

Cationic Rhodium Complex-catalysed Highly Selective Hydrosilylation of Propynylic Alcohols: a Convenient Synthesis of (*E*)- γ -Silyl Allylic Alcohols

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Cationic rhodium complex-catalysed hydrosilylation of alk-1-yneols including propynylic alcohols with triethylsilane is highly selective to give (*E*)-1-triethylsilyl alk-1-enols as products in excellent yields.

Neutral rhodium complex-catalysed hydrosilylation of alk-1-yne gives (*Z*)-vinylsilanes as the major product *via* the *trans* addition of Si-H across the carbon-carbon triple bond.¹ In contrast to the extensive amount of the work on the neutral rhodium complex-catalysed hydrosilylation of alk-1-yne, catalysis by cationic rhodium complexes has not been reported. In the course of the study of solvent effects on hydrosilylation, we noticed reversal of stereoselectivity for cationic rhodium complex catalysis, *i.e.* cationic rhodium complex-catalysed hydrosilylation of hex-1-yne with triethylsilane was highly selective giving (*E*)-1-triethylsilylhex-1-ene

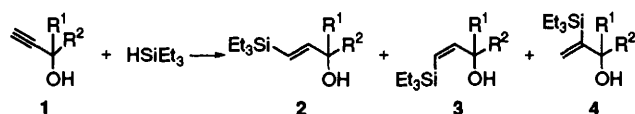


Table 1 Cationic rhodium complex-catalysed hydrosilylation of propynylic alcohols^a

| Entry | Substrate | Conditions T ^o /C (t/h) | Yield/% ^b | Product distribution ^c 2 : 3 : 4 |
|----------------|-----------|---------------------------------------|----------------------|---|
| 1 ^d | | room temp. (30 min) | 90 | >99 : 1 : 0 |
| 2 | | 50 (4 h) | 95 | >99 : 1 : 0 |
| 3 | | 50 (16 h) | 91 | 100 : 0 : 0 |
| 4 | | 50 (3 h) | 87 | 100 : 0 : 0 |
| 5 | | 50 (2 h) | 90 | 100 : 0 : 0 |
| 6 | | 50 (4 h) | 82 | 100 : 0 : 0 |
| 7 | | 50 (16 h) | 84 | 100 : 0 : 0 |
| 8 | | 50 (16 h) | 92 | 100 : 0 : 0 |
| 9 | | 50 (16 h) | 94 | 100 : 0 : 0 |

^a A mixture of propynylic alcohol (4 or 8 mmol), Et₃SiH (1.5 equiv.) acetone (6 or 12 ml) [Rh(cod)₂]BF₄ (0.5 mol%), PPh₃ (1 mol%) was stirred under argon. ^b Isolated yield. ^c Determined by 270 MHz ¹H NMR spectroscopy. ^d [Rh(cod)₂]BF₄ (0.2 mol%), PPh₃ (0.4 mol%).

as a product with 99% selectivity.² The catalyst system [Rh(cod)₂]BF₄-2PPh₃ is shown to be highly selective for the hydrosilylation of alk-1-yne.

The hydrosilylation of propynylic alcohols (Scheme 1) is the most straightforward method for the preparation of (*E*)- γ -silyl allylic alcohols **2**, which are useful building blocks, particularly as a source of chiral secondary alcohols.³ Reaction using the widely employed Speier catalyst resulted in the non-selective formation of γ - and β -silyl allylic alcohol.⁴ To raise the reaction to a synthetically useful level, the selectivity must be improved. Recently, some improvements were made by the use of a platinum(0) complex.⁵ However, the reaction has a serious limitation since dimethylphenylsilane, a more reactive hydrosilane, must be used to obtain (*E*)- γ -silyl allylic alcohols **2** in >95% selectivity. Furthermore, the platinum(0) complexes used are not easily accessible. More widely applicable and general hydrosilylation is desired and with our new and powerful catalyst in hand, we succeeded in highly selective hydrosilylation of propynylic alcohols with triethylsilane.

Propynylic alcohols were reacted with triethylsilane in the presence of a catalytic amount of [Rh(cod)₂]BF₄-2PPh₃. Results are summarized in Table 1. Whereas rhodium complexes have been reported to catalyse the dehydrogenative silylation of alcohols,⁶ no silylation occurred in the present reactions, which could therefore be carried out without requiring protection of the alcohol functionality. The hydrosilylation of propynylic alcohols was highly selective to give (*E*)- γ -silyl allylic alcohols **2** as products. The reaction of **1a** was rapid and was complete within 30 min at room temperature. Both secondary and tertiary propynylic alcohols were less reactive than **1a**, and to obtain the corresponding product in high yield, it was necessary to raise the temperature to 50 °C. For substrates bearing a carbon-carbon double bond, reaction occurred chemoselectively at the carbon-carbon triple bond (entries 4 and 5). The double-bond geometry of the starting alcohol was completely retained. γ -Silyl diallylic alcohols such as **2d** and **2e** were reported to be useful starting materials in the synthesis of cyclopentenones. They were easily oxidized to β -silylsubstituted divinyl ketones, which readily cyclize to give cyclopentenones.⁷ The hydrosilylation described here provides a more convenient and direct route to such alcohols. Hydrosilylation of but-1-yn-4-ol with triethylsilane gave (*E*)-1-triethylsilylbut-1-en-4-ol exclusively in 97% yield.

By contrast, [Rh(cod)Cl]₂-catalysed hydrosilylation of **1b** with triethylsilane was (*Z*)-selective to give products in 25% yield. The ratio of **2b** : **3b** : **4b** was 10 : 83 : 7. The reaction was quite sluggish (48 h under dioxane reflux).

Further development and synthetic application of these (*E*)- γ -silyl allylic alcohols are underway in our laboratory and will be reported in due course.

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