

Tri(*t*-butyl)phosphine-assisted selective hydrosilylation of terminal alkynes

Wei Wu^{*}, Xiao Yun Zhang, Shou Xing Kang, Yan Min Gao

Department of Chemistry, China University of Petroleum (East China), Qingdao 266555, China

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Abstract

A highly efficient and regio-/stereoselective method of hydrosilylating terminal alkynes was developed using Pt(DVDS)-tri(*t*-butyl)phosphine catalyst system at room temperature. *Trans*-products or *alpha*-products were obtained almost exclusively depending on the alkynes and silanes employed.

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Keywords: Hydrosilylation; Terminal alkynes; Tri(*t*-butyl)phosphine; Platinum

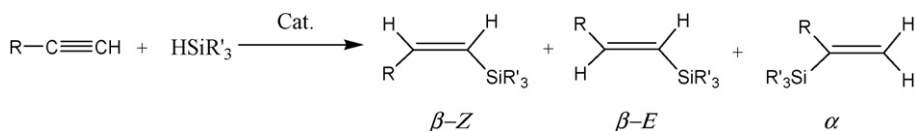
Catalytic hydrosilylation of alkynes is one of the most convenient and straightforward methods for the synthesis of vinylsilanes that are important building blocks in organic synthesis [1–3]. Because the hydrosilylation of terminal alkynes usually give a primary mixture of three isomeric vinylsilanes (β -*Z*, β -*E*, and α , Scheme 1), the major consideration in this conversion is the regio- and stereoselectivities.

Many catalyst systems, such as Pt [4], Ru [5], Rh [6], Pd [7], etc., have been developed for hydrosilylating alkynes since the first report using Speier's catalyst [8]. It was found that the control of the selectivity, in most cases, was capriciously affected by various factors such as types of alkynes and silanes, metal species and reaction conditions including solvent, temperature and reaction time [5], etc.

Among the aforementioned catalyst systems, platinum is still a better choice for the highly efficient formation of stereospecific vinylsilanes, for that it is generally applicable, convenient and easy accessible. The reactions are usually clean and no detectable byproducts can be found, although the vinylsilane isomer distribution may vary. Other conventional metal catalysts, like rhodium, ruthenium and palladium, usually show certain catalytic activity toward cyclotrimerization and/or dimerization of alkynes thus result in unsatisfactory yields, or they are only effective to certain activated silanes (such as trichloro-, trialkoxyl, and di/triphenylsilanes) [9]. Recently we found the regio-/stereoselectivity of Pt-catalyzed hydrosilylation can be greatly improved by addition of certain kind of bulky ligand [10]. Tri(*t*-butyl)phosphine, which is readily available and have been proven to be highly efficient for a one-pot hydrocarbonation [11], could be an excellent candidate for this purpose. Herein, we report a rapid and efficient room-temperature method for the highly stereo- and regioselective hydrosilylation of terminal alkynes using the Pt(DVDS)/P(*t*-Bu)₃ catalyst system.

^{*} Corresponding author.

E-mail address: wwu257@163.com (W. Wu).

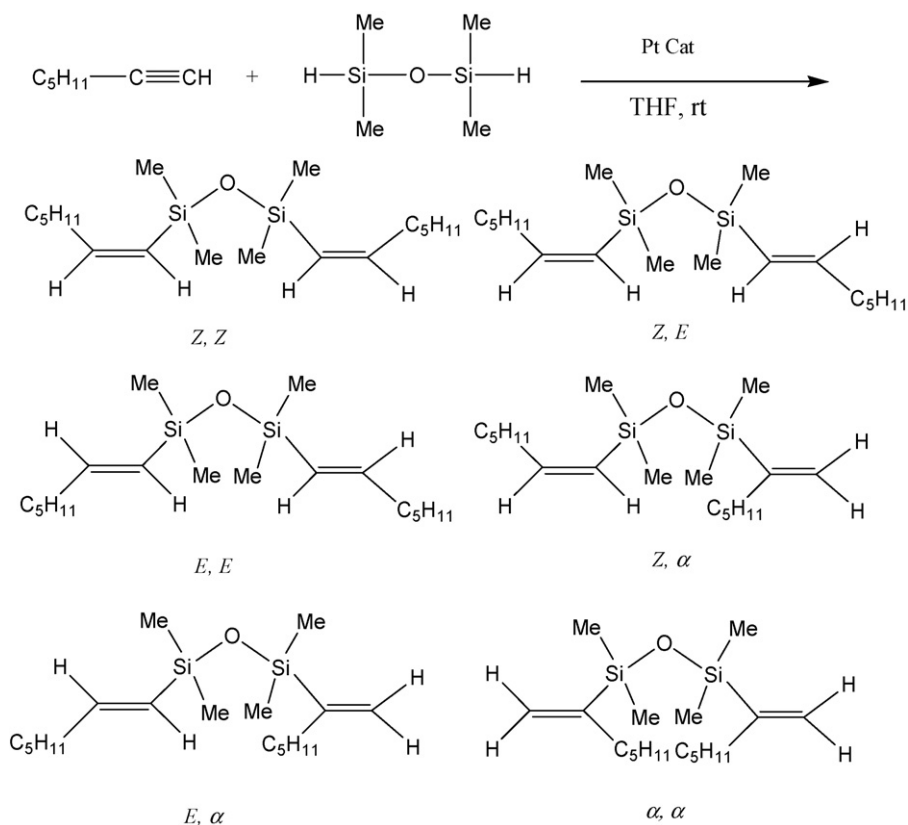


Scheme 1.

To begin our study, 1-heptyne was reacted with 1,1,3,3-tetramethyldisiloxane in THF with a variety of phosphorus ligands being examined. 1,1,3,3-tetramethyldisiloxane can combine with two equivalents of 1-heptyne, giving six possibilities of product isomers as shown in Scheme 2. The effect of ligand on the catalytic selectivity can be well observed from the product isomer distribution.

As shown in Table 1, the use of H_2PtCl_6 as a catalyst led to 69% isolated yield of the hydrosilylation products as an isomer mixture. Five isomers were present with the *E,E*-isomer as the main component (53%). In all cases, the least possible α,α -isomer was not found. The use of Pt (DVDS) (DVDS: 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) complex as a catalyst resulted in an increase in both the yield of the products and the *E,E* isomer ratio under the same reaction conditions. The use of HMPT, PPh_3 and $\text{P}(o\text{-MeC}_6\text{H}_4)_3$ increased the yields but the selectivity were still not good. $\text{P}(\text{OEt})_3$ and $\text{P}(\text{OPh})_3$ were totally unacceptable because of the low yield and poor selectivity under this condition. Notably, the employment of $\text{P}(t\text{-Bu})_3$ as ligand resulted in both excellent yield and improved selectivity, giving only three isomers with the *E,E*-isomer ratio up to 91%. Thus Pt(DVDS)/ $\text{P}(t\text{-Bu})_3$ was selected as catalyst for the following hydrosilylation of various terminal alkynes.

Under the optimized conditions, a variety of alkynes bearing various functional groups were hydrosilylated with triethylsilane, and triphenylsilane (Table 2). Hydrosilylation of heptyne with triethylsilane catalyzed by Pt(DVDS) without the phosphine ligand was also included for comparison (in parentheses, entries 1 and 2). The use of Pt(DVDS)/ $\text{P}(t\text{-Bu})_3$ as catalyst provided excellent yields in all cases. When triethylsilane was used, very high *trans* selectivity was



Scheme 2.

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