



# An effective hydrosilylation of alkynes in supercritical CO<sub>2</sub> – A green approach to alkenyl silanes



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## ARTICLE INFO

### Article history:

Received 13 July 2017

Revised 29 September 2017

Accepted 5 October 2017

### Keywords:

Hydrosilylation  
Alkyne functionalization  
Supercritical CO<sub>2</sub>  
Homogeneous catalysis  
Platinum  
Green process

## ABSTRACT

Hydrosilylation of a wide group of alkynes (terminal and internal) with four structurally different silanes has been for the first time performed in supercritical CO<sub>2</sub> (scCO<sub>2</sub>). The results clearly showed the advantages as well as the limitations of using of scCO<sub>2</sub> as a reaction and extraction medium for hydrosilylation of numerous alkynes with different functionality and volatility. Procedures for the synthesis and isolation of over forty silyl ethenes were described, among which more than twenty for the first time. Obtained products were fully characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR, GC–MS, and EA. Moreover, by X-ray crystallography, the molecular structures of (*E*)-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-2,5-dimethylhex-3-ene-2,5-diol (**3n**) and (*E*)-triethyl(2-(triphenylsilyl)vinyl)silane (**12a**) have been determined for the first time.

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## 1. Introduction

Transition-metal catalyzed hydrosilylation of alkynes is one of the most straightforward and effective ways for the synthesis of alkenyl-functionalized silanes [1–8]. The process occurs with 100% atom efficiency and depending on the type of a catalyst and reaction conditions, it gives the opportunity for the selective formation of all theoretically possible isomers of Si–H addition to both terminal and internal carbon-carbon triple bonds (C≡C). The obtained alkenyl silanes, due to their versatility, low cost, lack of toxicity, wide functionality, and high chemical stability, are considered as an important class of organosilicon building blocks for the synthesis of molecules, polymers, and natural products. For example, they can be used in palladium or rhodium-catalyzed cross-coupling reactions and in the Tamao-Fleming oxidation providing carbonyl derivatives [9–14].

Although hydrosilylation of alkenes and alkynes with silanes or siloxanes has been widely studied, new strategies, which can increase the process effectiveness, decrease its costs and make it more environmentally friendly are continuously searched for. In our group, we have tried to overcome these challenges by applying the procedures based on the use of highly active and selective cat-

alytic systems containing the precious or nonprecious metals which often can be applied multiple times, ensure easy product separation, and can be performed in nontoxic and nonvolatile solvents such as ionic liquids (IL) [15–30].

Recently, our research interest has been directed to the use of scCO<sub>2</sub> as a reaction and extraction medium for the hydrosilylation of carbon-carbon triple bond in alkynes. The characteristic features of scCO<sub>2</sub> include low critical parameters (73.8 bar, 31.2 °C, 0.456 g/mL) low price, non-flammability, wide availability due to its natural abundance, tunable density and solvent-like properties (through temperature and pressure variations) [31–36]. All of these make it a perfect medium allowing the recovery of catalyst, easy product separation, and significantly reduce cost of the isolation. Moreover, silicon-containing and unsaturated organic compounds are generally soluble in scCO<sub>2</sub>. It has been reported that even small organosilicon substituents such as SiMe<sub>3</sub> attached to ligands, significantly increase the solubility of transition metal complexes in scCO<sub>2</sub> [37–39]. The effect of silyl groups is the same as perfluorinated ones, and therefore organosilicon compounds are predominantly well soluble in nonpolar scCO<sub>2</sub>. This property gives the opportunity for the hydrosilylation of a wide spectrum of reagents as well as the extraction of the resulting hydrosilylation products.

Despite many advantages of synthetic methods based on scCO<sub>2</sub>, the hydrosilylation of carbon-carbon unsaturated bonds in this

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medium has been poorly explored. Up to date, only seven reports on the hydrosilylation of carbon-carbon double bond (C=C) have been published. Among them, just two concern the synthesis of molecular compounds by the hydrosilylation of perfluoro, alkyl or aryl olefins with dimethoxymethyl-, triethoxy- and triethylsilane, in the presence of  $\text{RhCl}(\text{PR}_3)_3$  or  $\text{RuCl}_2(\text{PR}_3)_2$  ( $\text{R}$  = phenyl, or perfluoroarene) [40,41]. The remaining papers refer to the synthesis of macromolecular systems, obtained by the hydrosilylation of perfluoro-1-hexene, bifunctional olefins or oligo(vinylsiloxanes) with poly(methylhydrosiloxanes) or modified silica, mostly in the presence of Karstedt's catalyst ( $\text{Pt}_2(\text{dvs})_3$ ) or 2,2'-azobis(2-methyl propionitrile) (AIBN) as radical initiator [42–46]. Moreover, there are no reports on the hydrosilylation of C≡C bond in  $\text{scCO}_2$  at all.

In view of the above-mentioned information, we decided to describe for the first time the synthesis of alkenyl silanes performed in  $\text{scCO}_2$ , afforded by hydrosilylation of a wide range of terminal and internal alkynes with different types of silanes, in the presence of Karstedt's catalyst.

The main purposes of our studies were: (i) to examine if the tested reagents can form homogeneous solutions in  $\text{scCO}_2$  (observations through the sapphire windows of the reactor), (ii) to determine if the chosen reagents can react in the presence of  $\text{Pt}_2(\text{dvs})_3$ , and how the  $\text{scCO}_2$  affects the catalyst activity and selectivity, (iii) finally to establish which products of hydrosilylation can be extracted with  $\text{scCO}_2$  in high yields and purity (Fig. 1).

Such studies will clearly show for which set of reagents and hydrosilylation products the use of  $\text{scCO}_2$  as a reaction and extraction medium can be successful, and for which, other media should be used.

## 2. Results and discussion

In the studies, seventeen structurally different alkynes were reacted with four silanes in  $\text{scCO}_2$  or toluene (or THF) under different reaction conditions. A wide range of internal and terminal alkynes, as well as organosilicon compounds with different functional groups, were applied to check if the physicochemical properties and the type of groups attached to the silicon atom or to the  $\text{C}_{\text{sp}}$  atom in alkyne, affects the possibilities to carry out the reaction in  $\text{scCO}_2$ . The set of alkynes contained terminal and internal symmetrically disubstituted alkyl as well as aryl alkynes. Some of them possessed the functionalities like hydroxyl,  $-\text{OSiMe}_3$ ,  $-\text{OCH}_3$ , bromo or boronic acid pinacol ester. On the other hand, among tested

silanes were 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1a**), triethoxysilane (**1b**), triethylsilane (**1c**), and triphenylsilane (**1d**). Both groups of reagents were composed of compounds with different molecular weight ( $M_w$ ) and physical properties such as boiling (b.p.) and melting (m.p.) points or solubility, which are the factors having a significant influence on the effectiveness of the process performed in  $\text{scCO}_2$  and the extraction of resulting products with this medium. Selected physical properties of all tested herein alkynes and silanes are presented in Supporting Information (Table S1).

The commercially available Karstedt's catalyst ( $\text{Pt}_2(\text{dvs})_3$ ) [47,48], well-known for its high activity in hydrosilylation of both terminal and internal carbon-carbon multiple bonds, was used. So far, it has been mainly applied for the modification of alkenes with a wide spectrum of functionalities (also with steric hindrance), in a wide range of temperatures, in the air or inert atmosphere [49–51]. Other catalytic systems could be considered, however, due to the lack of information concerning the alkyne hydrosilylation in  $\text{scCO}_2$ , the Karstedt's catalyst seems to be the most reasonable choice for the first tests of the reactivity of structurally different alkynes with silanes performed in this medium. The presence of tetramethyldivinylsiloxanes as ligands coordinated to the Pt atom will have also the positive impact on the solubility of the catalyst in compressed  $\text{CO}_2$ . Although the Karstedt's catalyst has been widely used in alkene hydrosilylation, we have found only a few examples of its use in hydrosilylation of alkynes [52–61]. There is no work concerning detailed studies on the hydrosilylation of structurally different alkynes with various silanes, catalyzed by  $\text{Pt}_2(\text{dvs})_3$ , performed in conventional media.

Since the Karstedt's catalyst is one of the most effective and widespread catalysts among all used, in our opinion, more complex catalytic systems should be applied only in the processes in which Karstedt's one will prove to be not selective or inactive. Moreover, our choice of reagents and catalyst which are stable and easily available should be considered as an advantage of presented herein synthetic and isolation methods since it makes the process more versatile, practical and meeting the green chemistry requirements.

### 2.1. Hydrosilylation of alkynes with 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1a**)

At the first step of the study, the hydrosilylation of alkynes with 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1a**) was performed. Compound **1a** is a liquid with a molecular weight  $M_w$  equal 222.5 g/mol, b.p. at 142 °C and it is considered as a molecular model of

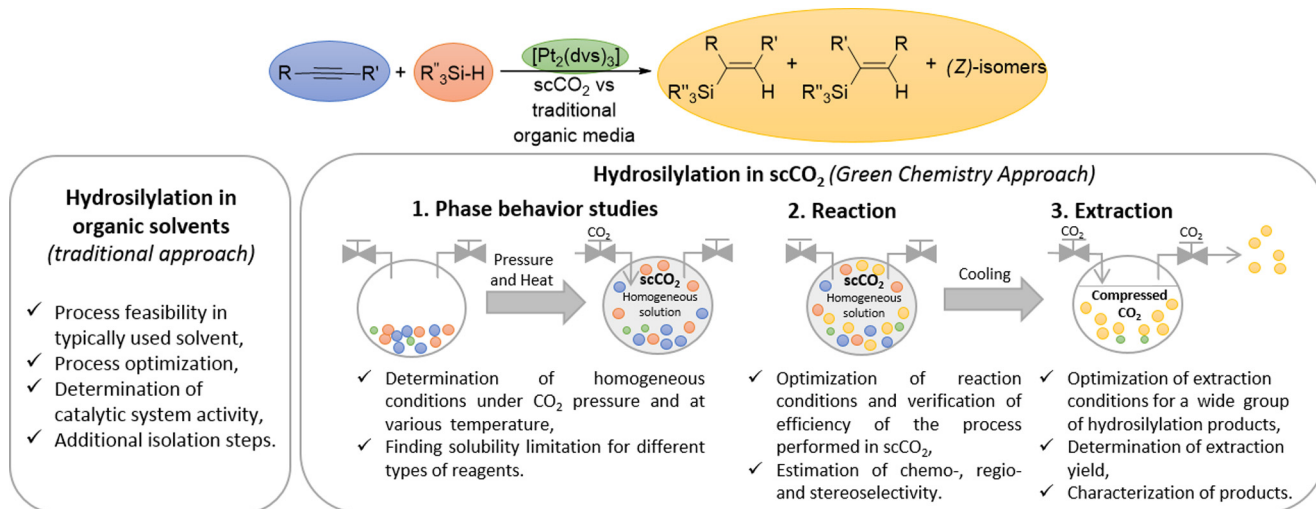


Fig. 1. Hydrosilylation of the terminal and internal alkynes with **1a-1d** performed in  $\text{scCO}_2$ .

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