Alkane Activation by a Highly Electrophilic Zirconium Hydride Complex Supported on Silica

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The silica-grafted zirconium hydride complex, synthesized by hydrogenolysis of the well-defined $\equiv$SiOZrNp$_3$, activates the C–H bonds of cyclooctane and methane as shown by the formation of the corresponding cyclooctyl- and methyl-zirconium complexes.

A great deal of interest is shown today in the activation of methane and higher alkanes. A number of complexes of transition metals of group III–V, lanthanides and actinides have recently been reported to activate the C–H bond of alkanes and aromatic hydrocarbons.[1] A common feature of these complexes is that the metal is in its highest oxidation state; it therefore, has a d^0 electron configuration and is consequently highly electrophilic. The first example of an intermolecular alkane activation reaction is the methyl exchange with methane in a lutetium complex, Scheme 1.[2]

We report here that a zirconium hydride complex, grafted onto the surface of silica, acquires such high electrophilic properties, that the reaction of σ-bond metathesis between the Zr hydride and the C–H bonds of cyclooctane and methane becomes feasible.

$$\mathrm{Cp'_2LuCH_3 + {}^{13}CH_4 \rightarrow Cp'_2Lu^{13}CH_3 + CH_4}$$

Scheme 1

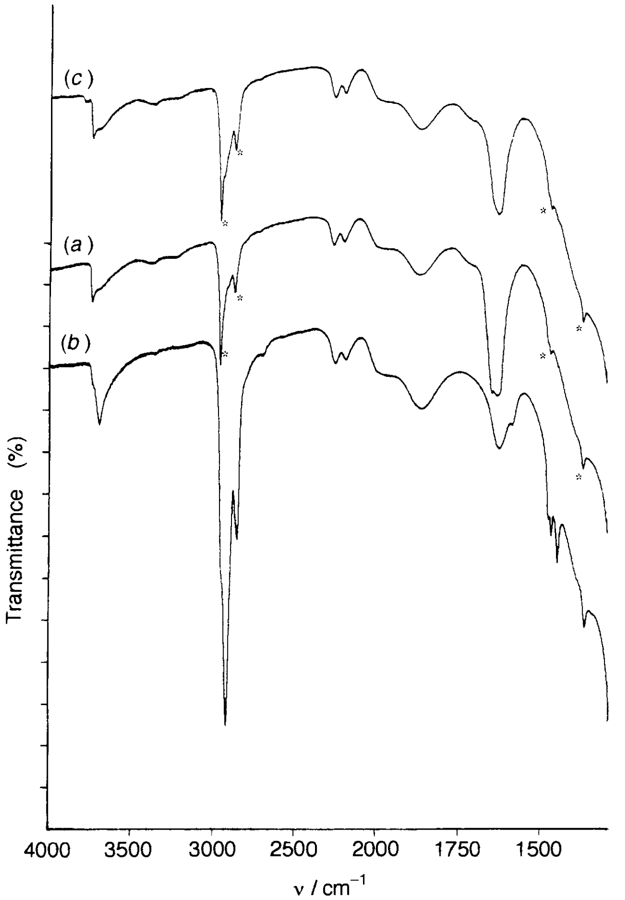

Fig. 1 IR spectra of: (*a*) $(\equiv$SiO)ZrNp$_3$ after reaction with H_2 (6 × 10^4 Pa, 423 K), followed by evacuation at room temperature; (*b*) (*a*) after reaction with cyclooctane (2.7 Pa, 298 K), followed by evacuation; (*c*) (*b*) after reaction with H_2 (6 × 10^4 Pa, 423 K). * Bands corresponding to neopentoxy ligands, formed by trace amounts of O_2.

Reaction of tetraneopentylzirconium, ZrNp$_4$, with the surface of a silica, previously dehydroxylated at 773 K, leads to a well-defined[3] surface complex, $\equiv$SiOZrNp$_3$, **1**, eqn. (1).

$$\mathrm{ZrNp_4 + {\equiv}SiO{-}H \rightarrow \underset{\mathbf{1}}{{\equiv}SiO{-}ZrNp_3} + NpH} \qquad (1)$$

A supported zirconium hydride surface complex, **2**, is formed by treatment of **1** with hydrogen [$p(H_2)$ 6 × 10^4 Pa; T 423 K]. **2** has been identified by IR spectroscopy [Fig. 1(*a*)], chemical reactivity and deuterium exchange experiments.[4] All subsequent studies on **2** have been carried out under strict exclusion of O_2 and H_2O. (The absence of Zr–OH is checked by IR spectroscopy.)

This supported zirconium hydride, **2**, [Zr]$_s$–H, reacts with cyclooctane at room temperature to form a Zr–cyclooctyl surface complex, eqn. (2). Support for reaction (2) is given by

$$\underset{\mathbf{2}}{\mathrm{[Zr]_s{-}H}} + \text{cyclooctane} \rightarrow \mathrm{[Zr]_s}\text{–cyclooctyl} + \mathrm{H_2} \qquad (2)$$

the following experimental evidence: (*i*) After gas-phase evacuation, the IR spectrum of the solid is modified: two bands, characteristic of ν(CH_2) vibrational modes at 2927 and 2857 cm^{-1}, and two bands, typical of δ(CH_2) vibrational modes at 1462 and 1447 cm^{-1} appear. Simultaneously, the intensity of the ν(Zr–H) band at 1635 cm^{-1} decreases strongly [Fig. 1(*b*)]. (*ii*) Gas-phase chromatography shows that the reaction between **2** and cyclooctane leads to the formation of molecular hydrogen in the gas phase. (*iii*) Treatment of the [Zr]$_s$–cyclooctyl, assumed to be formed, with hydrogen [$p(H_2)$ 5.33 Pa; T 343 K] regenerates the zirconium–hydride surface complex **1** [Fig. 1(*c*)]; cyclooctane as well as its hydrogenolysis products are detected in the gas phase. (*iv*) The appearance of a ν(CO) band at 1652 cm^{-1}, ascribed to an acyl ligand,[5] suggests that molecular CO is inserted into the Zr–C bond. Subsequent extraction of the organic ligands with HCl reveals the formation of cyclooctanal as the major component, eqn. (3). Surprisingly, this supported [Zr]$_s$–H **2** under moderate conditions [$p(CH_4)$ 5.3 × 10^4 Pa; T 423 K] is also reactive towards methane, eqn. (4).

$$\mathrm{[Zr]_s{-}R + CO \rightarrow [Zr]_s{-}C(O){-}R \xrightarrow{HCl} [Zr]_s{-}Cl + RCHO} \qquad (3)$$
$$\mathrm{R} = \text{cyclooctyl}$$

$$\mathrm{[Zr]_s{-}H + CH_4 \rightarrow [Zr]_s{-}CH_3 + H_2} \qquad (4)$$

Evidence for reaction (4) comes from the following data: (*i*) Upon introduction of CH_4 on **2** at 423 K, the intensity of the ν(Zr–H) band decreases. (*ii*) Molecular hydrogen is formed during this interaction. (*iii*) Analysis by mass spectrometry shows that subsequent hydrolysis with D_2O (2.7 × 10^3 Pa) liberates exclusively CH_3D, eqn. (5). (*iv*) The formation of [Zr]$_s$–$^{13}CH_3$ on reaction of **2** with $^{13}CH_4$ is confirmed by ^{13}C MAS NMR spectroscopy by the observation of a broad band at δ 36.[6]

$$\mathrm{[Zr]_s{-}CH_3 + D_2O \rightarrow [Zr]_s{-}OD + CH_3D} \qquad (5)$$

To our knowledge, no reaction of intermolecular alkane activation has previously been reported either on a molecular- or on a grafted-zirconium complex. The silica surface enhances the electrophilicity of the zirconium centre, allowing the reaction of C–H activation of alkanes. This increase in the electrophilic character of the metal is probably related to the stabilization of an 8e-Zr by the surface siloxy ligands, while molecular analogues are usually stabilized by two cyclopentadienyl ligands and thus have a 16e-configuration.

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3 IR spectrum (ν/cm^{-1}): 2953 (ν_{as} CH_3), 2864 ($\nu_s CH_2$), 1464 (δ_{as} CH_3), 1359 ($\delta_s CH_3$). ^{13}C MAS NMR δ 33 (CH_3), 32 [$C(CH_3)_3$]. F. Quignard, C. Lecuyer, A. Choplin, C. Bougault, F. Lefebvre, D. Olivier and J.-M. Basset *Inorg. Chem.*, submitted for publication.

4 IR spectrum: ν(Zr–H): 1635 cm^{-1}. F. Quignard, C. Lecuyer, A. Choplin, J. Corker, J. Evans and J.-M. Basset, unpublished results.

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