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## Ru(II)-Catalyzed RCM Reactions in the Construction of Silacycloalkenes and Silaspirenes.

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**Abstract:** Five-, six- and seven-membered silacycloalkenes have been prepared by carbon-carbon bond forming cyclisation of dienyl- and enynylsilanes under RCM conditions. The relative ease of ring formation from dienes was in the order six- > seven- > five-membered rings. A conjugated vinylsilacyclopentene was formed from a corresponding enyne substrate. Silaspirenes have been prepared from silacarbacycles by the same methodology.

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### Introduction

With increasing knowledge of the chemical behaviour of silacycles their potentials as reactants in organic synthesis gain importance.<sup>1</sup> The methods available for the preparation of five- and six-membered silacarbacycles were in a recent summary broadly classified as cycloadditions, ring enlargements of three- and four-membered cyclic silanes, ring closure of acyclic silanes by the formation of one Si-C bond or by the formation of two Si-C bonds, besides ring closure of acyclic silanes by C-C bond formation.<sup>2</sup>

Spiroannulated silacyclopentenes at the silicon atom have been prepared in low yields by reductive dehalogenation of 1,1-dichlorocyclocarbosilanes using sodium or potassium vapour at 300 °C in the presence of butadiene.<sup>3</sup> Five-membered spiroannulation in the synthesis of 5-silaspiro[4,4]nona-2,7-diene has been effected in a one-pot reaction from silyl tetrachloride and 1,3-butadiene with "active" magnesium.<sup>4</sup> The initial magnesium metalacycle intermediate reacts further to form 1,1-dichlorosilacyclopent-2,7-dienes. Repetition of the reaction sequence results in spiroannulation. The suggested intermediate has in another report been described as a good substrate for spiroannulation.<sup>5</sup> In another modification, the silicon reagent was a dialkoxy-dichlorosilane which was reacted with substituted butadiene.<sup>6</sup> Lewis acid mediated cascade cyclisation of diallylsilanes has been found to yield silacycles,<sup>7</sup> and of vinylbenzylsilanes to yield silatetraline.<sup>8</sup>

Ring closing metathesis (RCM) methodology has hitherto received little attention in the preparation of silacycles. Under this classification WOC14 has been used as a catalyst,<sup>9</sup> and the use of tungsten carbenoid complexes have been explored in the cyclisation of diallyldimethylsilane and homologs.<sup>10</sup> With the Schrock MoF6 catalyst, mainly silicon containing polymers have been obtained although a ten-membered silicon containing ring was found as a coproduct in some of these reactions.<sup>11</sup> Catalytically highly active carbenoid systems based on molybdenum complexes may be useful in cases when low chemoselectivity is acceptable.<sup>12</sup>

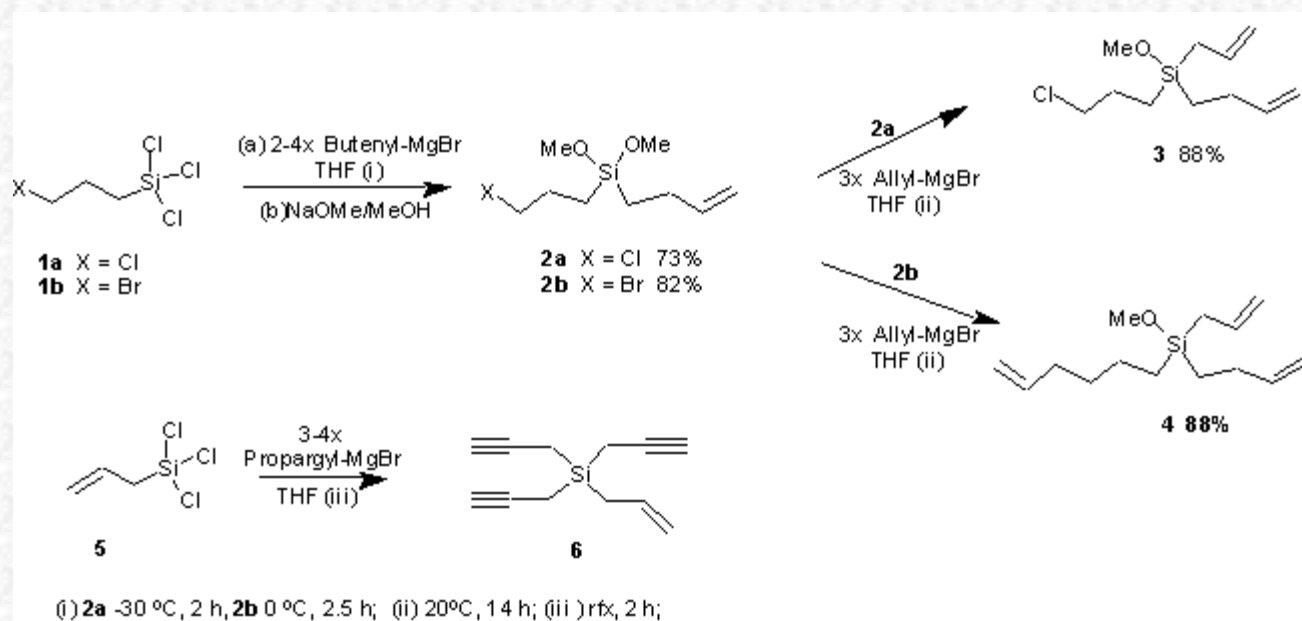
The Grubbs RCM methodology using as precatalyst bis(tricyclohexylphosphine)-benzylideneruthenium dichloride has become a very important tool with high substituent compatibility for ring-forming reactions of functionalized substrates.<sup>12-14</sup> We have used the Grubbs methodology extensively in the construction of heterospiranes as intermediates in amino acid syntheses.<sup>15</sup> The ring sizes available from the RCM reactions are in the main limited to five-, six- and seven-membered rings due to the reversible nature of metathesis reactions. Thermodynamic factors will

largely control whether oligomerization or cyclization can occur. Because of the strain of three-, four-, and eight- to eleven-membered rings, these will be difficult to prepare by metathesis. On the other hand, the method is highly applicable for the preparation of larger ring structures.<sup>16</sup> To our knowledge the use of Ru(II)-catalyzed RCM reactions has not been described for the preparation of silacarbacycles. However, the method has been applied for the preparation of cyclic siloxanes from appropriately functionalized alkoxy silanes.<sup>17</sup>

## Results and discussion

Preparations of some intermediate dienesilanes **3** and **4** and a triynesilane **6** for the RCM studies are shown in Scheme 1. Alkenylations or alkynylations at the silicon atom in the alkyltrichlorosilanes **1** were effected under Grignard conditions. The silicon-halogen bond is highly reactive. The silicon-oxygen bond in the form of an Si-OR bond can also be cleaved, but less readily than cleavage of a corresponding silicon-halogen bond. In general, the ease of substitution decreases with increasing number of substituents. These differences in reactivities may be exploited for selective, stepwise substitution reactions at the silicon center.

The lengths of the unsaturated chains were varied to provide substrates for formation of different ring-sizes in the RCM reactions leading to silacycloalkenes. The preparation of tetraalkylated substrates was essentially carried out as described for closely related molecules.<sup>18,19,20</sup> In the alkenylation and alkynylation reactions, large excess of Grignard reagent was used to effect a high conversion of the silane substrate. In our first reaction, butenylation of the *w*-chloropropylsilyl trichloride **1a** was effected at -30 °C to provide a monoalkenylated dichlorosilane. In the subsequent experiment with the bromosubstrate **1b**, the temperature was raised to 0 °C in which case a small amount of dialkenylated product was also seen. This byproduct, however, was readily removed by flash chromatography after prior conversion to its dialkoxy derivative **2b**. In general, the



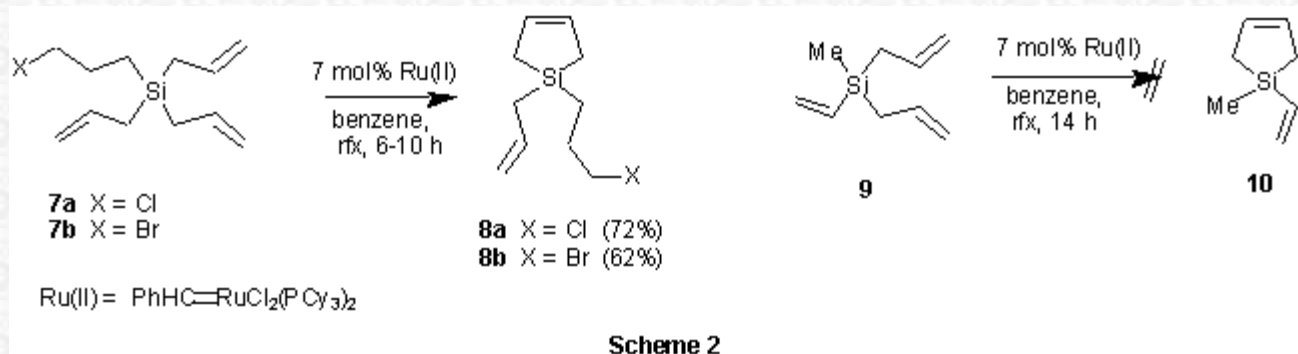
Scheme 1

remaining chlorine atoms in the initial alkylation products are easily exchanged with heteronucleophiles. Hydrolytic reactions therefore complicate the isolation and purification of the product. This problem was avoided by treatment of the crude product with methanolic sodium methoxide when the halogen substituents were replaced by methoxy groups. The methoxylated products can be purified by standard flash chromatography. Besides simplifying the isolation procedure, the methoxylated product can also be used as a substrate for further direct substitution reactions with organometallics under more vigorous conditions than for its halogen precursor. Alternatively, the methoxy group can be regarded as a protecting group which is to be cleaved by halogen acids. Silyl halides are generated in this reaction and can be used in subsequent transformations.

The dimethoxy derivatives were further investigated as substrates for organometallic substitution reactions. Treatment

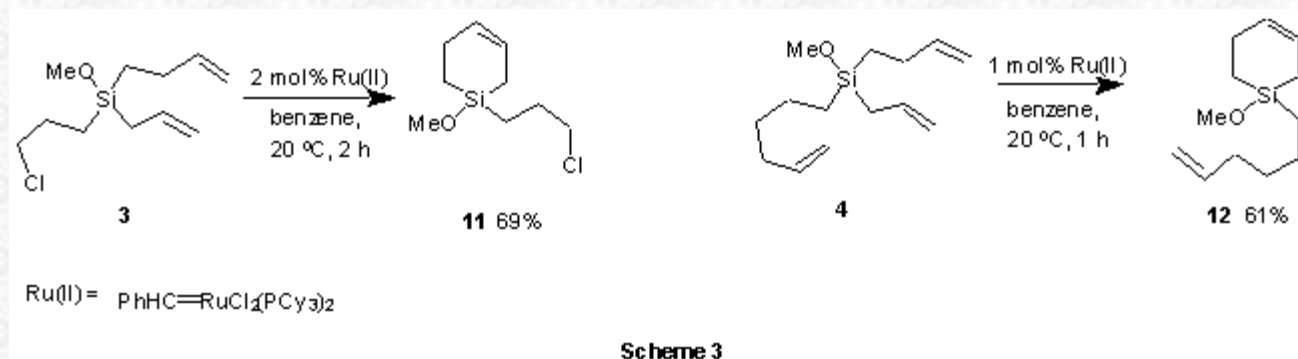
of the 3-chloropropyl derivative **2a** with 3.5 mol equivalents of allylmagnesium bromide in THF at ambient temperature led to replacement of one of the methoxy groups to furnish the monoallylated silane **3** in high yield. Use of the same conditions in the reaction of the 3-bromodimethoxysilane **2b**, however, resulted in diallylation. One methoxy group had been replaced and coupling had occurred at the bromopropyl carbon hereby providing a hexenylsilane **4** where all carbosubstituents are different.

For the alkynylation reaction, propargylmagnesium bromide was prepared as described from propargyl bromide and magnesium in the presence of catalytic amounts of HgCl<sub>2</sub>.<sup>21</sup> Under the conditions used, mixing of the reagents at -10 °C and subsequent heating under reflux for 2 h, the trialkynylated product **6** was obtained in 78% yield. A second product isolated in 7% yield (chromatography) was due to rearrangement of one of the propargyl groups into an allene group under the strongly basic conditions of the reaction. No attempts were made to study this as a route towards allene target molecules.<sup>22</sup>

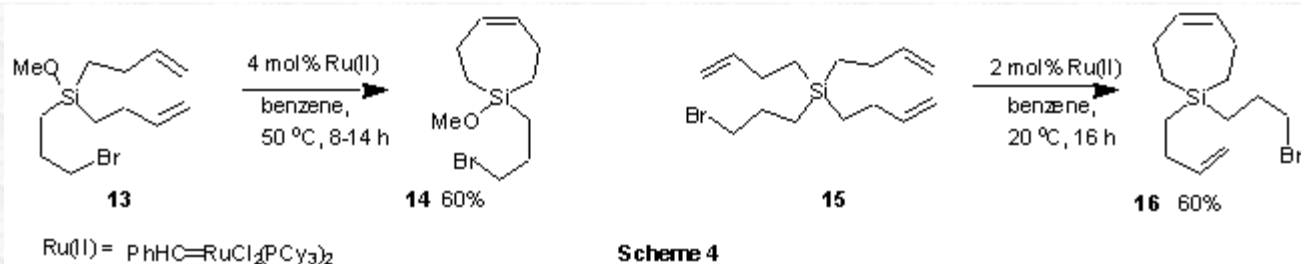


Scheme 2 shows Ru(II)-catalyzed RCM reactions for the formation of five-membered silacycloalkenes. Heating in benzene was a necessary requirement to effect ring-closure. Under these conditions the Ru(II)-catalyst system suffered from thermolytic decomposition. Therefore, when running relatively slow reactions at elevated temperature, additional catalyst has to be added at time intervals.<sup>23</sup> In all 7 mol% of catalyst was used.

In the diallylvinylsilane **9** a five-membered or the less favourable four-membered ring formation would in principle be possible by a metathesis reaction between the vinyl and an allyl group or between two allyl groups. Consumption of the substrate demanded up to 7 mol% catalyst in refluxing benzene. No silacycle was isolated from the reaction products. The vinylsilacyclopentene **10** has previously been prepared in 25% yield in a reaction between methylvinyl(dichloro)silane and the metallacycle from butadiene and magnesium.<sup>24</sup> The isomeric structure with the double bond in the 2,3-position would be available from the intramolecular Grignard reaction of 1-chloro-4-trichlorosilyl-*cis*-3-butene and methoxylation.<sup>25</sup> RCM reactions for silacyclopentene formation with other metal complexes and vinylsilane substrates have also been reported to be difficult to effect.<sup>26</sup>

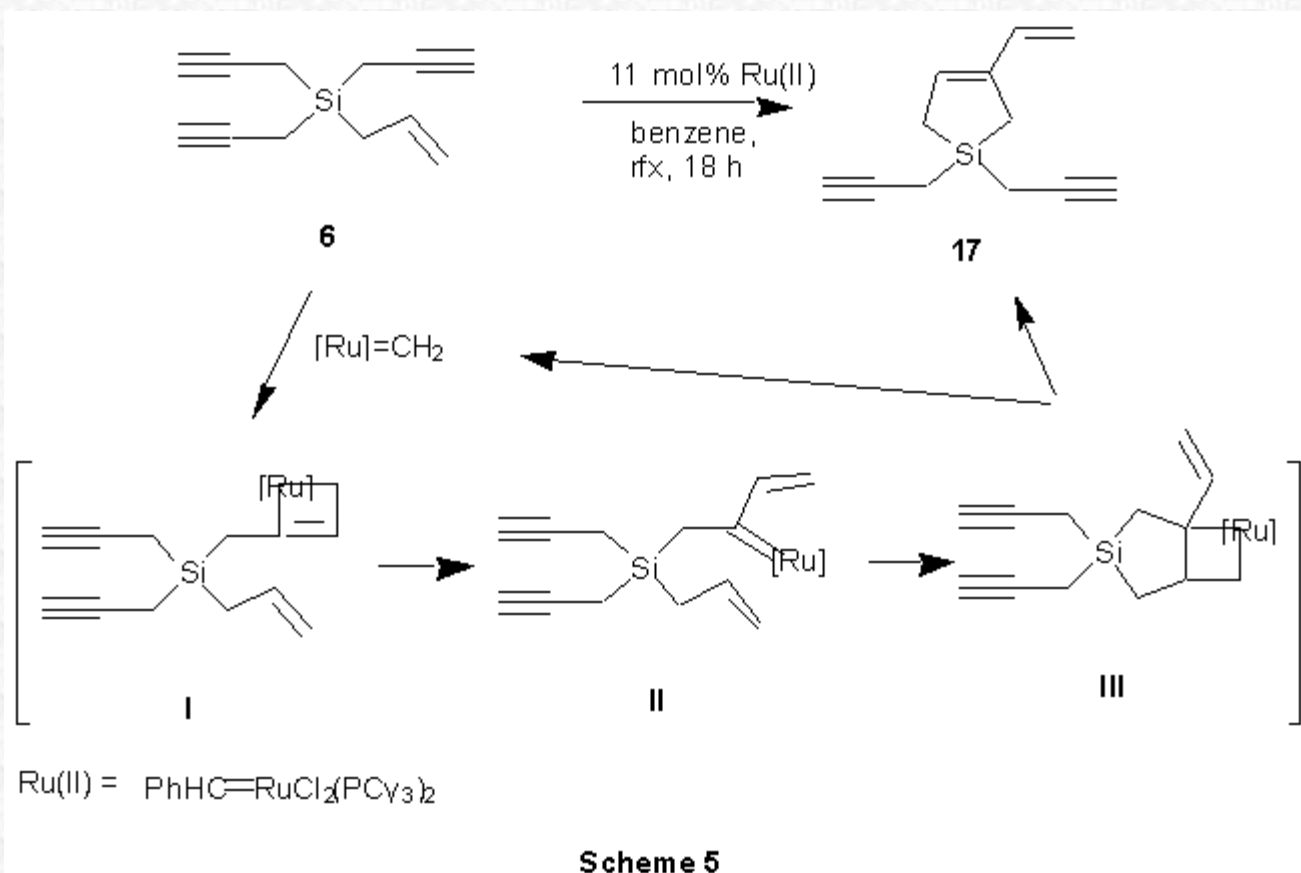


In six-membered ring formation shown in Scheme 3, the RCM reactions were run for a short time at ambient temperature using 1-2 mol% catalyst. Minor amounts of intermolecular RCM formed products could be detected. These products were removed during flash chromatography. Therefore, the initial intramolecular products can in principle be reacted further in intermolecular RCM reactions to furnish bis(silacycloalkenes).

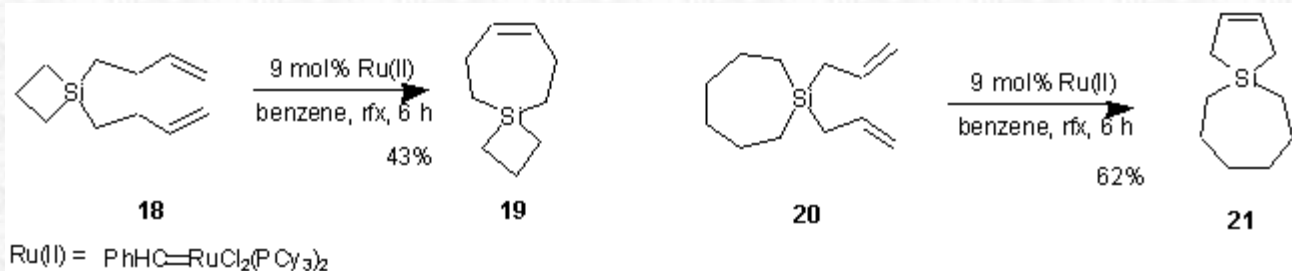


For the formation of the silacycloheptenes **14** and **16** larger amounts of catalyst and considerably longer reaction times were necessary than used for the silacyclohexenes.

As can be seen (*vide supra*), the reaction conditions for silacyclopentene formation **8** (Scheme 2) are significantly more vigorous than for the formation of the silacyclohexenes **11** and **12** (Scheme 3). The reaction conditions necessary for the formation of silacycloheptenes **14** and **16** occupy an intermediate position. These findings are in general agreement with our previous experience with RCM reactions in the formation of heterospiranes.<sup>15</sup>



When allyltripropargylsilane **6** in Scheme 5 was subjected to enyne RCM rearrangement conditions, a highly functionalized silacyclopentene **17** was formed. To effect the rearrangement, heating in benzene over an extended period of time was required and the catalyst had to be added at intervals. When the reaction was stopped after 18 h, 11 mol% of the catalyst had been consumed. The product **17** was isolated in 50% yield. In a comparison with the diene systems, it is important to know that enyne reactions differ from the diene RCM reactions. In the RCM reactions of dienes, the terminal methylenes are expelled as ethylenes during the ring closure. In the enyne reactions, on the other hand, the terminal alkylidene moiety of the alkene is transferred onto the alkyne carbon in the formation of the cyclic diene.<sup>28</sup> A rationalization of the process by the intermediate structures I-III is suggested in Scheme 5.



Silaspirane formation by RCM reactions is shown in Scheme 6. 9 mol% catalyst was used to effect the formation of the silaspirane **19** after heating in benzene solution for 6 h. The spiroannulated five-seven-member ring spirane **21** was obtained in 62% yield after heating in a benzene solution for 6 h. It seems likely that more favourable ring size silaspiranes would be available in a simple manner by this approach.

In conclusion, we have found carbon-carbon bond formation effected by Ru(II)-catalyzed RCM reactions to be a valuable method for the preparation of five-, six- and seven-membered silacycloalkenes and silacarbaspiroenes from dienyilsilanes. In a similar way, conjugated vinylsilacyclopentenes can be prepared from enyne disubstituted silanes.

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