

Communication

# Development of a well-defined silica-supported tungstenocarbonyne complex as efficient heterogeneous catalyst for alkyne metathesis

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## Abstract

The interaction of  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})(\text{OAr})_2]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**1**), with the hydroxyl groups of a silica dehydroxylated at 700 °C leads to  $[(\equiv\text{SiO})\text{W}(\text{OAr})_2(\equiv\text{C}-t\text{Bu})]$  (**2**) which was characterized by IR, solid-state NMR and mass balance analysis. This well-defined surface species is an efficient catalyst for the metathesis of pent-2-yne.

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## 1. Introduction

Alkene metathesis is now routinely used in organic synthesis [1–3]. Some recent and elegant applications are the synthesis of macrocycles by ring closing metathesis of a diene [4]. However, alkene metathesis meets some limitations as it gives mixtures of E and Z isomers, thus decreasing its potential as a highly stereoselective synthetic method. An approach to overcome this difficulty may be found with alkyne metathesis [5]. Indeed, the newly formed C≡C bond could then be stereo-selectively reduced to either E or Z, C=C isomers, or converted to another functionality. Up to now, several alkyne metathesis catalysts are known [5,6]. The catalyst developed by Schrock,  $[(t\text{BuO})_3\text{W}(\equiv\text{C}-t\text{Bu})]$ , is one of the most extensively used,

but the reaction proceeds usually at 80 °C [7,8]. Some other highly active alkyne metathesis catalysts have been synthesised by exchanging the amido ligand of molybdenum(VI) alkylidyne amide complexes with 4-nitrophenol [9–11]. Unfortunately, as in the case of olefin metathesis, these catalysts deactivate rapidly, apparently through a bimolecular dimerization pathway leading to a Mo≡Mo triple bond [12,13]. To avoid such a reaction, Moore et al. reported the grafting reaction of the molybdenum complex  $[\text{Mo}(\equiv\text{C}-t\text{Bu})(\text{NAr}(t\text{Bu}))_3]$  on amorphous silica pre-treated at 400 °C under dry O<sub>2</sub>, the purpose being to induce minimal changes in the electronic structure of the complex and to reduce its mobility [14]. This catalyst showed a high catalytic activity and a good stability. We have recently reported that the reaction of  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_3]$  with highly dehydroxylated silica affords the well-defined tungsten alkylidyne surface complex  $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_2]$  [15]. This system is active in olefin metathesis but displays only a stoichiometric activity in

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alkyne metathesis. The formation of the active species in olefin metathesis (a metal–carbene) passes probably by a  $\alpha$ -hydrogen elimination and this reaction can also be responsible of the lack of activity in alkyne metathesis [16,17]. The modification of the metal coordination sphere by replacing the two neopentyl moieties by ancillary ligands should therefore be of considerable interest: it could not only prevent the deactivation pathway by  $\alpha$ -hydrogen elimination, but it could also modify the performances of the catalytic system through the modulation of the steric and electronic parameters. We thus undertook the preparation of such supported catalysts, and we report here the synthesis and characterization of the new well-defined silica-supported bisaryloxycarbyne catalyst,  $[(\equiv\text{Si}-\text{O})\text{W}(\equiv\text{C}-t\text{Bu})(\text{OAr})_2]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ). In contrast to the  $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_2]$  complex, this system is active in alkyne metathesis [18].

## 2. Experimental

### 2.1. Preparation of $\text{SiO}_{2-(700)}$

Aerosil silica from Degussa (specific area of  $200 \text{ m}^2 \text{ g}^{-1}$ ), was partially dehydroxylated at  $700^\circ\text{C}$  under high vacuum ( $10^{-5}$  Torr) during 15 h. The resulting solid had a specific surface area of  $180 \text{ m}^2 \text{ g}^{-1}$  and contained  $0.7 \text{ OH nm}^{-2}$  as determined by reaction with  $\text{CH}_3\text{Li}$ .

### 2.2. Preparation of **2** by impregnation of **1** onto $\text{SiO}_{2-(700)}$

A mixture of  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})(\text{OAr})_2]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**1**) (300 mg, 0.443 mmol) in pentane (5 mL) and  $\text{SiO}_{2-(700)}$ . One gram was stirred at  $25^\circ\text{C}$  during 5 h. After filtration, the solid was washed five times with pentane and all volatile compounds were condensed into another reactor (of known volume) in order to quantify the neopentane evolved during the grafting reaction. The resulting yellow powder was dried under vacuum ( $10^{-5}$  Torr) to yield 1.094 g of **2**. Analysis by gas chromatography indicated the formation of  $150 \mu\text{mol}$  of neopentane during the grafting reaction ( $0.85 \pm 0.1 t\text{BuCH}_3/\text{W}$ ). Elemental analysis of **2**: W, 3.05 wt% and C, 5.52 wt%.

### 2.3. Preparation of **4** by impregnation of **3** onto $\text{SiO}_{2-(700)}$

A mixture of **3**,  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_3]$  (115 mg, 0.25 mmol) in pentane (5 mL) and  $\text{SiO}_{2-(700)}$ . 0.8 g was stirred at  $25^\circ\text{C}$  for 2 h. After filtration, the solid was washed five times with pentane and all volatile compounds were condensed into another reactor (of known volume) in order to quantify the neopentane evolved during grafting. The resulting brown powder was dried under vacuum ( $10^{-5}$  Torr) to yield 0.84 g of **4**. Analysis by gas chromatography indicated the formation of  $108 \mu\text{mol}$  of neopentane during the grafting ( $0.9 \pm 0.1 t\text{BuCH}_3/\text{W}$ ). Elemental analysis of **2**: W, 2.2 wt% and C, 2.2 wt%.

### 2.4. Reaction of acetonitrile with complex **2**

The solid **2** was contacted with acetonitrile (80 Torr, 1.63 mol%) in a reactor at  $25^\circ\text{C}$ . Small aliquots of the gas phase were analyzed by gas chromatography as a function of time.

### 2.5. Metathesis of pent-2-yne

The solids **2** or **4** were contacted with penty-2-yne (80 Torr, 1.63 mol% for **2** and 1.49 mol% for **4**) in a reactor at  $80^\circ\text{C}$ . Small aliquots of the gas phase were analyzed by gas chromatography as a function of time, allowing the determination of the conversion and selectivities.

## 3. Results and discussion

When a disk of silica (Aerosil Degussa  $200 \text{ m}^2 \text{ g}^{-1}$ ) treated at  $700^\circ\text{C}$  under vacuum ( $\text{SiO}_{2-(700)}$ ) is allowed to react with a pentane solution of  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})(\text{OAr})_2]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**1**), the IR spectroscopy shows the consumption of the free silanol groups ( $\nu_{\text{OH}} = 3747 \text{ cm}^{-1}$ ) (Fig. 1). Simultaneously, two groups of bands appear in the  $3100\text{--}2700 \text{ cm}^{-1}$  and  $1500\text{--}1300 \text{ cm}^{-1}$  regions. These bands are, respectively, assigned to  $\nu_{\text{CH}}$  and  $\delta_{\text{CH}}$  vibrations of the hydrocarbyl and phenoxy ligands. Moreover, two broad bands appear at  $3710 \text{ cm}^{-1}$  and  $3607 \text{ cm}^{-1}$ . The band at  $3710 \text{ cm}^{-1}$  is typical of residual surface hydroxyls in interaction with perhydrocarbyl groups, while that at  $3607 \text{ cm}^{-1}$  is attributed to other silanol groups in interaction with the aryloxy ligands of the grafted complex [19]. The free silanols do not reappear after washing of the unreacted complex with pentane; furthermore, the appearance of  $\nu_{\text{CH}}$  and  $\delta_{\text{CH}}$  bands, and the presence of  $t\text{BuCH}_3$  evolved in the gas phase support a chemical grafting of the tungsten complex on silica.

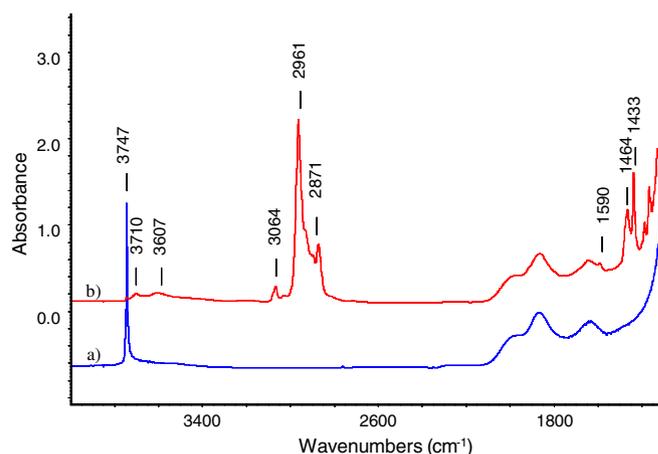


Fig. 1. Infrared spectra of the grafting reaction of  $[\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})(\text{OAr})_2]$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) (**1**) onto  $\text{SiO}_{2-(700)}$  by impregnation method: (a) silica partially dehydroxylated at  $700^\circ\text{C}$  for 15 h; (b) same sample after impregnation of **1** at  $25^\circ\text{C}$  for 4 h followed by washing in pentane and drying under vacuum.

To establish the mass balance, the reaction was carried out by impregnation on larger quantities of silica with a pentane solution of **1** (Table S1, entries 1, 2, 3 and 4, Supplementary material). The resulting yellow solid contained 1.9 and 3.63 wt% of W and C, respectively, corresponding to a C/W ratio of 29.1. These data are consistent with the removal of one neopentyl group per grafted W and formation of a monografted surface complex as a major species, which can be tentatively formulated as  $[(\equiv\text{SiO})(\text{W}\equiv\text{C}-t\text{Bu})(\text{OAr})_2]$  (**2**), (expected C/W ratio: 29) (Scheme 1).

Moreover, quantitative GC analyses revealed that 0.9 equiv. of 2,2-dimethylpropane per grafted W evolved during the grafting reaction, which is in agreement with the cleavage of about one neopentyl group in **1** and formation of one Si–O–W bond, as already observed with other molecular complexes [15,20–22]. The W loading is relatively low but it can be increased by increasing the reaction time. Thus, the behaviour of complex **1** is completely different from that of the perhydrocarbyl complexes of Ti, Zr, Hf or Ta, for which the grafting reaction takes place within 30 min to 1 h under similar conditions [20–23]. This observation is consistent with the presence in **1** of bulky aryloxy groups around the metal which prevents efficient protonolysis of the W–C bond by a surface silanol. Therefore, while  $\text{SiO}_{2-(700)}$  contains 0.26 mmol of surface hydroxyl groups per gram, the W elemental analysis shows that only 0.10 mmol (around 40%) are consumed during the grafting reaction. This observation is in agreement with the presence of residual silanols, as observed by IR spectroscopy (vide supra). Note that the grafted organometallic fragment  $\{\text{W}(\equiv\text{C}-t\text{Bu})(\text{OAr})_2\}$  has a projected surface area of about  $100 \text{ \AA}^2$ , which would afford a maximum W loading of 5.9 wt%.

Solid **2** was further characterized by solid-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The  $^1\text{H}$  MAS NMR spectrum of **2** (Fig. 2a) displays various signals assigned to the aromatic protons ( $\delta = 6.9$  ppm), the isopropyl methyne protons ( $\delta = 3.5$  ppm), and the methyl groups of the isopropyl and neopentylidyne groups ( $\delta = 1.0$  ppm, with a shoulder at 0.8 ppm). The  $^{13}\text{C}$  CP-MAS spectrum shows seven resolved peaks (Fig. 2b), which can be assigned to the aromatic carbons (163, 136 and 122 ppm for the *ipso*, *ortho* and undistinguished *meta* and *para* carbons, respectively), to the isopropyl groups (27 and 21 ppm, for the methyne

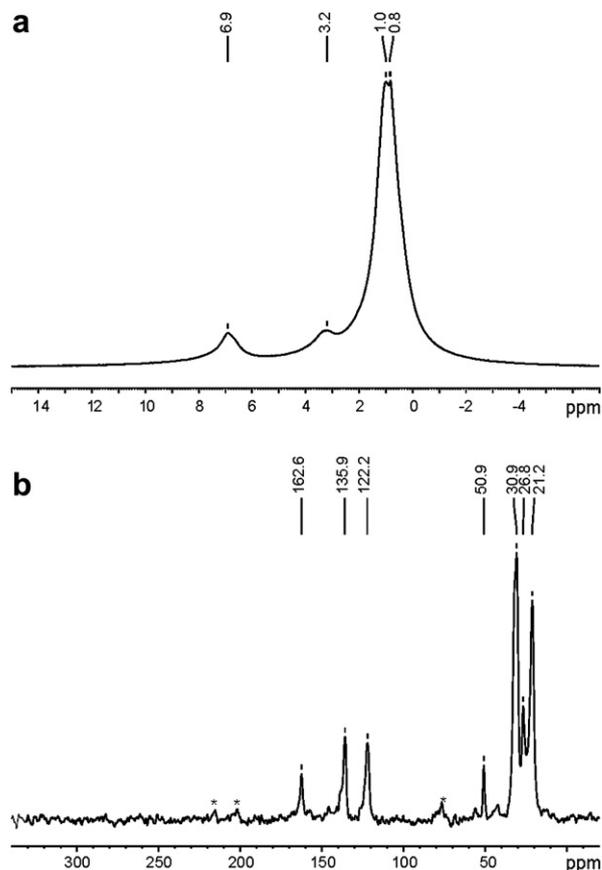
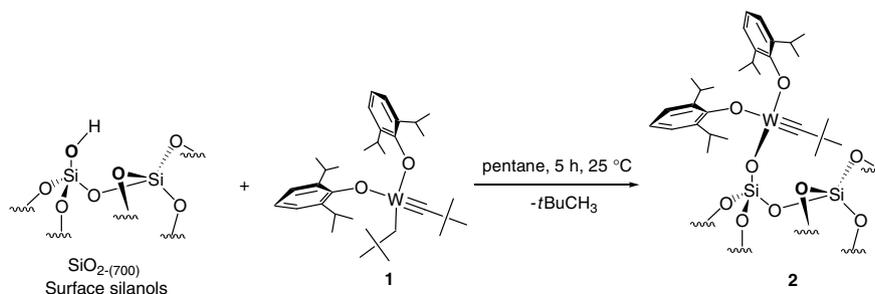
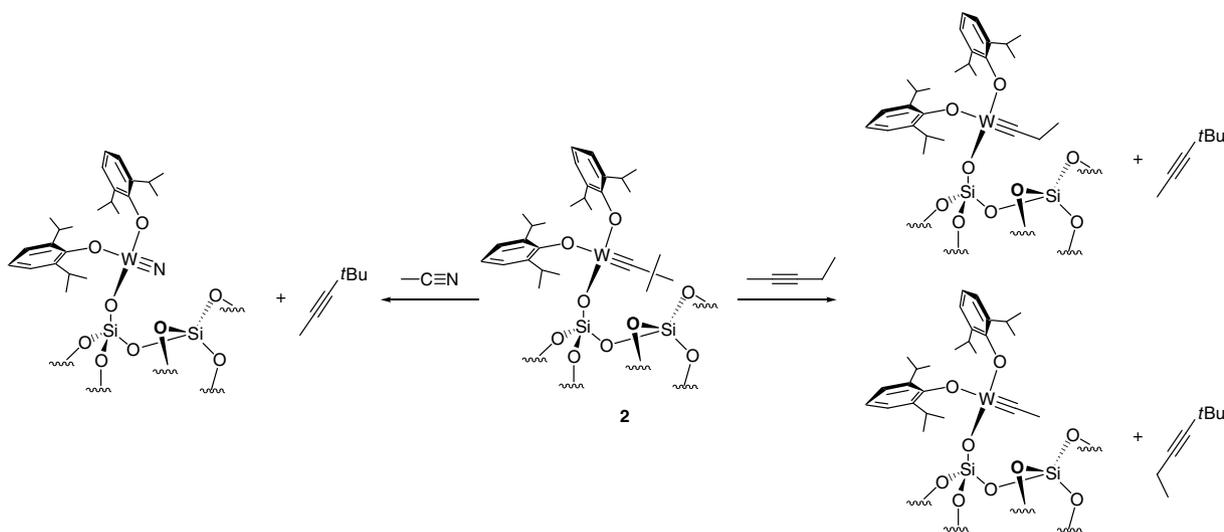


Fig. 2. (a)  $^1\text{H}$  MAS NMR spectrum of **2**. The spectrum was recorded with eight scans and a relaxation delay of 2 s. (b)  $^{13}\text{C}$  CP-MAS NMR spectrum of **2**. The spectrum was recorded with 50000 scans, a relaxation delay of 2 s and a CP contact time of 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transformation.

and methyl groups, respectively) and to the carbonyc *t*-butyl moiety (51 and 31 ppm for the quaternary carbon and the methyl groups, respectively). Unfortunately, despite extended measurement time, it has not been possible to detect the resonance of the carbonyc atom (a resonance should be expected at ca. 300 ppm), probably due to the fact that, (i) it is not surrounded by proton and, (ii) the signal is probably relatively broad due to the interaction with the metal. However the observation of the signal at 51 ppm (52.11 ppm in **1**) and the absence of any signal of a methy-



Scheme 1.



Scheme 2.

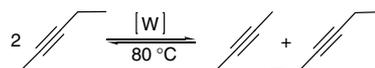
lenic carbon (like in **1**) at ca. 74 ppm support the above proposed structure [18].

Furthermore, these assignments were confirmed by  $^1\text{H}$ - $^{13}\text{C}$  2D HETCOR NMR (see Fig. S1 Supplementary material) which gave correlation cross-peaks ( $\delta\text{H}$  [ppm] in F1;  $\delta\text{C}$  [ppm] in F2) between  $^1\text{H}$  and  $^{13}\text{C}$  spectra for the methyl ( $\text{CH}(\text{CH}_3)_2$ ) (1.0; 21) and ( $\equiv\text{CC}(\text{CH}_3)_3$ ) (1.0; 31), the isopropyl ( $\text{CH}(\text{CH}_3)_2$ ) (3.5; 27), and the aromatic groups ( $\text{CH}$ -*para*,  $\text{CH}$ -*meta*) (6.9; 122). Accordingly, no correlation was observed for the peaks centered at 51 and 163 ppm, thus confirming their respective assignments as *tert*-butyl quaternary and aromatic *ipso* carbons.

We have then studied the stoichiometric and catalytic reactivities of **2**. Treatment of **2** with acetonitrile (10 equiv.) in gas phase at 80 °C led to the evolution of 0.8 equiv. of 4,4 dimethylpent-2-yne (GC-MS) per grafted tungsten and to a red solid tentatively formulated as  $[(\equiv\text{Si}-\text{O})\text{W}(\equiv\text{N})(\text{OAr})_2]$  (Scheme 2), on the basis of the known reactivity of molecular analogues [18,24]. Further characterizations of this complex are in progress and will be reported in a forthcoming paper.

High oxidation state carbynic group 6 derivatives are known to catalyze the metathesis of internal alkynes [9,25]. Thus, the reaction of **2** with an excess of pent-2-yne was performed in a batch reactor at room temperature. After reaction the solid turned to orange and 0.65 equiv. per tungsten of a 1/1 mixture of 4,4 dimethylpent-2-yne ( $\text{Me}-\text{C}\equiv\text{C}-t\text{Bu}$ ) and 2,2 dimethylhex-3-yne ( $\text{Et}-\text{C}\equiv\text{C}-t\text{Bu}$ ) had evolved. These products arise from the interaction between pent-2-yne and the carbyne ligand, namely the initiation step for alkyne metathesis. The 1/1 ratio is consistent with a comparable stability of both possible metallacyclobutadiene intermediates [26], which is not influenced by 1,2- or 1,3-interactions due to the planarity of the cycle, at the difference of alkene metathesis [27].

The above results show that at room temperature only a stoichiometric reaction is observed with pent-2-yne.



Scheme 3.

However when pent-2-yne (80 Torr, 61 equiv. per W atom) was contacted with the above material (1.63 mol%) at 80 °C in a batch reactor, but-2-yne and hex-3-yne were formed in a 1/1 ratio and the thermodynamic equilibrium (corresponding to 30% conversion of pent-2-yne) was reached after 140 min (Scheme 3 and Fig. S2 in Supplementary material). The initial turnover frequency was 0.32 mol mol  $\text{W}^{-1}$  min $^{-1}$ . Interestingly, no oligomerization of the alkyne substrate or of the reaction products was evidenced either by GC after extraction of the solid or via the mass balance. This behaviour is different from that of similar homogeneous catalysts for which formation of heavy products is problematic [18].

The surface species **4**,  $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_2]$  [15] prepared by grafting reaction of  $\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_3$  (**3**), on silica dehydroxylated at 700 °C was fully inactive in the same reaction conditions, even if the initiation products 4,4 dimethylpent-2-yne ( $\text{Me}-\text{C}\equiv\text{C}-t\text{Bu}$ ) and 2,2 dimethyl hex-3-yne ( $\text{Et}-\text{C}\equiv\text{C}-t\text{Bu}$ ) (0.45 equiv. per W) were observed as in the case of species **2**. The substitution of the two aryloxy groups in complex **2** by two neopentyl ligands in complex **4**, allowed probably a  $\alpha$ -hydrogen migration from the neopentyl to form bis-carbene species [16,17] which has been proved to be active in olefin metathesis [15] but led to fast deactivation of the catalyst in alkyne metathesis reaction.

#### 4. Conclusions

According to elemental and mass balance analyses, and to IR and solid state NMR spectroscopies, complex **1** reacts with  $\text{SiO}_2-(700)$  leading to  $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{Bu})(\text{OAr})_2]$  (**2**),

as the major surface species. This surface complex exhibits high catalytic activity and good stability in metathesis of pent-2-yne in contrast to  $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{Bu})(\text{CH}_2-t\text{Bu})_2]$  (**4**), probably because deactivation by  $\alpha$ -hydrogen migration is prevented. The system is also resistant to alkyne polymerization, which is problematic for similar homogeneous catalysts. In addition, the surface species **2** reacts with acetonitrile, a reaction which can be considered as the first step of nitrile-alkyne cross-metathesis [28].

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.020](https://doi.org/10.1016/j.jorganchem.2008.02.020).

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