

Note

Reactivity of silica-supported zirconium neopentyl fragments with trimethylphosphine and acetone: Formation of unexpected reaction products

Virginie Riollet, Mostafa Taoufik, Jean-Marie Basset, Frédéric Lefebvre *

Laboratoire LC2P2, Equipe LCOMS, 43 Boulevard du 11 Novembre 1918, 69626 Villeurbanne Cedex, France

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Abstract

The reactivity of trimethylphosphine with $(\equiv\text{SiO})_x\text{ZrNp}_{4-x}$ species ($x = 1-3$) synthesized on silica dehydroxylated at various temperatures has been studied. Only the bi-grafted $(\equiv\text{SiO})_2\text{ZrNp}_2$ complex reacts, leading to the formation of a surface alkylidene and evolution of neopentane. In presence of acetone the three neopentyl zirconium species react by the same way with evolution of neopentane and formation of enolate $(\equiv\text{SiO})_x\text{Zr}[\text{OC}(\text{CH}_3)(\equiv\text{CH}_2)]_{4-x}$ species.

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The reactivity of silica with alkyl transition metal complexes has been extensively studied during last years by us and others [1–3]. When silica has been previously treated under vacuum at high temperature (typically 500 °C or higher) a clean reaction occurs with the silanol groups leading to a mono-grafted surface complex and evolution of alkane. When silica is treated at a lower temperature only few data were reported, most of them concluding to the formation of a well-defined bi-grafted complex on silica dehydroxylated at ca. 200 °C. Such a behaviour could be relatively surprising as silica dehydroxylated at low temperature contains a distribution of silanol groups as evidenced for example by solid-state ^1H MAS NMR or infrared spectroscopy: Most of them are hydrogen bonded and so could lead to multi-grafted species but there are also, as on silica dehydroxylated at high temperature where they are predominant, some isolated silanol groups which should lead to mono-grafted species. We decided then to study the reactivity of tetra-neopentyl zirconium with silica dehydro-

oxylated at various temperatures. Indeed if its reactivity with silica dehydroxylated at high temperature is well known [4,5], there is, up to now, no report on what occurs on more silanol rich supports. Some chemical reactions of the grafted species prepared by this way were also studied.

Fig. 1a shows the amount of evolved neopentane during the grafting reaction of tetra-neopentyl zirconium on silica dehydroxylated at various temperatures [6]. It can be seen that the amount of evolved neopentane per zirconium varies continuously between ca. 2 for a silica dehydroxylated at 200 °C and 1 for a silica dehydroxylated at 500 °C. This late result is in agreement with literature and corresponds to the formation of the mono-grafted tris-neopentyl zirconium complex $(\equiv\text{Si}-\text{O})\text{ZrNp}_3$ on the silica surface [4,5]. The evolution of two neopentane molecules on silica dehydroxylated at 200 °C has also been observed for the grafting reaction of other transition metal complexes [7,8]. However, it is not possible to conclude, on the basis of these results, to the formation of a well-defined bis-grafted $(\equiv\text{Si}-\text{O})_2\text{ZrNp}_2$ complex (as proposed for example for titanium or vanadium) or of a mixture of mono- and multi-grafted zirconium species. ^{13}C CP-MAS NMR seems

* Corresponding author.

E-mail address: lefebvre@cpe.fr (F. Lefebvre).

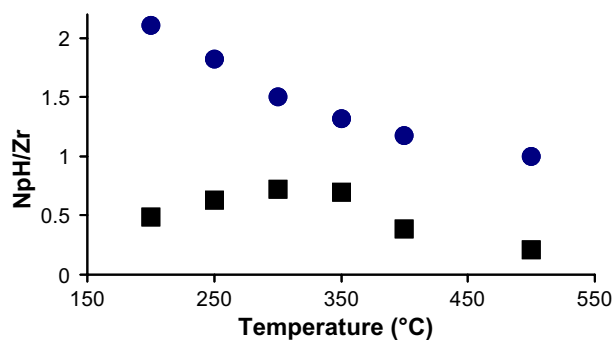


Fig. 1. Number of neopentane molecules evolved per grafted zirconium as a function of the dehydroxylation temperature of the starting silica during: (circles) the grafting step; (squares) the reaction of the grafted complex with PMe_3 .

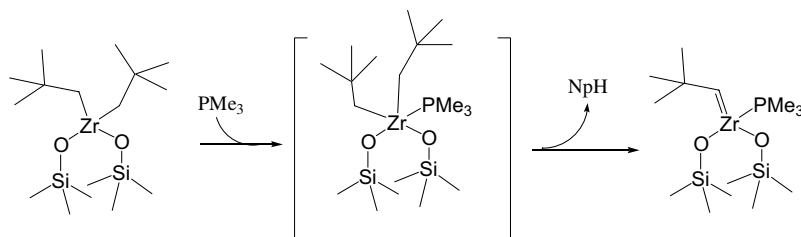
to be in agreement with the second hypothesis as the signal of the methylene carbon of the mono-grafted complex is observed at 96 ppm together with a broader signal at ca. 90 ppm which could correspond to multi-grafted species. However it will probably be difficult to conclude from physicochemical-characterizations because if there is a mixture of mono-, bi- and tri-grafted species (it seems reasonable to suppose that at least one neopentyl ligand remained on zirconium, simply because the tri-grafted complex should be so rigid that hydroxyl groups could not attack easily the last Zr–C bond), the amount of mono- and tri-grafted complexes should be equal and for example EXAFS should lead to a mean amount of two O and two C around Zr.

We searched then other proofs via chemical reactivity. The simplest reaction is thermolysis. It has been reported for other transition metal complexes [7] that heating at a moderate temperature a bis-grafted complex led to the formation of a surface alkylidene with evolution of the corresponding alkane. We tried then to study the thermolysis of $(\equiv\text{Si}-\text{O})_2\text{ZrNp}_2$ prepared on silica dehydroxylated at 200 °C. Indeed, if it is a mixture, the amount of evolved neopentane during this reaction should not be one per grafted zirconium as the tri-grafted complex cannot undergo a α -H abstraction followed by neopentane elimination. This reaction has also never been observed on mono-grafted species. Unfortunately, we were never able to obtain species where some neopentyl groups remained on the metal: In all cases all the organic groups were

removed, after a more or less large reaction time, even at 80 °C.

Another way to prepare alkylidene species starting from alkyl complexes is to coordinate a phosphine which will induce the α -H abstraction and the alkane elimination [9]. Such a reaction could also be used to discriminate between the two hypothesis for the nature of the zirconium species grafted on silica dehydroxylated at 200 °C, for the same reason than above (no reaction of the tri-grafted complex). Fig. 1b shows, for samples prepared on silica dehydroxylated at various temperatures, the amount of evolved neopentane after contacting the sample with trimethylphosphine during 48 h at room temperature (a kinetic study showed that the amount of neopentane did not vary after that time). The first conclusion is that the trisneopentyl zirconium fragment (prepared on silica dehydroxylated at 500 °C as a well-defined complex) does not react quantitatively, in our conditions, with trimethylphosphine as only a very small amount of neopentane is evolved. ^{31}P MAS NMR does not show any peak of coordinated phosphorus, only the signal of physisorbed trimethylphosphine being observed. A possible explanation is that the steric hindrance around zirconium is so high that trimethylphosphine cannot coordinate to it, preventing then the α -H abstraction and the neopentane evolution. The small experimental neopentane evolution could be due to the reaction of some grafted fragments located in special positions on the support where the steric hindrance is lower. In the case of silica dehydroxylated at 200 °C there is evolution of neopentane, so we can conclude that the bi-grafted species $(\equiv\text{SiO})_2\text{ZrNp}_2$ undergoes a reaction with the phosphine. But the most important feature is that the amount of neopentane is lower than 1 per zirconium, showing that there was not a well-defined bi-grafted complex on the surface but a mixture of mono-, di- and tri-grafted complexes. The amount of evolved neopentane indicates that on silica dehydroxylated at 200 °C ca. 60% of zirconium is present as a bi-grafted complex. The highest amount of this species (ca. 80%) is obtained on silica dehydroxylated at 300–350 °C.

By analogy with data obtained in solution on other transition metal complexes it can be proposed that a complex with the formula $(\equiv\text{SiO})_2\text{Zr}(\text{=CHCMe}_3)(\text{PMe}_3)$ has been formed upon reaction of $(\equiv\text{SiO})_2\text{ZrNp}_2$ with trimethylphosphine (Scheme 1). ^{31}P MAS NMR shows clearly a relatively broad peak at 58 ppm corresponding to the



Scheme 1.

coordinated phosphine (this peak cannot be attributed to trimethylphosphine oxide as it gives a signal at 36.2 ppm). Unfortunately ^{13}C NMR spectroscopy does not give interesting informations due to the presence of a mixture of species and the signal of the carbenic atom which should be a direct proof of the structure (expected at ca. 200–250 ppm as for tantalum carbenes [10]) is not seen.

Another proof of the presence of an alkylidene is the reaction with a ketone, which will lead to the evolution of an olefin and the formation of a metal oxo compound (pseudo-Wittig reaction) by a mechanism quite similar to that of olefin metathesis. When acetone is contacted with $(\equiv\text{SiO})_2\text{Zr}(\text{=CHCMe}_3)(\text{PMe}_3)$, no olefin is evolved, but all neopentyl groups are removed from the grafted species as neopentane. The same reaction occurs with the well-defined trisneopentyl zirconium fragment obtained on silica dehydroxylated at 500 °C, the three neopentyl groups being removed as neopentane. In order to understand what reaction occurred ^{13}C enriched on the methyl groups acetone was used and the resulting solid studied by solid-state ^{13}C CP-MAS NMR. The corresponding spectrum shows clearly two signals at 30 and 125 ppm which can be attributed to a methyl and an olefinic =CH_2 groups, respectively. The reaction can then be understood as an alcoholysis reaction of the Zr–Np bonds of the grafted complexes by the enol form of acetone, $\text{CH}_3\text{–CHOH=CH}_2$, leading to Zr–O–C(CH₃)=CH₂ species.

In conclusion these studies have shown some unexpected behaviours of grafted neopentyl zirconium complexes in presence of trimethylphosphine or of acetone: In the first

case only the bi-grafted species (never present as a well-defined species on the surface) reacts leading probably to an alkylidene complex while acetone reacts via its enol form leading to surface species containing terminal olefinic bonds. These bonds could be used as anchoring points for further modifications of the grafted complexes.

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