Si–C bond activation in the reaction of first generation Grubbs' catalyst with alkynylsilanes - formation of $[Cl_2\{P(C_6H_{11})_3\}_2Ru(=CHCH=CHPh)]$ and disiloxanes†

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Received 26th November 2009, Accepted 9th December 2009 First published as an Advance Article on the web 5th January 2010 DOI: 10.1039/b924945c

The first generation Grubbs catalyst $[Cl_2{P(C_6H_{11})_3}_2-Ru=C(H)Ph]$ reacts efficiently with alkynylsilanes in the presence of water to give the styryl carbene complex $[Cl_2{P(C_6H_{11})}_2 Ru=C(CH=CHPh)H]$ and disiloxane.

The activity of the family of Grubbs catalysts in metathesis transformations of carbon–carbon triple bonds such as in enyne metathesis,¹ alkyne² and diyne polymerization³ 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 $[Cl_2{P(C_6H_{11})_3}(H_2IMes)Ru=C(H)Ph]$ giving phosphane-free η^3 -vinylcarbene complexes.⁴ 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)^{5,6} and in cross metathesis (CM) of alkynylsilanes with olefins are known.^{5,7,8}

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,⁹ palladium catalysed cross-coupling silylacetylenes with organic halides,¹⁰ σ -bond metathesis of silylalkynes by uranium metallocene¹¹ as well as some other platinum,¹² rhodium¹³ or nickel¹⁴ 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 ¹H NMR spectroscopy indicated the disappearance of the signal $\delta = 20.63$ ppm assigned to the hydrogen atom at the carbene carbon in [Ru]=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 ¹H, ¹³C and ³¹P NMR spectroscopy revealed the formation of the styryl carbene complex (**3**) (isolated yield 48%). An alternative way of synthesising **3** is described in literature.¹⁵ No signal that could be attributed to the silyl group was observed in the ¹H 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.



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 ¹H 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 R-C=C-SiMe₃, where R = Me, Ph, SiMe₃ 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 ¹H NMR spectroscopy. The reaction of deuterium labelled alkylidene complex (1-d₆) with ethynyltrimethylsilane (**2a**) afforded complex **3**-d₆ (Scheme 2).



Moreover, reaction of 1 with 2a-d₁ leads to selective formation of 3-d₁ bearing a deuterium label at the β -carbon (Scheme 3).

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[†] Electronic supplementary information (ESI) available: Experimental details including optimized synthesis procedure for complex **3**. See DOI: 10.1039/b924945c

$$[Ru] = \stackrel{Ph}{\longrightarrow} + D \stackrel{Ru}{\longrightarrow} SiMe_3 \stackrel{H_2O(5 eq.)}{\longrightarrow} \stackrel{D}{\underset{[Ru]}{\longrightarrow}} \stackrel{Ph}{\longrightarrow} + Me_3SiOSiMe_3$$

$$1 \qquad 2a \cdot d_1 \qquad 3 \cdot d_1$$

$$[Ru] = Cl_2(PCy_3)_2Ru$$

Scheme 3

The positions occupied by the deuterium atoms in $3-d_6$ and $3-d_1$ suggested that the reactions proceed *via* the carbene mechanism.

To clarify the role of water in the process, the reaction of 1 with ethynyltrimethylsilane was performed under rigorous exclusion of water but with the controlled addition of a fivefold excess of D_2O . Deuterium was incorporated into the styrylcarbene complex and 3'-d₁ was formed (Scheme 4) confirming the participation of water in the reaction.



Scheme 4

¹H NMR spectroscopy indicated that the deuterium label was attached exclusively to the α -carbon atom. The analogous reaction of **1** with monodeuterated methanol likewise gave complex **3'**-d₁ and methoxytrimethylsilane. On the basis of these results it is reasonable to suppose that the reaction of **1** with ethynylsilane initially leads to an 1-(silyl)benzylidene complex [Cl₂{P(C₆H₁₁)₃}2Ru=C(SiR₃)CH=CHPh)] **(4)** via stoichiometric metathesis (Scheme 5). Although ruthenium alkylidene complexes bearing a silyl group at the α -carbon atom are very rare,^{16,17} such complexes must be involved in the catalytic cycles of the cross metathesis of silylacetylene with olefins⁷ and the homometathesis of vinylsilanes¹⁸ proceeding by the carbene mechanism. Presumably, the putative complex **4** immediately eliminates ClSiR₃ leading to a coordinatively unsaturated alkylidyne complex [Cl{P(C₆H₁₁)₃}₂Ru{=C(CH=CHPh)}] (Scheme 5).¹⁹



Scheme 5

The postulated elimination of ClSiR_3 very likely involves migration of the silyl group to the ruthenium and reductive elimination of chlorosilane. Migration of the silyl group to metal from α -carbon to form carbene (or carbyne) complexes was predicted by Caulton on the basis of considerable migratory aptitude of the SiR₃ group.²⁰ The formation of ruthenium alkylidyne complexes *via* elimination of HCl¹⁹ or HOAr²¹ from 1 was recently proposed. As soon as chlorosilane is formed it immediately reacts with water (alcohols or phenols) present in the system to form hydrochloride and silanol/disiloxane (alkoxy or phenoxysilane). The reaction of chlorosilane with water (alcohols or 4-methoxyphenol) is catalysed by $P(C_6H_{11})_3$ present in the reaction mixture and proceeds immediately after mixing the reagents (as confirmed in a separate experiment). In the last stage of the sequence (Scheme 5) the alkylidyne complex immediately reacts with hydrochloride to form complex 3. The formation of a ruthenium alkylidene complex *via* addition of HCl to an alkylidyne complex was recently reported.¹⁹

When monitoring the reaction (eq. 1) we never observed any signal which could be assigned to an alkylidyne complex. However, such an alkylidyne complex, once formed, is expected to immediately accept HCl to form **3**. Therefore, the alkylidyne complex will not accumulate in the mixture to a detectable level. This assumption was confirmed in a separate experiment. When the alkylidyne complex $[Cl{P(C_6H_{11})_3}_2Ru \equiv C(C_6H_4t-Bu-4)]^{19}$ was treated in C_6D_6 with an equimolar amount of chlorotrimethylsilane in the presence of an equimolar amount of water the immediate formation of $[Cl_2{P(C_6H_{11})_3}_2Ru = CH(C_6H_4t-Bu-4)]$ was observed.

In conclusion, unprecedented activation of alkynylsilanes by first generation Grubbs' catalyst is described. The reaction reported constitutes an alternative and easy route to ruthenium styrylcarbene complexes.²²

Acknowledgements

Financial support from the Ministry of Science and Higher Education (Poland), (project No. N 204 1935 33) is gratefully acknowledged.

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