

# Cross-Metathesis of Vinylsilanes with Styrene Catalyzed by Ruthenium–Carbene Complexes

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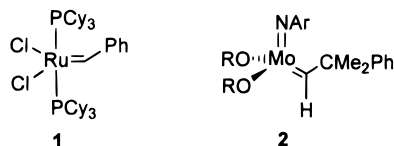
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The cross-metathesis of styrene with various vinylsilanes,  $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiR}_3$ , catalyzed by  $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$  (**1**) to give (*E*)-silylstyrene, (*E*)- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{SiR}_3$ , and ethylene is reported. The reaction proceeds even at room temperature and is highly selective. Very high conversions are observed when  $\text{R} = \text{OEt}$ ,  $\text{OSiMe}_3$  ( $\geq 95\%$ , 6 h, 2 mol % of **1**). The conversion significantly decreases with increasing substitution of Me for OR'. The metathesis is reversible. Therefore, removal of ethylene is critical for achieving high conversions. From the study of stoichiometric reactions of **1** with vinylsilanes it follows that in the series  $\text{SiR}_3 = \text{Si}(\text{OEt})_3$ ,  $\text{SiMe}(\text{OEt})_2$ ,  $\text{SiMe}_2\text{OEt}$ ,  $\text{SiMe}_3$  and  $\text{SiR}_3 = \text{Si}(\text{OSiMe}_3)_3$ ,  $\text{SiMe}(\text{OSiMe}_3)_2$ ,  $\text{SiMe}_2(\text{OSiMe}_3)$ ,  $\text{SiMe}_3$  the conversion rate increases, but simultaneously the selectivity of the metathesis decreases. The decreasing selectivity readily accounts for the decreasing efficiency in the catalytic metathesis. The product distribution of reactions of styrene-*d*<sub>8</sub> with  $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiR}_3$  ( $\text{R} = \text{OEt}$ ,  $\text{OSiMe}_3$ ) in the presence of **1** provides evidence for a metallacarbene mechanism involving  $[\text{Ru}]=\text{CHPh}$  and  $[\text{Ru}]=\text{CH}_2$  species.

## Introduction

Olefin metathesis such as ring-opening metathesis polymerization (ROMP) and the cross-metathesis of simple olefins catalyzed by carbene complex species of molybdenum, tungsten, or ruthenium has been known and utilized for a long time.<sup>1</sup> However, only recently have well-defined, functional-group-tolerant transition-metal carbene complexes such as **1**<sup>2</sup> and **2**<sup>3</sup> become available that efficiently catalyze ring-closing metathesis (RCM) and acyclic diene metathesis (ADMET) polymerization.



There are numerous accounts for ring-closing metathesis leading to carbo- and heterocycles catalyzed by complexes **1** and **2**.<sup>1c,4</sup> Even strained rings and macro-

cycles are accessible by RCM. Complexes of type **2** have also successfully been used as catalysts for the ADMET polymerization of 1,5-hexadiene and 1,9-decadiene.<sup>5</sup> The selective cross-metathesis of monosubstituted olefins catalyzed by **1** or **2** for the synthesis of different unsymmetrically substituted functionalized olefins has also been described.<sup>6–12</sup> Early examples include the selective cross-metathesis of olefins such as styrene,<sup>6</sup> acrylonitrile,<sup>7</sup> and allyltrimethylsilane,<sup>8,9</sup> with various olefins catalyzed by the molybdenum complex **2**. Recently, the ruthenium complex **1** has been employed as well.<sup>9–13</sup>

Although many metallacarbenes catalyze the metathesis of silicon-containing olefins, they are inactive in the metathesis of vinyl-substituted silanes and siloxanes.<sup>3b,14</sup> Studies using the classical heterogeneous systems  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  gave very poor results for vinyl-substituted silanes.<sup>15</sup> Only recently have the cross-metathesis of vinyl-substituted silsesquioxanes with alkenes,<sup>16</sup> the

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(1) For recent reviews see: (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997. (b) *Alkene Metathesis in Organic Synthesis*; Fuerstner, A., Ed.; Springer: Berlin, 1998. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413.

(2) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem.* **1995**, *107*, 2179; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(3) (a) Schrock, R. R.; Muzdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (b) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

(4) See e.g.: (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; Fuerstner, A., Ed.; Springer: Berlin, 1998; p 1.

(5) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649.

(6) Crowe, W. E.; Zhang, Z. J. *J. Am. Chem. Soc.* **1993**, *115*, 10998.

(7) Crowe, W. E.; Goldberg, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 5162.

(8) Crowe, W. E.; Goldberg, D. R.; Zhang, Z. J. *Tetrahedron Lett.* **1996**, *37*, 2117.

(9) Bruemmer, O.; Rueckert, A.; Blechert, S. *Chem. Eur. J.* **1997**, *3*, 441.

(10) Feng, J.; Schuster, M.; Blechert, S. *Synlett* **1997**, 129.

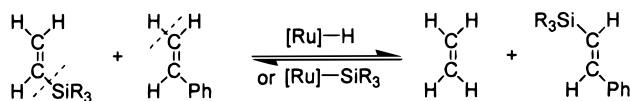
(11) Blanco, O. M.; Castedo, L. *Synlett* **1999**, 557.

(12) Roy, R.; Dominique, R.; Das, S. K. *J. Org. Chem.* **1999**, *64*, 5408.

(13) Gibson (née Thomas), S. E.; Gibson, V. C.; Keen, S. P. *Chem. Commun.* **1997**, 1107.

(14) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Devan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krueger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

Scheme 1



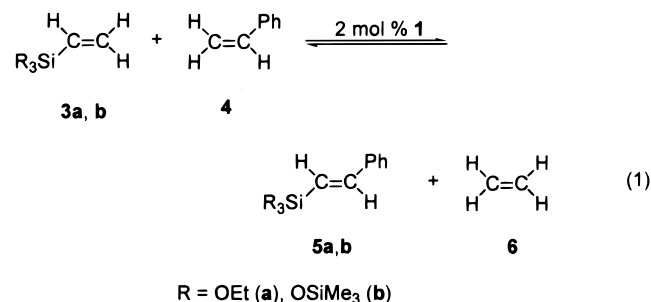
ADMET copolymerization of divinyl dimethylsilane with dienes,<sup>17</sup> and the RCM of acyclic silyl ether dienes<sup>18</sup> been reported.

A variety of ruthenium complexes (involving or generating Ru–H and Ru–Si bonds) were observed to induce the disproportionation of vinylsilanes and siloxanes and their cross-disproportionation (*trans*-silylation) with olefins (e.g., styrene) (Scheme 1) in the temperature range 60–110 °C. On the basis of a detailed study of the reactions a nonmetallacarbene mechanism proceeding through the cleavage of the =C–Si bond of the vinylsilane and the =C–H bond of the olefin was suggested.<sup>19</sup>

We now report on the highly selective cross-metathesis of vinylsilanes (vinylsiloxanes) with styrene proceeding under very mild conditions even at room temperature and provide evidence for a metallacarbene mechanism of these reactions that are catalyzed by **1**.

## Results

**Catalytic Examinations.** Treatment of a 1:1 mixture of the vinylsilanes H<sub>2</sub>C=C(H)SiR<sub>3</sub> (R = OEt (**3a**), OSiMe<sub>3</sub> (**3b**)) and styrene in benzene with 2 mol % of the ruthenium complex **1** gave rise to evolution of ethylene and formation of silylstyrenes **5a,b**, respectively (eq 1).



When the evolving ethylene was removed by a gentle stream of argon, the conversion of the vinylsilanes and styrene into **5a,b** and **6** was almost quantitative after 6 h at room temperature. The cross-metathesis was highly selective. Only the *E* isomer of **5a,b** was detected by <sup>1</sup>H NMR spectroscopy. Without purging with argon, the conversion of **3a** and **4** into **5a** and **6** dropped from 95 to 70%. When the metathesis was carried out in a closed system, applying otherwise analogous conditions, the conversion of vinyltriethoxysilane and styrene stopped after approximately 17% conversion. Conversely, applying a 10-fold excess of styrene **4** and

Table 1. Cross-Metathesis of Vinylsilanes with Styrene<sup>a</sup>

entry	SiR <sub>3</sub>	conversion (%) of H <sub>2</sub> C=C(H)SiR <sub>3</sub>	selectivity <sup>b</sup> (%) for Ph(H)C=C(H)SiR <sub>3</sub>
1	Si(OEt) <sub>3</sub>	17 <sup>c</sup>	96
2	Si(OEt) <sub>3</sub>	78	95
3	Si(OEt) <sub>3</sub>	95 <sup>d</sup>	95
4	Si(OEt) <sub>3</sub>	100 <sup>d,e</sup>	87 <sup>f</sup>
5	Si(OMe) <sub>3</sub>	76 <sup>d</sup>	95
6	Si(OSiMe <sub>3</sub> ) <sub>3</sub>	95 <sup>d</sup>	95
7	SiMe(OSiMe <sub>3</sub> ) <sub>2</sub>	15 <sup>d</sup>	95
8	SiMe <sub>2</sub> (OSiMe <sub>3</sub> )	5 <sup>d</sup>	<i>g</i>
9	SiMe(OEt) <sub>2</sub>	10 <sup>d</sup>	95
10	SiMe <sub>2</sub> (OEt)	3 <sup>d</sup>	<i>g</i>
11	SiMe <sub>3</sub>	<3	<i>g</i>

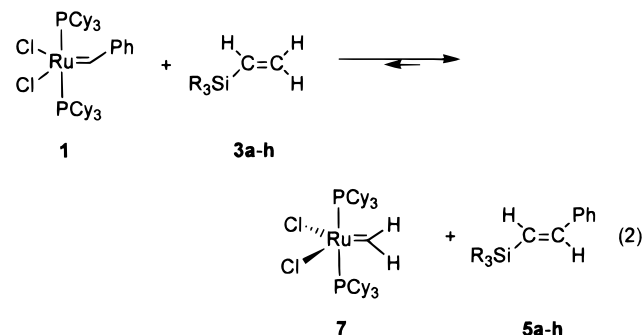
<sup>a</sup> [H<sub>2</sub>C=C(H)SiR<sub>3</sub>]:[H<sub>2</sub>C=C(H)Ph]:[**1**] = 1:1:(2 × 10<sup>-2</sup>), 6 h, benzene, room temperature. <sup>b</sup> Only the *E* isomer was detected by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Reaction performed in a closed system. <sup>d</sup> Ethylene was removed by a gentle argon flow. <sup>e</sup> 10-fold excess of styrene. <sup>f</sup> 9% (*E*)-stilbene. <sup>g</sup> The selectivity could not be determined, due to the low conversion.

purging the solution with argon led to complete conversion of **3a**; however, in addition to **5a** and **6**, 9% of the self-metathesis product of **4**, (*E*)-stilbene, was formed.

Removing ethylene was crucial for the efficiency of the reaction (Table 1, entries 1–4). Obviously, the cross-metathesis is reversible. The conclusion agrees well with earlier observations by Grubbs et al., who reported quantitative conversion of **1** into [Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru=CH<sub>2</sub>] by reaction with excess ethylene.<sup>2a</sup> No reaction was observed when 10 equiv of PCy<sub>3</sub> was added to the reaction mixture, indicating that dissociation of PCy<sub>3</sub> from **1** in a preequilibrium is essential for the catalysis.

Stepwise substitution of Me for OEt in **3a** or OSiMe<sub>3</sub> in **3b** considerably reduced the conversion (Table 1, entries 3, 9–11 and 6–8, 11) but did not significantly influence the selectivity of the catalysis. The effect on **3a** was slightly more pronounced than that on **3b**. In all catalytic experiments, usually traces of EtSiR<sub>3</sub> and SiR<sub>4</sub> as byproducts were detected by GC/MS.

**Stoichiometric Examinations.** To obtain additional information on the individual reaction steps of the catalytic cycle, the stoichiometric reactions of **1** with various vinylsilanes (eq 2) as well as the reactions of the methyldiene complex **7** with different olefins were also examined.



When equimolar amounts of **1** and **3a** or **3b** were mixed in benzene at room temperature (*c* = 0.012 mol/L

(15) (a) See for example: Finkelshtein, E. Sh.; Ushakov, N. V.; Portnykh, E. B. *J. Mol. Catal.* **1992**, *76*, 133. (b) Recently this subject was reexamined. See: Kawai, T.; Shiga, K.; Suzuki, T.; Iyoda, T. *J. Mol. Catal. A: Chem.* **1999**, *140*, 287.

(16) Feher, F. J.; Soulivong, D.; Eklund, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185.

(17) Wagener, K. B.; Smith, D. W., Jr. *Macromolecules* **1991**, *24*, 2649.

(18) Chang, S.; Grubbs, R. H. *Tetrahedron Lett.* **1997**, *38*, 4757.

(19) Marciniak, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320.

**Table 2. Metathesis of 1 with Vinylsilanes<sup>a</sup>**

entry	SiR <sub>3</sub>	conversion (%)		selectivity (%) <sup>b</sup> Ph(H)C=C(H)SiR <sub>3</sub> {H <sub>2</sub> C=C(H)Ph}
		H <sub>2</sub> C=C(H)SiR <sub>3</sub>	1	
1	Si(OEt) <sub>3</sub>	55	57	95 {5}
2	Si(OEt) <sub>3</sub> <sup>c</sup>		100	100
3	Si(OSiMe <sub>3</sub> ) <sub>3</sub>	55	55	100
4	Si(OMe) <sub>3</sub>	65	65	95 {5}
5	SiMe(OEt) <sub>2</sub>	70	70	65 {10}
6	SiMe <sub>2</sub> (OEt)	69	70	35 {7}
7	SiMe(OSiMe <sub>3</sub> ) <sub>2</sub>	75	71	75 {7}
8	SiMe <sub>2</sub> (OSiMe <sub>3</sub> )	93	75	32 {8}
9	SiMe <sub>3</sub>	95	84	15 {traces}

<sup>a</sup> [H<sub>2</sub>C=C(H)SiR<sub>3</sub>]:[1] = 1:1, 6 h, benzene, room temperature.

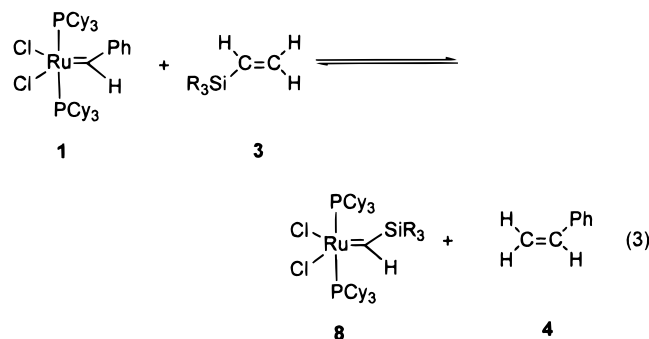
<sup>b</sup> Reported selectivities are based on consumption of 1 as determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> [H<sub>2</sub>C=C(H)Si(OEt)<sub>3</sub>]:[1] = 50:1, room temperature, 1 h, benzene.

each) 55% of 1 and 3a,b had been consumed after 6 h; that is, both olefins reacted with 1 at about the same rate. The selectivity for the conversion of 3a,b into 5a,b was very high (≥95%). In the reaction of 1 with 3a, in addition to 5a, the formation of small amounts of styrene was detected. When 3a was used in a 10-fold excess, the conversion of 1 was complete already after 1 h.

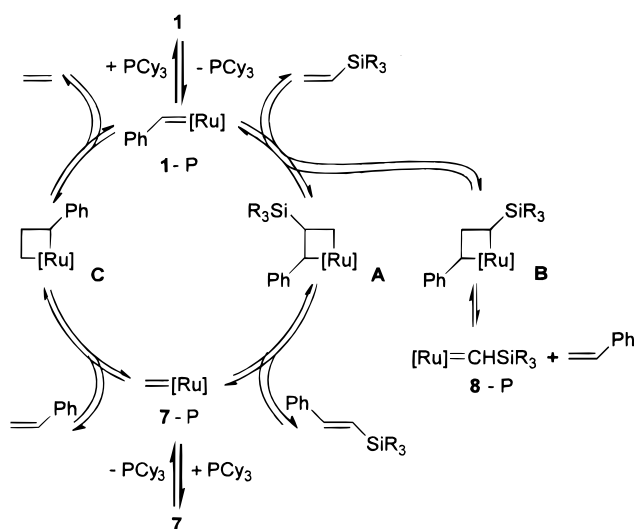
When triethoxyvinylsilane (3a) was replaced by trimethoxyvinylsilane (3c), the reaction rate increased. Analogously, stepwise substitution of Me for OEt in 3a (3a → 3d → 3e → 3h) or OSiMe<sub>3</sub> in 3b (3b → 3f → 3g → 3h) led to an increase in the conversion; however, this reduced the selectivity (Table 2). Thus, the fastest reaction, that of 1 with 3h, provided the lowest selectivity for the formation of silylstyrene. Complex 1 did not react with 5a in a productive way.

In general, the yield of the methyldene complex 7 was always much lower than that required by the mass balance and than that of the respective silylstyrene 5. Presumably, 7 (or an intermediate of the reaction) already significantly decomposed under the conditions that were used. This assumption is supported by the results of a study on the thermolysis of various ruthenium–carbene complexes.<sup>20</sup> Complex 7 was found to be considerably less stable than 1. The half-life of 7 at 55 °C in benzene was reported to be 40 min, as compared to 8 days for 1.<sup>20</sup>

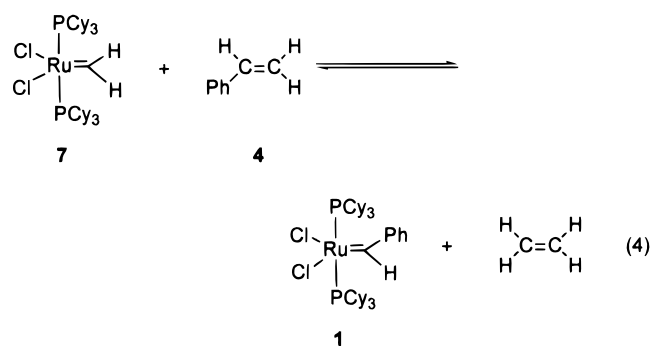
Usually, small amounts or traces of styrene (4) were also formed (eq 3). Presumably, 4 is derived from the



opposite regioselectivity in the addition of 3 to 1 to form the metallacyclic intermediate (see Scheme 2; B). However, it was not possible to detect the silylcarbene complex 8. Presumably, once formed, 8 rapidly decomposes.

**Scheme 2**

In principle, the reaction of 1 with 3 to form 7 and 5 (eq 2) is reversible. However, the equilibrium is far on the side of the products. A reaction of 7 with 5a or 5b (the reverse of that in eq 2) was detected only when the silyl- or siloxystyrenes were employed in a 50-fold excess.<sup>21</sup> No productive reaction between 7 and vinylsilanes such as 3a,b was observed even when the vinylsilanes were used in large excess. However, 7 reacted with styrene (eq 4), albeit slowly. After 6 h at



room temperature in C<sub>6</sub>D<sub>6</sub> ([7]:[styrene] = 1:1) 12% of styrene and 60% of 7 had been consumed. The selectivity for the formation of the benzylidene complex 1 was 95%, based on styrene consumption.

Decomposition of 7 as a side reaction may account for the difference between the consumption of 7 (60%) and the formation of 1 (12%).

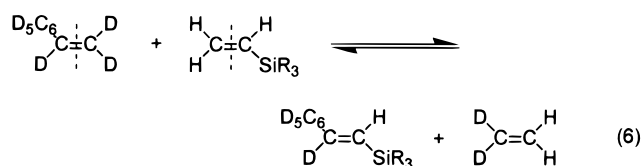
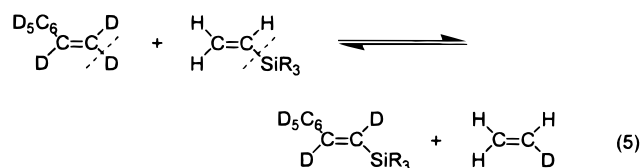
**Labeling Studies.** To distinguish between a non-metallacarbene mechanism,<sup>19</sup> such as that observed when [Ru(H)Cl(CO)(PPh<sub>3</sub>)<sub>3</sub>] or [RuCl(SiR<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] was used as the catalyst, and a metallacarbene mechanism,<sup>22</sup> the reaction of styrene-*d*<sub>8</sub> with 3a,b in the presence of 1 was investigated. In the case of a non-metallacarbene mechanism the formation of silylstyrene-*d*<sub>7</sub> and ethylene-*d* is to be expected (eq 5). In contrast, a metallacarbene mechanism should afford silylstyrene-*d*<sub>6</sub> and ethylene-*d*<sub>2</sub> (eq 6).

(21) The reaction of 7 with a 50-fold excess of (*E*)-Ph(H)C=C(H)Si(OEt)<sub>3</sub> (5b) afforded after 6 h at room temperature complex 1 in 8% yield (based on 7 used).

(22) Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

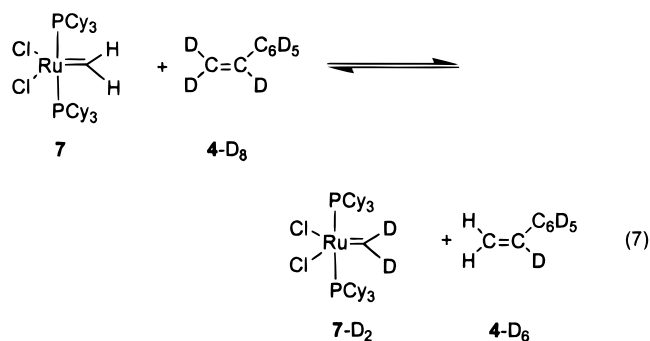
(20) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202.



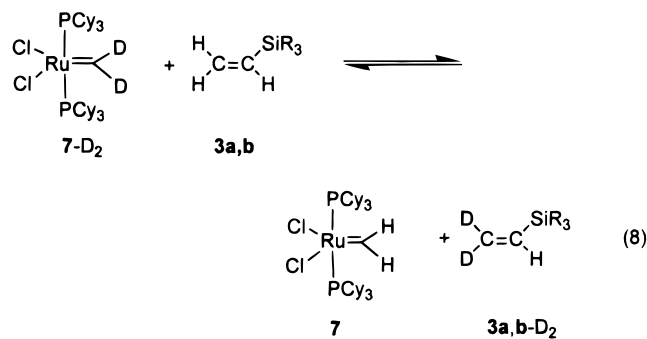


The analysis of the reaction mixture after 6 h at room temperature by  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy and GC-MS revealed that only  $\text{D}_2$  products,  $\text{D}_2\text{C}=\text{CH}_2$  and small amounts of  $\text{D}_2\text{C}=\text{C}(\text{H})\text{SiR}_3$ , and  $\text{D}_6$  products,  $\text{C}_6\text{D}_5(\text{D})\text{C}=\text{C}(\text{H})\text{SiR}_3$ , as well as small amounts of  $\text{H}_2\text{C}=\text{C}(\text{D})\text{C}_6\text{D}_5$ , were formed. A  $\text{D}_7$  olefin could not be detected. Therefore, a nonmetallacarbene mechanism (eq 5) can be excluded.

The formation of small amounts of styrene- $\text{D}_6$ ,  $\text{H}_2\text{C}=\text{C}(\text{D})\text{C}_6\text{D}_5$ , observed by  $^1\text{H}$  NMR spectroscopy is readily explained by methylidene exchange between  $\text{D}_2\text{C}=\text{C}(\text{D})\text{C}_6\text{D}_5$  and **7** (eq 7), which is formed in a follow-up reaction of complex **1** with  $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiR}_3$ .



The  $\text{D}_2$  vinylsilanes that were also observed in the reaction mixture presumably result from the reaction of **7-D<sub>2</sub>** with **3** (eq 8). **7-D<sub>2</sub>** has not been observed by  $^2\text{H}$  NMR spectroscopy, probably due to its small concentration.



### Discussion

These results demonstrate that complex **1** is an efficient precatalyst for the transformation of  $\text{H}_2\text{C}=\text{C}(\text{H})[\text{Si}(\text{OR})_3]$  and styrene into silylstyrene and ethylene. The reactions run smoothly even at room temperature. In contrast, complexes containing initially Ru-Si or Ru-H bonds such as  $[(\text{CO})(\text{PPh}_3)_2\text{ClRu-SiR}_3]$  (R

= Me, OEt) or  $[(\text{CO})(\text{PPh}_3)_3\text{ClRu-H}]$  require elevated temperatures (60–110 °C). Mechanistically, the reactions of these ruthenium complexes and of compound **1** significantly differ. The reactions catalyzed by Ru-Si and Ru-H species were proposed to proceed by a migratory insertion of styrene into the Ru-Si bond (and of vinylsilane into the Ru-H bond) followed by  $\beta$ -H (and  $\beta$ -Si) elimination. From the labeling studies it follows that a similar mechanism can be excluded for those reactions that are catalyzed by ruthenium-carbene species. The results obtained with **1** are best rationalized by the catalytic cycle shown in Scheme 2.

Dissociation of  $\text{PCy}_3$  from **1** generates the catalytically active, very likely solvent-stabilized species **1-P**. Addition of vinylsilanes to **1-P** and oxidative cyclization gives either ruthenacycle **A** or **B**. Formation of **A** is strongly favored over formation of **B**. Ruthenacycle **A** collapses to give silylstyrene and **7-P**. Elimination of vinylsilane from ruthenacycle **B** regenerates **1-P**; elimination of styrene from **B** affords the silylcarbene complex **8-P**. Styrene has been detected in the stoichiometric reactions, although only minor amounts have been formed. It was not possible to isolate or even spectroscopically detect the silylcarbene complex **8**, which is the product of  $\text{PCy}_3$  addition to **8-P**. Several factors may account for the failure to detect **8** or **8-P**: instability of **8-P**, instability of **8**, and decomposition of the ruthenacycle **B** by  $\beta$ -elimination or another process.

Analogously, **A** and **C** can likewise decompose, albeit to a lesser extent than **B**. Metathesis and decomposition are competing processes. The relative importance of the decomposition pathways depends on the substituents at silicon and strongly increases with an increasing number of methyl groups. Addition of styrene to **7-P**, formation of the ruthenacycle **C**, and ethylene elimination complete the catalytic cycle. Vinylsilane-independent decomposition of **7-P**<sup>20</sup> constitutes the second factor reducing the concentration of the catalytically active species. The results of the stoichiometric investigations indicate that the reaction of **7-P** with styrene to give **1-P** and ethylene is the bottleneck in the catalytic cycle.

This mechanistic scheme deviates from that proposed earlier<sup>23</sup> for the ring-closing metathesis of  $\alpha,\omega$ -dienes catalyzed by  $[\text{X}_2(\text{PR}_3)_2\text{Ru}=\text{C}(\text{H})\text{CHCPh}_2]$ . Grubbs et al. suggested an initial coordination of the olefin to the complex followed either (a) by dissociation of  $\text{PR}_3$ , formation of the ruthenacycle, elimination of the metathesized olefin, and readdition of  $\text{PR}_3$  to regenerate the starting complex as the major (dissociative) pathway or (b) by formation of the ruthenacycle without  $\text{PR}_3$  dissociation (associative pathway). Such a mechanistic scheme involving bis-phosphine complexes in the catalytic cycle cannot account for the high conversion rates observed in the cross-metathesis of vinylsilanes with styrene (Table 1), since the reaction of **7** with styrene to form **1** and ethylene is too slow.<sup>24</sup> However, the monophosphine species **1-P** and **7-P** are expected to be highly reactive and to rapidly add the corresponding olefin.

The efficiency of the catalytic cycle is determined by several factors: (a) the pronounced preference of **1-P** for

(23) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

(24) The rate constant  $k_2$  for the reaction of **7** with styrene in benzene at 20 °C is  $k_2 = (3.5 \pm 0.7) \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ .

the reaction with vinylsilanes, (b) the high regioselectivity of vinylsilane addition to **1-P**, and (c) the preference of **7-P** for reaction with styrene. These conclusions are supported by the results of the stoichiometric studies of **1** and **7** with olefins.

Substitution of Me for OR in  $\text{H}_2\text{C}=\text{C}(\text{H})[\text{Si}(\text{OR})_3]$  gives rise to an increase in the conversion of the vinylsilanes in the stoichiometric reactions; however, this also reduces the selectivity for the formation of **A** relative to **B**. Since **B** may essentially be regarded as the “dead end” of the metathesis cycle, withdrawing catalytically active ruthenium species from the cycle, the cross-metathesis activity rapidly decreases (Table 1). The regioselectivity of vinylsilane addition to the  $\text{Ru}=\text{C}$  bond is governed by both electronic and steric factors. Stoichiometric studies indicate a preference for the addition of the more nucleophilic end of the  $\text{C}=\text{C}$  bond to the carbene carbon of the complex (formation of **A**). Conversely, steric factors seem to favor formation of 1,3-disubstituted ruthenacyclobutanes (type **B**).

### Experimental Section

**Materials and Methods.** Unless mentioned otherwise, all operations were performed by using standard Schlenk techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WM250 at 250 and 62.9 MHz, respectively.  $^2\text{H}$  NMR spectra were recorded on a JEOL JNM-GX400 at 61 MHz. The GC/MS analyses were performed on a HP 6890 gas chromatograph (HP-5MS 30 m capillary column) equipped with a HP 5973 mass selective detector. GC analyses were carried out on a Carlo Erba GC 6000 Series 2 (FS-OV-101 25 m capillary column) equipped with an FID. Chemicals were obtained from the following sources: vinylsilanes and Grubbs catalyst (**1**) from ABCR, decane, dodecane, anthracene, and styrene- $d_8$  from Aldrich, benzene and styrene from Riedel-de Haen, and benzene- $d_6$  from Deutero GmbH.  $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2]$  was prepared by the literature method.<sup>2a</sup> All liquid reagents were distilled, dried with molecular sieves, and degassed by repeated freeze–pump–thaw cycles. Benzene- $d_6$  was dried by passing through an alumina column and degassed as mentioned above. Benzene was dried and distilled over  $\text{CaH}_2$  under a dry argon atmosphere prior to use. The silylstyrenes **5** were identified by their  $^1\text{H}$  NMR spectra.<sup>19, 25–27</sup>

**Stoichiometric Reactions.** The stoichiometric reactions were performed in NMR tubes and controlled by  $^1\text{H}$  NMR spectroscopy. In a typical procedure  $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}]$  (**1**; 0.01 g,  $1.21 \times 10^{-5}$  mol) and anthracene (internal standard) were dissolved in 0.65 mL of  $\text{C}_6\text{D}_6$ . Then  $1.21 \times 10^{-5}$  mol of the corresponding vinylsilane was added by syringe. The NMR spectra of the reaction mixture were taken (a) immediately after the reagents had been dissolved and (b) 6 h later. Conversions and selectivities were calculated using the internal standard method.

**Catalytic Reactions.** In a typical procedure **1** (0.01 g,  $1.21 \times 10^{-5}$  mol) was dissolved in 1 mL of benzene. Then decane or dodecane (0.03 mL, internal standard), styrene (0.07 mL,  $6.1 \times 10^{-4}$  mol), and vinylsilane ( $6.1 \times 10^{-4}$  mol) were added. The reaction was carried out at room temperature in an open system. To remove ethylene from the system, a very gentle flow of argon was used. To prevent vapor from leaving the system, an efficient condenser was used. The progress of the reaction was controlled by gas chromatography. The conversion of the substrates was calculated using the internal standard method.

(25) Marciniak, B.; Pietraszuk, C.; Kujawa, M. *J. Mol. Catal. A: Chem.* **1998**, 133, 41.

(26) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, 55, 3609.

(27) For an extensive NMR study of silylstyrenes see: Liepins, E.; Goldberg, Yu.; Iorel, I.; Lukevics, E. *J. Organomet. Chem.* **1987**, 335, 301.

**Labeling Study.** The stoichiometric reactions of vinylsilanes with styrene- $d_8$  were performed in NMR tubes and controlled by NMR spectroscopy. In a typical procedure complex **1** (0.001 g,  $1.2 \times 10^{-6}$  mol) was dissolved in 0.65 mL of  $\text{C}_6\text{D}_6$  (or  $\text{C}_6\text{H}_6$ ). Then styrene- $d_8$  (0.0070 mL,  $6.1 \times 10^{-5}$  mol) and vinylsilane (0.0088 mL,  $6.1 \times 10^{-5}$  mol) were added by syringe. The reactions were carried out at room temperature in an open system. After 6 h, the reaction mixtures were analyzed by GC-MS and  $^1\text{H}$  NMR and  $^2\text{H}$  NMR spectroscopy.

Selected spectroscopic data of deuterated silylstyrenes are as follows.

**(E)-D<sub>5</sub>C<sub>6</sub>(D)C=C(H)[Si(OEt)<sub>3</sub>] (5a-d<sub>6</sub>):**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  6.28 (t,  $J_{\text{H,D}} = 2.7$  Hz, CHSi);  $^2\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm)  $\delta$  7.20 (d,  $J_{\text{H,D}} = 2.7$  Hz, CDPh); MS  $m/z$  (%) 79 (17), 103 (21), 118 (22), 136 (26), 137 (23), 147 (26), 152 (40), 155 (54), 181 (57), 199 (34), 227 (43), 228 (100), 257 (40), 272 ( $\text{M}^+$ , 16).

**(E)-D<sub>5</sub>C<sub>6</sub>(H)C=C(H)[Si(OSiMe<sub>3</sub>)<sub>3</sub>] (5b-d<sub>6</sub>):**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  6.34 (t,  $J_{\text{H,D}} = 2.7$  Hz, CHSi);  $^2\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm)  $\delta$  7.06 (s, broad, CDPh); MS  $m/z$  (%) 73 (23), 140 (8), 150 (12), 167 (100), 168 (17), 207 (21), 279 (24), 301 (12), 389 (10), 404 ( $\text{M}^+$ , 12).

**Synthesis of (E)-Ph(H)C=C(H)[Si(OEt)<sub>3</sub>] (5a).** The reaction was carried out under an argon atmosphere in a Schlenk vessel equipped with a condenser. Complex **1** (0.1 g,  $1.21 \times 10^{-4}$  mol) was dissolved in 10 mL of benzene. Then styrene (2.09 mL,  $1.82 \times 10^{-2}$  mol) and vinyltriethoxysilane (1.28 mL,  $6.1 \times 10^{-3}$  mol) were added. The solution was stirred for 6 h at room temperature in an open system. To remove ethylene from the system, a very gentle flow of argon was used. To prevent vapor from leaving the system, an efficient condenser was used. The progress of the reaction was controlled by gas chromatography. The product was isolated by distillation in vacuo. The fraction boiling at 94–98 °C/1 mmHg was collected (1.35 g, 83% based on vinylsilane used). Spectroscopic data:<sup>19</sup>  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  1.26 (t, 9 H,  $\text{CH}_3$ ), 3.93 (q, 6 H,  $\text{OCH}_2$ ), 6.38 (d,  $J_{\text{H,H}} = 19.3$  Hz, 1 H, CHSi), 7.49 (d, 1 H,  $J_{\text{H,H}} = 19.3$  Hz, CHPh), 7.10–7.40 (m, 5 H, Ph);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  18.55 ( $\text{CH}_3$ ), 58.70 ( $\text{OCH}_2$ ), 118.97 (CHSi), 149.16 (CHPh), 138.20 ( $\text{C}_{\text{ipso}}$ ), 127.07, 128.78, 128.81 (Ph); MS  $m/z$  (%) 63 (20), 79 (23), 103 (29), 118 (20), 119 (19), 131 (34), 147 (76), 149 (67), 176 (64), 193 (43), 251 (57), 266 ( $\text{M}^+$ , 10).

**(E)-Ph(H)C=C(H)[Si(OSiMe<sub>3</sub>)<sub>3</sub>] (5b).** This compound was prepared analogously to (E)-Ph(H)C=C(H)[Si(OEt)<sub>3</sub>] (bp 90–94 °C/0.9 mmHg, yield 79% based on vinylsilane used). Spectroscopic data:<sup>25</sup>  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  0.28 (s, 27 H,  $\text{CH}_3$ ), 6.42 (d,  $J_{\text{H,H}} = 19.0$  Hz, 1 H, CHSi), 7.35 (d,  $J_{\text{H,H}} = 19.0$  Hz, 1 H, CHPh), 7.05–7.40 (m, 5 H, Ph);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  1.93 ( $\text{CH}_3$ ), 122.95 (CHSi), 146.92 (CHPh), 138.38 ( $\text{C}_{\text{ipso}}$ ), 126.93, 128.62, 128.82 (Ph); MS  $m/z$  (%) 73 (25), 145 (20), 161 (100), 162 (17), 193 (14), 207 (22), 279 (22), 295 (12), 383 (9), 398 ( $\text{M}^+$ , 12).

**(E)-Ph(H)C=C(H)[Si(OMe)<sub>3</sub>] (5c).** This compound was prepared analogously to (E)-Ph(H)C=C(H)[Si(OEt)<sub>3</sub>] (bp 78–82 °C/1 mmHg, yield 75% based on vinylsilane used). Spectroscopic data:<sup>26</sup>  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  3.61 (s, 9 H,  $\text{OCH}_3$ ), 6.33 (d,  $J_{\text{H,H}} = 19.3$  Hz, 1 H, CHSi), 7.48 (d,  $J_{\text{H,H}} = 19.3$  Hz, 1 H, CHPh), 7.10–7.40 (m, 5 H, Ph);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  50.38 ( $\text{OCH}_3$ ), 117.18 (CHSi), 149.83 (CHPh), 138.00 ( $\text{C}_{\text{ipso}}$ ), 127.09, 128.78, 128.95 (Ph); MS  $m/z$  (%) 90 (40), 91 (66), 104 (38), 107 (35), 121 (34), 131 (19), 161 (30), 162 (100), 223 (54), 224 ( $\text{M}^+$ , 61).

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