Ethylene Polymerization

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Isolation of a Self-Activating Ethylene Trimerization Catalyst**

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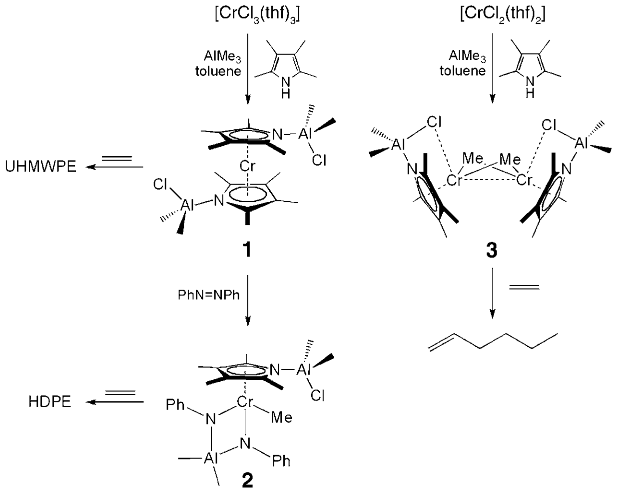
Among the many chemical elements that produce interesting catalysts for ethylene polymerization, without doubt, chromium occupies a special position. The heterogeneous Phillips polymerization system based on chromium-impregnated silica[1] is still among the most widely used, inexpensive, and best-performing catalytic systems for the worldwide commercial production of high-density polyethylene. Related and no less important is the ability of the same element to provide catalysts for selective ethylene trimerization.[2] In fact, chromium accounts for more than 90 % of all the existing ethylene oligomerization catalysts.[2,3] Even today, a pyrrole/chromium/AlR$_3$ catalyst is the only catalytic system commercially employed for the selective production of 1-hexene.[3] Furthermore, the sole existing homogeneous catalytic system that predominantly forms 1-octene is also based on chromium.[4]

In a modeling study on the ethylene trimerization system, Chevron Phillips recently reported the isolation of catalytically active chromium species acting as self-activating trimerization and polymerization catalysts.[5] This study has allowed the metal oxidation state to be linked to the particular catalytic behavior: chromium(I) is responsible for selective trimerization, whilst polyethylene is produced by divalent chromium. With the aim of generalizing and further clarifying these findings, we are currently investigating the chemistry of chromium with aluminatopyrrolyl anions.

By using a combination of tetramethylpyrrole, [CrCl$_3$(thf)$_3$], and AlMe$_3$, we have now obtained a chromocene-type complex [{η^5-2,3,4,5-Me$_4$C$_4$N(AlClMe$_2$)}$_2$Cr] (**1**; Scheme 1, Figure 1). The fact that a divalent species has been obtained although a trivalent starting material has been used is not surprising given that reduction of trivalent chromium to the divalent state is commonly observed upon treatment with aluminum alkyl compounds.[6] The magnetism of **1** ($\mu_{\text{eff}} = 2.77\,\mu_{\text{BM}}$) is as expected for medium-spin Cr$^{\text{II}}$ in an octahedral environment. It is interesting to note the structural difference with the related complex [{(2,3,4,5-C$_{12}$H$_4$N)AlEt$_2$Cl}$_2$Cr]



Scheme 1. Formation of complexes **1** and **2** from Cr$^{\text{III}}$ (polymerization of ethylene to ultrahigh molecular weight PE: $M_w = 2\,600\,000$, PDI = 1.7, 45 tonnes mol^{-1}) and **3** from Cr$^{\text{II}}$ (generation of 1-hexene).

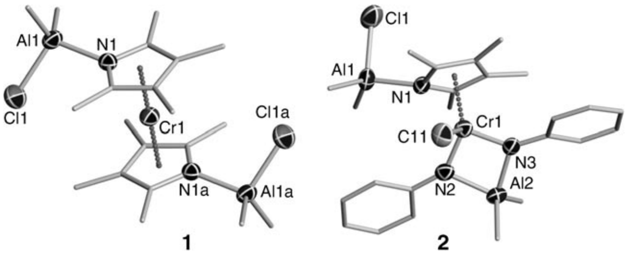


Figure 1. Plots of **1** and **2** with ellipsoids set at 50 % probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å] for **1**: Cr1–N1 2.224(2), Cr1–C1 2.274(3), Cr1–C2 2.341(3), Cr1–C3 2.312(3), Cr1–C4 2.260(3), C1–C2 1.396(4), C2–C3 1.425(5), C3–C4 1.396(4), N1–Al1 1.993(2). **2**: Cr1–N1 2.284(5), Cr1–C1 2.326(5), Cr1–C2 2.388(5), Cr1–C3 2.336(5), Cr1–C4 2.246(5), Cr1–C11 2.074(6), Cr1–N2 1.757(5), Cr1–N3 1.761(4), N2–Al2 1.966(5), N3–Al2 1.960(5).

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($\mu_{\text{eff}} = 4.78\,\mu_{\text{BM}}$) in which the two carbazolyl rings are σ-bonded to the metal center.[5] Complex **1** is thermally robust; it does not decompose upon heating in toluene at 100 °C for 12 h. Unlike chromocene, which is catalytically inactive unless supported onto silica,[7] this aluminatopyrrolyl chromium complex acts as an active homogeneous single-site, single-component polymerization catalyst, producing ultrahigh-molecular-weight polyethylene (UHMWPE; $M_w = 2\,650\,000$) with a very narrow polydispersity index (PDI) of 1.7 and melting points $T_m{}^1 = 145.7\,°\text{C}$ and $T_m{}^2 = 139.0\,°\text{C}$.

This system is reminiscent of a recently reported aluminatopyrrolyl-based vanadocene.[8] With a catalytic activity of $8 \times 10^5\,\text{g}_{\text{PE}}\,\text{mol}^{-1}\,\text{h}^{-1}$ (8 g UHMWPE from 10 μmol [Cr], $P = 600$ psi, toluene, $T = 110\,°\text{C}$, 1 h), complex **1** displays a somewhat higher catalytic activity and also produces UHMWPE. As in the vanadium case, questions arise about the catalytically active species formed during the self-activation process. A reasonable possibility is that dissociation of a neutral {(2,3,4,5-Me_4C_4N)AlMeCl} unit accompanied by methyl migration to the chromium center would produce the divalent complex [{η^5-2,3,4,5-$Me_4C_4N(AlClMe_2)$}CrMe] as the catalytically active species. Formation of a similar species has also been observed in the case of the vanadium analogue during the oxidation of the metal center. To study the possibility of alkyl transfer from aluminum to chromium in **1**, we deliberately oxidized the metal center by treatment with azobenzene. The reaction afforded a color change and deepening from the initial pale-turquoise to dark-brown, and yielded, after the addition of a small amount of THF, a pentavalent organochromium species [{η^5-2,3,4,5-$Me_4C_4N(AlMe_2Cl)$}CrMe(μ-NPh)$_2$AlMe$_2$][Me_3Al(thf)] (**2**; Scheme 1). The addition of a stoichiometric amount of THF after the reaction was only necessary to overcome the difficulties experienced for the crystallization of the complex. The structure of **2** (Figure 1) consists of the chromium atom π-bonded to one aluminatopyrrolide moiety (Me_4C_4N)$AlMe_2Cl$ in a structure reminiscent of a piano-stool half-sandwich compound.

The four-electron cleavage of azobenzene during the formation of **2** is indeed accompanied by the anticipated aluminum–pyrrolyl dissociation and alkyl transfer. Complex **2** shows the paramagnetism expected for the d^1 electronic configuration of a monomeric chromium(V) complex ($\mu_{\text{eff}} = 1.87\,\mu_{\text{BM}}$). The fact that the complex is pentavalent, and not hexavalent as might have been expected for the four-electron attack of the divalent metal center to azobenzene, is not completely surprising given the presence of reducing alkyl aluminum groups. The formation of **2** and alkyl transfer during the oxidative process is in agreement with the idea that a transient {[η^5-2,3,4,5-$Me_4C_4N(AlClMe_2)$]CrMe} complex may be generated during the self-activation process of **1** in the presence of ethylene. Although complex **2** is very different from **1**, it is also is a single-component catalyst. The catalytic activity was slightly higher than for **1** (11 g of PE from 10 μmol [Cr], activity $1.1 \times 10^6\,\text{g}_{\text{PE}}\,\text{mol}^{-1}\,\text{h}^{-1}$) under the best polymerization conditions ($P = 600$ psi, toluene, $T = 80\,°\text{C}$, 1 h). The molecular weight of the polymer is substantially lower than that formed by **1**. The polydispersity clearly reveals the presence of a single-site catalyst ($M_w = 850\,000$; PDI = 1.9, $T_m{}^1 = 139.03\,°\text{C}$, $T_m{}^2 = 133.27\,°\text{C}$).

When the reaction that afforded **1** was carried out with [$CrCl_2$(thf)$_2$] instead of the trivalent salt, a new species, [{η^5-2,3,4,5-$Me_4C_4N(AlClMe_2)$Cr}$_2$(μ-Me)$_2$] (**3**), was isolated in crystalline form in a low, yet reproducible yield. The structure (Figure 2), which closely resembles [{η^5-(Me_5C_5)Cr-(μ-Me)}$_2$],[9] has a comparably short Cr–Cr distance of 2.274(1). The positions of the chlorine atoms bonded to the two aluminum atoms have a partial occupancy by methyl groups (42 %). The complex has the expected small residual paramagnetism [$\mu_{\text{eff}} = 0.85\,\mu_{\text{BM}}$] for ligand-bridged dimers and does not thermally decompose at 100 °C even after a few hours. The ^{1}H NMR spectrum showed rather broad resonances for the two bridging methyl groups. The partial methyl occupancy of the positions that contain chloride bonded to aluminum gives rise to multiple sets of resonances, with relative intensities of 0.42:0.58 for [{η^5-2,3,4,5-Me_4C_4N-($AlClMe_2$)Cr}{η^5-2,3,4,5-$Me_4C_4N(AlMe_3)$Cr}(μ-Me)$_2$] and [{η^5-2,3,4,5-$Me_4C_4N(AlClMe_2)$Cr}$_2$(μ-Me)$_2$], respectively.

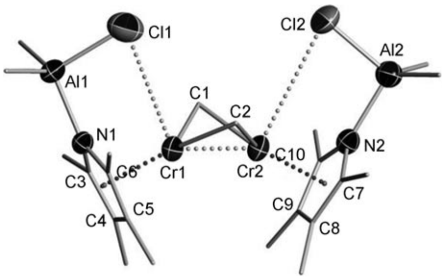


Figure 2. Plot of **3** with ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl1–Al1 2.187(3), Cr1–C1 2.181(5), Cr1–C2 2.198(5), Cr2–C1 2.172(4), Cr2–C2 2.180(5), Cr1–C3 2.306(5), Cr1–C4 2.341(5), Cr1–Cr2 2.274(1), Cr1–C5 2.339(5), Cr1–C6 2.317(4), Cr1–N1 2.350(4), Al1–N1 1.984(4), Cr1–C11 3.489(8), Cr2–Cl2 3.675(8), Cr1–centroid1 2.003(5), Cr2–centroid2 1.992(5); Cr2-Cr1-centroid1 152.9(3), Cr1-Cr2-centroid2 152.9(3).

Despite the close relationship with the species assumed to be generated during the self-activation of the polymerization catalyst **1**, complex **3** does not polymerize ethylene. In toluene, it is a moderately active self-activating oligomerization catalyst, producing a mixture of mainly 1-butene, 1-hexene, and 1-octene (Table 1, entry 1). However, when the reaction was performed with methylcyclohexane as solvent, 95 % pure 1-hexene (Table 1, entry 5) was formed with very good activity ($6.7 \times 10^5\,\text{g}\,\text{mol}^{-1}\,\text{h}^{-1}$). A further improvement in both activity and selectivity was observed when Me_2AlCl was added to the catalytic mixture (Table 1, entries 2,6). $AlMe_3$, on the other hand, had a poisoning effect on the catalyst. Accordingly, an isostructural compound **3a** containing lesser amount of chlorine (0.35 instead of 1.58 per dimer; see the Supporting Information), showed only marginal catalytic activity, confirming that the presence of chlorine is truly essential to catalytic activity. Species free of chlorine or with a definite stoichiometric ratio could not be properly characterized. Attempts to further activate **3** by treatment with $B(F_5C_5)_3$ resulted in no activity of any sort

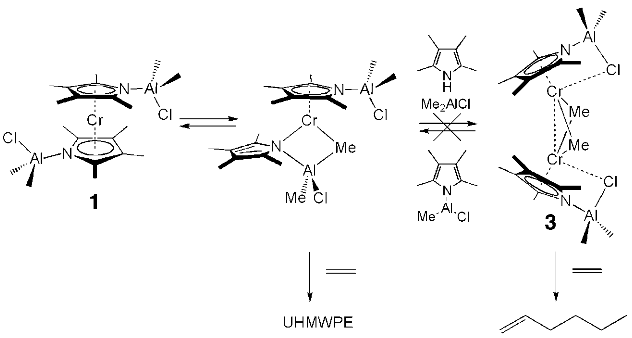
Table 1: Ethylene oligomerization by **3**.[a]

Entry	Solvent	Cocatalyst	PE [g] [b]	Oligom. [g]	Activity [$g\,mol^{-1}\,h^{-1}$]	C_4 [%]	C_6 [%]	C_8 [%]	C_{10} [%]	C_{12} [%]	C_{14} [%]	C_{16} [%]
1	toluene	–	trace	4.2	1.4×10^5	46	39	11	3	1	–	–
2	toluene	2.5 $AlMe_2Cl$	trace	18.3	6.1×10^5	33	52	11	3	1	–	–
3	toluene	2 TMP,[c] 3 $AlMe_2Cl$	trace	9.0	3.0×10^5	33	43	14	4	3	2	2
4	toluene	2 $B(C_6F_5)_3$	0.5	0.4	3.0×10^4[d]	24	44	18	14	–	–	–
5	methylcyclohexane	–	trace	20.2	6.7×10^5	2	95	2	1	–	–	–
6	methylcyclohexane	4 $AlMe_2Cl$	trace	36.7	1.2×10^6	–	97.5	0.2	0.2	0.1	–	–

[a] Standard conditions: loading 30 μmol of complex, $T = 105\,°C$, 100 mL of solvent, 36 bar of ethylene, 1 h reaction time. C_n = 1-*n*-ene. [b] Trace = less than 0.05 g of PE. [c] TMP = tetramethylpyrrole. [d] Based on PE + oligomers.

(Table 1, entry 4), which possibly indicates catalyst decomposition. In all the runs, only traces of polymer were observed.

Catalytic tests of **3** carried out in the presence of deliberately added equivalent amount of tetramethylpyrrole and Me_2AlCl did not switch the catalytic selectivity towards polymerization (Table 1, entry 3), thus excluding the possibility that complex **1** and **3** might be connected in the catalytic cycles via an aluminum–pyrrole dissociation/association process (Scheme 2). Therefore, the two species are not interconvertible despite their close relationship, and they show distinctively different catalytic behavior. Complex **3** is, to the best of our knowledge, only the second example of a self-activating trimerization catalyst producing 1-hexene with high selectivity. Its catalytic activity is one order of magnitude higher than the recently reported chromium(I) carbazolyl.[5]



Scheme 2. Non-interconvertibility of complexes **1** and **3**.

The catalytic behavior raises two main points. First, it seems to refute the possibility for "{η^5-2,3,4,5-Me_4C_4N-($AlClMe_2$)CrMe}" to be the catalytically active species in the self-activation of **1**. The two closely related species **1** and **3**, both bearing chromium in the divalent state, perform completely different catalytic processes. This might also indicate that, in the polymerization process promoted by **1**, both pyrrole rings possibly remain somehow connected to the chromium center. This is in line with the behavior of a closely related divalent carbazolyl derivative,[5] which is also a self-activating polymerization catalyst that produces UHMWPE. Second, the fact that **3** is an active self-activating selective trimerization catalyst and has the metal in the divalent state seems to contradict the recent findings that propose that only a chromium(I) aluminatopyrrolate complex should be capable of selective trimerization. On the other hand, it is certainly possible that complex **3** disproportionates in the presence of ethylene, generating the monovalent {η^5-2,3,4,5-Me_4C_4N-($AlClMe_2$)Cr} and the corresponding trivalent {η^5-2,3,4,5-Me_4C_4N($AlClMe_2$)$CrMe_2$} species. In fact, the coordination of a catalytically active chromium(I) species to toluene to form the corresponding η^6-arene complex is the only way to explain the spectacular poisoning effect of toluene, a feature never observed for divalent chromium.[10] The beneficial effect of added chlorine on the catalytic activity by the addition of stoichiometric amount of Me_2AlCl is ascribed to further chlorine enrichment of the coordinated aluminum residues.

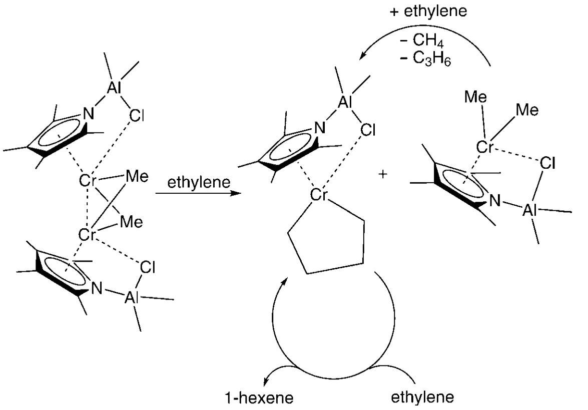
To support these ideas, we have evaluated the ΔG_{rxn} with the help of DFT calculations at the (PBE/TZVP) level for a few possible dimer dissociation scenarios (Table 2). Solvation effects (toluene versus cyclohexane) have also been taken

Table 2: Calculated thermodynamic parameters.[a]

Reaction	Cyclohexane ΔG_{298K}	Cyclohexane ΔG_{373K}	Cyclohexane, chlorine-free ΔG_{298K}	Toluene ΔG_{298K}	Toluene ΔG_{373K}
$\mathbf{3}\rightarrow 2[Cr^{II}L(CH_3)]$	9.8	5.7	11.2	10.7	6.6
$\mathbf{3}+2\,C_2H_4\rightarrow 2\,[Cr^{II}L(CH_3)(C_2H_4)]$	12.1	13.3	14.6	12.2	13.4
$\mathbf{3}\rightarrow[Cr^{III}L(CH_3)_2]+[Cr^{I}L]$	19.6	15.9	23.9	20.3	16.6
$\mathbf{3}+C_2H_4\rightarrow[Cr^{III}L(CH_3)_2]+[Cr^{I}L(C_2H_4)]$	10.9	9.8	15.0	11.5	10.4
$\mathbf{3}+2\,C_2H_4\rightarrow[Cr^{III}L(CH_3)_2]+[Cr^{III}L(C_4H_8)]$	−3.5	−0.8	0.7	−3.4	−0.7
$\mathbf{3}+3\,C_2H_4\rightarrow[Cr^{III}L(CH_3)_2]+[Cr^{III}L(C_4H_8)(C_2H_4)]$	11.2	16.4	11.9	10.8	16.0
$[Cr^{I}L]+C_6H_6\rightarrow[Cr^{I}L(C_6H_6)]$	−1.4	1.2	1.7	−3.0	−0.4
$\mathbf{3}+5\,C_2H_4\rightleftharpoons 2\,[CrL(C_4H_8)]+CH_4+C_3H_6$	−39.3	−33.3	−35.2	−39.0	−33.0

[a] Energies given in $kcal\,mol^{-1}$.

into consideration. The calculations clearly indicated that the solvation effects are only minor, thus confirming that the toluene poisoning effect may indeed be due to the formation of a chromium–arene species. Among the several possibilities taken under consideration, both homolytic and heterolytic dissociation exhibited positive values of ΔG_{rxn}. The results were not different when the same dissociations were calculated in the presence of ethylene to form the corresponding olefin complexes. Remarkably, ΔG_{rxn} became negative only in the case where the intermediate chromium(I) species, as obtained from the heterolytic dissociation, is reoxidized by two molecules of ethylene to form a chromacyclopentane ring (Scheme 3). Calculations predict that any one of the processes taken into consideration by using a chlorine-free compound (Me$_3$Al adducts) will only have more positive ΔG_{rxn} values (Table 2), which is also in agreement with the observed beneficial effect of chlorine feed on catalytic activity. Incidentally, these results explain the need for the use of dimethylaluminum chloride in the Chevron Phillips system, to which complex **3** is clearly closely related.



Scheme 3. Chromacylopentane ring formed from an intermediate chromium(I) species.

In conclusion, we have reported the preparation of a divalent chromium complex with a chromocene-type structural motif, which is a self-activating, single-site catalyst producing UHMWPE. A closely related species, with only one aluminatopyrrolyl ring and a dimeric structure, is instead an effective self-activating trimerization catalyst. The difference of catalytic behavior is explained by the fact that, in contrast to the "chromocene" type of complex, which maintains the divalent oxidation state, the dimeric complex disproportionates in the presence of ethylene to form a transient monovalent species.

Experimental Section

1: A solution of tetramethylpyrrole (0.233 g, 1.89 mmol) in toluene (15 mL) and a suspension of [CrCl$_3$(thf)$_3$] (0.400 g, 1.07 mmol) were combined after cooling to −35 °C. The resulting mixture was stirred for 5 min and treated with neat AlMe$_3$ (0.615 g, 8.53 mmol). The color changed immediately from purple to green. The solution was allowed to warm slowly to room temperature, and was then stirred for an additional 4 h. The solvent was evaporated under reduced pressure to yield green solid, which was redissolved in anhydrous hexane (20 mL). Dark bluish-green crystals were obtained after allowing the resulting solution to stand for one week at −15 °C (0.205 g, 0.43 mmol; yield 40 %). $\mu_{eff} = 2.77\,\mu_B$; elemental analysis (%) calcd for $C_{20}H_{36}Al_2Cl_2CrN_2$: C 49.90, H 7.54, N 5.82; found: C 49.87, H 7.52, N 5.79.

2: Method A: PhN=NPh (0.094 g, 0.52 mmol) was added to a solution of **1** (0.250 g, 0.52 mmol) in toluene (20 mL). The color of the mixture changed from red to brown during stirring for 4 h. The solvent was then removed in vacuo to yield a dark-brown solid, which was re-dissolved in freshly distilled hexane (15 mL). The solution was filtered to remove a small quantity of insoluble material. A dark brown amorphous compound was isolated after standing for one week at −35 °C. Upon addition of THF (0.52 mmol), the solid redissolved, and dark reddish brown crystals of **2** separated at room temperature after 6 days (0.105 g, 0.20 mmol; yield 31 %). $\mu_{eff} = 1.87\,\mu_B$; elemental analysis (%) calcd for $C_{32}H_{54}Al_3ClCrN_3O$: C 57.78, H 8.18, N 6.32; found: C 57.66, H 8.15, N 6.29. Method B: A solution of tetramethylpyrrole (0.291 g, 2.36 mmol) in toluene (20 mL) and a suspension of [CrCl$_3$(thf)$_3$] (0.500 g, 1.334 mmol) in toluene (25 mL) were cooled to −35 °C prior to mixing. The combined mixture was stirred for 5 min, followed by the addition of neat AlMe$_3$ (0.769 g, 10.67 mmol). An immediate color change from purple to green was observed. The solution was allowed to warm slowly to room temperature, and was then stirred for an additional 4 h. The addition of PhN=NPh (0.243 g, 1.33 mmol) and further stirring overnight resulted in a color change from green to reddish-brown. The solvent was evaporated under reduced pressure and the resulting reddish-brown solid was dissolved in anhydrous hexane. A small amount of insoluble material was removed by centrifugation, and reddish-brown crystals of **2** were obtained upon standing at room temperature for 5 days (0.191 g, 0.37 mmol; yield 28 %).

3: A solution of tetramethylpyrrole (0.9 g, 7.31 mmol) in toluene (5 mL) was combined with a suspension of [CrCl$_2$(thf)$_2$] (0.97 g 3.63 mmol) in toluene (4 mL), stirred for 20 min, and cooled to −30 °C. Neat AlMe$_3$ (1.05 g, 14.57 mmol) was pre-cooled to −30 °C and added to the resulting mixture. The solution was allowed to warm slowly to room temperature, and was then stirred for additional 4 h. Then the suspension was centrifuged, and the solvent of the clear solution was removed under reduced pressure. The resulting dark oil was redissolved in anhydrous hexane (5 mL). Dark purple crystals were obtained after allowing the resulting solution to stand for 2 days at −30 °C (0.36 g, 0.65 mmol; yield 35 %). ^{1}H NMR (500.177 MHz, [D$_8$]THF, 25 °C): $\delta = 36.4$ ($\Delta\omega_{1/2} = 700$ Hz, 6 H, μ-Me^A), 23.7 ($\Delta\omega_{1/2} = 700$ Hz, 6 H, μ-Me^B), 3.21 ($\Delta\omega_{1/2} = 35$ Hz, 6 H, $C_4NMe_2\mathit{Me}_2{}^A$), 2.83 ($\Delta\omega_{1/2} = 31$ Hz, 6 H, $C_4N\mathit{Me}_2Me_2{}^A$), 2.49 ($\Delta\omega_{1/2} = 23$ Hz, 12 H, $C_4N\mathit{Me}_2Me_2{}^B$), 1.77 ($\Delta\omega_{1/2} = 22$ Hz, 12 H, $C_4NMe_2\mathit{Me}_2{}^B$), 1.57 (6 H, $C_4NMe_2\mathit{Me}_2{}^A$, overlapped with resonance at 1.54 ppm), 1.54 (6 H, $C_4N\mathit{Me}_2Me_2{}^A$, overlapped with resonance at 1.57 ppm), 0.33 ($\Delta\omega_{1/2} = 13$ Hz, 9 H, $Al\mathit{Me}_3{}^A$), 0.10 (12 H, $Al\mathit{Me}_2Cl^B$, overlapped with resonance at 0.05 ppm), 0.05 ppm (6 H, $Al\mathit{Me}_2Cl^A$, overlapped with resonance at 0.10 ppm). Elemental analysis (%) calcd for $C_{22.42}H_{43.26}Al_2Cl_{1.58}Cr_2N_2$: C 48.53, H 7.86, N 5.05; found: C 48.77, H 7.89, N 5.01. Fractional stoichiometry is due to split Cl/Me occupation.

Polymerization/oligomerization: Samples were tested in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in toluene (100 mL) under N$_2$ prior to loading the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene; the pressure was maintained throughout the run. Polymerizations were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. Molecular weight and molecular weight distributions of the resulting polymers were determined by gel permeation chromatography on a PL-GPC210 equipped with a refractive index and a viscosity detector and a 3 × PLgel 10 μm Mixed-B column set at 135 °C using 1,2,4-trichlorobenzene as solvent. The molecular weight of the polyethylenes was referenced to polystyrene standards. Results of the oligomerization were assessed by NMR for activity and GC-MS for reaction mixture composition.

Crystal data for **1**: $C_{20}H_{36}Al_2Cl_2CrN_2$, $M_r = 481.37$, orthorhombic, $Pbca$, $T = 200(2)$ K, $a = 9.8897(11)$, $b = 14.3759(15)$, $c = 18.2210(19)$ Å, $V = 2590.5(5)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo}_{\mathrm{K}a}) = 0.787$ mm^{-1}; 20370 reflections collected, 2624 unique ($R_{int} = 0.0359$), GOF = 1.068, final R_1 ($I > 2s(I)$) = 0.0470, $wR_2 = 0.1228$. **2**: $C_{32}H_{54}Al_3L_3ClCrN_3O$, $M_r = 665.17$, monoclinic, $P2_1$, $T = 200(2)$ K, $a = 8.894(11)$, $b = 13.062(16)$, $c = 16.16(2)$ Å, $\beta = 95.804(17)°$, $V = 1868(4)$ Å^3, $Z = 2$, $\mu(\mathrm{Mo}_{\mathrm{K}a}) = 1.183$ mm^{-1}; 13311 reflections collected, 6354 unique ($R_{int} = 0.0551$), GOF = 1.025, final R_1 ($I > 2s(I)$) = 0.0678, $wR_2 = 0.1806$. **3**: $C_{22.42}H_{43.26}Al_2L_2Cl_{1.58}Cr_2N_2$, $M_r = 554.86$, orthorhombic, $Pna2_1$, $T = 200(2)$ K, $a = 21.313(10)$, $b = 9.226(4)$, $c = 15.055(7)$, $V = 2960(2)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo}_{\mathrm{K}a}) = 1.245$ mm^{-1}; 17311 reflections collected, 5037 unique ($R_{\mathrm{int}} = 0.0396$), GOF = 1.039, final R_1 ($I > 2s(I)$) = 0.0433, $wR_2 = 0.1188$. CCDC 720466 (**1**), 720467 (**2**), and 720468 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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