

# Si–C bond activation in the reaction of first generation Grubbs' catalyst with alkynylsilanes - formation of $[\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Ru}(\text{=CHCH=CHPh})]$ and disiloxanes

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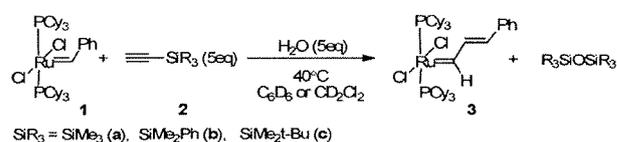
The first generation Grubbs catalyst  $[\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Ru}=\text{C}(\text{H})\text{Ph}]$  reacts efficiently with alkynylsilanes in the presence of water to give the styryl carbene complex  $[\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Ru}=\text{C}(\text{CH}=\text{CHPh})\text{H}]$  and disiloxane.

The activity of the family of Grubbs catalysts in metathesis transformations of carbon–carbon triple bonds such as in enyne metathesis,<sup>1</sup> alkyne<sup>2</sup> and diene polymerization<sup>3</sup> is well known. Until now, only a few reports have appeared on the reactivity of alkynes in equimolar reactions with Grubbs type ruthenium carbene complexes. Grubbs reported the reaction of electron-rich disubstituted alkynes with  $[\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2(\text{H}_2\text{IMes})\text{Ru}=\text{C}(\text{H})\text{Ph}]$  giving phosphane-free  $\eta^3$ -vinylcarbene complexes.<sup>4</sup> The reactivity of alkynes bearing a silyl group directly attached to the carbon–carbon triple bond towards Grubbs catalysts has not been studied in detail. Only a few examples of the activity of Grubbs catalysts in enyne ring-closing metathesis (RCM)<sup>5,6</sup> and in cross metathesis (CM) of alkynylsilanes with olefins are known.<sup>5,7,8</sup>

In this communication we report on the cleavage of the carbon–silicon bond accompanying the reaction of a first generation Grubbs catalyst (**1**) with ethynylsilanes in the presence of water. The known examples of the cleavage of the Si–C bond in silylacetylenes by transition metal complexes include 1,2-silyl migration accompanying the formation of vinylidene complexes of various transition metals,<sup>9</sup> palladium catalysed cross-coupling silylacetylenes with organic halides,<sup>10</sup>  $\sigma$ -bond metathesis of silylalkynes by uranium metallocene<sup>11</sup> as well as some other platinum,<sup>12</sup> rhodium<sup>13</sup> or nickel<sup>14</sup> catalysed reactions.

When we treated a first generation Grubbs catalyst (**1**) with stoichiometric amounts of ethynyltrimethylsilane in benzene at 40 °C in the presence of water, a gradual change in the colour of the solution from violet to red was observed. GC-MS analysis of the reaction mixture indicated the conversion of silylacetylene and the formation of hexamethyldisiloxane. Monitoring the process by <sup>1</sup>H NMR spectroscopy indicated the disappearance of the signal  $\delta = 20.63$  ppm assigned to the hydrogen atom at the carbene carbon in  $[\text{Ru}]=\text{CHPh}$  (**1**) and the simultaneous formation of a new signal, a doublet at  $\delta = 19.75$  ppm ( $J = 10.4$  Hz). After 5 h 55% of **1** was consumed. The reaction of **1** with a five-fold excess of ethynylsilane

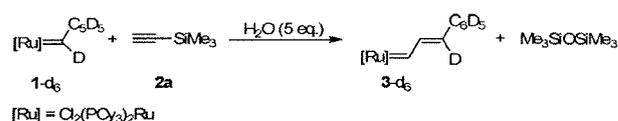
and water led to the complete conversion of **1** within 5 h. An orange solid precipitated when acetone was added to the concentrated post-reaction mixture. Analysis of the purified complex by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy revealed the formation of the styryl carbene complex (**3**) (isolated yield 48%). An alternative way of synthesising **3** is described in literature.<sup>15</sup> No signal that could be attributed to the silyl group was observed in the <sup>1</sup>H NMR spectrum of complex **3**. The GC-MS analysis of the post-reaction mixture indicated disiloxane to be the only silicon containing product. The reaction is summarized in Scheme 1.



Scheme 1

The reactions of **1** with other silylalkynes instead of ethynyltrimethylsilane proceeded analogously, giving **3** and a corresponding disiloxane. The yields of complex **3** measured on the basis of <sup>1</sup>H NMR spectra were found to be nearly independent of the substituents at silicon (43, 40 and 38%, respectively), however, they increased significantly (85% for reaction with the use of **2a**) when instead of benzene, methylene chloride was used as the solvent. No reaction was observed when internal silylacetylenes of the type  $\text{R}-\text{C}\equiv\text{C}-\text{SiMe}_3$ , where  $\text{R} = \text{Me}, \text{Ph}, \text{SiMe}_3$  were used as reagents.

A dramatic decrease in the yield of **3** was observed upon addition of three equivalents of phosphine to the reaction mixture. Therefore, we believe that dissociation of phosphine precedes the coordination of acetylene and the subsequent transformations. In order to elucidate the mechanism of formation of the vinylcarbene complex, experiments with deuterium labelled reagents were performed and monitored by <sup>1</sup>H NMR spectroscopy. The reaction of deuterium labelled alkylidene complex (**1-d<sub>6</sub>**) with ethynyltrimethylsilane (**2a**) afforded complex **3-d<sub>6</sub>** (Scheme 2).



Scheme 2

Moreover, reaction of **1** with **2a-d<sub>1</sub>** leads to selective formation of **3-d<sub>1</sub>**, bearing a deuterium label at the  $\beta$ -carbon (Scheme 3).

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