[Cp*Cr(C_6F_5)(Me)(Py)] as a Living Chromium(III) Catalyst for the "Aufbaureaktion"

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The reaction of [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ (**1**) with 2 equiv of MeLi in THF yields the methyl-bridged Cr(III) dimer [Cp*Cr(C_6F_5)(μ-Me)]$_2$ (**2**). This dinuclear compound is very soluble in hydrocarbon solvent and has been isolated in low yield (6%). Compound **2** reacts with pyridine to afford [Cp*Cr(C_6F_5)(Me)(Py)] (**3**), which has been isolated in a 67% yield. Compound **3** is a 15-electron, coordinatively saturated chromium(III) species that has been characterized by NMR, magnetometry, and EA. The structures of **1**, **2**, and **3** have been determined by single-crystal X-ray diffraction. Compounds **1** and **2** exist in the form of centrosymmetrical dimers with bridging chloride and methyl ligands, respectively. Mononuclear compound **3** adopts the expected three-legged piano stool geometry. Compound **2** polymerizes ethylene in toluene under 1 atm of ethylene at room temperature in the absence of any activators. Compound **3** is not catalytically active by itself. Yet, the addition of excess $AlEt_3$ to a solution of **3** in toluene leads to a catalytic system that readily oligomerizes ethylene. Oligomerization experiments carried out with $[\mathbf{3}] = 10^{-3}$ M and $[AlEt_3] = 4.5 \times 10^{-2}$ M for 15 min lead to the production of ethylene oligomers with an activity of 221 kg mol Cr^{-1} h^{-1}. As indicated by gas chromatography, the Poisson distribution formula accounts for the molecular weight distribution of the growing ethylene oligomers during this reaction, which is indicative of a living polymerization system. Experiments carried out at higher $AlEt_3$ concentrations ($[\mathbf{3}] = 10^{-3}$ M and $[AlEt_3] = 9 \times 10^{-2}$ M) lead to a lower activity (150 kg mol Cr^{-1} h^{-1}) but still present the characteristic features of a living polymerization system. These results are interpreted on the basis of a catalytic cycle in which the chain grows at chromium and is transferred to aluminum via an alkyl-bridged chromium−aluminum bimetallic intermediate.

Introduction

Linear primary alcohols constitute important elementary building blocks that serve for the preparation of detergents, lubricants, and cosmetic products among others. These alcohols are typically produced by processes based on the "Aufbaureaktion",[1] which involves the multiple insertion of ethylene molecules in the aluminum−carbon bond of a trialkylaluminum at elevated temperature and pressure. While this reaction is successfully utilized in several industrial plants, important drawbacks remain. In particular, selectivity is often affected by the formation of olefin and associated branching. Moreover, a number of safety problems linked to elevated temperatures, pressures, and possible runaway reactions are encountered when dealing with the current technology. For these reasons, much focus has been placed on the development of processes that allow for the oligomerization of ethylene under milder conditions. In this domain, Ni-based catalysts, also referred to as SHOP catalysts, hold a prominent place in the production of α-olefins.[2] The past few years have witnessed the emergence of an alternative strategy that relies on the synergy of a transition metal catalyst and a main group alkyl derivative.[3−7] In such systems, the chain effectively grows at the transition metal centers and undergoes reversible transfer to the main group center. Typically, this will involve alkyl-aluminum, -magnesium, and -zinc derivatives as the main group alkyl derivative and an olefin polymerization catalyst.[3−7] If the rate of chain transfer between the transition metal and the main group metal is fast and β-H processes do not occur, the molecular weight of the resulting ethylene oligomers follows a strict Poisson distribution. The latter is economically very attractive because it provides the narrowest molecular weight distribution available for any polymerization processes. For this reason, the

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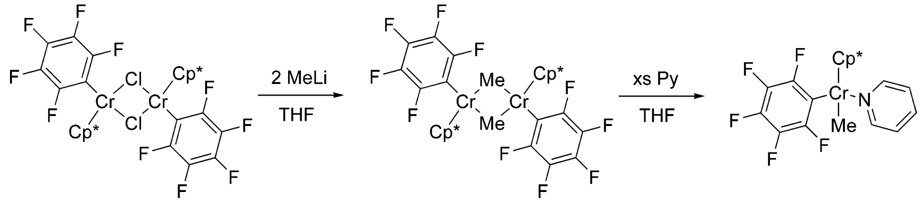
10.1021/om049675r CCC: $27.50

Scheme 1



1 **2** **3**

Poisson distribution supplants the Schultz–Flory distribution usually obtained when β-H processes are operative.

Following the discovery of heterogeneous chromium catalysts such as the Phillips catalyst (CrO_3/SiO_2)[8] or the Union Carbide catalyst (Cp_2Cr/SiO_2),[9] the study of homogeneous chromium species for the oligomerization and polymerization of ethylene has attracted a great deal of attention. In addition to promoting the trimerization of olefins,[10] a number chromium complexes also catalyze olefin polymerization reactions. In this category, those featuring a cyclopentadienide chromium(III) moiety have received the most attention and have served as homogeneous models for the Union Carbide catalyst.[11–16] While the exact molecular structure of such cyclopentadienide chromium(III) catalysts can be varied, Theopold has clearly established that the presence of a $Cr-C_{alkyl}$ σ-bond as well as a vacancy in the coordination sphere of the metal constitute the basic prerequisites for catalytic activity toward ethylene.[17] Although ethylene polymerization reactions have received the most attention, Bazan showed that catalytic systems such as $[Cp^*Cr(Me)_2(PMe_3)]/B(C_6F_5)_3$ and $[Cp^*Cr(Me)_2(PMe_3)]$/MAO are also competent for ethylene oligomerization reactions when combined with a trialkylaluminum.[18] As part of our contribution to this research area, we recently communicated a pentafluorophenyl chromium(III) complex, $[Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})]$, that also promotes the oligomerization of ethylene when combined with triethylaluminum.[19] Unlike other systems, $[Cp^*Cr(C_6F_5)(\eta^3\text{-Bz})]$ does not necessitate the use of an activator and produces linear alkyl chains that strictly follow the Poisson distribution. Herein, we would like to report the synthesis and characterization of several pentafluorophenyl–chromium complexes including $[Cp^*Cr(C_6F_5)(Me)(Py)]$ (**3**), which can be used as a catalyst for the living "Aufbaureaktion".

Results and Discussion

Treatment of $[Cp^*CrCl_2]_2$ with 1 equiv of C_6F_5Li at −78 °C affords $[Cp^*Cr(C_6F_5)(\mu\text{-Cl})]_2$ (**1**) as previously reported.[19] Unlike $[CpCr(X)(\mu\text{-X})]_2$ (X = F, Cl, Br, I),[20,21] compound **1** fails to react with pyridine and does not afford the corresponding monomeric adduct. This inertness indicates that the chloride-bridged dimer is very stable. Possibly, the stability of this dimer results from the electron-withdrawing nature of the C_6F_5 group, which increases the Lewis acidity of the chromium center. The reaction of **1** with 2 equiv of MeLi in THF yields the methyl-bridged chromium(III) dimer $[Cp^*Cr(C_6F_5)(\mu\text{-Me})]_2$ (**2**) (Scheme 1). Although this compound appears to form in high yield, it is difficult to isolate because of its high solubility in hydrocarbon solvents. It was obtained in less than 10% yield by recrystallization from pentane. Compound **2** is very air-sensitive and readily reacts with pyridine to afford $[Cp^*Cr(C_6F_5)(Me)(Py)]$ (**3**) (Scheme 1). This reaction is analogous to that observed in the case of $[Cp^*Cr(Me)(\mu\text{-Me})]_2$,[22] which converts into $[Cp^*Cr(Me)_2(Py)]$ upon treatment with pyridine. Analytically pure **3** was obtained in a 67% yield by addition of pyridine to the reaction mixture of **1** and MeLi. Compound **3** is a 15-electron, coordinatively saturated, chromium(III) species. The room-temperature magnetic moment (μ_{eff}) of 3.65 μ_B is close to the value expected for three unpaired d-electrons (3.87 μ_B).

The structures of **1**–**3** have been determined by single-crystal X-ray diffraction. Pertinent crystallo-

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Table 1. Crystal Data, Data Collection, and Structure Refinement for 1, 2, and 3

	1	**2**	**3**
Crystal Data			
formula	$C_{32}H_{30}Cl_2Cr_2F_{10}$	$C_{34}H_{36}Cr_2F_{10}$	$C_{22}H_{23}CrF_5N$
M_r	779.46	738.62	448.41
cryst size (mm^3)	0.4 × 0.21 × 0.11	0.5 × 0.5 × 0.3	0.27 × 0.10 × 0.09
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a (Å)	14.113(4)	9.6564(18)	11.229(4)
b (Å)	15.617(4)	11.053(2)	13.255(5)
c (Å)	29.042(7)	14.406(3)	16.119(6)
α (deg)	90.00	90.00	105.477(7)
β (deg)	95.474(5)	98.197(3)	109.348(7)
γ (deg)	90.00	90.00	102.192(7)
V (Å^3)	6372(3)	1521.9(5)	2059.8(13)
Z, Z'	16, 8	4, 2	2, 4
ρ_{calc} (g cm^{-3})	1.625	1.612	1.446
μ(Mo Kα) (mm^{-1})	0.931	0.800	0.607
F(000)	3152	756	924
Data Collection			
T/K	110(2)	110	110
scan mode	ω	ω	ω
hkl range	−16→13, −17→14,−33→33	−11→11, −12→13,−17→9	−11→13, −15→15,−19→14
no. of measd reflns	29 874	7770	10 716
no. of unique reflns, [R_{int}]	9981 [0.0581]	2685 [0.0456]	7084 [0.0870]
no. of reflns used for refinement	9981	2685	7084
Refinement			
no. of refined params	829	220	535
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0652, 0.1459	0.0327, 0.0867	0.0697, 0.1374
ρ_{fin}(max/min) (e Å^{-3})	1.593, −0.514	0.359, −0.255	0.675, −0.379

[a] $R_1 = (F_o - F_c)/F_o$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; for **1**, $a = 0.0600$, $b = 0$; for **2**, $a = 0.0505$, $b = 0$; for **3**, $a = 0.00$, $b = 0.0494$.

graphic data have been assembled in Table 1. Compound **1** crystallizes in the $P2(1)/c$ monoclinic space group. The asymmetric unit contains four independent Cp*Cr(C_6F_5)(Cl) moieties. Two of these moieties are associated in a [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ dimer. The other two moieties constitute the halves of two crystallographically centrosymmetrical [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ dimers. Altogether, the structures of the three independent [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ are analogous to that of other Cp*Cr chloro complexes (Figure 1).[17a,c,23] The coordination geometry about the chromium center is pseudooctohedral. The average Cr−Cl of 2.375 Å is comparable to the Cr−Cl distances observed in other chromium(III) chloride-bridged complexes such as [CpCr(Me)(μ-Cl)]$_2$ (av 2.356 Å),[24] [Cp*Cr(CH_2SiMe_3)(μ-Cl)]$_2$ (av 2.394 Å),[17a] or [Cp*Cr(Bz)(μ-Cl)]$_2$ (av 2.383 Å).[17c] The two C_6F_5 groups are coordinated to the chromium centers trans to each other. The average length of the Cr−C bond (2.106 Å) formed between the chromium center and the ipso-carbon of the pentafluorophenyl group is virtually identical to that found in [Cp*Cr(C_6F_5)(η^3-Bz)] (Cr(1)−C(11) = 2.109(3) Å).[19] In **2**, each chromium atom is bonded to one Cp* ligand, one terminal C_6F_5 group, and two bridging methyl ligands, thus completing the familiar pseudooctahedral coordination environment of the three-legged piano stool geometry (Figure 2). The lengths of the Cr−C bonds formed by the bridging methyl group (Cr(1)−C(1A) = 2.156(2) and Cr(1)−C(1) = 2.205(2) Å) are similar to those found in other methyl-bridged chromium species such as [Cp*Cr(Me)(μ-Me)]$_2$ (Cr−C = 2.206(4), 2.170(5) Å).[22a] As in **1**, the two C_6F_5 groups are coordinated to the chromium centers trans to each other and form a Cr(1)−C(12) bond of 2.1375(19) Å, which is similar to **1**. The Cr−Cr distance of 2.6971(7) Å in **2**, which is slightly longer than that found in [Cp*Cr(Me)(μ-Me)]$_2$ (2.606(2) Å), indicates the presence of a weak metal−metal bond.[22] Compound **3** crystallizes with two molecules in the asymmetric unit. Both independent molecules, arbitrarily denoted as molecule **A** and molecule **B**, adopt the expected three-legged piano stool geometry and feature very similar structures

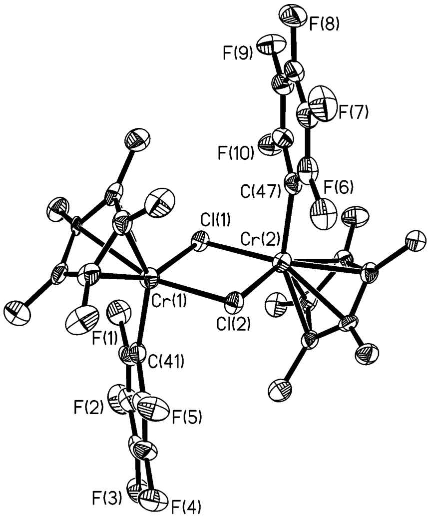


Figure 1. Molecular structure of [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ (**1**). Selected interatomic distances (Å) and angles (deg) for one of the independent molecules. The distances and angles corresponding to the other two independent molecules can be found in the Supporting Information. Cr(1)−C(41) 2.109(6), Cr(1)−Cl(2) 2.3701(18), Cr(1)−Cl(1) 2.3801(18), Cr(2)−C(47) 2.099(6), Cr(2)−Cl(1) 2.3708(18), Cr(2)−Cl(2) 2.3779(18), C(41)−Cr(1)−Cl(2) 96.45(17), C(41)−Cr(1)−Cl(1) 95.33(17), Cl(2)−Cr(1)−Cl(1) 89.55(6), C(47)−Cr(2)−Cl(1) 93.99(17), C(47)−Cr(2)−Cl(2) 97.33(17), Cl(1)−Cr(2)−Cl(2) 89.58(6), Cr(2)−Cl(1)−Cr(1) 90.39(6), Cr(1)−Cl(2)−Cr(2) 90.46(6).

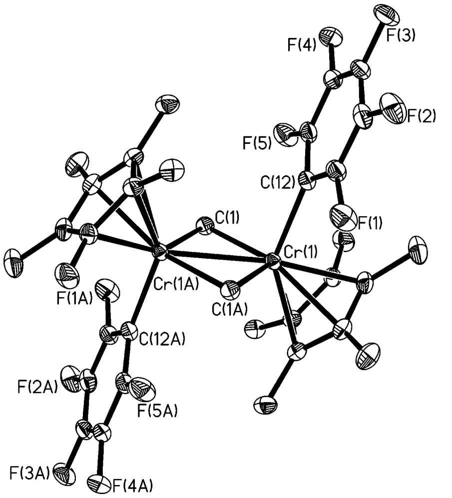


Figure 2. Molecular structure of [Cp*Cr $(C_6F_5)(\mu\text{-}CH_3)]_2$ (**2**). Selected interatomic distances (Å) and angles (deg): Cr(1)−C(12), 2.1375(19); Cr(1)−C(1A), 2.156(2); Cr(1)−C(1), 2.205(2); Cr(1)−Cr(1A), 2.6971(7); C(12)−Cr(1)−C(1A), 98.33(8); C(12)−Cr(1)−C(1), 96.28(7); C(1A)−Cr(1)−C(1), 103.61(6); C(12)−Cr(1)−Cr(1A), 101.85(5); C(1A)−Cr(1)−Cr(1A), 52.62(5); C(1)−Cr(1)−Cr(1A), 50.99(5); Cr(1A)−C(1)−Cr(1), 76.39(6).

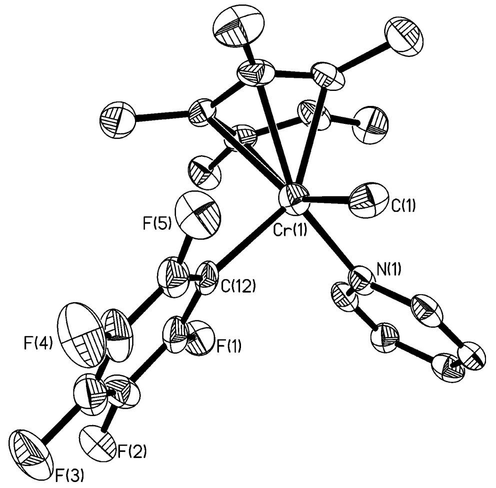


Figure 3. Molecular structure of [Cp*Cr(C_6F_5)(Me)(Py)] (**3**). Selected interatomic distances (Å) and angles (deg) for molecule **A**, the distances and angles corresponding to the other independent molecule (**B**) are indicated in square brackets: Cr(1)−C(1), 2.073(7) [2.075(7)]; Cr(1)−N(1), 2.116(6) [2.114(6)]; Cr(1)−C(12) 2.126(6) [2.116(6)]; C(1)−Cr(1)−N(1), 92.2(2) [92.1(2)]; C(1)−Cr(1)−C(12), 95.2(3) [94.3(3)]; N(1)−Cr(1)−C(12), 98.0(2) [99.0(2)].

(Figure 3). As expected, the bond formed between the chromium center and the terminal methyl group (Cr(1)−C(1) 2.073(7) Å for **A** and Cr(2)−C(18) 2.075(7) Å for **B**) is shorter than those observed in **2** for the bridging methyl group (Cr(1)−C(1A) = 2.156(2) Å and Cr(1)−C(1) = 2.205(2) Å). The pentafluorophenyl ligand is terminally ligated to the chromium center and forms a Cr−C bond (Cr(1)−C(12) 2.126(6) Å for **A** and Cr(2)−C(29) 2.116(6) Å for **B**) comparable to that found in the mononuclear complex [Cp*Cr$(C_6F_5)(\eta^3$-Bz)] (Cr(1)−C(11) = 2.109(3) Å).

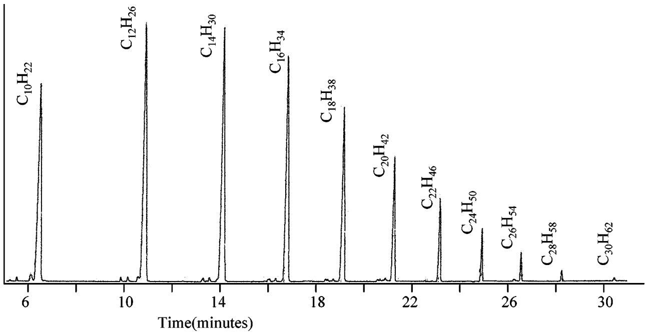
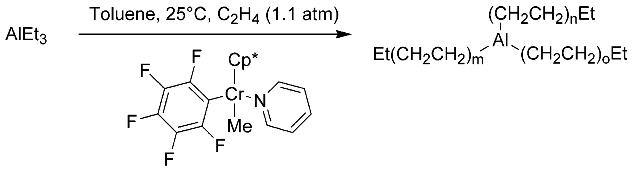


Figure 4. GC traces of the alkanes produced after hydrolysis from the reaction of ethylene with **3** and $AlEt_3$ ([**3**] = 10^{-3} M, [$AlEt_3$]/[**3**] = 90; P = 1.1 atm, T = 25 °C).

Scheme 2[a]



3

[a] m, n, o = integers

Although compound **2** polymerizes ethylene in toluene under 1 atm of ethylene at room temperature as observed for [Cp*Cr$(C_6F_5)(\eta^3$-Bz)],[19] the difficulties associated with its isolation as well as its high air sensitivity impeded a detailed investigation of its catalytic properties. For these reasons, we turned our attention to compound **3**. Unlike for **2** and [Cp*Cr(C_6F_5)-$(\eta^3$-Bz)], pure **3** is not catalytically active when dissolved in toluene and exposed to ethylene. This lack of activity is to be expected in the case of coordinatively saturated derivatives such as **3**. Fortunately, the simple addition of excess $AlEt_3$ to a solution of **3** in toluene leads to a catalytic system that readily oligomerizes ethylene (Scheme 2). Presumably, the Lewis acidic $AlEt_3$ is able to abstract a ligand, thereby generating an unsaturated chromium center. For example, when a solution of **3** in toluene (10^{-3} M) containing a 45-fold excess of $AlEt_3$ is exposed to ethylene (1.1 atm) at room temperature, rapid consumption of ethylene is observed (2.76 g after 15 min, activity = 221 kg mol Cr^{-1} h^{-1}). While no precipitation occurs during the first 13−14 min, a small amount of precipitate is typically observed after 14−15 min. The precipitate most likely consists of the trialkylaluminum species bearing the longer alkyl chains. After 15 min exposure to ethylene, hydrolysis of the reaction mixture leads to the formation of linear alkanes with an average chain length of 32 ±1 carbon units, as determined from ^{1}H NMR spectroscopy. This number corresponds almost exactly to the ratio of ethylene consumed per ethyl group (31.2). When the same experiment is carried out with a 90-fold excess of $AlEt_3$, 1.88 g of ethylene are consumed in 15 min, indicating a lower activity (150 kg mol Cr^{-1} h^{-1}). Under these conditions, shorter ethylene oligomers are produced (average chain length = 12 ± 1 carbon), and the formation of a precipitate toward the end of the reaction is not observed. Gas chromatography analysis of the longer oligomers (≥C10) shows that the chain length distribution closely matches that predicted by the Pois-

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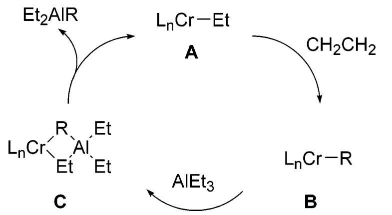
Scheme 3. Proposed Catalytic Cycle for the Oligomerization Reaction (R = oligomer, L = ligands)



son distribution formula (eq 1, Figure 4) and is indicative of a living polymerization system.[25]

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

(ν = av number of added ethylene, x = number of ethylene units, $n = 2x$)

These observations parallel those made previously with [Cp*Cr(Me)$_2$(PMe$_3$)]/B(C$_6$F$_5$)$_3$, [Cp*Cr(Me)$_2$(PMe$_3$)]/MAO, or [Cp*Cr(C$_6$F$_5$)(η^3-Bz)] as catalysts.[18,19] As previously suggested, the inhibitory effect observed at higher AlEt$_3$ concentration most likely results from saturation of the transition metal center through the formation of a heterobimetallic complex of type **C** (Scheme 3), whose concentration increases at higher AlEt$_3$ concentrations. Cationic examples of such bimetallic intermediates have been postulated by Bazan[18] and are also known in zirconium chemistry.[26] These observations are in agreement with a proposed catalytic cycle in which the growing alkyl chain is transferred from chromium to aluminum (Scheme 3). While the exact nature of the active chromium species is unknown, we propose that this exchange reaction involves a bridged chromium−aluminum complex of type **C**.

To get more detailed insight of the progress of the oligomerization reaction as a function of time, the reaction mixture of a typical oligomerization experiment ([**3**] = 10^{-3} M, [AlEt$_3$] = 45/[**3**]) was sampled every 3 min, hydrolyzed, and analyzed by gas chromatography (Figure 5). The molecular weight distribution observed at each time interval closely matches the Poisson distribution. A similar observation was made by Gibson et al. in the case of an iron-catalyzed ethylene oligomerization on zinc dialkyls.[27] In the present case, the average numbers of added ethylene (ν) that provides the best fit for each experimental distributions are ν = 2.5, 5.4, 8.8, and 11.6 after 3, 6, 9, and 12 min, respectively. A plot of the average number of added ethylene (ν) versus time indicates that ν increases linearly with time. This feature is in agreement with the existence of a living polymerization system; it also shows that, in the fairly narrow window of the growth reaction, the oligomerization rate remains essentially constant and is not influenced by the increasing length of the chains.

Conclusion

The synthetic results presented herein indicate that chromium(III) complexes bearing a Cp* ligand as well as a C$_6$F$_5$ ligand can be readily prepared and isolated. While the methyl derivative [Cp*Cr(C$_6$F$_5$)(μ-Me)]$_2$ (**2**) is very air sensitive and somewhat difficult to isolate, its corresponding pyridine adduct, namely, [Cp*Cr(C$_6$F$_5$)(Me)(Py)] (**3**), can be isolated in high yield and stored for an extended amount of time under a dry, inert atmosphere. In the presence of excess AlEt$_3$, this compound promotes the oligomerization of ethylene. Its activity is comparable to that of [Cp*Cr(C$_6$F$_5$)(η^3-Bz)].[19] Remarkably, **3** is a neutral catalyst that promotes the "Aufbaureaktion" in the absence of MAO or B(C$_6$F$_5$)$_3$. In contrast to the conventional "Aufbaureaktion", which requires elevated temperatures and ethylene pressures, the use of **3** allows for the living oligomerization of ethylene at room temperature and under 1 atm of ethylene.

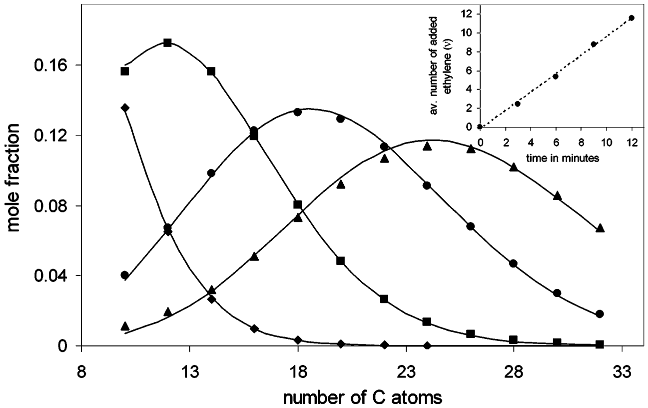


Figure 5. Experimental and calculated chain length distribution of the alkanes formed, after hydrolysis of the reaction mixture obtained at 3 min intervals, by the reaction of ethylene with **3** and AlEt$_3$ ([**3**] = 10^{-3} M, [AlEt$_3$]/[**3**] = 45; P = 1.1 atm, T = 25 °C). (◆: 3 min, ν = 2.5. ■: 6 min, ν = 5.4. ●: 9 min, ν = 8.8. ▲: 12 min, ν = 11.6). The inset (top right) shows a plot of the average number of added ethylene (ν) versus time.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere using standard glovebox and vacuum-line techniques. MeLi (1.5 M diethyl ether solution) was obtained from Aldrich. Pyridine, toluene, THF, hexanes, and pentane were dried over sodium and distilled prior to use. ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 298 K. The chemical shifts are reported in ppm relative to SiMe$_4$. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Gas chromatography analyses were performed in the temperature range 70−290 °C using Hewlett-Packard, HP 6890 Series, column specifications: Agilent Technologies Inc. HP5, 30 m × 0.25 mm; phase: 5% phenyl poly(dimethylsiloxane), 0.25 μm. The GC response was calibrated with a standard containing C$_{14}$H$_{30}$, C$_{15}$H$_{32}$, and C$_{16}$H$_{34}$ in 0.033 wt % in hexane. Magnetic susceptibility measurements were carried out with a Quantum Design SQUID MPMS-XL magnetometer. DC magnetic measurements were performed with an applied field of 1000 G in the 2−300 K temperature range. Data were corrected for the diamagnetic contributions calculated from the Pascal constants.[28] The magnetic moment was derived from the susceptibility at room temperature. [Cp*Cr(C$_6$F$_5$)(μ-Cl)]$_2$ (**1**) was synthesized as previously reported.[19]

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[27] Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; Van Meurs, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 489−491.

[28] *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; John Wiley & Sons: New York, 1976.

Crystallography. Crystals of **1** were grown from CH_2Cl_2 at −30 °C. Crystals of **2** and **3** were obtained upon cooling of pentane solutions (vide infra). The crystals were mounted onto a glass fiber with Apiezon grease. The crystallographic measurements were performed on a Bruker SMART 1000 X-ray three-circle diffractometer. The goniometer was controlled using the SMART software suite, version 5.625. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 5 cm from the crystal sample (CCD-PXL-KAF2, SMART 1000, 512 × 512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube ($K_\alpha = 0.70173$ Å with a potential of 50 kV and a current of 40 mA) and filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). For all three measurements, dark currents were obtained for the appropriate exposure time of 10 s and a rotation exposure was taken to determine crystal quality and the X-ray beam intersection with the detector. The beam intersection coordinates were compared to the configured coordinates, and changes were made accordingly. The rotation exposure indicated acceptable crystal quality, and the unit cell determination was undertaken. Sixty data frames were taken at widths of 0.3° with an exposure time of 10 s. Over 100 reflections were centered, and their positions were determined. These reflections were used in the autoindexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the *hkl* overlays on several frames of data, including zone photographs. The cell was verified and refined using at least 500 reflections obtained after data collections. After careful examination of the unit cell, a standard data collection procedure was initiated. This procedure consists of collection of one hemisphere of data collected using omega scans, involving the collection of 1265 0.3° frames at fixed angles for ϕ, 2θ, and χ ($2\theta = -28°$, $\chi = 54.73°$), while varying omega. Each frame was exposed for 10 or 15 s and contrasted against a 10 or 15 s dark current exposure. The total data collection was performed at 110 K. No significant intensity fluctuations of equivalent reflections were observed. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program SAINT V6.63. The integration method employed a three-dimensional profiling algorithm, and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data were merged and scaled to produce a suitable data set. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 6.1) allowed for the location of the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to carbon were placed in idealized positions [C−H = 0.96 Å, $U_{iso}(H) = 1.2U_{iso}(C)$].

Synthesis of [Cp*Cr(C_6F_5)(μ-Me)]$_2$ (2). MeLi (0.51 mmol) was added to a solution of [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ (**1**) (0.20 g, 0.25 mmol) in THF (30 mL) at room temperature, upon which the color of the solution changed from dark blue to dark bluish-brown. Following stirring for 18 h, the solvent was removed under vacuum, and the residue was extracted with pentane. The resulting solution was filtered and the filtrate concentrated to 15 mL. Cooling to −30 °C for 7 days gave dark purple crystals of **2** (0.012 g, 0.016 mmol, 6.4%). ^{1}H NMR (benzene-d_6) δ: 0.28 (br, CH_3), 2.27 (br, Cp*). Satisfactory analysis could not be obtained because of the high air-sensitive nature of the compound.

Synthesis of [Cp*Cr(C_6F_5)(Me)(Py)] (3). MeLi (0.54 mmol) and subsequently pyridine (0.1 mL) were added to a solution of [Cp*Cr(C_6F_5)(μ-Cl)]$_2$ (**1**) (0.21 g, 0.27 mmol) in THF (30 mL) at room temperature. The solution was stirred for 18 h, during which time the color of the solution turned to dark brown. The solvent was removed under vacuum, and the resulting residue was extracted with pentane (30 mL). The pentane solution was filtered and concentrated to 15 mL. The solution was cooled to 5 °C for 2 days to give dark red crystals of **3** (0.162 g, 0.36 mmol, 67%). Anal. Calcd for $C_{22}H_{23}CrF_5N$: C, 58.93; H, 5.13. Found: C, 58.42; H, 5.21. ^{1}H NMR (benzene-d_6) δ: 2.2 (br, Me-Cp*), 22.65 (br). $\mu_{eff} = 3.65\ \mu_B$.

General Ethylene Oligomerization Experiments. The catalyst (50 μmol) was placed in a 200 mL Schlenk flask and dissolved in toluene (50 mL). Following addition of the appropriate amount of $AlEt_3$, 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 using water (10 mL) at 0 °C. The toluene layer was separated for ^{1}H NMR and gas chromatography analysis.

Ethylene Oligomerization Using 3 as a Catalyst with $AlEt_3$. A Schlenk flask was charged with a toluene solution (50 mL) of **3** (0.022 g, 0.050 mmol) and $AlEt_3$ (0.513 g, 4.50 mmol). The ethylene oligomerization reaction was carried out as described above. After 15 min, 1.88 g of ethylene had been consumed, giving an activity of 150 kg mol Cr^{-1} h^{-1}. Following quenching, gas chromatography analysis of the alkanes in the crude toluene phase provided an average chain length of 12 ± 1 carbon units. The same experiment carried out with **3** (0.022 g, 0.050 mmol) and $AlEt_3$ (0.256 g, 2.25 mmol) led to an ethylene consumption of 2.76 g and an activity of 221 kg mol Cr^{-1} h^{-1}. Following quenching, ^{1}H NMR analysis of the alkanes (δ (ppm): 1.30 (br, CH_2, 62 H), 0.91 (br, CH_3, 6 H)) in the crude toluene phase provided an average chain length of 32 ± 1 carbon units. The average molecular weight of the sample exceeded the range that can be reliably analyzed with our gas chromatograph. In a separate experiment carried out with **3** (0.022 g, 0.050 mmol) and $AlEt_3$ (0.256 g, 2.25 mmol), aliquots (1 mL) were taken by syringe at 3, 6, 9, and 12 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): $\nu = 2.5$, 5.4, 8.8, and 11.6 after 3, 6, 9, and 12 min, respectively.

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Supporting Information Available: Molecular weight distribution analysis. X-ray crystallographic data for **1**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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