) (a) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408. (b) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1993**, *12*, 988.

6. Catalytic Mechanisms. We could clearly observe most of the elementary processes responsible for the hydrosilation of **1** catalyzed by $RuHCl(CO)(PPh_3)_3$ (**2**). The experimental data are consistent with the catalytic processes depicted in Scheme 1, which is comprised of two catalytic cycles, the Chalk−Harrod cycle **A** and the modified Chalk−Harrod cycle **C**, and their interconnecting processes **B** and **D**.

The first stage is the insertion of **1** into the Ru−H bond of **2**, giving dienyl complex **8** (process **i** in cycle **A**). This reaction takes place instantly under the catalytic conditions with liberation of PPh_3 (eq 2). Complex **8** then reacts with hydrosilane in two reaction processes, process **ii** in cycle **A** and process **B**, which compete with each other under the catalytic conditions (eq 3 and Table 3). Process **ii** provides 1,4-bis(silyl)-1,3-butadiene **3** with regeneration of **2**, while process **B** forms allylsilane **4** and silyl complex **9**.

Silyl complex **9** thus generated in the system is the key intermediate for catalytic cycle **C**. Insertion of **1** to **9** (process **iii**) proceeds via formal *trans*-addition (eqs 5 and 6). The resulting dienyl complex **11** then reacts with hydrosilane to give hydrosilation products **5** and **6** (process **iv**). This reaction proceeds rapidly in the absence of free PPh_3 and regenerates silyl complex **9**, selectively (Table 4, entries 1 and 3). Therefore, cycle **C** is operative in high selectivity by using **9** as the catalyst, which is coordinated with two PPh_3 ligands and realizes the catalytic system without free PPh_3 (Table 5, entries 1−3). On the other hand, when the catalytic reaction is conducted with catalyst **9** in the presence of added PPh_3, the reaction of **11** with hydrosilane is effectively retarded by free PPh_3 and thereby complex **11** also undergoes β-hydrogen elimination (process **D**) to give 1,4-bis(silyl)-1,3-butenyne **7** and hydride complex **2** (Table 4, entries 2 and 4). The resulting **2** starts cycle **A** again. Consequently, the catalytic hydrosilation provides significant amounts of **3**, **4**, and **7** in addition to **5** and **6**, especially in the reaction with $HSiEt_3$ (Table 5, entry 4).

Conclusion

The present catalytic reaction involves both hydridoruthenium (**2**) and silylruthenium (**9**) as the reaction intermediates. The stoichiometric reactions in eqs 2 and 5 have suggested that **2** is much more reactive than **9** toward the insertion of **1**. The difference in the reactivities was further supported by the following experiment. Thus the treatment of a 1:1 mixture of **2** and **9b** with **1** (1 equiv) in $CDCl_3$ at room temperature led to the selective conversion of **2** to **8** while **9b** remained unreacted (see Experimental Section). Despite the much higher reactivity of **2** than **9**, however, the modified Chalk−Harrod cycle **C** predominates over the Chalk−Harrod cycle **A** when $HSiMePh_2$ and $HSiMe_2Ph$ are employed. This is mainly due to the selectivities in the reactions of dienyl complexes **8** and **11** with hydrosilanes. Thus the reaction of **8** with $HSiMePh_2$ or $HSiMe_2Ph$ in cycle **A** provides a considerable amount of **9**, while the reactions of **11** with these hydrosilanes in cycle **C** form **9** in high selectivity. In these situations the catalytic cycle is effectively shifted from **A** to **C** and cycle **C** is operative in high selectivity. Therefore, we may consider that the selection of the catalytic cycles (i.e., the Chalk−Harrod cycle **A** or the modified Chalk−Harrod cycle **C**) takes place at the product-forming steps.

Recently, Aizenberg and Milstein examined the reductive elimination of $Ir(CH_3)(H)(SiR_3)(PMe_3)_3$ (SiR_3 = $Si(OEt)_3$, $SiPh_3$, and $SiEt_3$) and found that more alkyl substituents at silicon facilitate more the C−Si reductive elimination than the C−H reductive elimination.[7e] In our case, however, the relative ease of the C−Si and C−H bond formation is not so clearly correlated with the nature of silyl groups (see Tables 3 and 4), but the structures of dienylruthenium complexes serve as the more important factors to control the selectivity. Thus terminal dienyl complex **8** reacts with hydrosilane to provide comparable amounts of hydride and silyl complexes **2** and **9** via the C−Si and C−H coupling reactions, respectively, while internal dienyl complex **11** exclusively forms silyl complex **9** along with the formation of the C−H coupling products **5** and **6**. The exact reason for the difference in the selectivities is presently uncertain and is the subject to be clarified in due course.

Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere with standard Schlenk techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on JEOL JNM-A400 (^{1}H NMR, 399.65 MHz) and Varian Mercury 300 (^{1}H NMR, 300.11 MHz; ^{13}C NMR, 75.46 MHz; ^{31}P NMR, 121.49 MHz) spectrometers. Chemical shifts are reported in δ ppm referred to an internal $SiMe_4$ standard for ^{1}H and ^{13}C NMR and to an external 85% H_3PO_4 standard for ^{31}P NMR. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV, capillary column). GLC analysis was performed with a GL Sciences GC-353 instrument equipped with a FID detector and a capillary column (TC-1, 30 m). THF, Et_2O, benzene, and hexane were dried over sodium benzophenone ketyl and distilled just before use. CH_2Cl_2 was dried over CaH_2 and distilled just before use. $CDCl_3$ was purified by passage though an Al_2O_3 column and dried over Molecular Sieves 4A. Benzene-d_6 and toluene-d_8 were dried over $LiAlH_4$, vacuum transferred, and stored under a nitrogen atmosphere. 1-(Trimethylsilyl)-1-buten-3-yne (**1**)[8d] and $RuHCl(CO)(PPh_3)_3$ (**2**)[19] were synthesized according to the literature. 1-(Trimethylsilyl)-4-(triethylsilyl)-1-buten-3-yne and 1-(trimethylsilyl)-4-(dimethylphenylsilyl)-1-buten-3-yne were prepared by lithiation of **1** with BuLi, followed by treatment with $ClSiEt_3$ and $ClSiMe_2Ph$, respectively. All other compounds were obtained from commercial sources and used without purification.

Catalytic Hydrosilation of 1 (Tables 1 and 5). A typical procedure (entry 1 in Table 1) is as follows. The complex $RuHCl(CO)(PPh_3)_3$ (**2**; 5.7 mg, 6.0 μmol) was placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas at room temperature. 1-(Trimethylsilyl)-1-buten-3-yne (**1**; 14.9 mg, 0.120 mmol) and anisole (4.0 μL, 0.037 mmol) as an internal standard for ^{1}H NMR analysis were added. All components were dissolved in $CDCl_3$ (0.6 mL), and $HSiMePh_2$ (23.8 mg, 0.120 mmol) was added. The sample tube was placed in an oil bath controlled to 30 °C, and the reaction progress was monitored by ^{1}H NMR spectroscopy at intervals. The amounts of **1** and reaction products were determined by measuring the relative peak integration of the methyl protons of anisole (δ 3.81), acetylenic proton of **1** (δ 2.94), and olefinic protons of the products. After 64 h substrate **1** was consumed and products **3a**, **4a**, **5a**, **6a**, and **7a** were formed in a 6:4:81:6:3 ratio in totally 100% yield. The product ratio was also confirmed by GLC. All the catalytic reactions reported in this paper were similarly conducted. In every run the silation products were obtained in totally (100 ± 3)% yield.

Identification of the catalytic reaction products was performed by NMR spectroscopy and GC-mass spectrometry without their isolation. The geometries around the C=C bonds were determined on the basis of $^3J_{H-H}$ coupling constants appearing on the olefinic proton signals except for **4a**−**c**, whose geometries could not be determined due to the almost identical chemical shifts of two olefinic protons. The allenyl structures of **5a**−**c** were supported by the observations of characteristic signals at around δ 212 in the ^{13}C{^{1}H} NMR spectra, assignable to the center carbon of the allenyl group.

***(1E,3E)*-1-(Methyldiphenylsilyl)-4-(trimethylsilyl)-1,3-butadiene (3a).** ^{1}H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 6.57−6.69 (m, 2H, =CH), 6.20 (d, J = 17.0 Hz, 1H, =CH), 5.94 (d, J = 17.4 Hz, 1H, =CH), 0.68 (s, 3H, $Si(CH_3)Ph_2$),

(19) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

0.11 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 322 (M^+, 5), 307 (9), 229 (8), 197 (100), 172 (11), 135 (17), 105 (11), 73 (20), 45 (13).

1-(Methyldiphenylsilyl)-4-(trimethylsilyl)-2-butene (4a). ^1H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 5.26−5.30 (m, 2H, ═CH), 2.02 (d, J = 6.8 Hz, 2H, CH_2), 1.38 (d, J = 6.8 Hz, 2H, CH_2), 0.73 (s, 3H, $Si(CH_3)Ph_2$), −0.09 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 324 (M^+, 3), 197 (100), 181 (5), 135 (8), 105 (7), 73 (13), 45 (9).

1-(Methyldiphenylsilyl)-4-(trimethylsilyl)-1,2-butadiene (5a). ^1H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 5.27 (dt, J = 6.9 and 3.4 Hz, 1H, ═CH), 4.85 (dt, J = 6.9 and 8.5 Hz, 1H, ═CH), 1.29 (m, 2H, CH_2), 0.64 (s, 3H, $Si(CH_3)Ph_2$), −0.01 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 213.2 (═C═), 136.7 (Ph), 134.6 (Ph), 129.3 (Ph), 127.7 (Ph), 80.6 (═CH), 78.8 (═CH), 16.2 (CH_2), −1.9 ($Si(CH_3)Ph_2$), −3.5 ($Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 322 (M^+, 6), 307 (6), 229 (12), 197 (100), 172 (50), 135 (67), 105 (22), 73 (62), 45 (28).

(*1Z*,*3E*)-1-(Methyldiphenylsilyl)-4-(trimethylsilyl)-1,3-butadiene (6a). ^1H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 6.90 (dd, J = 14.3 and 11.5 Hz, 1H, ═CH), 6.53 (dd, J = 18.1 and 11.5 Hz, 1H, ═CH), 5.98 (d, J = 14.3 Hz, 1H, ═CH), 5.92 (d, J = 18.1 Hz, 1H, ═CH), 0.57 (s, 3H, $Si(CH_3)Ph_2$), −0.19 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 322 (M^+, 1), 305 (1), 244 (16), 197 (9), 172 (21), 135 (100), 121 (8), 105 (11), 73 (30), 59 (13), 45 (12).

(*1E*)-1-(Trimethylsilyl)-4-(methyldiphenylsilyl)-1-buten-3-yne (7a). ^1H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 6.65 (d, J = 19.2 Hz, 1H, ═CH), 6.08 (d, J = 19.2 Hz, 1H, ═CH), 0.71 (s, 3H, $Si(CH_3)Ph_2$), −0.10 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 320 (M^+, 3), 305 (12), 244 (16), 197 (16), 172 (21), 135 (100), 121 (11), 105 (15), 73 (31), 59 (16), 43 (14).

(*1E*,*3E*)-1-(Dimethylphenylsilyl)-4-(trimethylsilyl)-1,3-butadiene (3b). ^1H NMR ($CDCl_3$): δ 7.50−7.57 (m, 2H, Ph), 7.34−7.42 (m, 3H, Ph), 6.52−6.65 (m, 2H, ═CH), 6.03 (d, J = 17.5 Hz, 1H, ═CH), 5.94 (d, J = 17.0 Hz, 1H, ═CH), 0.37 (s, 6H, $Si(CH_3)_2Ph$), 0.10 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 260 (M^+, 1), 245 (4), 186 (21), 172 (30), 135 (37), 73 (100), 59 (29), 43 (26).

1-(Dimethylphenylsilyl)-4-(trimethylsilyl)-2-butene (4b). ^1H NMR ($CDCl_3$): δ 7.50−7.57 (m, 2H, Ph), 7.34−7.42 (m, 3H, Ph), 5.22−5.28 (m, 2H, ═CH), 1.68 (d, J = 6.4 Hz, 2H, CH_2), 1.40 (d, J = 6.6 Hz, 2H, CH_2), 0.27 (s, 6H, $Si(CH_3)_2Ph$), −0.04 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 262 (M^+, 3), 135 (100), 112 (13), 97 (8), 73 (21), 43 (17).

1-(Dimethylphenylsilyl)-4-(trimethylsilyl)-1,2-butadiene (5b). ^1H NMR ($CDCl_3$): δ 7.50−7.57 (m, 2H, Ph), 7.34−7.42 (m, 3H, Ph), 5.05 (ddd, J = 6.9, 3.8 and 3.0 Hz, 1H, ═CH), 4.81 (ddd, J = 8.5, 8.5 and 6.9 Hz, 1H, ═CH), 1.22−1.38 (m, 2H, CH_2), 0.36 (s, 6H, $Si(CH_3)_2$-Ph), 0.03 (S, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 212.1 (═C═), 138.9 (Ph), 133.7 (Ph), 129.0 (Ph), 127.7 (Ph), 80.4 (═CH), 80.0 (═CH), 16.4 (CH_2), −1.8 ($Si(CH_3)_2Ph$), −2.1 ($Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 260 (M^+, 4), 245 (4), 186 (11), 172 (33), 135 (100), 73 (85), 43 (33).

(*1Z*,*3E*)-1-(Dimethylphenylsilyl)-4-(trimethylsilyl)-1,3-butadiene (6b). ^1H NMR ($CDCl_3$): δ 7.50−7.57 (m, 2H, Ph), 7.34−7.42 (m, 3H, Ph), 6.89 (dd, J = 13.5 and 10.7 Hz, 1H, ═CH), 6.64 (dd, J = 17.9 and 10.4 Hz, 1H, ═CH), 5.91 (d, J = 17.9 Hz, 1H, ═CH), 5.82 (d, J = 13.7 Hz, 1H, ═CH), 0.44 (s, 3H, $Si(CH_3)_2Ph$), −0.01 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 260 (M^+, 1), 245 (1), 186 (20), 172 (29), 135 (43), 73 (100), 59 (26), 43 (25).

(*1E*)-1-(Trimethylsilyl)-4-(dimethylphenylsilyl)-1-buten-3-yne (7b). ^1H NMR ($CDCl_3$): δ 7.52−7.66 (m, 4H, Ph), 7.36−7.42 (m, 6H, Ph), 6.58 (d, J = 19.2 Hz, 1H, ═CH), 6.02 (d, J = 19.2 Hz, 1H, ═CH), 0.44 (s, 3H, $Si(CH_3)_2Ph$), −0.08 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 258 (M^+, 15), 243 (100), 227 (11), 185 (13), 159 (29), 145 (13), 135 (48), 73 (28), 59 (19), 43 (36).

(*1E*,*3E*)-1-(Triethylsilyl)-4-(trimethylsilyl)-1,3-butadiene (3c). ^1H NMR ($CDCl_3$): δ 6.49−6.60 (m, 2H, ═CH), 5.89 (d, J = 17.4 Hz, 1H, ═CH), 5.86 (d, J = 17.0 Hz, 1H, ═CH), 0.95 (t, J = 7.7 Hz, 9H, $SiCH_2CH_3$), 0.59 (q, J = 7.7 Hz, 6H, $SiCH_2$), 0.10 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 240 (M^+, 3), 225 (5), 211 (35), 183 (48), 155 (21), 124 (34), 101 (40), 73 (100), 59 (69), 45 (42).

1-(Triethylsilyl)-4-(trimethylsilyl)-2-butene (4c). ^1H NMR ($CDCl_3$): δ 5.21−5.25 (m, 2H, ═CH), 1.63 (d, J = 6.2 Hz, 2H, CH_2), 1.40 (d, J = 6.6 Hz, 2H, CH_2), 0.95 (t, J = 7.7 Hz, 9H, $SiCH_2CH_3$), 0.59 (q, J = 7.7 Hz, 6H, $SiCH_2$), −0.01 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 242 (M^+, 8), 213 (1), 115 (85), 87 (100), 73 (58), 59 (59), 45 (30).

1-(Triethylsilyl)-4-(trimethylsilyl)-1,2-butadiene (5c). ^1H NMR ($CDCl_3$): δ 4.81 (ddd, J = 6.9, 3.8, and 3.3 Hz, 1H, ═CH), 4.70 (td J = 8.2 and 6.9 Hz, 1H, ═CH), 1.26 (m, 2H, CH_2), 0.95 (t, J = 7.7 Hz, 9H, $SiCH_2CH_3$), 0.59 (q, J = 7.7 Hz, 6H, $SiCH_2$), 0.03 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 211.8 (═C═), 78.8 (═CH), 77.7 (═CH), 16.5 (CH_2), 7.3 ($SiCH_2CH_3$), 3.9 ($SiCH_2$), −1.9 ($Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 240 (M^+, 3), 223 (1), 211 (27), 183 (77), 155 (31), 115 (36), 109 (29), 87 (99), 73 (100), 59 (81), 45 (67).

(*1Z*,*3E*)-1-(Triethylsilyl)-4-(trimethylsilyl)-1,3-butadiene (6c). ^1H NMR ($CDCl_3$): δ 6.88 (dd, J = 14.0 and 10.7 Hz, 1H, ═CH), 6.71 (dd, J = 17.9 and 10.7 Hz, 1H, ═CH), 5.91 (d, J = 17.9 Hz, 1H, ═CH), 5.62 (d, J = 14.0 Hz, 1H, ═CH), 0.95 (t, J = 7.7 Hz, 9H, $SiCH_2CH_3$), 0.59 (q, J = 7.7 Hz, 6H, $SiCH_2$), 0.10 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 240 (M^+, 2), 211 (21), 183 (17), 155 (7), 138 (8), 124 (27), 101 (45), 87 (43), 73 (100), 59 (58), 45 (47).

(*1E*)-1-(Trimethylsilyl)-4-(triethylsilyl)-1-buten-3-yne (7c). ^1H NMR ($CDCl_3$): δ 6.51 (d, J = 19.2 Hz, 1H, ═CH), 5.99 (d, J = 19.2 Hz, 1H, ═CH), 0.95 (t, J = 7.7 Hz, 9H, $SiCH_2CH_3$), 0.59 (q, J = 7.7 Hz, 6H, $SiCH_2$), 0.09 (s, 9H, $Si(CH_3)_3$). MS, *m*/*z* (rel intensity, %): 238 (M^+, 1), 210 (26), 195 (11), 181 (68), 167 (13), 153 (100), 139 (14), 127 (10), 113 (8), 97 (10), 83 (32), 73 (31), 59 (39), 45 (26).

Preparation of $Ru(CH═CHCH═CHSiMe_3)Cl(CO)(PPh_3)_2$ (8) (Eq 2). The complex $RuHCl(CO)(PPh_3)_3$ (**2**; 5.7 mg, 6.0 μmol) was charged into an NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas. $CDCl_3$ and 1-(trimethylsilyl)-1-buten-3-yne (**1**; 14.9 mg, 6.0 μmol) were added by means of a syringe at room temperature. The color of the solution instantly changed from pale yellow to red. The $^{31}P\{^1H\}$ NMR spectrum of the solution exhibited two singlets at δ 31.2 and −4.7 in a 2:1 ratio, assignable to **8** and free PPh_3, respectively. No trace of the signals of **2** [δ 39.6 (br, 2P) and 13.5 (br, 1P)] was observed. The NMR data of **8** are listed in Table 2.

The same reaction was examined in a 100-mg sample of **2** in a Schlenk tube. The reaction solution was concentrated to dryness at room temperature to give a red oily material, which was dissolved in CH_2Cl_2 (ca. 0.5 mL), and then Et_2O (ca. 1 mL) was carefully layered. The solvent layer was allowed to stand at −20 °C overnight, giving a reddish brown solid (87 mg). The $^{31}P\{^1H\}$ NMR spectrum revealed the formation of a complicated mixture, and thereby complex **8** could not be isolated.

Reactions of 8 with Hydrosilanes (Table 3). A typical procedure (entry 2) is as follows. A $CDCl_3$ solution (0.6 mL) of **8** (6 μmol) was prepared by the procedure describe above. Anisole (1.0 μL, 9.2 μmol) as an internal standard for ^1H NMR analysis and $HSiMe_2Ph$ (16.4 mg, 0.120 mmol) were added at room temperature. The color of the solution instantly changed from red to orange. $^{31}P\{^1H\}$ NMR analysis of the solution revealed the formation of $RuHCl(CO)(PPh_3)_3$ (**2**; δ 39.6 (br) and 13.5 (br)) and $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (**9b**; δ 33.4 (s)) in a 69:31 ratio with consumption of **8**. Complex **9b** was identified by using an authentic sample, independently prepared from $RuHCl(CO)(PPh_3)_3$ (**2**) and $CH_2═CHSiMe_2Ph$ (vide infra). ^1H NMR analysis of the reaction solution revealed the formation of **3b** and **4b** in 68 and 32% yields, respectively. The reactions of **8** with $HSiMePh_2$ and $HSiEt_3$ were similarly conducted. For both cases, the reaction progress was slow and it took 3 h for completion as confirmed by ^1H NMR spectroscopy.

Preparation of $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (9b) (Eq 4). The complex $RuHCl(CO)(PPh_3)_3$ (**2**; 150 mg, 0.157 mmol) was suspended in THF (20 mL), and $CH_2═CH(SiMe_2Ph)$ (128 mg, 0.787 mmol) was added at room temperature. The mixture was refluxed with stirring for 12 h to give an orange solution. Volatile materials were removed by pumping at room temperature, and the residue was purified by silica gel column chromatography with a 1:1 mixture of CH_2Cl_2 and benzene as eluent. The orange elution band was collected and concentrated to dryness. The resulting oily product was treated with Et_2O (4 mL) at 0

°C to form orange crystals of **9b**, which was collected by filtration and dried under vacuum (48 mg, 37% yield). ^{1}H NMR ($CDCl_3$): δ 7.17−7.43 (m, 33H, Ph), 7.06 (m, 2H, SiPh), 0.50 (s, 6H, $SiCH_3$). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 33.4 (s). IR (KBr): ν_{CO} 1913 cm^{-1}. Anal. Calcd for $C_{45}H_{41}ClOP_2RuSi$: C, 65.56; H, 5.01. Found: C, 65.32; H, 4.95.

Similarly prepared were $Ru(SiMePh_2)Cl(CO)(PPh_3)_2$ (**9a**, 58% yield) and $Ru(SiEt_3)Cl(CO)(PPh_3)_2$ (**9c**, 28% yield). Complex **9c** was identified by comparison of the NMR data with those reported.[4b] The identification data for **9a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.18−7.40 (m, 34H, Ph), 7.07 (t, J = 7.5 Hz, 2H, SiPh), 6.91 (t, J = 7.5 Hz, 4H, SiPh), 0.71 (s, $SiCH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.3 (s). IR (KBr): ν_{CO} 1913 cm^{-1}. Anal. Calcd for $C_{50}H_{43}ClOP_2RuSi$: C, 67.75; H, 4.89. Found: C, 67.49; H, 4.87.

Reaction of 9b with 1 (Eq 5). The complex $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (**9b**; 4.9 mg, 6.0 μmol) was placed in an NMR sample tube equipped with a rubber septum cap. The system was replaced with nitrogen gas, and toluene (1.0 μL, 9.4 μmol) and $CDCl_3$ (0.6 mL) were added. After **9b** was dissolved, 1-(trimethylsilyl)-1-buten-3-yne (**1**; 14.9 mg, 0.120 mmol) was added, and then the tube was placed in an NMR sample probe controlled to 30.0 ± 0.1 °C. The reaction progress with time was followed by measuring relative peak integration of methyl protons of toluene (δ 2.36) and **9b** (δ 0.50) in ^{1}H NMR spectra. The reactions in C_6D_6 and in the presence of added PPh_3 (0.33 equiv) were similarly investigated.

Preparation of Ru[C(=CHSiMe$_2$Ph)CH=CHSiMe$_3$]Cl(CO)(PPh$_3$)$_2$ (11b). To a Schlenk tube containing $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (**9b**; 200 mg, 0.243 mmol) was added THF (10 mL) under a nitrogen atmosphere. 1-(Trimethylsilyl)-1-buten-3-yne (**1**; 90.6 mg, 0.729 mmol) was added. The homogeneous solution was stirred at room temperature for 3 h and then evaporated to dryness by pumping. The resulting orange solid was dissolved in Et_2O (ca.6 mL), the volume of mixture was reduced to ca. 2 mL, and the solution was allowed to stand at −70 °C overnight to give yellow crystals of **11b**. The product was collected by filtration, washed with Et_2O (0.5 mL) at −78 °C, and dried under vacuum (180 mg, 78% yield). The ^{1}H and ^{31}P NMR data are listed in Table 2. IR (KBr): ν_{CO} 1926 cm^{-1}. Anal. Calcd for $C_{52}H_{53}ClOP_2RuSi_2$: C, 65.84; H, 5.63. Found: C, 65.45; H, 5.68.

Ru[C(=CHSiMePh$_2$)CH=CHSiMe$_3$]Cl(CO)(PPh$_3$)$_2$ (**11a**; 56% isolated yield) was similarly prepared. The ^{1}H and ^{31}P{^{1}H} NMR data are reported in Table 2. Additional data are as follows. IR (KBr): ν_{CO} 1926 cm^{-1}. Anal. Calcd for $C_{57}H_{55}ClOP_2RuSi_2$: C, 67.74; H, 5.49. Found: C, 67.47; H, 5.22.

Complex **11b** was independently prepared starting from **2**. To an NMR sample tube containing $RuHCl(CO)(PPh_3)_3$ (**2**; 5.0 mg, 5.2 μmol) were added C_6D_6 (0.6 mL) and 1-(trimethylsilyl)-4-(dimethylphenylsilyl)-1-buten-3-yne (8.1 mg, 31 μmol) at room temperature. The initially heterogeneous mixture gradually turned to a homogeneous orange solution over 30 min. The ^{31}P{^{1}H} NMR spectrum of the reaction solution indicated the selective formation of **11b** with liberation of 1 equiv of PPh_3. The ^{1}H and ^{31}P{^{1}H} NMR data observed were in fair agreement with the data of **11b** listed in Table 2.

Reaction of 9c with 1 (Figure 1). The complex $Ru(SiEt_3)Cl(CO)(PPh_3)_2$ (**9c**; 7.1 mg, 8.8 μmol) was placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with nitrogen gas at room temperature. $CDCl_3$ (0.8 mL) and anisole (1.0 μL, 9.2 μmol) as an internal standard for ^{1}H NMR analysis were added. After **9c** was dissolved, 1-(trimethylsilyl)-1-buten-3-yne (**1**; 5.1 mg, 0.041 mmol) was added. The sample tube was placed in an NMR sample probe controlled to 30.0 ± 0.1 °C. The amounts of ruthenium complexes at intervals were determined by ^{31}P{^{1}H} NMR spectroscopy: **9c** (δ 35.1 (s)), **11c** (δ 32.2 (br)), **8** (δ 31.2 (s)). At a later stage of the reaction (>70% conversion of **9c**), three singlets arising from unidentified ruthenium species were observed at δ 31.6 (br), 31.3 (s), and 30.8 (s).

Since complex **11c** could not be isolated from the above reaction system, its authentic sample was independently prepared by the reaction of $RuHCl(CO)(PPh_3)_3$ (**2**) with $Et_3SiC{\equiv}CCH{=}CHSiMe_3$. To a THF suspension (10 mL) of **2** (100 mg, 0.105 mmol) was added 1-(trimethylsilyl)-4-(triethylsilyl)-1-buten-3-yne (150 mg, 0.630 mmol). The heterogeneous mixture was stirred at room temperature, giving a homogeneous orange solution. The stirring was continued for 12 h, and then the reaction solution was concentrated to dryness by pumping. The resulting orange solid was subjected to silica gel column chromatography with use of a 1:1 mixture of CH_2Cl_2 and benzene as eluent. The orange elution band was collected and evaporated under reduced pressure to give an orange solid of **11c** (27 mg, 28% isolated yield). The complex thus obtained was stable in solution at low temperature (<0 °C) but readily decomposed at room temperature. Therefore, its elemental analysis could not be carried out. ^{1}H NMR ($CDCl_3$, −20 °C): δ 7.74−6.93 (m, 30H, Ph), 5.79 (d, J = 17.7, 1H, =C*H*), 4.97 (d, J = 17.7, 1H, =C*H*), 4.41 (s, 1H, =C*H*), 0.63 (br, 9H, Si(CH$_2$C*H*$_3$)$_3$), 0.18 (br, 6H, Si(C*H*$_2$CH$_3$)$_3$), −0.04 (s, 9H, Si(C*H*$_3$)$_3$. ^{31}P-{^{1}H} NMR ($CDCl_3$, room temperature): 32.2 (br).

Reactions of 11a and 11b with Hydrosilanes (Table 4). To an NMR sample tube containing Ru[C(=CHSiMe$_2$Ph)CH=CHSiMe$_3$]Cl(CO)(PPh$_3$)$_2$ (**11b**; 5.7 mg, 6.0 μmol) were added $CDCl_3$ (0.6 mL) and anisole (1.0 μL, 9.2 μmol) as an internal standard for NMR analysis. After **11b** was dissolved, $HSiMe_2Ph$ (16.4 mg, 0.120 mmol) was added. The color of the solution instantly changed from yellow to orange yellow. ^{1}H NMR analysis of the solution revealed the formation of **5b** and **6b** in 90 and 10% yield, respectively, as confirmed by measuring the relative peak integration of the methyl protons of anisole (δ 3.81) and the olefinic protons of **5b** (δ 4.81) and **6b** (δ 5.91). Furthermore, the ^{31}P{^{1}H} NMR analysis indicated the selective formation of **9b** (δ 33.4).

The reaction of **11b** with $HSiMe_2Ph$ in the presence of 1 equiv of added PPh_3 was similarly examined. In this case, the formation of **7b** (δ 6.02) in addition to **5b** and **6b** and the formation of **2** (δ 39.6) in addition to **9b** were confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, respectively. The reactions of **11a** with $HSiMePh_2$ in the presence and absence of free PPh_3 were similarly investigated.

Kinetic Study of the Reaction of 11b with HSiMe$_2$Ph in Benzene-d_6. Complex **11b** (4.9 mg, 6.0 μmol) was loaded to an NMR sample tube at room temperature, and the tube was capped with a rubber septum. The system was replaced with nitrogen gas, and anisole (1.0 mL, 9.2 mmol) and C_6D_6 (0.6 mL) were added by means of a syringe. After **11b** was dissolved, $HSiMe_2Ph$ (16.4 mg, 0.120 mmol) was added, and then the sample tube was placed in an NMR sample probe controlled to 30.0 ± 0.1 °C. The amounts of **11b** (δ 6.24) at intervals were determined by measuring the relative peak integration of the olefinic proton signal of **11b** at δ 6.24 and the methyl proton signal of anisole at δ 3.28 in ^{1}H NMR spectra.

Competition Reaction of 2 and 9b with 1. To an NMR sample tube containing $RuHCl(CO)(PPh_3)_3$ (**2**; 5.7 mg, 6.0 μmol) and $Ru(SiMe_2Ph)Cl(CO)(PPh_3)_2$ (**9b**; 4.9 mg, 6.0 μmol) were added $CDCl_3$ (0.6 mL) and anisole (1.0 μL, 9.2 μmol) under a nitrogen atmosphere at room temperature. After the complexes were dissolved, 1-(trimethylsilyl)-1-buten-3-yne (14.9 mg, 6.0 μmol) was added. The color of the solution instantly changed from yellow to red. ^{1}H and ^{31}P{^{1}H} NMR analysis of the solution revealed the selective formation of **8** with consumption of **2**. Complex **9b** remained unreacted.

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