

# Cross-coupling of vinyl-disilacyclobutane with olefins catalyzed by $[\text{RuH}(\text{Cl})(\text{CO})(\text{PCy}_3)_2]^\star$

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## Abstract

Cross-coupling of vinyl-disilacyclobutane with a variety of olefins in the presence of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PCy}_3)_2]$  leads to stereoselective formation of functionalized vinyl-disilacyclobutanes. Analogous homo-coupling of vinyl-disilacyclobutane leads to the formation of *E*- and *gem*-bis(silyl)ethenes. The reaction offers a new route for synthesis of attractive monomers for ring opening polymerization (ROP).

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## 1. Introduction

Recent progress in the synthetic routes leading to the substituted disilacyclobutanes has enabled the preparation of a wide range of poly(silylenemethylene)s via ring opening polymerization (ROP) (Scheme 1) [1]. By using reactive functionalities on silicon new polymers of this type bearing various side chains on the polymer backbone can be formed [2].

Four membered silacyclobutane ring is susceptible to ROP even without any catalyst present [1].

In the last two decades, we have developed two new catalytic reactions occurring between the same parent substances, i.e., silylative coupling (SC) (also called *trans*-silylation or silyl group transfer) and cross-metathesis (CM) of alkenes (Scheme 2) with vinylsilanes which have

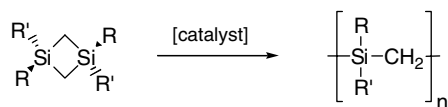
provided a universal route for the synthesis of molecular compounds with vinylsilicon functionality. While the cross-metathesis is catalyzed by well-defined Ru and Mo carbenes the silylative coupling is catalyzed by complexes initiating or generating  $[\text{M}]-\text{H}$  or  $[\text{M}]-\text{Si}$  bonds (where  $\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$ ) (for recent reviews, see [3–5]).

The mechanism of catalysis of SC proved by Wakatsuki et al. [6] and by us [7] involves insertion of vinylsilane into the  $[\text{M}]-\text{H}$  bond followed by  $\beta$ -silyl elimination which generates  $[\text{M}]-\text{Si}$  complex and ethylene, followed by insertion of alkene into  $[\text{M}]-\text{Si}$  bond followed by  $\beta$ -elimination with elimination of substituted vinylsilane and regeneration of  $[\text{Ru}]-\text{H}$  complex. Functionalization of vinylsubstituted cyclosiloxanes, cyclosilazane [8] and octavinylsilsequioxane [9], stereoselective synthesis of amides [10] and boranes [11] having a vinylsilicon functionality are recent examples of this new synthetic route.

Herein, we report the effective homo-coupling of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane and its cross-coupling with olefins catalyzed by ruthenium complexes containing  $[\text{Ru}]-\text{H}$  bonds leading to respective substituted vinylsilanes.

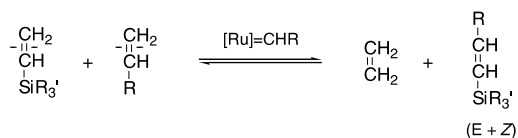
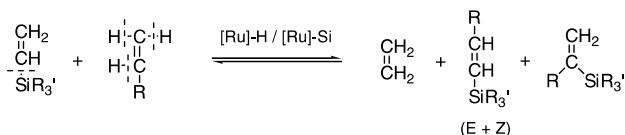
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Scheme 1.

## Cross-metathesis (CM)

Silylative Coupling (*trans*-silylation) (SC)

Scheme 2.

## 2. Results and discussion

When the solution of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane (**2**) in toluene was treated in the presence of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PCy}_3)_2]$  at 110 °C for 18 h over 99% conversion was observed and the mixture of (*E* + *gem*) bis(trimethyldisilacyclobutyl)ethene was formed with the total yield 75% (Scheme 3).

The process was carried out at 110 °C for 18 h. After that time products (*E* + *gem*) was yielded. In case the reaction was performed in the presence of the first or second generation of Grubbs catalysts  $[\text{RuCl}_2(\text{PCy}_3)_2]$ -

(=CHPh)] and  $[\text{RuCl}_2(\text{PCy}_3)(\text{IMesH}_2)(=\text{CHPh})]$ , respectively, no conversion was observed.

*Trans*-silylation of **2** with a variety of olefins occurs regio- and stereoselectively and lead to exclusive formation of *E*-isomer (Scheme 4).

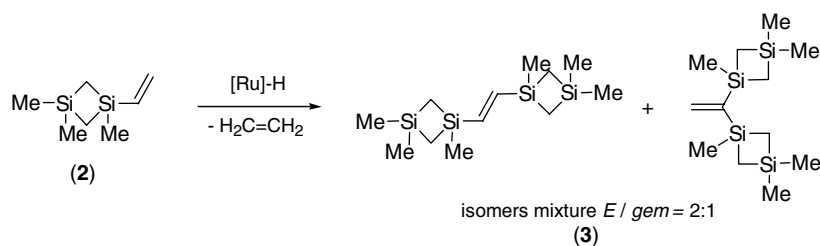
In order to avoid vinyldisilacyclobutane homo-coupling, olefins were used in excess. The experimental data for the reactions were compiled in Table 1.

In contrast to effective silylative coupling the cross-metathesis of **2** with the olefins does not proceed in the presence of Grubbs catalysts. Apparently, reported earlier decomposition of Grubbs catalyst takes place in the system [12].

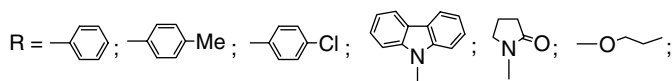
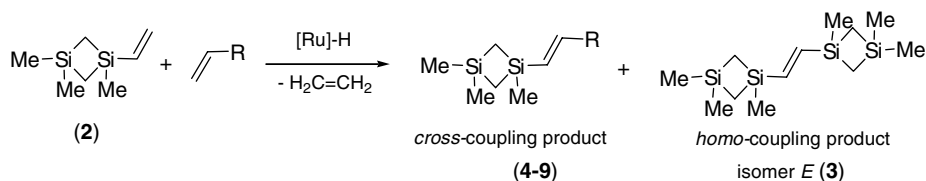
To learn more about the mechanism of the reaction, experiment with deuterium-labelled styrene- $\text{d}_8$  was performed. Thus, the reaction of vinyldisilacyclobutane (**2**) with styrene- $\text{d}_8$  permits a distinction between the mechanism of the silylative coupling (*trans*-silylation) and metallacarbene mechanism. In the case of a *trans*-silylation the formation of silyl-styrene- $\text{d}_7$  and ethylene- $\text{d}_1$  is expected (Scheme 5). In contrast, the metallacarbenes mechanism should afford silyl-styrene- $\text{d}_6$  and ethylene- $\text{d}_2$ .

The GC–MS analysis of the reaction mixture after 20 min, i.e., in the initial stage of the reaction, when the conversion did not exceed 10%.

A comparison of the fragments of mass spectra of silyl-styrene- $\text{d}_0$  ( $m/z = 232\text{M}^+$ ) (obtained in a control experiment, Fig. 1(a)) with the corresponding ones of silyl-styrene- $\text{d}$  obtained in a reaction according to Scheme 5, reveals a shift of the signals of the analogous fragments by 7 units, which suggests the formation of silyl-styrene- $\text{d}_7$  ( $m/z = 239\text{M}^+$ ). Moreover, the mass distribution presented in the spectrum (Fig. 1(b)) and



Scheme 3.



Scheme 4.

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