

Ruthenium-catalyzed cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane: Selective formation of a five-membered silacycle

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Abstract

The cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane (**1**) in the presence of ruthenium–diphosphine complexes has been examined. A ruthenium–dppe (**8**) or a ruthenium–dppv (**12**) complex selectively catalyzed the reaction and 1,1,2,3,3-pentamethyl-1,3-disilylcyclopent-4-ene (**3**) was isolated as the major product. The reaction was also carried out in the presence of a deuterated ruthenium–PⁱPr₃ complex and the incorporation of deuterium to 1,1,4,4-tetramethyl-1,4-disilacyclohex-2-ene (**2**) was observed. The mechanism of this reaction has been proposed.

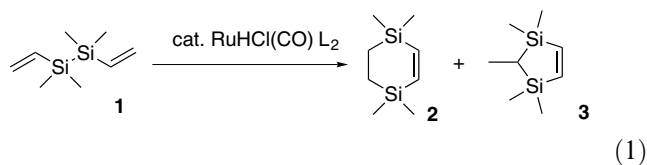
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1. Introduction

Activation of the Si–Si bond by transition metal catalysts [1] is a useful method for the synthesis of a variety of organosilicon compounds, which have been widely used in organic chemistry [2]. During the studies of some ruthenium-catalyzed reactions of organosilicon compounds [3], we found a new ruthenium-catalyzed cycloisomerization reaction of 1,1,2,2-tetramethyl-1,2-divinyldisilane (**1**, Eq. 1), which involves the cleavage of a silicon–silicon bond [4]. The formation of 1,1,4,4-tetramethyl-1,4-disilacyclohex-2-ene (**2**) and 1,1,2,3,3-pentamethyl-1,3-disilylcyclopent-4-ene (**3**) was observed, and compound **2** was isolated

as the major product in the presence of a ruthenium catalyst such as RuHCl(CO)(PⁱPr₃)₂ (**4**) or RuHCl(CO)(PPh₃)₃ (**5**). However, the selective formation of **3** has not been realized. In order to examine the possibility of the selective formation of the cyclic compound **3**, and also to obtain mechanistic insight to this reaction, we reexamined this reaction by use of ruthenium catalysts with various phosphine ligands. In this paper, we report the successful synthesis of **3** and the results of the reactions carried out in the presence of a deuterium-labeled ruthenium complex.



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2. Results and discussion

2.1. Ruthenium-catalyzed cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane (**1**)

We carried out the reaction of **1** in the presence of ruthenium–diphosphine complexes and the result was summarized in Table 1. While the catalytic activity of **6** (entry 3) was comparable to that of **5** (entry 2) [4], the catalytic activity of the ruthenium–diphosphine complexes such as **7–12** was significantly different. As shown in entries 4–8, the progress of the reaction was much slower in most examples, and the reaction did not complete even after prolonged heating (48 h) at 60 °C in THF. It is also noteworthy that the ratio of the product was significantly different when the reaction was carried out in the presence of **8**, and the five-membered silacycle **3** was isolated as the major product for the first time in this reaction (entry 5).

The selective formation of **3** in the presence of a ruthenium–diphosphine catalyst **8** led us to further examine this reaction at higher temperature. 1,2-Dichloroethane was selected as a solvent with higher boiling point and the reaction was carried out at 80 °C (entries 9–10). When compound **8** was employed as the catalyst, the starting material completely disappeared and the isomer ratio **2/3** was 13/87 (entry 9). On the other hand, the highly selective conversion of **1** to **3** was observed when the reaction was

carried out in the presence of RuHCl(CO)(PPh₃)dppv (**12**), though the rate of the reaction was very slow (entry 10). We finally chose 1,4-dioxane as the solvent and carried out the reaction at 100 °C (entries 11–14). While the isomer ratio remained unchanged even when the reaction was carried out at 100 °C, the complete conversion of **1** was observed. When the reaction was carried out at 100 °C for 48 h and in the presence of **12**, the product, which mainly consists of **3**, was isolated in 44% yield (entry 14) [5].

2.2. Cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane (**1**) in the presence of a deuterated ruthenium complex

With hope to provide mechanistic insight to the reaction, we carried out the reaction of **1** in the presence of a deuterated ruthenium complex generated in situ (Eq. 2). Thus, **4-d** (80% atom D) was synthesized by the reaction of **4** with an excess (10 equiv.) of Et₃SiD (97% atom D) [6]. To a solution of **4-d** in benzene was added **1** and the incorporation of deuterium to the product **2** was examined by GC–MS. The analysis indicated the formation of partially (15% atom D) deuterated **2** at the earlier stage (20 min) of the reaction. The deuteration of a mixture of **2** and **3** in the presence of **4-d** was also examined and the formation of a very small portion (4% atom D) of deuterated **2** and **3** was observed after prolonged heating (200 min) of the reaction mixture (Eq. 3) [7].

Table 1
Ruthenium-catalyzed cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane (**1**)

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion ^d (%)	Ratio ^e (2/3)	Isolated yield (%)
1 ^{a,b}	RuHCl(CO)(P ^t Pr ₃) ₂ (4)	THF	60	20	–	76/24	60
2 ^{a,c}	RuHCl(CO)(PPh ₃) ₃ (5)	THF	60	48	92	93/7	–
3	RuHCl(CO)(PPh ₃) ₂ py (6)	THF	60	48	100	92/8	–
4	RuHCl(CO)(PPh ₃)dppm (7)	THF	60	48	Trace	–	–
5	RuHCl(CO)(PPh ₃)dppe (8)	THF	60	48	26	13/87	–
6	RuHCl(CO)(PPh ₃)dppp (9)	THF	60	48	35	87/13	–
7	RuHCl(CO)(PPh ₃)dppb (10)	THF	60	48	48	94/6	–
8	RuHCl(CO)(PPh ₃)dppf (11)	THF	60	48	65	94/6	–
9 ^f	RuHCl(CO)(PPh ₃)dppe (8)	(CH ₂ Cl) ₂	80	72	100	13/87	–
10 ^f	RuHCl(CO)(PPh ₃)dppv (12)	(CH ₂ Cl) ₂	80	90	28	2/98	–
11 ^f	RuHCl(CO)(PPh ₃) ₃ (5)	1,4-dioxane	100	5	100	94/6	–
12 ^f	RuHCl(CO)(PPh ₃)dppm (7)	1,4-dioxane	100	24	100	93/7	–
13 ^g	RuHCl(CO)(PPh ₃)dppe (8)	1,4-dioxane	100	24	100	12/88	40
14 ^g	RuHCl(CO)(PPh ₃)dppv (12)	1,4-dioxane	100	48	100	2/98	44

^a Ref. [4].

^b Reaction conditions: **1**, 11.9 mmol, catalyst 0.055 mmol, solvent 25 ml.

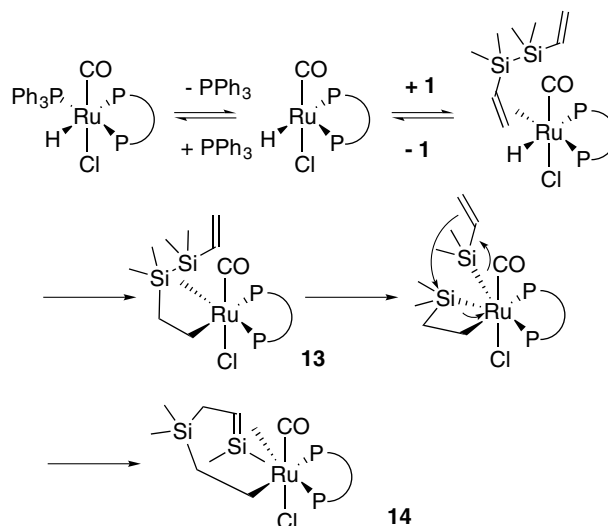
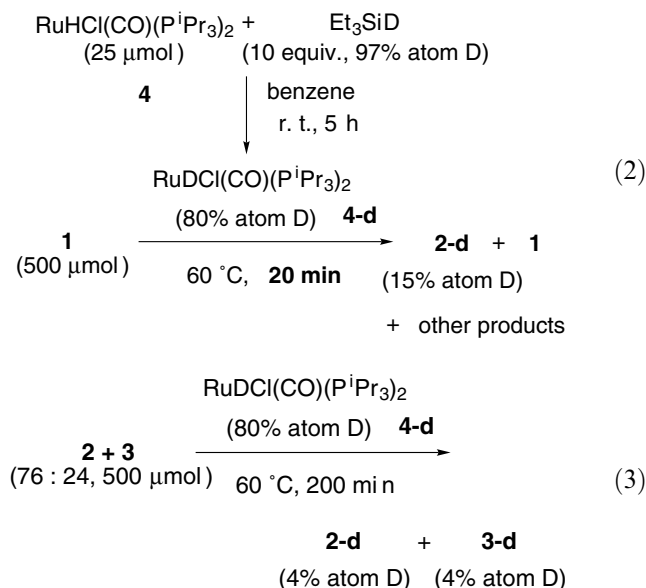
^c Reaction conditions: **1**, 1 mmol, catalyst 0.02 mmol, solvent 5 ml.

^d Determined by the integration of the signals appeared in GC–MS (**2 + 3**)/(**1 + 2 + 3**). This value has been used as a semiquantitative benchmark to monitor the progress of the reactions, and no calibration was performed.

^e Determined by GC–MS. Though no calibration was performed, the value correlated fairly well with the ratio determined by ¹H NMR.

^f Reaction conditions: **1**, 1 mmol, catalyst 0.02 mmol, solvent 1 ml.

^g Reaction conditions: **1**, 10 mmol, catalyst 0.05 mmol, solvent 5 ml.



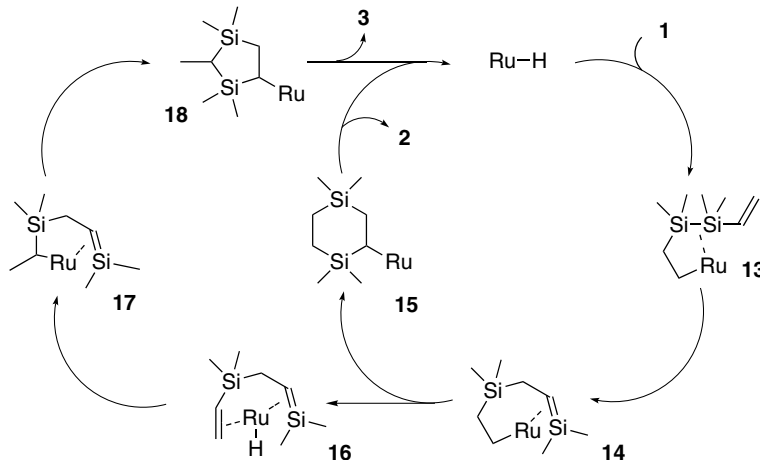
Scheme 2.

2.3. Proposed mechanism and the effect of the diphosphine ligand on the catalytic activity and selectivity of the cycloisomerization

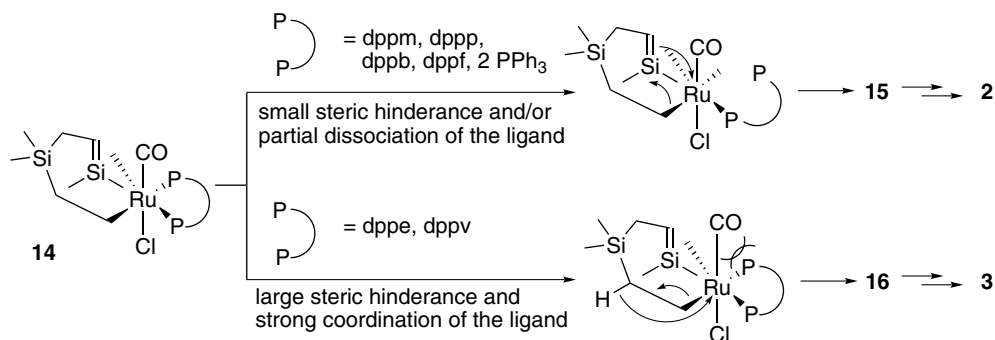
We have already proposed the mechanism of this reaction as shown in Scheme 1 [4]. Thus, the hydorruthenation of **1** would initially take place and the sterically less congested complex **13** would be formed. The ruthenium-assisted isomerization [8] (1,3-shift of the silyl group) of **13** would be the key step for this reaction, which would lead to the formation of **14**. This process might proceed via the insertion of the Ru species to the Si–Si σ bond, followed by the C–Si bond formation as depicted in Scheme 2. The intramolecular insertion of Ru–C bond to the C=Si double bond would lead to the formation of **15**, a six-membered silacycle which would give **2** as the product. Alternatively, the β -hydride elimination might take place, and the insertion of Ru–H

bond to the C=C double bond followed by the insertion of Ru–C to the C=Si double bond would lead to the formation of the five-membered silacycle **3** as the product.

The rate of the reaction was low when the reaction was carried out in the presence of a ruthenium–diphosphine complex, while the selective formation of **3** was observed when the reaction was carried out in the presence of **8** or **12**. Jun and co-workers [9] reported the catalytic activity of the ruthenium–diphosphine complexes **8–12** in the hydrogenation reaction which does not correlate to the activity of **8–12** observed in the present study. Since they assumed that the initial equilibrium stage would be the most important factor for the hydrogenation reaction they reported, the rate-determining step of the cycloisomerization reaction would not be related to the initial equilibrium stage. A reasonable assumption is that the conversion of **14** to **15** (or **16**) is the rate-determining step. The large steric hindrance



Scheme 1.



Scheme 3.

induced by the strong binding of the dppv or dppe to the ruthenium metal, which leads to the formation of a stable five-membered ruthenacycle, might inhibit the interaction of Ru–C bond with the silylene moiety and retard the conversion of **14** to **15**. Therefore, the formation of **16** might be a more favorable pathway when **8** or **12** was used as the catalyst. This conversion might also be accompanied by the partial dissociation of the bidentate ligand (Scheme 3) [10].

The insertion of the Ru–H bond to the C=C double bond has been proposed as the initial step of this reaction. The observed incorporation of deuterium to **2** in the presence of **4-d** or **12-d** is a supporting evidence for this proposal. Since the rate of H–D exchange between **2** and **3** with **4-d** was much slower, it is likely that the incorporation is accompanied with the conversion of **1** to **2** (or **3**).

In summary, we carried out the isomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane in the presence of ruthenium–diphosphine complexes and observed the highly selective formation of five-membered silacycle **3** in the presence of a ruthenium–dppv complex **12**. The incorporation of deuterium of the complex **4-d** to **2** was observed. Our study revealed the significant effect of the diphosphine ligand on the selectivity of the reaction and provided mechanistic insight to the isomerization reaction. Further studies including the synthesis of functionalized polymers from **3** are in progress.

3. Experimental

3.1. General procedure

All reactions were carried out under argon atmosphere. 1,1,2,2-Tetramethyl-1,2-divinyldisilane (**1**) [11], ruthenium catalysts **4** [12], **5** [13], **6** [14], **7–11** [15], **12** [9], and Et₃SiD [16] were prepared as reported in the literature. Other reagents were commercially available and used without further purification.

3.2. Reaction of **1** with RuHCl(CO)(PⁱPr₃)₂ (**4**) (Table 1, entry 1)

To a two-necked flask fitted with a reflux condenser were added RuHCl(CO)(PⁱPr₃)₂ (26.3 mg, 0.054 mmol), **1** (2.02 g, 11.9 mmol), and dry THF (25 ml) and the solution was stirred at 60 °C for 20 h. The reaction mixture was evaporated under reduced pressure and the residual oil was distilled (70 °C/35 mmHg, Kugelrohr) to give a mixture of two isomers of **2** [4] and **3** [4] as colorless oil (1.21 g, 60% yield, **2/3** = 76/24).

3.3. Reactions of **1** with ruthenium catalysts (Table 1, entries 2–12)

To a screw-capped tube were added the ruthenium catalyst (0.02 mmol), **1** (0.17 g, 1.0 mmol), and dry degassed solvent (5 ml for entries 2–8, or 1 ml for entries 9–12) and the solution was stirred and heated as described in Table 1. The progress of reaction was monitored and the ratio of the products was analyzed by GC–MS.

3.4. Reaction of **1** with RuHCl(CO)(PPh₃)dppe (**8**) or RuHCl(CO)(PPh₃)dppv (**12**) (Table 1, entries 13 and 14)

To a two-necked flask fitted with a reflux condenser was added the ruthenium catalyst (0.05 mmol), **1** (1.70 g, 10.0 mmol), and dry degassed 1,4-dioxane (5 ml) and the solution was stirred at 100 °C as described in Table 1. The reaction mixture was evaporated under reduced pressure and the residual oil was purified by distillation (70 °C/35 mmHg, Kugelrohr) to give a mixture of **2** [4] and **3** [4] as a colorless oil.

Data for **2**: GC–MS, *m/e* 170; ¹H NMR (270 MHz, CDCl₃) δ 0.05 (s, 12H), 0.82 (s, 4H), 6.79 (s, 2H), ¹³C NMR (68 MHz, CDCl₃) δ –2.3, 7.5, 150.6.

Data for **3**: GC–MS, *m/e* 170; ¹H NMR (270 MHz, CDCl₃) δ –0.10 (q, 1H, *J* = 7.75 Hz), 0.07 (s, 6H), 0.12 (s, 6H), 1.04 (d, 3H, *J* = 7.75 Hz), 7.02 (s, 2H);

^{13}C NMR (68 MHz, CDCl_3) δ -3.2, -0.5, 1.7, 8.3, 155.0.

3.5. Procedure for the reaction of **1** with $\text{RuDCl}(\text{CO})-(\text{P}^i\text{Pr}_3)_2$ [6] (**4-d**) and $\text{RuDCl}(\text{CO})(\text{PPh}_3)\text{dppv}$ (**12-d**)

To a solution of $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (0.025 mmol) in dry degassed benzene (2.5 ml) was added Et_3SiD (0.25 mmol) and the mixture was stirred at room temperature for 5 h. Then, disilane **1** (0.5 mmol) was added and the mixture was heated at 60 °C. Analysis by GC-MS revealed that a small amount (5%) of the product **2** was formed, which was partly deuterated (15% atom D) after 20 min.

The deuteration of mixture of **2** and **3** in the presence of $\text{RuDCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ was also examined under the same condition as above and a very small portion of **2** (**3**) was deuterated (4% atom D) after heating the mixture for 200 min.

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