

Synthesis, structure and catalytic properties of $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ toward ethylene in the presence of AlEt_3

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Abstract

Treatment of $[\text{Cp}^*\text{CrCl}(\text{C}_6\text{F}_5)]_2$ with BnMgCl (Bn = benzyl) in $\text{Et}_2\text{O}/\text{THF}$ affords $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ (**1**) which has been isolated in 72% yield. This compound whose magnetic moment is equal to of $4.037 \mu_{\text{B}}$ has been characterized by NMR and single crystal X-ray analysis. Compound **1** alone does not polymerize ethylene when dissolved in toluene. However, addition of excess AlEt_3 to a solution of **1** in toluene leads to a catalytically active system which readily oligomerizes ethylene under standard conditions. Oligomerization experiments carried out with $[\text{1}] = 10^{-3} \text{ M}$ and $[\text{AlEt}_3] = 9 \times 10^{-2} \text{ M}$ for 15 min lead to the production of ethylene oligomers with an activity of $280 \text{ kg mol Cr}^{-1} \text{ h}^{-1}$. The experimental molecular weight distribution observed at intermediate times during the reaction is satisfactorily accounted for by the Poisson distribution formula, which is indicative of a living polymerization system. These observations are in agreement with a catalytic cycle in which the growing alkyl chain is transferred from chromium to aluminum via a bimetallic complex in which the chromium and aluminum centers are bridged by an alkyl group and the growing polymer chain.

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1. Introduction

The catalytic production of linear hydrocarbons by oligomerization of ethylene under mild conditions is an area of active research [1,2]. In this context, recent efforts have focused on the use of transition metal catalysts in combination with a main group alkyl derivatives [3–7]. In these systems, the transition metal catalysts promotes ethylene oligomerization and reversibly transfers the growing chain to the main group alkyl [3–7]. As part of our contribution to this chemistry, we have studied homogeneous Cr(III) catalysts [8–15] that feature a pentafluorophenyl ligand bound to the metal center [16,17]. In combination with AlEt_3 and under 1 atm of ethylene, we found that derivatives such as

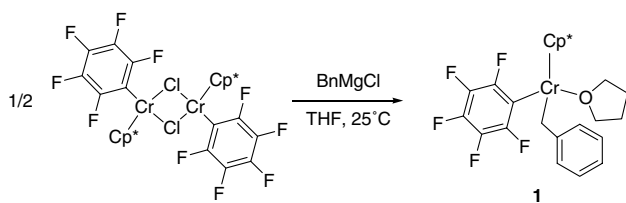
$[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\eta^3\text{-Bn})]$ (Bn = benzyl) catalyze the “Aufbaureaktion” and produce linear alkyl chains whose molecular weights strictly follow the Poisson distribution [16]. In a continuation of these efforts, we would like to report the synthesis, structure and catalytic properties of $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ (**1**) toward ethylene in the presence of AlEt_3 .

2. Results and discussion

2.1. Synthesis and characterization

Treatment of $[\text{Cp}^*\text{CrCl}(\text{C}_6\text{F}_5)]_2$ with BnMgCl in $\text{Et}_2\text{O}/\text{THF}$ followed by solvent evaporation to dryness and extraction with pentane gives the mononuclear Cr(III)–THF adduct $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ (**1**) as dark purple crystals in 72% yield (Scheme 1).

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Scheme 1.

Compound **1** is highly soluble in hydrocarbon solvents; it is thermally stable and can be kept in an inert atmosphere for extended amount of time at room temperature. The Cp* methyl signal in the ^1H NMR spectrum appears at $\delta = -3.42$ is close to that observed for $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\eta^3\text{-Bn})]$ ($\delta = 3.6$). The room temperature magnetic moment μ_{eff} of $4.037 \mu_{\text{B}}$ is in agreement with the presence of three unpaired d-electrons at the Cr(III) center. The structure of **1** has been determined by single crystal X-ray diffraction. Pertinent crystallographic data have been assembled in Table 1. The coordination geometry about the chromium center is pseudooctahedral and the complex adopts a structure reminiscent of a three-legged piano-stool. Examination of the crystal structure confirms the presence of a pentafluorophenyl, a THF, and a κ^1 -benzyl ligand bound to the chromium

Table 1
Crystal data, data collection, and structure refinement for **1**

Crystal data	1
Formula	$\text{C}_{27}\text{H}_{30}\text{CrF}_5\text{O}$
M_r	517.51
Crystal size (mm^3)	$0.77 \times 0.75 \times 0.47$
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (\AA)	16.695(13)
b (\AA)	8.710(7)
c (\AA)	17.153(13)
α ($^\circ$)	90.00
β ($^\circ$)	100.720(13)
γ ($^\circ$)	90.00
V (\AA^3)	2451(3)
Z	4
ρ_{calc} (g cm^{-3})	1.402
μ (Mo K α) (mm^{-1})	0.522
Absorption correction	Empirical
$F(000)$ (e)	1076
T (K)	110(2)
Theta range ($^\circ$)	1.56–23.28
hkl range	$-18 \leq h \leq 18, -9 \leq k \leq 9,$ $-18 \leq l \leq 13$
Measured reflections	10,508
Unique reflections [R_{int}]	3516 [0.0669]
Reflections used for refinement	3516
Refined parameters	308
$R_1,^a wR_2,^b [I > 2\sigma(I)]$	0.0507, 0.1186
ρ_{fin} (max/min) (e \AA^{-3})	0.780 and -0.621

^a $R_1 = \sum (|F_o^2| - |F_c|) / |F_o|$;

^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2) / 3$.

center. The length of the Cr–C bond (Cr(1)–C(8) 2.120(4) \AA) formed between the chromium center and the *ipso*-carbon of the pentafluorophenyl group is similar to that observed in related complexes such as $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\eta^3\text{-Bn})]$ (2.109(3) \AA), $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Me})(\text{Py})]$ (2.126(6) \AA), and $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\mu\text{-Me})_2]$ (2.104 \AA) [16,17]. The lengths of the Cr–C bond formed by the terminal benzyl ligand (Cr(1)–C(1) 2.122(4) \AA) are similar to the value reported for $[\text{Cp}^*\text{Cr}(\text{Py})(\text{Bn})_2]$ (2.125(9) and 2.139(9) \AA) [15c] (see Fig. 1).

2.2. Ethylene oligomerization

Compound **1** alone is not catalytically active when dissolved in toluene and exposed to ethylene, which is not surprising since the chromium center of **1** is coordinatively saturated [10]. As in the case of $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Me})(\text{Py})]$ [17], addition of excess AlEt_3 to a solution of **1** in toluene activates the catalyst which readily oligomerizes ethylene (Scheme 2). This activation

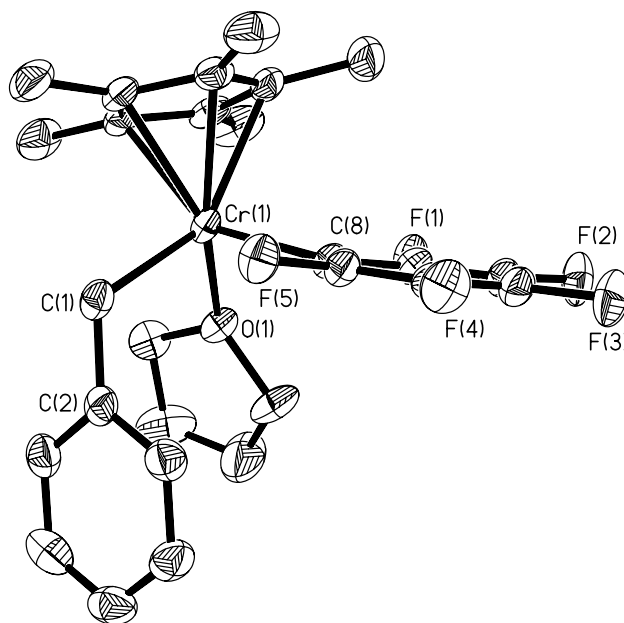
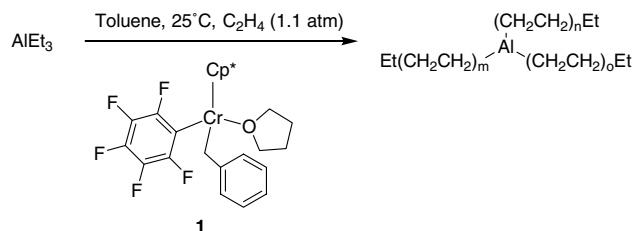


Fig. 1. ORTEP view of **1** (50% ellipsoids). Selected interatomic distances (\AA) and angles ($^\circ$): Cr(1)–O(1) 2.072(3), Cr(1)–C(8) 2.120(4), Cr(1)–C(1) 2.122(4); O(1)–Cr(1)–C(8) 96.03(13), O(1)–Cr(1)–C(1) 93.11(13), C(8)–Cr(1)–C(1) 102.52(14).



Scheme 2. $m, n, o = \text{integers}$.

suggests that the Lewis acidic AlEt_3 is able to abstract the THF ligand thereby generating an unsaturated chromium center. Interestingly, the chloro-derivative $[\text{Cp}^*\text{CrCl}(\text{C}_6\text{F}_5)_2]$ is not activated by AlEt_3 . When a 50 mL solution of **1** in toluene (10^{-3} M) containing a 90-fold excess of AlEt_3 is exposed to ethylene (1.1 atm) at 25° , 3.5 g of ethylene is consumed in 15 min without formation of a precipitate. The activity of this system ($280 \text{ kg mol Cr}^{-1} \text{ h}^{-1}$) is similar to those observed for $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\eta^3\text{-Bn})]$ ($211 \text{ kg mol Cr}^{-1} \text{ h}^{-1}$) and $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Me})(\text{Py})]$ ($150 \text{ kg mol Cr}^{-1} \text{ h}^{-1}$) under similar conditions [16,17]. Hydrolysis of the resulting mixture results in the formation of linear alkanes with an average chain length of 21 ± 1 carbon units, as determined from the integrated ^1H NMR spectrum of the toluene phase. As previously suggested, these observations are in agreement with a catalytic cycle where the growing alkyl chain is transferred from chromium to aluminum. This transfer is thought to occur via a bimetallic complex in which the chromium and aluminum centers are bridged by an alkyl group and the growing polymer chain [13,17]. Cationic examples of such bimetallic intermediates are also known in zirconium chemistry [18] and were first postulated by Bazan for $\text{Cp}^*\text{Cr}(\text{III})$ complexes [13]

$$\chi_n = \text{mole fraction of } \text{C}_{2x}\text{H}_{4x+2} \\ = (v^{(x-1)} \cdot e^{-v}) / (x-1)! \quad (1)$$

(v = average number of added ethylene, x = number of ethylene units, $n = 2x$).

The progress of a typical oligomerization reaction ($[\text{I}] = 10^{-3}$ M, $[\text{AlEt}_3] = 63 \times [\text{I}]$) was monitored as a function of time. The reaction mixture was sampled every three minutes, hydrolyzed and analyzed by GC. The experimental molecular weight distribution observed at each time interval could be satisfactorily accounted for

by the Poisson distribution formula (Eq. (1) and Fig. 2) [19] yielding an average number of added ethylene $v = 2.5, 4.3, 6.2, 8.1$ and 11.9 after 3, 6, 9, 12 and 15 min, respectively. Similar observations have been made by Gibson et al. in the case of an iron-catalyzed ethylene oligomerization on zinc dialkyls [20] and by us with $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Me})(\text{Py})]$ [17]. As indicated by the linearity of the plot of the average number of added ethylene (v) versus time (Fig. 3), the oligomerization rate remains essentially constant and does not appear influenced in the narrow window of the growth reaction. The slope of the line fitting this experimental data corresponds to the rate of ethylene insertion into the growing oligomers and is equal to $2.25 \times 10^{-2} (\text{mol C}_2\text{H}_2) \times (\text{mol growing oligomer})^{-1} \times \text{s}^{-1}$. Since ethylene insertion takes place at the chromium center, the rate of ethylene insertion at

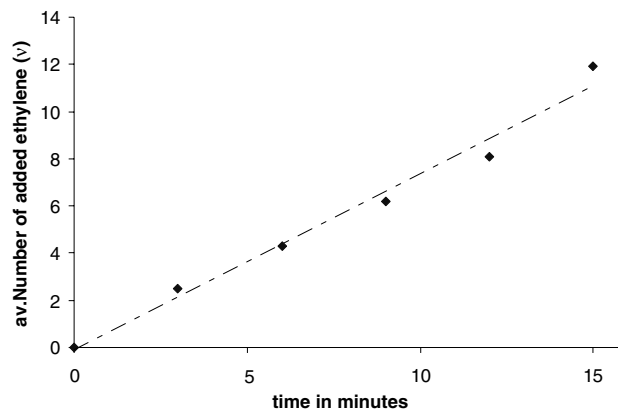


Fig. 3. Plot of the average number of added ethylene (v) versus time for the oligomerization of ethylene catalyzed by **1** and AlEt_3 ($[\text{I}] = 10^{-3}$ M, $[\text{AlEt}_3]/[\text{I}] = 63$; $P = 1.1$ atm, $T = 25^\circ\text{C}$).

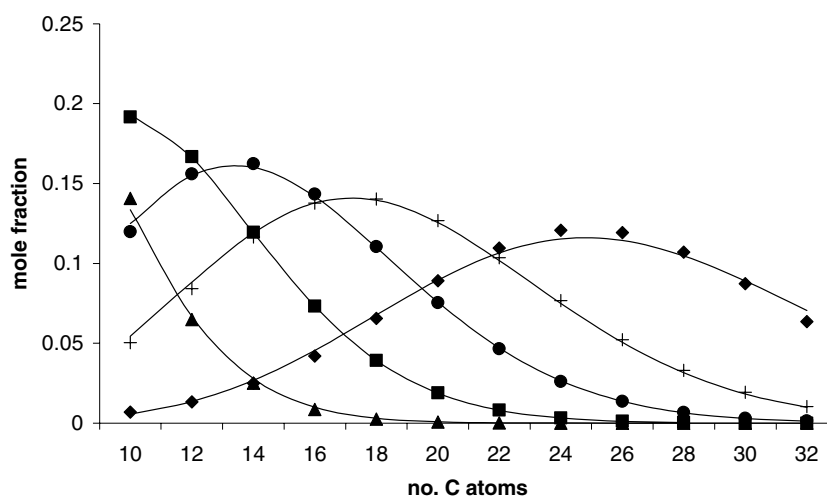


Fig. 2. Experimental (points) and calculated (thin lines) chain length distribution of the alkanes formed, after hydrolysis of the reaction mixture obtained at 3 min intervals, by the reaction of ethylene with **1** and AlEt_3 ($[\text{I}] = 10^{-3}$ M, $[\text{AlEt}_3]/[\text{I}] = 63$; $P = 1.1$ atm, $T = 25^\circ\text{C}$). (▲: 3 min, $v = 2.5$. ●: 6 min, $v = 4.3$. ●: 9 min, $v = 6.2$. +: 12 min, $v = 8.1$. ◆: 15 min, $v = 11.9$).

chromium is equal to $4.2 (\text{mol C}_2\text{H}_2) \times (\text{mol Cr})^{-1} \times \text{s}^{-1}$. Because a strict Poisson distribution is observed, it is justified to assume that each insertion is immediately followed by a transfer of the chain from the chromium to the aluminum center. As a result, the rate of ethylene insertion at chromium represents a lower limit for the rate of chain exchange between the chromium and aluminum centers under the present experimental conditions ($[\mathbf{1}] = 10^{-3} \text{ M}$, $[\text{AlEt}_3] = 63 \times [\mathbf{1}]$).

3. Conclusion

The results reported in this paper indicate that $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ (**1**) promotes the “Aufbau-reaktion” in the absence of MAO or $\text{B}(\text{C}_6\text{F}_5)_3$ at room temperature and under 1 atm of ethylene. The molecular weight distribution of the linear alkanes produced by this system strictly follows a Poisson distribution thus indicating that the oligomerization process is “living”. The activity of complex **1** toward ethylene in the presence of AlEt_3 is comparable to that of $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\eta^3\text{-Bn})]$ which suggests that $\text{Cp}^*\text{CrC}_6\text{F}_5$ alkyl complexes bearing donor ligands are useful precatalysts. From these results, as well as those described in our previous papers [16,17], it can be concluded that the presence of an alkyl ligand serves as a minimum requirement for the catalytic activity of $\text{Cp}^*\text{Cr}(\text{III})\text{C}_6\text{F}_5$ complexes toward ethylene in the presence of AlEt_3 .

4. Experimental

4.1. General procedures

All experimental manipulations were carried out under a N_2 atmosphere using standard Schlenk procedures and a glove box. Solvents were dried over sodium and distilled before use. The ethylene gas used in the oligomerization experiments was passed through a P_2O_5 column. NMR spectra were recorded on a Varian VXR-300 instrument at 298 K. The chemical shifts are reported in ppm with reference to the residual proton in the incompletely deuterated solvent. Atlantic Micro-lab (Norcross, GA) performed the elemental analyses. GC analyses were performed with temperature range of 70–280 °C using Hewlett Packard, HP 6890 Series, column specifications: J&W Scientific Inc., CyclodexB 30 m \times 0.25 mm \times 0.25 μm . Anhydrous CrCl_3 was purchased from Strem Chemical Co. $[\text{Cp}^*\text{CrCl}_2]_2$ [21], $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\mu\text{-Cl})_2]$ [17] and Cp^*Li [22] were synthesized by the literature procedures. PhCH_2MgCl was synthesized by addition of PhCH_2Cl (1 mL, 8.70 mmol) to a diethylether (100 mL) solution of Mg (1.1 g, 44 mmol) followed by stirring for 3 h. The concentration of the solution is calculated by acid–base titration.

4.2. Crystallography

The crystallographic measurement for **1** was performed using a Siemens SMART-CCD area detector diffractometer, with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). 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 260778 contains the supplementary crystallographic data for this paper.

4.3. Synthesis of $[\text{Cp}^*\text{Cr}(\text{C}_6\text{F}_5)(\text{Bn})(\text{THF})]$ (**1**)

An Et_2O solution of PhCH_2MgCl (0.80 mmol) was added to a solution of $[\text{Cp}^*\text{CrCl}(\text{C}_6\text{F}_5)]_2$ (0.20 g, 0.256 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. The solvent was removed under vacuum. The resulting residue was dissolved in pentane (40 mL) and the solution was filtered. Next, the solution was concentrated to approximately 20 mL and cooled to $-40 \text{ }^\circ\text{C}$ for 3 days to give dark crystals of **1** (0.191 g, 0.37 mmol, 72%). Satisfactory elemental analysis could not be obtained due to the air sensitive nature of the compound. Each batch was controlled by NMR as well as by measurement of the unit cell. ^1H NMR ($[\text{D}_6]$ benzene): $\delta = -30.04$ (br s), -3.42 (br s, $\text{CH}_3\text{-Cp}^*$), $0.22\text{--}2.10$ (m), 30.04 (br s). $\mu_{\text{eff}} = 4.037 \mu_{\text{B}}$.

4.4. Ethylene oligomerization experiments

A schlenk flask was charged with a toluene solution (50 mL) of **1** (0.026 g, 0.050 mmol) and AlEt_3 (0.513 g, 4.50 mmol). The flask was weighed, placed in a room-temperature water bath and connected to an ethylene manifold. The flask was then evacuated for 5 s and refilled with 1.1 atm of ethylene to which it remained exposed for 15 min. After 15 min, 3.50 g of ethylene had been consumed giving an activity of $280 \text{ kg mol Cr}^{-1} \text{ h}^{-1}$. Following quenching using water (10 mL) at $0 \text{ }^\circ\text{C}$, ^1H NMR analysis of the alkanes δ : 1.35 (br, CH_2 , 38H), 0.94 (br, CH_3 , 6H) in the crude toluene phase provided an average chain length of 21 ± 1 carbon units.

In a separate experiment carried out with **1** (0.026 g, 0.050 mmol) and AlEt_3 (0.360 g, 3.15 mmol) in toluene under the same conditions, aliquots (1 mL) were taken by syringe at 3, 6, 9, 12 and 15 min. Each aliquot was quenched with water (1 mL) and analyzed by gas chromatography. The experimental distributions were fitted using the Poisson formula which gave the following average numbers of added ethylene (ν): $\nu = 2.5, 4.3, 6.2, 8.1$ and 11.9 after 3, 6, 9, 12 and 15 min, respectively.

5. Supplementary material

Crystallographic data for the structural analysis of **1** have been deposited at the Cambridge Crystallographic Data Center and assigned the CCDC number 260778. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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