Activation and Functionalisation of the C–H Bonds of Methane and Higher Alkanes by a Silica-supported Tantalum Hydride Complex

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Silica-supported tantalum hydride activates at low temperature the C–H and the C–D bonds of cyclooctane and CD_4, respectively, to form the corresponding cyclooctyl and perdeuteriomethyl-tantalum surface complexes; these complexes are transformed under molecular oxygen into the corresponding tantalum-alkoxy derivatives which with acetic acid give rise to the corresponding alkylacetates.

The valorisation of methane and higher alkanes still constitutes a major scientific challenge. In the field of classical organometallic chemistry, numerous complexes of transition metals of Groups 3–5, lanthanides and actinides have been reported to activate the C–H bond of methane, higher alkanes and aromatics.[1] These highly electrophilic complexes with a d^0 configuration are commonly believed to activate the C–H bond of alkanes by a σ-bond metathesis mechanism.[1e,2,3] Recently, we have reported that, in the field of surface organometallic chemistry, a silica-supported zirconium hydride, very likely $(\equiv SiO)_3Zr–H$ with a d^0 configuration, was able to activate stoichiometrically the C–H bond of alkanes or methane, at 25 and 120 °C, respectively, to form the corresponding zirconium-alkyls.[4,5] The same grafted complex as well as its hafnium analogue was also found to catalyse the low temperature hydrogenolysis of several alkanes such as propane, *n*-butane, isobutane or neopentane.[5,6,7] The unexpected high activity of these surface organometallic fragments in catalytic conditions which usually require much higher temperatures in classical heterogeneous catalysis, has been ascribed to the high electrophilic character of these metals which are formally eight electron species, associated with the immobilisation and isolation of the zirconium centres which prevent dimerisation or more generally deactivation.

We have therefore tried to see if other silica-supported early transition metal hydrides could lead to similar types of C–H bond activation, one of the objectives being a possible functionalisation after activation. We report here that a silica-supported tantalum-hydride is also able to activate cyclooctane and methane to form the corresponding tantalum-alkyl surface species. We also demonstrate that these surface tantalum-alkyls can be transformed under molecular oxygen into the corresponding tantalum-alkoxy derivatives which with acetic acid gives the corresponding alkylacetates.

We have recently reported that the reaction of the trisneopentyl(neopentylidene)tantalum complex $Ta(–CH_2–CMe_3)_3(=CH–CMe_3)$[8] **1** with the silanol groups of a silica previously dehydroxylated at 500 °C ($silica_{500}$), leads to the formation of two surface species: $\equiv SiO–Ta(–CH_2–CMe_3)_2(=CH–CMe_3)$ **2a** (*ca.* 65%) and $(\equiv SiO)_2Ta(–CH_2–CMe_3)(=CH–CMe_3)$ **2b** (*ca.* 35%), with liberation of neopentane.† These two grafted complexes have been characterized by elemental analysis, chemical reactivity with D_2O and acetone (pseudo-Wittig reaction) and by FT-IR and ^{13}C CP-MAS NMR spectroscopies.[9]

When **2a** and **2b** are treated under hydrogen (1 atm; 150 °C for 15 h), supported tantalum-hydride $[Ta]_s–H$ **3** is formed, characterized by an IR band at ν 1830 and shoulders at 1815 and 1855 cm^{-1} [Fig. 1(*a*)]. Simultaneously, neopentane is evolved in the gas phase as well as methane, ethane, propane and isobutane resulting either from a partial hydrogenolysis of the neopentyl or neopentylidene ligands or more likely from the hydrogenolysis of the neopentane released during the hydrogenolysis of these hydrocarbyl ligands.

Complex **3** exchanges reversibly with deuterium at room temperature as evidenced by the reversible shift under D_2 and then H_2 of the three IR bands at 1815, 1830 and 1855 cm^{-1}. Complex **3** reacts with water to liberate hydrogen and with MeI to form CH_4. Although full characterization of **3** is still in progress, it seems that an eight electron Ta^{III} monohydride $(\equiv SiO)_2Ta(H)$ linked to the silica surface by two siloxy fragments is the major (if not unique) component.‡

Complex **3** reacts spontaneously at room temperature with a vapour of cyclooctane (5 torr) to form a tantalum-cyclooctyl surface complex **4** [eqn. (1)]. Evidence for reaction (1) is as

$$[Ta]_S–H + cyclo\text{-}C_8H_{16} \rightarrow [Ta]_S–cyclo\text{-}C_8H_{15} + H_2 \quad (1)$$

follows: (*a*) after gas phase evacuation, IR bands at 2929, 2857 [$\nu(CH_2)$] and 1477, 1468, 1448 cm^{-1} [$\delta(CH_2)$] characteristic of methylene groups appear on the silica disc [Fig. 1(*b*)]; these bands are resistant to prolonged evacuation at room temp. under which conditions physisorbed cyclooctane is removed (independent experiment). Simultaneously, the intensity of the IR bands at 1815, 1830 and 1855 cm^{-1} decreases; (*b*) the reaction produces molecular hydrogen as evidenced by GC; (*c*) introduction of water vapour on the surface complex **4**, resulting from the reaction of **3** with cyclooctane, liberates cyclooctane and the IR bands corresponding to $\nu(CH_2)$, and $\delta(CH_2)$ vibration modes disappear [Fig. 1(*c*)]; (*d*) after introduction of dry oxygen (200 torr; 25 °C) on the presumed tantalum-cyclooctyl species **4**, a new surface complex is formed which is resistant to hydrolysis; further introduction of a vapour of acetic acid (15 torr) liberates cyclooctyl-acetate as a major product; this demonstrates that oxygen has been inserted into the Ta–C bond, probably *via* a peroxo intermediate as known in molecular chemistry,[10] to form

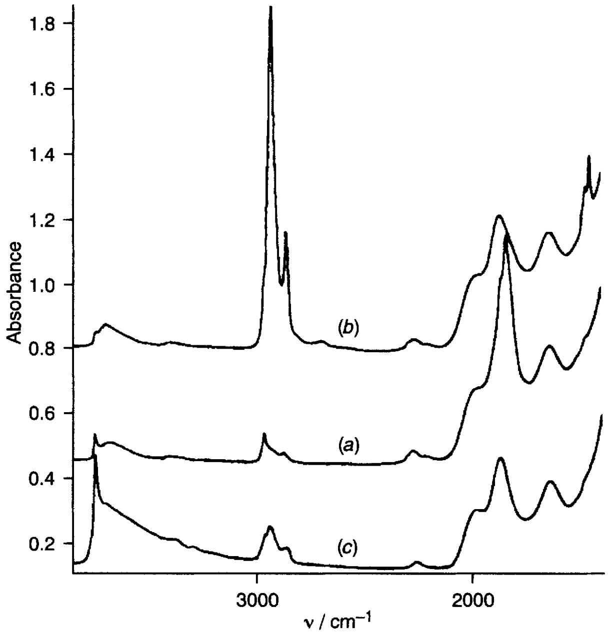
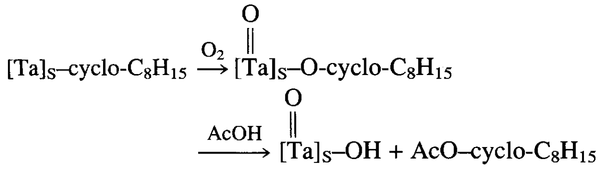


Fig. 1 IR spectra of (*a*) the silica-supported tantalum hydride complex **3**, (*b*) the cyclooctyl-tantalum complex **4** formed by reaction of **3** with cyclooctane, (*c*) the complex **4** after reaction with water

a cyclooctyloxy-tantalum and presumably a tantalum oxo species [eqn. (2)]. The presence of an oxo ligand is further



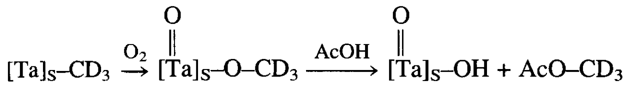
$$[\mathrm{Ta}]_S\text{–cyclo-}C_8H_{15} \xrightarrow{O_2} \overset{O}{\overset{\|}{[\mathrm{Ta}]}}_S\text{–O-cyclo-}C_8H_{15} \xrightarrow{AcOH} \overset{O}{\overset{\|}{[\mathrm{Ta}]}}_S\text{–OH} + \text{AcO–cyclo-}C_8H_{15} \quad (2)$$

supported by its reaction with Bu^tNCO which affords the evolution of CO_2 and an expected supported imido-tantalum complex,[11] the elementary analysis of which gives a 0.97 N : Ta ratio.

Complex **3** also reacts with CD_4 at 100–150 °C to form a tantalum-perdeuteriomethyl species [eqn. (3)]. Evidence for

$$[\mathrm{Ta}]_S\text{–H} + CD_4 \rightarrow [\mathrm{Ta}]_S\text{–}CD_3 + HD \quad (3)$$

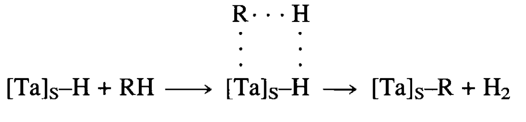
this activation is the introduction of CD_4 on **3** which results in the disappearance of the hydride bands at 1815, 1830 and 1855 cm^{-1}. Simultaneously the IR spectrum of this species shows a band of small intensity at 2251 cm^{-1}, characteristic of a CD_3 species. Subsequent treatment with dry oxygen and then with acetic acid leads to the formation of $MeCOOCD_3$ characterized by GC–MS. The following reaction sequence is therefore implied [eqn. (4)].



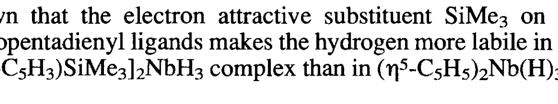
$$[\mathrm{Ta}]_S\text{–}CD_3 \xrightarrow{O_2} \overset{O}{\overset{\|}{[\mathrm{Ta}]}}_S\text{–O–}CD_3 \xrightarrow{AcOH} \overset{O}{\overset{\|}{[\mathrm{Ta}]}}_S\text{–OH} + \text{AcO–}CD_3 \quad (4)$$

To our knowledge, this is the first example of an intermolecular alkane activation on a supported tantalum hydride. Photolytic or thermal reaction of benzene with $(\eta^5\text{-}C_5H_5)Ta(Me)(PMe_3)$ has already been reported;[12] an oxidative addition of benzene was assumed but the presence of $(Bu^t)_2SiH_2$ proved to be necessary; the role of the silane was to favour the liberation of methane before the activation of benzene; $(Bu^t)_2SiH_2$ also induced the exchange of the phenyl group with C_6D_6 on the obtained complex. Thermal or photochemical reaction of $(\eta^5\text{-}C_5H_5)_2Ta(H)_3$ with hydrosilanes R_3SiH has also been reported.[13,14] In the case of $PhMe_2SiH$ only the symmetrical adduct $(\eta^5\text{-}C_5H_5)Ta(H)SiMe_2Ph(H)$ supported by an X-ray structure determination was obtained;[13] the other isomers $(\eta^5\text{-}C_5H_5)Ta(H)_2(SiR_3)$ with the silyl group in the lateral position were also observed as minor components in the case of SiH_4, $MeSiH_3$, Me_2SiH_2, Me_3SiH, Me_2SiHCl or $(MeO)_3SiH$.[14] In both case, hydrogen was assumed to be released before the oxidative addition of the silane.

This kind of mechanism differs from that which is usually mentioned in the case of early transition metals, lanthanides or actinides, for which a σ-bond metathesis process is invoked.[1e,2,3] In the present case of supported tantalum-hydride $[\mathrm{Ta}]_S\text{–H}$ **3**, it may be attractive to propose a σ-bond metathesis mechanism since no hydride is left on the surface after alkane activation [eqn. (5)]. However, we cannot yet exclude an oxidative addition of the C–H bond of alkanes on a tantalum(III) surface species followed by an elimination of hydrogen [eqn. (6)]. Some results in the case of niobium have shown that the electron attractive substituent $SiMe_3$ on the cyclopentadienyl ligands makes the hydrogen more labile in the $[(\eta^5\text{-}C_5H_3)SiMe_3]_2NbH_3$ complex than in $(\eta^5\text{-}C_5H_5)_2Nb(H)_3$.[15]



$$[\mathrm{Ta}]_S\text{–H} + RH \longrightarrow \begin{array}{c} R\cdots H \\ \vdots \quad \vdots \\ [\mathrm{Ta}]_S\text{–H} \end{array} \longrightarrow [\mathrm{Ta}]_S\text{–R} + H_2 \quad (5)$$



$$[\mathrm{Ta}]_S\text{–H} + RH \longrightarrow \begin{array}{l} \quad /R \\ [\mathrm{Ta}]_S\text{–H} \\ \quad \backslash H \end{array} \longrightarrow [\mathrm{Ta}]_S\text{–R} + H_2 \quad (6)$$

In the same way, the presence of siloxy ligands coordinated to tantalum instead of the cyclopentadienyl ligands should make the metal far more electrophilic and may favour the departure of hydrogen.

Moreover, the present supported tantalum-hydride $[\mathrm{Ta}]_S\text{–H}$ **3** proves to be far more active towards C–H bond activation than the corresponding molecular complexes; indeed, complex **3** reacts spontaneously at room temperature with cyclooctane whereas irradiation or heating to 100 °C are required to form the corresponding molecular Ta-alkyl or -silyl complexes. This is probably due to the direct grafting of tantalum on silica which results (*a*) in the formation of ≡Si–O–Ta bonds which will make the tantalum very electrophilic, (*b*) in the isolation of the metallic centres and (*c*) in the stabilisation of highly co-ordinatively unsaturated species, all parameters which are difficult to govern in solution.

The subsequent oxidation step illustrates the possibility of selectively introducing an oxygen atom into the alkane molecule.

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Footnotes

† $[Ta(\text{–}CH_2\text{–}CMe_3)_3(\text{=}CH\text{–}CMe_3)]$ was prepared according to a published procedure;[8] it was sublimed under vacuum (80 °C, 10^{-4} torr) on freshly dehydroxylated (500 °C, 15 h, 10^{-4} torr) silica (Aerosil Degussa, 200 $m^2\ g^{-1}$) according to break and seal techniques; unreacted complex was removed by evacuation at the same temperature. The solid samples thus obtained were *ca.* 5 mass% Ta. All further reactants were carefully dried over freshly regenerated molecular sieves and when necessary deoxygenated over deoxo traps. The IR spectra were recorded from a glass cell with CaF_2 windows, on a FT-IR Nicolet 550 spectrometer. Gas phases were analysed by GC.

‡ The full characterization of complex **3** will be published elsewhere.

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