

Journal of Organometallic Chemistry, 402 (1991) 27–33
Elsevier Sequoia S.A., Lausanne
JOM 21273

Platinum-catalyzed elimination–addition reactions of trisilylethenes

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(Received July 6th, 1990)

Abstract

(*E*)-1-Hexyldimethylsilyl-1,2-bis(trimethylsilyl)ethene (**1**) and (*E*)-1-(3'-butyl-1',3'-tetramethyldisiloxanyl)-1,2-bis(trimethylsilyl)ethene (**7**) undergo isomerization–redistribution reactions catalyzed by platinum. Each of them is converted into its (*Z*)-isomer and ethenes bearing one trimethylsilyl group and two substituted silyl groups as major products. The proposed mechanism for the reactions involves a sequence of eliminations of hydrosilanes from the ethenes and re-addition to them. Oxygen greatly affects the reaction, apparently accelerating *anti*-elimination of hydrosilanes.

Introduction

We have previously reported that the platinum-catalyzed hydrosilylations of disilylethyne with high boiling silanes produced various unexpected disilylethyne and trisilylethenes in addition to the expected adducts [1,2]. The proposed mechanisms of formation of various products involved: (1) direct silyl group exchange reactions between disilylethyne and hydrosilanes, and (2) elimination–addition reactions of primary adducts. It was shown that mechanism (1) was predominant in the presence of oxygen i.e. in dry air.

Upon further mechanistic investigations, we have found that trisilylethenes undergo isomerization and redistribution reactions catalyzed by platinum. The isomerization and redistribution reactions can be accounted for by the elimination–addition sequence. These findings lead us to believe that the mechanism responsible for formation of unexpected products in the hydrosilylation of disilylethyne is a combination of (1) and (2).

In this paper we describe the isomerization–redistribution reactions of trisilylethenes. We also report significant effects of oxygen on the isomerization–redistribution reactions.

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Results and discussion

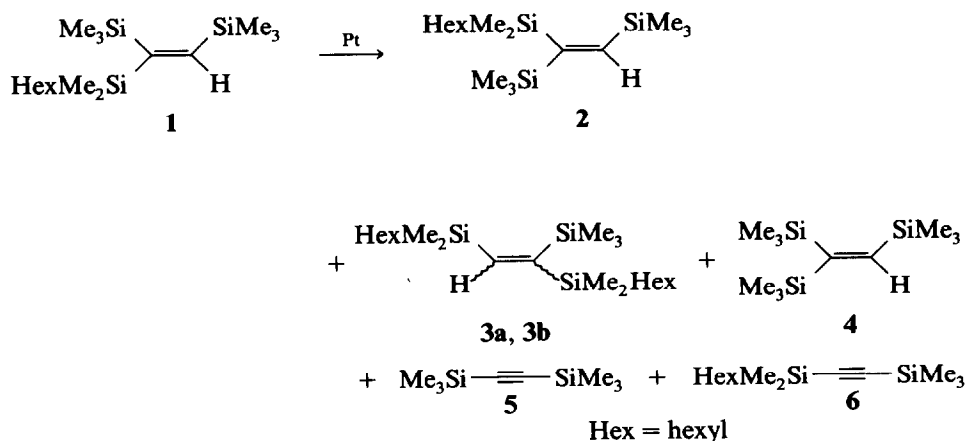
Reactions of 1

(*E*)-1-Hexyldimethylsilyl-1,2-bis(trimethylsilyl)ethene (**1**) underwent isomerization–redistribution reactions under various conditions, with the results listed in Table 1. Each figure in the Table shows the GC peak area for each compound as a percentage of the total area for all peaks. Signals of less than 1.0% are omitted, so that the total of the peak areas is not necessarily 100%. Without the platinum catalyst [tris(tetramethyldivinylsiloxane)diplatinum(0)] no detectable reaction took place. The reactions proceeded slowly and reached stationary states after 7 hours at 130 °C. Identification of the structures of the principal compounds are described in the experimental section.

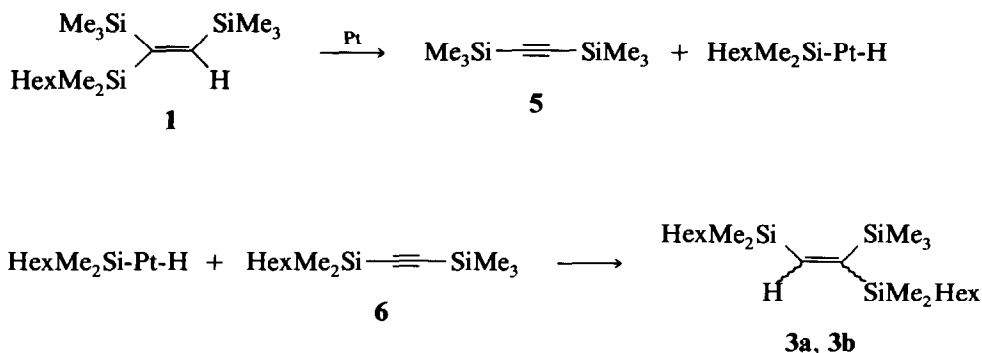
The products from reaction of **1** consisted of its *Z*-isomer (**2**) and bis(hexyldimethylsilyl)trimethylsilylethene (**3a,3b** given in the order of their GC retention times with the geometries not determined), along with small amounts of tris(trimethylsilyl)ethene (**4**), bis(trimethylsilyl)ethyne (**5**) and hexyldimethylsilyltrimethylsilylethyne (**6**) (Scheme 1).

The formation of **5** and **6** can be taken as direct evidence that elimination reactions took place. However, no hexyldimethylsilane, one of the elimination products, was detected by GC except when it was deliberately added in runs 4 and 5. This can be accounted for in terms of the formation of a Si–Pt^{II}–H intermediate rather than the free silane by platinum-catalyzed elimination. Such an intermediate would add to **6** to give **3** (Scheme 2), or simply add back to **5** to give **1**. Trace amounts of trimethylsilane were detected occasionally, which implies that Me₃Si–Pt–H decomposes more easily due to the high volatility of the silane.

In run 1, the detected amounts of **4** and **5** were relatively small compared with that of **3** even though the amount of the latter should be the same as the total of **4** and **5**. A possible explanation for this discrepancy is that both **4** and **5** escaped with the highly volatile trimethylsilane even though a reflux condenser was used. This is evidenced by the differences between runs 1 and 2. In run 2 where evaporation was



Scheme 1



Scheme 2

suppressed, the detected amounts of **4** and **5** were much larger. The weight loss from run 1 was 5.1%, which means that about 10 mol% of trimethylsilyl groups were lost if it is assumed that the evaporated materials were **4**, **5** and trimethylsilane. The weight loss from run 2 was 3.2%, corresponding to 7 mol% loss of trimethylsilyl groups.

The effect of atmosphere was significant. Apparently the active platinum species under nitrogen differed from those under air, which is consistent with observations in the hydrosilylation of bis(trimethylsilyl)ethyne reported previously [2]. Comparison of runs 1 and 3 shows that platinum under air (Pt-A hereafter) enhances the formation of **2** and platinum under nitrogen (Pt-N) enhances the formation of **3**. On the assumption that the platinum-catalyzed addition proceeds solely in the *syn*-manner [3], **2** must be formed by addition of $\text{Me}_3\text{Si-Pt-H}$ to **6**. Because $\text{Me}_3\text{Si-Pt-H}$ and **6** can be formed by *anti*-elimination reaction from **1**, formation of **2** can be regarded as a consequence of *anti*-elimination. This leads to the conclusion that Pt-A enhances *anti*-elimination. The formation of **3** needs $\text{HexMe}_2\text{Si-Pt-H}$ and **6**. Because $\text{HexMe}_2\text{Si-Pt-H}$ is produced by *syn*-elimination and **6** is produced by *anti*-elimination, the formation of **3** can be taken as a consequence of both eliminations. Consequently Pt-N caused both eliminations.

In order to confirm that Pt-A enhances the formation of **2**, an experiment involving a change of the atmosphere was performed. The result is shown in Fig. 1. The atmosphere was changed from nitrogen to air after 3 hours at 160 °C. It can be seen that the introduction of air caused an acceleration of the formation of **2**. This difference between Pt-A and Pt-N may be related to the platinum colloid formation reported by Lewis and Lewis [4].

In run 4, in which hexyldimethylsilane was added, **3b** was the only major product. This suggests another possible mechanism leading to formation of **3**, namely, that **1** is hydrosilylated by hexyldimethylsilane to form a saturated intermediate which undergoes rapid elimination of trimethylsilane to give **3** (Scheme 3).

The third possible isomer of **1**, 1-hexyldimethylsilyl-2,2-bis(trimethylsilyl)ethene, was not detected. According to the proposed elimination-addition mechanism, it could have been produced if the $\text{Me}_3\text{Si-Pt-H}$ intermediate underwent rotation before the re-addition. The reason that the intermediate does not do so is not clear, but the short life of the $\text{Me}_3\text{Si-Pt-H}$ due to the high volatility of trimethylsilane may inhibit the rotation-addition sequence. The absence of the third isomer can be

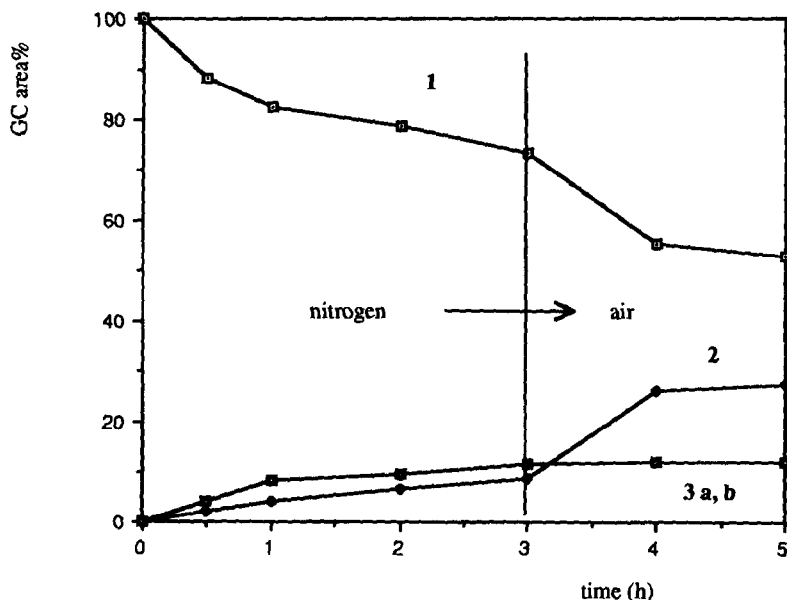
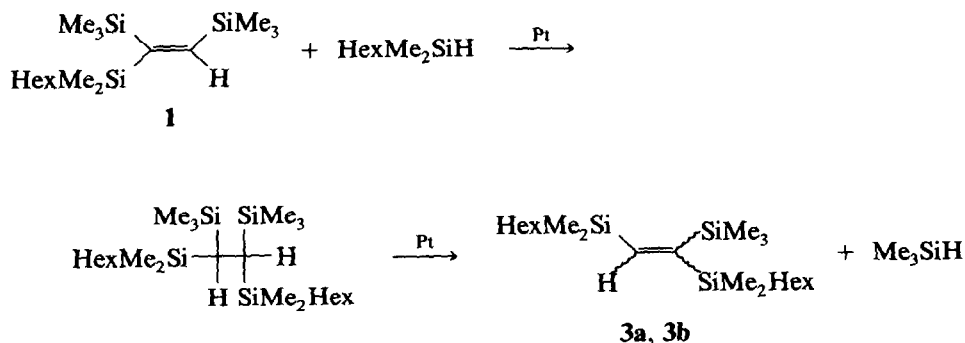


Fig. 1. Reaction of trisilylene 1 with platinum at 160 °C with atmosphere change.

taken as an indication that the elimination reaction is not a stepwise but a concerted reaction. The possibility of random silyl group redistribution can also be ruled out.

Thus the elimination–addition mechanism can account for the formation of every product in Table 1. However, there are some alternative explanations. One possible explanation for the formation of isomer 2 is that there is a simple *cis*–*trans* isomerization catalyzed by platinum. This type of reaction was reported by Chicote, et al. for the complex of platinum and dialkyl maleate [5], but there seems to be no great steric preference for 2 compared with 1 as in the case of maleate–fumarate isomerization. Another possible mechanism was proposed by Dickers et al. [6]. They reported isomerization of (*E*)-1-triethylsilyl-1-hexene catalyzed by rhodium and proposed a mechanism for this isomerization involving a saturated intermediate (addition product of SiH to ethene) and subsequent elimination (similar mechanism



Scheme 3

Table 1

Reactions of trisilylethene **1** (130 °C, 7 h)

Run	1	2	3	4	5
Atmosphere	N ₂	N ₂	air ^a	N ₂	air ^a
Pressure	normal	sealed	normal	normal	normal
Addition of HexMe ₂ SiH ^b	no	no	no	yes	yes
Products (GC area%)					
1	77.0	72.0	53.3	89.8	62.1
2	7.9	7.2	36.1	tr.	26.3
3a	0.9	0.8	0.8	0.3	1.4
3b	9.4	8.3	1.3	5.7	3.6
4	1.1	3.6	1.6	tr.	tr.
5	1.6	4.9	tr.	0.7	0.6
6	2.0	2.2	1.2	1.2	tr.

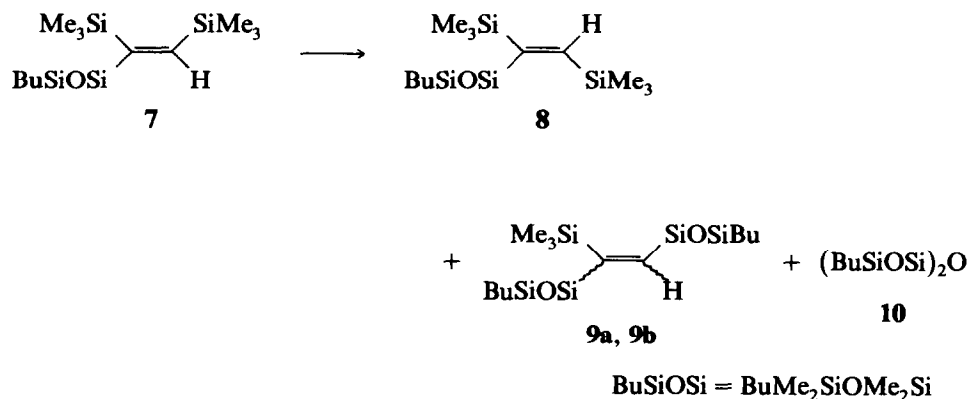
^a Dried by passage through CaCl₂ tube. ^b 10 mol% of **1**.

to Scheme 3). Their evidence for this mechanism is that hydrosilane is needed for the isomerization. This mechanism should not be applicable in the present study because hydrosilane suppresses the isomerization (compare runs 1 and 4, or runs 3 and 5).

Reactions of **7**

The same reactions (under normal pressure, without hydrosilane) were carried out using (*E*)-1-(3'-butyl-1',3'-tetramethyldisiloxanyl)-1,2-bis(trimethylsilyl)ethene (**7**). The compounds produced are shown in Scheme 4 and the results are listed in Table 2.

The results are more or less the same as those in Table 1, although the difference between nitrogen and air atmospheres is not as large as that in Table 1. The amounts of ethynes (corresponding to **5** and **6** in Table 1) formed were very small, indicating that re-addition of the eliminated silane was easier in the case of **7** than that of **1**. This is consistent with the results presented in our earlier report [2]



Scheme 4

Table 2

Reactions of trisilylethene **7** (130 °C, 7 h)

Run	6	7
Atmosphere	N ₂	air ^a
Products (GC area%)		
7	82.8	79.4
8	11.2	15.0
9a	3.4	tr.
9b	0.3	nil
10	nil	2.3

^a Dried by passage through CaCl₂ tube.

showing that the amounts of substituted ethynes were smaller in hydrosilylation with BuMe₂SiOMe₂SiH than with hexyldimethylsilane.

Experimental

Materials

Tris(tetramethyldivinylidisiloxane)diplatinum(0) was prepared as described previously [7*]. The preparations and identifications of **1** (purity: 99% by GC) and **7** (purity: 97%) were as described elsewhere [2].

Isomerization–redistribution reaction under normal pressure

1 or **7** (1.0 g, 3.2 mmol and 2.8 mmol, respectively) was mixed with the platinum catalyst (0.2 μmol) and the mixture was divided into two parts, each of which was then put into a 5 ml pear-shaped flask fitted with a reflux condenser. Vacuum was applied to one flask down to 0.1 mmHg at room temperature, and the flask was then filled with nitrogen (high purity grade). This procedure was repeated twice and finally the top of the reflux condenser was connected to a manifold with constant nitrogen flow. The other flask (for experiment under air) was connected, through the reflux condenser, to a CaCl₂ drying tube (30 cm) with its other end open to air. The flasks were placed in an oil bath kept at 130 °C. The reaction mixture was analyzed by GC periodically. For reactions under nitrogen with added hexyldimethylsilane (10 mol%), the vacuum was applied with cooling of the flask (liquid nitrogen) and the nitrogen purge procedure was repeated for four times.

Isomerization–redistribution reaction in a sealed ampoule

A reaction mixture was prepared in a 2 ml ampoule and the air was replaced with nitrogen as described above. The sealed ampoule was kept in the oil bath for 7 h then cooled to room temperature and opened. The weight loss was measured immediately, and GC analysis then carried out.

Structure determination of **2–6**

Because of their very close retention times and similar mass spectral data in GC-MS, **2** was judged to be an isomer of **1**. The other isomer [1-hexyldimethylsilyl-

* Reference number with asterisk indicates a note in the list of references.

2,2-bis(trimethylsilyl)ethene] had been independently synthesized and shown to have slightly different retention time from **2** [8]. When **1** was irradiated with UV light (medium pressure mercury lamp, 150 W), it isomerized (50/50 by GC at photostationary state) to form a compound having exactly the same retention time as **2**. On the basis of the theory of photochemistry of olefins, only *E-Z* isomerization should have taken place. Thus, **2** was determined to be the *Z*-isomer of **1**. The structures of **3**, **4**, **5** and **6** were determined by GC-MS and those of **4**, **5** and **6** were confirmed by the agreement of GC retention time with authentic samples. GC-MS data (70 eV) *m/e* (relative abundance) **3**: 369 (0.5%, $M^+ - \text{Me}$), 300 (5%, $M^+ - \text{hexyl} + 1$), 143 (17%), 73 (61%), 59 (100%). **4**: 244 (33%, M^+), 229 (17%, $M^+ - \text{Me}$), 156 (100%). **5**: 170 (12%, M^+), 155 (100%, $M^+ - \text{Me}$), 73 (47%). **6**: 240 (0.3%, M^+), 225 (13%, $M^+ - \text{Me}$), 156 (86%, $M^+ - \text{hexyl} + 1$), 155 (97%, $M^+ - \text{hexyl}$), 73 (100%).

Structure determination of **8-10**

By the reasoning described above, **8** was judged to be the *Z*-isomer of **7**. The identities of **9** and **10** were assigned from GC-MS data.

GC-MS *m/e* **9**: 476 (2) M^+ ; 461 (3) $M^+ - \text{methyl}$; 419 (2) $M^+ - \text{butyl}$; 133 (100); 73 (75). **10**: 379 (2) $M^+ - \text{methyl}$; 337 (18) $M^+ - \text{butyl}$; 115 (32); 73 (100).

Measurements

GC analyses were performed with a Hewlett Packard 5890 gas chromatograph fitted with a FID and an HP-1 glass capillary column (25 m). Peak areas were determined with a Hewlett Packard 3392 integrator. GC-MS data were obtained using a Hewlett Packard 5995 gas chromatograph/mass spectrometer.

References and notes

- 1 T. Suzuki and P.Y. Lo, *J. Organomet. Chem.*, 391 (1990) 19.
- 2 T. Suzuki and P.Y. Lo, *J. Organomet. Chem.*, 396 (1990) 299.
- 3 I. Ojima, in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Vol. 2, Wiley, New York, 1989, p. 1479.
- 4 L.N. Lewis and N. Lewis, *J. Am. Chem. Soc.*, 108 (1986) 7228.
- 5 M.T. Chicote, M. Green, J.L. Spencer, F.G.A. Stone and J. Vicente, *J. Chem. Soc. Dalton Trans.*, (1979) 536.
- 6 H.M. Dickers, R.N. Haszeldine, A.P. Mather and R.V. Parish, *J. Organomet. Chem.*, 161 (1978) 91.
- 7 "Solution A" in G. Chandra, P.Y. Lo, P.B. Hitchcock and M.F. Lappert, *Organometallics*, 6 (1987) 191. The structure of active species has been determined and reported in N.J.W. Warhurst, Ph.D. Thesis, University of Sussex, 1990.
- 8 T. Suzuki, unpublished work.