Catalyst Design

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Chromium Catalysts Supported by a Nonspectator NPN Ligand: Isolation of Single-Component Chromium Polymerization Catalysts**

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Ethylene oligomerization and polymerization can be regarded as belonging to the same type of C−C bond-forming reactions. In fact, the highly desirable selective tri- and tetramerization processes may be simply considered to be polymerizations precisely truncated at an early stage. However, it is commonly accepted that the mechanisms are completely different (oxidative addition followed by ring expansion for oligomerization[1] versus migratory insertion for polymerization[2]), and therefore the two processes are conceptually distinct. On the other hand, it is not obvious to which mechanism oligomerization affording a Schultz–Flory distribution of products belongs. Furthermore, the fact that even the best chromium-based oligomerization catalysts invariably produce small amounts of polyethylene (PE) as an undesirable side product suggests that the two processes may be closely linked. Addressing these important questions cannot be dissociated from understanding of the factors which govern the selectivity of the same catalyst towards one or the other type of transformation.

Chromium is an ideal substrate for this research, since effective catalysts for both ethylene polymerization[3] and oligomerization (including selective tri-[4] and even tetramerization[5]) have been reported for this element. All homogeneous chromium-based catalyst systems reported to date invariably consist of a di- or trivalent chromium precursor and an activator.[3] However, understanding of these systems remains limited, since even the oxidation state of the metal in the catalytically active species is still debated. The nature of the transition metal is not the only important factor, since the cocatalyst can also have a profound effect on catalyst selectivity.[6] Thus, obtaining single-component catalysts by treating a catalyst precursor with different aluminum alkyls may reveal the metal oxidation state of the catalytically active species. In turn, this may provide significant information towards understanding the factors which govern the C−C bond-forming reaction.

Herein we describe the preparation and testing of a chromium-based catalyst system supported by a nonspectator ligand. Activation with different cocatalysts gave spectacular changes in catalyst selectivity, while attempts to isolate the catalytically active species resulted in the characterization of two unprecedented single-component polymerization catalysts.

Wass et al., Bercaw et al., and Overett et al. have clearly demonstrated the potential of the combination of nitrogen and phosphorous donor atoms in a three-atom array for obtaining selective trimerization[4f,g,j,k] and tetramerization catalysts.[5] Our previous mechanistic studies on selective trimerization led us to believe that a stable cationic organo–chromium(III) species might be the key to selectivity for the oligomerization process.[7d] These two arguments prompted us to use the established $(t\mathrm{BuNPN}t\mathrm{Bu})_2{}^{2-}$ dianion,[8] since the particular geometry of the cage defined by the four-membered P_2N_2 ring of the ligand with two additional N donor atoms was assumed to be unsuited to accommodating the square-planar geometry of d^4 $\mathrm{Cr^{II}}$.

In spite of our expectations for facial, octahedral d^3 trivalent complexes, the reaction of the dianion, in the form of the dilithium salt, with either $[\mathrm{CrCl_2(thf)_2}]$ or $[\mathrm{CrCl_3(thf)_3}]$ produced the same divalent, distorted square-planar complex $[(t\mathrm{BuNPN}t\mathrm{Bu})_2\mathrm{Cr}]$ (**1**; Scheme 1). In this species the dianion was cleaved into two $(t\mathrm{BuNPN}t\mathrm{Bu})^-$ monoanions, a transformation occasionally observed but only with main-group elements.[8h,j,9]

When activated with methyl alumoxane (MAO), **1** yielded a statistical distribution of ethylene oligomers (including waxes) but with unprecedented activity. It proved difficult to control the reaction temperature with catalyst concentrations as low as 5 µm. The catalyst was found to be thermally robust, as tests with higher catalyst loading easily reached and maintained temperatures above 110 °C for prolonged periods of time. The activity gradually increases with increasing Al:Cr ratio, but this did not affect the product distribution. Interestingly, the selectivity of **1** was completely determined by the nature of the activator (Table 1). While MAO resulted in oligomerization of ethylene, activation with $(i\mathrm{Bu_2Al})_2(\mu\text{-O})$ gave low-molecular-weight polyethylene with a similarly high activity as when activated with MAO. Notably, small amounts of a mixture of exclusively 1-hexene and 1-octene (av ratio 85:15) were formed as side product. In an attempt to track the

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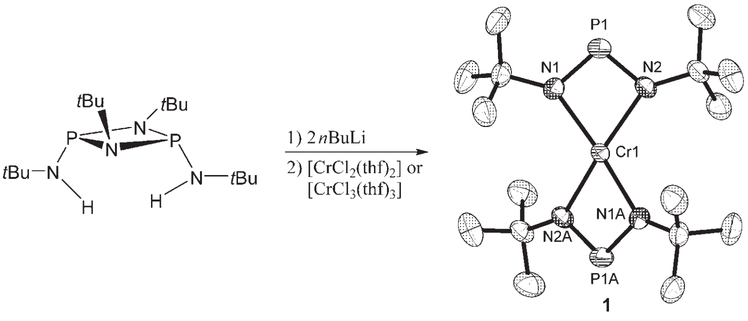
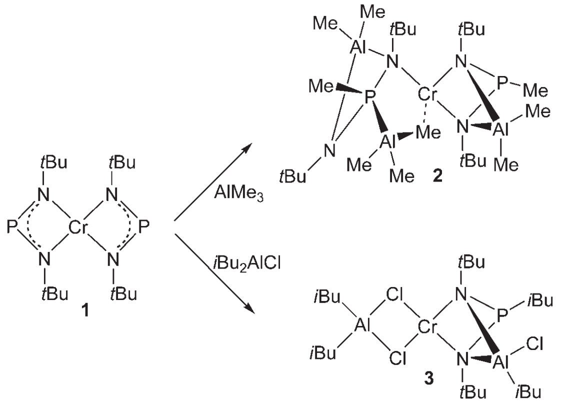


Scheme 1. Synthesis and partial thermal-ellipsoid plot of **1** with ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Cr1–N1 2.098(3), Cr1–N2 2.103(3); N1-Cr1-N2 70.50(10), N1-Cr1-N1a 158.10(16), N1-Cr1-N2a 114.08(11).

origin of the oligomers, it was argued that possibly Al*i*Bu$_3$ present in $(i\mathrm{Bu}_2\mathrm{Al})_2(\mu\text{-O})$ was responsible for oligomerization. In fact, on activation with Al*i*Bu$_3$, complex **1** indeed gave 1-hexene with excellent selectivity (> 99.9 by GC). Although the activity was substantially lower than that obtained by activation with MAO, it was still similar to that of the other existing selective catalysts.[4g,7]

This intriguing diversity of catalytic behavior depending on the activator clearly indicates that different catalytically active species are generated from the reaction of **1** with the alkyl aluminum reagents. Therefore, we attempted to isolate such species by reaction of **1** with various aluminum alkyls. In all cases, the reactions were surprisingly clean and produced crystalline or microcrystalline materials. However, only when **1** was treated with AlMe$_3$ or *i*Bu$_2$AlCl (Scheme 2), was it possible to elucidate the structures by single-crystal X-ray diffraction. Both complexes **2** and **3** contain chromium in the divalent state. In spite of their different appearance, the two reactions have in fact followed a similar trend, in the sense that the P atom has been alkylated in both cases. Also the resulting $[t\mathrm{BuNP(R)N}t\mathrm{Bu}]^{2-}$ dianion uses the two N donor atoms to bridge the chromium center to an AlX$_2$ [X = Me (**2**); Cl, *i*Bu (**3**)] residue to afford an $[\mathrm{RP(N}t\mathrm{Bu)_2AlX_2}]^-$ anion. The difference between the two complexes is that **3** contains one $[\mathrm{RP(N}t\mathrm{Bu)_2AlX_2}]^-$ ligand with chromium bonded to a second Al*i*Bu$_2$ residue through two bridging chloride ligands, while complex **2** contains two $[\mathrm{RP(N}t\mathrm{Bu)_2AlX_2}]^-$ ligands. Coordination of the alkylated phosphorus atom of the second ligand in **2** to an additional AlMe$_3$ moiety prevents it from binding to chromium like the other does. Consequently, one of the two aluminum methyl groups occupies the fourth coordination site of the distorted square-planar chromium atom (Figure 1).

Since the anionic charge of the $[\mathrm{RP(N}t\mathrm{Bu)_2AlX_2}]^-$ ligand is located at the aluminum center that, at least for Al3, is situated relatively far from the chromium center, the structure can be regarded as having a formally dicationic chromium center stabilized by two anionic $[\mathrm{RP(N}t\mathrm{Bu)_2AlX_2}]^-$ ligands. Interestingly, such a structure resembles the earlier reported divalent chromium tetramerization catalyst precursor $[\{\mathrm{CyN(PPh_2)_2}\}_2\mathrm{CrClAlMe_3}]^+$, in which a formally cationic chromium center is stabilized by one $(\mathrm{Me_3AlCl})^-$ fragment



Scheme 2. Reaction of **1** with aluminum alkyls.

Table 1: Ethylene oligomerization and polymerization reactions with **1**–**3** as single-component catalysts or in combination with cocatalysts.[a]

Entry	Cat.	c_{cat} [μmol]	Cocat.	Al:Cr	PE [g]	M_n [g mol^{-1}]	PDI	Activity [g mmol^{-1} h^{-1}]	Oligomers[d] amount [mL]	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	α
1	**1**	5	MAO	2000	0.9	310[c]	1.4	23600	59	45.2	29.7	11.0	6.6	3.8	2.1	0.58
2	**1**	5	MAO	1000	0.9	420[c]	1.3	6400	16	40.0	23.9	15.4	9.1	5.3	2.8	0.61
3[b]	**1**	5	MAO	1000	trace	–		4800	12	41.5	25.1	15.8	9.0	4.8	2.5	0.57
4	**1**	5	MAO	500	3.4	440[c]	1.4	400	1	44.1	23.2	12.1	7.9	4.9	4.4	0.62
5	**1**	5	Al*i*Bu$_3$	1000	1.5	400[c]	1.3	800	2	> 99.9	–	–	–	–	–	–
6	**1**	5	Al*i*Bu$_3$	500	trace	–		400	1	> 99.9	–	–	–	–	–	–
7	**1**	1	$(i\mathrm{Bu}_2\mathrm{Al})_2(\mu\text{-O})$	1000	16.4	34940	3.7	32800	2	82.5	17.5	–	–	–	–	–
8	**1**	1	$(i\mathrm{Bu}_2\mathrm{Al})_2(\mu\text{-O})$	500	12.2	12760	3.0	24400	2	85.0	15.0	–	–	–	–	–
9	**2**	10	–	–	11.2	37990	3.2	2240	0	–	–	–	–	–	–	–
10	**2**	5	MAO	2000	0.2	490[c]	1.3	18800	47	45.3	26.1	14.2	8.3	4.7	2.1	0.57
11	**2**	5	MAO	1000	0.1	500[c]	1.2	18000	45	39.2	26.0	15.3	9.8	6.3	3.4	0.64
12	**2**	5	Al*i*Bu$_3$	1000	1.4			560	0	–	–	–	-	-	–	–
13	**3**	10	–	–	16.5	26780	2.8	3300	0	–	–	–	–	–	–	–
14	**3**	5	MAO	2000	1.2	450[c]	1.3	34000	85	35.2	26.3	15.8	11.5	7.1	4.1	0.67
15	**3**	5	MAO	1000	0.7	410[c]	1.2	27600	69	36.7	26.5	15.9	10.6	6.5	3.8	0.64
16	**3**	5	Al*i*Bu$_3$	1000	3.6	11420	4.3	920	0	–	–	–	–	–	–	–

[a] Standard conditions: $T = 50\,°\mathrm{C}$, 100 mL of toluene, 35 bar of ethylene, 30 min reaction time. [b] 5 bar of ethylene. [c] Waxes. [d] The oligomer distribution is given in %.

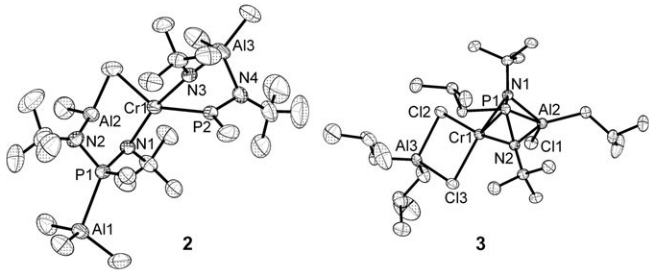


Figure 1. Selected bond lengths [Å] and angles [°] for **2**: Cr1—N1 2.135(3), Cr1—N3 2.136(3), Cr1—C14 2.344(5), Cr1—P2 2.3505(12), N1—Al2 1.940(3), N2—Al2 1.839(3), Al2—C14 2.025(5), P1—N1 1.736(3), P1—N2 1.667(3), Al1—P1 2.5549(15), Al3—N3 1.993(3), Al3—N4 1.876(4), P2—N3 1.710(3), P2—N4 1.648(4); N1-Cr1-N3 167.32(12), N1-Cr1-C14 89.40(14), N3-Cr1-C14 103.24(14), N1-Cr1-P2 122.95(9), N3-Cr1-P2 44.50(9), C14-Cr1-P2 145.67(12), Al2-C14-Cr1 78.08(16). Selected bond lengths [Å] and angles [°] for **3**: Cr1—N2 2.1256(12), Cr1—N1 2.1305(13), Cr1—Cl3 2.4041(5), Cr1—Cl2 2.4063(5), Al3—Cl3 2.2764(7), Al3—Cl2 2.2765(7), Al2—N1 1.9209(13), Al2—N2 1.9283(13), Al2—C13 1.9370(16), P1—N1 1.7651(14), P1—N2 1.7730(14); N2-Cr1-N1 65.26(5), N2-Cr1-Cl3 104.24(4), N1-Cr1-Cl3 169.42(4), N2-Cr1-Cl2 169.26(4), N1-Cr1-Cl2 104.67(4), Cl3-Cr1-Cl2 85.713(17), Cl3-Al3-Cl2 91.88(2), N1-Al2-N2 73.20(6), N1-P1-N2 80.88(6).

and two diphosphinoamine ligands.[7b] In contrast to this complex, which required a cocatalyst for any catalytic activity to be observed, **2** is a single-component catalyst. Simple exposure of **2** to ethylene (35 bar, 50 °C) yielded polyethylene with moderate activity. Treatment of **2** with MAO again led to a drastic switch in selectivity towards a statistical distribution of ethylene oligomers (including some waxes) with a similar remarkable activity to that of the **1**/MAO system (compare entries 1–4 with entries 10 and 11 in Table 1). Surprisingly, attempts at activating both **1** and **2** with an excess of AlMe$_3$ in fact had the opposite effect of totally deactivating the system.

Complex **3** also acts as a single-component ethylene polymerization catalyst with similar activity to **2**. Different from **2**, there are no free coordination sites around chromium in **3**, nor are Cr—C bonds present which could possibly act as polymerization initiators. In analogy with **2**, attempts to activate **1** and **3** with an excess of *i*Bu$_2$AlCl did not produce any catalytic transformation. Treatment of **3** with MAO instead afforded an ethylene oligomerization catalyst even more active than **1** with a nearly constant activity over a period of at least 30 min. The most probable explanation for the single-component activity of **3** is migration of an alkyl group from the AlR residue leading to "[*i*BuP(N*t*Bu))$_2$Al*i*BuCl]Cr*i*Bu", which again can be regarded as an ionic structure containing a cationic chromium alkyl. Alkyl shuttling from the alkylated P atom is another possibility which cannot be ruled out at this stage. Since **2**, **3**, and (*i*Bu$_2$Al)$_2$(μ-O)-activated **1** yield polymers of similar molecular weight, it is probable that closely related active species are generated in the three systems.

The unexpected behavior of the initially intended (*t*BuNPN*t*Bu)$_2^{2-}$ ligand system gave access to a nonspectator (*t*BuNPN*t*Bu)$^-$ anion, which readily reacts with aluminum alkyls. The resulting [RP(N*t*Bu)$_2$AlX$_2$]$^-$ anions afford thermally stable, single-component chromium catalysts. To the best of our knowledge, homogeneous single-component catalysts based on chromium have been reported only once before.[10] This desirable behavior is ascribed to two characteristics of the [RP(N*t*Bu)$_2$AlX$_2$]$^-$ monoanion: 1) it has the potential to transfer an alkyl group to chromium (either from P or from the Al residue), which evidently affords robust chromium alkyl species, and 2) it establishes a structure in which the Lewis acidity of the aluminum residue enhances the positive charge on chromium. Complexes **2** and **3** can reasonably be regarded as representative of the fate of **1** in the early stage of its activation. Formation of such species, which possibly survive in small amounts in the presence of the large excess of activators, might be responsible for the presence of the polymer commonly observed during oligomerization. The intriguing selective trimerization obtained on activation of **1** with Al*i*Bu$_3$ remains unexplained at this stage and it is the target of current investigation.

Experimental Section

Samples were tested in a 200-mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighed amount of catalyst was dissolved in 10 mL of toluene under N$_2$ and injected into the preheated reactor already charged with cocatalyst and toluene (total volume 100 mL). Solutions were heated with a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by 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. Molecular weight and molecular-weight distributions of the polymers were determined by means of gel permeation chromatography on a PL-GPC210 equipped with refractive-index and viscosity detectors and a 3 × PLgel 10 μm MIXED-B column set at 135 °C with 1,2,4-trichlorobenzene as solvent. The molecular weight of PE was referenced to polystyrene ($M_w = 65500$, PDI = 1.02) standards. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by using an aluminum oxide solvent purification system. Samples for magnetic susceptibility were preweighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey magnetic susceptibility balance. Data for X-ray crystal structure determination were collected with a Bruker diffractometer equipped with a 1K Smart CCD area detector. [CrCl$_2$(thf)$_2$] was prepared according to standard procedures. The ligand *cis*-{*t*Bu(H)NP[(μ-N)*t*Bu]$_2$PN(H)*t*Bu} was prepared according to a literature procedure.[6b] The reagents *i*Bu$_2$AlCl (Aldrich), AlMe$_3$ (Aldrich), (*i*Bu$_2$Al)$_2$(μ-O), and MAO (Chemtura and Aldrich) were used as received. Mass spectra were recorded on a Micromass Quattro-LC Electrospray Triple Quadrupole Mass Spectrometer. All the experiments were done in the negative mode with toluene as the main solvent by using 2.5 % of toluene in acetonitrile, capillary voltage 4.00–4.20 kV, cone voltage 40 kV, and a desolvation temperature of 220 °C. Diamagnetic corrections were applied to the calculations of the magnetic moments.

1: A solution of *cis*-{*t*Bu(H)NP[(μ-N)*t*Bu]$_2$PN(H)*t*Bu} (0.348 g, 1 mmol) in THF (20 mL) was treated with *n*BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 0 °C. The mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of [CrCl$_2$(thf)$_2$] (0.268 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue redissolved in toluene. The resulting suspension was centrifuged and the solution was stored at −30 °C. Brown crystals of **1** separated over two days and were filtered, washed with cold hexanes (10 mL), and dried in vacuo to give analytically pure compound (0.294 g, 74 %). $\mu_{\mathrm{eff}} = 4.98\,\mu_B$; ESI-MS (assignment, rel. intensity): m/z: 397.0 ([M−H]$^-$, 42), 341.1

($[M-C_4H_9]^-$, 98), 324.0 ($[M-C_4H_9-NH_3]^-$, 100); C,H,N analysis (%) found (calcd for $C_{16}H_{36}CrN_4P_2$): C 48.23 (48.25), H 9.11 (9.17), N 14.06 (13.91).

2: A solution of **1** (0.398 g, 1 mmol) in toluene (20 mL) was treated with trimethylaluminum (0.288 g, 4 mmol) at room temperature and stirred for 10 min. The solvent was removed in vacuo and then hexanes (10 mL) were added. Storing the resulting solution at −30 °C for 3 d afforded small purple crystals of **2**, which were collected by filtration, washed with cold hexanes, and dried in vacuo (0.386 g, 63 %). $\mu_{eff} = 4.97\,\mu_B$; ESI-MS (assignment, rel. intensity): m/z: 613.9 ($[M-H]^-$, 48), 703.2 (multiple signals, $[M+\text{toluene}-H]^-$, 100; experiments with [D$_8$]toluene gave the expected isotopic pattern), 571.0 ($[M-C_3H_7]^-$, 88); C,H,N analysis (%) found (calcd for $C_{25}H_{63}Al_3CrN_4P_2$): C 48.93 (48.77), H 10.18 (9.98), N 9.13 (9.15).

3: A solution of **1** (0.398 g, 1 mmol) in toluene (20 mL) was treated with diisobutylaluminum chloride (0.704 g, 4 mmol) at room temperature and stirred for 10 min. The solvent was removed in vacuo and then hexanes were added. The solution was stored in a −30 °C freezer for 3 d. The resulting product was collected by filtration, washed with cold hexanes, and dried in vacuo to give **3** as blue crystals (0.282 g, 46 %). $\mu_{eff} = 5.24\,\mu_B$; ESI-MS (assignment, rel. intensity): m/z: 613.8 (multiple signals, $[M-H]^-$, 20), 690.0 (multiple signals, $[M+\text{toluene}-CH_2]^-$, 28; experiments with [D$_8$]toluene gave the expected isotopic pattern), 577.0 ($[M-Cl]^-$, 100); C,H,N analysis found (calcd for $C_{24}H_{54}Al_2Cl_3CrN_2P$): C 46.95 (46.68), H 8.87 (8.71), N 4.56 (4.63).

Crystal data for **1**: $C_{16}H_{36}CrN_4P_2$, formula weight 398.43, orthorhombic, $Pccn$, $Z = 4$, $a = 16.166(4)$, $b = 11.929(3)$, $c = 11.814(3)$ Å, $V = 2278.1(11)$ Å^3, $D = 1.162$ Mg m^{-3}; $\mu = 0.647$ mm^{-1}; $F(000) = 856$; $R_1 = 0.0446$, $wR_2 = 0.1054$; GoF = 1.118; for **2**: $C_{25}H_{63}Al_3CrN_4P_2$, formula weight 614.67, triclinic, $P\bar{1}$, $Z = 2$, $a = 9.3177(13)$, $b = 11.7323(16)$, $c = 17.301(2)$ Å, $\alpha = 90.963(2)$, $\beta = 95.876(2)$, $\gamma = 94.465(2)°$; $V = 1875.0(4)$ Å^3, $D = 1.087$ Mg m^{-3}; $\mu = 0.479$ mm^{-1}; $F(000) = 766$; $R_1 = 0.0568$, $wR_2 = 0.1327$; GoF = 0.993; for **3**: $C_{24}H_{54}Al_2Cl_3CrN_2P$, formula weight 613.97, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 8.6978(14)$, $b = 16.930(3)$, $c = 23.134(4)$ Å, $V = 3406.6(10$ Å^3, $D = 1.197$ Mg m^{-3}; $\mu = 0.685$ mm^{-1}; $F(000) = 1312$; $R_1 = 0.0275$, $wR_2 = 0.0622$; GoF = 1.041.

CCDC 676890 (**1**), 676891 (**2**), 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

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