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Synthesis and Characterization of Silica-Stabilized Chromium(IV) Alkylidene Complexes

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Oxide-supported Cr catalysts are used in commercial processes to polymerize α-olefins, particularly ethylene.[1,2] These much-studied heterogeneous systems are so complex that an atomic-level understanding of the polymerization process has not yet been achieved.[3] In particular, the mechanism of initiation of polymerization remains obscure.[4] However, in light of the widely held belief that polymer chains grow by insertion of the olefin into a surface Cr−C σ-bond, it is surprising that silica-supported catalysts based on cyclopentadienyl derivatives or inorganic chromate are much more active than those prepared from σ-alkyl Cr complexes.[5,6]

The activity of transition metal alkylidene complexes in homogeneous olefin metathesis and alkyne polymerization has long been exploited.[7] The possible participation of a Cr alkylidene in the active site of heterogeneous polymerization catalysts has been suggested on the basis of spectroscopic evidence[8] and product analysis.[9] Unfortunately, molecular Cr complexes which polymerize olefins remain rare,[10,11] and high valent Cr alkylidenes are virtually unknown.[12]

We set out to synthesize silica-supported alkyl chromium complexes in order to attempt the insertion of ethylene into a preformed Cr−C σ-bond. We previously reported that tetraneopentylchromium(IV) reacts with the hydroxyl groups of amorphous silica (partially dehydroxylated by thermal treatment in vacuo at 200 °C)[13] to give a bis(neopentyl)chromium(IV) surface complex, **1**, eq 1.[6]

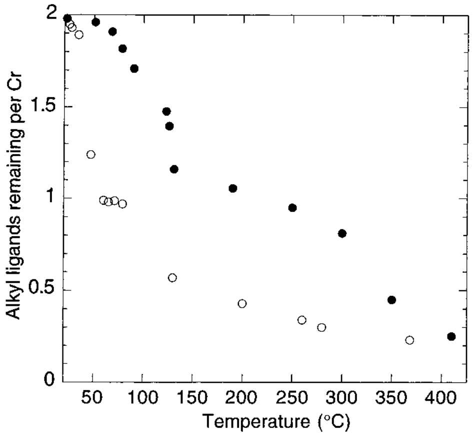

Figure 1. Thermal transformations of ($\equiv$SiO)$_2$Cr(CH$_2$C(CH$_3$)$_3$)$_2$ (open circles) and ($\equiv$SiO)$_2$Cr(CH$_2$Si(CH$_3$)$_3$)$_2$ (filled circles) in vacuum.

$$2{\equiv}\mathrm{SiOH} + \mathrm{Cr(CH_2C(CH_3)_3)_4} \rightarrow \underset{\mathbf{1}}{(\equiv\mathrm{SiO})_2\mathrm{Cr(CH_2C(CH_3)_3)_2}} + 2(\mathrm{CH_3})_4\mathrm{C} \quad (1)$$

The maximum loading of **1** on Aerosil-200 corresponds to 2.0% Cr by mass or 0.40 mmol Cr/g silica. The surface hydroxyl groups are >90% consumed by this reaction: in the IR spectrum, very little residual intensity remains for the ν(O−H) stretching vibration. Like its molecular precursor, **1** is extremely reactive toward O_2 but unreactive toward H_2O vapor (10 Torr) and ethylene (80 Torr) at room temperature over periods of several days. However, when **1** was heated to 100 °C in the presence of ethylene, polyethylene was formed. During a subsequent study of the thermal stability of **1**, we discovered a reaction which produces a long-lived Cr(IV) neopentylidene complex.

Upon heating **1** in vacuum (ca. 10^{-4} Torr) at 70 °C for 4 h, (0.92 ± 0.04) neopentyl ligands per Cr (average of nine experiments) were liberated as neopentane, and a new surface Cr species, **2**, was formed. Figure 1 shows the temperature region of stability for **2**, which decomposes gradually as the temperature is raised above 80 °C. After thermolysis of **1** at 70 °C, the absorbance in the ν(C−H) region of the IR spectrum of a self-supporting silica disk was (0.48 ± 0.03) of its original intensity (by *in situ* integration, average of eight experiments). We note that there are insufficient remaining hydroxyl groups available on the silica surface to undergo a quantitative reaction with **1**. Instead, we propose that the neopentane is generated by α-H elimination,[14] which simultaneously forms a Cr(IV) neopentylidene species, **2**, eq 2.

$$\underset{\mathbf{1}}{(\equiv\mathrm{SiO})_2\mathrm{Cr(CH_2C(CH_3)_3)_2}} \rightarrow \underset{\mathbf{2}}{(\equiv\mathrm{SiO})_2\mathrm{Cr{=}CHC(CH_3)_3}} + \mathrm{C(CH_3)_4} \quad (2)$$

Reaction of **2** with anhydrous HCl(g) (20 Torr, room temperature, 1 h) liberated 0.9 ± 0.1 neopentane/Cr, while a reaction with DCl(g) under similar conditions gave 71% neopentane-d_2. The magnetic moment of **2** is 2.77 μ_B/Cr,[15] consistent with noninteracting d^2 Cr(IV) surface complexes. The alkylidene

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(13) The silica used in all experiments was Degussa Aerosil-200, a nonporous pyrogenic silica with a surface area of 200 m^2/g. After this material is treated in vacuum at 200 °C, there are approximately 0.86 mmol OH/g silica (B. A. Morrow; A. J. McFarlan, *Langmuir* **1991**, *7*, 1695−1701). All reactions with silica-supported complexes were gas−solid reactions, following strict high vacuum protocol as previously described.[6]

(14) The kinetics of this reaction were followed by monitoring the evolution of neopentane. The curve is a single exponential, indicating first-order kinetics, as expected, with $k = 0.0046$ min^{-1} at 70 °C.

(15) The magnetic susceptibility was measured in vacuum as a function of temperature between 2 and 300 K with a 3 kG field on a SQUID magnetometer. The data were fit ($R = 0.9998$) to a Curie−Weiss model with a constant (SiO_2) background, giving a Néel temperature of 0.7 K.

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complex **2** has no precedent in molecular chemistry, although thermolysis of bis(alkyl) complexes is a well-documented route to metal alkylidenes.[16,17] The thermal decomposition of $Cr(CH_2X(CH_3)_3)_4$ (X is C or Si) was reported to liberate neopentane, although no intermediates were isolated.[18,19] However, thermolysis of $TiCH_2C(CH_3)_3)_4$ to give transient $Ti(CH_2C(CH_3)_3)_2({=}CHC(CH_3)_3)$ was recently inferred from kinetic isotope effects.[20] On the silica surface, the formation of a surface Ta(V) neopentylidene was suggested to occur by α-H elimination.[21] We propose that the unusual and unsaturated complex **2** is stabilized on the silica surface by its immobility, which prevents bimolecular dimerization and/or disproportionation reactions.

The mechanism of neopentane formation was confirmed by thermolysis of **1** prepared with neopentyl ligands labeled with deuterium in the α positions. $Cr(CD_2C(CH_3)_3)_4$ (90% α-D_2, 10% α-H_2) was synthesized by reaction of $BrMgCD_2C(CH_3)_3$[22] with $CrCl_3(THF)_3$.[23] The reaction of this compound with silica gave $({\equiv}SiO)_2Cr(CD_2C(CH_3)_3)_2$, with two ν(C−D) vibrations at 2163 and 2103 cm^{-1}, and was accompanied by the liberation of neopentane-d_2 (90%) and neopentane-d_0 (10%).[24] Heating this material in vacuum at 70 °C led to the disappearance of the ν(C−D) vibrations and liberated 61% neopentane-d_3 (calc. 71%) and 39% neopentane-d_2. Whereas thermolysis of unlabeled **1** is half complete in 2.5 h at 70 °C, thermolysis of **1** labeled with deuterium in the α-positions is only half complete in 7.5 h at the same temperature. This difference in reactivity is not consistent with metallacycle formation by γ-elimination, nor with Cr−C bond homolysis, and supports our assignment of the mechanism as α-H elimination. Substantial kinetic isotope effects for α-H/D elimination have been previously reported for transition metal neopentyl complexes,[25] including, most recently, the thermolysis of tetraneopentyltitanium.[20] The subsequent reaction of $({\equiv}SiO)_2Cr{=}CDC(CH_3)_3$ with anhydrous DCl(g) (20 Torr, room temperature, 1 h) gave 81% neopentane-d_3 and no neopentane-d_4.[26]

Spectroscopic evidence for the alkylidene nature of the paramagnetic surface complex **2** is difficult to obtain. Its IR spectrum does not contain a low frequency ν(CH) mode, although these vibrations are sometimes masked by other C−H modes.[7,27] We therefore probed the chemistry of **2** with some characteristic test reactions for high-valent metal alkylidenes. The reaction of **2** with Br_2(g) gave 1,1-dibromo-2,2-dimethylpropane,[28] eq 3, within a few minutes at room temperature, as expected for an electrophilic attack on a metal−carbon double bond.[29] The room-temperature reaction of **2** with acetone vapor immediately gave a trace of the expected olefin 2,4,4-trimethyl-2-pentene from the pseudo-Wittig reaction,[30] eq 4, as well as the condensation product 4-methyl-3-penten-2-one. These reactions are completely consistent with the characterization of **2** as a terminal alkylidene complex.

$$({\equiv}SiO)_2Cr{=}CHC(CH_3)_3 + Br_2 \rightarrow C(CH_3)_3(CHBr_2) \quad (3)$$

$$({\equiv}SiO)_2Cr{=}CHC(CH_3)_3 + (CH_3)_2CO \rightarrow (CH_3)_2C{=}CHC(CH_3)_3 \quad (4)$$

A similar bis(alkyl)complex, $({\equiv}SiO)_2Cr(CH_2Si(CH_3)_3)_2$, **3**,[6] eliminates one of its ligands at 150 °C, Figure 1, and we suggest that the product is also an alkylidene complex $({\equiv}SiO)_2Cr{=}CHSi(CH_3)_3$, **4**. In this reaction, the gases evolved during thermolysis include not only tetramethylsilane but also a mixture of hydrocarbons, including methane. The greater thermal stability of **3** compared to **1** is consistent with weaker M−C bonds in the latter, a phenomenon which has been attributed to greater steric crowding,[25] and has been confirmed kinetically for $Ta(CH_2E(CH_3)_3)_5$ (E is C or Si).[31]

Since there are so few literature reports of high-valent Cr alkylidene complexes, their reactivity is of great interest. When either **2** or **4** were exposed to 20 Torr ethylene at room temperature, we observed immediate ethylene polymerization. Intense bands at 2924 and 2850 cm^{-1}, assigned to the C−H stretching vibrations of polyethylene,[32] saturated the IR spectrum within minutes. Small quantities of $C_{2n}H_{4n}$ α-olefins (1-butene, 1-hexene, etc.) were also detected, as has been previously noted for the Phillips catalyst.[33] The Cr was extracted from the polyethylene with alkaline H_2O_2,[34] and then the polymer was dissolved in 1,2,4-trichlorobenzene. Its ^1H and ^{13}C NMR spectra[35] at 350 K consist of sharp lines at 1.33 and 30.13 ppm, respectively.[36] Polymerization also occurred when 80 Torr propylene was added to **2**, but the reaction was at least an order of magnitude slower than the polymerization of ethylene.

The initiation of polymerization may involve [2 + 2] addition at the alkylidene to form a metallacyclobutane, resembling the olefin metathesis transition state.[37] The mechanism of this reaction and other reactions of these unusual surface-stabilized alkylidene species are under investigation in our laboratory. The use of the silica surface to isolate these unsaturated complexes suggests that other highly reactive transients may also be trapped in this way.

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