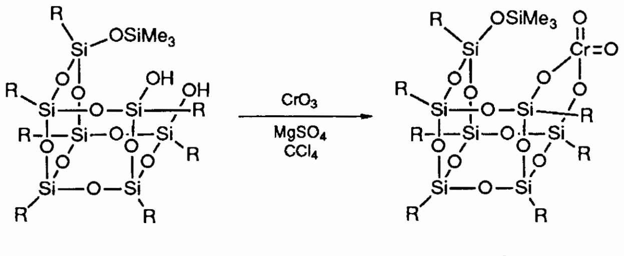
Polyhedral Oligometallasilasesquioxanes as Models for Silica-supported Catalysts: Chromium attached to Two Vicinal Siloxy Groups

Frank J. Feher* and Rusty L. Blanski

Department of Chemistry, University of California, Irvine, CA 92717, USA

The reaction of $[(\text{cyclo-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2]$ with CrO_3 leads to the formation of $[(\text{cyclo-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)CrO_2]$, a new crystallographically characterized silyl-chromate complex that catalyses the polymerization of ethylene in the presence of trialkylaluminium reagents.

Silica-supported chromium catalysts are used extensively for the coordination polymerization of ethylene.[1,2] The commercial importance of these systems has spawned an intense effort to identify likely catalytic species and mechanisms by which they form, function and decay. The Phillips polymerization catalyst,[1] in particular, has been the subject of many detailed studies, but precious little can be gleaned from the 'deluge of conjecture'[1d] to support any single mechanism unambiguously. Many of the difficulties associated with studying these systems are inherent in any study of heterogeneous catalysis, but some problems clearly stem from a general lack of well defined, homogeneous chromium catalysts for alkene polymerization.[3] In this paper we report the synthesis of one such model, a chromium-containing polyhedral oligometallasilasesquioxane (POMSS) that is capable of polymerizing ethylene in the presence of Me_3Al. Although the active catalyst in this system has yet to be identified, the polyethylene produced is similar to that obtained from Phillips-like catalysts, suggesting that a detailed study of chromium-containing POMSS may provide new insight into the chemistry of Phillips-like polymerization catalysts.



1 R = cyclo-C_6H_{11}

2

The reaction[†] of the bissilanol **1**[4a] with CrO_3 and $MgSO_4$ in CCl_4 gives a quantitative (NMR) yield of chromate ester **2**, which was unambiguously identified on the basis of multinuclear NMR data[‡] and a single-crystal X-ray diffraction study[§] (Fig. 1).

Chromate **2** is one of the few chromate esters that have been structurally characterized,[5] but the interatomic distances and interbond angles appear to be normal.[6] The local structure around Cr is, in fact, similar to that observed for $(Ph_3SiO)_2CrO_2$.[5a] The CrO_4 moiety is nearly tetrahedral, with Cr–O single bond lengths of 1.731(4) Å and Cr=O double bond lengths of 1.574(4) and 1.557(5) Å. Within the limits of experimental uncertainty the two Cr–O–Si bond angles are equal (135.3°) and all Si–O interatomic distances and angles are within the ranges typically observed for cyclohexylsilasesquioxanes.[4]

Like its bis-triphenyl silyl analogue,[7] chromate **2** is a strong oxidant that readily oxidizes stilbene to benzaldehyde (77 °C; CCl_4; 1 h). However, unlike $(Ph_3SiO)_2CrO_2$, which only polymerizes ethylene under forcing conditions,[7,8] chromate **2** is a good precatalyst for the polymerization of ethylene. The addition of Me_3Al (2–10 equiv.) to benzene solutions of **2** produces dark-orange solutions which readily polymerize ethylene. At room temperature, ethylene pressures of 1 atm[¶] and chromium concentrations of 3.1 μmol dm^{-3}, ethylene polymerization typically proceeds for several hundred turnovers (~3 h) before gelation of the solution prevents further uptake of ethylene and leads to deactivation of the catalyst. GPC analysis of the polymer indicated M_n and M_w values of 8890 and 30 680, respectively, and a differential scanning calorimetry curve for the polymer exhibited no detectable exotherm prior to the onset of crystalline melting at 130.7 °C. Consistent with the relatively high T_m, IR and NMR spectra[9] indicate that the polymer is composed of essentially linear polyethylene chains with methyl and vinyl termini. For a polymerization performed at 550 psig of ethylene using 0.088 mmol of **2** (C_6H_6; 25 °C), more than 3200 turnovers were observed before the reaction mixture completely solidified. The average molecular weights, polydispersity and T_m were 61 400 (M_n), 376 500 (M_w), 6.13 and 132.1 °C.

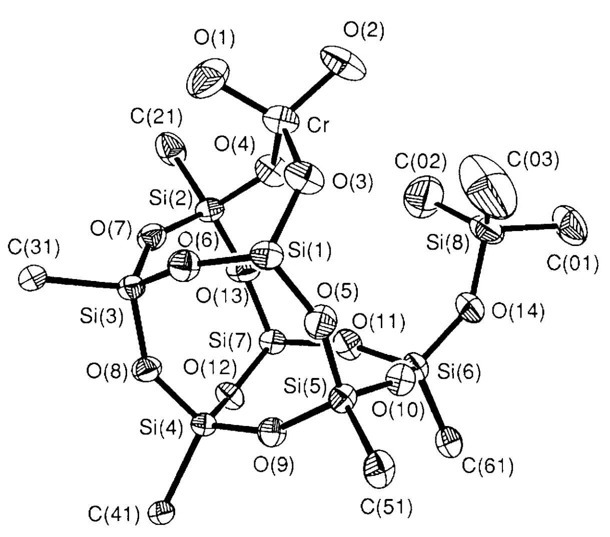


Fig. 1 Perspective ORTEP plot of **2**. For clarity, thermal ellipsoids are shown at 50% probability and only C attached to Si [except Si(1) and S(7)] are shown. Selected interatomic distances (Å) and interbond angles (°) are: Cr–O(1) 1.557(5), Cr–O(2) 1.574(4), Cr–O(3) 1.731(4), Cr–O(4) 1.730(4), O(1)–Cr–O(2) 109.4(2), O(1)–Cr–O(3) 110.0(2), O(1)–Cr–O(4) 109.9(2), O(2)–Cr–O(3) 108.3(2), O(2)–Cr–O(4) 109.8(2), O(3)–Cr–O(4) 109.5(2), Si(1)–O(3)–Cr 135.4(2), Si(2)–O(4)–Cr 135.2(2), other Si–O–Si 145–149.

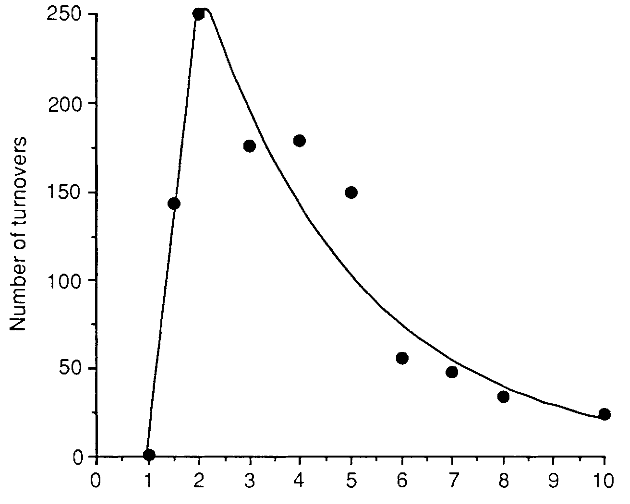


Fig. 2 Dependence of polymerization activity (*i.e.*, average number of turnovers per Cr) on the number of equivalents of Me_3Al added to **2**. All reactions were run under identical conditions (31 μmol of **2**; C_6H_6; 25 °C; 720 Torr) and quenched with propan-2-ol after 3 h.

The activity of the catalyst mixture is sensitive to the amount of Me_3Al used to generate the active catalyst(s). As shown in Fig. 2, polymer production (~1 atm; 25 °C; 3 h) is maximized when approximately two equivalents of Me_3Al are used as cocatalyst. In contrast, the reaction of $(Ph_3SiO)_2CrO_2$ with Me_3Al under identical conditions causes rapid reduction of the chromium complex to a dirty greenish-orange solution

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[†] In a typical reaction, a mixture of disilanol **1** (5.00 g, 4.25 mmol), CrO_3 (2.00 g, 14.2 mmol), and $MgSO_4$ (8.00 g) in CCl_4 (250 ml) was stirred overnight in the dark. Vacuum filtration and evaporation of the volatile material (25 °C in the dark; 10^{-3} Torr) gave an amorphous orange foam, which was recrystallized from a minimum of hexane (−40 °C; 3 days) to give **2** as bright orange, somewhat photosensitive crystals in 75% yield (4.0 g).

[‡] *Spectroscopic data* for **2**: ^1H NMR (500 MHz; C_6D_6; 25 °C): δ 2.00 (m, 14H), 1.63 (br m, 35H), 1.15 (br m, 28H) and 0.43 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz; C_6D_6; 25 °C): δ 28.03, 27.91, 27.88, 27.71, 27.64, 27.59, 27.55, 27.47, 27.18 and 26.88 (s, CH_2); 25.45, 24.70, 24.29, 23.67 and 23.47 (s, 1 : 2 : 2 : 1 : 1 for *C*H); 1.94 [s$(CH_3)_3SiO$]; $^{29}Si\{^1H\}$ NMR (99.36 MHz; C_6D_6–C_6H_6; 25 °C): δ 10.38 (s, $SiMe_3$); −60.15, −67.03, −68.81, and −69.57 (s, 2 : 2 : 1 : 2 for cyclohexyl-SiO_3); m.p. 155.5 °C (decomp.).

[§] *Crystal data* for **2** (n-hexane): $C_{51}H_{100}CrO_{14}Si_8$, M_r = 1214.0, monoclinic, space group $P2_1/c$, a = 11.051(2); b = 23.778(5); c = 25.182(5) Å, β = 91.40(3)°, U = 6615(2) Å^3, D_c = 1.219 g cm^{-3}, Z = 4, $F(000)$ = 2616 electrons, μ(Mo-Kα) = 3.63 cm^{-1}. Current R 0.0608 (R_w 0.0661) for 685 variables refined against 6881 unique, observed $[|F_o| > 4.0\sigma(|F_o|)]$ reflections measured at 173 K on a Siemens R3m/V diffractometer in the range $4.0 < 2\theta < 50.0°$. The structure was solved by direct methods (SHELXTL PLUS) and refined using full matrix least squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms with fixed isotropic U values (0.08 Å^2) were contrained to idealized geometries (C–H 0.95 Å) using a standard riding model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[¶] For reactions performed at 1 atm, Matheson polymerization grade ethylene (99.9%) was purified by slowly bubbling through tri-n-octylaluminium, followed by two freeze (−196 °C)–pump (10^{-3} Torr)–thaw (25 °C) degas cycles. For reactions performed at 550 psig, the ethylene was used without further purification.

that slowly produces trivial amounts of polyethylene. We have not extensively explored the use of other cocatalysts, but we have observed similar activities using Et_3Al instead of Me_3Al.

The identity of the active polymerization catalyst in our system is currently not known, but the much greater reactivity of chromate **2** compared to $(Ph_3SiO)_2CrO_2$ suggests that the chromium-containing silasesquioxane framework remains intact. It also appears that the active catalyst is formed by the reduction of **2** because anaerobic aqueous quenching of reaction mixtures during the course of polymerization produces green solutions containing negligible concentrations of Cr^{VI} (by iodometry). The green colour could be interpreted (or misinterpreted!) as evidence for a Cr^{III} catalyst, but there is no direct evidence for such a species. Further speculation about the oxidation state or the identity of the active catalyst(s) would be inappropriate without additional data. Efforts to elucidate the active catalyst in this interesting system are currently in progress.

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References

1 (*a*) M. P. McDaniel, C. H. Leigh and S. M. Wharry, *J. Catal.*, 1989, **120**, 170; (*b*) H. L. Krauss in *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, eds. W. Kaminsky and H. Sinn, Springer-Verlag, New York, 1988, pp. 163–168; (*c*) M. P. McDaniel, *Adv. Catal.*, 1985, **33**, 47; (*d*) M. P. McDaniel in *Transition Metal Catalyzed Polymerization, Part B*, ed. R. P. Quirk, Harwood Academic Press, New York, 1983, pp. 713–735; (*e*) J. P. Hogan, *J. Polym. Sci., Pt A-1*, 1970, **8**, 2637; (*f*) T. W. Woo and S. I. Woo, *J. Catal.*, 1990, **123**, 215.

2 (*a*) F. J. Karol, *Catal. Rev. Sci. Eng.*, 1984, **26**, 557; (*b*) F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson and W. L. Carrick, *J. Polym. Sci., Pt A-1*, 1972, **10**, 2621.

3 *Cf.* (*a*) B. J. Thomas and K. H. Theopold, *J. Am. Chem. Soc.*, 1988, **110**, 5902; (*b*) K. H. Theopold, Acc. Chem. Res., 1990, **23**, 263.

4 (*a*) F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741; (*b*) F. J. Feher and D. A. Newman, *J. Am. Chem. Soc.*, 1990, **112**, 1931; (*c*) F. J. Feher, T. A. Budzichowski and K. J. Weller, *J. Am. Chem. Soc.*, 1989, **111**, 7288; (*d*) F. J. Feher, *J. Am. Chem. Soc.*, 1986, **108**, 3850; (*e*) F. J. Feher, S. L. Gonzales and J. W. Ziller, *Inorg. Chem.*, 1988, **27**, 3440.

5 (*a*) B. Stensland and P. Kierkegaard, *Acta Chem. Scand.*, 1970, **24**, 211; (*b*) P. Stavropoulos, N. Bryson, M.-T. Youinou and J. A. Osborn, *Inorg. Chem.*, 1990, **29**, 1807.

6 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988.

7 L. M. Baker and W. L. Carrick, *J. Org. Chem.*, 1970, **35**, 773.

8 W. L. Carrick, R. J. Turbett, F. J. Karol, G. L. Karapinka, A. S. Fox and R. N. Johnson, *J. Polym. Sci., Pt A-1*, 1972, **10**, 2609.

9 (*a*) C. Groeneveld, P. P. M. M. Wittgen, H. P. M. Swinned, A. Wernsen and G. C. A. Schuit, *J. Catal.*, 1983, **83**, 346; (*b*) J. Spevacek, *Polymer*, 1978, **19**, 1149.