Alkane Metathesis with the Tantalum Methylidene [(≡SiO)Ta(=CH₂)Me₂]/[(≡SiO)₂Ta(=CH₂)Me] Generated from Well-Defined Surface Organometallic Complex [(≡SiO)TaᵛMe₄]

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ⓢ *Supporting Information*

ABSTRACT: By grafting TaMe₅ on Aerosil₇₀₀, a stable, well-defined, silica-supported tetramethyl tantalum(V) complex, [(≡SiO)TaMe₄], is obtained on the silica surface. After thermal treatment at 150 °C, the complex is transformed into two surface tantalum methylidenes, [(≡SiO)₂Ta(=CH₂)Me] and [(≡SiO)Ta(=CH₂)-Me₂], which are active in alkane metathesis and comparable to the previously reported [(≡SiO)₂TaHₓ]. Here we present the first experimental study to isolate and identify a surface tantalum carbene as the intermediate in alkane metathesis. A systematic experimental study reveals a new reasonable pathway for this reaction.

The catalytic transformation of alkanes remains one of the most important challenges in chemistry, considering the inertness of the C−H and C−C bonds but also the application potential,[1] for converting short alkanes into longer chain analogues usually is a value-adding process. Our work in this area began with the discovery of the highly electrophilic metal hydride [(≡SiO)₃Zr-H] supported on silica, which is able to activate the C−H and C−C bonds of alkanes at very moderate temperature and transform polyethylene into diesel-range gasoline.[2] Later, in 1997, we reported the discovery of the highly electrophilic tantalum hydride supported on a silica surface, [(≡SiO)₂TaHₓ],[3] which can catalytically transform alkanes into their lower and higher homologues (eq 1, T > 25 °C). By analogy to

$$2C_nH_{2n+2} \rightleftharpoons C_{n-i}H_{2(n-i)+2} + C_{n+i}H_{2(n+i)+2}$$

$$n \geq 2, \quad i = 1, 2, ..., (n-1) \quad (1)$$
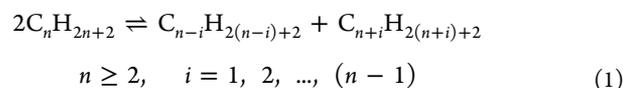
olefin metathesis, and different from "tandem metathesis of paraffins",[1b,f,4] this reaction was dubbed "alkane metathesis".[3a,5] An alumina-supported tungsten hydride, W(H)₃/Al₂O₃, was found to have better activity in subsequent studies.[6]

A clear understanding of the reaction mechanism is essential for catalyst design and improvement of the catalyst's reactivity and selectivity. We previously performed a series of mechanistic studies with [(≡SiO)₂TaHₓ] as the catalyst,[5,7] including kinetic studies, isotope distribution studies, solid-state (SS) NMR, density functional theory (DFT) calculations, determination of the effect of substrates, etc. On the basis of those results, we concluded that, besides C−H bond activation leading to metal−alkyls and metal hydride olefins, intermediates should be involved similar to those involved in olefin metathesis. We proposed that the reaction occurred on a multifunctional, single-site [(≡SiO)Ta(=CH₂)(H)] intermediate species and involved (i) C−H bond activation on the metal hydride (Ta-H), (ii) α-H or β-H elimination on the tantalum−alkyl formed, (iii) olefin metathesis on the carbene moiety (Ta=CH₂) with metallocyclobutane as a key intermediate, and (iv) hydrogenation of the newly formed olefins on the metal hydride (Ta-H).[8]

However, [(≡SiO)₂TaHₓ]-catalyzed alkane metathesis always involves hydrogenolysis as a competing reaction,[9] which is the major initial reaction and sometimes has higher reaction rates than alkane metathesis. The high reactivity of the proposed [(≡SiO)₂Ta(=CH₂)H] intermediate species makes it very difficult to identify its existence and the reaction pathway. [(≡SiO)Ta(=CHt-Bu)(CH₂t-Bu)₂] and some other metal neopentyl species are also able to catalyze alkane metathesis, albeit at a lower rate.[7c] To determine the reaction mechanism, we focused on isolating the methylidene intermediate and showing direct evidence for the reaction pathway.

Inspired by our recent syntheses of various surface methyl-metal compounds, e.g., [(≡SiO)WMe₅],[10] [(≡SiO)Ta-Me₂Cl₂],[11] and [(≡SiO)Ta(=CH₂)Cl₂],[12] here we report the isolation of an alkane metathesis intermediate, the surface tantalum methylidene [(≡SiO)ₓTa(=CH₂)Me₃₋ₓ] (x = 1, 2), which is the simplest analogue of the presumed active species [(≡SiO)Ta(=CH₂)(H)]. This compound was prepared by thermal treatment of the well-defined surface tantalum species [(≡SiO)TaMe₄] (Scheme 1). Both [(≡SiO)TaMe₄] **2** and tantalum methylidene methyl compounds **3a** and **3b** can catalyze the alkane metathesis reaction with a reactivity comparable to that of [(≡SiO)₂TaHₓ]. By performing a systematic study of the

Scheme 1. Production of $[(\equiv SiO)TaMe_4]$ and $[(\equiv SiO)Ta(=CH_2)Me_2]/[(\equiv SiO)_2Ta(=CH_2)Me]$
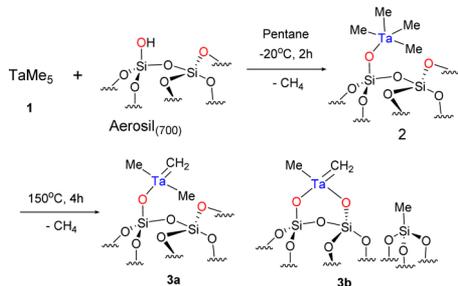
reaction mechanism, we found that the Ta—Me bond can directly activate C—H as an initiation step.

$[(\equiv SiO)TaMe_4]$ can be easily and efficiently prepared by grafting $TaMe_5$ (synthesized *in situ*, see SI, Figure S1) onto the surface of $Aerosil_{700}$.[13] After washing three times with pentane and evacuation at room temperature $(10^{-5}$ mbar) for 3 h, grayish powder product **2** was obtained (Scheme 1). After chemisorption of $TaMe_5$, the IR peak of the silanols at 3747 cm^{-1} disappeared, and new bands appeared at 2932 cm^{-1} for ν(C—H) and 1397 cm^{-1} for δ(C—H) (SI, Figure S2). The ^{1}H MAS SS-NMR spectrum of **2** displays a main signal at 0.9 ppm (Figure 1A
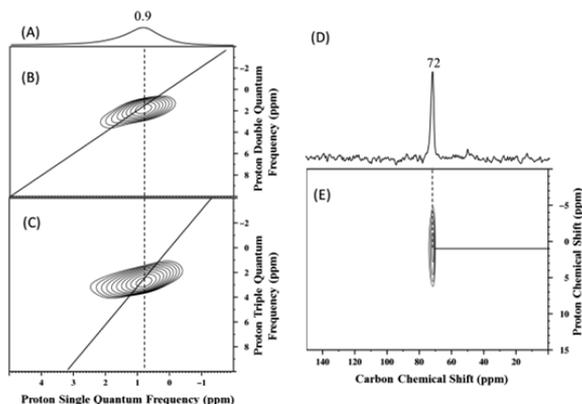
Figure 1. (A) ^{1}H MAS NMR, (B,C) 2D contour plots of the aliphatic region of the DQ and TQ proton SS-NMR correlation spectra, (D) ^{13}C CP-MAS NMR, and (E) 2D contour plot of the aliphatic region of the ^{1}H—^{13}C HETCOR spectrum of $[(\equiv SiO)TaMe_4]$.

and SI, Figure S4) and a weak-intensity peak at 1.90 ppm, assigned to the small amount of unreacted silanols. The ^{13}C-enriched compound **2*** (97% enriched) was synthesized with the same protocol starting from $^{13}CH_3I$ for better carbon NMR sensitivity. The ^{13}C CP-MAS NMR spectrum of **2*** gives only one signal at 72 ppm. ^{1}H—^{13}C HETCOR NMR recorded with a contact time of 0.2 s shows that the proton signal at 0.9 ppm is correlated with the carbon signal at 72 ppm (Figure 1E). The ^{1}H—^{1}H double- (DQ) and triple-quantum (TQ) correlation spectra under 22 kHz MAS (Figure 1B,C) support that the signal belongs to a methyl group,[4b] as autocorrelation peaks are observed on the diagonal of the two-dimensional (2D) DQ and TQ spectra (0.9 ppm in F2, and 1.8 and 2.7 ppm in F1, respectively). Elemental analysis gives 5.30% Ta, 1.41% C, and 0.33% H, with <0.1% Cl and a ratio of Ta/C/H = 1/4.0±0.3/11.5±1.0 (theoretical ratio 1/4.0/12.0). Hydrolysis and hydrogenolysis of **2** produced 4.0 ± 0.3 and 3.8 ± 0.3 mol of methane

per mole of tantalum, respectively. This compound is quite stable at room temperature, and no decomposition is detected after storage for more than 1 week; i.e., there is no change in the SS-NMR spectrum.

After $[(\equiv SiO)TaMe_4]$ was heated at 150 °C for 4 h, methane was the only product in the gas phase (1.1 ± 0.2 equiv of methane per mole of tantalum). IR shows that the bands at 2932 cm^{-1} for ν(C—H) and 1397 cm^{-1} for δ(C—H) both decreased after the treatment (SI, Figure S3). The ^{1}H MAS NMR spectrum (Figure 2A and SI, Figure S5) shows that the peak at 0.9 ppm disappears
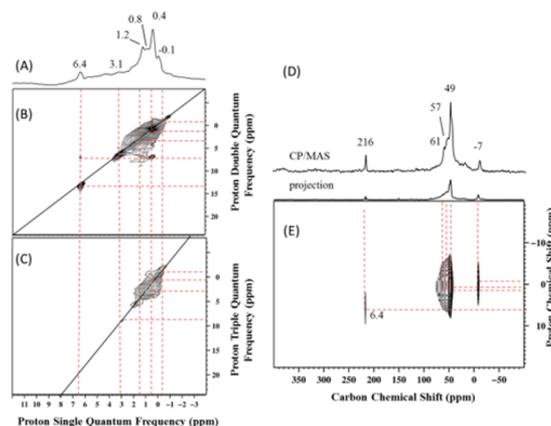
Figure 2. (A) ^{1}H MAS NMR, (B,C) 2D contour plots of the aliphatic region of the DQ and TQ quantum proton SS-NMR correlation spectra, (D) ^{13}C CP-MAS NMR, and (E) 2D contour plot of the aliphatic region of ^{1}H—^{13}C HETCOR spectrum of $[(\equiv SiO)Ta(=CH_2)Me_2]/[(\equiv SiO)_2Ta(=CH_2)Me]$.

and five new peaks appear at 6.4, 3.1, 1.2, 0.4, and −0.1 ppm. The latter four signals autocorrelate in 2D DQ and TQ ^{1}H—^{1}H homonuclear dipolar correlation spectra and thus can be assigned to Ta-Me groups (Figure 2B,C). The peak at 6.4 ppm can be assigned to Ta=CH$_2$, as an autocorrelation is limited to the DQ. The signal at −0.1 ppm is attributed to $\equiv$Si—Me groups resulting from the surface methyl transfer, which is also supported by the autocorrelation in DQ and TQ (Figure 2B,C). The ^{13}C CP-MAS NMR spectrum (^{13}C, 97% enriched) gives parallel results (Figure 2D): the peak at 72 ppm ascribed to $[(\equiv SiO)TaMe_4]$ disappears after the thermal treatment, and new peaks are observed at 216, 61, 57, 49, and −7 ppm. The 2D ^{1}H—^{13}C HETCOR NMR spectrum with a short contact time of 0.2 ms shows that the CH$_3$ protons (3.1, 1.2, and 0.4 ppm) correlate with carbon atoms (61, 57, and 49 ppm, respectively), and the proton signal at 6.4 ppm has strong correlation with the carbon signal at 216 ppm (Figure 2E). These data support the assignment of the methylidene moiety, Ta=CH$_2$. The carbon peak at −7 ppm correlates with proton peak at −0.1 ppm attributed to $\equiv$Si—Me group, suggesting the formation of bipodal species **3b**.[11] By analogy with our recent NMR and DFT study on $[(\equiv SiO)W(\equiv CH)Me_2]$,[10] as well as the ^{1}H—^{1}H correlation observed between the methyl groups and the methylidene moiety in DQ and TQ experiments (Figure 2B,C), the methyl groups at ^{13}C 49 and 57 ppm and ^{1}H 0.4 and 1.2 ppm can be assigned to the monopodal species **3a**, while the methyl groups at ^{13}C 61 ppm and ^{1}H 3.1 ppm are assigned to the bipodal species **3b**. Elemental analysis gives 5.41% Ta, 1.04% C, and 0.25% H, with a ratio of Ta/C/H = 1/2.9±0.3/8.2±1.0.

Because the methylidene species **3** is much more thermally stable than precursor **2**, hydrolysis of **3** produced 2.6 ± 0.2 mol of

Table 1. Alkane Metathesis with $[(\equiv SiO)Ta(=CH_2)Me_2]/[(\equiv SiO)_2Ta(=CH_2)Me]$ As Prepared

alkane[a]	TON[b]	C1	C2	C3	C4	C5	C6	C7	C8
					product selectivity (%)				
ethane	18 (2.8)	50.6	–	46.5	1.3(0.2)[c]				
propane	49 (7.8)	11.6	45.4	–	32.8(6.5)	5.5(1.7)	0.9(0.2)		
butane	65 (10.4)	5.3	15.1	41.9	–(2.6)	29.3(3.4)	3.8(0.9)	1.2	
pentane	119(18.0)	1.0	2.7	17.2	21.8(0.5)	–(1.7)	42.5(0.8)	9.0(1.1)	2.5

[a]After 120 h of reaction in a batch reactor (Ta/alkane ratio ≈ 630, 150 °C, 0.95 atm). [b]TON is expressed in moles of alkane transformed per mole of Ta. The values in parentheses are conversions. [c]The percentage of the isomer partition.

methane per mole of tantalum. All these characterization data support the generation of the tantalum methylidene species on the silica surface as a mixture of $[(\equiv SiO)Ta(=CH_2)Me_2]$ and $[(\equiv SiO)_2Ta(=CH_2)Me][\equiv Si-Me]$. Several attempts to avoid the formation of the bipodal species failed, as the methyl transfer to silicon is an easy process when the Ta-methyl is close to a highly reactive ≡Si-O-Si≡.

These methyl methylidene species—the simplest homologues of the proposed active species, $[(\equiv SiO_2)Ta(=CH_2)H]$—also are important intermediates themselves. Alkane metathesis with $[(\equiv SiO)Ta(=CH_2)Me_2]/[(\equiv SiO)_2Ta(=CH_2)Me]$ as catalyst was performed with our previously reported standard conditions in a batch reactor. When propane (630 equiv) was brought into contact with **3** at 150 °C, after 120 h, the propane was converted into methane (11.6%), ethane (45.4%), butanes (32.8%), and pentanes (5.5%) with a conversion of 7.8%, which gives a turnover number (TON) of 49. The results for ethane, butane, and pentane are listed in Table 1. These results are comparable with the catalytic results obtained using $[(\equiv SiO)_2TaH_x]$.[3a] We also found that **2** (the precursor) has productivity and selectivity similar to those of **3** in alkane metathesis, which indicates that the alkane metathesis catalyzed by **2** and **3** might go through the same reaction pathway.

Further insight into the mechanism was achieved by labeling experiments. The reaction of $[(\equiv SiO)TaMe*_4]$ (98% labeled) and $^{13}CH_3$-CH_3 (50% ^{13}C-labeled) was monitored by SS-NMR. Within the first hour, **2** was converted into methylidene: strong peaks corresponding to **3** were observed, while the peak at 72 ppm for **2** disappeared (SI, Figure S6). After 6 h, the intensity of the peak for the methylidene group at 216 ppm sharply decreased, and another carbene species, presumably a Ta-ethylidene, appeared at 220 ppm (SI, Figure S7). Starting from compound **3***, after reacting with $^{13}CH_3$-CH_3 for 5 h, a similar ^{13}C SS-NMR spectrum was obtained (SI, Figure S8). These results support that **2** and **3** catalyze the alkane metathesis via the same pathway.

Isotopic distribution in the alkane metathesis reaction was then followed by GC-MS. When **2** and **3** were reacted with a stoichiometric amount of C_5D_{12} (for details see SI) at 150 °C, after a few minutes, CH_3D was observed as the main product in the gas phase, with trace amount of metathesis products (SI, Figures S15 and S16). This indicates that the Ta−CH_3 bond can directly activate the C−D bond of C_5D_{12} and produce monodeuterated methane, likely by σ-bond metathesis. The alkane metathesis mechanism we proposed previously involves an initial elementary step of C−H bond activation with surface Ta-H,[7b,e] leading to a Ta-alkyl. Here we demonstrate that the C−H activation could be achieved with a Ta-alkyl group via σ-bond metathesis. When the reaction with C_5D_{12} was performed under the same experimental conditions as the reaction with C_5H_{12} (Table 1), the rate decreased by a factor of 2.4, suggesting a possible kinetic isotope effect.[14]

When ^{13}C-labeled $[(\equiv SiO)TaMe*_4]$ reacts with a stoichiometric amount of C_5H_{12} (150 °C, 250 mbar), $^{13}CH_4$ is produced without any ^{13}C-labeled metathesis product, indicating that the labeled methyl or methylidene group does not take part in the metathesis step of this reaction (SI, Figures S17−S20). Generally, only alkane products are found in the gas phase after the alkane metathesis reaction (SI, Figure S9). However, after reaction with ethane for 4 h, upon hydrolysis, the surface organometallic species gives not only alkanes but also alkene products (as propene and four different butenes; SI, Figure S10).[7f] By varying the contact time, we already observed that alkenes are produced in the reaction as intermediates,[7e] probably by β-H elimination from the Ta-alkyls. SS-NMR results also support that after reaction of $[(\equiv SiO)TaMe_4]$ with $^{13}CH_3$-CH_3 for a few hours, the ^{13}C MAS NMR (SI, Figure S7) shows two peaks at 105 and 118 ppm corresponding to alkenes (they disappear from the NMR spectrum after hydrolysis with H_2O). If, instead, the surface species is hydrolyzed with D_2O, partially deuterated alkane products are identified by GC-MS at M+1, M+2, and M+3 (singly, doubly, and triply deuterated alkanes); the peaks are found with high intensity (SI, Figures S21−S24). Meanwhile, the ethane produced in this treatment is found as $C_2H_4D_2$ with a main peak at M+2, indicating the ethyl group exists on the surface mainly as a Ta=$CHCH_3$ moiety.

Next we monitored the metathesis reaction by *in situ* IR (SI, Figures S11 and S12). A small peak at 2270 cm^{-1}, generally assigned to ≡Si-H (SI, Figure S13), is observed after reaction of $[(\equiv SiO)TaMe_4]$ with ethane or pentane for 6 h. The presence of this ≡Si-H indicates the formation of the Ta-H intermediate (likely monopodal) in the reaction, which would react with the surface ≡Si-O-Si≡ bridge as a secondary reaction to produce the ≡Si-H moiety. The formation of the Ta-H also is supported by formation of H_2 in the reaction as a byproduct (SI, Scheme S1). Furthermore, the addition of 0.5% H_2 to the alkane has little effect on the reaction (SI, Table S2).

The metathesis reaction also was performed under dynamic conditions in a fixed-bed reactor coupled with an *in situ* GC detector. Contacting **2** (0.043 mmol Ta) with ethane (1 bar, 3.0 mL/min, ~3.1 mol of ethane/(mol of Ta·min)) at 150 °C in a dynamic reactor gave a mixture of hydrogen, methane, propane, isobutane, and butane as the products with time (SI, Figure S14a). Trace amounts of ethylene, propylene, and butenes were also detected. Methane was produced in a large quantity initially and reached a maximum at 50 min, and then it decreased quickly to a level similar to that of propane, which may be due to the generation of methylidene species and σ-bond metathesis with the C−H group of the alkanes. The production of propane and hydrogen also reached a maximun with time and then decreased slowly. In total, approximately 0.592 mmol of methane, 0.441 mmol of propane (0.151 mmol less than methane, 3.2 equiv relative to Ta), and 0.038 mmol of hydrogen (0.8 equiv relative

to Ta) were produced. The TON reached 22, and the catalyst slowly lost its activity after 1200 min (SI, Figure S14b).

On the basis of the experimental results from this and our previous studies,[6,7] the following mechanism is proposed (Scheme 2): **3** as the active species reacts with alkane to produce

Scheme 2. Proposed Mechanism for Ethane Metathesis with the Precursor $[(\equiv SiO)TaMe_4]$
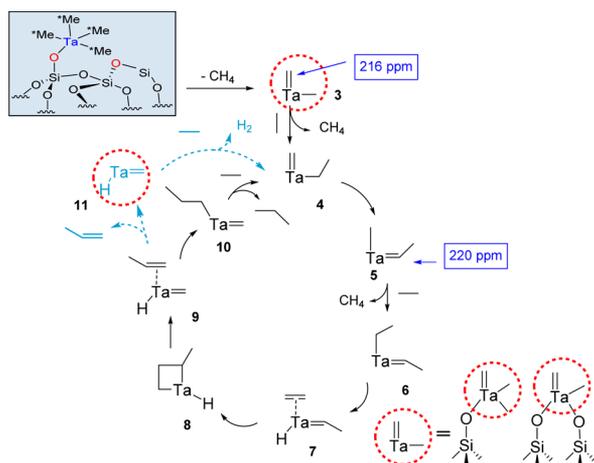
methane and Ta-alkyl species **4**, followed by α-H abstraction, producing ethylidene species **5**, which is supported by the observed new ^{13}C NMR peak at 220 ppm (SI, Figure S7) and production of $C_2H_4D_2$ in the hydrolysis treatment. Further σ-bond metathesis with ethane removes the methyl group (original methylidene moiety) to produce **6**; intermediate species **7** is produced with a following β-H abstraction. The metathesis product is produced following the metallocyclobutane mechanism described by Chauvin[15] via intermediates **8** and **9**. Intramolecular insertion of the formed higher olefin into the tantalum hydride, followed by σ-bond metathesis between ethane and propyl-tantalum, gives the metathesis product. Alternatively, propylene can dissociate to produce **11**, leaving a possibility of σ-bond metathesis between ethane and the tantalum hydride. The Ta–H intermediate species **7**–**9** can lead to surface $\equiv$Si-H by reaction with the siloxane bridge, or to H_2 by reaction with alkane via σ-bond metathesis. The catalyst possibly is deactivated because of these secondary reactions, and these byproducts lead to different deuterated alkanes when they meet D_2O.

In summary, we present the first experimental study to isolate the tantalum methylidene intermediate species **3** for alkane metathesis, prepared easily from the well-defined surface species $[(\equiv SiO)TaMe_4]$. Both **2** and **3** have reactivity and selectivity in alkane metathesis comparable to those previously reported for $[(\equiv SiO)_2TaH_x]$, and catalyze this reaction via the same pathway. The reaction intermediates for alkane metathesis are identified for the first time by SS-NMR and other characterization methods. We have developed a new catalyst for alkane metathesis which can be prepared easily, opening a new way for catalyst design.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experiment details, and IR, NMR, GC, MS, and other characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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