Reactions of Ruthenium−Benzylidene Complexes with Bis(trimethylsilyl)ethene and Trimethylsilylstyrenes: Olefin Metathesis versus β-$SiMe_3$ Elimination/Reductive Elimination

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The benzylidene complexes $[Cl_2(PCy_3)_2Ru{=}C(C_6H_4R\text{-}p)H]$ [R = H (**1a**), Cl (**1b**), OMe (**1c**)] react with (*E*)-bis(trimethylsilyl)ethene (**2**) to give 3,3-bis(trimethylsilyl)-1-arylprop-1-ene, $H[H(SiMe_3)_2C]C{=}C(C_6H_4R\text{-}p)H$ (**3a**−**c**). Analogously, reaction of **1a** with trimethylsilylstilbene gives $H(Ph)C{=}C(SiMe_3)H$ (**4a**). In contrast, reaction of **1a** with *para*-methoxysubstituted trimethylsilylstilbene, $H(Me_3Si)C{=}C(C_6H_4OMe\text{-}p)H$ (**4b**), affords mixtures of the cross-metathesis product, $H(Me_3Si)C{=}C(Ph)H$, and various propene derivatives. Labeling experiments have been carried out. The mechanism of these reactions is discussed.

Introduction

The discovery of well-defined, functional group tolerant molybdenum[1] and ruthenium carbene complexes[2] has opened new opportunities for the application of metathesis in organic and polymer synthesis.[3] Remarkable progress has also been achieved in the chemistry of vinylsilanes. Lately, several papers on the metathetical conversion of vinylsilanes catalyzed by molybdenum−alkylidene complexes have appeared.[4]

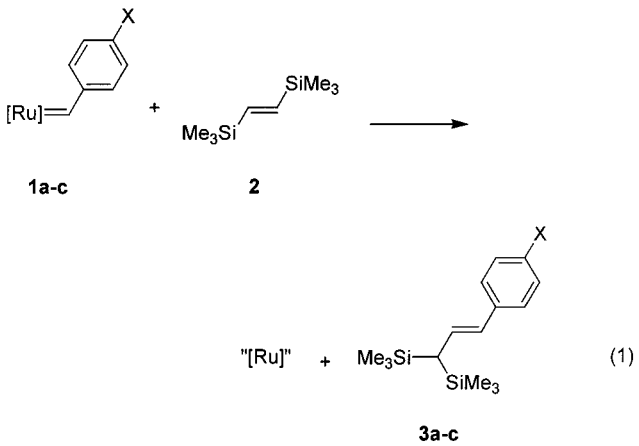
We recently reported on the highly selective cross-metathesis of styrene,[5a] substituted styrenes, alkenes, and selected allyl derivatives,[5b] $H_2C{=}C(R)H$, with several vinyl silanes, $H_2C{=}C(SiR_3)H$, to give $H(R)C{=}C(SiR_3)H$ (mostly *trans* isomer) and ethylene catalyzed by **1a**.[2,6]

Very high conversions even at room temperature were observed when R = OR′ (R′ = Et, $SiMe_3$); however, the conversion significantly decreased with increasing substitution of Me for OR′.[5a] The near inactivity of trimethyl(vinyl)silane in the cross-metathesis was explained by rapid decomposition of the ruthenacyclobutanes by β-elimination.[5a,7] A detailed analysis of the products formed in the stoichiometric reaction of **1a** and *para*-substituted derivatives thereof with trimethyl(vinyl)silane revealed considerable amounts of several allylsilanes containing the C_3 fragment of the ruthenacycle.[7]

We now present the results of studies of the stoichiometric reaction of several ruthenium−benzylidene complexes with internal Me_3Si-substituted olefins.

Results

Addition of 1 equiv of (*E*)-bis(trimethylsilyl)ethene (**2**) to solutions of $[Cl_2(PCy_3)_2Ru{=}C(Ph)H]$ (**1a**) in CD_2Cl_2 gave β-styrenylbis(trimethylsilyl)ethene (eq 1). After ca. 6 h (18 h) at room temperature slightly more than 50% (85%) of the starting compounds had been consumed. Only a single organic product (**3a**) had been formed. **3a** was identified on the basis of its spectroscopic data (MS, ^1H, ^{13}C NMR).



When CD_2Cl_2 is replaced by benzene-d_6 as the solvent, the reaction rate drops to about 50% (Table 1). Loss of

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(5) (a) Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913−917. (b) Pietraszuk, C.; Fischer, H.; Kujawa, M.; Marciniec, B. *Tetrahedron Lett.* **2001**, *42*, 1175−1178.
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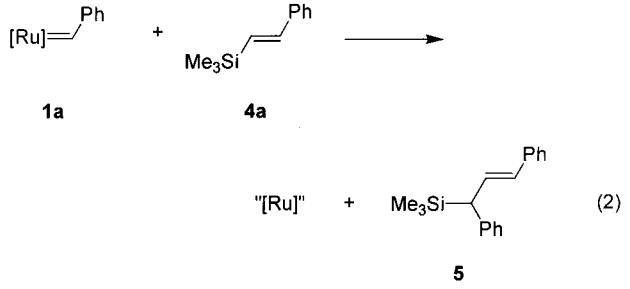
Table 1. Reaction of $[Cl_2(PCy_3)_2Ru{=}C(C_6H_4X\text{-}p)H]$ (1a−c) with (*E*)-$H(Me_3Si)C{=}C(SiMe_3)H$ (2) ([1a−c]:[2] = 1:1) at Room Temperature in CD_2Cl_2 (C_6D_6 in parentheses)

X	time [h]	conversion of **2** [%]	conversion of **1a−c** [%]	selectivity for **3a−c** [%]
H	1	11 (5)	11 (5)	100 (100)
	6	55 (35)	56 (37)	98 (99)
	18	85 (45)	88 (45)	98 (98)
Cl	1	8	8	100
	6	54	57	98
	18	80	85	98
OMe	1	4	4	100
	6	35	38	96
	18	66	70	94

one PCy_3 ligand from **1a** is presumed to initiate the reaction. This transforms **1a** into a catalytically active species. Very likely, the formation of **3a** is also initiated by PCy_3 dissociation from **1a** followed by addition of **2** to the resulting species. PCy_3 was detected in the reaction mixture. Interaction with dichloromethane may stabilize the intermediate. A related species, $[(Me_3CO)_2(PCy_3)Ru{=}C(Ph)H]$, has recently been isolated and fully characterized.[9]

The 4-chloro- and 4-methoxy-substituted benzylidene complexes **1b** and **1c** react with **2** in a similar way to afford the propene derivatives **3b** and **3c** (eq 1), respectively. Both reactions proceeded slightly slower than the reaction of **1a** with **2** (Table 1). The kinetic investigation of these reactions, performed in CD_2Cl_2 at 24 °C under pseudo-first-order conditions, revealed a ratio of reaction rates of **1a**:**1b**:**1c** = 1.31:1.15:1.

Reaction of complex **1a** with the silylstyrene **4a** afforded 1,3-diphenyl-3-(trimethylsilyl)prop-1-ene (eq 2) in very high selectivity.



The reaction proceeded considerably slower than the analogous reaction with **2**. Increasing the temperature to 50 °C led to an increase in the reaction rate but simultaneously to a decrease in the selectivity. Then, some *E*-stilbene is formed in addition to **5**. The selectivity at 50 °C also decreased with increasing reaction time (Table 2).

Substrate-independent decomposition of **1a** in addition to the reaction with **4a** may account for the reduced selectivity and for the higher conversion of **1a** compared to that of the olefin **4a**. The half-life for the thermolytic decomposition of **1a** in C_6D_6 at 55 °C was reported to be 8 days.[8] In CD_2Cl_2 the half-life is expected to be less (see above). Substituted carbenes such as **1a** were found

Table 2. Reaction of 1a with (*E*)-$H(SiMe_3)C{=}C(Ph)H$ (4a) in CD_2Cl_2 ([1a]:[4a] = 1:1)'

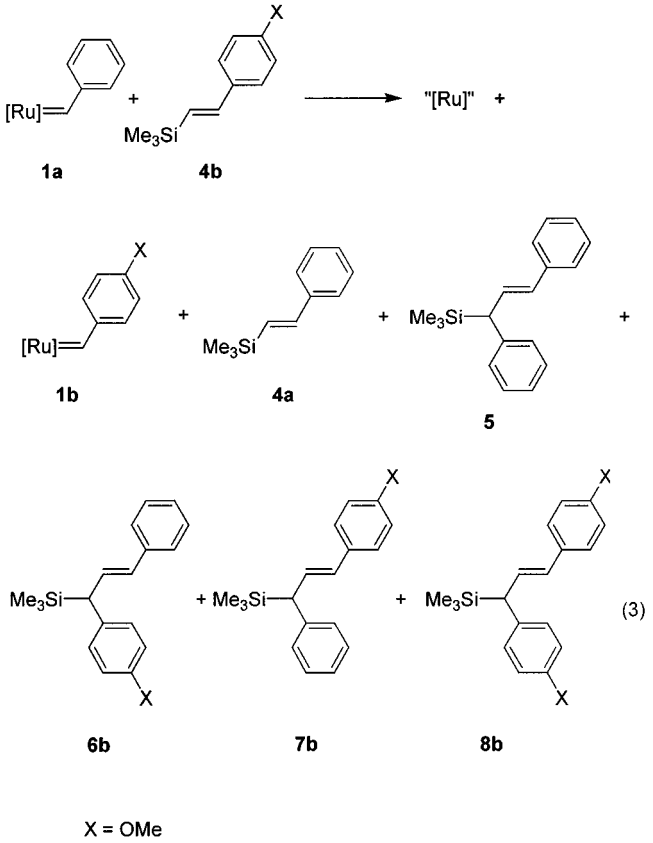
conditions	time [h]	conversion of **4a** [%]	conversion of **1a** [%]	selectivity for **5** [%]
rt	1	0	0	
	6	7	8	100
	18	21	22	100
50 °C	1	11	20	97
	6	40	58	85
	18	51	73	80

Table 3. Reaction of 1a with 4b in CD_2Cl_2 at 50 °C ([1a]:[4b] = 1:1)'

	distribution of the silyl group [%]					
time [h]	**4b**	**4a**	**5**	**6**	**7**	**8**
1	53	39	2	2	3	4
6	34	43	7	5	7	4
18	25	25	12	9	12	8

to decompose through bimolecular pathways, giving, among other compounds, the dimer of the carbene ligand.

When the substituted silylstyrene **4b** was employed instead of **4a**, a mixture of propene derivatives (**5**, **6b**−**8b**) and, in addition, considerable amounts of the olefin metathesis product **4a** (eq 3, Table 3) were formed.



Compounds **6b** and **7b** are those isomers expected from the reaction of **4b** with **1a**. The propene derivatives **5** and **8b** are secondary products derived from the reaction of the olefin metathesis products (**1b** and **4a**) with the starting compounds **1a** and **4b**. Compound **5** presumably is formed in the reaction of **1a** with **4a**, and **8b** in the reaction of **1b** with **4b**.

As expected, in the course of the reaction the combined concentration of the starting olefin and the

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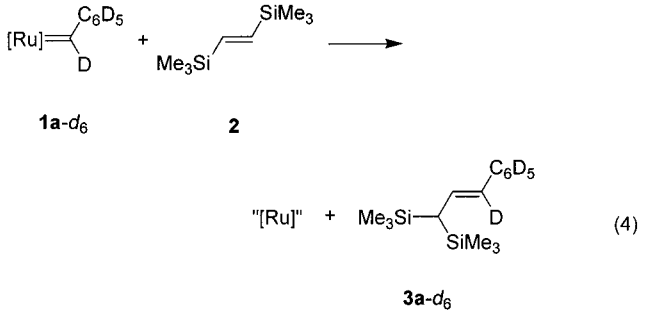
(9) Sanford, M. S.; Henling, L. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem.* **2000**, *112*, 3593−3595; *Angew. Chem., Int. Ed.* **2000**, *39*, 3451−3453.

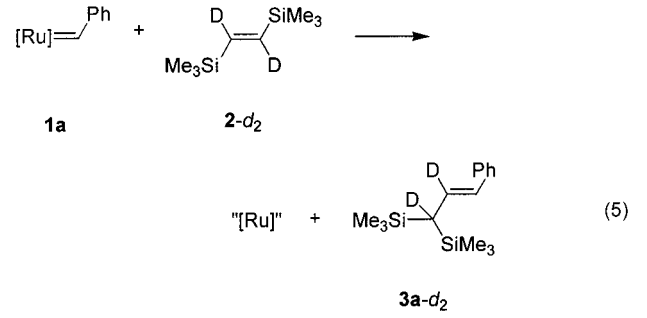
metathesis-produced olefin decreased and that of the propene derivative increased. However, the ratio of the primary (**6b** + **7b**) to the secondary propene derivatives (**5** + **8b**) remained constant. These results indicate that olefin metathesis is rapid with respect to propene derivative formation.

Labeling Studies. This conclusion was confirmed by the results of several labeling studies. When the deuterated benzylidene complex **1a**-d_6 was treated with 1 equiv of the nondeuterated (*E*)-1,2-bis(trimethylsilyl)-ethene, the deuterium label was found only at C1 of the resulting (*E*)-1-phenyl 3,3-bis(trimethylsilyl)prop-1-ene **3a**-d_6 (eq 4).



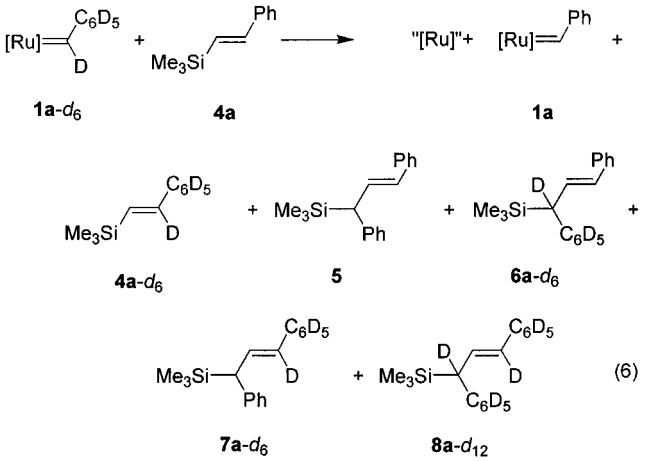
1a-d_6 **2** **3a**-d_6 (4)

Conversely, when 1,2-dideuterated (*E*)-1,2-bis(trimethylsilyl)ethene **2**-d_2 was used in the reaction with nondeuterated **1a**, the deuterium labels were found exclusively in the 2- and 3-position of **3a**-d_2 (eq 5).



1a **2**-d_2 **3a**-d_2 (5)

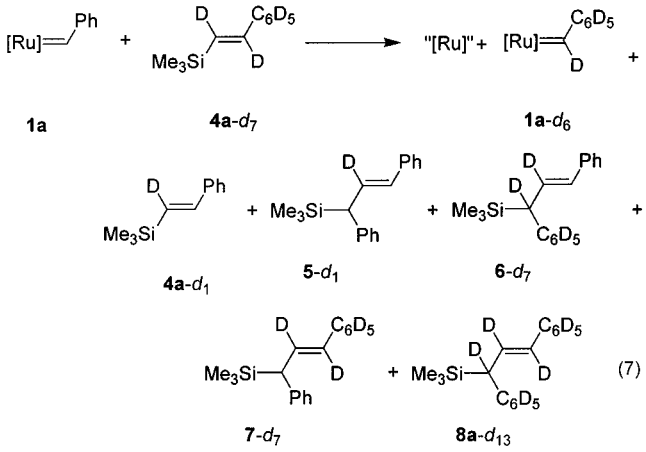
Treatment of **1a**-d_6 with nondeuterated silylstyrene **4a** gave rise to a mixture of **4a**-d_6, nondeuterated **5**, and various partially deuterated diphenylsilylpropenes (eq 6), as confirmed by ^{1}H NMR spectroscopy and GC/MS. Please note that **6a**-d_6, **7a**-d_6, and **8a**-d_{12} are isotopomers of **5**.



1a-d_6 **4a** **1a** **4a**-d_6 **5** **6a**-d_6 **7a**-d_6 **8a**-d_{12} (6)

Only the formation of **4a**-d_6 deuterated adjacent to the C_6D_5 substituent was observed. Propene derivatives deuterated in the 2-position were not detected. Although it was not possible to separate these propene derivatives by gas chromatography, the mass spectrum of the mixture of isotopomers allowed the determination of the product ratio: **5**:(**6a**-d_6 + **7a**-d_6):**8a**-d_{12} = 1:2.2:0.8. From the analysis of the integrals of the ^{1}H resonances of the hydrogen atoms in the 1- and 3-position it followed that **6a**-d_6 and **7a**-d_6 were formed in a ratio close to 1.

Finally, analysis of the product mixture obtained from **1a** and heptadeuterated **4a** (**4a**-d_7) revealed the formation of d_1-, d_7-, and d_{13}-products (eq 7).



1a **4a**-d_7 **1a**-d_6 **4a**-d_1 **5**-d_1 **6**-d_7 **7**-d_7 **8a**-d_{13} (7)

From the mass spectrum a product ratio of **5**-d_1:(**6a**-d_7 + **7a**-d_7):**8a**-d_{13} = 1:2.2:0.8 was deduced. The ^{1}H NMR spectrum indicated that the ratio of the isotopomers was again close to 1.

Discussion

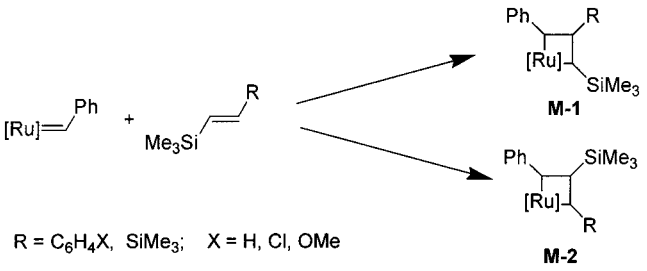
These results demonstrate that the ruthenium benzylidene complexes react with internal vinylsilanes in two different ways: (A) by mutual exchange of =C(R^1)-R^2 units (olefin metathesis) and (B) by formal transfer of the benzylidene ligand to the vinylsilane, rearrangement, and formation of silyl-substituted propene derivatives. It has been shown that reactions of these ruthenium benzylidene complexes with olefinic substrates are initiated by loss of a PR_3 ligand. Therefore, in both types of reactions of **1a**−**c** with **2** and **4a**,**b**, olefin metathesis, and propene derivative formation, the initial reaction steps are loss of a PCy_3 ligand, followed by addition of the olefin and formation of a ruthenacyclobutane. Depending on the regiochemistry of olefin addition, two isomeric metallacycles[10] are possible, **M-1** and **M-2** (Scheme 1).

By succeeding ring-opening and olefin decoordination metallacycle **M-1** can break down into either **C-1** and olefin **O-1** or **C-2** and olefin **O-2**. The analogous reaction of **M-2** affords either **C-2** and **O-2** or **C-3** and **O-3** (Scheme 2). **C-2** and **O-2** result from nonproductive olefin metathesis.

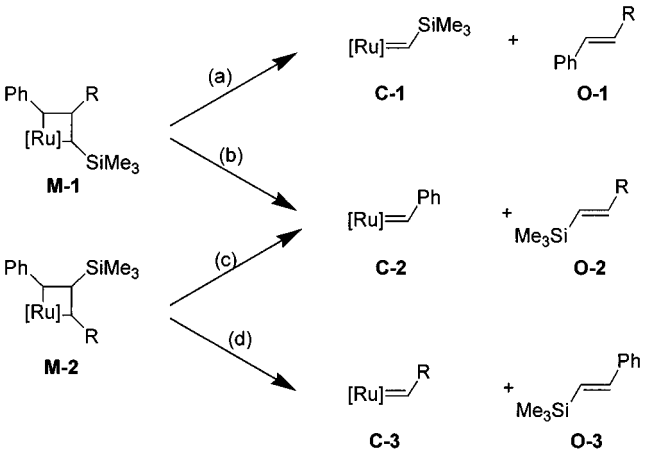
At room temperature, neither **C-1** nor **O-1** has been detected in the reaction mixture. In contrast, the metathesis products **O-3** and **C-3** are rapidly formed (eq

(10) For a review on the chemistry of metallacycles see: Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241−2290.

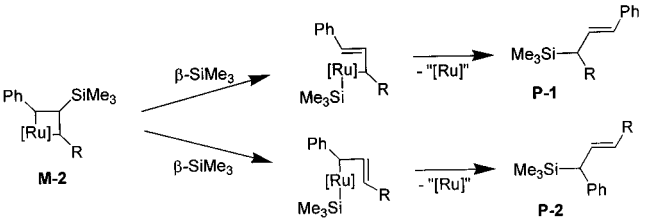
Scheme 1



Scheme 2



Scheme 3



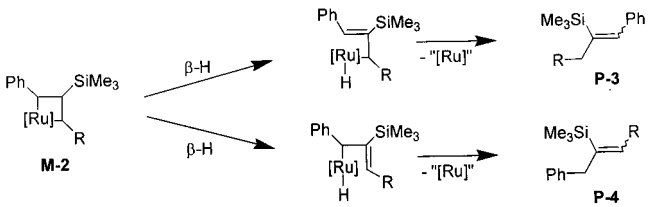
3, Table 3). Therefore either **M-1** preferentially breaks down into **C-2** and **O-2** or, more likely, olefin addition to the intermediate obtained by loss of PCy_3 from **1a** and cyclization are highly regioselective in favor of formation of metallacycle **M-2**.

The formation of the propene derivatives is readily explained by β-elimination followed by reductive elimination. The migration of SiR_3 groups is well known and was proposed to play an important role in a variety of catalytic processes in organosilicon chemistry.[11] A mechanism involving β-elimination and reductive elimination in the formation of the propene derivatives is also supported by the results of the labeling experiments. Thus, β-$SiMe_3$ migration in **M-2** and reductive elimination afford **P-1** and **P-2** (Scheme 3).

Migration of the β-H atom in **M-2** and subsequent reductive elimination would give rise to the propene derivatives **P-3** and **P-4** (Scheme 4).[12]

However, propene derivatives carrying a Me_3Si group in the β-position such as **P-3** or **P-4** have not been

Scheme 4



observed. Analogously, products derived from β-H elimination in **M-1** have likewise not been detected. Obviously, β-H elimination is strongly disfavored compared to β-$SiMe_3$ elimination.

Elimination of the β-R group in **M-1** followed by reductive elimination leads to **P-1** and **P-5** (Scheme 5).

Whereas propene derivatives **P-1** have been detected in the reaction mixtures (e.g., **6b**, eq 3), **P-5** has not been observed. However, **P-1** is also the product of β-$SiMe_3$ elimination in **M-2** and reductive elimination (Scheme 3). Since both $SiMe_3$ elimination products, **P-1** (**6b**) and **P-2** (**7b**), are formed in nearly equal amounts, we would expect that **P-1** and **P-5** likewise should be formed in equal amounts or, at least, **P-5** should be detectable. From the failure to observe propene derivative **P-5** in the reactions in eqs 3 and 7 we conclude that **P-1** is derived from **M-2**.

From the high selectivity of the product formation in the reaction of **1a** with (*E*)-bis(trimethylsilyl)ethene (**2**) (eq 1) it follows that a breakdown of the metallacycle **M-3** (Scheme 6) to form [Ru]=C($SiMe_3$)H species and H(Ph)C=C($SiMe_3$)H is strongly disfavored. In fact, in none of the reactions (eqs 1−7) have [Ru]=C($SiMe_3$)H species been detected. Furthermore, β-$SiMe_3$ migration and ring-opening are highly selective. There is a pronounced preference for the pathway **M-3** → **C-4** → **3a** as compared to **M-3** → **C-5** → **9** (Scheme 6).

From the results of the reactions in eqs 1−3 and from the labeling experiments several conclusions can be drawn:

(1) The reactivity of the olefins toward the benzylidene complexes considerably decreases in the series **2** > **4a**,**b** > propene derivatives. Thus, in the course of the reactions the propene derivatives accumulate.

(2) There is a strong preference for the formation of metallacycles of type **M-2** compared to **M-1**. In fact, all products can be traced to **M-2**.

(3) Olefin metathesis is considerably faster than the formation of the propene derivatives.

(4) The formation of propene derivatives is readily explained by β-$SiMe_3$ elimination followed by reductive elimination. Migration of a β-aryl group is very unlikely. There is no indication for a β-H elimination.

(5) The selectivity of β-$SiMe_3$ elimination and reductive elimination strongly depends on the substituents.

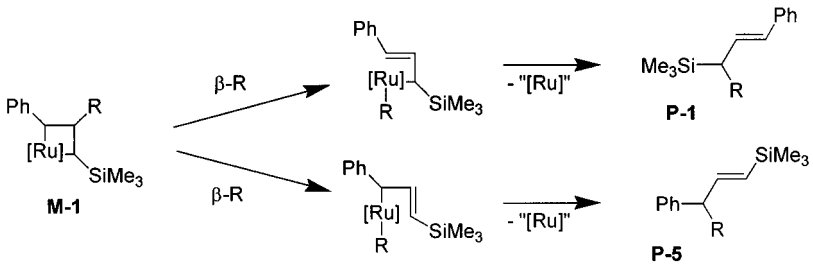
Experimental Section

Materials and Methods. Unless mentioned otherwise, all operations were performed by using standard Schlenk tech-

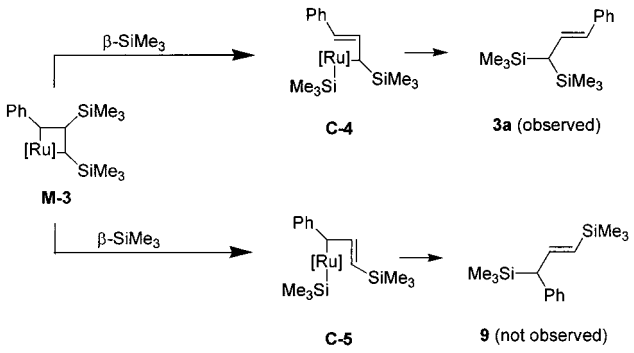
(11) See for example: (a) Seki, Y.; Takeshita, K.; Kawamoto, K. *J. Organomet. Chem.* **1989**, *369*, 117−123. (b) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703−704. (c) Marciniec, B. *New J. Chem.* **1997**, *21*, 815−824. (d) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320−4326. (e) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Organometallics* **1999**, *18*, 2033−2036.

(12) For β-H elimination decomposition pathways see for example: (a) Leconte, M.; Basset, J. M.; Quignard, F.; Larroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, pp 371−420. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, pp 532−536.

Scheme 5



Scheme 6



niques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM250 at 250 and 62.9 MHz, respectively, or on a Varian Gemini and Mercury 300 at 300 and 75.46 MHz. ^{2}H NMR spectra were recorded on a JEOL JNM-GX400 at 61 MHz. All spectra were recorded at room temperature. Chemical shifts are reported im ppm relative to the residual solvent peak. The GC/MS analyses were performed on a HP 6890 gas chromatograph (HP-5MS 30m capillary column) equipped with a HP 5973 mass selective detector or AMD 604/402. GC analyses were carried out on a Carlo Erba GC 6000 Series 2 (FS-OV-101 25m capillary column) equipped with an FID. Chemicals were obtained from the following sources: $[Cl_2(PCy_3)_2Ru{=}C(Ph)H]$ (**1a**) from ABCR, benzene and styrene from Riedel-de Haen, benzene-d_6 from Deutero GmbH, anthracene and styrene-d_8 from Aldrich. $[Cl_2(PCy_3)_2Ru{=}C(Me)H]$,[13] $H(Me_3Si)C{=}C(SiMe_3)H$ (**2**),[14] and $H(Me_3Si)C{=}C(Ph)H$ (**4a**),[11d] were prepared by published methods. All liquid reagents were dried with molecular sieves and degassed by repeated freeze−pump−thaw cycles. Benzene-d_6 was dried and distilled over CaH_2 under a dry argon atmosphere prior to use. Due to insufficient materials from TLC separation of mixtures, some compounds were analyzed by ^{1}H NMR spectroscopy (**4a**-d_7 and **6a**-d_6) or by ^{1}H NMR and mass spectroscopy only (**3a**-d_2 and **3a**-d_6).

$[Cl_2(PCy_3)_2Ru{=}C(C_6H_4Cl$-*p*$)H]$ (1b). 4-Chlorostyrene (0.084 mL, 6.57×10^{-4} mol) was added to a solution of $[Cl_2(PCy_3)_2Ru{=}C(Me)H]$ (0.1 g, 1.31×10^{-4} mol) in 3 mL of benzene. The mixture was stirred at room temperature for 3 h. Then benzene was removed in vacuo. The residue was treated with 3 mL of methanol and then filtered, washed with methanol, and dried in vacuo. Yield: 0.029 g (26%). All spectroscopic data agree with those published in the literature.[2]

$[Cl_2(PCy_3)_2Ru{=}C(C_6H_4OMe$-*p*$)H]$ (1c)[2] and $[Cl_2(PCy_3)_2Ru{=}C(C_6D_5)D]$ (1a-d_6) were prepared in a similar manner.

$H(Me_3Si)C{=}C(C_6H_4OMe$-*p*$)H$ (4b).[15] In a 20 mL glass ampule $[RuHCl(CO)(PPh_3)_3]$ (0.019 g, 2.0×10^{-5} mol) was dissolved in 0.3 mL of benzene. Then vinyltrimethylsilane (0.3 mL, 0.002 mol) and 4-methoxystyrene (1.34 mL, 0.01 mol) were added. The ampule was sealed in air and heated at 100 °C for 24 h. The product was isolated by distillation (71−74 °C/0.6 mmHg) and recrystalized from methanol. Yield (after recryst): 0.19 g (44%, based on vinyltrimethylsilane); ^{1}H NMR (CD_2Cl_2, ppm) δ 0.20 (s, 9 H, $SiMe_3$), 3.29 (s, 3 H, OMe), 6.39 (d, 1 H, J = 19.1 Hz, $=C(H)SiMe_3$), 6.78 (d, 2 H, J = 18.9 Hz, $=C(H)C_6H_4OMe$), 6.98 (d, 1 H, J = 19.1 Hz, Ph), 7.32 (d, 2 H, J = 8.8 Hz, Ph); ^{13}C NMR (C_6D_6, ppm) δ 0.8 ($SiMe_3$), 54.9 (OMe), 114.3 (Ph), 126.3 (=CH), 128.1, 131.8 (Ph), 144.0 (=*C*Ph), 160,2 (Ph); MS *m*/*z* (%) 206 (M^+, 52), 191 (100), 175 (32), 165 (39), 161 (6), 151 (5), 145 (6), 135 (5), 115 (3), 105 (2), 95 (4), 89 (5), 73 (5), 59 (16).

$D(Me_3Si)C{=}C(C_6D_5)D$ (4a-d_7) was prepared analogously to **4a**,[11d] but starting from styrene-d_8 and $D(Me_3Si)C{=}CD_2$: ^{1}H NMR (C_6D_6, ppm) δ 0.19 (Me); ^{2}H NMR (C_6H_6, ppm) δ 6.47 [$=C(D)SiMe_3$], 6.94 [$=C(D)C_6D_5$]; ^{13}C NMR ($CDCl_3$, ppm) δ −1.3 (Me), 125.9, 127.4, 128.0 (Ph), 129.0 (=CSi), 138.2 (Ph), 143.2 (=*C*Ph); MS *m*/*z* (%) 183 (M^+, 35), 168 (100), 151 (32), 151 (32), 140 (27), 110 (7), 84 (4), 73 (4), 60 (27).

$D(Me_3Si)C{=}C(SiMe_3)D$ (2-d_2) was prepared according to the literature procedure for the nondeuterated analogue **2**[14] by using $D(Me_3Si)C{=}CD_2$ instead of $H(Me_3Si)C{=}CH_2$ as a substrate: ^{1}H NMR ($CDCl_3$, ppm) δ 0.06 (Me); ^{2}H NMR (C_6H_6, ppm) δ 6.80 (=CD); ^{13}C NMR ($CDCl_3$, ppm) δ −1.6 ($SiMe_3$), 150.2 (J_{CD} = 20.7 Hz, =CD); MS *m*/*z* (%) 174 (M^+, 19), 159 (37), 143 (2), 101 (18), 84 (5), 73 (100).

Stoichiometric Reactions. All stoichiometric reactions were performed in NMR tubes and controlled by ^{1}H NMR spectroscopy. In a typical procedure $[Cl_2(PCy_3)_2Ru{=}C(Ph)H]$ (0.01 g, 1.21×10^{-5} mol) and anthracene (internal standard) were dissolved in 0.65 mL of C_6D_6. Then 1.21×10^{-5} mol of the corresponding olefin was added by syringe. The NMR spectra of the reaction mixture were measured immediately after the reagents had been mixed as well as 1 h, 6 h, and 18 h later. Conversions and selectivities were calculated using the internal standard method.[16]

$H[H(Me_3Si)_2C]C{=}C(Ph)H$ (3a). Compound **3a** was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.63), colorless liquid. Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.07 (s, 18 H, $SiMe_3$), 1.10 (dd, 1 H, J = 9.7, 1.3 Hz, C*H*$SiMe_3$), 6.14−6.21 (m, 2 H, C*H*=C*H*), 7.00−7.30 (m, 5 H, Ph); ^{13}C NMR (C_6D_6, ppm) δ −0.3 ($SiMe_3$), 26.7 (*C*$SiMe_3$); 128.8 (=CH), 129.6 (=*C*Ph); 125.8, 126.4, 128.5 (Ph); MS *m*/*z* (%) 262 (M^+, 28), 247 (12), 174 (65), 159 (82), 145 (7), 131 (9), 115 (3), 105 (4), 73 (100), 59 (14).

$H[H(Me_3Si)_2C]C{=}C(C_6H_4Cl$-*p*$)H$ (3b). Compound **3b** was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.60). Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.07 (s, 18 H, $SiMe_3$); 1.07 (d, 1 H, J = 11.2 Hz, C*H*$SiMe_3$), 5.93−6.12 (m, 2 H, =CH), 6.97 (m, 2 H, J = 8.4 Hz, C_6H_4), 7.12 (d, 2 H, J = 8.4 Hz, C_6H_4); ^{13}C NMR (C_6D_6, ppm) δ 0.4 ($SiMe_3$), 27.5 (*C*$SiMe_3$), 127.8 (=CH), 131.1 (=*C*Ph), 127.4, 129.4, 132.3, 137.9 (Ph); MS *m*/*z* (%) 296 (M^+, 12), 281 (5), 208

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(17), 193 (11), 173 (15), 145 (6), 115 (2), 93 (3), 73 (100), 59 (7); mass calcd for $C_{15}H_{25}Si_2{}^{35}Cl$, 296.11835; determined, 296.11901.

H[H(Me$_3$Si)$_2$C]C=C(C$_6$H$_4$OMe-*p*)H (3c). Compound **3c** was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.33). Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.11 (s, 18 H, $SiMe_3$), 1.12 (d, 1 H, J = 11.0 Hz, $CHSiMe_3$), 3.33 (s, 3 H, MeO), 6.01−6.23 (m, 2 H, =CH), 6.80 (d, 2 H, J = 8.6 Hz, C_6H_4), 7.23 (d, 2 H, J = 8.6 Hz, C_6H_4); ^{13}C NMR (C_6D_6, ppm) δ −0.2 ($SiMe_3$), 26.3 (*C*$SiMe_3$); 54.8 (OMe), 126.9 (=CH), 130.8 (=*C*Ph); 114.4, 126.9, 132.0, 159.0 (Ph); MS *m*/*z* (%) 292 (M^+, 20), 277 (32), 204 (8), 189 (65), 165 (4), 159 (3), 145 (3), 131 (3), 115 (5), 73 (100), 59 (9); mass calcd for $C_{16}H_{28}Si_2O$, 292.16739; determined, 292.16788.

H[H(Me$_3$Si)$_2$C]C=C(C$_6$D$_5$)D (3a-*d*$_6$). Compound **3a**-d_6 was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.63). Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.08 (s, 9 H, $SiMe_3$), 1.25 (d, 1 H, J = 11.9 Hz, $CHSiMe_3$), 6.18 (d of broad peaks, 1 H, J = 12.2 Hz, =CH); MS *m*/*z* (%) 268 (M^+, 28), 253 (11), 180 (61), 165 (46), 150 (3), 140 (4), 73 (100), 59 (10).

D[D(Me$_3$Si)$_2$C]C=C(Ph)H (3a-*d*$_2$). Compound **3a**-d_2 was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.63). Spectroscopic data: ^{1}H NMR ($CDCl_3$, ppm) δ 0.07 (s, 9 H, $SiMe_3$), 6.13 (s, broad peak, 1 H, =CH), 7.1−7.3 (m, 5 H, Ph); MS *m*/*z* (%) 264 (M^+, 25), 249 (11), 176 (59), 161 (76), 146 (5), 135 (6), 73 (100), 59 (8).

H[H(Ph)(Me$_3$Si)C]C=C(Ph)H (5). Compound **5** was isolated from the reaction mixture by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.55), colorless liquid. Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ −0.04 (s, 9 H, $SiMe_3$), 2.99 (d, 1 H, J = 9.8 Hz, C*H*($SiMe_3$)Ph), 6.33 (d, 1 H, J = 15.0 Hz, =CHPh), 6.61 (dd, 1 H, J = 9.5, 15 Hz, =CH), 7.0−7.4 (m, 10 H, Ph); MS *m*/*z* (%) 266 (M^+, 25), 251 (1), 193 (5), 191 (5), 178 (6), 173 (3), 165 (4), 145 (2), 135 (5), 115 (16), 91 (7), 73 (100). All spectroscopic data agree well with those reported in ref 17.

H[H(C$_6$H$_4$OMe-*p*)(Me$_3$Si)C]C=C(Ph)H (6b) and H[H(Ph)(Me$_3$Si)C]C=C(C$_6$H$_4$OMe-*p*)H (7b). A mixture of compounds **6b** and **7b** was prepared by the reaction of **1b** with **4** (CH_2Cl_2, 50 °C, 24 h) and isolated by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.47). (**6b**) Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.08 (s, 9 H, $SiMe_3$), 3.10 (d, 1 H, J = 10.0 Hz, C*H*($SiMe_3$)), 3.78 (s, 3H, OMe); 6.31 (d, 1 H, J = 15.5 Hz, =CHPh), 6.45 (dd, 1 H, J = 15.5, 10.0 Hz, =CH), 6.82 (d, 2H, J = 8.5 Hz, Ph); 7.15 (d, 2H, J = 8.5, Ph); 7.10−7.40 (m, 4H, Ph); MS *m*/*z* (%) 296 (M^+, 6), 281 (100), 223 (13), 203 (7), 191(6), 178 (7), 165 (7), 145 (8), 115 (23), 91 (5), 73 (49); mass calcd for $C_{19}H_{24}OSi$: 296.15964; determined, 296.16002. (**7b**) Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.01 (s, 9 H, $SiMe_3$), 3.07 (d, 1 H, J = 9.9 Hz, C*H*($SiMe_3$)), 3.77 (s, 3H, OMe); 6.34 (d, 1 H, J = 16.0 Hz, =CHPh), 6.56 (dd, 1 H, J = 16.0, 9.9 Hz, =CH), 6.83 (d, 2H, J = 8.6 Hz, Ph); 7.07 (d, 2H, J = 8.6, Ph); 7.10−7.40 (m, 4H, Ph); MS *m*/*z* (%) 296 (M^+, 5), 281 (100), 223 (13), 203 (7), 191(6), 178 (7), 165 (7), 145 (8), 115 (24), 91 (6), 73 (51); mass calcd for $C_{19}H_{24}OSi$, 296.15964; determined, 296.15998.

H[H(C$_6$H$_4$OMe-*p*)(Me$_3$Si)C]C=C(C$_6$H$_4$OMe-*p*)H (8b). Compound **8b** was prepared from the reaction of **1c** with **4b** (CH_2Cl_2, 50 °C, 24 h) and isolated by TLC (silica, hexane/CH_2Cl_2, 1:1, R_f = 0.20). Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) δ 0.08 (s, 9 H, $SiMe_3$), 3.03 (d, 1 H, J = 9.6 Hz, C*H*($SiMe_3$)), 3.77 (s, 3H, OMe); 6.28 (d, 1 H, J = 15.7 Hz, =CHPh), 6.40 (dd, 1 H, J = 9.6, 15.7 Hz, =CH), 6.80−6.86 (m, 4H, Ph); 7.06 (d, 2H, J = 8.6 Hz, Ph); 7.28 (d, 2H, J = 8.6 Hz, Ph); ^{13}C NMR ($CDCl_3$, ppm) δ −1.1 ($SiMe_3$), 42.7 (*C*$SiMe_3$); 56.2 (OMe), 129.0 (=CH), 132.5 (=*C*HCH); 126.8, 127.9, 128.2, 128.3 (Ph); MS *m*/*z* (%) 326 (M^+, 3), 311 (100), 253 (22), 203 (9), 178 (5), 165 (3), 165 (7), 121 (8), 115 (4), 73 (26); mass calcd for $C_{20}H_{26}O_2Si$, 326.17020; determined, 326.17071.

Reaction of 1a-*d*$_6$ with 4a. In an NMR tube 0.0052 g (6.25 × 10^{-6} mol) of **1a**-d_6 was dissolved in 0.7 mL of C_6D_6. Then 0.0011 g (6.25 × 10^{-6} mol) of **4a** was added. The tube was sealed and placed in a heating chamber at 50 °C for 6 h. Then the ^{1}H NMR spectrum of the reaction mixture was recorded.

6a-*d*$_6$ + 7a-*d*$_6$: ^{1}H NMR (C_6D_6, ppm) δ −0.04 s ($SiMe_3$, **6a**-d_6 + **7a**-d_6), 2.99 (d, J = 9.8 Hz, CHSi, **7a**-d_6), 6.32 (d, br, J = 15 Hz, =C*H*Ph, **6a**-d_6), 6.60 (2 d, J = 9.8 and 15 Hz, =CH, **6a**-d_6 + **7a**-d_6), 7.0−7.4 (m, Ph, **6a**-d_6 + **7a**-d_6).

Reaction of 1a with 4a-*d*$_7$. The reaction was carried out analogously to that of **1a**-d_6 with **4a**.

6a-*d*$_7$ + 7a-*d*$_7$: ^{1}H NMR (C_6D_6, ppm) δ −0.04 s ($SiMe_3$, **6a**-d_7 + **7a**-d_7), 2.99 (s, CHSi, **7a**-d_7), 6.32 (s, br, =CHPh, **6a**-d_7), 7.0−7.4 (m, Ph, **6a**-d_7 + **7a**-d_7).

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Supporting Information Available: ^{1}H NMR spectra of **2**-d_2, **3a**-d_2, **3a**-d_6, **3b**, **3c**, **4a**-d_7, **4b**, **6a**, **6a**-d_6/**7a**-d_6, and **6a**-d_7/**7a**-d_7 as well as ^{13}C NMR spectra of **2**-d_2, **3b**, **3c**, **4a**-d_7, and **4b**. The material is available free of charge via the Internet at http://pubs.acs.org.

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