Silica-supported alkylidene complexes: their preparation, characterization and reactivity, especially towards olefins

Marcel C. Beaudoin, Omisola Womiloju, Anqiu Fu, Jamila Amor Nait Ajjou, Gordon L. Rice, Susannah L. Scott*

Department of Chemistry, Center for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

Abstract

When silica is employed as a bidentate ligand to bis(alkyl) complexes of the early first-row transition metals, rare terminal alkylidene fragments are readily formed and stabilized. These materials have the empirical formula $(\equiv SiO)_2M=CHEMe_3$, where M is Ti, V, or Cr and E is C or Si, incorporating two covalent interactions with oxygens of the silica surface which serve to immobilize the grafted complexes. The silica-supported alkylidene complexes undergo several typical reactions, including electrophilic cleavage with H^+ and Br_2, metathetical exchange with acetone and styrene, and addition of a silane. Reaction with ethylene leads to oligomerization/polymerization, for which the material with M = Cr is particularly effective. The mechanism of initiation of polymerization, as well as the influence of the silica support (fumed versus precipitated) on the composition of the active sites, is discussed.
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1. Introduction

Many examples of alkylidene ligands bound to high-valent complexes of Mo, W, Ta and Nb are extant in the literature, and a large number have been characterized by X-ray diffraction as well as spectroscopy [1,2]. Alkylidene complexes of other transition metals, while not isolated, are believed to be formed in situ during activation of inorganic catalyst precursors with alkylating agents. The utility of well-defined complexes has been extensively demonstrated in the polymerization of alkynes [3], metathesis polymerization of alkenes [4], and olefination of ketones [3].

The demonstration of the alkylidene ligand as an active site for olefin activation has led to wide acceptance of the Chauvin mechanism for olefin metathesis [5]. There are also intriguing possibilities for the participation of alkylidene ligands in Ziegler–Natta polymerization [6], although evidence for such systems is scarce [7]. The formation of alkylidene ligands on heterogeneous catalysts used for metathesis (oxide-supported Mo, W or Re) [8,9] and polymerization (oxide-supported Cr) [10,11] has been suggested, although in most cases such ligands are difficult to detect since the fraction of active sites is very low, typically ≤1% [12].

One versatile route to molecular alkylidene complexes is thermally-induced α-H abstraction from a bis(alkyl) complex [2,13–15]. During our investigation of bis(alkyl) complexes of Ti(IV), V(IV) and

* Corresponding author. Fax: +1-613-562-5170.
*E-mail address:* sscott@science.uottawa.ca (S.L. Scott).

Cr(IV) supported by silica as a ligand, we discovered such a family of α-H abstraction reactions. They give rise to stable terminal alkylidene complexes, rare in the first-row transition series, which undergo reactions characteristic of high-valent molecular alkylidene complexes of their heavier congeners, as well as some which are less well-documented in solution but which are potentially relevant to mechanisms in heterogeneous catalysis, such as initiation of olefin oligomerization and polymerization.

2. Results and discussion

2.1. Preparation and characterization of silica-supported bis(alkyl) metal complexes

The homoleptic metal alkyls MR_4 (where M is Ti or Cr and R is CH_2CMe_3; M is V or Cr and R is CH_2SiMe_3) react at room temperature with the hydroxyl groups present on the surface of a non-porous Aerosil silica partially dehydroxylated at $200\,^\circ C$. The resulting material contains alkylmetal fragments grafted onto the silica surface, as shown by their in situ IR spectrum, seen for $M = Cr$ and $R = CH_2CMe_3$ in Fig. 1A and B (curve a). The appearance of vibrations characteristic of the hydrocarbon modes of the organic ligands is accompanied by the disappearance of the band at $3747\,cm^{-1}$ assigned to the $\nu(O-H)$ vibration of mutually non-interacting surface hydroxyl groups, designated $\equiv SiOH$. At the same time, RH is liberated into the gas phase, where it was confirmed to be the sole volatile product of the reaction. The surface-modified silicas acquire colors characteristic of their grafted organometallic fragments, viz. yellow, green and orange for $M = Ti$, V and Cr, respectively.

When the experiment is performed as a gas–solid reaction in which the organometallic complex is sublimed in vacuo onto a silica powder or self-supporting disk, the reaction occurs with a well-defined and reproducible stoichiometry (Table 1). The amount of protonated ligand RH liberated into the gas phase represents two equivalents for each metal complex grafted onto the silica surface, Eq. (1):

$$2(\equiv SiOH) + MR_4 \rightarrow (\equiv SiO)_2MR_2 + 2RH \qquad (1)$$
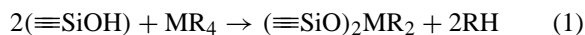
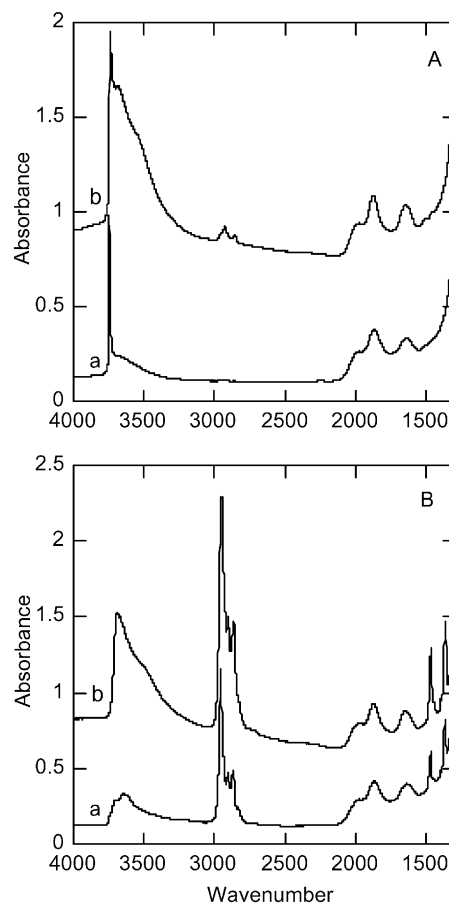This 2:1 grafting stoichiometry was previously reported by several groups for the reactions of MR_4

Fig. 1. IR spectra of silicas modified by $Cr(CH_2CMe_3)_4$. Frame (A) shows the spectra of (a) Aerosil-200 and (b) Sylopol-952, both partially dehydroxylated at $200\,^\circ C$. Frame (B) shows the spectra of the same samples after reaction with an excess of the organochromium reagent and desorption of unreacted material.

($M = Ti$, Zr, Hf; R = allyl, neosilyl, neopentyl, norbornyl, benzyl) on pyrogenic silicas pretreated at $200\,^\circ C$ [16–19], and contrasts with the 1:1 stoichiometry reported for reactions on such silicas treated at $400\,^\circ C$ or above [17,20–24]. On this basis, Ballard speculated that the majority of hydroxyl groups on the $200\,^\circ C$ silica surface do not occur randomly, but rather are distributed in pairs [17]. He also observed that the paired structure is lost once the silica is heated to $450\,^\circ C$, upon which the grafting stoichiometry changes to give supported complexes with the formula $\equiv SiOMR_3$. Others have argued that the observation of an overall 2:1 stoichiometry implies only an average

Table 1
Stoichiometry of grafting and thermolysis of Aerosil-200-supported organometallic complexes[a]

Molecular complex	Products of grafting[b]		Products of thermolysis[b]
	RH $(mmol\,g^{-1})^{c,d}$	M $(mmol\,g^{-1})^{d}$	RH $(mmol\,g^{-1})^{c,d}$
$Ti(CH_2CMe_3)_4$	0.83 ± 0.03 (13)	0.42 ± 0.02 (8)	0.41 ± 0.03 (10)
$V(CH_2SiMe_3)_4$	0.79 ± 0.02 (5)	0.39 ± 0.01 (5)	0.37 ± 0.04 (15)
$Cr(CH_2SiMe_3)_4$	0.71 ± 0.01 (3)	0.37 ± 0.01 (3)	0.34 ± 0.01 (11)
$Cr(CH_2CMe_3)_4$	0.71 ± 0.01 (6)	0.37 ± 0.01 (6)	0.34 ± 0.01 (29)

[a] The silica was partially dehydroxylated by thermal treatment in vacuo at 200 °C, resulting in an accessible OH content of 0.86 mmol g^{-1}.

[b] Errors are standard deviations. Values in parentheses are the number of independent experiments on which each measurement was made. Only experiments in which complete reaction of the surface hydroxyls was achieved are averaged, although it was established that neither the grafting nor the thermolysis stoichiometric ratios (RH/M) change at lower metal loadings.

[c] RH represents the only hydrocarbon product detected, either CMe_4 or $SiMe_4$.

[d] Values are normalized per gram of silica.

composition $(\equiv SiO)_2MR_2$, with important contributions from $\equiv SiOMR_3$ and $(\equiv SiO)_3MR$ [23,25].

We observed the grafting stoichiometry shown in Eq. (1) regardless of metal loading on Aerosil-200 silica, up to a maximum of ca. 2 wt.% M. The surface reaction is self-limiting, i.e. metal loadings above 2 wt.% (ca. 0.4 mmol g^{-1}) were not achieved, and experiments in which more MR_4 was added resulted in later desorption of unreacted MR_4 from the silica surface to a liquid N_2 cold trap. These results imply that grafting occurs exclusively on surface hydroxyl sites, since the number of accessible hydroxyl sites on this silica (0.86 mmol g^{-1}) is close to 2 M.

Silica-supported complexes derived from VR_4 and CrR_4 are paramagnetic and give no observable ^{13}C CP/MAS spectra. However, it was possible to derive magnetic moments for the surface organometallic fragments from variable temperature magnetic susceptibility measurements on the metal-modified silicas. Both $(\equiv SiO)_2V(CH_2SiMe_3)_2$ and $(\equiv SiO)_2Cr(CH_2CMe_3)_2$ showed Curie–Weiss behavior down to 4 K. The values derived for μ_{eff} are 1.57 and 2.68 B.M., respectively, consistent with magnetically isolated d^1 and d^2 sites. The ^{13}C CP/MAS spectrum for diamagnetic $(\equiv SiO)_2Ti(CH_2CMe_3)_2$ shows the methylene, quaternary and methyl carbons at 112, 35 and 32 ppm (Fig. 2). The spectrum is similar to those reported for $\equiv SiOM(CH_2CMe_3)_3$ (M = Ti [24], Zr [20], Hf [21]), although in those cases the methylene carbon was not detected. The ^{29}Si CP/MAS spectrum of $(\equiv SiO)_2Ti(CH_2CMe_3)_2$ shows no peak due to $\equiv SiNp$, confirming the absence of neopentyl transfer to silicon atoms of the surface during grafting.

2.2. Formation of silica-supported alkylidene complexes

Each of the silica-supported bis(alkyl) metal complexes is stable at room temperature provided it is scrupulously protected from air. However, each undergoes a thermal transformation in vacuo resulting in the evolution of a further equivalent of RH (Table 1). These reactions occur with a precise stoichiometry, regardless of the loading of the metal complex on silica, and argue strongly for compositional uniformity of the supported organometallic fragments. Since, at full loading, virtually no accessible hydroxyls remain, and since the presence of strong metal–oxygen bonds to the surface effectively prohibits mobility of
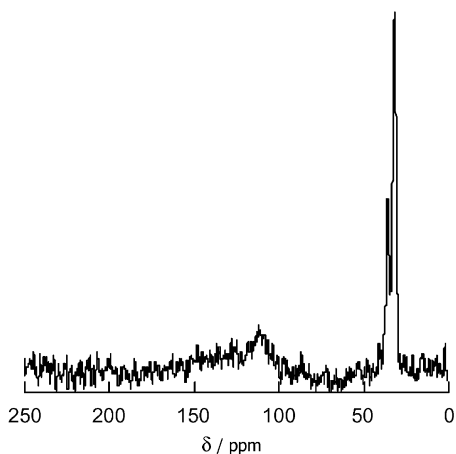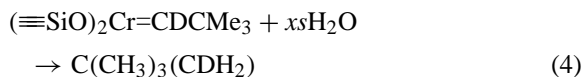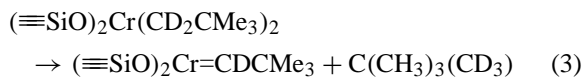

Fig. 2. ^{13}C CP/MAS NMR spectrum of $(\equiv SiO)_2Ti(CH_2CMe_3)_2$ (1.2 wt.% Ti).

the supported organometallic fragments, the thermal transformation is inferred to be intramolecular. Furthermore, we assert that it consists of α-H abstraction to generate essentially quantitatively the corresponding silica-supported alkylidene complexes (Eq. (2)):

$$(\equiv SiO)_2M(CH_2EMe_3)_2$$
$$\rightarrow (\equiv SiO)_2M=CHEMe_3 + EMe_4 \quad (E = C, Si) \tag{2}$$
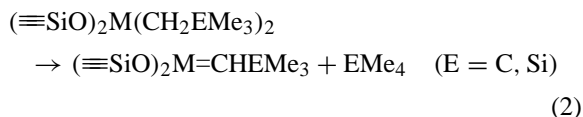
Such reactions are analogous to the formation of transient neopentylidene complexes deduced from isotope labeling studies [26] and predicted by calculation [27] for thermolysis of $Ti(CH_2CMe_3)_4$. Other mechanisms of decomposition of the molecular complex, such as γ-H abstraction and Ti–C homolysis, are calculated to have higher barriers [28] and have been ruled out experimentally [26]. In contrast, thermolysis of $Cr(CH_2CMe_3)_4$ has been suggested to proceed via γ-H abstraction to give a transient chromacyclobutane intermediate [29]. Additional evidence implicating reaction at the α-H was therefore sought for M = Cr. An isotope-labeling experiment in which the α-H atoms of $(\equiv SiO)_2Cr(CH_2CMe_3)_2$ were replaced by D, via grafting of $Cr(CD_2CMe_3)_4$, and subsequent thermolysis, produced neopentane identified by GC/MS as predominantly $C(CH_3)_3(CD_3)$ (Eq. (3)) [30]. Protonolysis of the presumed $(\equiv SiO)_2Cr=CDCMe_3$ product with water vapor yielded the expected $C(CH_3)_3(CDH_2)$ (Eq. (4)):

$$(\equiv SiO)_2Cr(CD_2CMe_3)_2$$
$$\rightarrow (\equiv SiO)_2Cr=CDCMe_3 + C(CH_3)_3(CD_3) \tag{3}$$

$$(\equiv SiO)_2Cr=CDCMe_3 + xsH_2O$$
$$\rightarrow C(CH_3)_3(CDH_2) \tag{4}$$

Similarly, reaction of $(\equiv SiO)_2Cr(CH_2CMe_3)_2$ with DCl gave mostly $C(CH_3)_3(CH_2D)$, while treatment of $(\equiv SiO)_2Cr=CHCMe_3$ gave mostly $C(CH_3)_3(CD_2H)$ (Eq. (5)):

$$(\equiv SiO)_2Cr=CHCMe_3 + xsDCl$$
$$\rightarrow C(CH_3)_3(CHD_2) \tag{5}$$
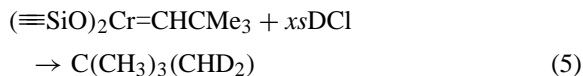
As well, electrophilic cleavage of the neopentylidene ligand with Br_2 yielded $C(CH_3)_3(CBr_2H)$ (Eq. (6)):

$$(\equiv SiO)_2Cr=CHCMe_3 + xsBr_2$$
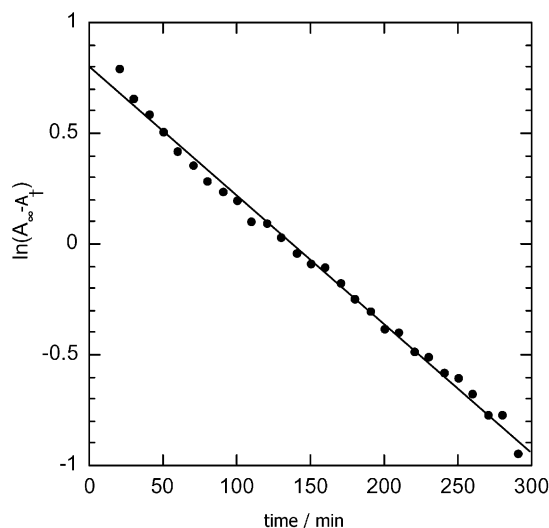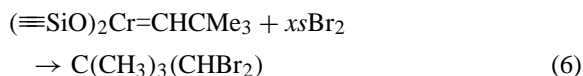$$\rightarrow C(CH_3)_3(CHBr_2) \tag{6}$$

Fig. 3. Kinetics of evolution of CMe_4 from $(\equiv SiO)_2$ $Ti(CH_2CMe_3)_2$ at $70\,^\circ C$, monitored by integrating the absorbance of the $\nu(C–H)$ region in the gas phase IR spectrum above the modified silica. The line is the fit to the linearized first-order integrated rate equation.

The α-H abstraction reactions of $(\equiv SiO)_2M(CH_2 EMe_3)_2$ occur at characteristic temperatures, depending on the identities of M and E. Each of the reactions exhibits first-order kinetic behavior, shown for M = Ti in Fig. 3, as expected for an intramolecular transformation. Rate constants were measured by following the evolution of hydrocarbon RH in the gas phase by in situ IR spectroscopy. The values obtained for α-H abstraction/elimination at ca. $70\,^\circ C$ are $k = 1.93 \times 10^{-4}$, 1.10×10^{-4}, 0.90×10^{-4} and ca. $0.2 \times 10^{-4}\,s^{-1}$ for $(\equiv SiO)_2V(CH_2SiMe_3)_2$, $(\equiv SiO)_2Ti(CH_2CMe_3)_2$, $(\equiv SiO)_2Cr(CH_2CMe_3)_2$ and $(\equiv SiO)_2Cr(CH_2SiMe_3)_2$, respectively. The rate constant for thermolysis of $(\equiv SiO)_2Cr(CD_2CMe_3)_2$ at this temperature is $0.28 \times 10^{-4}\,s^{-1}$, yielding a kinetic isotope effect $k_H/k_D = 3.2$. This effect is temperature-dependent [31], implying a multi-step mechanism for the transformation where M = Cr.

Similar reactions were not observed for the complexes $\equiv SiOM(CH_2EMe_3)_3$, which show much greater thermal stability than their bis(alkyl) analogues. We speculate that greater metal electrophilicity in the bis(siloxide)-substituted complexes may facilitate α-H abstraction, however, steric effects

cannot be ruled out. Also, coordination of an adjacent siloxane ligand $\equiv Si_2O$ to $(\equiv SiO)_2M(CH_2EMe_3)_2$ may enhance the rate of formation of the alkylidene complex.

IR spectra of the silica-supported metal alkylidenes are not diagnostic since no especially low frequency vibration was detected for the C_α–H stretching mode [32] (suggesting that the supported complexes are not so electron-deficient as their empirical formula $(\equiv SiO)_2M=CHEMe_3$ implies, vide infra). However, in each case, the integrated absorbance of the C–H vibrations decreased by 50%, consistent with the loss of one alkyl ligand. No $\nu(M=C)$ vibration was identified due to the high absorbance of the silica support below $1300\,cm^{-1}$. The magnetic moments of $(\equiv SiO)_2V=CHSiMe_3$ and $(\equiv SiO)_2Cr=CHCMe_3$ were measured to be 1.63 and 2.77 B.M., respectively, confirming that the oxidation states and mononuclearity of the supported metal alkylidenes remain unchanged from that of their precursors $(\equiv SiO)_2M(CH_2EMe_3)_2$.

The natural abundance ^{13}C CP/MAS NMR spectrum of $(\equiv SiO)_2Ti=CHCMe_3$ does not display any new low field signal attributable to the alkylidene carbon. This finding is similar to a previous report for a silica-supported Ta neopentylidene complex [33], and is presumably due to its low abundance, low cross-polarization efficiency and rigidity of the alkylidene carbon.

## 2.3. Reactions of silica-supported alkylidene complexes

Isolable high-valent alkylidene complexes of the early first-row transition metals are relatively rare [1,34–38]. Their reactivity has thus been much less investigated compared to heavier congeners. However, there are many "characteristic" reactions of metal alkylidenes of the second and third-row metals, which are considered diagnostic of M=C functionality [32]. The degree of resemblance between these molecular complexes and silica-supported alkylidene complexes was therefore explored through reactivity.

Reactions of silica-supported alkylidene complexes with electrophiles such as H^+ and Br_2 are described earlier. The pseudo-Wittig reaction of $(\equiv SiO)_2$ $Cr=CHCMe_3$ with acetone yields 2,5,5-trimethyl-

pent-1-ene [39] (Eq. (7)):

$$(\equiv SiO)_2Cr=CHCMe_3 + xsMe_2C=O$$
$$\rightarrow Me_2C=CHCMe_3 \qquad (7)$$
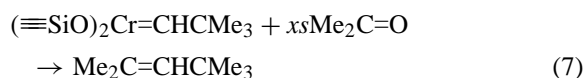
Olefin metathesis products neohexene and trimethylvinylsilane were detected upon reaction of $(\equiv SiO)_2$ $M=CHEMe_3$ (M = V, Cr) with styrene (Eq. (8)):

$$(\equiv SiO)_2M=CHEMe_3 + xsPhCH=CH_2$$
$$\rightarrow H_2C=CHEMe_3 \quad (E = C, Si) \qquad (8)$$
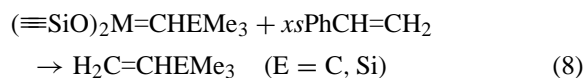
The initial surface organometallic product is presumably the benzylidene complex $(\equiv SiO)_2M=CHPh$, which was not isolated since it appears to undergo subsequent reaction with styrene.

In contrast, reaction of $(\equiv SiO)_2M=CHEMe_3$ with excess ethylene yielded no olefin metathesis products, consistent with the observations made for reactions of Ta(V) and Cr(VI) neopentylidene complexes [35,40]. Ethylene uptake was instead characterized by oligomerization/polymerization. The nature of the reaction was strongly metal-dependent: for M = Cr, polymerization was rapid and extensive, whereas ethylene uptake self-terminated after addition of ca. 40 eq. C_2H_4 for M = V and Ti (Fig. 4). Traces of linear α-olefins (1-hexene, 1-octene, etc.) were also detected. When $(\equiv SiO)_2Cr=CHCMe_3$ was dosed with a very small amount (ca. 1 equivalent) of ethylene, the volatiles detected were primarily the C_7 olefins 4,4-dimethylpent-2-ene, 4,4-dimethylpent-1-ene and 2,3,3-trimethylbutene. The origin of these products is likely the coupling of a neopentylidene ligand with ethylene. In support of this hypothesis, reaction of $(\equiv SiO)_2Cr=CHCMe_3$ with a small amount of C_2D_4 generated $(CD_3)CD=CHC(CH_3)_3$, identified by its MS fragmentation pattern.

Surface organometallic complexes with the general formula $(\equiv SiO)_2MR_2$ (M = Ti, Zr, Hf) have been reported to react with H_2 to give supported metal hydride complexes which hydrogenate [19,41] and polymerize [16,42,43] olefins. The formation of spectroscopically detectable hydrido complexes generally results in a dramatic increase in polymerization activity [44,45], however, hydrogenation of the silica-supported complexes requires elevated temperatures (100–200 °C) and results, in particular for M = Ti, in a number of different supported hydride complexes as well as partial reduction of the metal. Therefore, the possibility

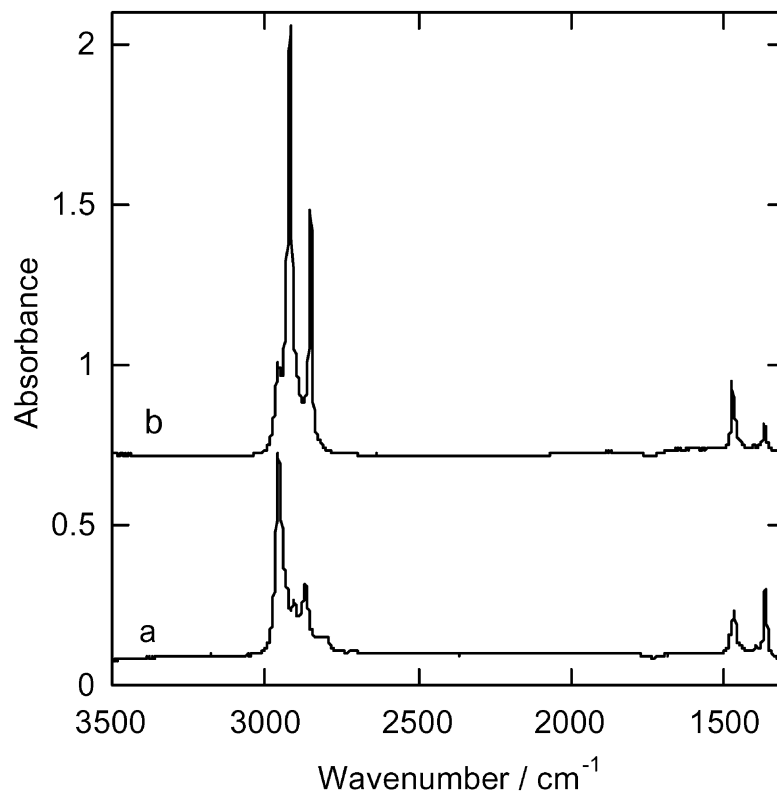Fig. 4. IR difference spectra of (a) ($\equiv$SiO)$_2$Ti(CH$_2$CMe$_3$)$_2$, (b) after addition of C$_2$H$_4$. The background spectrum of silica was removed by subtraction.

of forming hydrido complexes of the silica-supported first-row metals under milder conditions, i.e. directly from the supported alkylidenes, was explored.

Exposure of ($\equiv$SiO)$_2$Cr=CHEMe$_3$ to 100 Torr H$_2$ at room temperature resulted in no discernable reaction, as judged by a lack of change in the IR spectrum, even after several days. Upon heating, the onset of hydrogenation was noted at ca. 150 °C, accompanied by formation of volatile hydrocarbons such as methane, ethane and propane in addition to neopentane (E = C) and SiMe$_4$ (E = Si). The intermediacy of surface Cr–H species is inferred, however, the quantities formed were too small to permit spectroscopic detection.

An alternate low temperature route to metal hydrides from alkylidenes is the addition of a silane across M=C, reported recently for M = Ta [46,47]. Although ($\equiv$SiO)$_2$Cr=CHCMe$_3$ gave no reaction when treated with Me$_3$SiH, even after several days at room

temperature, a reaction occurred readily with 70 Torr Et$_2$SiH$_2$ vapor. In the IR spectrum, the integrated intensity of the vibrations in the ν(C–H) region increased to approximately double its initial value, while two new hydride vibrations were detected at 2137 and 2078 cm^{-1} (Fig. 5). The frequency of the higher energy mode closely resembles the spectrum of Et$_2$SiH$_2$, which consists of two closely-spaced bands at 2140 and 2133 cm^{-1}. The lower energy mode is inferred to belong to ν(Cr–H). The reaction with Et$_2$SiH$_2$ is formulated as addition of the silane across the Cr=C bond (Eq. (9)):

$$(\equiv SiO)_2Cr=CHCMe_3 + xsEt_2SiH_2$$
$$\rightarrow (\equiv SiO)_2(H)CrC(H)(SiHEt_2)(CMe_3) \qquad (9)$$
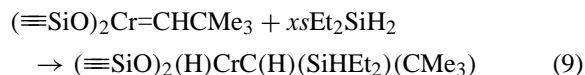
The presence of a surface Cr hydride was further confirmed by exposure of the sample to CH$_3$I, upon which methane was detected in the gas phase above

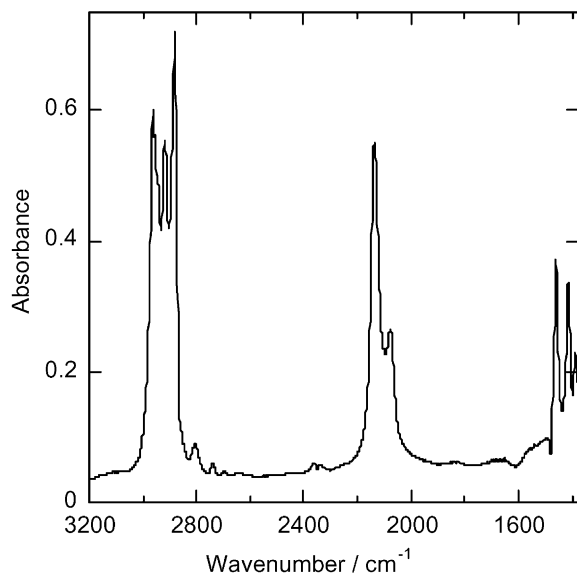Fig. 5. IR difference spectrum showing new vibrations appearing after reaction of $(\equiv SiO)_2Cr=CHCMe_3$ with Et_2SiH_2 (spectrum of $(\equiv SiO)_2Cr=CHCMe_3$ before reaction removed by spectral subtraction).

the sample by its characteristic IR spectrum. Furthermore, exposure of the Et_2SiH_2-treated sample to D_2 resulted in a very slow loss of $\nu(Cr–H)$ intensity and the appearance of a weak band at $1557\,cm^{-1}$, consistent with the conversion of Cr–H to Cr–D. The hydride complex is also an active catalyst for ethylene polymerization; details will be reported later.

The silica-supported alkylidene complexes described here are not electrophilic enough to activate the C–H bonds of arenes, as has been reported for transient $[(2,6-{}^iPr_2–C_6H_3)N)_2Cr=CHCMe_3]$ [35] or alkanes, similar to $Cp^*W(NO)(CHCMe_3)$ [48]. Although the formula $(\equiv SiO)_2M=CHEMe_3$ as written suggests a high degree of coordinative unsaturation, this is almost certainly mitigated by the abundance of surface oxygens within coordination distance of M (vide infra).

2.4. Effect of silica support

The Aerosil silica used in all of the experiments described above is a highly pure, non-porous combustion aerosol with irregularly shaped primary particles of average diameter 12 nm. It is further known

from small-angle neutron and X-ray scattering measurements that the surfaces of such fumed silica particles are smooth (surface fractal dimension $D_s = 2.0$) down to the molecular length-scale [49]. The extent of hydroxylation of the surface exerts a strong effect on subsequent reaction chemistry with MR_4, yielding either $(\equiv SiO)_2MR_2$ or $\equiv SiOMR_3$, as described earlier.

Despite the empirical evidence for formulation of the alkylidene complexes as $(\equiv SiO)_2M=CHEMe_3$, the coordination number of the metal in these or the bis(alkyl) complexes which precede them has not yet been established. Indeed, we believe it is highly unlikely that three-coordinate complexes persist in the presence of many possible oxygen donor atoms disposed in proximity around the silica-supported alkylidene complexes. Association with the oxygen of a nearby siloxane bridge to form a pseudo-tetrahedral surface complex is a likely possibility (Eq. (10)):

$$(\equiv SiO)_2M=CHEMe_3 + \equiv SiOSi\equiv$$
$$\rightarrow (\equiv SiO)_2(\equiv Si_2O)M=CHEMe_3 \qquad (10)$$
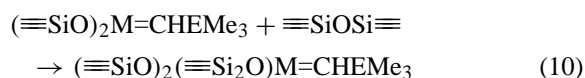
Since the strength of the metal–siloxane interaction may influence reactivity of the silica-supported alkylidenes, and the nature of the silica is known to be particularly important in determining the activity of supported polymerization catalysts [42,50], evidence for siloxane participation in the coordination sphere was sought by varying the nature of the silica.

Grafting of $Cr(CH_2EMe_3)_4$ on a porous silica gel, Sylopol-952, was accomplished in the same fashion as the reaction on Aerosil. After thermal treatment in vacuo at $200\,°C$, the accessible hydroxyl content of this silica, $1.25\,mmol\,g^{-1}$, is significantly higher than that of Aerosil-200. Regardless of loading, the reaction of $Cr(CH_2EMe_3)_4$ with the surface OH groups of Sylopol-952 occurs with the same stoichiometry as on Aerosil-200. For E = C, the reaction results in the liberation of (2.0 ± 0.3) CMe_4 per grafted Cr (average of four experiments). Thus, the surface complexes on Sylopol silica are formulated as $(\equiv SiO)_2Cr(CH_2EMe_3)_2$. The IR spectra of the supported organochromium fragments is very similar on porous and non-porous silicas (Fig. 1) with the exception that a much larger fraction of the hydroxyls which appear in the IR spectrum of the Cr-modified Sylopol silica are inaccessible to organochromium reagents.

Thermolysis of $(\equiv SiO)_2Cr(CH_2CMe_3)_2$ supported on Sylopol-952 at $70\,^{\circ}C$ resulted in the evolution of 1.1 ± 0.2 eq. CMe_4 as the exclusive volatile product. The rate constant, $k = 0.98 \times 10^{-4}\,s^{-1}$, is similar to that measured for the material prepared with Aerosil-200 ($k = 0.90 \times 10^{-4}\,s^{-1}$). Therefore, we suggest that a neopentylidene complex of Cr(IV) is again formed, and that the nature of the silica support does not appear to substantially influence either grafting or α-H abstraction. Nevertheless, evidence for an effect of the silica "ligand" on the subsequent reactivity of supported alkylidene complexes was found in their reactions with ethylene (vide infra).

2.5. Initiation of ethylene polymerization

The rate law for polymerization of low pressures (40–400 Torr) of C_2H_4 over $(\equiv SiO)_2Cr=CHCMe_3$ on Aerosil-200 has been investigated and the kinetics reported in some detail [51]. The gas–solid reaction displays no observable induction period at room temperature, no deactivation occurs during the course of polymerization and there is no evidence for mass transport effects. Mechanistic investigation of the reaction, including measurement of the activation parameters and the absence of a primary kinetic isotope effect, rules out alkylidene complexes as propagating intermediates (which appeared in earlier proposals for polymerization mechanisms over Phillips catalysts [10,11]), and agrees with the findings of computational investigations [52,53]. Furthermore, the formation of neopentylidene-containing olefins during polymerization suggests that the alkylidene ligand is eliminated from the supported catalyst upon exposure to ethylene during a fast initiation reaction. High-valent Cr alkylidenes have been predicted to undergo reductive elimination upon reaction with olefins, in contrast to Mo and W analogues which favor metathesis [54].

Although the mechanism of polymerization has been studied extensively for cationic, d^0 complexes of group IV, many other electron configurations are known to be consistent with appreciable activity. The d^2 configuration (i.e. Cr(IV)) in our homologous series of silica-supported complexes is by far the most active. The involvement of a cationic silica-supported Cr(IV) complex was suggested in a computational study [52], but its formation is considered unlikely, since protonation of the alkylidene ligand by a surface

silanol would also undoubtedly be accompanied by the formation of a covalent metal–siloxide interaction [53].

The precise nature of the initiation is still unclear. However, it seems reasonable to postulate an interaction between ethylene and $(\equiv SiO)_2Cr=CHCMe_3$ to generate the chromacyclobutane analogous to that required by its metathetical reaction with styrene (Eq. (8)). Calculations on a model Cr ethylidene system predict a highly exothermic $(2 + 2)$ addition of ethylene with almost no barrier [52]. Although neohexene, the olefin metathesis product, was not detected, formation of 2,3,3-trimethylbutene suggests that de-insertion of neohexene can occur, followed by rotation of the coordinated olefin. However, it must rapidly re-add to $(\equiv SiO)_2Cr=CH_2$ to generate the chromacyclobutane with the *tert*-butyl substituent in the β-position (Scheme 1). This mechanism of isomerization, albeit for the transformation of the β-substituted metallacyclobutane to the α-substituted isomer, has been demonstrated for a titanocene complex [55].

Extrusion of 4,4-dimethylpentenes from an α-*t*-butyltitanacyclobutane has been observed [38,40], with a suggested mechanism of β-H elimination to the allyl hydride complex, followed by reductive elimination [32,38]. On our catalyst, the immediate organometallic product may be the reduced ethylene complex, or the chromacyclopentane, via the cyclization of two coordinated C_2H_4 at the reduced Cr site. Both find precedent in experimental studies of tantalacyclobutane decomposition in the presence of olefins [38,40], observations of ethene trimerization by homogeneous Cr [56,57] and Ta [58] catalysts, and theoretical calculations on Cr(IV) model complexes [53].

Spontaneous extrusion of C_7 olefins is thus inferred to precede the formation of polyethylene on the active sites. This observation allows us to estimate the number of such sites in two ways. First, the $\nu(C–H)$ intensity in the in situ IR spectrum decreases to approximately two-thirds of its initial value upon exposure of $(\equiv SiO)_2Cr=CHCMe_3$ to C_2D_4, implying that one-third of the neopentylidene ligands were eliminated. Second, treatment of the polymer-enshrouded catalyst with HCl after polymerization resulted in the liberation of 0.67 eq. of neopentane per Cr, suggesting that two-thirds of the neopentylidene sites did not react with ethylene. In agreement with these findings,
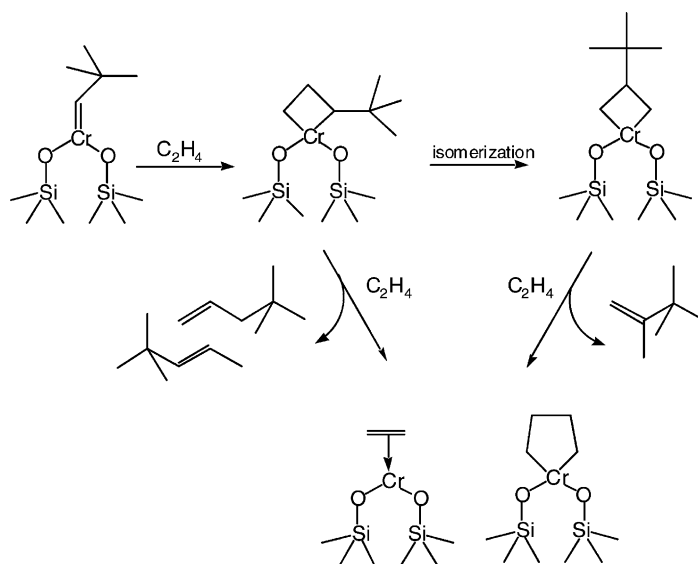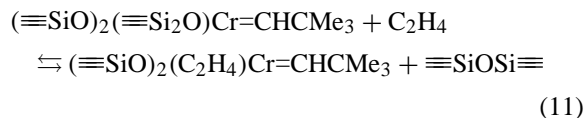
Scheme 1.

selective poisoning of the active sites with substoichiometric amounts of O_2 resulted in complete inhibition of polymerization activity for ca. 60 Torr C_2H_4 when the amount of O_2 added corresponded to 20% of total Cr [59].

The inability of a substantial fraction of neopentylidene sites to add ethylene, despite the presumed facility of this reaction, suggests that initiation is inhibited by another, stronger interaction, such as the coordination of an adjacent siloxane oxygen as in Eq. (10). Since the strength of the interaction is presumably dependent on geometric considerations, which might be expected to vary for different sites on the silica surface, it is reasonable to assume that ethylene can displace the siloxane ligand in some but not all of the supported complexes (Eq. (11)):

$$(\equiv SiO)_2(\equiv Si_2O)Cr=CHCMe_3 + C_2H_4$$
$$\leftrightarrows (\equiv SiO)_2(C_2H_4)Cr=CHCMe_3 + \equiv SiOSi\equiv$$

(11)

According to this explanation, higher pressures of C_2H_4 should be able to activate more neopentylidene sites, due to displacement of the equilibrium shown in Eq. (11) to the right. In agreement with this hypothesis, the threshold for inhibition of polymerization activity by O_2 increased from 20 to 30% poisoning of the Cr sites when the C_2H_4 pressure was raised from 60 to 250 Torr. The distribution of binding constants for C_2H_4 may also contribute to the broad polydispersities (typically $15 < M_w/M_n < 20$) of the polyethylene produced over both "single-site" $(\equiv SiO)_2Cr=CHCMe_3$ [59] and heterogeneous Cr/SiO_2 catalysts in general.

The reaction of $(\equiv SiO)_2Cr=CHCMe_3$, supported on Sylopol-952, with 40 Torr C_2H_4 is not spontaneous at room temperature. This finding was surprising in view of the very similar stoichiometry of the grafting reaction and IR spectrum compared to the Aerosil-200 reaction. Upon further investigation, we discovered that polymerization does occur in the presence of 1 atm C_2H_4. We propose that spectroscopically undetected (thus far) siloxane coordination results in a stronger interaction with the potential active sites on the surface of Sylopol-952 than on Aerosil-200 surface, thereby inhibiting polymerization at lower pressures. This phenomenon is suggested to be a consequence of the surface roughness of the silica gel (with a surface fractal dimension close to 3.0 [60]), resulting in greater proximity of adjacent siloxanes to the grafted Cr sites.

3. Experimental

Aerosil^{TM}-200 (BET surface area $183\,m^2\,g^{-1}$) is an amorphous, non-porous fumed silica manufactured by Degussa Corp. Sylopol-952 (BET surface area $309\,m^2\,g^{-1}$) is a precipitated silica gel from Grace–Davison. The content of accessible hydroxyls on each silica, after partial dehydroxylation, was measured by $VOCl_3$ chemisorption [61]. $Ti(CH_2CMe_3)_4$, $V(CH_2SiMe_3)_4$, $Cr(CH_2CMe_3)_4$ and $Cr(CH_2SiMe_3)_4$ were prepared by literature procedures and purified by sublimation [62–65]. Vacuum techniques for the preparation and characterization of bis(alkyl) and alkylidene complexes grafted onto silica surfaces, including selective deuterium isotope labeling, have previously been described in detail [22,31]. Since the supported organometallic complexes are highly air-sensitive, all manipulations were performed following strict high vacuum protocols, using breakseal techniques.

High purity C_2H_4 (Matheson), H_2 (Air Products) and C_2D_4 (98% D, Cambridge Isotopes) were further purified by passing each one through a trap containing a mixture of BTS Deoxo Catalyst (Caledon Laboratories Ltd.) and $3\,\text{Å}$ molecular sieves (Aldrich), then stored in glass high vacuum bulbs. The desired gas was transferred into the in situ reactor containing the catalyst through a high vacuum line (base pressure $<10^{-4}$ Torr) equipped with a capacitance manometer reading absolute pressures. Liquid reagents were purchased from Aldrich, dried over molecular sieves and stored under vacuum in glass vessels equipped with high vacuum Teflon stopcocks. Vapor phase transfer into the reactors was achieved via the vacuum manifold.

All IR experiments were performed in situ, in reactors with IR-transparent KCl windows. In experiments with a single gaseous product, quantitation of the volatile organic component was also achieved by IR, using the gas phase spectra of known pressures of pure compounds to construct calibration curves. For NMR experiments, the Ti-modified silica was prepared in powdered form in a Schlenk tube equipped with a high vacuum stopcock and 5 mm o.d. Pyrex NMR tubes welded onto the main body of the Schlenk tube at right angles. Samples were transferred in vacuo into the NMR tubes and sealed at 30 mm lengths with a torch, to give tubes containing approximately 50 mg of sample. The ^{13}C and ^{29}Si CP/MAS (cross polarization/magic angle spinning) NMR spectra were recorded on a Bruker ASX-200 spectrometer at frequencies of 50.32 and 39.75 MHz, respectively. ^{13}C spectra were collected at a spin rate of 4 kHz using a 4.4 ms 90° proton pulse with a contact time of 2 ms and relaxation delay of 2 s and treated with 20 Hz line broadening. For ^{29}Si spectra, the contact time was 10 ms and the relaxation delay 1 s.

Mixtures of volatile organic products were analyzed by GC and/or GC/MS. Metal analyses were performed by colorimetry after quantitative extraction from the modified silicas, following previously described procedures [66].

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