Journal of Organometallic Chemistry 744 (2013) 3–6

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

$[(\equiv SiO)Ta^V(=CH_2)Cl_2]$, the first tantalum methylidene species prepared and identified on the silica surface

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ARTICLE INFO

Article history:
Received 16 March 2013
Received in revised form
29 April 2013
Accepted 29 April 2013

Dedicated to Professor Wolfgang Herrmann, at the occasion of his 65th birthday.

Keywords:
Surface tantalum methylidene
Surface organometallics chemistry
α-Hydrogen abstraction
Kinetics

ABSTRACT

A novel surface tantalum methylidene $[(\equiv SiO)Ta^V(=CH_2)Cl_2]$ was obtained via thermal decomposition of the well-defined surface species $[(\equiv SiO)Ta^VCl_2Me_2]$. This first surface tantalum methylidene ever synthesized has been fully characterized and the kinetics of the α-hydrogen abstraction reaction has also been investigated in the heterogeneous system.

1. Introduction

Since the first discovery by Schrock of metal alkylidenes, these complexes have played an important role in the development of organometallic chemistry, olefin metathesis and generally catalysis [1,2]. Particularly, high oxidation state tantalum alkylidenes, prepared from the corresponding metal alkyl complex [3–5], have been found to be key intermediates involved in olefin metathesis catalysis. The late transition metal alkylidenes as ruthenium imidazole compound discovered by Herrmann [6,7] have led to another climax in this research field.

In heterogeneous catalysis, the study of surface supported catalyst is essential for the improvement of catalytic performances [8,9]. By comparison with their well-studied homogeneous counterpart, surface metal alkylidenes compounds reported are much fewer [10–16], the existence of such species often supported by only infrared spectroscopy or chemical reactivity [17–19].

Tantalum alkylidene compounds reported so far is even less abundant. Our group has reported the first fully characterized surface tantalum alkylidene, $[(\equiv SiO)(=CHt\text{-}Bu)(CH_2t\text{-}Bu)_2]$, but other examples are very limited [14,16]. So far the direct grafting on the silanols of silica with the tantalum (alkyl)(alkylidene) precursors have failed mostly because the silanol group add into the tantalum carbon double bond rather than the expected replacement of the alkyl group [20]. Meanwhile, in solution metal alkyl precursors substituted with small groups are unstable and often produce alkylidene, alkylidyne or even non identified products due to multiple α-hydrogen abstraction or bimolecular reactions [21,22].

We have always been interested in developing diversity of the surface organometallic chemistry of tantalum alkylidene. Here, we synthesized a novel surface tantalum methylidene complex $[(\equiv SiO)Ta^VCl_2(=CH_2)]$ on the silica surface, which derived from thermal decomposition of the well-defined surface binary methyl organometallic compound $[(\equiv SiO)Ta^VCl_2Me_2]$ that we reported recently [23]

2. Experimental and results

When $[(\equiv SiO)Ta^VCl_2Me_2]$ was thermally treated, methane was observed as the main product with traces of ethane and ethylene. From earlier work from Schrock, it is assumed that the formation of methane results from α-hydrogen abstraction and transfer to the remaining methyl [2]. Therefore, an immobilized tantalum methylidene complex should be observable since the bimolecular decomposition could be avoided on the silica surface (Scheme 1).

Upon heating $[(\equiv SiO)Ta^VCl_2Me_2]$ **1** at 140 °C for 24 h in a well-sealed Schlenk tube, gas calibration analysis found that 1 mmol of

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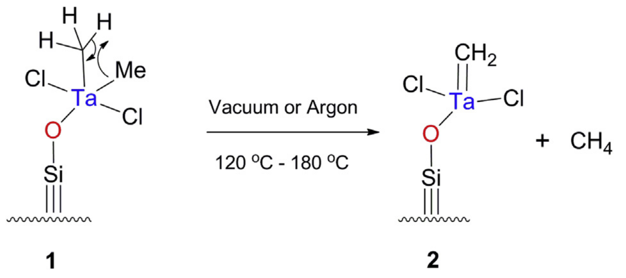
http://dx.doi.org/10.1016/j.jorganchem.2013.04.050



Scheme 1. The synthesis of [(≡SiO)Ta^V(=CH$_2$)Cl$_2$] **2**.

[(≡SiO)Ta^{V}Cl$_2$Me$_2$] **1** produced 0.93 mmol of methane. Another 0.90 mmol of methane was produced upon hydrolysis of the surface complex. Infrared spectroscopy shows this complex exhibits two peaks for the C–H stretching vibrations (2961, 2858 cm^{-1}). Elemental analysis shows a ratio of Ta:Cl:C = 1 ± 0.1:1.89 ± 0.1:0.97 ± 0.1 (expected: 1:2:1) in agreement with the expected monopodal methylidene species.

2.1. NMR study

^{1}H- MAS NMR spectrum of species **2** displays 4 peaks at 0.0, 1.2, 1.9 and 7.5 ppm (Fig. 1b). The weak signal at 0.0 ppm is probably due to methane or trace amount of ≡SiMe (*vide infra* for further comments, Fig. S3). One broad peak at 7.5 ppm is due to the methylidene group of [(≡SiO)Ta^V(=C**H$_2$**)Cl$_2$]. The peak at 1.9 ppm corresponds to unreacted silanols on the silica surface, which appears as a shoulder peak of the methyl group NMR signal of [(≡SiO)Ta^{V}Cl$_2$Me$_2$] (Fig. 1a), it is more easily detected after heat decomposition, with the same intensity. The small peak at 1.2 ppm corresponds to traces of the starting material on the silica surface.

Proton double (DQ)- and triple (TQ)-quantum correlation spectra under 22 kHz MAS provide autocorrelation peaks observed on the diagonal of the 2D DQ spectrum for all the protons (Fig. 1c) and only an autocorrelation peak is observed in the TQ spectrum for the peak at 1.2 ppm (1.2 ppm in F2 and 3.7 ppm in F1) (Fig. 1d). The fact that the signal at 7.5 ppm exhibits autocorrelation in the double quantum autocorrelation but does not exhibit an autocorrelation in the triple quantum is a proof that it is a CH$_2$ species. These results confirm that the signal at 7.49 ppm corresponds to a (=CH$_2$) group [24].

For a higher resolution of the ^{13}C CP MAS NMR spectroscopy, ^{13}C labeled [(≡SiO)Ta^{V}Cl$_2$Me$_2$] **1*** (97%) was synthesized. After heating the sample to 140 K, the ^{13}C CP/MAS NMR spectrum of **2*** displays formation of a novel peaks at 230 ppm (Fig. 2b) for an sp^2 carbon. Other ^{13}C NMR signals belong to the remained trace amount of [(≡SiO)Ta^{V}Cl$_2$Me$_2$] on the silica surface.

2D ^{1}H–^{13}C HETCOR NMR analysis (Fig. 2c) with short contact time (0.2 ms) shows a clear correlation between the methylidene protons at 7.5 ppm and the carbon at 230 ppm, confirming the existence of tantalum methylidene species on the surface.

2.2. *Kinetics study of the conversion of [(≡SiO)Ta^{V}Cl$_2$Me$_2$] to [(≡SiO)Ta^V(=CH$_2$)Cl$_2$]*

In order to determine the kinetics of formation of this methylidene species, the reaction was firstly performed in a fixed bed reactor with a PID control unit, **1** was heated under argon flow

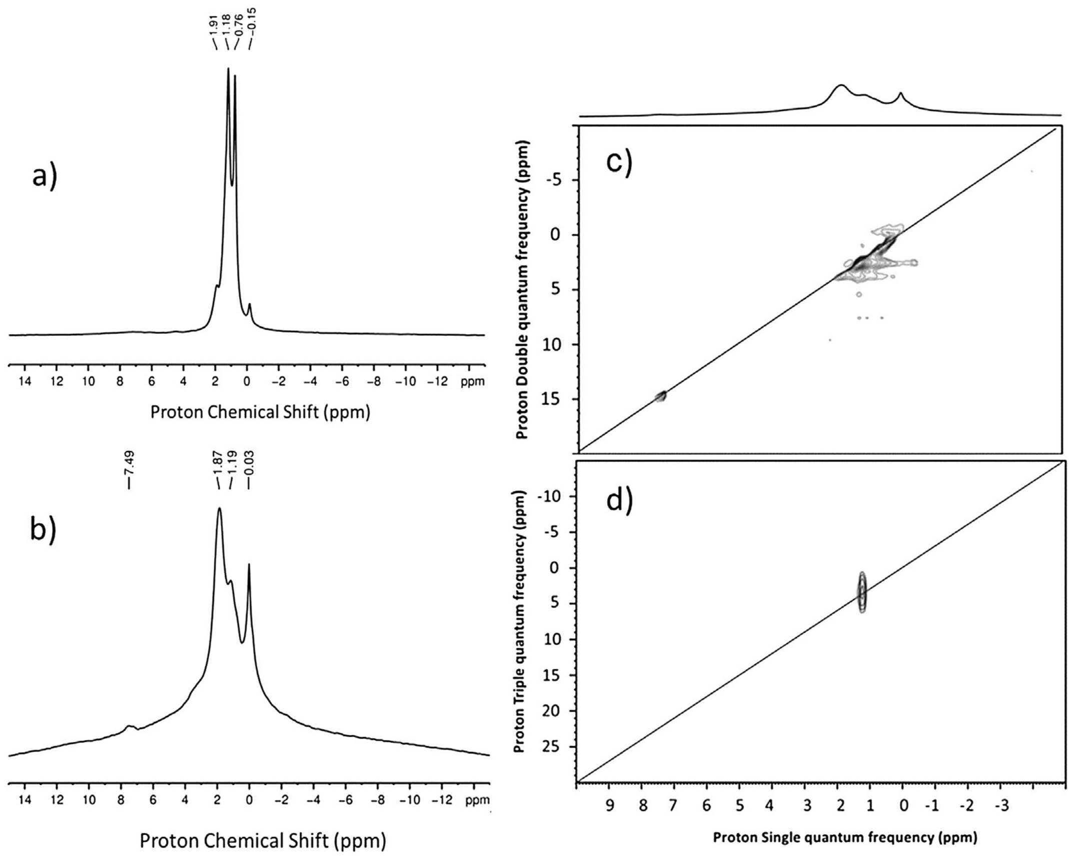


Fig. 1. (a) ^{1}H MAS NMR of [(≡SiO)Ta^{V}Me$_2$Cl$_2$], (b) ^{1}H MAS NMR of [(≡SiO)Ta^V(=CH$_2$)Cl$_2$] (c), (d) two dimensional contour plots of the aliphatic region of the double (DQ) and triple (TQ) quantum proton solid-state NMR correlation spectra of [(≡SiO)Ta^V(=CH$_2$)Cl$_2$] (more details see Supplementary material).

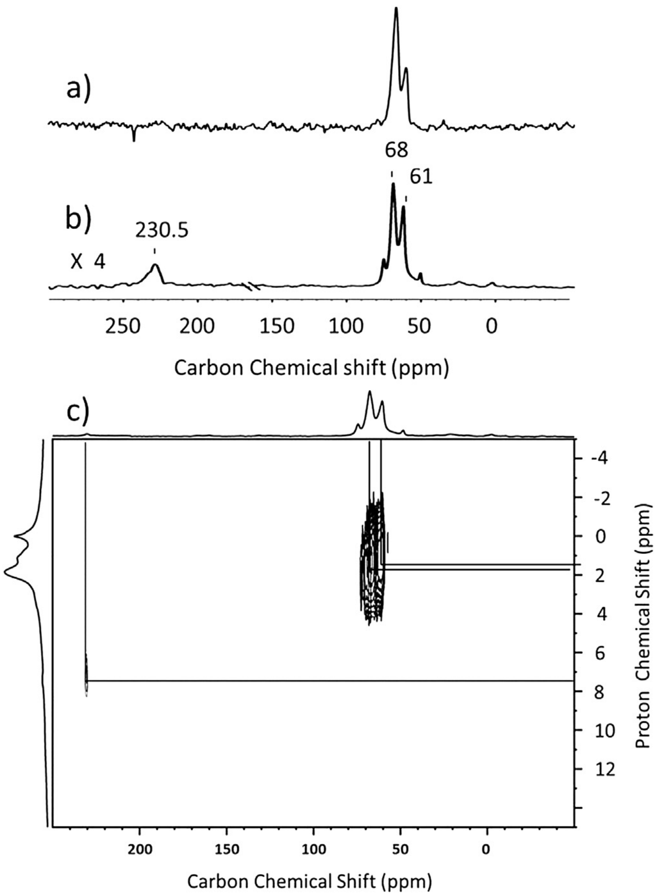


Fig. 2. (a) ^{13}C CP MAS spectrum of $[(\equiv SiO)Ta^{V}Me_2Cl_2]$, (b) ^{13}C CP MAS spectrum (c) and contour plot of the aliphatic region of a ^{1}H–^{13}C HETCOR spectrum recorded with a contact times of 0.2 ms spectrum of $[(\equiv SiO)Ta^{V}(=CH_2)Cl_2]$ (experimental details are given in Supplementary material).

(atmosphere pressure, 17.1 mL/min) at 140 °C (more information see Supplementary material), methane was observed with traces amounts (less than 0.1%) of ethane and ethylene (Fig. 3). Methane accounts for more than 99.8% of the gaseous products; combined with the former results, we can take the methane generation rate as the reaction rate, online GC monitoring found the methane generation rate decreased exponentially with the time. The equation fits with a first-order kinetics reaction, in agreement with studies of Schrock [25] and Xue [26], which reported also a first order kinetics for the conversion of $Ta(CH_2XMe_3)_5$ into $Ta(=CHXMe_3)(CH_2XMe_3)_3$ (X = C, Si).

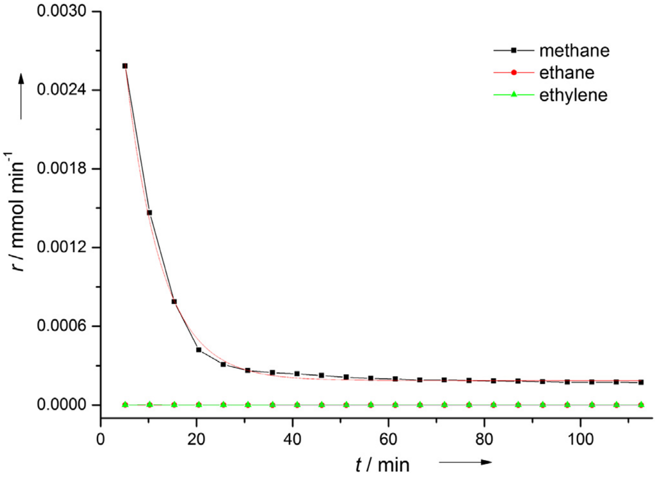


Fig. 3. The thermal decomposition of $[(\equiv SiO)Ta^{V}Cl_2Me_2]$ at 140 °C in a fixed bed reactor (black line, experimental data; red line, exponential fitting with first order law) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

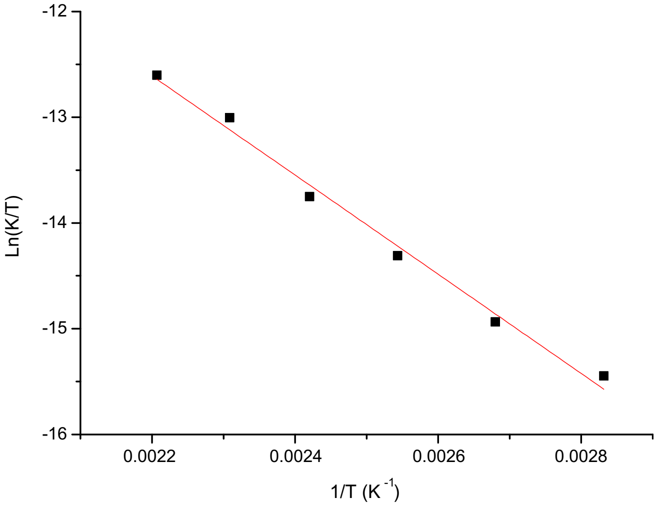


Fig. 4. Eyring plot of the reaction ($\ln(k/T)$ vs $1/T$).

To obtain the thermodynamics parameters, thermal decomposition of $[(\equiv SiO)Ta^{V}Cl_2Me_2]$ was monitored under a static condition (experimental details see Supplementary material). In a well-sealed Schlenk tube with known volume, $[(\equiv SiO)Ta^{V}Cl_2Me_2]$ was decomposed at specified temperature, the quantity of the methane produced was quantified.

The thermal decomposition at six different temperatures (between 353.1 and 453.1 K) has been determined (see Supplementary material). Eyring plot of $\ln(k/T)$ vs $1/T$ gave an activation enthalpy of $\Delta H^{\pm} = 9.3 \pm 0.2$ kcal/mol and an activation entropy of $\Delta S^{\pm} = -26.0 \pm 1.5$ (eu) for the conversion of **1** to **2** (Fig. 4). Arrhenius plot gave the $\Delta H = 10.1 \pm 0.2$ (kcal/mol) and $\Delta S = -39.0 \pm 2$ (eu) (see Fig. S7). These values close to the experimental values Schrock observed for the α-hydrogen abstraction of $TaCp(CH_2CMe_3)Cl_2$ in chloroform ($\Delta H = 10.7 \pm 0.5$ (kcal/mol), $\Delta S = -36.0 \pm 2$ (eu)) [25,26], also comparable to the DFT calculated value for α-H abstraction of $TaMe_5$ ($\Delta H = 7.2$ kcal/mol) [27]. Further application and catalysis research works are still in progress.

3. Conclusions

By employing surface organometallic chemistry, we have been able to synthesize a novel tantalum methylidene species on the silica surface, $[(\equiv SiO)Ta^{V}(=CH_2)Cl_2]$, and monitored its formation by α-H abstraction. The thermodynamic values supported a monomolecular α-hydrogen abstraction mechanism and highlights how surface organometallic species is an effective tool to study a transformation which would not be otherwise observable in a homogeneous system.

Acknowledgements

We thanks KAUST for the financial support and YC gratefully acknowledges generous donation from SABIC.

Appendix A. Supplementary material

Supplementary material associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2013.04.050.

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