DOI: 10.1002/ange.200803434

Catalyst Design

Isolation of Single-Component Trimerization and Polymerization Chromium Catalysts: The Role of the Metal Oxidation State**

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Chromium catalysts account for over 90% of the patent and scientific literature of ethylene oligomerization.[1] This metal also provides many potent polymerization catalysts.[2] Therefore, its complexes are ideal systems for studying the factors that determine catalyst activity and selectivity for polymerization or selective oligomerization of ethylene, respectively. One of the main unsolved issues in all the chromium systems is the metal oxidation states responsible for either ethylene polymerization or selective oligomerization. Given the completely different nature of the two mechanisms (nonredox[3] versus redox[4]), the metal oxidation state is expected to play a critical role in determining the type of process and its selectivity. Whereas trivalent chromium complexes are generally used as catalyst precursors for both polymerization and oligomerization, it is well-established that trivalent organochromium species have the tendency to spontaneously reduce towards the +2 or even lower oxidation states.[5] Accordingly, chromium(II) complexes can also be catalyst precursors for both polymerization and oligomerization processes and regularly display a catalytic activity higher than their trivalent counterparts.[6] Conversely, further reduction towards the monovalent state is also a realistic alternative scenario.[7] A Cr^I intermediate might be sufficiently reducing to start the redox ring-expansion mechanism, leading to oligomerization. Furthermore, the tendency of Cr^I to form π complexes with ethylene and even with arenes is documented.[8] Seminal work by Jolly and co-workers has further demonstrated the tendency of a deliberately prepared seven-membered metallacycle to reductively eliminate towards Cr^I and 1-hexene.[7b] Although not a catalyst system for trimerization, this system lends substantial credibility to the ring-expansion mechanism powered by the Cr^I/Cr^{III} redox couple, and encourages further efforts to isolate and prepare Cr^I derivatives.

Isolating active intermediates of the catalytic cycle is central to the clarification of different aspects of the complex mechanistic puzzle and, most of all, addressing the problem of selectivity. For this purpose, we have recently analyzed two established selective oligomerization systems,[5] demonstrating that the Cr^{III} precursor is readily reduced to the +2 oxidation state. By isolating reactive intermediates, we also realized that the Cr^{II} complex may be reoxidized to Cr^{III} by disproportionation,[5d] suggesting that Cr^{II} produces polyethylene or a Schulz-Flory distribution of ethylene oligomers by a nonredox Cossee-Arlman mechanism, whereas Cr^{III} might form a redox couple with Cr^I that is responsible for selective ethylene oligomerization.

To gain greater insight into the chromium oxidation state, we have focused on the highly active and selective Phillips trimerization catalyst.[1a] This remarkable system consists of a mixture of pyrrole, a chromium salt, and a mixture of Et_3Al and Et_2AlCl. The ratio AlX_3/Cr [X = Et, Cl] was unusually low in this system (<10:1), suggesting that a single-component, catalytically active species could be isolated and characterized and, in turn, elucidating the metal oxidation state responsible for such an outstanding selective catalytic activity. Herein we report our findings.

As expected, isolation of pyrrole-based single-component catalysts proved problematic, with the preferred 1,2-dimethylpyrrole ligand, as recommended by the original Phillips patent,[1a] yielding only oily or microcrystalline products. By using 2,3,4,5-tetrahydro-1*H*-carbazole (also recommended in the Phillips patent) and Cr(2-ethylhexanoate)$_3$, $[CrCl_3(thf)_3]$, or $[CrCl_2(thf)_2]$ in the presence of $AlEt_3$ and $AlEt_2Cl$, we isolated characterizable products. By using $[CrCl_3(thf)_3]$ or $[CrCl_2(thf)_2]$ and following the method, outlined in the patent, of treating the chromium precursor with a mixture of the ligand and $AlEt_3$, the same square-planar Cr^{II} species, $[Cr\{\eta^2\text{-}AlEt_2Cl(2,3,4,5\text{-}C_{12}H_4N)\}_2]$ (**1**) was obtained as a blue paramagnetic crystalline material ($\mu_{eff} = 4.78\ \mu_B$, Scheme 1). The use of $AlEt_2Cl$ in combination with $AlEt_3$, as required by the patent method,[1a] did not substantially modify the outcome of the reaction in this case. Conversely, when halogen-free chromium(III) octanoate (also suggested in the original patent)[1] was used, the presence of $AlEt_2Cl$ was crucial to the successful isolation of a characterizable material. The reaction afforded the new paramagnetic Cr^I species $[Cr\{\eta^6,\eta^6\text{-}(C_{12}H_{12}NAlEt_2)_2(\mu\text{-}Cl)\}]$ (**2**) in crystalline form. Complex **2** can also be obtained from the one-electron reduction of **1** with potassium metal. The magnetic moment of **2** ($\mu_{eff} = 1.87\ \mu_B$) was as expected for the low-spin configuration of d^5 Cr^I in a pseudooctahedral ligand field with a formal electron count of 17.

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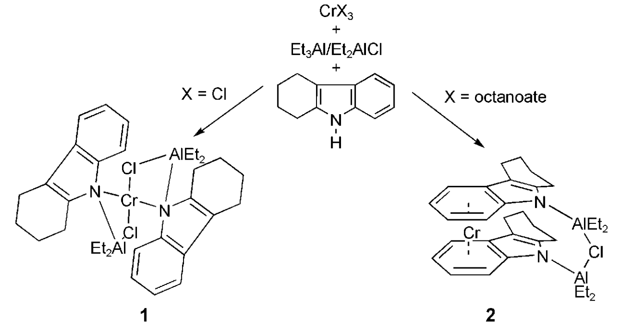
[**] This work was supported by the Natural Science and Engineering Council of Canada (NSERC) and by the Dutch Polymer Institute. W. K. Gerritsen (University Eindhoven) is gratefully acknowledged for the GPC analysis.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803434.



Scheme 1. Synthesis of complexes **1** and **2**.

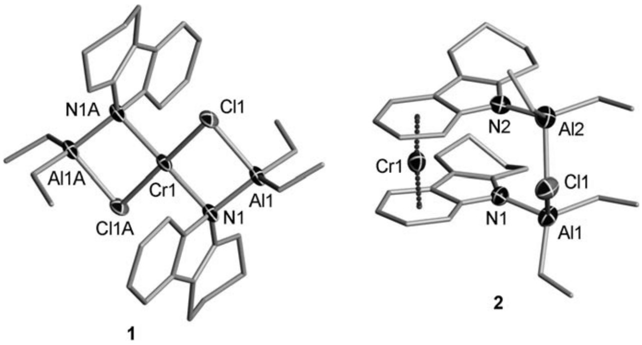


Figure 1. Partial molecular structures of **1** and **2** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles: **1**: Cr1-N1 2.1477(17), Cr1-Cl1 2.3589(9), Al1-N1 1.9510(15), Al1-Cl1 2.3139(10), N1-Cr1-Cl1 84.21(5), Al1-Cl1-Cr1 83.23(4), N1-Al1-Cl1 89.97(6), Cl1A-Cr1-Cl1 180.0, N1A-Cr1-Cl1 95.79(5); **2**: Al1-N1 1.887(4), Al1-Cl1 2.326(2), Al2-Cl1 2.337(2), Al2-N2 1.884(4), N1-Al1-Cl1 103.56(14), Al1-Cl1-Al2 117.55(8), N2-Al2-Cl1 101.26(14), Cr1-centroid 1.64(5), centroid-Cr1-centroid 176.2(5).

The formation under identical conditions of **1** and **2**, containing Cr^{II} and Cr^{I}, respectively, depending on the counteranion of the chromium starting salt, clearly reiterates the ease of chromium reduction in these systems. The further reduction to the monovalent state, as obtained by using a nonchlorinated starting material, is not completely surprising. It can be readily explained by assuming more extensive alkylation of the octanoate, compared to the chloride, in the early stage of the reaction. Interestingly, the structure of **2** contains one chlorine atom, acquired from $AlEt_2Cl$.

In all cases, the connectivity has been elucidated by single-crystal X-ray structure determinations (Figure 1). Complexes **1** and **2** display either the characteristic square-planar or sandwich coordination geometry, as expected for high-spin d^4 Cr^{II} and low-spin d^5 Cr^{I} ions, respectively. In complex **1**, the coordination environment is defined by the N atoms of the carbazolyl ligands, which, in turn, bridge an $AlEt_2Cl$ residue. The chlorine atoms bridge between the aluminum atoms and chromium atom, thus occupying the two remaining coordination sites of the square-planar chromium center. Complex **2** comprises a chromium(I) center sandwiched between the phenyl moieties of the two carbazolyl ligands, in a structure closely reminiscent of chromium(I) bis(arene) complexes.[9] Each nitrogen atom of the carbazolyl anions is σ bonded to an Et_2Al residue. The two aluminum atoms are connected through one residual chlorine atom, which is too distant from chromium to form a bonding interaction.

Complex **1** acts as a single-component ethylene polymerization catalyst, initiating a fast polymerization reaction upon simple exposure to ethylene gas (Table 1). An interesting comparison can be made between this species and the recently reported $[V(\eta^5\text{-}\{2,5\text{-}Me_2C_4H_2N(AlClMe_2)\})_2]$, which also acts as a single-component, single-site polymerization catalyst.[10] The unique ability of this species to be catalytically active without a preformed V−C bond was explained by assuming ring slippage and switching of the pyrrolide bonding mode from π to σ, prior to dissociation and alkyl transfer from Al to V. From this point of view, the σ-ligated complex **1** may be regarded as being one stage further toward self-transformation into the catalytically active species, only requiring alkyl transfer and dissociation of the neutral $(L)AlR_2$ residue. The square-planar coordination geometry, as dictated by the d^4 electronic configuration of Cr^{II}, is clearly the factor responsible for this difference to the vanadium catalyst.

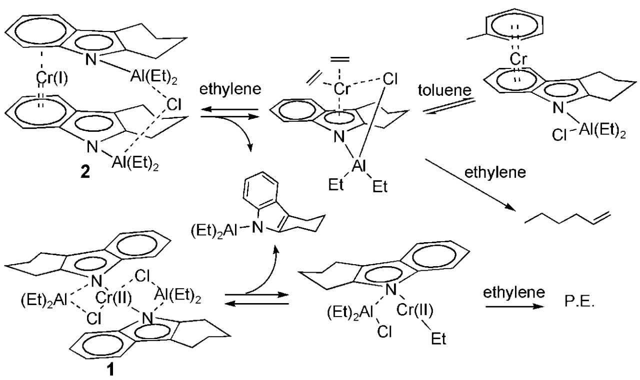
The monovalent state of chromium is known to be stabilized by aromatic compunds (for example, toluene used as a solvent), with which it forms catalytically inactive η^6-arene compounds.[8] Accordingly, monovalent **2** produces only insignificant traces of polymer while in solution in aromatic solvents (Table 1). However, in methylcyclohexane,

Table 1: Catalytic performances of complexes **1**–**3**

Catalyst	Solvent	Cocatalyst	Activity [g mmol^{-1} h^{-1}]	Polymer [g]	Total olig. [mL]	1-hexene [%]	C$_8$ [%]	C$_{10}$ (isomers) [%]
(1,2-dimethylpyrrole)[a]	methylcyclohexane	$AlEt_3$ (7 equiv) $AlEt_2Cl$ (7 equiv)	1170	0.2	11.5	92	4	4
(2,3,4,5-tetrahydro-1*H*-carbazole)[a]	methylcyclohexane	$AlEt_3$ (7 equiv) $AlEt_2Cl$ (7 equiv)	150	Traces	1.5	93	4	3
1	methylcyclohexane	none	320	3.2	none	–	–	–
2	methylcyclohexane	none	220	Traces	2.2	93	4	3
2	toluene	none	20	0.2	traces	<1	–	–
3	methylcyclohexane	none	270	traces	2.7	30	17	10

[a] Benchmark chromium catalysts with the stated ligands.[1a] All runs carried out under 600 psi at 115 °C for 30 min. with 20 μmol of catalyst in a total volume of 100 mL.

2 is an unprecedented single-component trimerization catalyst, producing 1-hexene with only trace amounts of higher oligomers. As in the Phillips catalytic system, **2** is inactive in toluene, even at elevated temperatures.[1a] The poisoning behavior of toluene in the Phillips catalytic systems can now be understood in terms of the nature of the catalytically active species (Scheme 2). Assuming that complex **2** dissociates one ligand to vacate the necessary coordination sites, in a similar manner to $[V(\eta^5\text{-}\{2,5\text{-}Me_2C_4H_2N(AlClMe_2)\})_2]$, it is conceivable that toluene could simply form an inert $\{Cr^I(\pi\text{-arene})\}$ structure.[8] The same ligand dissociation in methylcyclohexane would allow ethylene to coordinate, without the unfavorable competition of other π systems. In contrast to complex **1**, dissociation of a $LAlR_2$ fragment from **2** does not imply alkyl transfer, which is, furthermore, unnecessary for trimerization by a redox ring-expansion mechanism.



Scheme 2. Catalytic activity of complexes **1** and **2**. P.E. = polyethylene.

In the original Phillips method, 1,2-dimethylpyrrole is the preferred ligand, and gives by far the best activity. This ligand does not incorporate a condensed aromatic ring and, therefore, formation of a complex analogue to **2** is not possible, raising the question whether a monovalent species might still be generated with standard pyrrolide anions. In an attempt to address this issue we have carried out a preparation similar to that for **1**, using simple pyrrole. The reaction afforded an insoluble material which, however, could still be crystallized if a stoichiometric amount of bis(trimethylsilyl)acetylene was added as a trapping agent. The complex, formulated as $[\{Cr(\eta^5\text{-}C_4H_4NAlEt_2Cl)\}_2\{\mu^2,\eta^2\text{-}C_2(SiMe_3)_2\}_2]$ (**3**) is nearly diamagnetic, with the same small residual paramagnetism often detected for dinuclear chromium compounds with a short Cr⋯Cr contact (in this case, 2.3 Å). The structure (Figure 2) consists of a symmetry-generated dimer, with each chromium center π bonded to a pyrrolyl($AlEt_3$) anion. The bridging interaction between the two Cr-containing residues is provided by the two alkynes which are μ^2,η^2-side-on bonded to both metal centers. Complex **3** is the first example of a well-characterized Cr(alkyne) complex not to contain phosphine or carbonyl ligands. Its formation is the result of the oxidative addition of a transient monovalent Cr species to the alkyne, affording what appears to be a trivalent species, given the elongation of the coordinated alkyne C–C bond, which is clearly indicative of a two-electron reduction. Complex **3** is a nonselective, single-component oligomerization catalyst (Table 1). As a trivalent chromium complex,[11] this species was not expected to be a single-component selective catalyst. In fact, the lack of selectivity seems to rule out that alkyne reductive elimination might occur by simple dissociation. In this event, it would have been reasonable to expect the same level of selectivity reported in the Phillips patent. Thus, dimer versus monomer dissociation probably generates empty coordination sites and in turn initiates the catalytic cycle. Unsurprisingly, the activity was only moderate, albeit significant, and no evidence for incorporation of alkyne in the oligomers was detected in the GC of catalytic mixtures. No evidence for alkyne dissociation could be found in the NMR spectra of the reaction mixtures. Again, unless one assumes that alkyl transfer from aluminum to chromium occurs, there is no initiating Cr–R function in this system.

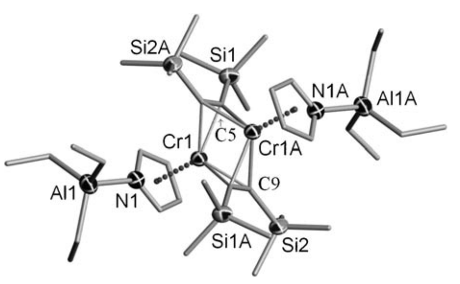


Figure 2. Molecular structure of **3** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:Cr1-Cr1A 2.2992(15), Cr1-centroid 1.94(6), Cr1-C5 2.063(5), Cr1-C9 2.060(5), Cr1-C5A 2.075(5), Cr1-C9A 2.088(4), Al1-N1 2.015(4), C5-C9A 1.343(6), Si1-C5 1.875(5), C9-Cr1-C5 100.67(18), C9A-C5-Si1 140.1(4).

In summary, this study, on a system closely related to the commercial Phillips ethylene trimerization system, has elucidated a link between the metal oxidation state and the type of catalytic behavior: Cr^{III} led to nonselective oligomerization, Cr^{II} to polymerization and Cr^I to selective trimerization. Although these findings give a reasonably realistic picture of the complexity of an important catalytic system, they certainly cannot be generalized at such an early stage. For example, the three complexes also differ by chlorine content, which, in principle, could be another factor affecting the catalytic behavior. Nonetheless, an attractive working hypothesis for the design of novel trimerization catalysts emerged with zwitterionic ligands facially bound to Cr^I.

Experimental Section

Polymerization and oligomerization results: Samples were tested in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighed amount of catalyst was dissolved in toluene (10 mL) under N_2 and injected into the preheated reactor already charged with co-catalyst and toluene (total volume 100 mL). Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. The oligo/polymerizations were quenched by venting the reactor and addition of EtOH and HCl. The resulting polymer was isolated by filtration, sonicated with an acidified ethanol solution, rinsed, and thoroughly dried prior to mass determination. Oligomers were analyzed using

GC and ^{1}H NMR spectroscopy. Gel-permeation chromatography (GPC) analysis of the polyethylene was referenced to polystyrene ($M_w = 65\,500$, PDI = 1.02) standards. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent-purification system. Samples for magnetic susceptibility analysis were preweighed inside a drybox equipped with an analytical balance, and measured on a Johnson–Matthey magnetic susceptibility balance. [$CrCl_2(thf)_2$] and [$CrCl_3(thf)_3$] were prepared according to standard procedures. Cr(2-ethylhexanoate) was used as received (Strem). Pyrrole and 2,5-dimethylpyrrole (Aldrich) were purified by distillation and recrystallization, respectively, before use. 2,3-Dimethylindole and 2,3,4,5-tetrahydrocarbazole (Aldrich) were used as received. The alkylaluminum reagents $AlEt_2Cl$ (Aldrich), $AlEt_3$ (Aldrich), and MAO (Chemtura) were used as received. Mass spectra were recorded on a Micromass Quattro-LC Electrospray-Triple Quadrupole Mass Spectrometer. Experiments were carried out in the negative mode.

Synthesis of [Cr{η^2-$AlEt_2Cl$(2,3,4,5-$C_{12}H_4N$)}$_2$] (**1**): Method A: A purple suspension of [$CrCl_3(thf)_3$] (374 mg, 1 mmol) in pentane (5 mL) was added a colorless solution of 2,3,4,5-tetrahydrocarbazole (340 mg, 2 mmol) in pentane (5 mL) containing $AlEt_3$ (684 mg, 6 mmol). The resulting deep-green solution was centrifuged and allowed to stand for 3 days at −35 °C, affording **1** (259 mg, 0.41 mmol, 41 %) as blue crystals.

Method B: A blue suspension of [$CrCl_2(thf)_2$] (267 mg, 1 mmol) in pentane (10 mL) was added to a colorless solution of 2,3,4,5-tetrahydrocarbazole (340 mg, 2 mmol) in pentane (10 mL) containing $AlEt_3$ (684 mg, 6 mmol), resulting in a blue solution. The solution was stirred for a period of 1 h, centrifuged, and stored at −35 °C for 3 days affording blue crystals of **1** (530 mg, 0.84 mmol, 84 %). Elemental analysis (%) calcd for $C_{32}H_{44}Al_2Cl_2CrN_2$: C 60.60, H 7.00, N 4.42; found: C 60.00, H 6.98, N 4.38.

Synthesis of [Cr{η^6,η^6-($C_{12}H_{12}NAlEt_2$)$_2$(μ-Cl)}] (**2**): Method A: A green solution of Cr(2-ethylhexanoate)$_3$ (481 mg, 1 mmol) in toluene (10 mL) was added to a solution of $AlEt_3$ (570 mg, 6 mmol) and 2,3,4,5-tetrahydrocarbazole (340 mg, 2 mmol) in toluene (10 mL). The mixture was stirred for 10 min and afforded a brown solution. Addition of $AlEt_2Cl$ (170 mg, 1 mmol), filtration, and layering with hexanes for one week at −35 °C afforded **2** as brown crystals (97 mg, 0.16 mmol, 16 %).

Method B: The addition of finely divided potassium (40 mg, 1 mmol) to a blue solution of **1** (632 mg, 1 mmol) in toluene (10 mL) and stirring for 24 h gradually turned the color of the mixture to dark brown. The solution was filtered to remove solids, layered with hexanes, and stored at −35 °C for one week, affording **2** as dark brown crystals (540 mg, 0.90 mmol, 90 %). Elemental analysis calcd for $C_{32}H_{44}Al_2ClCrN_2$: C 64.26, H 7.42, N 4.68; found: C 64.23, H 7.41, N 4.67.

Synthesis of [{Cr(η^5-$C_4H_4NAlEt_2Cl$)}$_2${μ^2,η^2-$C_2(SiMe_3)_2$}$_2$](**3**): A purple suspension of [$CrCl_3(thf)_3$] (374 mg, 1 mmol) and pyrrole (134 mg, 2 mmol) in hexane (5 mL) was combined with a colorless solution of $AlEt_3$ (798 mg, 7 mmol) and $C_2(SiMe_3)_2$ (170 mg, 1 mmol) in hexanes (5 mL), resulting in a dark green solution. The solution was stirred for 1 h, centrifuged, and stored at −35 °C for 3 days to give **1** as dark green crystals (140 mg, 0.17 mmol, 34 %). Further product was isolated by concentrating the solution to half the volume and storing for an additional week at −35 °C (total yield 44 %). ^{1}H NMR (500 MHz, [D$_8$]toluene): $\delta = 3.34$ (m, 4H; Pyr), 1.43 (br m 12H; $SiMe_3$), 1.20 (br m 12H; $SiMe_3$), 1.01 (m, 4H; Pyr), 0.86 (br m, 12H; $SiMe_3$), 0.12 (br s, $AlCH_2CH_3$), −0.12 ppm (br s, 18H; $AlCH_2CH_3$); ^{13}C{^{1}H} NMR (125.7 MHz, [D$_8$]toluene): $\delta = 70.8$ (s, Pyr), 32.1 (s, $SiMe_3$), 25.0 (s, Pyr), 23.1 (s, $AlCH_2CH_3$), 14.4 (s, $SiMe_3$), 10.4 (s, $SiMe_3$), 9.5 (s, $C_2(SiMe_3)_2$), −5.8 ppm ($AlCH_2CH_3$). ESI MS (toluene/NEt3 0.2 %, rel. int.): m/z 804.1 (75) [{M−H}$^-$], 732.1 (100) [{M−$SiMe_3$}$^-$]. Elemental analysis calcd for $C_{36}H_{74}Al_2Cr_2N_2Si_4$: C 53.69, H 9.26, N 3.48; found: C 53.67, H 9.21, N 3.47.

Crystallographic data: Data for X-ray crystal structure determination were collected with a Bruker diffractometer equipped with a 1 K Smart CCD area detector and solved by direct methods.

1: $C_{32}H_{44}Al_2Cl_2CrN_2$, $M_r = 633.55$, monoclinic, $P21/n$, $T = 200(2)$ K, $a = 10.053(5)$ Å, $b = 9.809(5)$ Å $c = 8.263(2)$ Å, $\beta = 92.743(9)°$, $V = 1606.9(13)$ Å^3, $Z = 2$, 4471 unique ($R_{int} = 0.0391$), GOF = 1.068, final $R1[I > 2\sigma(I)] = 0.0376$, $wR^2 = 0.0914$. **2**: $C_{32}H_{44}Al_2ClCrN_2$, $M_r = 598.10$, monoclinic, $P2(1)$, $T = 203(2)$ K, $a = 10.543(7)$ Å, $b = 28.920(19)$ $c = 10.762(7)$ Å, $\beta = 110.679(9)°$, $V = 3070(3)$ Å^3, $Z = 4$, 10 848 unique reflections [$R_{int} = 0.0546$], GOF = 0.997, final $R1[I > 2\sigma(I)] = 0.0552$, $wR^2 = 0.1262$. **3**: $C_{36}H_{74}Al_2Cr_2N_2Si_4$, $M_r = 805.29$, monoclinic, $P21/n$, $T = 203(2)$ K, $a = 11.4912(16)$, $b = 12.3763(18)$, $c = 16.618(2)$, $\beta = 99.366(2)$, $V = 2331.8$ Å^3, $Z = 2$, 1804 unique reflections ($R_{int} = 0.0329$), GOF = 1.0151, final $R1[I > 2\sigma(I)] = 0.0613$ and $wR^2 = 0.1356$. CCDC 676890 (**1**), 676891 (**2**), and 676892 (**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

Received: July 16, 2008
Revised: August 14, 2008

Keywords: alkenes · chromium · homogeneous catalysis · oligomerization · polymerization

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