Oligomerization

A Neutral Chromium(III) Catalyst for the Living "Aufbaureaktion"[**]

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The commercial production of linear primary alcohols is typically achieved by processes based on the "Aufbaureaktion".[1] These processes, which involve the reaction of

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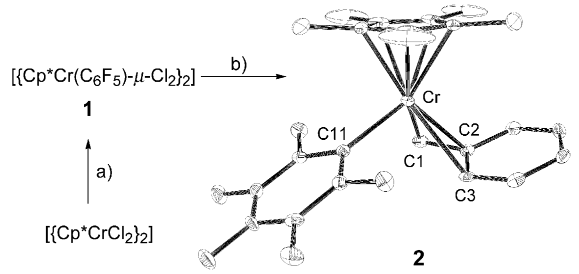
triethylaluminum with ethylene, feature several drawbacks including elevated temperatures and pressures, olefin formation by β-H elimination, and branching. In addition, a number of safety problems associated with the use of ethylene under high pressures and possible runaway reactions are encountered when dealing with the current technology. Parallel developments in the field of olefin polymerization have demonstrated the potential of organometallic complexes as highly active catalysts.[2] Cationic cyclopentadienide chromium(III) complexes are important examples of such catalysts and display high olefin polymerization activities at room temperature and under 1 atm of ethylene.[3–8] As demonstarted by Theopold and co-workers, neutral chromium(III) complexes that are coordinatively unsaturated and that feature a Cr–C_{alkyl} σ bond are also catalytically active.[9]

A series of recent reports demonstrate that cationic olefin-polymerization catalysts can be combined with alkyl aluminum, alkyl magnesium, and alkyl zinc derivatives to afford ethylene oligomers.[10–14] So far, some of the most impressive results have been obtained with cationic chromium(III) complexes.[15–18] Because of the high costs associated with the use of activators such as methylaluminoxane (MAO) or $B(C_6F_5)_3$, we have focused on neutral catalysts and report herein the chemistry of pentafluorophenyl chromium(III) complexes.

[{Cp*$CrCl_2$}$_2$] reacts with C_6F_5Li in Et_2O/THF at −78 °C to afford [{Cp*Cr(C_6F_5)(μ-Cl)}$_2$] (**1**) in 73 % yield in the form of dark blue crystals. As with other Cp*Cr chloro complexes, **1** most likely exists as a chloride-bridged dimer.[9c] Compound **1** is also formed by the reaction of [{Cp*$CrCl_2$}$_2$] with [{(C_6F_5)$AlMe_2$}$_2$] or [{(C_6F_5)$AlEt_2$}$_2$] (1 equiv) in toluene at room temperature. Similar C_6F_5-transfer reactions have been documented by Bochmann and Sarsfield in the case of zirconocene complexes.[19] Complex **1** has a room-temperature magnetic moment μ_{eff} of 4.36 μ_B, which is in agreement with the presence of two antiferromagnetically coupled Cr^{III} centers. The ^{1}H NMR spectrum shows a broad resonance at $\delta = -35.2$ corresponding to the Cp* methyl signal. Compound **1** reacts with BnMgCl in Et_2O/THF to afford mononuclear [Cp*Cr(C_6F_5)(η^3-Bn)] (**2**, Bn = benzyl) as dark brown crystals in 64 % yield (Scheme 1).

Compound **2** is highly soluble in hydrocarbon solvents; it is thermally stable and can be kept under an inert atmosphere for extended amounts of time at room temperature. The signal for the Cp* methyl in the ^{1}H NMR spectrum differs from that of **1** and appears at $\delta = -3.6$ ppm. The room-temperature magnetic moment μ_{eff} of 3.83 μ_B is in agreement with the presence of three unpaired d electrons at the Cr^{III} center. The X-ray crystal structure of **2** (Scheme 1) shows relatively short bond lengths for Cr–C1 (2.118(3) Å), Cr–C2 (2.282(3) Å), and Cr–C3 (2.410(3) Å),[20] indicating that the benzyl ligand is η^3 coordinated to the chromium center. This coordination mode is confirmed by the relatively short C1–C2 bond (1.437(4) Å) and the elongated C2–C3 bond (1.417(4) Å). These metrical parameters are similar to those found in [Cp*Cr(η^1-Bn)(μ-η^3:η^6-Bn)CrCp*], which also features a η^3-benzyl ligand.[9d] The pentafluorophenyl ligand in **2** is terminally ligated to the chromium center (Cr–C11 2.109(3) Å).



Scheme 1. Synthesis and crystal structure of **2**. a) C_6F_5Li, Et_2O/THF, −78 °C; b) BnMgCl, Et_2O/THF, 25 °C.

Compound **2** catalyzes the polymerization of ethylene. In the absence of any added activator, exposure of a solution of **2** in toluene (10^{-3} M) to ethylene (1.1 atm) at room temperature leads to the rapid precipitation of polyethylene. Under these conditions, the activity (266 kg mol Cr^{-1} h^{-1}) is greater than that previously reported for other neutral chromium complexes.[9] In the presence of $AlEt_3$, compound **2** catalyzes the formation of AlRR′R″ species in which R, R′, and R″ are ethylene oligomers. For example, when a solution of **2** in toluene (10^{-3} M) containing a 90-fold excess of $AlEt_3$ is exposed to ethylene (1.1 atm) for 15 min at room temperature, 2.64 g of ethylene are readily consumed without precipitation of polyethylene. The ^{1}H NMR spectrum of the crude reaction mixture confirmed the formation of AlRR′R″ species. Under these conditions, the activity of the catalytic system is 211 kg mol Cr^{-1} h^{-1}. Hydrolysis of the reaction mixture leads to the formation of linear alkanes with an average chain length of 17 ± 1 carbon units, as determined from the integrated ^{1}H NMR spectrum. As shown by gas chromatography, the chain length of the resulting alkanes ranges from C6 to C32.

The catalytic system formed by **2** and $AlEt_3$ presents the features of a living polymerization. The reaction resumes after extended interruption of the ethylene feed. Moreover, the observed chain length distribution closely matches that predicted by the Poisson distribution formula [Eq. (1),

$$\chi_n = \text{mole fraction of } C_{2x}H_{4x+2} = (\nu^{(x-1)}\, e^{-\nu})/(x-1)! \qquad (1)$$

ν = average number of added ethylene units, x = number of ethylene units, $n = 2x$; Figure 1].[21] The data obtained from the oligomerization reactions are summarized in Table 1. For entries 1 and 2, the chain-length distribution could be accurately determined. In these cases the value of ν that provides the best fit to the observed distribution approaches the value that is derived experimentally from the amount of ethylene units consumed per AlEt group (Figure 1).

Although we have not been able to confirm the exact nature of the catalytically active species, we have observed that the activity decreases as the [$AlEt_3$]/[**2**] ratio increases (Table 1). Similar inhibitory effects are not uncommon in chromium[15] or zirconium chemistry[22] and, as previously suggested, most likely result from saturation of the transition metal center through formation of a heterobimetallic complex of type **C** (see Scheme 2), whose concentration increases at higher $AlEt_3$ concentrations. As expected, increasing the

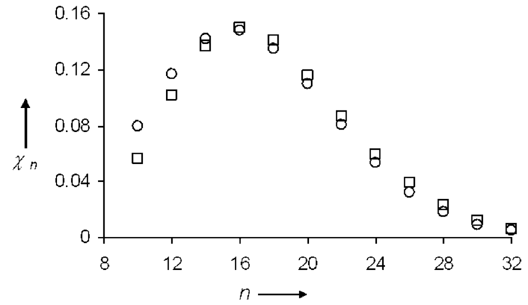


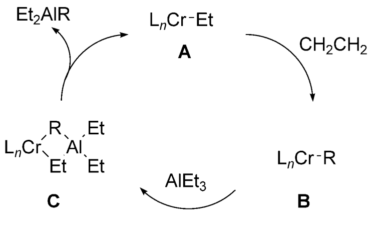
Figure 1. The experimental (□) and calculated (○, Poisson distribution, $\nu = 7.3$; see Equation (1)) mol fraction χ_n as a function of the number of carbon atoms n in the alkanes formed after hydrolysis of the mixtures obtained from the reaction of ethylene with **2** and $AlEt_3$ for 15 min. Reaction conditions: $[AlEt_3]/[\mathbf{2}] = 90$, $p = 1.1$ atm, $T = 25$ °C.

Table 1: Data obtained for the oligomerization reactions.[a]

Entry	$[AlEt_3]/[\mathbf{2}]$	Activity[b]	Avg chain length[c]
1	90	211	17 ± 1
2	135	155	9 ± 1
3	180	41	–[d]
4	450	24	–[d]

[a] Reaction conditions: $[\mathbf{2}] = 10^{-3}$ M, $p = 1.1$ atm, $T = 25$ °C, 15 min reaction time. [b] Amount of ethylene (kg) consumed per mol of **2** per hour. [c] Determined by ^1H NMR spectroscopy after hydrolysis of the reaction mixture. [d] The average chain length was too small for accurate determination.

$[AlEt_3]/[\mathbf{2}]$ molar ratio results in the production of shorter chains. While polyethylene formation is observed at low $[AlEt_3]/[\mathbf{2}]$ ratios, reactions carried out at greater ratios do not result in the precipitation of any polymer and afford only shorter chains. These observations are in agreement with a catalytic cycle in which the growing alkyl chain is transferred from chromium to aluminum (Scheme 2). We propose that this exchange reaction involves a bridged chromium–aluminum complex of type **C**.



Scheme 2. Proposed catalytic cycle for the oligomerization reaction. L = ligands, R = oligomer.

In conclusion, we report for the first time the use of a neutral catalyst that promotes the Aufbaureaktion in the absence of any activators. In contrast to the conventional Aufbaureaktion, which requires elevated temperatures and ethylene pressures, the process that we describe produces linear alkanes at room temperature and under 1 atm of ethylene. Moreover, this method features the characteristics of a living polymerization. The molecular-weight distribution of the resulting ethylene oligomers is narrow and well accounted for by the Poisson distribution formula.

Experimental Section

1: ***Caution: solutions of C_6F_5Li are potentially unstable and should not be warmed above −78°C.*** A solution of C_6F_5Li was prepared at −78°C by the addition of *n*BuLi (6.71 mmol) to C_6F_5Br (0.85 mL, 6.71 mmol) in Et_2O (50 mL) and then added at −78°C to a solution of $[\{Cp^*CrCl_2\}_2]$, which was prepared by the addition of Cp*Li (0.90 g, 6.33 mmol) to $CrCl_3$ (1.00 g, 6.31 mmol) in THF (50 mL). The resulting mixture was allowed to warm to room temperature and stirred for 18 h, during which time the color turned to dark blue. The solvents were removed under vacuum, and the residue was extracted with toluene (200 mL) and filtered. The filtrate was concentrated to 80 mL and mixed with hexanes (50 mL). Cooling to −20°C afforded dark blue crystals of **1** after 3 d (1.81 g, 2.32 mmol, 73.6%). Elemental analysis: calcd for $C_{32}H_{30}Cr_2Cl_2F_{10}$: C 49.28, H 3.85; found: C 49.20, H 3.89; ^1H NMR ($[D_8]$toluene): $\delta = -35.21$ ppm (brs, Cp*); $\mu_{eff} = 4.36\ \mu_B$ (room temperature).

2: A solution of BnMgCl (0.80 mmol) in Et_2O was added to **1** (0.31 g, 0.40 mmol) in THF (50 mL) at room temperature. The color of the solution turned to dark purple, and the mixture was stirred for 18 h. Following removal of the solvent under vacuum, the residue was suspended in toluene (20 mL) and stirred for 15 min. After repeated removal of the solvent under vacuum, the residue was extracted with pentane (100 mL), filtered, and concentrated to 20 mL. Cooling to 5°C for 2 d afforded dark brown crystals of **2** (0.23 g, 0.51 mmol, 64%). Satisfactory elemental analysis could not be obtained since **2** is very air-sensitive. Each batch was controlled by NMR spectroscopy as well as by measurement of the unit cell. ^1H NMR ($[D_6]$benzene): $\delta = -29.5$ (brs), −3.7 (brs, CH_3-Cp*), 30.2 ppm (brs); $\mu_{eff} = 3.83\ \mu_B$.

Ethylene oligomerization experiments: In a 200-mL Schlenk flask, catalyst **2** (22.5 mg, 50 μmol) was dissolved in toluene (50 mL). Following addition of the appropriate amount of $AlEt_3$ ($[AlEt_3]/[\mathbf{2}] = 0$, 90, 135, 180, 450), the flask was weighed, placed in a room-temperature water bath, and connected to an ethylene manifold. Before each experiment, the flask was evacuated for 5 s and refilled with 1.1 atm of ethylene, to which it remained exposed for 15 min. The ethylene feed was then discontinued and the flask was weighed for activity measurements. The reaction was quenched with water (10 mL) at 0°C. The toluene layer was separated for analysis by ^1H NMR spectroscopy and gas chromatography.

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[20] Crystal structure analysis of **2** ($C_{23}H_{22}CrF_5$): $M_r = 445.41$, monoclinic, space group $P2(1)/c$, $a = 9.3808$ (19), $b = 11.592$ (2), $c = 18.143$ (4) Å, $\beta = 92.004$ (4)°, $V = 1971.6(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.501$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 110$ (2) K, 12137 measured reflections, 4529 unique reflections, $R_{int} = 0.0647$, $\mu = 0.632$ mm^{-1}, $R1$ ($I > 2\sigma$) = 0.0538 for 262 parameters. The crystal was mounted onto a glass fiber with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. CCDC-220136 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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