

Hydrogenolysis of Cycloalkanes on a Tantalum Hydride Complex Supported on Silica and Insight into the Deactivation Pathway by the Combined Use of 1D Solid-State NMR and EXAFS Spectroscopies

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Abstract: Hydrogenolysis of cyclic alkanes is catalysed by $[(\equiv\text{SiO})_2\text{Ta-H}]$ (**1**) at 160 °C and leads to lower alkanes and cyclic alkanes including cyclopentane. The turnover number is correlated with the number of carbon atoms of the cyclic alkanes, and therefore while cycloheptane is readily transformed, cyclopentane does not give any product (< 1 %). The mechanism of ring contraction probably involves carbene de-insertion as a key carbon-carbon bond-cleavage

step. The reluctance of cyclopentane to undergo hydrogenolysis was further studied: under the reaction conditions cyclopentane reacts with **1** to give the corresponding cyclopentyl derivative $[(\equiv\text{SiO})_2\text{Ta-C}_5\text{H}_9]$ (**13**), which evolves towards cyclopentadienyl derivative

$[(\equiv\text{SiO})_2\text{Ta}(\text{C}_5\text{H}_5)]$ (**14**) according to both solid-state NMR and EXAFS spectroscopies. This latter complex is inactive in the hydrogenolysis of alkanes, and therefore the formation of cyclopentane in the hydrogenolysis of various cyclic alkanes is probably responsible for the de-activation of the catalyst by formation of cyclopentadienyl complexes.

Keywords: alkanes • EXAFS spectroscopy • hydrogenolysis • NMR spectroscopy • tantalum

Introduction

Hydrogenolysis of cyclic alkanes has been widely studied on metal particles, and has given rise to numerous mechanistic debates over the past thirty years.^[1] Most of the mechanisms involve an “ensemble” of adjacent metal atoms or preferably two metal centres in the carbon-carbon bond-cleavage step, since such types of arrangements are readily found on metallic surfaces. On the other hand, it is possible to generate “isolated” metal centres directly attached to the support by covalent metal-oxygen bonds. This is achieved by surface organometallic chemistry.^[2] For example, the reaction of an organometallic complex like $[\text{Ta}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_3]$

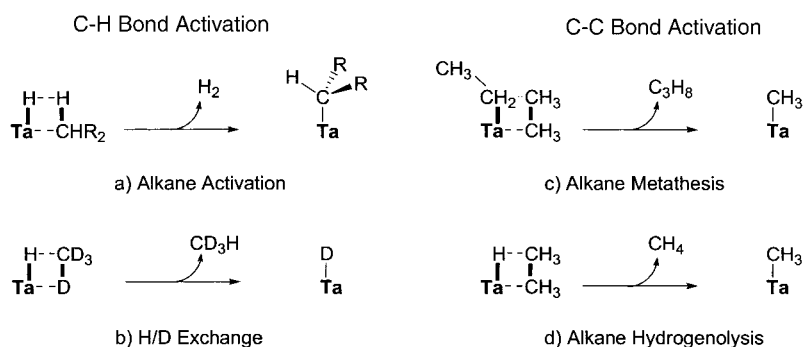
with a partially dehydroxylated silica generates $[(\equiv\text{SiO})_x\text{Ta}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_{3-x}]$ ($x=1$ or 2 or both, depending on the temperature of pretreatment of silica).^[3] Upon treatment under hydrogen at 150 °C, these surface complexes rearrange into $[(\equiv\text{SiO})_2\text{Ta-H}]$ (**1**), and under these conditions the neopentane evolved undergoes hydrogenolysis to methane.^[4] This new surface complex can readily be considered as an isolated atom of tantalum in an oxidation state of III stabilized by two siloxy (surface) and the hydride (external) ligands.

This hydride of unusual structure, for both molecular and surface chemistry, exhibits tremendous reactivity towards alkanes (Scheme 1): a) it readily activates their C-H bonds at low temperatures (25–80 °C) to give the corresponding surface alkyl complexes with evolution of molecular hydrogen,^[4, 5] b) it catalyses H/D exchange in mixtures of deuterated and nondeuterated alkanes including methane,^[6] c) it transforms acyclic alkanes into their lower and higher homologues under mild conditions (alkane metathesis),^[7] and d) it catalyses the hydrogenolysis of acyclic alkanes into methane at low temperatures in the presence of H₂.^[8] In the latter reaction, it has clearly been shown that the key step for carbon-carbon bond cleavage was different from a β -alkyl transfer, in contrast to supported Group 4 metal hydrides.^[9, 10] In our continuing effort to understand the reactivity of **1** with alkanes, we investigated the hydrogenolysis of cyclic alkanes, and the results are disclosed below.

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Scheme 1. Reactivity of [(≡SiO)₂Ta-H] (**1**) toward alkanes.

Results and Discussion

Hydrogenolysis of cycloalkanes:^[11] This reaction was carried out with various cyclic alkanes under identical conditions: a mixture of hydrogen (360 equiv), a cycloalkane (14.5 equiv) and a catalytic amount of **1** (1 equiv) was heated at 160 °C. Under these conditions, cycloheptane is converted into a mixture of acyclic alkanes from methane to heptanes and cyclic alkanes (cyclopentane, cyclohexane, and methylcyclohexane; see Figure 1 a and Figure 2). Their proportions are in agreement with what would be expected based on the difference in the respective free energies of reaction, which favour the formation of cyclohexane over that of methylcyclohexane and heptane (Table 1). Cyclohexane and methylcyclohexane are also transformed into a mixture of acyclic and cyclic alkanes (Figure 1 b–d and Figure 2), while cyclopentane gives no product (<1%). The hydrogenolysis of meth-

ylcyclopentane is noteworthy since it forms a mixture of acyclic alkanes, cyclopentane and the ring-expansion product cyclohexane (for the free energy of reaction, see Table 1, entry 7).

In all cases the activity of the catalyst decreases rapidly, and after 20 h little or no conversion is observed, in agreement with deactivation of **1**. The percentage conversion varies as a function of the ring size of the

starting alkane and its substituents as follows: cycloheptane > methylcyclohexane > cyclohexane > methylcyclopentane > cyclopentane.

The formation of smaller cyclic compounds must involve a carbon–carbon activation step followed by rearrangement of the carbon–carbon bond skeleton by ring expansion or contraction,^[12] while the formation of acyclic alkanes probably arises from the ring opening of the corresponding cyclic alkane (vide infra for mechanistic discussion) followed by the subsequent hydrogenolysis of the open alkane chains.^[8] In some cases, for example, methyl-substituted cycloalkanes (methylcyclopentane and methylcyclohexane), direct cleavage of the pendant methyl substituent is clear from the higher selectivity in methane compared to other acyclic alkanes (Figure 1 c, d).

We previously described the hydrogenolysis of acyclic alkanes in the presence of **1** and showed that successive

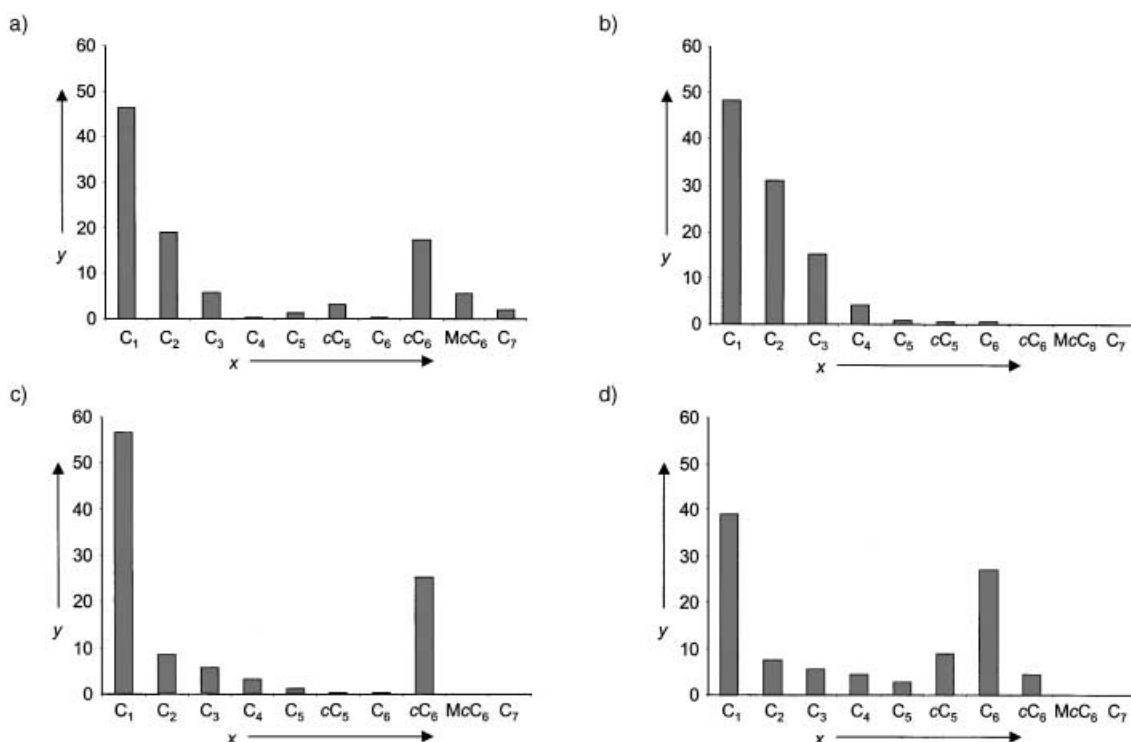


Figure 1. Product distribution (selectivities) after 50 h of reaction. a) cycloheptane, b) cyclohexane, c) methylcyclohexane and d) methylcyclopentane. x axis: products (C₁ = methane, C₂ = ethane, C₃ = propane, C₄ = butanes, C₅ = pentanes, cC₅ = cyclopentane, C₆ = hexanes, cC₆ = cyclohexane, McC₆ = methylcyclohexane and C₇ = heptanes. y = selectivity for cycloalkane [%].

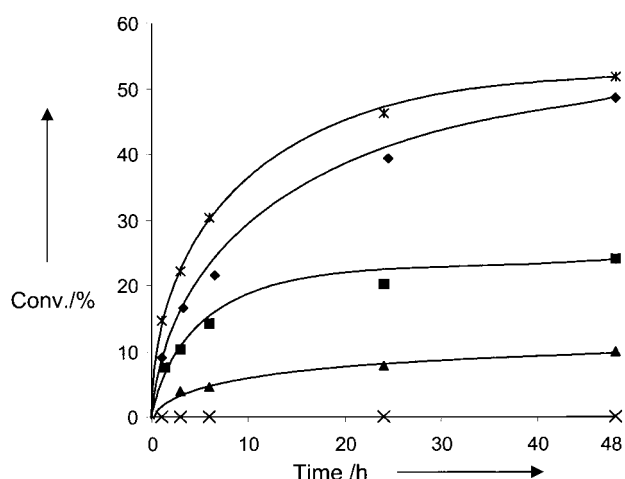


Figure 2. Conversion of cycloalkane as a function of time. Cycloheptane (*), methylcyclohexane (♦), cyclohexane (■), methylcyclopentane (▲), cyclopentane (×).

Table 1. Thermodynamic data for the hydrogenolysis of cycloalkanes.

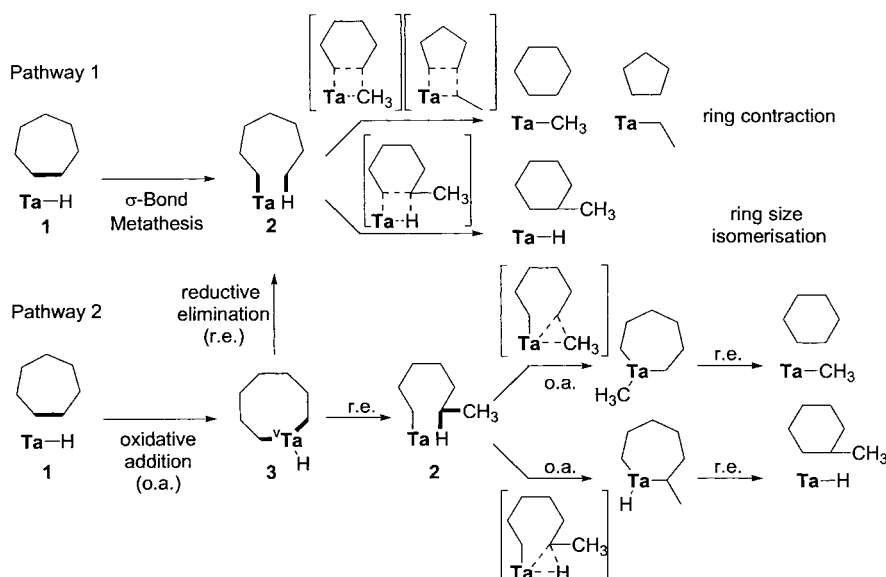
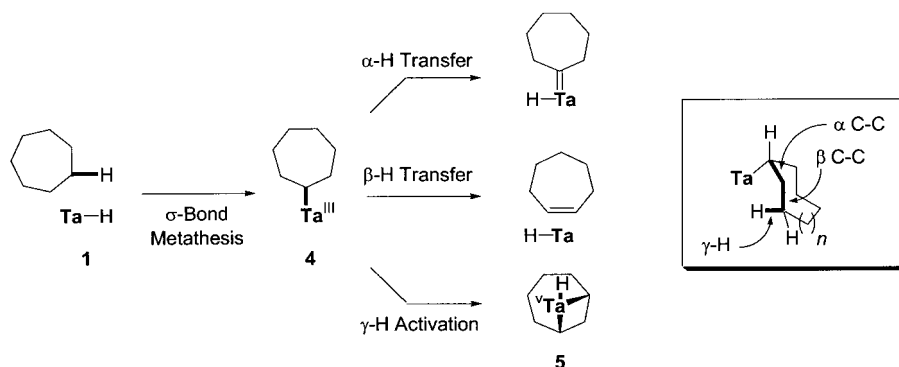
Entry	Reaction	ΔG_{450} [kcal mol ⁻¹]
1		-20.0
2		-8.7
3		-15.4
4		-11.6
5		-11.3
6		-12.2
7		-0.6
8		-6.2
9		-8.6

cleavage of one carbon atom at a time was preferred over a two-carbon cleavage process like a β -alkyl transfer.^[8] We have therefore proposed a mechanism for carbon-carbon bond cleavage based on a σ -bond metathesis mechanism (vide supra, Scheme 1), but also pointed out that **1**, a d² transition-metal complex, could also participate in oxidative pathways (e.g., direct oxidative addition^[13] and α -alkyl transfer (carbene de-insertion) processes).^[14, 15] In the case of cycloalkanes, more specifically cycloheptane, C-C bond activation by a σ -bond metathesis mechanism would lead to the formation of **2**, which could then undergo a series of intramolecular C-C or C-H bond activations by a similar σ -bond metathesis mechanism^[16] to form cyclohexane and methylcyclohexane, respectively (Scheme 2, Pathway 1). The formation of cyclopentane in the hydrogenolysis of cycloheptane could occur either by subsequent hydrogenolysis of cyclo-

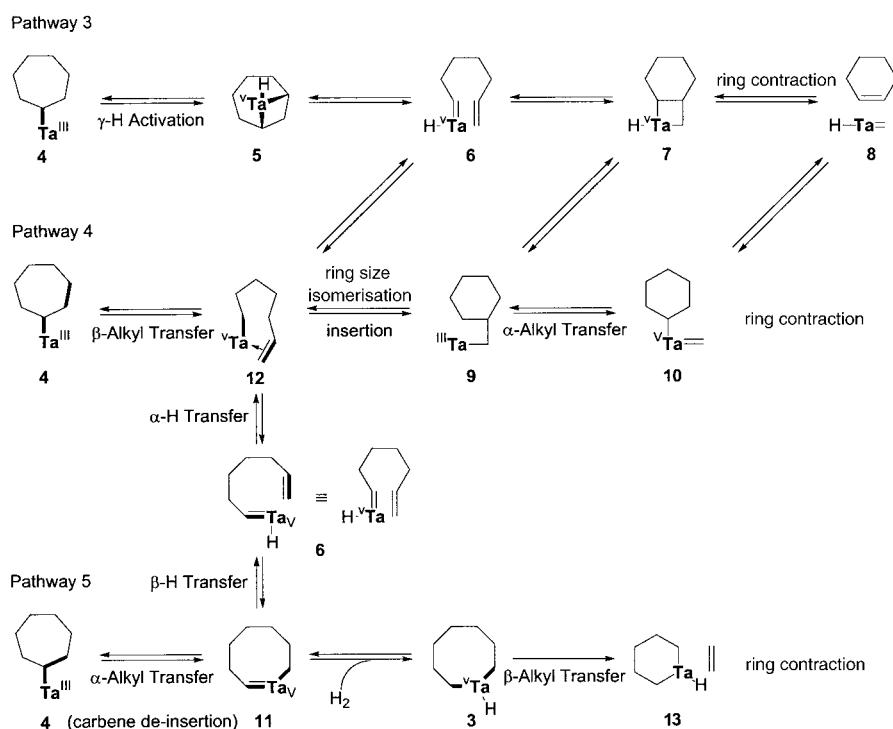
hexane or directly by cleavage of a terminal ethyl group in place of the methyl group in **2**. Direct oxidative addition of cycloalkane to **1** (Scheme 2, Pathway 2)^[13] could also take place and generate the surface intermediate **3**. This process can also explain the formation of acyclic alkanes, and the smaller cyclic alkanes would have to be formed via a route similar to that delineated for a σ -bond metathesis mechanism, but in which the steps would involve successive oxidative addition and reductive elimination. Note that the formation of cyclohexane and methylcyclohexane by intramolecular oxidative addition or σ -bond metathesis mechanisms in the intermediate **2** must involve the formation of metallacycloheptane intermediates or the corresponding transition states (activation of the C-H and C-C bonds in the ω position of **2**). The high selectivity for cyclohexane derivatives via these rather disfavoured pathways probably argues for an alternative mechanism.

Additionally, it is known that the activation of C-H bonds is often faster than that of C-C bonds, despite the lower bond energies of the latter.^[17] In fact the chemistry observed for silica-supported Group 4 metal hydrides shows exactly this principle; that is, β -alkyl transfer is the key step for carbon-carbon activation (intramolecular process), yet the first step, which is required for the carbon-carbon bond activation step, is in fact an intermolecular C-H bond activation by σ -bond metathesis. The C-H bond activation of cycloheptane on the surface complex **1** would give **4**. In fact this reaction has been shown to take place, and the corresponding cycloalkyl tantalum surface species characterised.^[4, 5] This surface complex can itself participate in various intramolecular C-C and C-H bond activations. Firstly, activation of a proton in the α , β or γ position in **4** (also called α - or β -H transfer and γ -H abstraction^[18]) generates alkylidene hydride,^[19] olefin hydride or metallacyclobutane^[20] (**5**) intermediates (Scheme 3). While the first two processes can be involved in H-scrambling reactions, they do not contribute to carbon-carbon activation. On the other hand, the latter generates a metallacyclobutane **5**, which is a key intermediate for carbon-carbon cleavage, for example, in olefin metathesis (Scheme 4, Pathway 3).^[20, 21] The formation of smaller cyclic products can readily be explained by a combination of rearrangements and hydrogenolysis of metallacyclobutanes as delineated in Scheme 4 (**6** \rightarrow **7** \rightarrow **8**, **7** \rightarrow **9** and **8** \rightarrow **10**).

Secondly, the intermediate **4** could also directly undergo intramolecular activation of a carbon-carbon bond in the α or in the β position (Scheme 4, Pathways 4 and 5). Pathway 5 corresponds to an α -alkyl transfer,^[14, 15] which gives an intermediate **11** that can readily transform into either intermediate **3** upon hydrogen addition or **12** via successive β -H and α -H transfer steps. While the former pathway (via **3**) could potentially account for the two-carbon ring-contraction product (cyclopentane) or smaller linear products (pentane) via a β -alkyl transfer (Scheme 4: **3** \rightarrow **13**),^[22] it cannot readily explain the formation of one-carbon ring-contraction products. On the other hand, the conversion of **11** to **6** and/or **12** by simple hydrogen-transfer processes does allow the formation of all the products to be explained. Carbon-carbon activation in the β position in intermediate **4** (Pathway 4) can be regarded as a β -alkyl transfer,^[23] depending on whether one

Scheme 2. σ -Bond metathesis versus oxidative addition pathway: intermolecular C–C bond activation.

Scheme 3. Intramolecular C–H bond activation.



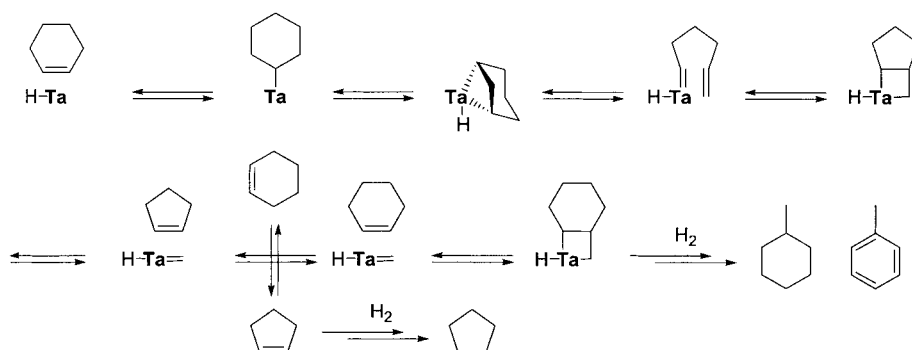
Scheme 4. Intramolecular C–C bond activation.

considers that the oxidation state of the metal centre has changed or not (metallacyclopentane versus π -olefin complex). This pathway gives ω -alkenyl complexes like **12**, which can readily undergo insertion to give **9**, either directly or via **6**, and hence leads to the formation of smaller ring systems (cyclohexane or methylcyclopentane). Note that most intermediates (**5**, **11** and **12**) can readily fall into one or another carbon–carbon activation manifold, since α - and β -H transfer processes are very common for Group 5 transition metals.^[19]

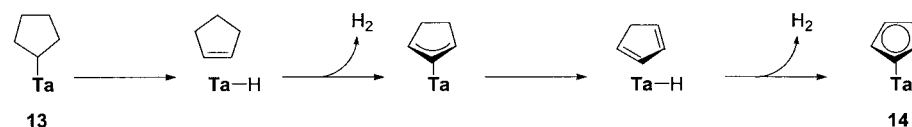
In the case of the hydrogenolysis of Group 4 metal hydrides, the ring contraction was best explained by a β -alkyl transfer mechanism—like for acyclic alkanes—and was very dependent on the alkane ring size (cycloheptane > cyclohexane (no reaction)).^[9b] This was readily explained by the necessity for the metal–carbon and carbon–carbon bonds to be in a *syn*-coplanar arrangement to undergo a β -alkyl transfer and thereby carbon–carbon cleavage. In the case of **1**, a similar trend in ring size dependence was also observed (vide supra), yet cyclohexane undergoes hydrogenolysis, which is not observed with Group 4 metal hydrides. This, along with the formation of one-carbon ring-contraction products, speaks for a mechanistic difference between Group 4 metal hydrides and **1**. While it is difficult to point to a specific mechanism in this system, it seems that metallacyclobutane and carbene intermediates are more likely than σ -bond metathesis or direct oxidative addition, since they both involve transition states with seven-membered rings.

To probe this mechanism the reaction of cyclohexene with **1** was also investigated. At 150 °C, in the absence of H₂,

cyclohexene is mainly transformed into cyclohexane (2.8 equiv), cyclohexadiene (0.001 equiv) and benzene (0.6 equiv) in a disproportionation reaction.^[24] Moreover cyclopentane (0.1 equiv), cyclopentadiene (0.02 equiv), toluene (0.01 equiv) and methylcyclohexane (0.01 equiv) are also observed. Despite their presence in small amounts, their formation is consistent with ring-opening/ring-closing metathesis pathways in which cyclohexene is transformed into cyclopentene and methylcyclohexene, which under the reaction conditions are transformed into cyclopentane, cyclopentadiene, methylcyclohexane and toluene (Scheme 5). This speaks in favour of metallacyclobutane/carbene mechanism, which is to be related to that found on metallic surfaces, for which carbene de-insertion was proposed to be a key step in carbon–carbon bond cleavage.^[1]



Scheme 5. Proposed pathway for the reaction of cyclohexene with **1**.



Scheme 6. Intramolecular dehydrogenation of a cyclopentyl ligand to give a Cp ligand.

Besides these mechanistic intricacies, the lack of reactivity of cyclopentane towards **1** in the presence of H₂ is still puzzling, and its reactivity towards **1** has been investigated in more details in the hope of understanding this difference in reactivity compared to higher cycloalkanes.

Activation of cyclopentane: The activation of cycloalkanes at low temperatures (<80 °C) has already been studied, and it was reported that this reaction yielded the corresponding cycloalkyl complex (**4** in the case of cycloheptane) with the formation of H₂ (ca. 1 equiv).^[4, 5] Nonetheless, their stability at higher temperatures, that is, those of hydrogenolysis (160 °C), has not been investigated. Therefore, the stability of the cyclopentyl derivative **13** was further studied (Scheme 6), first by using in situ IR spectroscopy (see Supporting Information). Reaction of cyclopentane with **1** at room temperature is slow and is not complete, since a residual band (55 %) at 1820 cm⁻¹ associated with Ta–H remains unchanged. At 80 °C this IR band has disappeared to the extent of 75 %. Heating this species further under static vacuum leads to changes in the IR bands associated with ν(C–H) such as the appearance of

bands above 3000 cm⁻¹ in agreement with the formation of C_{sp³}–H fragments. To gain further insight, this reaction was also monitored by solid-state NMR spectroscopy by treating ¹³C-labelled cyclopentane with **1** at various temperatures. The solid-state ¹³C NMR spectrum is indeed consistent with the formation of **13** as a major surface species, since the signals are typical of those of cyclopentyl derivatives (Figure 3b).^[25] On the other hand, the ¹H NMR spectrum displays a peak at δ = 6.3 ppm, in agreement with the formation of small amounts of unsaturated hydrocarbyl species (Figure 3a). Heating the putative **13** at 150, 200 or 250 °C for 12 h gives rise to the evolution of H₂ (1–2 equiv/Ta). It also leads to an increase of the proportion of the signal at δ = 6.3 ppm in the solid-state ¹H NMR spectrum (Figure 3a, c, e and g). At 250 °C this signal predominates, and most of the signal at δ = 0.8 ppm has disappeared. At the same time, the signal at δ = 27 ppm in the ¹³C NMR spectrum has almost vanished (Figure 3h). These data are most consistent with the transformation of **13** into the cyclopentadienyl derivative [(≡SiO)₂TaCp] (**14**).^[26] Elemental analyses of these surface complexes gave 5–6 carbon atoms per Ta center, independent of the temperature of treatment (>80 °C), which is consistent with the presence of mainly a C₅ compound/Ta. Hydrolysis gave only a small amount of CpH (0.01 equiv/Ta; the reaction was probably not quantitative due to the reluctance of Cp complexes to undergo hydrolysis). All the data are in agreement with the formation of [(≡SiO)₂TaCp] (**14**). More-

over, EXAFS on samples treated at room temperature and at 200 °C confirms the evolution of the surface species from [(≡SiO)₂Ta–C₅H₉] (**13**), a major species at room temperature, into [(≡SiO)₂TaCp] (**14**) at higher temperatures. EXAFS on the sample prepared at room temperature is most consistent with about two oxygen neighbours located at 1.91 Å along with one carbon atom per Ta center at 2.03 Å^[27, 28] (Figure 4). For the sample treated at higher temperatures (e.g., 200 °C), EXAFS is consistent with a tantalum atom surrounded by an average of 4.6 neighbouring carbon atoms at 2.42 Å (Cp) along with about two oxygen atoms at 1.94 Å (Figure 5).^[27] These data are again fully consistent with 1) the formation of **13** from the activation of cyclopentane on **1**, and 2) its evolution towards cyclopentadienyl derivative **14** at higher temperatures. The NMR data also show that the proportion of Cp derivatives increases with the reaction temperature, which would speak for tantalum sites with different reactivities.

The formation of cyclopentadienyl surface complexes from cyclopentyl derivatives leads to the presence of less electrophilic surface complexes (12- versus 8-electron complexes if oxygen atoms are considered to be pure σ-donor

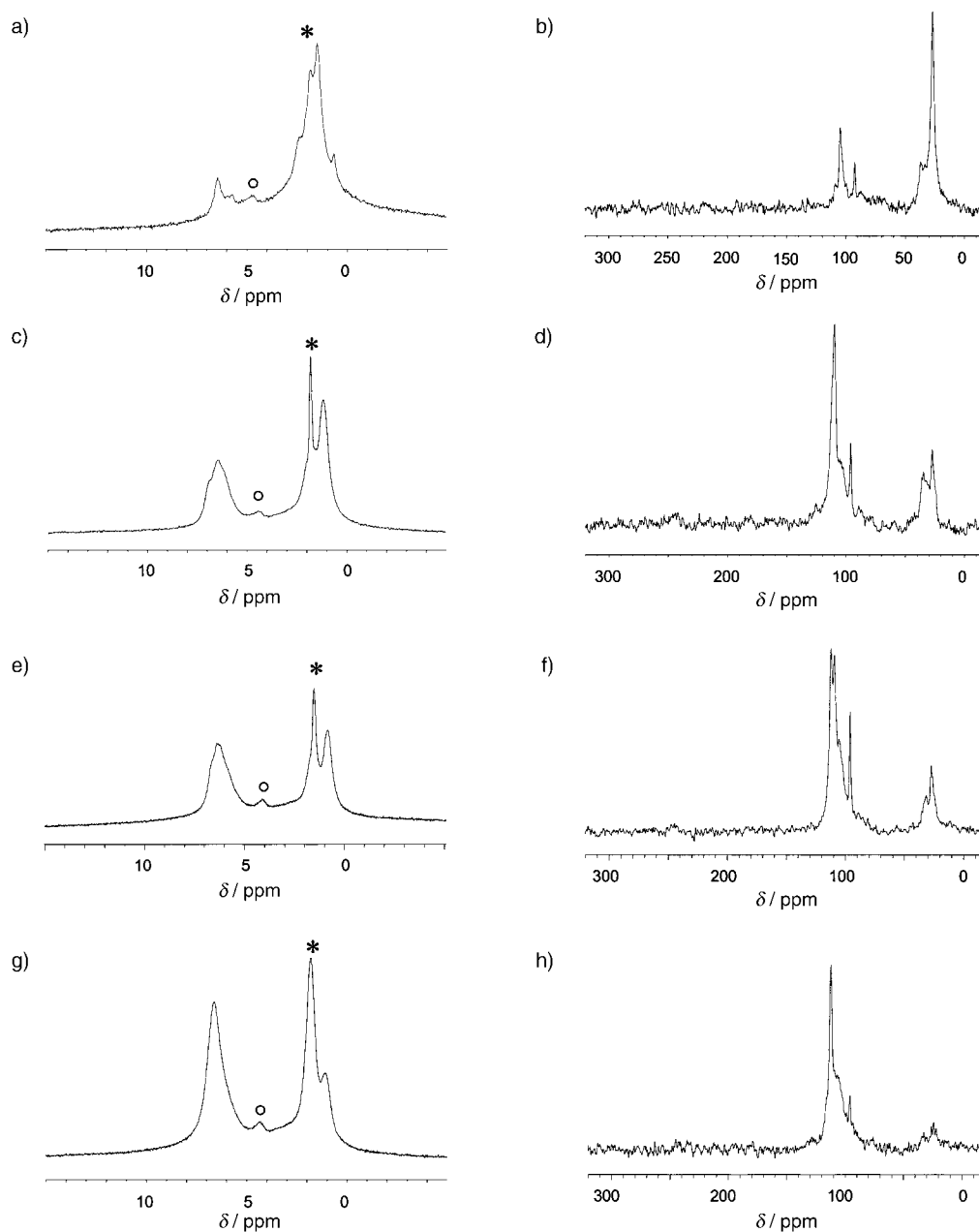


Figure 3. Solid-state NMR spectrum of **1** after reaction with ^{13}C -labelled cyclopentane at various temperatures. 25 °C: a) ^1H MAS NMR ($l_b = 1$ Hz); b) ^{13}C CP/MAS NMR ($l_b = 50$ Hz). 150 °C: c) ^1H MAS NMR ($l_b = 1$ Hz); d) ^{13}C CP/MAS NMR ($l_b = 50$ Hz). 200 °C: e) ^1H MAS NMR ($l_b = 1$ Hz); f) ^{13}C CP/MAS NMR ($l_b = 50$ Hz). 250 °C: g) ^1H MAS NMR ($l_b = 1$ Hz); h) ^{13}C CP/MAS NMR ($l_b = 50$ Hz). * = (SiOH); o = (SiH).

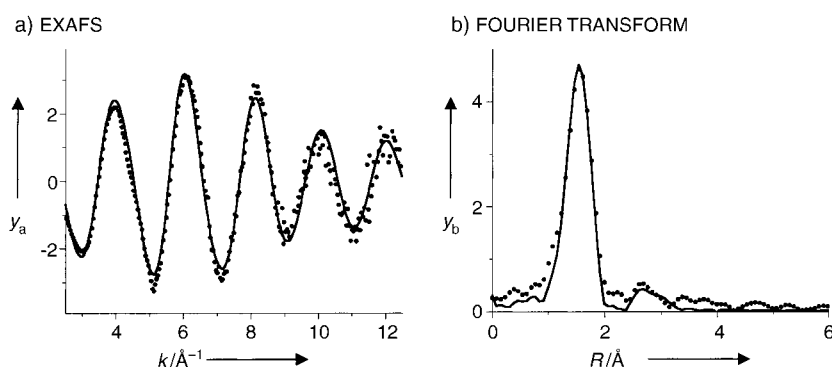


Figure 4. EXAFS of **1** after reaction with cyclopentane at 25 °C. Experimental (\bullet), simulated (—). $y_a = k^3\chi(k)$. $y_b = |F(R)|$. $\rho = 5.6\%$, $d_{\text{Ta-O}} = 0.1909$ nm ($N_{\text{O}} = 1.9 - \sigma = 0.057$), $d_{\text{Ta-C}} = 0.2028$ nm ($N_{\text{C}} = 1.0 - \sigma = 0.058$), $d_{\text{Ta-Si}} = 0.330$ nm ($N_{\text{Si}} = 2.0 - \sigma = 0.144$).

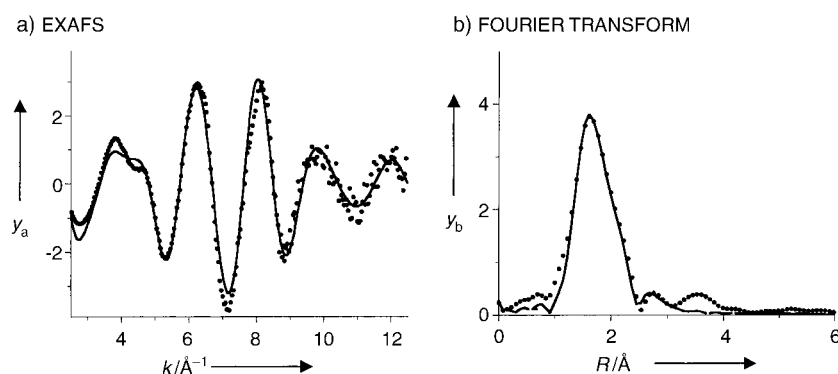


Figure 5. EXAFS of **1** after reaction with cyclopentane at 200 °C. Experimental (●), simulated (—). $y_a = k^3\chi(k)$. $y_b = |F(R)|$. $\rho = 4.7\%$, $d_{\text{Ta-O}} = 0.1941$ nm ($N_{\text{O}} = 2.4 - \sigma = 0.072$), $d_{\text{Ta-C}} = 0.2416$ nm ($N_{\text{C}} = 4.6 - \sigma = 0.089$), $d_{\text{Ta-Si}} = 0.334$ nm ($N_{\text{Si}} = 2.0 - \sigma = 0.173$).

ligands). In fact these species do not catalyse the hydrogenolysis of acyclic alkanes. Since cycloalkanes generate cyclopentane during their hydrogenolysis, it is therefore possible that the corresponding cyclopentyl derivatives formed will be transformed into cyclopentadienyl surface complexes, which are inactive. Thus, the hydrogenolysis of cyclic alkanes generates its own poison (cyclopentane), which explains the fast deactivation and the low conversion in these cases, in contrast to what has been observed for acyclic alkanes.^[8] Solid-state ^1H NMR spectra of a catalyst after its use in the hydrogenolysis of cyclohexane at 160 °C do indeed display similar spectral feature (i.e., typical signals at $\delta = 6\text{--}7$ ppm of the cyclopentadienyl tantalum species, see Supporting Information) as that of **1** treated with cyclopentane under the same conditions, even in the presence of H_2 , which further confirms that the active sites have been transformed into inactive cyclopentadienyl derivatives, formation of which corresponds to the deactivation pathway.

Conclusion

We have shown that cycloalkanes undergo hydrogenolysis under mild conditions, albeit with low turnovers; the activities are much lower than those obtained with acyclic alkanes. A key feature is the ring contraction of cycloalkanes under hydrogenolysis conditions, which probably occurs via carbene intermediates (carbene de-insertion/metallacyclobutane). The order of reactivity of cycloalkanes is as follows: cycloheptane > methylcyclohexane > cyclohexane > methylcyclopentane \gg cyclopentane. Cyclopentane does not undergo hydrogenolysis, while it readily reacts with **1** to give a cyclopentyl surface complex as a major surface species. This cyclopentyl derivative evolves upon heating towards the cyclopentadienyl derivative **15**, which is inactive in the hydrogenolysis of cyclic or acyclic alkanes. This species has been characterized by the combined use of chemical analysis, 1D NMR and EXAFS spectroscopies. Since cyclopentane is formed in the hydrogenolysis of higher cycloalkanes, cyclopentane is transformed into cyclopentadienyl species (which are inactive in the hydrogenolysis of alkanes) and the hydrogenolysis of cycloalkanes on **1** provides an aged catalyst with similar spectroscopic features to that of the model

cyclopentadienyl surface complex **14**, we propose that the deactivation observed in the hydrogenolysis of all cycloalkanes is most consistent with the formation of cyclopentadienyl derivatives as inactive species under hydrogenolysis conditions.

Experimental Section

Preparation of **1** was carried out according to the literature procedure.^[4] Gaseous alkanes and H_2 were dried over freshly regenerated molecular sieves (3 Å) and deoxo traps before addition. Liquid alkanes were dried on sodium and degassed. All reactions were carried out with the same batch of catalyst in the strict absence of oxygen and water.

Solid-state NMR spectroscopy: 1D MAS ^1H and ^{13}C CP/MAS solid-state NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 and 75 MHz for ^1H and ^{13}C , respectively. The samples were introduced under Ar in a zirconia rotor, which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz. Chemical shifts are given with respect to TMS as an external standard, with a precision of 0.2–0.3 and 1 ppm for ^1H and ^{13}C NMR, respectively. For CP/MAS ^{13}C NMR, the following sequence was used: 90° pulse on the protons (impulsion length 3.8 μs), then a cross-polarization step with a contact time typically set to 5 or 10 ms and finally recording of the ^{13}C signal under high-power proton decoupling. The delay between each scan was set to 1 s. For ^1H and CP/MAS ^{13}C NMR spectra, apodisation functions (exponential) corresponding to line broadenings (lb) of 1 and 50 Hz were applied, respectively.

EXAFS spectroscopy: X-ray absorption spectra were recorded at LURE (Orsay, France) on the DCI storage ring (1.85 GeV positrons, with an average current of ca. 300 mA). They were collected in the transmission mode at the tantalum L_{III} edge, from 9700 to 11000 eV. EXAFS analysis was performed with software written by Michalowicz.^[29] The background absorption μ_0 was calculated by using a theoretical expression developed by Lengeler and Eisenberger,^[30] and the single atomic absorption of the absorber μ_i was interpolated by a sixth-degree polynomial. The pseudoradial distribution $|F(R)|$ was obtained by Fourier transformation of the weighted $\omega(k)k^3\chi(k)$ spectrum, where k is the intensity of the photoelectron wave vector, $\chi(k) = [(\mu - \mu_i)/(\mu_1 - \mu_0)]$ is the oscillatory part of the absorption coefficient normalised to the structureless (atomic-like) background ($\mu_1 - \mu_0$) and $\omega(k)$ is a window using a Kaiser function defined between 2.5 and 12.5 \AA^{-1} . The best removal of low-frequency noise was checked by this Fourier transformation. Fits were carried out by using FEFF 7 theoretical phase and amplitude files.^[31] The structural parameters which were fitted are the number of neighbours around the tantalum atom N , the tantalum–neighbour distance R and the Debye–Waller factor σ , accounting for both thermal and structural disorders. The fit residue ρ is calculated by Equation (1), where $\chi_{\text{exptl}}(k)$ and $\chi_{\text{calcd}}(k)$ designate respectively the experimental and simulated oscillatory parts of the absorption coefficient.

$$\rho = \frac{\sum_k [k^3\chi_{\text{exptl}}(k) - k^3\chi_{\text{calcd}}(k)]^2}{\sum_k [k^3\chi_{\text{exptl}}(k)]^2} \quad (1)$$

Hydrogenolysis of cycloalkanes: The catalyst **1** (135 mg, 31.7×10^{-6} mol of Ta, 1 equiv) was weighed and loaded into a Pyrex batch reactor (440 mL) in a glove box. After evacuation of the reactor, the cycloalkane (19 Torr, 14.5 equiv) followed by H_2 (470 Torr, 360 equiv) were introduced, and the reaction mixture was heated with an oil bath at 160 ± 1 °C. During the reaction, aliquots were expanded in a small volume, brought to atmospheric pressure and analysed by gas chromatography to follow the evolution of lighter compounds quantitatively (methane to butanes) and

heavier compounds only qualitatively (HP 5890 apparatus, Al₂O₃/KCl on fused silica column, 50 m × 0.32 mm). At the end of the reaction, 2 mL of a 1 M solution of internal standard (2,2-dimethylpentane) in octane was added to the reaction mixture, and the composition of heavier compounds (> butanes) was determined by GC analysis (mass balance was found to be 100, 92, 87 and 81 % for cycloheptane, methylcyclohexane, cyclohexane and methylcyclopentane, respectively). All the compounds were identified by GC/MS. Selectivities *S_i* were calculated as the amount of product *i* divided by the sum of the amounts of products.

Activation at room temperature: The surface complex **1** (68 mg, 18.8 × 10⁻⁶ mol of Ta, 1 equiv) was loaded into a glove box in a Pyrex reactor and then contacted at room temperature with cyclopentane vapour. After 3 h the reactor was evacuated at this temperature for 60 min, and the solid was loaded into an NMR rotor in a glove box.

Activation of cyclopentane at other temperatures: The same procedure as described above was performed, but after addition of cyclopentane at room temperature the reactor was heated at the desired temperature for 12 h, evacuated at 150 °C under vacuum for 10 min, and the solid loaded into the NMR rotor for NMR analysis.

Reaction of cyclohexene with **1:** The surface complex **1** (68 mg, 18.8 × 10⁻⁶ mol of Ta, 1 equiv) was loaded into a glove box in a Pyrex reactor and then contacted at room temperature with cyclohexene vapor (20 equiv). After 12 h an aliquot was expanded in a small volume, brought to atmospheric pressure and analyzed by GC and GC/MS.

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