Regio- and Stereoselective Hydrosilylation of 1,4-Bis(trimethylsilyl)-3-buten-1-ynes

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(Received March 19, 1997; CL-970199)

Four kinds of regio- and stereoisomers of hydrosilylation products of 1,4-bis(trimethylsilyl)-3-buten-1-yne (**1**) could be independently prepared in over 93% selectivities by proper choice of catalysts and cis and trans geometries of **1**.

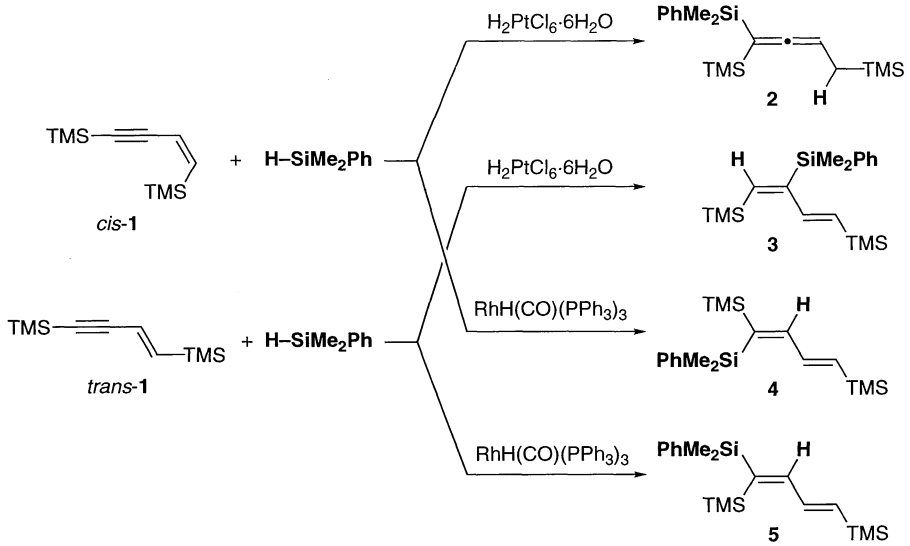
Catalytic hydrosilylation of conjugated enynes has been investigated by several research groups and shown to give allenylsilanes and dienylsilanes, which are useful intermediates in organic synthesis.[1] We have been interested in the use of cis and trans isomers of 1,4-bis(trimethylsilyl)-3-buten-1-ynes (*cis*-**1** and *trans*-**1**, respectively) as substrates of catalytic hydrosilylation, because both isomers are readily accessible from a common starting material, (trimethylsilyl)acetylene.[1c,2,3] It has been expected that the difference in the geometry of starting enynes (cis or trans) would be reflected in the regio- and stereochemistries of the reaction, leading to the selective synthesis of isomers of hydrosilylation products. We report herein that such reactions could be realized in high selectivities by proper choice of hydrosilylation catalysts.

Scheme 1 outlines the results. One of the most interesting findings in this study is an alteration in the regiochemistry (1,4- or 1,2-addition) depending on the trans and cis geometries of enynes, that was observed for the platinum-catalyzed reactions. Another point should be noted is clear dependence of the stereochemistry upon the geometries in the rhodium-catalyzed reactions; *cis*-**1** and *trans*-**1** gave *anti*- and *syn*-addition products **4** and **5**, respectively.

The representative data are listed in Table 1. Treatment of *cis*-**1** with $HSiMe_2Ph$ (1.1 equiv.) in the presence of a catalytic amount of $H_2PtCl_6{\cdot}6H_2O$ (0.5 mol%) led to 1,4-addition of hydrosilane across the enyne skeleton to give allenylsilane **2** in 96% selectivity (Entry 1). Almost the same selectivity for allenylsilane formation was observed with $HSiMePh_2$ in place of $HSiMe_2Ph$, though the reactivity of $HSiMePh_2$ was considerably lower than that of $HSiMe_2Ph$.[4,5] On the other hand, the platinum-catalyzed hydrosilylation of *trans*-**1** with $HSiMe_2Ph$ mainly provided 1,2-addition product **3** (Entry 2).[6]

In the rhodium-catalyzed reactions, 1,2-addition of hydrosilane across the triple bond took place for both enyne isomers (Entries 3–5). It was noted that the orientation of addition observed for the rhodium-catalyzed systems was opposite to the platinum-catalyzed 1,2-addition of *trans*-**1** (Entry 2). The selectivity was highly sensitive to the sort of catalyst employed and $RhH(CO)(PPh_3)_3$ was the only rhodium complex that provides over 90% selectivities.[7] Although the reaction of *trans*-**1** with $HSiMe_2Ph$ gave only 81% selectivity of **5** (Entry 4), the selectivity could be improved to 96% by using $HSiMePh_2$ (Entry 5).

The stereochemical courses of the rhodium-catalyzed hydrosilylation were clearly dictated by the cis and trans geometries of starting enynes. Of the reaction courses shown in Scheme 1, the *syn*-addition to *trans*-**1** giving **5** is a commonly observed process for the catalytic hydrosilylation of acetylene derivatives. On the other hand, the *anti*-addition to *cis*-**1** to give **4** deserves a discussion. It should be noted that the *anti*-addition involved cis to trans isomerization of the ene part of *cis*-**1**. This phenomenon can be reasonably understood by the hydrosilylation process in Scheme 2. The first step is *syn*-addition of a silylrhodium species to the triple bond of *cis*-**1** to afford a methylene-π-allyl complex **6**, which has a bulky trimethylsilyl group at the anti position of the π-allyl moiety. The steric demand in the *anti*-π-allyl complex **6** may be



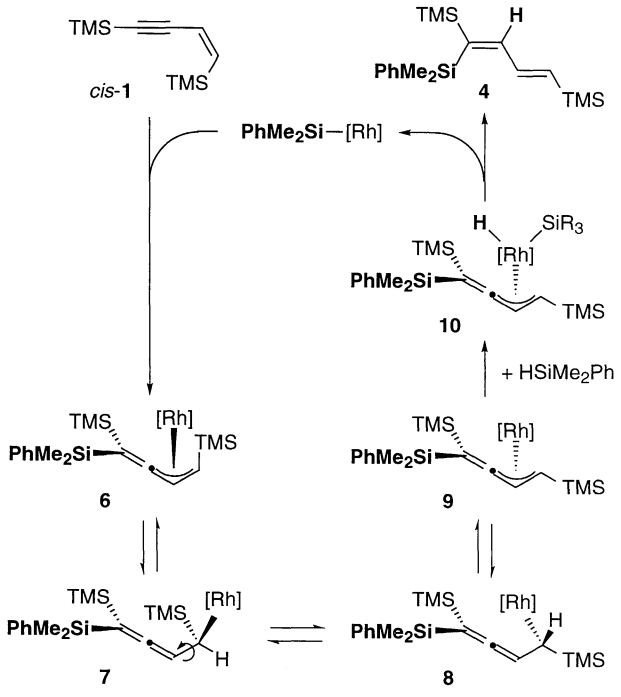
Scheme 1.

Table 1. Catalytic hydrosilylation of *trans*- and *cis*-1,4-bis(trimethylsilyl)-3-buten-1-ynes (**1**) with $HSiMe_2Ph$[a]

Entry	Enyne	Catalyst	Reaction time/h	Product ratio[b]				Total yield /%
				2	**3**	**4**	**5**	
1	*cis*-**1**	$H_2PtCl_6 \cdot 6H_2O$	2	**96**	4	0	0	93
2	*trans*-**1**	$H_2PtCl_6 \cdot 6H_2O$	3	0	**93**	0	7	100
3	*cis*-**1**	$RhH(CO)(PPh_3)_3$	19	0	0	**95**	5	98
4	*trans*-**1**	$RhH(CO)(PPh_3)_3$	19	10	0	9	**81**	96
5[c]	*trans*-**1**	$RhH(CO)(PPh_3)_3$	24	4	0	0	**96**	99

[a]All reactions were examined with 0.5 mol% of catalyst and 1.1 equivalents per **1** of $HSiMe_2Ph$ at 80 °C without solvent. [b]Determined by ^1H NMR analysis of a mixture of the reaction products after separation of catalyst by column chromatography (Al_2O_3, hexane). [c]The reaction was performed with $HSiMePh_2$ in place of $HSiMe_2Ph$.

effectively reduced by its isomerization to the *syn*-π-allyl isomer **9** via allenylmethyl intermediates **7** and **8**. As seen from the scheme, the rhodium moiety is shifted from the syn position to the anti position with respect to the R_3Si group during the isomerization. Therefore, after the oxidative addition of hydrosilane to **9** followed by the reductive elimination of the methylene-π-allyl and hydrido ligands from **10**, the *anti*-addition product **4** is produced with the cis to trans isomerization of the ene part.



Scheme 2.

Supplementary Material (4 pages) including experimental procedures and spectroscopic data of new compounds are available on request to the author by facsimile (+81-6-605-2978).

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. Partial financial supports from Asahi Glass Foundation and Tokuyama Science Foundation are gratefully acknowledged.

References and Notes

1 a) For review see: T. Hiyama and T. Kusumoto, in "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 8, Chap. 3.12, p. 772; b) M. Ishikawa, A. Naka, and J. Ohshita, *Organometallics*, **11**, 3004 (1992); c) J. Ohshita, K. Furumori, A. Matsuguchi, and M. Ishikawa, *J. Org. Chem.*, **55**, 3277 (1990); d) T. Kusumoto, K. Ando, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **65**, 1280 (1992); e) T. Kusumoto and T. Hiyama, *Chem. Lett.*, **1985**, 1405; f) M. Licchelli and A. Greco, *Tetrahedron Lett.*, **28**, 3719 (1987); g) H. Bock and H. Seidl, *J. Am. Chem. Soc.*, **90**, 5694 (1968).

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4 The reaction of *cis*-**1** with $HSiMePh_2$ (1.1 equiv.) at 80 °C for 69 h in the presence of the platinum catalyst (0.5 mol%) gave 1-(diphenylmethylsilyl)-1,4-bis(trimethylsilyl)-1,2-butadiene in 94% selectivity.

5 The predominant formation of allenylsilane **2** was also observed with $RuHCl(CO)(PPh_3)_3$ catalyst, though the catalytic activity was much lower than the platinum catalyst. For example, the reaction of *cis*-**1** with $HSiMe_2Ph$ (1.5 equiv.) in the presence of 2.5 mol% of $RuHCl(CO)(PPh_3)_3$ at 80 °C for 134 h gave **2** in 86% selectivity, together with **4** (6%) and **5** (8%).

6 The catalytic hydrosilylation of *cis*-**1** and *trans*-**1** could be conducted in almost the same selectivities as in Entries 1 and 2 using phosphine-free platinum catalysts such as $Pt(cod)_2$ and $PtCl_2(cod)$, while the selectivity was low when PPh_3-coordinated complexes ($PtCl_2(PPh_3)_2$ and $Pt(PPh_3)_4$) were employed as catalysts.

7 The product ratio in the hydrosilylation of *trans*-**1** with $HSiMePh_2$ at 80 °C catalyzed by other rhodium complexes: $RhCl(PPh_3)_3$, **2/4/5** = 17/11/68; $[Rh(cod)_2]BF_4$, **2/3/5** = 5/44/51, [Rh(cod)(dppp)]BF_4, **2/3/5** = 2/48/50; TpRh(cod), **2/3/5** = 4/21/75.