From Synthesis to Chemical Reactivity of Supported d^0 Complexes. Part 1. An *in situ* Infrared Spectroscopic Study of Silica-anchored Zirconium Hydrides†

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Silica-anchored zirconium hydride complexes have been synthesized by controlled hydrogenolysis of a tris(neopentyl)zirconium surface complex. They have been characterized spectroscopically and their chemical reactivity compared to related molecular analogues. The mechanism of their formation is discussed. High reactivity and thermal stability seem to be correlated to the presence around Zr of the 'solid' ligand; its influence is discussed in terms of electronic and immobilizing effects.

Recently, we have reported the remarkable stoichiometric and catalytic activity towards the σ C–H bonds of alkanes of silica-supported zirconium hydrides, derived from silica-anchored tris(neopentyl)zirconium.[1,2] During the same time, the chemistry of a silica(zirconium) dihydride was described by King and Schwartz:[3] the unexpected low reactivity of this complex, when compared to that of related molecular zirconium hydrides, was correlated to the co-ordination of three surface oxygens per Zr, in a multiple bonding fashion (π bonding of the lone pair of p electrons). Differences in the procedures of synthesis seem to produce different kinds of silica-supported zirconium hydrides. We wish to report here the synthesis, the *in situ* spectroscopic and chemical characterization of grafted zirconium hydrides, which show a reactivity very similar to related molecular complexes.

Experimental

Reagents.—Silica (Aerosil from Degussa, 200 $m^2\ g^{-1}$) was treated for 12 h, at 423, 523 or 773 K under vacuum (10^{-5} Torr). Tetrakis(neopentyl)zirconium, $[Zr(CH_2CMe_3)_4]$, was prepared from $ZrCl_4$ (Aldrich) according to a published procedure.[4] Hydrogen, alkanes and olefins (Air Liquide) were purified before use by passing through deoxo and molecular-sieve traps. Deuterium was purified by flowing through a liquid-nitrogen trap. Organic reagents (Aldrich) were dried by classical techniques and degassed by freeze and thaw cycles prior to use.

Techniques.—Qualitative and quantitative analysis by chromatography (GC) were performed on an Intersmat 120 FID chromatograph equipped with a capillary column, KCl–Al_2O_3 (50 m × 0.3 mm) for the hydrocarbons and Carbowax/Chromosorb for the oxygenated compounds. Elemental analysis was performed by Mikroanalytisches Labor Pascher, Remagen (Germany). IR spectra were recorded on a Nicolet 10 MX-FT instrument.

All experiments were performed under strict exclusion of air and water, using standard high-vacuum line equipment (10^{-4}–10^{-5} Torr). Sublimation of $[Zr(CH_2CMe_3)_4]$ on SiO_2 at 333 K and all the following steps for the study of the chemical reactivity were performed in a cell specially designed for *in situ* preparations under a rigorously controlled atmosphere.[5] These procedures avoid the use of solvents, whose vibrational spectra may overlap those of the surface complexes of interest, and any transfer from one vessel to another, which may be a source of destruction of the very air- and moisture-sensitive zirconium alkyl and hydride surface complexes.

Results and Discussion

Chemical Reactivity of the Surface Hydride Complexes.—The reaction of $[Zr(CH_2CMe_3)_4]$ with the surface of silica previously dehydroxylated at 773 K, $SiO_2(773)$, leads to the formation of only one surface complex, $\geqslant SiO{-}Zr(CH_2CMe_3)_3$ **1**.[6] Subsequent reaction of **1** with hydrogen at 423 K gives solid **2**, characterized by vibrational bands in two different frequency ranges: two bands arise at 2253 and 2195 cm^{-1} (zone **A**) and a group of overlapping bands centred at 1635 cm^{-1} (zone **B**) are observed [Fig. 1(*a*)]. These bands were tentatively assigned to surface silanes, $\geqslant Si{-}H$, and surface zirconium hydrides, $[Zr]_s{-}H$, respectively, on the basis of infrared data of molecular analogues, *i.e.* $SiH(RO)_3$[3] and $[ZrH_2(\eta^5\text{-}C_5H_5)]$,[7] and on their different ability to exchange with deuterium.[8] The observation of more than one band in both frequency ranges strongly suggests the occurence of more than one surface silicon and zirconium hydride respectively.

The chemical reactivity of molecular zirconium hydrides and of silanes is reportedly very different, the former being much more reactive than the latter. These differences will help us to check our preliminary infrared assignments. We describe here reactions known to be specific to hydride complexes of the early transition metals in their d^0 configuration. All reactions were followed by *in situ* infrared spectroscopy.

Reactivity.—*Towards oxygen.* When dry O_2 (30 Torr, 298 K) is introduced on a self supported disk of **2**, the intensity of the **B** bands decreases immediately [Fig. 1(*a*), (*b*)]. After 15 min, only a band of weak intensity is observed at 1646 cm^{-1}; after 16 h, no band of significant intensity remains in this frequency range. Simultaneously, a band is observed at 3760 cm^{-1}, whose intensity increases with time. This band can reasonably be attributed to a (Zr)O–H vibration.[9] The intensity of the **A** bands does not vary during the time of exposure to O_2 and simultaneously, no gas evolution is detected by GC (hydrocarbon, H_2).

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† *Non-SI unit employed:* Torr ≈ 133 Pa.

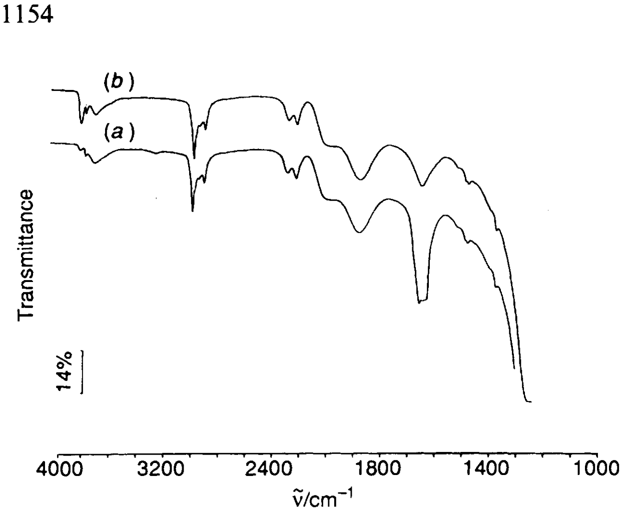


Fig. 1 Reactivity of **2** with O_2. IR spectra of (*a*) solid **2**, (*b*) solid **2** after introduction of O_2 (30 Torr, 298 K, 15 min)

Towards water. Hydrolysis was performed with D_2O (5 Torr, 298 K). The vibrational **B** bands disappear instantaneously, while the **A** bands are slightly broadened. New bands are observed at 2785w, 2759m, 2705s (br) and *ca.* 2600vbr cm^{-1}. The two broad low-frequency bands may be assigned to OD groups interacting *via* hydrogen bonding. The band at 2759 cm^{-1} is typical of isolated deuteriated silanol groups; their formation can result either from the opening of a siloxane bridge, $\geqslant$Si–O–Si$\leqslant$, a process known to be reversible on the surface of silica [equation (1)], or from the rupture of a $\geqslant$Si–O–Zr$\leqslant$ bridge [equation (2)].

$$\geqslant \mathrm{Si{-}O{-}Si} \leqslant + \mathrm{D_2O} \longrightarrow 2 \geqslant \mathrm{Si{-}OD} \qquad (1)$$

$$\geqslant \mathrm{Si{-}O{-}ZrX_3} + \mathrm{D_2O} \longrightarrow \geqslant \mathrm{Si{-}OD} + [\mathrm{DO{-}ZrX_3}] \qquad (2)$$

Analysis of the gas phase formed above a large sample evidences the concomitant formation of hydrogen.

Alkaline hydrolysis of **2** with a solution of $KOH-H_2O$ suppresses both the **A** and **B** bands; H_2 is liberated.

Towards halogenated hydrocarbons. The reactivity of halogenated hydrocarbons, R–X (X = Cl, Br or I), with metal hydrides, MH_x, is reportedly high[10–12] while these same reactants are inert towards Si–H bonds without any catalyst.[13,14] We studied the reactivity of **2** with various R–X, *i.e.* MeI, EtBr and PrCl.

The reaction of MeI with **2** was previously described:[8] it involves exclusively the **B** hydrides. The liberation of 1 mol CH_4 per mol $[Zr]_s$ suggests the presence of an average of one hydride ligand per surface zirconium. Similarly, the reaction with EtBr (20 Torr) or PrCl (20 Torr) at room temperature produces instantaneously ethane or propane respectively with the simultaneous disappearance of all the **B** bands. Apparently, the nature of the halide has no influence on the reactivity of these **B** hydrides towards halogenated hydrocarbons.

Towards alcohols. When anhydrous propan-2-ol (20 Torr, 298 K) is introduced on a disk of **2**, trace amounts of H_2 are detected by GC. The infrared spectrum (after evacuation of excess alcohol) changes as follows [Fig. 2(*a*), (*b*)]: total disappearance of the **B** vibrational bands, broadening of the **A** bands so that only essentially one band is distinguished. The appearance of the ν(C–H) vibrational bands at 2971, 2936 and 2871 cm^{-1} as well as the δ(C–H) bands at 1466, 1382, 1369 and 1338 cm^{-1} are characteristic of an isopropyl fragment.[15] These data suggest that the **B** hydrides are easily alcoholysed, but not the **A** hydrides.

Towards acetone. When anhydrous acetone (40 Torr, 298 K) is introduced on a self supported disk of **2**, drastic changes are observed: total disappearance of the **B** bands, occurence of two new very broad bands at *ca.* 3650 and 3400 cm^{-1}, assignable to hydrogen-bonded hydroxyl groups and four new strong bands in the ν(CO) range at 1750, 1730, 1673 and 1590 cm^{-1}. The ν(C–H) bands at 2971, 2936 and 2871 cm^{-1} as well as the δ(C–H) bands at 1466, 1455, 1445, 1361 and 1338 cm^{-1} characteristic of an alkoxide species[15] appear simultaneously. The two **A** bands remain and a third band is observed at 2230 cm^{-1} [Fig. 2(*c*)].

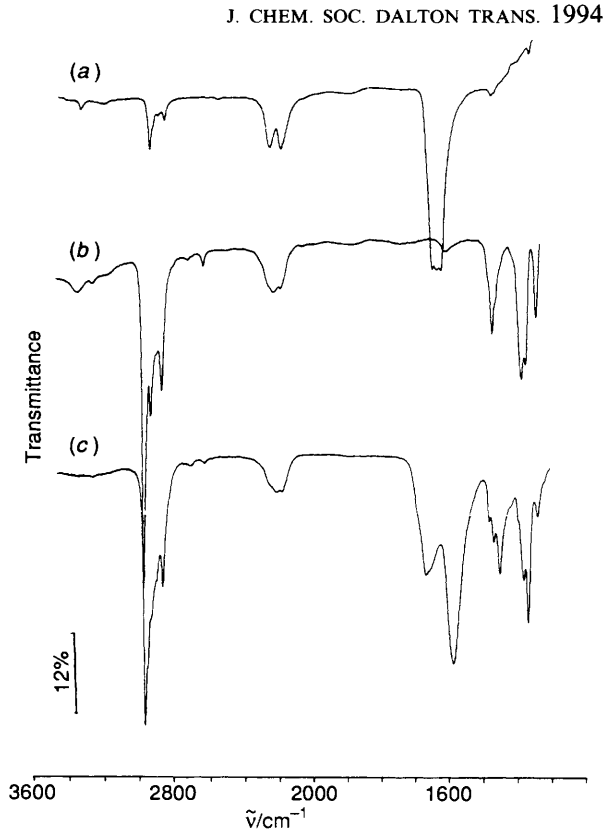


Fig. 2 Reactivity of **2** with propan-2-ol and acetone. IR spectra, after subtraction of the spectrum of $SiO_2(733)$, of (*a*) solid **2**, (*b*) solid **2** after introduction of propan-2-ol (20 Torr, 298 K) and subsequent evacuation and (*c*) solid **2** after introduction of acetone (40 Torr, 298 K) and subsequent evacuation

Evacuation of the system results in the removal of the bands at 3400, 1750 and 1730 cm^{-1} and an intensity decrease of the band at 1673 cm^{-1}. These bands can reasonably be attributed to gaseous acetone (1750 cm^{-1}) and acetone weakly coordinated to the solid. The two remaining ν(CO) bands must be assigned to more strongly held acetone, by donor–acceptor complexation to a surface Lewis acid for example.[16,17] Subsequent reaction with gaseous HCl affords only propan-2-ol (as identified by GC).

Towards olefins. Introduction of ethylene (15 Torr, 298 K) on **2** leads to an immediate reaction, as evidenced by the total consumption of the **B** bands and the growth of very intense bands at 2950vs, 2850s, 1485m and 1365m cm^{-1}, a spectrum typical of polyethylene;[18] polymer formation results from a multiple insertion of ethylene, a reaction well known with zirconium hydride complexes.[19,20]

When propene (20 Torr, 298 K) is introduced on **2**, the infrared spectrum is modified as follows: total disappearance of all **B** bands, appearance of ν(C–H) bands at 2959, 2915, 2873 and 2844 cm^{-1} and δ(C–H) bands at 1459 and 1377 cm^{-1}, characteristic of an alkyl fragment [Fig. 3(*a*), (*b*)]. Subsequent reaction with H_2 (600 Torr) at 423 K restores the initial spectrum.

Isobutene reacts similarly to propene and leads to the formation of isobutyl ligands, characterized by ν(C–H) bands at 2960, 2932 and 2869 cm^{-1}, and δ(C–H) bands at 1468 and 1367 cm^{-1}.

With all the studied olefins, no changes could be detected in

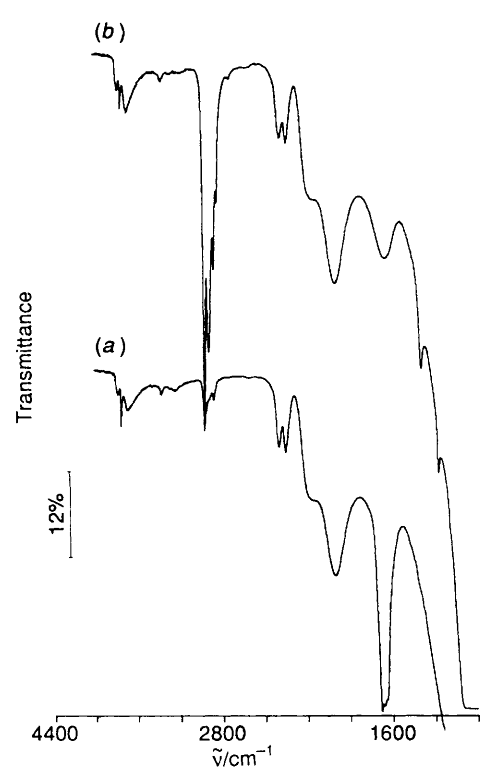


Fig. 3 Reactivity of **2** with olefins. IR spectra of (*a*) solid **2**; (*b*) solid **2** after introduction of propene (20 Torr, 298 K) and subsequent evacuation

the **A** region of the IR spectrum, strongly suggesting the inertness of surface silanes towards these reactants.

With alkanes. Complex **2** reacts under mild conditions with cyclooctane (5 Torr, 298 K) and methane (400 Torr, 423 K) as deduced from IR data. Hydrogen evolution occurs simultaneously.[8] With methane, the formation of $[Zr]_s$–$^{13}CH_3$ by reaction with $^{13}CH_4$ is confirmed by the observation of a broad band at δ 36[21] in the ^{13}C magic angle spinning (MAS) NMR spectrum, a value very far from the chemical shifts expected for $Si(CH_3)_{4-x}(OR)_x$ (δ −1.9 to −10.3, x = 1–3).[22] Deuteriolysis liberates exclusively CH_3D (mass spectral analysis).

Neopentane (30 Torr) reacts at room temperature as evidenced by a significant modification of the shape of the **B** bands; after 17 h, only a rather weak band remains at 1635 cm^{-1} and no further changes occur even at *ca.* 333 K (Fig. 4).

Propane (200 Torr) behaves similarly towards **2**: the reaction takes place at room temperature as evidenced by the intensity decrease of the **B** bands. After 30 min of contact time at 373 K, these bands are totally consumed, while bands typical of an alkyl fragment, different from a neopentyl fragment, are observed at 2966, 2935, 2877, 1464 and 1380 cm^{-1}.

With all alkanes, no modifications are detected in the **A** region of the IR spectrum, sign of no reactivity of the relevant hydrides.

Towards deuterium. Introduction of D_2 (90 Torr, 298 K) on **2** induces time-dependent changes. Thus, after 5 min of contact, only one band, moderately broad, remains at 1635 cm^{-1} [Fig. 5(*a*), (*b*)]. Its intensity slowly decreases with time [Fig. 5(*c*)]. Simultaneously, only very minor changes of the relative intensities of the two **A** bands can be observed. Subsequent reaction with H_2 (100 Torr, 298 K) indicates the total reversibility of the process [Fig. 5(*d*), (*e*)]. The kinetics of the reaction of **2** with D_2 (or the reverse reaction) is sharply increased with temperature: it is completed in about 3 h when performed at 423 K.

In conclusion, hydrogenolysis of $\geqslant SiO\text{–}Zr(CH_2CMe_3)_3$ leads unexpectedly to a complex mixture of surface complexes.

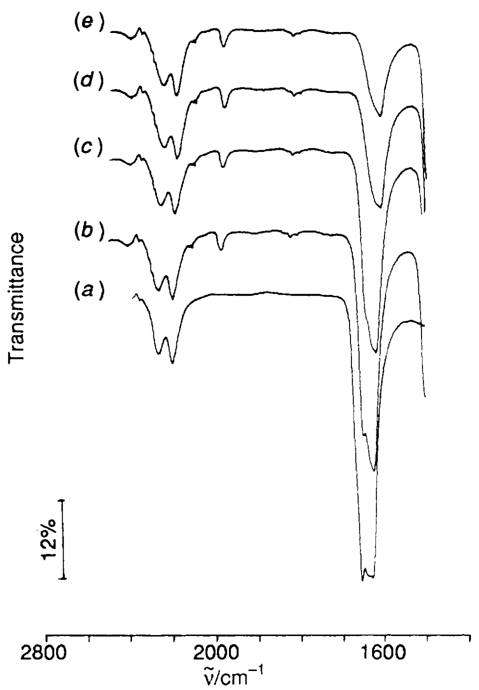
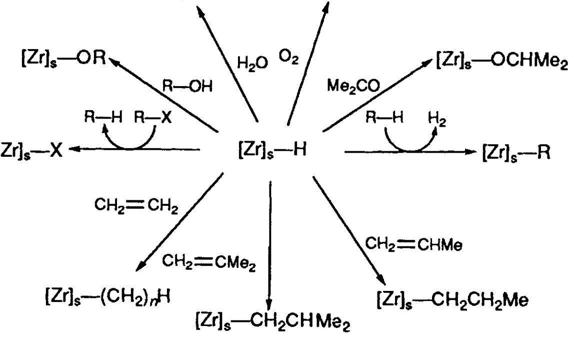


Fig. 4 Reactivity of **2** with neopentane. IR spectra, after subtraction of the spectrum of SiO_2(773), of (*a*) solid **2** after introduction of neopentane (30 Torr, 298 K) (*b*) after 15 min, (*c*) after 30 min, (*d*) after 18 h and (*e*) after 1 h at 333 K



Scheme 1 Summary of reactions of silica-anchored zirconium hydride

The liberation of molecular hydrogen and the simultaneous disappearance of both **A** and **B** vibrational bands by hydrolysis (neutral or alkaline) clearly show that both types of complexes are surface hydrides.

The **B** type surface complexes show, definitely, all the well-known chemical properties of zirconium hydrides and related Groups 3, 4, lanthanide and actinide d^0 hydride complexes towards halogenated hydrocarbons, alcohols, olefins and ketones.[8,23–31] (Scheme 1).

A direct comparison of the vibrational frequencies of these supported zirconium hydrides with either those of molecular analogues[32] such as $[ZrH_2(\eta^5\text{-}C_5Me_5)_2]$[ν(Zr–H$_t$) 1555 cm^{-1}], $[\{[ZrH(\eta^5\text{-}C_5H_5)_2]H\}_x]$ [ν(Zr–H$_t$) 1520 cm^{-1}, ν(Zr–H$_b$) 1285 cm^{-1}], $[ZrH(\eta^5\text{-}C_5Me_5)_2(OMe)]$ [ν(Zr–H$_t$) 1590 cm^{-1}] or of surface zirconium hydride sites resulting from heterolytic dissociation of H_2 on ZrO_2[33] [ν(Zr–H$_t$) 1562 cm^{-1}, ν(Zr–H$_b$) 1371 cm^{-1}] strongly suggests that our silica-supported zirconium hydrides possess terminal hydride ligands (H$_t$). The presence of bridging hydride (H$_b$) ligands could not be evidenced: no band could be observed in the expected frequency range, *i.e.* near 1280 cm^{-1}.

The **A** surface hydrides are chemically inert at room temperature towards all studied reactants, except alkaline

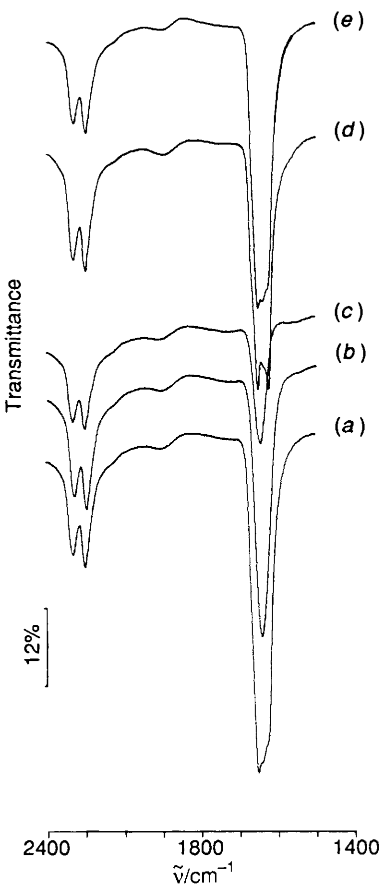
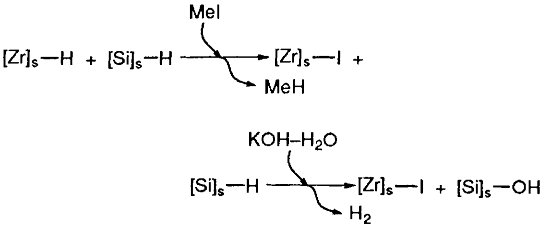


Fig. 5 Reactivity of **2** with D_2. IR spectra, after subtraction of the spectrum of $SiO_2(773)$, of (*a*) solid **2** after introduction of D_2 (90 Torr, 298 K), (*b*) after 5 min, (*c*) after 16 h, then evacuation and reintroduction of H_2 (100 Torr, 298 K), (*d*) after 5 min and (*e*) after 16 h

water. The direct comparison of the vibrational frequencies and of the known reactivity of molecular complexes, such as $SiH(OMe)_3$[3] and $SiHR_3$[34] allows us to confirm the formation of surface silanes [Si]–H.

Among the reactions described (see above) two of these should allow the determination of the average number of hydride ligands for the surface-hydride complexes. The amount of methane released (reaction with MeI) reflects the average number of hydride ligands per surface-zirconium atoms, while the amount of hydrogen (reaction with $KOH-H_2O$) is directly correlated to the average number of hydride ligands transferred from zirconium to silicon [equation (3)].



$$[Zr]_s{-}H + [Si]_s{-}H \xrightarrow{MeI} [Zr]_s{-}I + MeH$$

$$[Si]_s{-}H \xrightarrow{KOH-H_2O} [Zr]_s{-}I + [Si]_s{-}OH + H_2 \qquad (3)$$

Experimentally, an average number of one hydride ligand per Zr atom and one Si–H bond formed by surface zirconium is observed *i.e.* a total of two hydride ligands, a number difficult to reconcile with a total number of three hydride ligands expected from the stoichiometry of **1**. Nevertheless, the above results are based on the hypothesis of occurrence on the surface of exclusively zirconium(IV) species: in fact, one observes very often accidental formation of neopentoxy zirconium complexes, which are unreactive towards H_2, and of zirconium(III) entities.[35,36]

The multiplicity of the infrared bands and the different kinetic behaviour of the H–D exchange reaction clearly show that more than one type of $[Zr]_s$–H species exists on the surface; they may differ by the number of siloxy ligands, a consequence of the related formation of Si–H entities.

Given the high potentiality of such immobilized zirconium hydride complexes in the field of catalysis, it appears, at first, highly desirable to obtain only one well-defined surface zirconium hydride. Among the parameters which may orient the reaction of their formation, the temperature may be important: it may influence both the hydrogenolysis of the Zr–C bonds and the hydride transfer and thus modify the nature and/or the relative concentration of the resulting surface hydrides, Zr–H and Si–H.

Influence of the Temperature of Hydrogenolysis and of the Degree of Dehydroxylation of Silica.—When H_2 (400 Torr, 298 K) is introduced on **1**, no changes occur in the IR spectrum below 343 K. After *ca.* 2 h at 343 K, two weak bands appear at 2256 and 1635 cm⁻¹, while the intensity of the bands typical of ν(CH) and δ(CH) vibrations decreases only slightly. These changes are time dependent [Fig. 6]. After 42 h, the spectrum is identical to the one obtained after reaction of **2** with H_2 (2 h, 423 K). This strongly suggests that temperature is not the key factor for obtaining only one type of surface Zr–H. Apparently, an increase in temperature simply accelerates the rate of the reaction of hydrogenolysis of the Zr–C bond. Higher temperatures cannot be used given that silica-supported zirconium hydrides decompose above 473 K.

The number of possible zirconium hydride surface species can be large if related to the initial number of neopentyl ligands around Zr. This latter number may be varied *via* the degree of hydroxylation of silica; thus, with less dehydroxylated silicas (evacuated at 523 or 423 K for example), the formation of $(\geqslant SiO)_xZr(CH_2CMe_3)_{4-x}$ ($x > 2$) was proposed.[37,38] The reaction of these surface neopentyl zirconium complexes with H_2 (400 Torr, 423 K) leads to surface hydride species, characterized by a broad band around 1635 cm⁻¹, which is apparently multiple with $SiO_2(523)$ but single with $SiO_2(423)$ (Fig. 7).

Given the kinetic selectivity of the reaction of exchange of Zr–H with D_2 (see above), we used this reaction to test if only one surface Zr hydride was obtained. Thus, introduction of D_2 (100 Torr) on this latter sample [$SiO_2(423)$] leads to the total disappearence of the band at 1635 cm⁻¹ after 30 min at 423 K. Reintroduction of H_2 (100 Torr, 298 K) provokes the immediate reappearance of two bands at 1643 and 1615 cm⁻¹, and progressive restoration of the complete initial spectrum with time (Fig. 8). This confirms that the band at 1635 cm⁻¹ is also multiple in the case of $SiO_2(423)$, suggesting that only the relative amount of each surface zirconium hydride complex varies with the degree of dehydroxylation of silica.

Hydrogenolysis of **1** is certainly a four-centre mechanism[39,40] occurring successively on the three neopentyl ligands. Hydride transfer takes place as soon as the first hydride ligand is present on the zirconium centre. Whatever the temperature of hydrogenolysis ($343 < T < 423$ K) and whatever the degree of dehydroxylation of silica ($423 < T < 773$ K), both hydrides are thus always obtained simultaneously. Nevertheless given the fact that one should not use **2** at temperatures above the temperature of dehydroxylation of silica (to avoid liberation of molecular water), we think that it will be preferable to work with silica(773) for most applications.

Conclusion

Formation of a complex mixture of surface zirconium and silicon hydrides by hydrogenolysis of $\geqslant SiO{-}Zr(CH_2CMe_3)_3$ was confirmed; simple parameters, such as temperature of

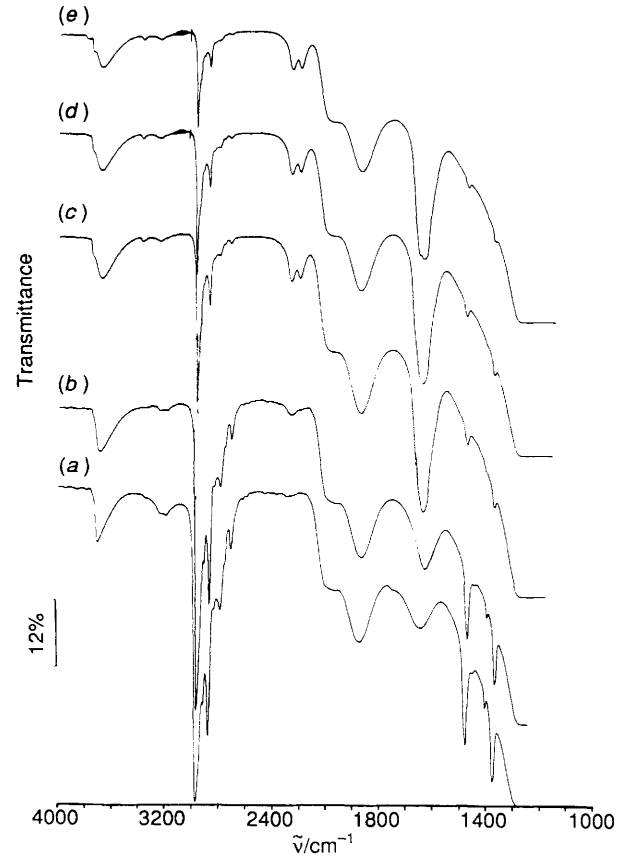


Fig. 6 Reaction of **1** with H_2. IR spectra of (*a*) solid **1** after introduction of H_2 (400 Torr, 343 K) and after 2 (*b*), 18 (*c*), 24 (*d*) and 42 h (*e*)

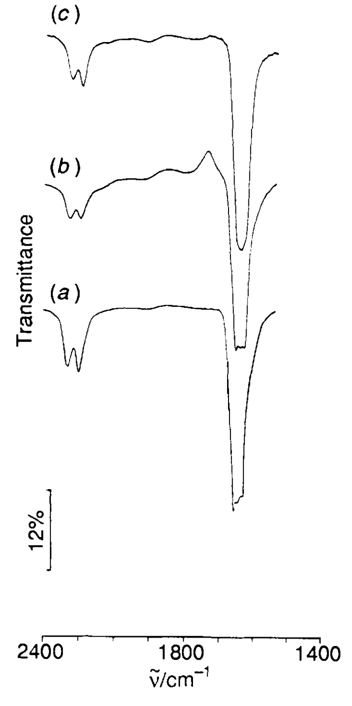


Fig. 7 Influence of the temperature of dehydroxylation of silica (*a*) **2**–SiO_2(773), (*b*) **2**–SiO_2(523) and (*c*) **2**–SiO_2(423)

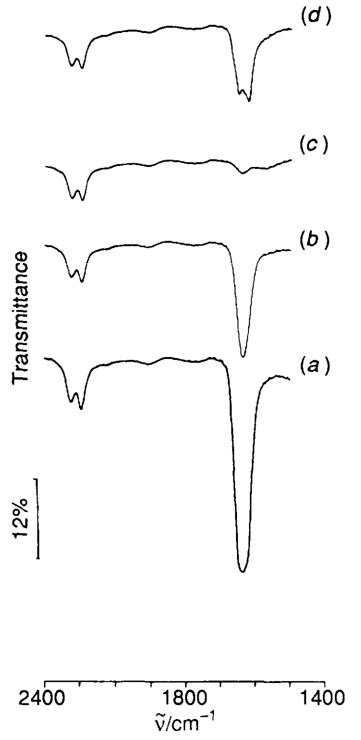


Fig. 8 Reaction of deuterium exchange on **2**–SiO_2(423). IR spectra of: (*a*) **2**–SiO_2(423) after introduction of D_2 (100 Torr), (*b*) 298 K, 10 min, (*c*) 423 K, 30 min and (*d*) 423 K, 30 min after evacuation and subsequent reintroduction of H_2 (100 Torr, 298 K)

reaction and degree of surface dehydroxylation cannot orient the reaction towards the selective formation of either type of hydride species.

No significant differences in reactivity could be evidenced for the different zirconium surface hydrides. Some reactions, such as H–H activation (H–D exchange), and C–H activation, which are directly correlated to the electrophilicity of the zirconium centre, are kinetically sensitive to the nature of the zirconium hydride complex. This may be correlated to the zirconium ligand environment, and more precisely to the number of siloxy ligands. Kinetic data, on similar molecular complexes, reveal indeed that alkoxide substitution greatly depresses the rate of hydrogenolysis. This effect is explained in terms of a decrease of the metal electrophilicity, arising from the π-donor character of the alkoxy ligands.[41] These silica-anchored zirconium hydrides react, chemically, like the molecular hydrides of elements of Groups 3 or 4, or of lanthanides or actinides in d^0 or f^0 configurations: *viz.* insertion of olefins and ketones into M–H bonds and C–H activation of alkanes.[42] The observation of C–H bond activation of alkanes arises because the 'solid' ligand induces differences relative to molecular zirconium complexes which may be related to electronic effects and/or immobilizing properties. Formally an 8e$^-$ species, if one considers the surface zirconium as four-co-ordinated, or a 10e$^-$ species, if one considers the co-ordination of a surface oxygen atom *via* a two-electron donor bond, the surface zirconium hydrides are in any case highly electron deficient entities when compared to the 16e$^-$ cyclopentadienyl-stabilized molecular complexes. Immobilization of these hydrides on a solid surface also accounts for their remarkable stability toward temperature (up to 473 K) and dimerization.

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