



## Review

## Well-defined silica supported metallocarbenes: Formation and reactivity

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## ABSTRACT

This overview describes how well-defined silica supported metallocarbenes are prepared, what is their mechanism of formation, what is their reactivity towards alkanes and alkenes, and these data are compared with the current knowledge of modern organometallic chemistry.

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## 1. Introduction

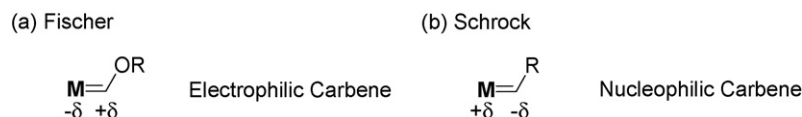
Metallocarbenes belong to an important class of ligands in organometallic chemistry. They are divided in two sub-classes depending on the substitution at the  $C_{sp^2}$  carbon doubly bonded to the metal: (1) Fischer type carbenes, which usually contain a heteroatom in the  $\alpha$ -position and are electrophilic; (2) Schrock type carbenes or alkylidenes, which contain H and/or alkyl substituent and are nucleophilic (Scheme 1).

While the former display interesting stoichiometric reactivities, which have been exploited in organic synthesis [1,2], the latter display both stoichiometric and catalytic reactivities (they are key intermediates in alkene metathesis) and will be discussed in more details thereafter both in term of structure and reactivity [3]. First, these Schrock type carbene ligands have often a distorted geometry

at the carbon directly linked to the metal centre: wide M–C–C bond angle, acute M–C–H bond angle and an elongated C–H bond, which is due to the presence of an  $\alpha$ -H agostic interaction (Scheme 2a). This typically gives rise to lower  $\nu(C-H)$  and  $J_{C-H}$  values in IR and NMR spectroscopies, respectively [3–6]. In the case of  $d^0$  early transition metal complexes, carbenes react with  $\sigma$ -bonds, such as the O–H bond of alcohols [7], or even the C–H bond of unactivated alkanes (Scheme 2b) [8].

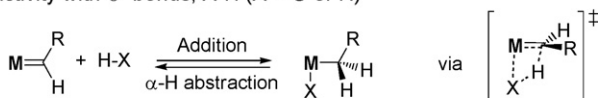
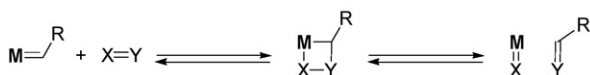
These reactions take place through  $\sigma$ -bond metathesis; the corresponding reverse reaction ( $\alpha$ -H abstraction) is often encountered in the formation of alkylidene ligands. Moreover, metallocarbenes can also react with  $\pi$ -bond systems (Scheme 2c). The reaction with alkenes gives metallacyclobutanes via a [2+2]-cycloaddition and the reverse reaction (cycloreversion) yields either the original carbene plus the alkene or two new ones. This overall transalkylation ( $\pi$ -bond metathesis) is catalytic and is the basis of the Chauvin mechanism in alkene metathesis [9–11]. In contrast, the corresponding reaction with aldehydes or ketones is irreversible

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Scheme 1.

## (a) Agostic interaction

(b) Reactivity with  $\sigma$ -bonds, X-H (X = O or R)(c) Reactivity with  $\pi$ -bonds, X=Y (X = O or  $\text{CR}_2$ ; Y =  $\text{CR}_2$ )

Scheme 2.

and yields alkenes, and is therefore related to the Wittig reaction, hence its name “pseudo-Wittig reaction”.

In this review, we will outline (1) how well-defined alkylidene surface complexes are formed on silica surfaces and (2) the reactivity of these systems, especially focusing on the difference and similarity of molecular and surface chemistry.

## 2. Discussion

### 2.1. Generality on silica

The bulk of silica is constituted of tetrahedral  $\text{SiO}_4$  units (Scheme 3), and its surface is amorphous and can be described as a complex assembly of cyclic structures of various sizes (typically between 6 and 12 member ring) using  $\text{SiO}_4$  as building block [12,13]. The surface  $\text{SiO}_4$  units can contain hydroxyl functionality, leading to different types of silanols: geminal, vicinal and isolated. The specific surface area is typically comprised between 50 and 400  $\text{m}^2/\text{g}$ , but higher surface areas are found in the case of mesoporous silica. Up to 700 °C, partial dehydroxylation under vacuum does not change the specific surface area of non-porous silica, while the OH concentration varies with the temperature treatment. At higher temperatures, there is a loss of specific surface area combined with

the formation of highly reactive siloxane bridges, e.g. four member ring siloxane bridge. The dehydroxylation process takes place first by desorption of physisorbed water, followed by condensation of vicinal OH groups above 150–200 °C. Partial dehydroxylation leads to the formation of isolated hydroxyl groups. At 200–300 °C, this treatment yields very hydroxyl rich silica surfaces (0.86 mmol/g), which are mainly composed of vicinal OH, while a treatment at 700 °C ( $\text{SiO}_{2-(700)}$ ) allows the statistical distribution of isolated OH groups at an average distance of ca. 13 Å, which corresponds to 0.26 mmol OH/g.

### 2.2. Formation of well-defined silica supported metallocarbene complexes

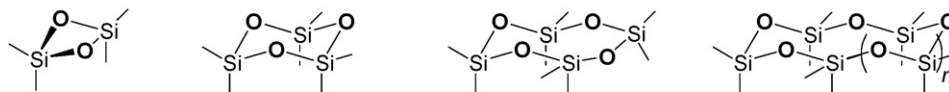
Most silica supported metallocarbene complexes have been obtained by grafting on silica, and more specifically  $\text{SiO}_{2-(700)}$ . They are typically tetra-coordinated and have a  $d^0$  configuration:  $[\text{Ta}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_3]$ ,  $[(\text{R}^1\text{N}\equiv)\text{Mo}(\text{=CHR}^2)(\text{CH}_2\text{R}^3)_2]$ ,  $[(\text{R}^1\text{N}\equiv)\text{Mo}(\text{=CHR}^2)(\text{NR}_2)_2]$ ,  $[(\text{R}^1\text{N}\equiv)\text{Mo}(\text{=CHR}^2)(\text{OR})_2]$  and  $[(t\text{BuC}\equiv)\text{Re}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ . They can be described with the following general formula  $[(\text{E})\text{M}(\text{=CHR}^2)(\text{X})_2]$ , where  $\text{E}=\text{X}$ ,  $\text{NR}^1$  or  $\text{C}t\text{Bu}$ ,  $\text{R}^2 = t\text{Bu}$  or  $\text{CMe}_2\text{Ph}$ . These complexes can graft on the surface OH group of silica through different possible competitive ways (Scheme 4):

- *Pathway 1*: a direct electrophilic cleavage of one M–X bond by the surface O–H group via  $\sigma$ -bond metathesis, yielding XH and the corresponding surface alkylidene complex  $[(\equiv\text{SiO})(\text{E})\text{M}(\text{=CHR}^2)(\text{X})]$ , where one X ligand has been replaced by a siloxy.
- *Pathway 2*: an addition of the O–H group onto the alkylidene ( $\text{M}=\text{CHR}$ ), giving  $[(\equiv\text{SiO})(\text{E})\text{M}(\text{CH}_2\text{R}^2)(\text{X})_2]$ , which can decompose via an  $\alpha$ -H abstraction process to yield  $[(\equiv\text{SiO})(\text{E})\text{M}(\text{=CH}t\text{Bu})(\text{X})]$  along with XH.

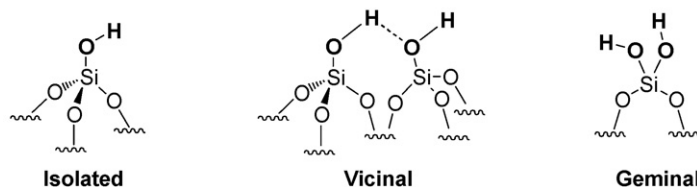
Note that there has been no evidence for the reaction of the E ligand with surface O–H group for  $\text{E}=\text{NR}^1$  (imido) or  $\text{C}t\text{Bu}$  (alkylidyne).

Depending on the grafted complex, grafting has been shown to occur in several ways: either selectively via one process of the two possible pathways or via both competing pathways. The grafting mechanisms are typically investigated as follows: (1) using

### (a) Siloxane bridges



### (b) Silanols



Scheme 3.

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