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Reactivity of 1-allylsilatrane in ruthenium-catalyzed silylative coupling with olefins – mechanistic considerations

https://doi.org/10.1515/hc-2020-0006
Received February 13, 2019; accepted October 16, 2019.

Abstract: We have developed a new effective route for obtaining (E)-vinyl-substituted silatranes via ruthenium-catalyzed silylative coupling of 1-allylsilatrane with olefins. Experimental research allowed us also to propose the mechanism of the process based on stoichiometric reactions.

Introduction

Silatranes make a widely studied class of organosilicon compounds characterized by cage tricyclic structure, pentacoordinate silicon center with donor-acceptor transannular Si ← N bond, and interesting biological properties [1-3]. In the last three decades, research on silatranes covered several areas, including organic and organometallic synthesis [4-6], materials chemistry [7-9] as well as biochemistry and medicine [10-13]

Given the variety of silatrane derivatives, allylsilatranes are hardly explored, which stands in stark contrast to the wide range of applications of allylsilanes in organic synthesis (e.g., in allylation of carbonyl compounds or olefin metathesis, for review see [14]). 1-Allylsilatrane (or allylsilatrane) **1** is the simplest representative of allyl-substituted silatranes (Figure 1).

In literature, there are not many reports concerning the structural aspects of **1** and its reactivity. The crystal structure of **1** was determined in low temperature, and its correlation to hyperconjugation between the Si-C σ-electrons and the C=C π-system was discussed [15]. Allylsilatrane was functionalized in catalytic hydrosilylation and hydrogermylation, as well as in non-catalytic hydrostannation [16].

Platinum-catalyzed hydrosilylation of **1** was used in the preparation of oligosiloxanes with silatrane cages, which may find potential applications in lithium-ion conductive matrices [17]. There are also reports of reactivity of **1** toward electrophiles and nucleophiles [18,19] and dienes [20] (in Diels-Alder reactions).

In the last two decades, our group has developed a catalytic transformation involving vinylmetalloids and olefins, i.e., ruthenium-catalyzed *trans*-metalation, which leads to functionalized alkenyl-substituted boronates, silanes and germanes (Scheme 1) [21].

In our previous study, we have reported the reactivity of vinylsilatrane in stereoselective *trans*-silylation with styrene derivatives catalyzed by $RuHCl(CO)(PCy_3)_2$, which leads to (*E*)-substituted alkenylsilatranes. We have also presented a detailed mechanism of this process, supported by studies and DFT calculations [22].

In this paper, we describe for the first time the reactivity of allylsilatrane in ruthenium-catalyzed *trans*-silylation with olefins. Experimental examination, such as catalytic tests and stoichiometric reactions, allowed us to propose a mechanism for this transformation.

Results and discussion

Synthesis of allylsilatrane

Allylsilatrane **1** was prepared in the transesterification reaction of allyltrimethoxysilane with triethanolamine in

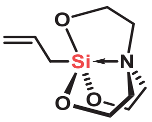

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Figure 1 Structure of 1-allylsilatrane.

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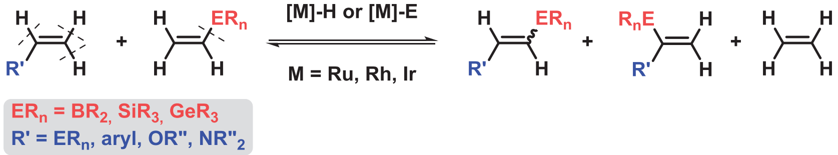
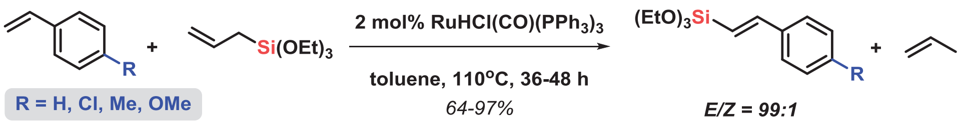
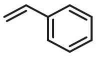
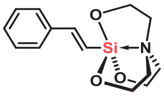
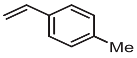
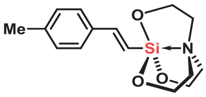
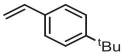
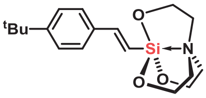
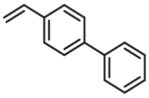
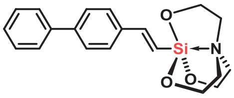


Scheme 1 Ruthenium catalyzed *trans*-metalation of olefins with vinylmetalloids.



Scheme 2 Ruthenium-catalyzed silylation of olefins with triethoxyallylsilane.

Table 1 allylsilatrane 100 mg (0.46 mmol), olefin (**1-3**) 0.92 mmol, olefin (**4**) 0.46 mmol, 2 mol% RuHCl(CO)(PCy$_3$)$_2$, 110°C, toluene (3 mL), open system, 24 h

	Olefin	Product	Isolated yield [%]
1			87
2			90
3			92
4			93

boiling xylene in 82% yield, which is a slightly modified procedure based on the work of Corriu et al. [19] **1** Was isolated as white, powdery flakes stable in air and toward moisture.

Reactivity of allylsilatrane in *trans*-silylation with olefins

In 1999, Murai et al. presented an alternative protocol for the silylation of olefins by using allylsilanes as silylating agents [23]. The process was then dubbed as dehydrogenative silylation, even though it is a different variant of the silylative coupling reaction which proceeds with the evolution of propene instead of ethylene. The authors studied the reactions of allyltrimethyl- and allyltriethoxysilane with selected styrenes in the presence of RuHCl(CO)(PPh$_3$)$_3$ and isolated several (*E*)-triethoxystyrylsilanes.

We were able to use **1** as a silylating reagent for the catalytic synthesis of (*E*)-styrylsilatranes with selected styrenes in the presence of 2 mol% RuHCl(CO)(PCy$_3$)$_2$, which is the most efficient catalyst for the silylative coupling reaction (Table 1, Scheme 3).

Examination of the ^{1}H ^{13}C ^{29}Si NMR spectra, showed full conversion of **1** and confirmed that the reaction was (*E*)-selective. The same products could also be obtained when 1-vinylsilatrane acted as a silylating reagent, which was previously mentioned [22]. However, contrary to Murai's report, the product of dimerization of **1** was not observed.

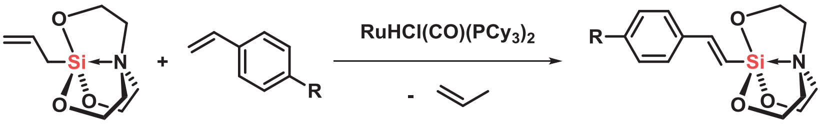
Nevertheless, the homocoupling of **1** catalyzed by 2 mol% of RuHCl(CO)(PCy$_3$)$_2$ gave 1-silatranyl-2-(silatranylmethyl)ethene in 90% yield as a mixture of E/Z isomers (Scheme 4).

Mechanistic implications

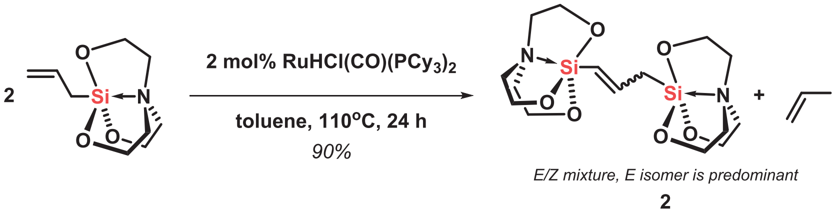
The equimolar reaction of **1** with RuHCl(CO)(PCy$_3$)$_2$ in toluene-d_8 carried out in a closed system (Young NMR tube) proved that the gas product of the reaction was propene (Scheme 5), which was confirmed by ^{1}H NMR analysis. However, the ^{1}H NMR spectrum also showed that the Ru–H proton signal did not entirely disappear, which was explained as a result of the regeneration of the complex during the initial stage of the catalytic cycle.

As the Ru-silatranyl complex is also the same intermediate in the coupling reaction of vinylsilatrane with olefins, we added styrene to the equimolar reaction system, which after 12 h was fully converted to (*E*)-styrylsilatrane **5** (Scheme 6).

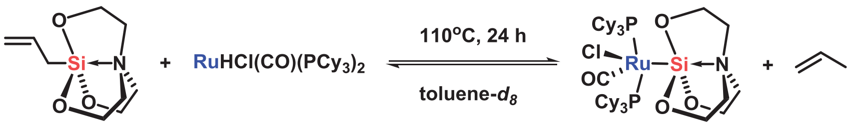
Based on our experimental evidence and Murai's work, as well as our previous study on silylative coupling of vinylsilatrane, we proposed a general mechanism for the first part of the catalytic cycle of ruthenium-catalyzed silylative coupling of **1** with olefins (Scheme 7).



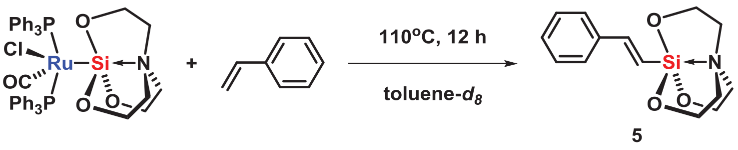
Scheme 3 *Trans*-silylation of **1** with styrenes catalyzed by $RuHCl(CO)(PCy_3)_2$.



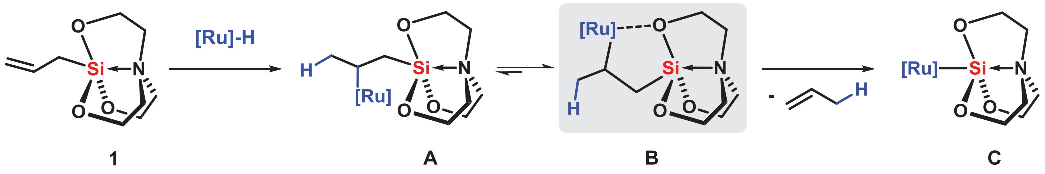
Scheme 4 Homocoupling of allylsilatrane.



Scheme 5 The equimolar reaction of **1** with $RuHCl(CO)(PCy_3)_2$.



Scheme 6 The equimolar reaction of **1** with $RuHCl(CO)(PCy_3)_2$.



Scheme 7 Proposed mechanism for the first half of the catalytic cycle of silylative coupling of 1-allylsilatrane with olefins.

Allylsilatrane **1** undergoes a 1,2-migratory insertion into the Ru–H bond of the ruthenium complex and forms intermediate **A,** which subsequently converts to more stable conformer **B** due to coordination of ruthenium center to the oxygen atom of silatrane framework. The ruthenium-silatranyl complex **C** is formed *via* β-elimination of propene molecule. The second part of the catalytic cycle is identical to the one present in coupling reaction of vinylsilatrane with olefins, which we previously mentioned [22].

Conclusions

We have developed catalytic *trans*-silylation of allylsilatrane with olefins leading to (*E*)-vinyl-substituted silatranes - the same products as those coming with vinylsilatrane as the substrate in very good yields. The mechanism for the coupling reaction of allylsilatrane with styrenes was studied by catalytic and stoichiometric reactions — the evolution of propene and formation of ruthenium-silatranyl species was confirmed. We also obtained a product of allylsilatrane homocoupling reaction — (*E*)-1-silatranyl-2-(silatranylmethyl)ethene.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Science Centre (OPUS project UMO-2017/27/B/ST5/00149). This research was supported in part by PL-Grid Infrastructure.

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