Molecular Heterogeneous Metathesis Catalysts: an Attempted Synthesis of Surface-anchored Alkylidenetungsten Complexes

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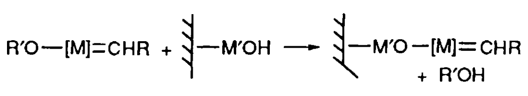
The reactivity of the two alkylidynetungsten complexes, $[W(\equiv CCMe_3)(CH_2CMe_3)_3]$ and $[W(\equiv CCMe_3)Cl_3(dme)]$ (dme = 1,2-dimethoxyethane), was determined with the surface of different inorganic oxides, such as silica, alumina, silica–alumina and niobia; their catalytic activity was tested for the metathesis of *cis*-pent-2-ene. The most efficient solids resulted from the interaction of these complexes with the surface of partially dehydroxylated niobia and silica–alumina. An attempt to identify the surface complexes on niobia (most active system) and silica (less active system) revealed the presence of a number of different anchored complexes, some of them bearing a neopentylidene ligand. The possible correlation between catalytic activity and some of the most probable surface entities is discussed.

The reactivity of organometallic complexes with the surface functional groups of amorphous inorganic oxides has been extensively studied during the last twenty years; the rules which govern this chemistry compare with those of molecular organometallic chemistry.[1] Among the objectives of such studies is the synthesis of surface-anchored complexes with a predefined co-ordination sphere. With these heterogeneous molecular complexes, the metal atom is surrounded by two distinct types of ligands, (*i*) the 'solid' ligands, generally non-labile oxy-type surface ligands which anchor the complex to the solid surface and (*ii*) the 'classical' ligands, which influence the chemical reactivity of the complex *via* their steric and electronic properties and/or their lability, as it occurs with homogeneous catalysts. Stability and/or chemical reactivity of the anchored complexes may thus be enhanced, when compared to their molecular counterparts, by immobilization and/or ligand-substitution effects. Thus, for example, zirconium hydride complexes, when supported on a partially dehydroxylated silica, are thermally very stable (up to 473 K under H_2) and present a high reactivity towards the C–H bonds of alkanes, such as methane, propane or cyclooctane,[2] a reactivity not yet reported with complexes such as $[ZrH_2(\eta^5\text{-}C_5H_5)_2]$ for example.

We wish to report here our approach to the synthesis of supported tungsten-based molecular complexes, catalysts for the reaction of olefin metathesis. Given that the most active well characterized homogeneous tungsten-based catalysts are alkylidenetungsten(VI) complexes,[3,4] proceeding *via* the metallocarbene mechanism of Chauvin and co-workers,[5] we decided to try to synthesize a surface alkylidenetungsten(VI) complex. If one considers on the one hand the surface chemical properties (redox, acid–base) of amorphous inorganic oxides[6] and on the other hand the different methods of synthesis of molecular alkylidene complexes, then at least three different types of precursor complexes can reasonably be envisaged in order to achieve our goal. (*i*) Alkylidyne complexes. Direct protonation of the carbynic W≡C bond by surface Brönsted acids [equation (1)] would lead to the formation of the desired surface-anchored alkylidene complexes. (*ii*) Alkoxyalkylidene complexes. The simple substitution of an alkoxy ligand by a surface M'O entity (M' = Si, Al . . .) is expected [equation (2)]. This reaction must occur under conditions where the alkylidene moiety is unreactive towards the surface functional groups. (*iii*) Polyalkyl complexes. The first reaction must result in the anchoring of the complex to the surface; this may occur *via* an alkyl or another ligand (electrophilic attack by a surface proton). Subsequently, an α-H abstraction on an alkyl ligand, with elimination of the alkane [equation (3)] would lead to the expected surface alkylidene complex. All these reactions [equations (1)–(3)] have been described with molecular complexes.[7–9]


(1)

$$[M]\equiv CR + HX \longrightarrow \underset{X\quad H}{[M]=CR}$$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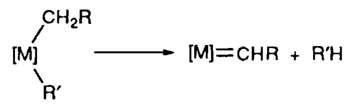

(3)

$$\overset{CH_2R}{\underset{R'}{[M]}} \longrightarrow [M]=CHR + R'H$$

Reaction (1), in principle a one-step synthesis of a surface-grafted alkylidene complex, was first investigated using $[W(CCMe_3)(CH_2CMe_3)_3]$ **1** and $[W(CCMe_3)Cl_3(dme)]$ (dme = 1,2-dimethoxyethane) **2** as precursor complexes. The choice of the inorganic oxide is crucial for the catalytic properties of the resultant supported complex.[10] We report our results concerning the influence of the surface properties of some inorganic oxides on their reactivity with complexes **1** and **2** and the catalytic properties of these solids for olefin metathesis. Some aspects of the relevant surface organometallic chemistry will be given and discussed in relation with the most probable nature of the active sites.

Experimental

Reagents.—Complexes $[W(CCMe_3)(CH_2CMe_3)_3]$ **1** and

[$W(CCMe_3)Cl_3(dme)$] **2** were prepared as previously described.[11] The oxides γ-Al_2O_3 (Degussa, 100 m^2 g^{-1}), SiO_2 (Degussa, 200 m^2 g^{-1}), SiO_2–Al_2O_3 (24.3% Al_2O_3, Ketjen, 374 m^2 g^{-1}) and Nb_2O_5 (CBMM, 100 m^2 g^{-1}, previously calcined at 723 K under O_2) were treated under vacuum (10^{-4} Torr $\approx 1.33 \times 10^{-2}$ Pa) overnight, at the desired temperature. Solvents (Prolabo) were distilled under nitrogen over sodium–benzophenone (pentane, hexane, heptane), P_2O_5 (methylene chloride) or $CaCl_2$ (acetone) and stored under argon on molecular sieves (4 Å). *cis*-Pent-2-ene, pent-1-ene (Aldrich), *trans*-2,5-dimethylhex-3-ene (Fluka) were stored on molecular sieves (4 Å); allyl bromide (Aldrich) was distilled prior use.

Synthesis of the Catalysts.—The catalysts were prepared at room temperature under argon using Schlenk-tube techniques. The pretreated inorganic oxides (typically 2 g) were impregnated with a solution of the complex. With **1**, *n*-hexane was used as solvent and the gas phase was analysed, after *ca.* 15 min of interaction, by gas chromatography (GC) using *n*-butane as an internal standard. With **2**, methylene chloride was used as solvent; HCl formed during the reaction was trapped by a NaOH solution. After *ca.* 30 min of reaction, acid back-titration of the excess alkali gave the amount of HCl released during the reaction. In all cases, the solids were washed with the appropriate solvent in order to remove unreacted complex, dried under vacuum and then stored at 248 K under argon (or vacuum) until the determination of their properties.

Determination of the Catalytic Properties.—All experiments of metathesis of *cis*-pent-2-ene were carried out under argon, at room temperature. Aliquots of the same solid sample, prepared as described above, were transferred under argon to a Pyrex batch reactor and suspended under magnetic stirring in *n*-hexane. *cis*-Pent-2-ene was introduced *via* a syringe. Analysis of the gas phase was performed on an Intersmat IGC FL chromatograph, equipped with a flame ionization detector and an Al_2O_3–KCl on fused-silica capillary column (50 m × 0.32 mm). The conversion of *cis*-pent-2-ene was calculated according to equation (4). The reactions of exchange between

$$\text{conversion} = \frac{2[\text{butenes}]}{[\text{butenes}] + [\text{pentenes}]} \times 100 \qquad (4)$$

the surface alkylidene and pent-1-ene, *trans*-2,5-dimethylhex-3-ene and allyl bromide respectively were performed under analogous conditions, but using *n*-heptane as solvent and *n*-pentane as internal standard. The reaction between the surface complexes and acetone was followed by GC analysis of the liquid phase (*n*-hexane : solvent) and using *n*-heptane as internal standard. Typically 0.1 cm^3 acetone was introduced on a sample with a content of *ca.* 10^{-4} mol tungsten.

*Carbon-*13 *CP MAS* (*Cross-polarization Magic Angle Spinning*) *NMR Studies.*—Solid-state NMR spectra were recorded on a Bruker MSL spectrometer, operating at 75.4 MHz and equipped with a double-bearing probe allowing spinning frequencies of 3–4 kHz. The conditions of cross polarization were a 5 ms contact time, 90° for ^1H = 6.2 μs. Typically 11 000 scans were accumulated with a delay of 5 s. Chemical shifts are given relative to external $SiMe_4$.

Results

We determined first which types of inorganic oxide(s) were able to react chemically with complexes **1** and **2**, with formation of a true surface-anchored complex. Next, we analysed the catalytic properties of these anchored complexes for the reaction of metathesis of *cis*-pent-2-ene. Finally, we selected the best catalytic systems in order to identify the active surface complexes.

Influence of the Nature of the Support on its Reactivity with Complexes 1 *and* 2 *and on the Catalytic Properties of the Resulting Solids.*—Four inorganic oxides were chosen, which present different surface acid–base properties, *e.g.* silica, alumina, niobia and silica–alumina.[6,12] For two of them, namely silica and niobia, the concentration and/or the nature of the surface functional groups were varied *via* the temperature (T/K) of evacuation of the solids, prior to reaction with the complexes.

When these four oxides are impregnated with a solution of either complex **1** or **2**, the liquid phase is instantaneously decolourized, while the solids, initially white, take up a colour (Table 1). In the case of SiO_2, this phenomenon is slow. With complex **1**, a yellow-orange powder, all the oxides become yellow, except $Nb_2O_5[573]$, which turns dark grey. With complex **2**, a purple powder, most solids take up a colour different from that of the precursor complex, *i.e.* either yellow (SiO_2, Nb_2O_5) or green (SiO_2–Al_2O_3). Only γ-Al_2O_3 takes up a colour similar to that of the precursor complex, *i.e.* purple. These observations suggest that, in most cases, dramatic changes of the ligand field around tungsten and/or the oxidation state of tungsten have occurred. The simultaneous evolution of neopentane or HCl, respectively, suggests that a true chemical reaction has indeed occurred between the complexes **1** and **2** and the different inorganic oxides.

The maximum amount of complex which can precisely react with a given surface, $M_xO_y[T]$, was determined from preliminary experiments using a large excess of precursor complex (Table 1). Thus, for all subsequent experiments, designed for the quantitative determination of the amount of gas released, the amount of precursor complex introduced on the inorganic oxide ($[W]_{in}$) was chosen below or close to these values.

With complex **1**, the amount of neopentane liberated comprised between 1.2 and 1.8 mol per mol $[W]_s$. This amount decreases only slightly as the temperature of pretreatment of the support increases (Table 1). The reaction of complex **2** with these same oxides releases only a small amount of HCl (0.2–0.5 mol per mol $[W]_s$), except with $SiO_2[473]$ for which a value close to 1.5 mol per mol $[W]_s$ is obtained.

The catalytic properties of some of these solids were determined at room temperature for the metathesis of *cis*-pent-2-ene. Complex **1**, inactive in solution, becomes active when supported on any of the four oxides studied [Fig. 1(*a*)]. The performances seem to be correlated mainly to the nature of the support itself, and to some extent to its degree of dehydroxylation (at least for Nb_2O_5 and SiO_2 in the range of tested T). This favourable effect of the support decreases as follows: SiO_2–$Al_2O_3[773] \approx Nb_2O_5[573] > Al_2O_3[673] \approx Nb_2O_5[393] \gg SiO_2[473] \approx SiO_2[773]$. With complex **2**, the influence of these same parameters is more dramatic [Fig. 1(*b*)]. Thus, the activity of supported **2** decreases as follows: SiO_2–$Al_2O_3[773] > Al_2O_3[673] > Nb_2O_5[573] > Nb_2O_5[413] \gg SiO_2[473, 773] = 0$. As far as activity is concerned SiO_2–$Al_2O_3[773]$ is the best support for both complexes, but the relevant catalysts are not selective: double-bond migration occurs even at low conversions, and consequently cross-metathesis reactions take place between pent-1-ene and pent-2-enes. Niobium oxide appears to be a good support in both cases; the catalytic activity is lower for the trichloroneopentylidyne complex, despite the presence of more electron-withdrawing ligands. Given these differences, we decided to study the niobia-supported systems in some more detail.

Characterization of Niobium-oxide-supported 1 *and* 2.—*Spectroscopic investigations.* The observed colour changes suggest that a true chemical reaction occurs between niobium oxide and complex **1** or **2**. We first tried to identify the surface species by IR and CP MAS NMR spectroscopies.

When complex **1** is introduced *in situ* on a disc of $Nb_2O_5[573]$, the vibrational ν(OH) band at 3693 cm^{-1}

Table 1 Qualitative characterization of the solids resulting from the reaction of complex **1** or **2** with different inorganic oxides

Inorganic oxide[T/K][a]	Complex	$[W]_{in}$[b] (%)	$[W]_{exp}$[b,c] (%)	Colour	Neopentane/ mol per mol $[W]_s$	HCl/ mol per mol $[W]_s$
SiO_2[473]	**1**	5.5	3.8	Yellow-orange	1.3	—
SiO_2[473]	**1**	9	6.2	Yellow-orange	*d*	—
SiO_2[473]	**2**	3.0	1.5	Yellow	—	1.5
SiO_2[773]	**1**	8	6.4	Yellow	*d*	—
SiO_2[773]	**1**	2	2.0	Yellow	1.2	—
SiO_2[773]	**2**	6	1.3	Yellow	—	0.3
γ-Al_2O_3[673]	**1**	0.4	0.4	Yellow	1.3	—
γ-Al_2O_3[673]	**2**	0.4	0.4	Purple	—	0.4
SiO_2–Al_2O_3[773]	**1**	9	5.5	Yellow	1.4	—
SiO_2–Al_2O_3[773]	**1**	5	5	Yellow	*d*	—
SiO_2–Al_2O_3[773]	**2**	3.2	3.1	Green	—	*d*
SiO_2–Al_2O_3[773]	**2**	1.5	1.5	Green	—	0.2
Nb_2O_5[393]	**1**	0.9	0.87	Beige	1.8	—
Nb_2O_5[393]	**2**	0.6	0.58	Beige	—	0.5
Nb_2O_5[573]	**1**	0.5	0.5	Dark grey	1.4	—
Nb_2O_5[573]	**1**	1.2	1.1	Dark grey	*d*	—
Nb_2O_5[573]	**2**	0.7	0.66	Yellow	—	0.2

[a] Temperature, T, of pretreatment of the inorganic oxide. [b] By weight. [c] Determined experimentally by elemental analysis. [d] Not determined.

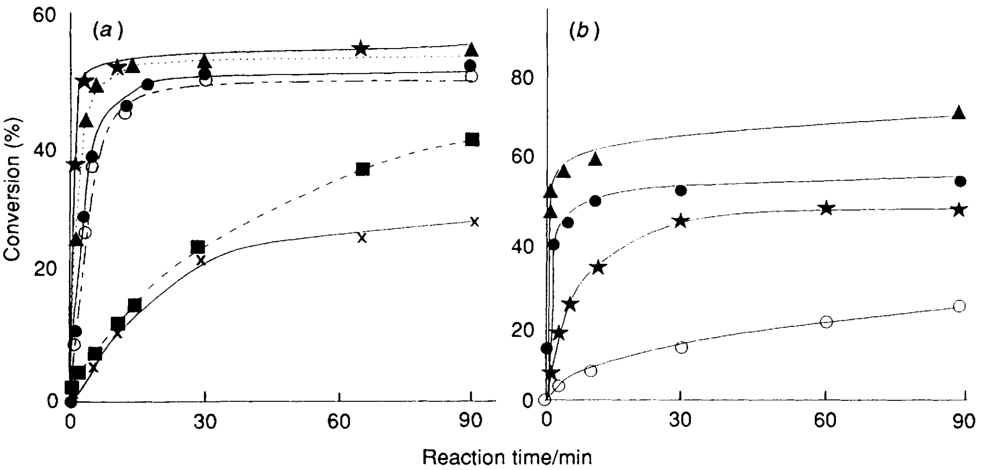


Fig. 1 Catalytic activity of complex **1** (*a*) and **2** (*b*), when supported on SiO_2–Al_2O_3[773] (▲), Nb_2O_5[573] (★), Nb_2O_5[393] (○), SiO_2[473] (■), SiO_2[773] (×) or Al_2O_3[693] (●). Experimental conditions: $[W]_s$: *cis*-pent-2-ene = 1 : 1000, solvent = *n*-hexane and T = 298 K

disappears instantaneously, while ν(CH) bands at 2950, 2902 and 2861 cm^{-1} and δ(CH) bands at 1464, 1388, 1324, 1263, 1233, 1195, 1153 and 1115 cm^{-1}, typical of neopentyl groups appear. Simultaneously, the IR spectrum of the gas phase reveals the presence of neopentane.[13]

Carbon-13 CP MAS NMR spectra were recorded on similar samples of complex **1** or **2** with Nb_2O_5[573]. With Nb_2O_5, the spectrum shows a broad peak at *ca.* δ 32. The possible presence of one or more of the three types of ligands, *i.e.* neopentyl, neopentylidene and neopentylidyne, around tungsten in different surface complexes hampers any reasonable assignment of the NMR peaks [Fig. 2(*a*)]. With **2**–Nb_2O_5[573] two signals, at δ 35 and 31, are observed [Fig. 2 (*b*)]. By comparison with the MAS NMR spectrum of an authentic sample of complex **2** [Fig. 2(*c*)], one of these signals (possibly that at δ 35) might be attributed to a CH_3 group (C_γ) of a neopentylidyne ligand; the other one may be assigned to a CH_3 group of either a neopentylidene or neopentyl ligand. No other signal could be detected. It must be emphasized that even in the case of unsupported complex **2** we could not detect, under our experimental conditions, any signal assignable to a C_α (*i.e.* a carbon in the α position to tungsten).

These data clearly indicate that full identification of the surface-grafted complexes cannot be achieved by spectroscopic techniques. They nevertheless confirm the participation of the Brönsted acidic surface hydroxyl groups to the surface reaction and the presence in all cases of molecular entities with a neopentyl 'backbone'.

Influence of the temperature [T] *of evacuation of niobia on* (*a*) *the amount of neopentane or* HCl *released during the impregnation step.* The reaction leading to the bonding of complexes **1** and **2** to the surface may involve either the alkylidyne ligand and/or the alkyl or even chlorine ligands respectively. In the first case, no gas evolution should occur, while in the second case liberation of neopentane or HCl respectively should take place. Quantitative analysis of the gas phase during impregnation of niobia by the solution of complex was thus performed and studied as function of T.

Analysis of the experimental data (Table 2) reveals that the amount of neopentane or HCl released during impregnation decreases as the temperature of pretreatment of Nb_2O_5 increases. This behaviour compares well with the variation of the concentration of Brönsted acid sites on the surface of Nb_2O_5 with temperature [Fig. 3(*c*)].

(*b*) *The catalytic activity for the metathesis of* cis-*pent-2-ene.* The surface acidic properties of niobia vary with the tem-

Table 2 Characterization of the surface complexes resulting from the reaction of complex **1** or **2** with $Nb_2O_5[T]$. Influence of the evacuation temperature T/K of niobia

Complex	$Nb_2O_5[T]$	$[W]^a$ (%)	Neopentane or HCl/ mol per mol $[W]_s$	2,4,4-trimethylpent-2-ene^b/ mol per mol $[W]_s$	Initial turnover rate^c/ min^{-1}
1	393	0.87	1.8	0.2	100
1	473	0.41	1.3	*d*	*d*
1	573	0.51	1.4	0.3	370
1	673	0.54	1.0	0.2	170
2	393	0.58	0.5	0.5	10
2	473	0.48	0.1	0.65	*d*
2	573	0.66	0.2	0.8	60
2	673	0.39	—	0.6	20

^{a} By weight; determined by elemental analysis. ^{b} Results from a pseudo-Wittig-type reaction of the surface complex with acetone. ^{c} For metathesis of *cis*-pent-2-ene, $[W]_s$: [olefin] = 1 : 1000, solvent = *n*-hexane and T = 298 K. ^{d} Not determined.

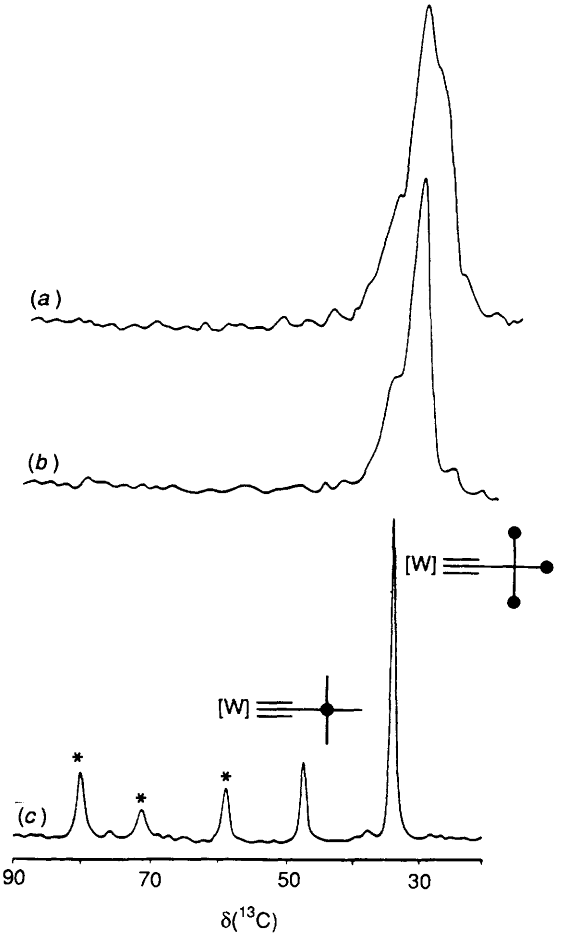


Fig. 2 Carbon-13 CP MAS NMR spectra of (*a*) $1\text{-}Nb_2O_5[573]$, (*b*) $2\text{-}Nb_2O_5[573]$ and (*c*) pure **2**. Asterisked peaks are attributed to dme

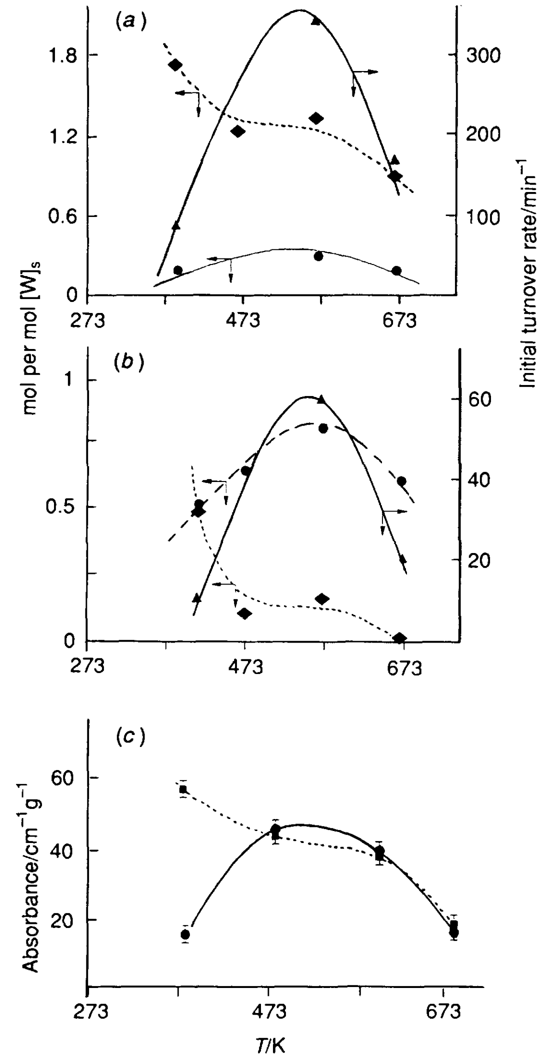


Fig. 3 Variation with the evacuation temperature (T) of niobia of the catalytic activity for *cis*-pent-2-ene metathesis (▲), the concentration of neopentylidene-bearing species (●) and the amount of evolved gases (◆) for $1\text{-}Nb_2O_5$ (*a*) and $2\text{-}Nb_2O_5$ (*b*). Variation of the concentration of surface Brönsted (1543 cm^{-1}) (■) and Lewis (1448 cm^{-1}) (●) acid sites with T (*c*) (from ref. 10)

perature of pretreatment.[10,14] This latter parameter may affect not only the reaction of niobia with complex **1** or **2**, but also the catalytic properties of these solids.

All the samples were prepared with a tungsten concentration close to 0.5% (by weight), *i.e.* a concentration far from total surface coverage (no unreacted complex should be present, see Table 1). The catalytic activities of these samples were studied under mild conditions, as described in the Experimental section. Initial turnover rates are given in Table 2 as a function of T. For both niobia-supported complexes, a maximum activity is observed when niobia is pretreated at *ca.* 573 K [Fig. 3(*a*) and 3(*b*)]. A very similar variation is observed for the Lewis-acid concentration on the surface of Nb_2O_5 [Fig. 3(*c*)]. It should be mentioned that, whatever the temperature of pretreatment, the activity of **1**-niobia is larger than that of **2**-niobia, despite the presence of electron-withdrawing ligands with **2**.[15]

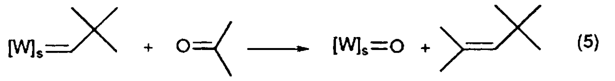
None of these data allows a precise description of the surface complexes. Their reactivity towards reactants, specifically of metal alkylidene complexes, such as acetone and olefins, was thus studied.

Table 3 Chemical reactivity of the surface complexes resulting from the reaction between complex **1** and $Nb_2O_5[573]$ or $SiO_2[473]$ and from the reaction between complex **2** and $Nb_2O_5[573]$

Complex	Support [*T*]	[W]	[Neopentylidene][a]/ mol per mol $[W]_s$	[3,3-Dimethylbut-1-ene][b]/ mol per mol $[W]_s$	[3-methylbut-1-ene][c]/ mol per mol $[W]_s$	Initial turnover rate[d]/min^{-1}
2	$Nb_2O_5[573]$	0.66	0.8	0.4	0.01	60
1	$Nb_2O_5[573]$	0.5	0.3	0.1	0.3	370
1	$SiO_2[473]$	3.8	0.5	0.15	0.03	15

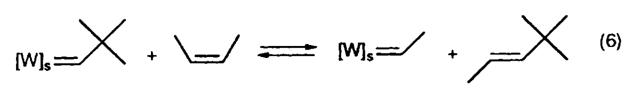
[a] Estimated from the amount of 2,4,4-trimethylpent-2-ene liberated by a Wittig-type reaction with acetone. [b] Product of allyl bromide reaction. [c] Product of *trans*-2,5-dimethylhex-3-ene reaction. [d] For metathesis of *cis*-pent-2-ene, $[W]_s$:[olefin] = 1 : 1000, solvent = *n*-hexane and *T* = 298 K.

(*c*) *The reactivity of* **1**-*niobia and* **2**-*niobia with acetone.* If the initial active site is a surface tungsten complex bearing a neopentylidene ligand, the catalytic activity may be correlated to the initial concentration of alkylidene ligands. The initial concentration of neopentylidene fragments, resulting from the reaction between $Nb_2O_5[T]$ and complex **1** or **2** respectively, was determined from the amount of 2,4,4-trimethylpent-2-ene liberated by the reaction of the relevant solids with acetone [equation (5)]. This Wittig-type reaction may not be quantitative, although yields comprised between 82 and 100% are generally reported.[16]


(5)

The results obtained with complexes **1** and **2** differ significantly; whatever *T*, the neopentylidene concentration appears to be 2–3 times larger with **2**-niobia than with **1**-niobia (Table 2). But, its variation with *T* is in any case rather smooth, a small maximum being observed in the 473–573 K temperature domain (Fig. 3). Thus, initial activity and concentration of neopentylidenetungsten complexes are not directly proportional; this suggests that different types of surface-active complexes, which do not necessarily directly involve an initially present neopentylidene ligand, may be present on the surface.

Reactivity of **1**-*niobia and* **2**-*niobia towards olefins.* The first step of any reaction of metathesis catalysed by a neopentylidene complex is the reaction of exchange of the neopentylidene ligand by the alkylidene fragment resulting from the olefin [equation (6)]. We first studied the behaviour of **1**-niobia and **2**-niobia towards pent-1-ene and allyl bromide, by analysing the first formed products. In both cases, 3,3-dimethylbut-1-ene is formed [equations (7) and (8)]. Only in the case of allyl bromide is the amount of 3,3-dimethylbut-1-ene large enough to be quantified (Table 3). With pent-1-ene, self metathesis takes place; in the case of allyl bromide, no such products were detected.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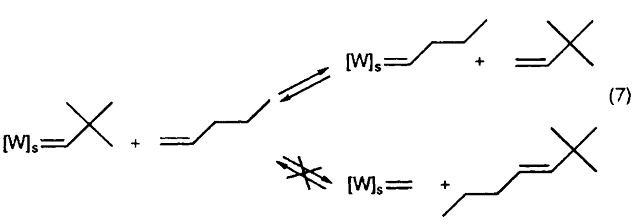
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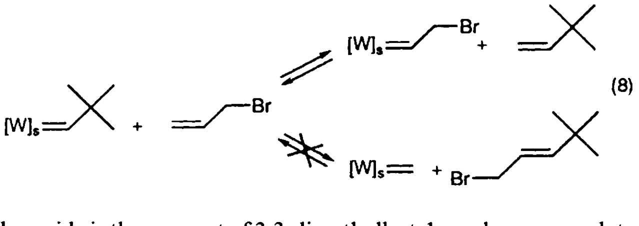
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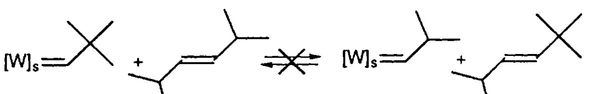
With *trans*-2,5-dimethylhex-3-ene, no 2,2,5-trimethylhex-3-ene, the product expected for metathetical exchange of this olefin with a neopentylidene ligand, could be detected [equation (9)] which may be related to the bulkiness of this olefin.


(9)

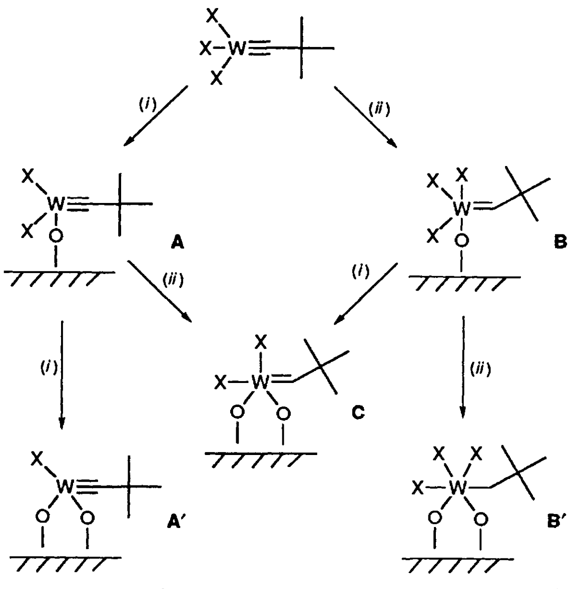
However, with complex **1**, the formation of several other olefins, namely 3-methylbut-1-ene (by far the major product), isobutene, 2,4-dimethylpent-2-ene, 5-methylhex-2-ene and traces of propene were observed. These unexpected results suggest that this bulky olefin reacts with a surface complex in a manner which does not involve a metathetical exchange of the olefin with the neopentylidene ligand. Among the mechanisms of formation of the first metallocarbene so far proposed in the literature,[3] the π-allyl mechanism, previously described for the system $ReO_3(Me)–Nb_2O_5$,[17] accounts for all the products. This mechanism implies that a reduced tungsten species [tungsten (⩽IV)] is formed initially by reaction between the precursor neopentylidynetungsten complexes and the surface of the niobia.

Characterization of Silica-supported **1** *and* **2**.—Under our experimental conditions, both **1**–SiO_2 and **2**–SiO_2 are poor catalysts or even inactive for the metathesis of *cis*-pent-2-ene (Fig. 1). Nevertheless, the reactivity of **1**–$SiO_2[473]$ towards acetone indicates the presence of a reasonable concentration of neopentylidenetungsten surface complexes, an amount apparently slightly larger than with **1**–$Nb_2O_5[573]$ (Table 3). The reactivity of these same solids towards allyl bromide is also similar to that of **1**–$Nb_2O_5[573]$, but the reactivity of **1**–SiO_2 and **1**–Nb_2O_5 towards *trans*-2,5-dimethylhex-3-ene is dramatically different, only a very small amount of 3-methylbut-1-ene is formed with **1**–$SiO_2[474]$. This is about ten times less than with **1**–$Nb_2O_5[573]$, but comparable to **2**–$Nb_2O_5[573]$.

Considering these data (Table 3), the activity of these supported tungsten complexes seems to be correlated to the concentration of the surface species giving rise to 3-methylbut-1-ene when treated with *trans*-2,5-dimethylhex-3-ene. Accordingly, the initially formed neopentylidene ligand would not necessarily be involved in the catalytic reaction.

Discussion

The neopentylidyne complexes $[W(CCMe_3)X_3]$ become (X = neopentyl) or are more (X = Cl) active metathesis catalysts when supported on inorganic oxides such as silica–alumina, niobia or alumina. Under the same experimental conditions, silica is only a very poor support. However, Weiss and Lössel,[18] who were the first to immobilize these same complexes on silica, obtained good catalysts for the metathesis of oct-1-ene at 344 or 395 K, when using a highly dehydroxylated silica (silica[1173]).



Scheme 1 Some of the possible complexes formed by reaction of complex **1** or **2** with the surface of inorganic oxides. Step (*i*) involves the electrophilic attack of a surface proton on an X ligand liberating HX, whereas step (*ii*) involves protonation of the carbynic W≡C bond by surface Brönsted acid

The formation of neopentane or HCl as the result of the complex–support interaction indicates that at least one type of *chemical* reaction takes place, which must be an electrophilic attack of surface protons on an X ligand [equation (10)]. This

$$X_3W(\equiv CCMe_3) + x\,H{-}O{-}\wr \longrightarrow (\wr{-}O)_xW(\equiv CCMe_3)X_{3-x} + x\,HX \qquad (10)$$

type of reaction leads to the anchoring of the complexes to the surface through a covalent bond between the tungsten atom and a surface oxygen. Because x, the number of moles of HX liberated per mole $[W]_s$, is not an integer whatever the support, one must consider that, even if reaction (10) is the only type of surface reaction, then at least two types of surface complexes are formed, differing by the number of bonds to the surface. Thus, with HX = neopentane, x is larger than 1; this suggests that reaction (10) may lead to at least two surface complexes, such as **A** and **A′** (Scheme 1). With X = Cl, x is smaller than 1 and a second type of reaction certainly occurs on the surface, which does not involve the chlorine ligands.

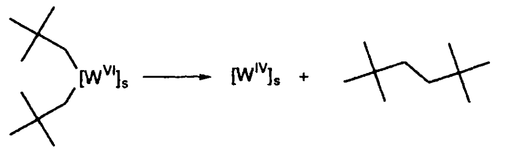
This latter hypothesis is corroborated by the following complementary observations. The Wittig-type reactivity of the supported complexes towards acetone, their capacity to exchange metathetically with olefins such as allyl bromide strongly suggest that among these surface complexes, some bear a neopentylidene ligand. The formation of this ligand can result from the protonation of the initial carbynic bond, W≡CR, by surface Brönsted acids [equation (1)]. This reaction leads also to tungsten complexes, covalently bonded to surface oxygen atoms (species **B**, Scheme 1).

When the surface complex bears at least two neopentyl ligands, an α-H abstraction may be envisaged, with elimination of neopentane [equation (3)]. Such surface complexes are not represented in Scheme 1 for sake of simplicity. If complex **1** was directly transformed *via* reaction (3) (perhaps mediated by the surface), then the resultant alkylidene complex would not be bonded to the surface. As none of the surface complexes could be removed by a solvent, reaction (3) can only involve a complex already grafted to the surface by another type of reaction, such as, for example, reactions (1) or (10).

It appears that in all the cases studied, and more specifically on niobia, at least two different types of reactions must occur on the surface. Their relative importance is a function of the degree of hydroxylation of the surface, of the surface acidity (type and strength) and of the nature of the ligand X. Scheme 1 represents most of the possible types of surface complexes which can result from such reactions. The formation of **A′**, **B′** and **C** relies on the existence of neighbouring hydroxyl groups, a situation which may be favoured on the less dehydroxylated surfaces.

The comparison of the reactivity of **1**–Nb_2O_5[573] and **2**–Nb_2O_5[573] with that of **1**–SiO_2[473] towards acetone, allyl bromide and *trans*-2,5-dimethylhex-3-ene respectively leads to the following observations. (*i*) The most active catalyst, *i.e.* **1**–Nb_2O_5[573] shows a low concentration of poorly exchangeable neopentylidene ligands, but the largest amount of 'reduced [W]' surface species; (*ii*) although the amount of exchangeable neopentylidene is large for **2**–Nb_2O_5[573], the catalytic activity of the solid is poor. This seems to be correlated to the absence of 'reduced [W]' species; and (*iii*) the correlation between the concentration of reduced [W] surface entities and catalytic activity seems to hold for **1**–SiO_2[473].

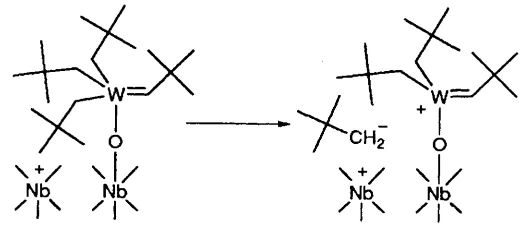
The process of formation of such 'reduced' species is not yet fully understood. It may result from a reaction of reductive coupling of neopentyl ligands with elimination of 2,2,5,5-tetramethylhexane [equation (11)], a reaction which can only



(11)

occur with complex **1** as precursor; this well known reaction occurs during the synthesis of **1**.[11] On the surface, complexes **A**, **B**, **B′** and **C** may undergo this type of reduction. Small amounts of dineopentane have been detected during impregnation of Nb_2O_5[573] with **1**, but could not be quantified.

The supported catalytic systems described here may nevertheless be even more complicated. Indeed, none of the species so far proposed on the basis of our experimental results and on the reported chemical reactivity of complexes **1** and **2** towards different reactants, can be reconciled with the observed relation between catalytic activity and concentration of surface Lewis-acid sites on niobia. Niobia, when compared to oxides such as silica–alumina for example, presents very strong Lewis-acid sites in the low-temperature domain (373–573 K) (this occurs only above 773 K for silica–alumina). Such strong Lewis-acid sites may be able to induce the heterolytic dissociation of a W–C bond resulting in the transfer of a neopentyl ligand from W to the Nb^{5+} Lewis-acid site. This reaction would lead to the formation on the surface of a cation-like tungsten(VI) complex, a species co-ordinatively and electronically unsaturated and thus a potential active site [equation (12)]. This type of reaction



(12)

takes place when $[ThMe_2(\eta^5\text{-}C_5Me_5)_2]$ is treated with a highly dehydroxylated alumina (Al_2O_3[1223]).[19] In the present case, the formation of cationic tungsten surface complexes would help to explain the variation in activity of **1**–Nb_2O_5 with the temperature of dehydroxylation, and its correlation with the number of surface Lewis-acid sites. It would also account for the low activity of **2**–Nb_2O_5 (Cl not transferred) and the poor catalytic properties of silica-supported **1** and **2**: indeed, silica does not present surface Lewis sites in the whole range of temperatures of dehydroxylation studied here (< 773 K). Identification of such cationic tungsten surface complexes is currently under investigation.

Conclusion

The interaction of the alkylidynetungsten(VI) complexes **1** and **2** with the surface of inorganic oxides such as alumina, niobia and silica–alumina, which all present surface acid sites, leads to supported molecular complexes, presenting good catalytic activities for the metathesis of *cis*-pent-2-ene. A variety of different surface complexes are formed, making it difficult to determine unambiguously the precise nature of the precursor(s) of the active site(s). Surface Brönsted-acid sites are involved in the process of grafting of the complexes to the surface and/or intervene in the formation of surface neopentylidenetungsten complexes. Surface Lewis-acid sites, such as Nb^{5+} for example, most probably induce the formation of a tetravalent cationic neopentylidenetungsten(VI) complex, which may well be the precursor of the most active species, owing to its high electronic and co-ordinative unsaturation. Partial reduction of tungsten (VI) must be considered, but its mechanism of formation is still not clear. These studies clearly reveal the influence of the support on the catalytic properties of supported **1** and **2**, by orienting the surface reaction preferentially towards one or the other surface complex. This is a well known situation in heterogeneous catalysis, although not always well understood.

Acknowledgements

The authors are grateful to Dr. J. L. Couturier for the generous donation of samples of the tungsten complexes and to Dr. F. Lefebvre for the MAS NMR experiments and to them both for fruitful discussions.

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Received 30*th December* 1993; *Paper* 3/07590G