Reactions of Tetraalkylchromium(IV) with Silica: Mechanism of Grafting and Characterization of Surface Organometallic Complexes

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The reactions of CrR_4 (**1**, R is neopentyl or trimethylsilylmethyl) with the surfaces of partially dehydroxylated silicas lead to the formation of discrete mononuclear surface organometallic fragments. The reaction stoichiometry depends on the density of surface hydroxyl groups. On silica subjected to prior dehydroxylation at 500 °C, one Cr is grafted per hydroxyl group and 1 equiv of alkane is evolved, giving $\equiv SiOCrR_3$, **2**. On silica dehydroxylated at 200 °C, each Cr is grafted onto two hydroxyl groups and 2 equiv of alkane are evolved, giving $(\equiv SiO)_2CrR_2$, **3**. When CrR_4 reacts with deuterated hydroxyl groups, unlabeled and monodeuteroalkanes are liberated. A chemisorption mechanism is proposed with competing protonation by surface hydroxyl groups and intramolecular α-H elimination. The chemisorbed Cr species retain the oxidation state and nuclearity of their parent molecular precursors, as shown by UV−vis and EPR spectra and magnetic susceptibility measurement. The surface organometallic complexes are unreactive toward water, CO, and olefins but highly sensitive to O_2. While **2** is thermally stable up to 100 °C, **3** smoothly eliminates one alkyl ligand as alkane at 60 °C.

Introduction

Chromium dispersed on the surfaces of inorganic oxides constitutes an important class of catalytically active materials. For example, CrO_3/SiO_2 and Cp_2Cr/SiO_2, developed at Phillips[1] and Union Carbide,[2] respectively, catalyze the polymerization of ethylene. These systems have been intensively studied, but a convincing characterization of the structure of the active site(s) has yet to be achieved.[3] One reason is the wide range of oxidation states and coordination geometries simultaneously present in these heterogeneous systems,[4] combined with the observation that only a small proportion of the surface Cr participates in the reaction.[5] Although Cr(II) has been proposed as the active valence state in both catalysts, evidence from molecular chemistry suggests that Cr in a higher oxidation state is likely to be more active.[6] Mechanisms have been written for the industrial catalysts in which alkyl and hydrido ligands bound to Cr(IV) are propagation sites.[7]

Recently, Chen *et al.* reported that Cr-substituted aluminophosphates (CrAPO) catalyze the selective oxidation of alcohols by *tert*-butyl hydroperoxide.[8] The proposed mechanism involves reduction of Cr(VI) to Cr(IV) by the alcohol, followed by reoxidation of Cr(IV) by the peroxide. In contrast, the mechanism for the catalytic oxidations of hydrocarbons using CrAPO[9] and Cr-substituted clays[10] was suggested to involve an alkylperoxochromium(VI) active site, whose oxidation state does not change during the reaction.

In order to examine the feasibility of these mechanisms, we decided to prepare oxide-supported Cr(IV). The incipient wetness method for synthesizing mixed oxides is obviously inappropriate since the lifetime of the aquachromium(IV) ion is very short ($t_{1/2}$ ca. 30 s).[11] The reaction of CrO_2Cl_2 with hydroxyl-terminated oxide surfaces is reported to lead to surface species of composition $(\equiv SiO)_2CrO_2$;[12] however, *in situ* reduction with H_2 gives a mixture of species and oxidation states.[3] Therefore, to prepare Cr(IV)-containing materials cleanly, we decided to use an organometallic precursor containing Cr(IV).

The homoleptic alkyls of Cr(IV) were first reported over 20 years ago,[13−15] and some are now structurally characterized.[16−18] The metal−carbon bonds are potential sites of reactivity toward hydroxyl-terminated surfaces of oxides. In this paper, we report the reactions of CrR_4 (R is neopentyl or trimethylsilylmethyl) with the silica surface and the reactivity and thermal stability of the grafted surface organometallic fragments.

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Experimental Section

The tetraalkylchromium(IV) complexes were prepared according to published procedures.[14,15] D_2O (Aldrich, 99% enriched), DCl (Cambridge Isotopes, 98% enriched), ethylene (Matheson, 99.99%), CO (Air Products, 99%), and HCl (Matheson, 99% anhydrous) were used as received.

Pyrogenic silica (Degussa Aerosil 200, 200 m^2/g) was used in all experiments. A standard pretreatment procedure was adopted to ensure reproducibility. For infrared experiments, the silica was pressed (125 kg/cm^2) into a 16 mm self-supporting disk containing 2−4 mg silica/cm^2. For all other experiments, the silica was compacted by pressing into thick disks which were then finely ground in a mortar. The silica was calcined at 500 °C in the presence of 300 Torr of dry ultrapure oxygen for 2 h, then partially dehydroxylated at 500 °C for 2 h in dynamic vacuum (10^{-4} Torr). This silica is referred to as silica-500. To obtain silica dehydroxylated at 200 °C, the silica-500 was rehydrated with water vapor at 200 °C and then dehydroxylated under dynamic vacuum at 200 °C for 2 h.

Deuterated silica was prepared by two different methods. Four cycles of treatment with D_2O vapor at 450 °C for 3 h followed by dynamic vacuum gave >90% deuteration of the surface hydroxyl groups. The extent of deuteration was judged by the relative decrease in intensity of the ν(O−H) vibration at 3747 cm^{-1}. Alternately, room temperature exposure to 80 Torr of DCl gave, immediately, >90% deuteration. Silica is not chlorinated by DCl at room temperature.[19]

Infrared experiments were performed in an all-glass *in situ* gas cell equipped with KCl windows. The cell is capable of holding static vacuum ($<10^{-3}$ Torr) for several days. In each experiment, CrR_4 was sublimed at room temperature *in vacuo* into a glass break-seal, which was then welded onto the infrared cell. After thermal treatment of the silica, the break-seal was broken and excess CrR_4 was sublimed *in vacuo* onto the silica surface. Unreacted CrR_4 was then desorbed from the silica surface by immersing the break-seal side arm for several hours in a liquid N_2 trap. The side arm was removed by sealing it off with a torch. Transmission infrared spectra were recorded on a Mattson Research Series FT-IR spectrometer equipped with a DTGS detector and purged with CO_2-free dry air. Surface spectra were recorded by coadding 32 scans at a resolution of 2 cm^{-1}.

All experiments other than IR were performed in high-vacuum Schlenk tubes using break-seals to admit CrR_4. For EPR experiments, 25 mg samples were transferred *in vacuo* into 8 mm o.d. cylindrical quartz tubes welded at right angles onto the Schlenk tubes. Variable temperature spectra were recorded on a Bruker ER 200 spectrometer operating at 9.450 GHz, with a sweep time of 500 s. For UV−vis experiments, 50 mg samples were transferred into 2 × 5 mm rectangular quartz tubes, also welded onto the Schlenk tube. Spectra were recorded on a Varian Cary 1E spectrometer equipped with an integrating sphere diffuse reflectance attachment and referenced to Spectralon.

Magnetic measurements were made on samples stored under vacuum in a sealed quartz sample holder. Susceptibility was measured as a function of temperature (4−300 K) on a Quantum Design SQUID magnetometer operating at 5 T and using a 3 cm Reciprocating Sample Option scan at 1 Hz with iterative regression, 10 cycles per measurement and 5 measurements per average.

Gases were analyzed qualitatively and quantitatively by IR spectroscopy, GC, MS, and absolute pressure measurements using a Baratron capacitance manometer. Gas phase IR spectra were recorded at a resolution of 0.75 cm^{-1}. Infrared calibration curves were prepared using gas standards with pressures in the range 1−10 Torr. Alkane products were quantified by integration of the ν(C−H) region of gas phase IR absorbance spectra. When present, HCl was removed by adsorption on powdered NaOH before analysis of the alkane. Gas chromatography analysis of hydrocarbons was performed on a Hewlett-Packard 5710A gas chromatograph with a Porasil packed column, isothermal at 22 °C. Mass spectra were recorded using a modified (ballistic electron emission) VG ZAB-2F mass spectrometer (VG Analytical, Manchester, U.K.). The sample was introduced into the mass spectrometer via the gas inlet system. The deuterium content of neopentane was calculated from the corrected relative intensities of the *tert*-butyl fragment peaks at $m/z = 57$ and 58.[20] The energy of the ionizing electrons was 70 eV; the reproducibility of the results was verified at various ionization energies (12, 15, or 30 eV).

At the end of each experiment, the reactor was opened and the silica sample was analyzed for Cr in air following a published procedure.[21] The sample (20−40 mg) was treated with 5 mL of 5 M NaOH to extract Cr from the silica surface. One milliliter of 30% H_2O_2 was added, and the yellow solution was boiled for 5 h and then diluted with water to 50 mL. Cr was analyzed as CrO_4^{2-} by its absorbance at 374 nm.

Results

The molecular complexes $Cr(CH_2C(CH_3)_3)_4$ (**1a**) and $Cr(CH_2Si(CH_3)_3)_4$ (**1b**) are volatile and air sensitive.[14,15] They are intensely colored maroon (**1a**, λ_{max} 474 nm in hexane) and purple (**1b**, λ_{max} 538 nm in ether) solids. Sublimation at room temperature of each complex onto silica-500 results in a change in the color of the silica to orange (**1a**) and pink (**1b**), and these colors are retained even after prolonged desorption of unreacted CrR_4 to a liquid N_2 trap. Diffuse reflectance spectra of the modified silicas contain bands slightly blue-shifted compared to those of the molecular precursors, with maxima at 456 and 513 nm for the neopentyl- and trimethylsilylmethyl-derived materials, respectively. The minimum at 413 nm in the spectrum of **1a** is very shallow in the spectrum of the modified silica. Also, the spectrum of silica modified with **1b** contains a poorly-resolved band at ca. 350 nm, which is not present in the spectrum of **1b**.

Stoichometry of the Reactions of CrR_4 with Silica. The quantity of accessible hydroxyl groups on the silica surface decreases as the silica is heated. At 200 °C, the hydroxyl density decreases to 2.6 OH/nm^2, and at 500 °C, it is 1.2 OH/nm^2.[22] Silicas subjected to these thermal treatments are referred to as silica-200 and silica-500, respectively.

The reaction between CrR_4 and silica-500 results in the evolution of the alkane RH as the only volatile product, confirmed by IR spectroscopy and GC. The quantity of RH was determined by absolute pressure measurements and by integration of the IR intensity in the ν(C−H) region. For example, when a 9.8 mg self-supporting disk of silica-500 was exposed to excess **1a**, 3.52 μmol of neopentane was evolved. After desorption of unreacted **1a**, chemisorbed Cr was extracted from the silica. The sample contained 1.87% Cr by mass or 3.57 μmol of Cr. From the known surface area and hydroxyl content of silica-500 before the reaction, the initial quantity of hydroxyl groups present on a 9.8 mg disk is 4.0 μmol.

On average, 0.92 ± 0.05 mol of RH is liberated per mol of grafted Cr on silica-500. These results suggest

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Table 1. Quantitative Product Analysis for the Reaction of CrR_4 with Silica[a]

		products of grafting				products of protonolysis	
	CrR_4[b]	mmol of Cr	Cr/OH[c]	mmol of RH	RH/Cr	mmol of RH	RH/Cr
silica-500	**1b**	0.050	0.13	0.048	0.95		
	1a	0.205	0.50	0.173	0.84	0.595	2.89
	1a	0.210	0.53	0.201	0.96		
	1a	0.247	0.62	0.216	0.87		
	1a	0.363	0.89	0.359	0.98		
silica-200	**1b**	0.041	0.05	0.080	1.94		
	1a	0.068	0.08	0.127	1.85		
	1a	0.168	0.20	0.310	1.85		
	1a	0.236	0.27	0.441	1.87	0.437	1.85
	1a	0.245	0.28	0.451	1.84		
	1a	0.250	0.29	0.465	1.86		
	1a	0.372	0.43	0.703	1.89	0.696	1.87

[a] All quantities are reported normalized per gram of silica. [b] R is $CH_2C(CH_3)_3$, **1a**, or $CH_2Si(CH_3)_3$, **1b**. [c] Ratio of the amount of chemisorbed Cr to the initial amount of surface hydroxyl groups: 0.40 mmol of OH/g of silica-500 and 0.86 of mmol OH/g of silica-200.

that the following stoichiometric reaction (eq 1) has occurred

$$\equiv\text{SiOH} + \underset{\substack{\textbf{1a}\\ \textbf{1b}}}{\text{CrR}_4} \rightarrow \underset{\substack{\textbf{2a}\ \text{R} = \text{CH}_2\text{C(CH}_3)_3\\ \textbf{2b}\ \text{R} = \text{CH}_2\text{Si(CH}_3)_3}}{\equiv\text{SiOCrR}_3} + \text{RH} \qquad (1)$$

where $\equiv$SiOH represents a hydroxyl group on the silica surface. The results for a representative range of Cr loadings are summarized in Table 1. The stoichiometry of eq 1 is observed, regardless of the Cr loading, in the range 0.13−0.89 Cr/OH. The highest Cr loading achieved was close to 1 Cr/OH, which suggests that the availability of surface hydroxyl groups determines the extent of chemisorption of CrR_4 on the silica-500 surface.

The products **2a** and **2b** retain three alkyl groups per Cr, and these groups are susceptible to protonolysis. Treatment with 10 Torr of HCl(g) causes the color of **2** to change to green and liberates 2.9 ± 0.1 RH/Cr, eq 2.

$$\underset{\textbf{2}}{\equiv\text{SiOCrR}_3} + \text{excess HCl} \rightarrow \text{“}\equiv\text{SiOCrCl}_3\text{”} + 3\ \text{RH} \qquad (2)$$

The product $\equiv SiOCrCl_3$ was not characterized further; however, Cr analysis after protonolysis confirmed that the metal remains chemisorbed rather than being liberated from the surface (for example, as volatile $CrCl_4$).[14]

On silica-200, a grafting reaction similar to eq 1 occurs, with liberation of RH as the only volatile product. However, in this case, an average of 1.87 ± 0.03 equiv of RH are liberated per chemisorbed Cr, consistent with the stoichiometry shown in eq 3. Once

$$2\equiv\text{SiOH} + \underset{\textbf{1a,b}}{\text{CrR}_4} \rightarrow \underset{\textbf{3a,b}}{(\equiv\text{SiO})_2\text{CrR}_2} + 2\text{RH} \qquad (3)$$

again, the stoichiometry is independent of Cr loading, Table 1. In addition, although silica-200 has a hydroxyl content approximately twice as high as that of silica-500, the maximum loading of Cr on silica-200 is not higher, ca. 0.4 mmol of Cr/g of silica. In this case, the maximum amount of grafted Cr is slightly less than 0.5 Cr/OH. The products **3a** and **3b** retain an average of only two alkyl ligands per Cr, confirmed by protonolysis with 10 Torr of HCl(g) to give 1.9 ± 0.1 RH/Cr, eq 4.

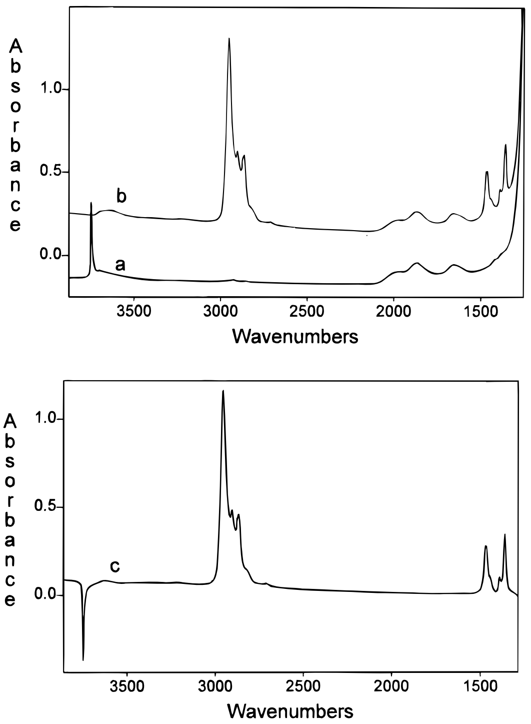

Figure 1. Transmission infrared spectra of: (a) a self-supporting disk of silica, partially dehydroxylated at 500 °C; (b) $(\equiv SiO)Cr(CH_2C(CH_3)_3)_3$, **2a**; (c) difference spectrum, b−a.

$$\underset{\textbf{3a,b}}{(\equiv\text{SiO})_2\text{CrR}_2} + \text{excess HCl} \rightarrow \text{“}(\equiv\text{SiO})_2\text{CrCl}_2\text{”} + 2\text{RH} \qquad (4)$$

Once again, the product $(\equiv SiO)_2CrCl_2$ was not characterized; it is included only to balance the reaction.

Infrared Spectroscopic Characterization. The reactions of **1a** and **1b** with silica were followed by *in situ* IR spectroscopy. Before reaction, the spectrum of a self-supporting disk of silica-500 has a sharp band at 3747 cm^{-1}, attributed to non-hydrogen-bonded surface hydroxyl groups, with a broad low-frequency shoulder assigned to hydroxyl groups that are perturbed by hydrogen bonding, Figure 1a. Broad bands at 1977, 1868, and 1647 cm^{-1} are overtones and combinations of the intense Si−O fundamental modes originating in the bulk of the silica, which render the silica virtually opaque below 1200 cm^{-1}. These bands are unchanged by any reactions which occur at the surface, and which, therefore, they do not alter the bulk structure of silica. When CrR_4 is sublimed onto a silica-500 disk, new bands characteristic of alkyl groups appear in the regions 3000−2800 cm^{-1} (C−H stretching), 1500−1300 cm^{-1} (methyl and methylene deformations), and 750−680 cm^{-1} (methyl rocking coupled to Si−C stretching, **1b** only), parts b and c of Figure 1. Simultaneously, the band at 3747 cm^{-1} disappears completely[23] and is not regenerated when unreacted CrR_4 is desorbed. The vibrations attributed to alkyl groups decrease only

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(23) A very broad band in the O−H stretching region remains after reaction with CrR_4. It is assigned to OH groups which are inaccessible, possibly located in the bulk of the silica structure. Morrow, B. A.; McFarlan, A. J. *Langmuir* **1991**, *7*, 1695−1701.

slightly in intensity during desorption. This result confirms that CrR_4 is irreversibly chemisorbed onto the silica surface and that the mode of chemisorption is reaction with surface hydroxyl groups.

On silica-200, similar IR spectral changes were recorded during the reactions of surface hydroxyl groups with **1a** and **1b**.

Nuclearity and Oxidation State of Grafted Complexes. The oxidation state of chromium in CrR_4 complexes has been demonstrated by EPR.[13−15,17,24,25] The spectra are characteristic of triplet d^2 systems, consisting of a broad line at room temperature which narrows upon cooling and splits into two lines separated by a small zero-field splitting, $D = 0.011$ (**1a**) and 0.063 cm^{-1} (**1b**).[15] The magnetic moments at room temperature are 2.7 (**1a**) and 2.9 μ_B (**1b**),[15] close to the spin-only value expected for a d^2 system, 2.83 μ_B.

The EPR spectra of the silica-supported complexes **2a** and **3a** are broad, featureless lines at 298 K. At 78 K, the appearance of an inflection point at $g = 1.984$ is evidence for zero-field splitting in the spectrum of **3a**. The resolution is comparable to that observed in the solution EPR spectrum of the molecular precursor $Cr(CH_2C(CH_3)_3)_4$, $g = 1.986$, at 180 K.

The silica-supported complexes are magnetically dilute, since they contain typically ca. 1% Cr in a diamagnetic silica matrix. The magnitudes of the room temperature moments are extremely small. However, at low temperature, the solids show typical Curie−Weiss behavior. The value of μ_{eff} for **3a** is 2.68 μ_B, which is the same as that of its molecular precursor **1a** and close to the spin-only value. There is evidence for very weak antiferromagnetic coupling from the Néel temperature, $\Theta = 7$ K. We conclude that the grafted species are essentially magnetically isolated, mononuclear, d^2 systems.

Mechanism of Grafting. The results in Table 1 suggest that CrR_4 is chemisorbed onto silica by reaction with the surface hydroxyl groups. In order to probe the mechanism of this reaction, chemisorption on deuterated silica was studied. Deuterium was incorporated into the hydroxyl groups of silica by repeated exchanges with D_2O or DCl, until >90% exchange was achieved. Reaction with **1a** liberated 1 (silica-500) or 2 (silica-200) equiv of neopentane, as before. The extent of deuterium incorporation into the neopentane was evaluated by mass spectrometry. Since the molecular ion peak for neopentane is very weak, the *tert*-butyl fragments were detected at $m/z = 57$ (C_4H_9) and 58 (C_4H_8D) instead. On silica-500, both unlabeled and monodeuteroneopentane were produced in the ratio 51:49 (±6, average of three experiments). On silica-200, neopentane-d_0 and -d_1 were detected in the ratio 40:60 (±3, average of four experiments).[26]

$$\equiv SiOD + Cr(CH_2C(CH_3)_3)_4 \rightarrow \equiv SiOCr(CH_2C(CH_3)_3)_3 + C(CH_3)_3(CH_2D) \quad (5)$$

$$\equiv SiOD + \equiv SiOCr(CH_2C(CH_3)_3)_3 \rightarrow (\equiv SiO)_2Cr(CH_2C(CH_3)_3)_2 + C(CH_3)_3(CH_2D) \quad (6)$$

A simple electrophilic attack of surface protons/deuterons on the metal−carbon bond was expected to produce >90% neopentane-d_1 on either silica-500 or silica-200, eqs 5−6. Equations 5 and 6 alone are therefore inadequate to explain the observed isotopomer ratios. A kinetic isotope effect may be responsible for the faster reaction of **1a** with ≡SiOH relative to ≡SiOD, accounting for a small part of the excess neopentane-d_0. However, on partially deuterated silica-200 with a Cr loading of 1.28 wt % (0.25 mmol of Cr/g of silica), similar decreases in intensity of the ν(O−H) and ν(O−D) modes at 3747 and 2762 cm^{-1}, respectively, were measured (0.42 and 0.38, respectively). Therefore, another proton source is responsible for the excess neopentane-d_0 that is liberated during grafting on deuterated silica. Since our experiments were performed *in vacuo* in the absence of solvent, the only other proton source is $Cr(CH_2C(CH_3)_3)_4$. We propose a competition between direct protonolysis, eqs 5−6, and H/D exchange of methylene protons with hydroxyl protons, eqs 7−8. On the basis of the observed isotope ratios in

$$\equiv SiOD + Cr(CH_2C(CH_3)_3)_4 \rightarrow \equiv SiOCr(CHDC(CH_3)_3)(CH_2C(CH_3)_3)_2 + C(CH_3)_4 \quad (7)$$

$$\equiv SiOD + \equiv SiOCr(CHDC(CH_3)_3)(CH_2C(CH_3)_3)_2 \rightarrow (\equiv SiO)_2Cr(CHDC(CH_3)_3)_2 + C(CH_3)_4 \quad (8)$$

the neopentane products, the fraction of D in the methylene positions of the surface neopentyl ligands should be 0.07 on silica-500 and 0.15 on silica-200, Scheme 1. The ν(C−D) mode is extremely weak and was not observed in the IR spectra of the grafted species.

Thermal Stability. Since catalysis with oxide-supported Cr is usually effected above room temperature (typically 80−120 °C),[3,8,9] we investigated the behavior of the grafted species as a function of temperature. The molecular complex **1a** is reported to be thermally stable in hexane at 80 °C for several days.[13] The silica-supported tris(alkyl) complexes **2** are also stable at 80 °C, giving less than 10% loss of alkyl ligands after 2 h (as judged by the change in ν(C−H) intensities in the IR). In contrast, the bis(alkyl) complex **3a** undergoes a transformation within 1 h at 60 °C which results in a reproducible decrease in the integrated ν(C−H) intensity of 49.8 ± 0.03% (average of three experiments), Figure 2, and the liberation of 0.89 ± 0.03 (average of four experiments) equiv of neopentane as the unique gas phase product.

The IR spectra in Figure 2 show that the quantity of surface hydroxyl groups does not decrease during thermolysis of **3a**. In fact, the intensity of the sharp band at 3747 cm^{-1} of the isolated hydroxyl groups increases slightly at the expense of the lower frequency broad band that is assigned to hydroxyl groups perturbed by hydrogen bonding. Therefore, unreacted surface hydroxyl groups are not the source of the protons which cause the liberation of neopentane. Since the reaction occurs *in vacuo* in the absence of solvent, the proton source must be the grafted species **3a** itself, eq 9. In agreement with the stoichiometry of eq 9, protonolysis of **4** with excess HCl liberated 0.89 ± 0.01 equiv of neopentane.

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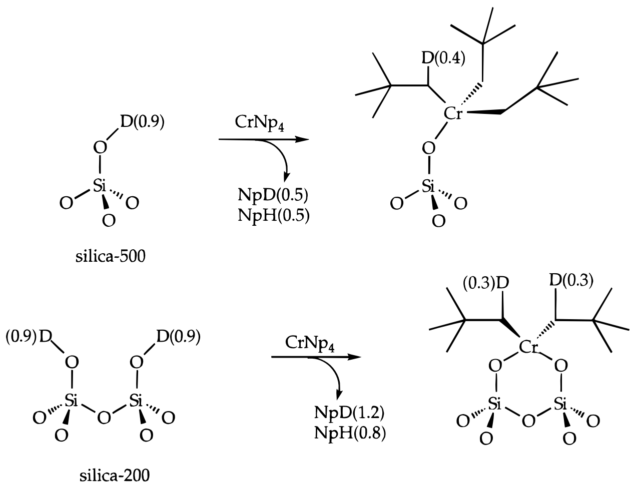
[26] The ratio of isotopomers of neopentane shows no dependence on Cr loading. Blank experiments verified that deuterated silica does not catalyze the H/D exchange of neopentane, nor does **3a**.

Scheme 1



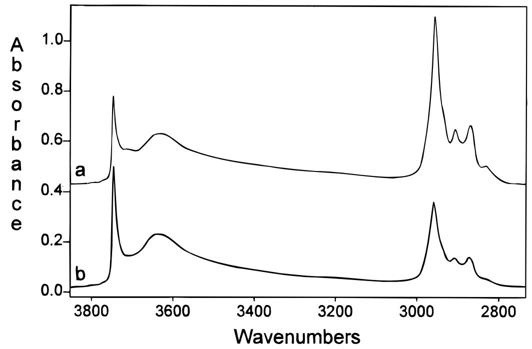


Figure 2. Transmission infrared spectra of: (a) $(\equiv SiO)_2Cr(CH_2C(CH_3)_3)_2$, **3a**, at room temperature; (b) after heating in vacuum at 60 °C for 2 h.

$$\underset{\mathbf{3a}}{(\equiv SiO)_2Cr(C_5H_{11})_2} \rightarrow \underset{\mathbf{4}}{(\equiv SiO)_2Cr(C_5H_{10})} + C(CH_3)_4 \qquad (9)$$

Thermolysis of **3a** was also attempted on deuterated silica. Neopentane-d_0 and neopentane-d_1 were observed in the ratio 49:51 (±6, average of three experiments). The expected ratio for α-elimination, in the absence of a kinetic isotope effect, is 85:15, based on the presumed amount of D incorporated into the methylene positions during grafting (see above). Reaction of **4** with DCl/HCl mixtures liberated neopentane-d_0, -d_1, and -d_2.

Reactivity. The grafted species **2** and **3** are unreactive toward water, like their molecular precursors **1**. Introduction of 50 Torr of water vapor into the reactor at room temperature gave no change in either the colors or the infrared spectra of the solids. However, these species are extremely sensitive to O_2. In the presence of 10 Torr of dry O_2, **2** and **3** immediately lose their characteristic colors to become yellow. The intensities of the bands in the ν(C−H) region of the IR spectrum decrease, and new bands appear in the region 1680−1570 cm^{-1}. The latter are characteristic of hydrocarbon oxidation products containing carbonyl groups. Also, CO and CO_2 were detected in the gas phase by IR spectroscopy. This deep oxidation was observed in all attempts to vary the temperature and pressure of O_2; consequently, we were not able to identify the initial product in the reactions of the surface species with O_2.

The complexes **2** and **3** also proved to be unreactive toward CO (20 Torr) and ethylene (10 Torr); no evidence for insertion was observed at room temperature. However, spectral changes were recorded after addition of NO. Although no modification occurred in the ν(C−H) region, two new bands were observed at 1854 and 1716 cm^{-1}, which persisted under dynamic vacuum. Pairs of bands in this region have been attributed to the symmetric and antisymmetric N−O stretching modes of bis(nitrosyl)chromium supported on silica.[27]

Compared to the bis(alkyl)chromium precursor **3**, the thermolysis product **4** is much more reactive. For example, it reacts instantly with water vapor. Further characterization and investigation of its reactivity is in progress.

Discussion

A brief report of the interaction of CrR_4 with silica concluded that only physisorption occurs, based on the similarity in color of the treated silica to the molecular precursors.[28] In this work, the differences in the UV−vis spectra of the molecular and grafted complexes are slight; therefore, we conclude that color is not a reliable indicator of whether a reaction occurs in these systems. The materials **2** and **3** contain irreversibly chemisorbed Cr species, formed by evolution of one or more alkyl ligands as alkane.

The reactivity of CrR_4 toward the hydroxyl groups of silica is somewhat unexpected, since these complexes are completely unreactive toward alcohols and even water.[14] However, the surface silanols of Aerosil are slightly acidic ($pK_a \sim 4$), and CrR_4 is known to undergo protonolysis by acids.[15] The average stoichiometries of the surface reactions on silica-500 and silica-200 are consistent with those reported for the grafting of homoleptic tetraalkyl complexes of Ti and Zr.[29−32] The reaction of CrR_4 with silica-500 gives a surface complex whose average formula is $\equiv SiOCrR_3$, **2**. In order to give the ratio R/Cr = 3, $(\equiv SiO)_2CrR_2$ can only be present if (a) unreacted CrR_4 is simultaneously present or (b) a reaction of CrR_4 with silica, which does not liberate RH, also occurs. The first possibility is excluded by the stability of the material to prolonged desorption; physisorbed volatile CrR_4 is completely removed under these conditions. The second possibility might be fulfilled by a reaction of CrR_4 with siloxane bridges, eq 10. Similar

$$\equiv SiOSi\equiv + CrR_4 \rightarrow \equiv SiOCrR_3 + \equiv SiR \qquad (10)$$

reactions have been observed on highly dehydroxylated silica with $Ni(\eta^3\text{-}C_3H_5)_2$,[33] $AlMe_3$,[34] and $Zr(CH_2C(CH_3)_3)_4$.[35] However, the occurrence of reaction 10 is inconsistent with the disappearance of 93% of the ν(C−H) intensity after protonolysis, since $\equiv SiR$ species are unreactive toward HCl. Therefore, we conclude that the average formula of **2** represents the true major species,

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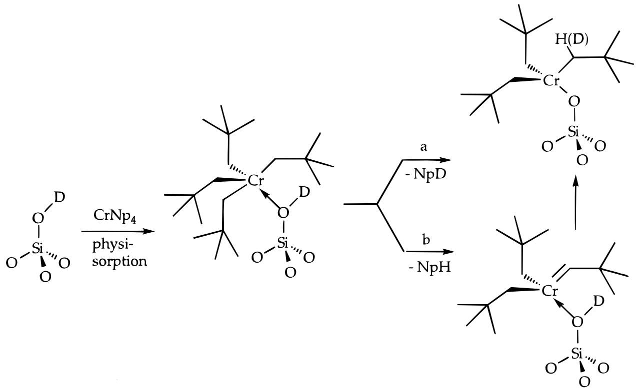
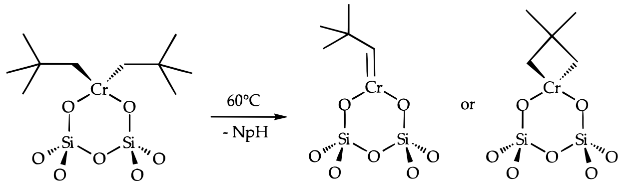
Scheme 2



Scheme 3



a tris(alkyl)chromium fragment, present on the silica-500 surface.

On silica-200, the average formula is $(\equiv SiO)_2CrR_2$, **3**. It seems reasonable to suppose that **3** is formed stepwise from **2** by reaction with an adjacent $\equiv$SiOH, due to the greater availability of the latter on silica-200. Using cristobalite as a model for the amorphous silica, the closest approach between the oxygen atoms of surface hydroxyl groups in the same row is ca. 2.5 Å,[36] creating a reasonable bidentate binding geometry for the silica "ligand". The proposed reaction is shown in eq 11.

$$\underset{\mathbf{2}}{\equiv SiOCrR_3} + \equiv SiOH \rightarrow \underset{\mathbf{3}}{(\equiv SiO)_2CrR_2} + RH \qquad (11)$$

Therefore, we expected to obtain a mixture of **2** and **3** on silica-200, in a ratio which depends on the relative rates of reactions 11 and 1. In order to achieve the average ratio R/Cr = 2, the amount of **2** present must be balanced by an equal amount of a monoalkyl species $(\equiv SiO)_3CrR$. The latter is considered unlikely, since the required third hydroxyl group is in an adjacent row, over 5 Å away.[37] On silica-200, we conclude that the major species is **3** with the average ratio R/Cr = 2. In this respect, it seems reasonable that reaction 11 should be faster than reaction 1, since the second substitution takes place while the organometallic fragment is immobilized in position next to a hydroxyl group. The second hydroxyl group will be sterically encumbered by the presence of the surface organometallic fragment and, therefore, unlikely to be available for reaction with physisorbed CrR_4.

The projected surface area occupied by the tris(neopentyl) fragment **3a** was estimated by molecular modeling to be 90 Å^2; the total area occupied by these fragments at our highest loading, 0.36 mmol of Cr/g of silica-500, is therefore 200 m^2, which represents a full monolayer on Aerosil-200 (surface area 200 m^2/g). On silica-200, the maximum loading (0.40 mmol of Cr/g of silica-200) of the bis(neopentyl) fragment **3a**, with an estimated surface area of 60 Å^2, occupies 145 m^2/g.

The grafting process appears to involve exchange of surface protons/deuterons into the alkyl ligands, in addition to direct cleavage of the metal−carbon bond by the surface hydroxyl groups. A possible mechanism is shown in Scheme 2. The physisorbed tetraalkyl complex that is interacting with a hydroxyl group eliminates alkane with a proton derived from either a surface hydroxyl group or an α-H of another alkyl ligand. In the latter case, an alkylidene intermediate would be formed, which then undergoes addition of $\equiv$SiO−H across the Cr=C bond.

The driving force for the transformation of the five-coordinate physisorbed complex to the bis(alkyl)alkylidene species may be the relief of steric crowding, similar to the spontaneous decomposition of $Ta(CH_2CCH_3)_5$ to $Ta(=CHC(CH_3)_3)(CH_2CCH_3)_3$.[20] On silica-200, analogous branching of the mechanism may be expected in the reaction of the second alkyl ligand with $\equiv$SiOH. The formation of an alkylidene intermediate in the grafting of MR_4 (M is Ti, Zr, Hf) on silica has not previously been reported.

Gentle thermolysis of **3** at 60 °C liberates one of the alkyl ligands as alkane. The product **4** may be formulated as either an alkylidene or a metallacycle, Scheme 3. Although we cannot at this time exclude the possibility of a metallacyclic complex, the liberation of equal amounts of neopentane-d_0 and -d_1 from thermolysis of **3** on deuterated silica is more consistent with α-H/D elimination from one of the four methylene positions thought to incorporate D during grafting than from one of the 18 methyl positions. Even so, a large kinetic preference for the cleavage of a C−D bond vs a C−H bond is required to explain the observed isotope distribution. As evidence for **4**, treatment with DCl liberates a mixture of isotopomers, including neopentane-d_2. Although Fischer carbene complexes of low-valent Cr are well-known,[38] alkylidenes of high-valent Cr in high-oxidation states are extremely rare in the literature.[39−41] No doubt, the immobility of the grafted complex contributes to its stability.

The silica-supported complexes **2** and **3** show little reactivity, except toward O_2. No reactivity toward ethylene was observed at room temperature,[28] although Cr(IV) alkyls and hydrides have been proposed as active centers for polymerization in Cr/silica catalysts.[7] However, since those polymerizations are typically run at 80−120 °C, it is possible that less coordinatively saturated species, such as **4**, are responsible for the activity. Indeed, **4** catalyzes the polymerization of olefins, such as ethylene and propylene, at room temperature.[42]

Conclusion

Well-defined silica-supported paramagnetic alkylchromium(IV) complexes have been characterized, and

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their average stoichiometries are consistent with tris(alkyl) and bis(alkyl) complexes which predominate on silica-500 and silica-200, respectively. The surface complexes do not interact magnetically. They are robust and unreactive toward a number of gases, except O_2. An interesting thermal transformation has been observed, which we believe represents an entry point to more reactive surface species of Cr(IV).

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Supporting Information Available: UV−vis diffuse reflectance spectra, EPR spectra, and magnetic susceptiblity data for **2** and **3** (3 pages). Ordering information is given on any current masthead page.

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