From Synthesis to Chemical Reactivity of Supported d^0 Complexes. Part 2.[1] Reactivity of Silica-anchored Alkylzirconium Complexes. An Attempt toward Functionalization of Alkanes†

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Silica-anchored alkyl zirconium complexes $[Zr]_s$–R (R = cyclooctyl, Pr or Me) have been generated by reaction of $[Zr]_s$–H complexes with the relevant alkanes. Their stoichiometric reactivity towards molecules such as carbon monoxide and olefins was studied in order to estimate the potential of such systems to activate and functionalize alkanes catalytically.

Activation of the σ C–H bond of alkanes by organometallic complexes is now a well documented reaction.[2] Most interesting nevertheless are reactions which would lead to a catalytic functionalization of alkanes, *i.e.* to their transformation into an alcohol, aldehyde, acid, thiol or a higher olefin. Very few examples have so far been published.[3] Recently, we have reported the synthesis of zirconium hydride complexes, $[Zr]_S$–H **1**, anchored to the surface of a partially dehydroxylated silica.[1] These supported complexes activate, under mild conditions, the C–H bond of alkanes such as methane, propane, neopentane and cyclooctane.[4] The resulting surface alkylzirconium complexes can be considered as intermediates in a catalytic cycle of functionalization of alkanes. We have so far selected the reactions of acylation of alkanes and of methylation of olefins[5] [equations (1) and (2)]. We have now studied some related

$$R\text{–}H + CO + C_3H_6 \longrightarrow R\text{–}C(O)\text{–}C_3H_7 \qquad (1)$$

$$CH_4 + C_3H_6 \longrightarrow CH_3\text{–}C_3H_7 \qquad (2)$$

stoichiometric reactions, which may be reasonable steps of a potential catalytic cycle and then analysed the possibilities to render reactions (1) and (2) catalytic.

Experimental

Reagents.—Silica (Aerosil from Degussa, 200 m^2 g^{-1}) was treated for 12 h, at 773 K under vacuum (10^{-5} Torr). Tetra(neopentyl)zirconium, $Zr(CH_2CMe_3)_4$, was prepared from $ZrCl_4$ (Aldrich) according to a published procedure.[6] Hydrogen, alkanes and olefins (Air Liquide) were purified before use by passing through a deoxo catalyst and molecular sieves traps.

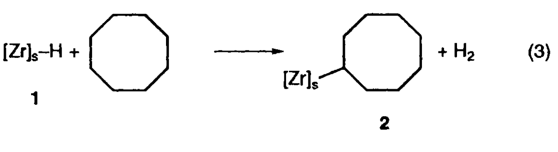
Techniques.—Qualitative and quantitative GC analyses of the gas phase were performed on an Intersmat 120 FID chromatograph equipped with a capillary column containing $KCl\text{–}Al_2O_3$ (50 m × 0.3 mm) for the hydrocarbons and Carbowax/Chromosorb for the oxygenated compounds. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen (Germany). Infrared spectra were recorded on a Nicolet 10 MX-FT spectrometer.

All experiments were performed under strict exclusion of air and water, using standard high-vacuum-line equipment (10^{-4}–10^{-5} Torr) and break-seal techniques. 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.[7] These procedures avoid the use of solvents, the vibrational spectra of which 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 sensitive zirconium alkyl and hydride surface complexes.

Results

Supported zirconium hydride complexes, $[Zr]_S$–H, are able to activate the σ C–H bond of alkanes:[4] this reaction leads to the formation of surface alkylzirconium complexes, $[Zr]_S$–R, and molecular hydrogen. We report here the reactivities of such $[Zr]_S$–R complexes, considered as the intermediates in any stoichiometric or catalytic reaction of alkane functionalization on such electrophilic systems.

Stoichiometric Acylation of Alkanes.—(*a*) *Cyclooctane.* The surface $[Zr]_S$–cyclooctyl complex **2** is obtained by room-temperature reaction of $[Zr]_S$–H with cyclooctane [equation (3)]:[4] the reaction is quantitative [Fig. 1(*a*), (*b*)].



(3)

The direct carbonylation of alkanes is thermodynamically possible only in the presence of an olefin. We have therefore studied the stoichiometric reactivity of **2** towards CO, and then that of the resulting complex with propene. The choice of propene as the olefin was dictated by its lower propensity to polymerize on this type of complex.[2,8] The expected functionalized alkane may then be liberated by hydrogenolysis of the Zr–C bond(s) of the final surface complex.

(*i*) *Reactivity of* $[Zr]_S$*–cyclooctyl towards* CO. When CO (30 Torr, 298 K) is introduced on to complex **2** at room temperature no immediate modification of the IR spectrum in

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

the 4000–1200 cm^{-1} range is observed. Only after 12 h at 343 K a new band is observed in the ν(CO) region, at 1642 cm^{-1} [Fig. 1(*c*)]; the low frequency and weak intensity suggest that it may be assigned to an acyl type ligand.[9–11] Reaction of this solid with gaseous HCl gives rise to the formation of cyclooctylmethanal (as revealed by GC–mass spectrometry) and to a surface species characterized by a strong band at 1600 cm^{-1}. These data suggest that CO has indeed inserted into the Zr–C (cyclooctyl) bond. Although the wavenumbers typical for molecular acylzirconium complexes are generally *ca.* 100 cm^{-1} below our observed value, one cannot rule out an η^2 co-ordination of the CO moiety, caused by the high oxophilicity of Zr^{IV};[9] a direct comparison of the ν(CO) frequencies for molecular and silica-supported complexes can be misleading due to major differences in the ligand environment of Zr (≡Si–O *versus e.g.* C_5H_5 or C_5Me_5 ligands) (Scheme 1, complex **2a**).

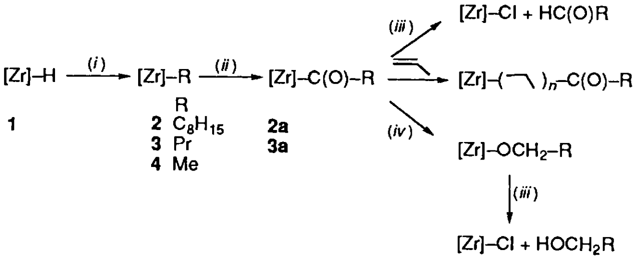
(*ii*) *Reactivity of* $[Zr]_S$–$C(O)C_8H_{15}$ *towards* H_2. Introduction of dry H_2 (200 Torr, 298 K) on a disc of complex **2a** provokes the disappearance of the acyl band at 1642 cm^{-1}, and some minor changes in the ν(CH) and δ(CH_x) region. Subsequent reaction with gaseous HCl liberates cyclooctylmethanol, as determined by GC (comparison with an authentic sample) and trace amounts of cyclooctylmethanal. The presence of cyclooctylmethanol as the major extracted compound strongly suggests that under H_2 the acyl ligand is transformed into an alkoxide ligand (Scheme 1), a reaction which may be compared to the formation of a methoxide ligand when $Zr(C_5Me_5)H_2$ is treated with CO and H_2.[12,13]

(*iii*) *Reactivity of* $[Zr]_S$–$C(O)C_8H_{15}$ *towards propene.* When propene (40 Torr, 343 K) is introduced on a disc of complex **2a** vibrational bands appear at 2957s, 2917s, 2872w, 2843w and 1461m, 1378m cm^{-1}, typical of ν(CH) and δ(CH_x) of acyclic alkyl groups[14] [Fig. 1(*d*)]. The ν(CO) band at 1642 cm^{-1} is unperturbed, suggesting that the carbonyl O atom is still co-ordinated to the very oxophilic zirconium centre. Subsequent introduction of gaseous HCl in the cell does not lead to any gaseous product (GC–mass spectrometry), but to a surface species characterized by a very strong broad ν(CO) band at 1600 cm^{-1} with a shoulder near 1665 cm^{-1}. This suggests the formation of a heavy product, resulting from mono or multiple insertion of propene into the Zr–C(O) bond. Neither cyclooctylmethanal nor butanal was detected, suggesting the absence of side reactions due to incomplete transformation of $[Zr]_S$–H to $[Zr]_S$–$C(O)C_8H_{15}$. The IR band at 1600 cm^{-1} may be attributed to the formation of a ketone, strongly adsorbed on the surface *via* an interaction between O(ketone) and a strong Lewis acid centre, such as for example the zirconium(IV) centres. When a carbonyl compound such as pentanone is adsorbed on SiO_2(500), two strong vibrational bands are observed at *ca.* 1720 and 1740 cm^{-1}, which are assigned respectively to free ketone and hydrogen-bonded ketone.

(*b*) *Propane.* The surface propylzirconium complex **3** is obtained by reaction of $[Zr]_S$–H with propane (400 Torr) at 373 K:[1] the reaction is complete after less than 30 min as deduced from the disappearance of the bands, centred at 1635 cm^{-1}, characteristic of Zr–H stretching vibrations.

Reactivity of $[Zr]_S$–Pr *towards* CO. A disc of complex **3** immediately becomes yellow when CO (30 Torr) is introduced at room temperature. Simultaneously, the IR spectrum shows, in the ν(CO) frequency range, two new weak bands, at 2026 and 1935 cm^{-1} respectively [Fig. 2(*a*)]. After treatment at 343 K (16 h) these two bands vanish and a band of low intensity is now observable at 1642 cm^{-1} [Fig. 2(*b*)]. These data show that **3** is able to co-ordinate at least two CO molecules to the zirconium:[9] the zirconium centres are indeed highly co-ordinatively and electronically unsaturated. Insertion of CO into the Zr–Pr bond is only observed at higher temperatures and is concomitant with the removal of the CO ligands. The presence of the acyl ligand in **3a** is further confirmed by the formation of small amounts of *n*- and iso-butanal by reaction of **3a** with gaseous HCl (GC analysis). Semiquantitative analysis indicates that the ratio *n*-C_4:iso-C_4 is close to 4:1. The strong IR band at 1600 cm^{-1} resulting from this same reaction can be tentatively assigned, as previously, to an aldehyde strongly adsorbed on the surface (co-ordination to a highly electrophilic Zr).

The chemical reactivity of supported alkylzirconium complexes is summarized in Scheme 1. The reactivity towards CO of the surface alkyl zirconium complexes compares very well with that reported for a number of molecular analogues, such as $Zr(C_5H_5)R_2$ (R = H, Me or CH_2CMe_3).[10–12,15] Thus, CO inserts into the Zr–C bonds with formation of an acyl complex. Nevertheless the substitution of the two cyclopentadienyl ligands by 'solid' siloxide ligands induces a number of differences, which may be explained by electronic effects. The electron deficiency of the 'solid' ligand (a one-electron siloxide



Scheme 1 (*i*) RH; (*ii*) CO; (*iii*) HCl; (*iv*) H_2

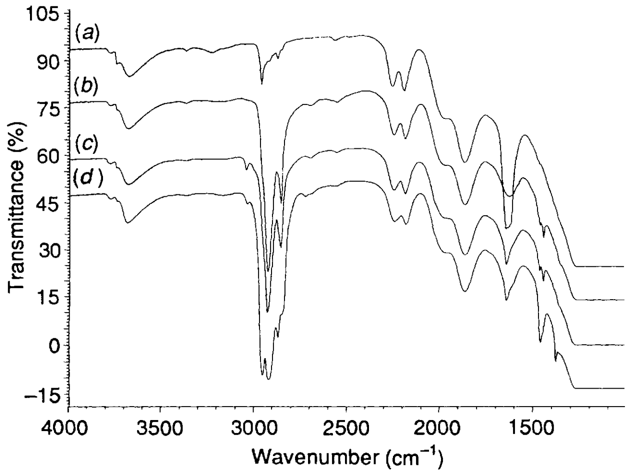


Fig. 1 Reactivity of $[Zr]_S$–cyclooctyl **2** towards CO. Infrared spectra of: (*a*) $[Zr]_S$–H, (*b*) $[Zr]_S$–cyclooctyl, (*c*) (*b*) after introduction of CO (30 Torr, 343 K, 12 h) and subsequent evacuation; (*d*) (*c*) after introduction of propene (40 Torr, 343 K) and subsequent evacuation

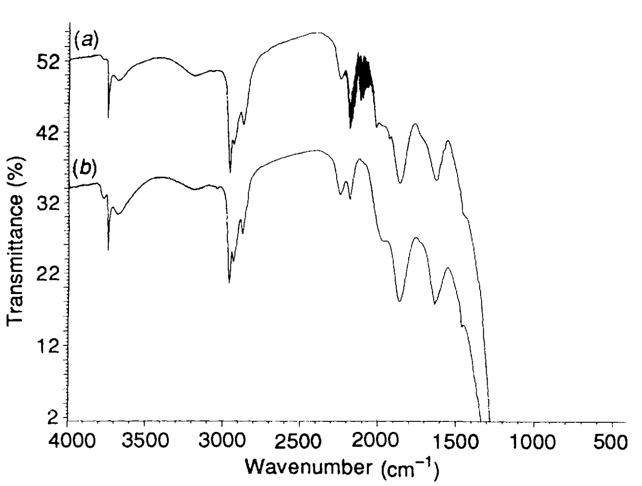


Fig. 2 Reactivity of $[Zr]_S$–Pr **3** towards CO. Infrared spectra of **3**: (*a*) after introduction of CO (30 Torr, 298 K), (*b*) (*a*) after heating (343 K, 16 h) and subsequent evacuation

ligand replacing a five-electron C_5H_5 ligand) generates a highly electronically unsaturated zirconium centre, able readily to co-ordinate, at room temperature, at least two CO molecules (as observed by IR spectroscopy, when R = Pr). The d_π–p_π interaction between O (siloxide ligand) and Zr is certainly responsible for the sharp decrease in the rate of insertion of CO. A similar phenomenon was observed with molecular zirconium complexes bearing alkoxide ligands.[16]

Methylation of Olefins.—Silica-supported methylzirconium complexes **4** are synthesised *via* reaction of **1** with methane (400 Torr, 423 K) [Fig. 3(*a*), (*b*)].

Reactivity of $[Zr]_S$–Me *towards olefins.* When ethylene (5 Torr, 298 K) is introduced on a disc of complex **4** the infrared spectrum exhibits a drastic increase in intensity of the $\nu(CH_2)$ and $\delta(CH_2)$ bands at 2860vs, 2820s and 1475m, 1460 (sh) cm^{-1}, respectively [Fig. 3(*c*)]: it is then very similar to the spectrum of polyethylene.[17] The reaction is completed within *ca.* 15 min; no gaseous reaction product could be detected by GC or IR spectroscopy. Elemental analysis of the disc indicates a ratio C : Zr close to 49 : 1 suggesting that an average of *ca.* 24 (C_2H_4) units have been inserted successively into the Zr–C bond(s).

When the same experiment is performed with propene (5 Torr, 298 K) there is an overall increase in the intensity of the ν(CH) bands and $\nu(CH_2)$ bands appear. Analysis of the gas phase after 30 min of reaction reveals the presence of propene only. Increasing the temperature of reaction (353 K, 30 min) does not lead to any detectable differences in the IR spectrum. Acidic hydrolysis (gaseous HCl) of the solid, obtained under similar conditions, but on a larger sample (100 mg) liberates isobutane (24), propane (44) and methane (32%). No *n*-butane could be detected. The formation of C_4 hydrocarbons confirms that propene has inserted once into the Zr–C bonds of complex **4**. The absence of *n*-butane reveals that this insertion occurs in an anti-Markovnikov fashion. The liberation of propane suggests that activation of methane by **1** was not completed: indeed, propene is known to insert only once into the Zr–H bond.[1] Finally, the presence of methane may be a strong indication of an incomplete reaction of **4** with propene (for this larger sample the amount of propene introduced was sub-stoichiometric).

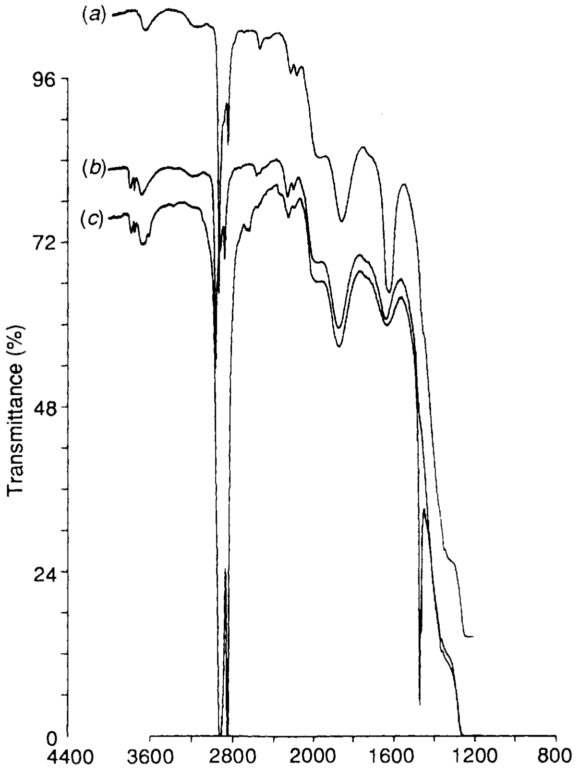


Fig. 3 Reactivity of $[Zr]_S$–Me **4** (2.63% w/w Zr) towards ethylene. Infrared spectra of (*a*) $[Zr]_S$–H, (*b*) (*a*) after introduction of CH_4 (423 K, 400 Torr, 15 h) and subsequent evacuation, (*c*) (*b*) after introduction of C_2H_4 (5 Torr, 298 K, 15 min)

When isobutene (5 Torr, 298 K) is allowed to react with complex **4**, an immediate increase in the intensity of the ν(CH) and $\delta(CH)_x$ vibrational bands and a concomitant evolution of methane are observed (liberation of methane is not due to accidental hydrolysis, as checked by IR spectroscopy). Subsequent hydrolysis of the solid *via* HCl liberates exclusively isobutene (GC analysis).

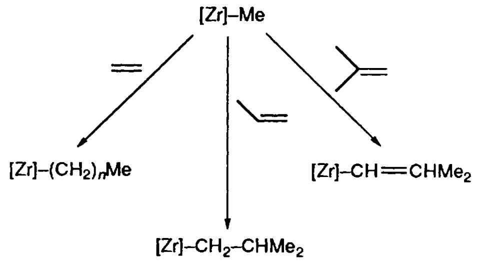
We conclude that the reactivity of silica-anchored methyl zirconium complexes towards olefins depends dramatically on the nature of the olefin and more precisely on its degree of substitution (Scheme 2). Ethylene rapidly polymerizes, as a result of multiple insertion into the Zr–C bond. Propene undergoes only one insertion in an anti-Markovnikov fashion to afford the isobutyl derivative. Isobutene does not insert, but undergoes a vinylic C–H bond activation (probably *via* a four-centre mechanism) which liberates methane and leads to a surface isobutenyl fragment. This type of reactivity compares well with that reported for the molecular methyl scandium complex $Sc(C_5Me_5)_2Me$.[18]

Discussion

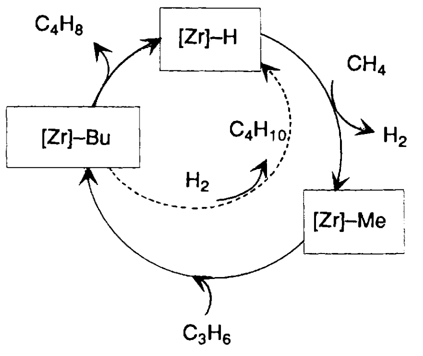
The chemical reactivity of silica-supported $[Zr]_S$–R complexes (R = alkyl), resulting from C–H activation of alkanes by the related zirconium hydride complexes, confirms the high electrophilic character of the zirconium centre, a fact certainly directly correlated to the stabilization of a formally eight-electron entity by the silica surface. Thus, the behaviour of these complexes, particularly towards olefins, compares well with that of the highly electrophilic $Sc(C_5Me_5)_2Me$ complex.[18]

The stoichiometric synthesis of cyclooctylmethanal, cyclooctylmethanol, butanal and isobutanal from the corresponding alkanes was performed on these systems.

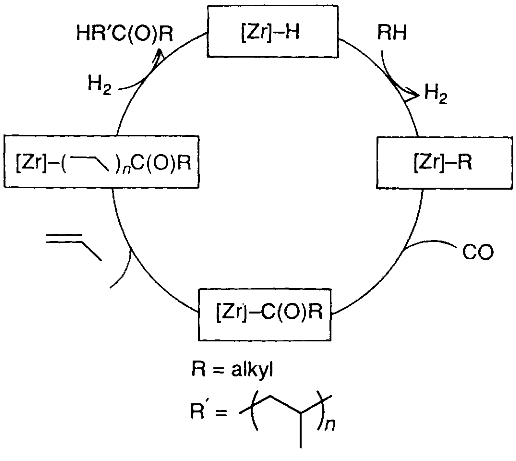
Based on thermodynamics and on the established reactions (see above), two catalytic cycles can in principle be envisaged, which would lead either to the carbonylation of an alkane or to the alkylation of an olefin; both cycles are based on $[Zr]_S$–H as the potential active sites (Schemes 3 and 4).



Scheme 2



Scheme 3



Scheme 4

Preliminary experiments were performed with methane and propene, under the following experimental conditions: CH_4: C_3H_6 = 10:1; C_3H_6: Zr = 40:1 and 473 K (*i.e.* the temperature necessary to activate CH_4). Analysis of the reaction products reveals the formation of mainly C_4 unsaturated hydrocarbons, of propane and small amounts of lower (C_2) as well as heavier hydrocarbons. In the absence of methane among the reactants, propene shows a very poor reactivity (reaction of homologation). The formation of mainly unsaturated C_4 hydrocarbons is quite surprising: it is thermodynamically unfavourable at moderate temperatures (< 473 K). Clearly hydrogen was transferred to some hydrogen acceptor. The concomitant formation of propane strongly suggests that propene acts in this capacity.[19] From a mechanistic point of view one must then consider that the step which restores the catalytic site may be a β-H elimination on the [Zr]-Bu complex.[18,20] The [Zr]-Me site is then restored *via* C-H activation of methane. Experiments using $^{13}CH_4$ or CD_4 are currently under investigation, in order to confirm the incorporation of the methyl unit into the C_4 hydrocarbons or the role of methane as the source of hydrogen.

The case of catalytic acylation of alkanes is *a priori* more complicated, due to the presence of the oxygen atom of carbon monoxide and the well known strong oxophilicity of Zr. Thus a number of secondary reactions such as polymerization of the olefin, insertion of ketones into [Zr]-H bonds and reduction of the acyl to an alkoxy ligand under H_2 must be avoided. Studies are currently in progress in order to determine the appropriate conditions for catalytic alkane acylation to occur on these molecular anchored entities.

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