Journal Name

ARTICLE

From Polyethylene Waxes to HDPE Using a α,α'-Bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl-Chromium(III) Chloride Pre-catalyst in Ethylene Polymerisation

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(Chuanbing Huang and Shizhen Du made an equal contribution in this work)

Abstract: Five examples of α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl-chromium(III) chlorides (aryl = 2,6-Me$_2$Ph **Cr1**, 2,6-Et$_2$Ph **Cr2**, 2,6-i-Pr$_2$Ph **Cr3**, 2,4,6-Me$_3$Ph **Cr4**, 2,6-Et$_2$-4-MePh **Cr5**) have been synthesized by the one-pot template reaction of α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine, CrCl$_3$·6H$_2$O and the corresponding aniline. The molecular structures of **Cr1** and **Cr4** reveal distorted octahedral geometries with the N,N,N-ligand adopting a *mer*-configuration. On activation with an aluminium alkyl co-catalyst, **Cr1 − Cr5** exhibited high catalytic activities in ethylene polymerization and showed outstanding thermal stability operating effectively at 80 °C with activities up to 1.49×10^7 g of PE (mol of Cr)$^{-1}$ h^{-1}. Significantly, the nature of the co-catalyst employed had a dramatic effect on the molecular weight of the polymeric material obtained. For example, using diethylaluminium chloride (Et$_2$AlCl) in combination with **Cr4** gave high density/high molecular weight polyethylene with broad molecular weight distributions (30.9–39.3). By contrast, using modified methylaluminoxane (MMAO), strictly linear polyethylene waxes of lower molecular weight and narrow molecular weight distribution (1.6-2.0) were obtained with vinyl end-groups.

Introduction

Besides the vast market for commodity-type polyolefinic materials, there is a growing demand for speciality polyethylenes capable of displaying new and unique properties that is attracting attention in both the industrial and academic communities alike.[1] Chromium-based catalysts are well known for their applications in ethylene oligomerization and polymerization,[2] some examples include the heterogeneous Phillips catalyst[3] for manufacturing high density polyethylene (HDPE) and a variety of homogeneous systems for generating 1-hexene[4] and/or 1-octene.[5] The mechanism of catalysis involving these chromium complexes has been thoroughly investigated.[6] Elsewhere, inspired by the discovery that high molecular weight polyethylene can be achieved using iron or cobalt catalysts,[7] bis(imino)pyridyl-chromium complexes (**A**, Chart 1) have emerged as being particularly productive in ethylene oligomerization and/or polymerization.[8]

Subsequently numerous other tridentate nitrogen-donors have been developed as ligand frameworks for both late-transition metal[1,7] as well as chromium-based pre-catalysts.[9] To enhance catalytic performances, N,N,N-ligands based on cycloalkyl-fused pyridines have been successfully employed to support cobalt and iron pre-catalysts.[10] More recently α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl-M (M = Fe or Co) complexes incorporating a central pyridine fused by two seven-membered rings have proved highly efficient catalysts affording strictly linear vinyl-polyethylenes.[11]

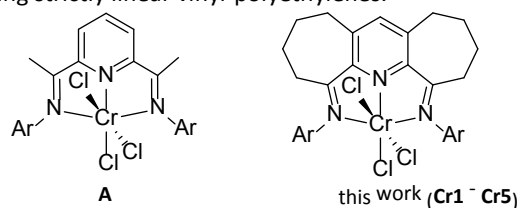

Chart 1 Chromium(III) pre-catalyst development

Herein, we report the synthesis of a new family of α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl-chromium trichlorides (**Cr1 − Cr5**, Chart 1) and their performance as pre-catalysts in ethylene polymerization. On activation with diethylaluminium chloride (Et$_2$AlCl), good activities were observed for all the chromium complexes studied affording highly linear and high molecular weight polyethylene. On the other hand, using modified methylaluminoxane (MMAO) as activator, the catalytic activities were not only significantly

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higher but also the materials obtained were of much lower molecular weight displaying properties characteristic of polyethylene waxes with vinyl end-groups; an observation also noted using bis(imino)pyridyl-chromium(III) complexes (**A**, Chart 1).[8b] In addition to an in-depth catalytic evaluation including studies of the polymer properties, we also disclose the synthetic and characterization details for the five chromium(III) complexes.

Results and Discussion

Synthesis and Characterization of Cr1 – Cr5

In previous work we have shown that the free α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridines, α,α'-(ArN)-2,3:5,6-$(C_5H_8)_2C_5HN$, suffer from instability issues owing to ready decomposition via pathways involving imine-enamine tautomerization.[10e] To circumvent this problem, a template approach has proved successful in which the complexed N,N,N-ligand can be prepared by a one-pot reaction of the precursor ketone, metal salt and corresponding aniline.[11] Similarly, [α,α'-(ArN)-2,3:5,6-$(C_5H_8)_2C_5HN$]CrCl$_3$ (Ar = 2,6-Me$_2$Ph **Cr1**, 2,6-Et$_2$Ph **Cr2**, 2,6-i-Pr$_2$Ph **Cr3**, 2,4,6-Me$_3$Ph **Cr4**, 2,6-Et$_2$-4-MePh **Cr5**) could be prepared in good yield by interaction of α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine, CrCl$_3$·6H$_2$O and an excess of the corresponding aniline in acetic acid at reflux for 3 hours (Scheme 1). All the chromium complexes were characterized by FT-IR spectroscopy and by elemental analysis. With regard to their IR spectra, all the chromium complexes displayed absorption bands around 1610 cm^{-1} consistent with coordination of the imine nitrogen atoms.[10,11] In addition, crystals of **Cr1** and **Cr4** have been subject to single crystal X-ray diffraction studies.
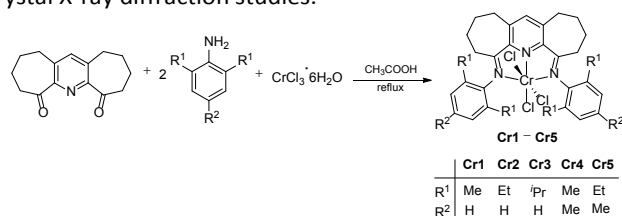
Scheme 1 Synthetic route to chromium(III) chlorides, **Cr1 – Cr5**

Molecular Structures

Single crystals of **Cr1** and **Cr4** suitable for the X-ray determinations were grown by the slow diffusion of heptane into a saturated dichloromethane solution of the respective complex at ambient temperature. Perspective views of **Cr1** and **Cr4** are given in Figures 1 and 2; selected bond distances and angles are listed in Table 1. Both structures are similar and will be discussed together. Each structure consists of a single chromium centre surrounded by three nitrogen donors belonging to the α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridine ligand and three chloride ligands to complete a geometry best described as distorted octahedral. The key difference between the structures arises in the nature of the N-aryl group; in **Cr1** it is a 2,6-dimethylphenyl group while in **Cr4** it is a 2,4,6-trimethylphenyl group. The

tridentate N,N,N-ligand adopts a *mer*-configuration with the plane formed by the three nitrogen atoms almost perpendicular

Table 1 Selected bond lengths (Å) and angles (°) for **Cr1** and **Cr4**

|	Cr1	Cr4
Bond lengths (Å)		
Cr1–N1	2.004(2)	2.003(3)
Cr1–N2	2.110(2)	2.122(3)
Cr1–N3	2.109(2)	2.128(3)
Cr1–Cl1	2.352(8)	2.3579(10)
Cr1–Cl2	2.312(8)	2.3034(10)
Cr1–Cl3	2.284(9)	2.2973(10)
N2–C2	1.297(3)	1.292(4)
N3–C14	1.297(3)	1.297(4)
Bond angles (°)		
N1–Cr1–N2	77.92(8)	77.61(10)
N1–Cr1–N3	77.73(8)	77.32(11)
N2–Cr1–N3	155.37(8)	154.31(11)
N1–Cr1–Cl1	81.07(6)	81.72(8)
N1–Cr1–Cl2	93.53(6)	94.43(8)
N1–Cr1–Cl3	173.47(6)	172.65(8)
N2–Cr1–Cl1	90.36(6)	91.85(7)
N2–Cr1–Cl2	90.58(6)	89.12(8)
N2–Cr1–Cl3	100.93(6)	102.07(7)
N3–Cr1–Cl1	89.50(6)	90.05(8)
N3–Cr1–Cl2	87.27(6)	87.28(8)
N3–Cr1–Cl3	103.68(6)	103.51(8)
C2–N2–Cr1	114.33(16)	113.9(2)
C14–N3–Cr1	114.18(16)	114.2(2)
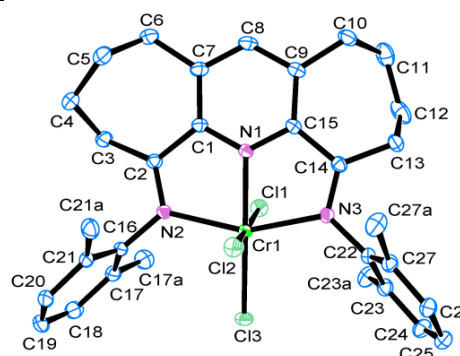
Figure 1 ORTEP drawing of **Cr1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.
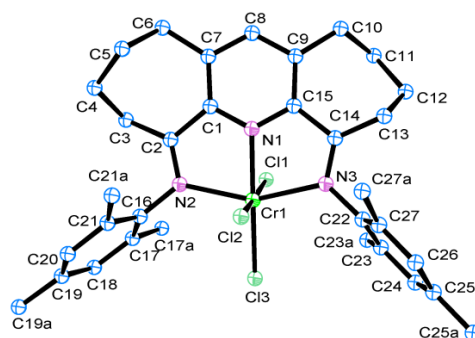
Figure 2 ORTEP drawing of **Cr4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and two molecules of CH_2Cl_2 have been omitted for clarity.

to the plane containing the three chloride ligands. The Cl1, Cl2, N2 and N3 atoms constitute the equatorial sites while N1 and Cl3 fill the two axial ones (N1–Cr1–Cl3, 173.47(6)° for **Cr1** and 172.65(8)° for **Cr4**). Similar structural features have been noted in related chromium complexes.[9,12] In addition, the N,N,N-coordination plane is close to perpendicular with respect to the two *N*-aryl rings. Taking **Cr1** as an example, the N,N,N-plane forms a dihedral angle of 78.68° with the N2–aryl ring, and 72.47° with the other N3–aryl ring, respectively. The central Cr–$N_{pyridine}$ (Cr1–N1, 2.004(2) **Cr1**, 2.003(3) Å **Cr4**) distance is shorter than those of the exterior Cr–N_{imino} distances (Cr1–N2 2.110(2) **Cr1**, 2.122(3) Å **Cr4**; Cr1–N3 2.109(2) **Cr1**, 2.128(3) Å **Cr4**), consistent with stronger bonding between the $N_{pyridine}$ and the metal centre. In comparison with cobalt(II) and iron(II) complexes bearing similar tridentate ligands, the M–$N_{pyridine}$ bond distance in **Cr1** and **Cr4** is notably shorter (Co-$N_{pyridine}$ 2.082 Å[11a] and Fe-$N_{pyridine}$ 2.132 Å[11b]), in accord with the higher oxidation state of these chromium complexes.

Ethylene Polymerization

Initially, **Cr4** was employed as the test pre-catalyst for the ethylene polymerization screen using five different alkylaluminium co-catalysts namely, diethylaluminium chloride (Et_2AlCl), dimethylaluminium chloride (Me_2AlCl), ethylaluminium sesquichloride (EASC), methylaluminoxane (MAO) and modified methylaluminoxane (MMAO). Typically the runs were performed in toluene using 10 atmospheres of ethylene pressure at 30 °C over a 30 minute time period (Table 2). Inspection of the data reveals the best activities were achieved using either Et_2AlCl or MMAO. Hence all further more detailed catalytic investigations were made using these two co-catalysts.

Table 2 Ethylene polymerization screen using **Cr4** with various co-catalysts [a]

Entry	Co-catalyst	Al/Cr	PE (g)	Activity[b]	M_W[c]	M_W/M_n[c]	T_m[d] (°C)
1	Et_2AlCl	400	0.37	2.47	799.8	39.3	135.0
2	Me_2AlCl	400	0.27	1.80	639.1	37.1	133.6
3	EASC	400	0.26	1.73	481.0	44.0	132.9
4	MAO	2000	0.32	2.13	515.3	42.4	132.3
5	MMAO	2000	0.56	3.73	20.0	22.5	127.2

[a] Conditions: 3.0 µmol **Cr4**, 100 mL toluene, 10 atm ethylene, 30 min, 30 °C; [b] 10^5 g·mol-1(Cr)·h-1, [c] M_W: Kg·mol-1, M_W and M_W/M_n determined by GPC; [d] Determined by DSC.

Catalytic evaluation with Cr1 – Cr5/Et_2AlCl

To ascertain the optimum reaction conditions for a catalyst composed of **Cr4** and Et_2AlCl, the molar ratio of aluminium to chromium, the reaction temperature and the reaction time were systematically explored with the ethylene pressure kept at 10 atmospheres (Table 3). In each case the polymeric product was characterized by Gel Permeation chromatography (GPC) and Differential Scanning calorimetry (DSC).

Firstly, on increasing the Al/Cr molar ratio from 200 to 600 at 30 °C over a 30 minutes (entries 1–5, Table 3), the highest

activity of 2.47 × 10^5 g of PE (mol of Cr)-1 h-1 was observed at an Al/Cr molar ratio of 400 (entry 3, Table 3). Broad molecular weight distributions are a characteristic of the polyethylenes obtained (35.3–39.3) indicating multi-site behaviour for the active species. With regard to the molecular weight of the polyethylenes, they were found to lower from 1068.3 to 670.1 Kg·mol-1 as the amount of Et_2AlCl increased, suggesting that large amounts of co-catalyst enhanced the possibility of chain transfer from the active chromium species to the aluminium co-catalyst, resulting in shorter-chain polymers.[13] This molecular weight trend is borne out in the GPC curves for the five different runs (Figure 3).
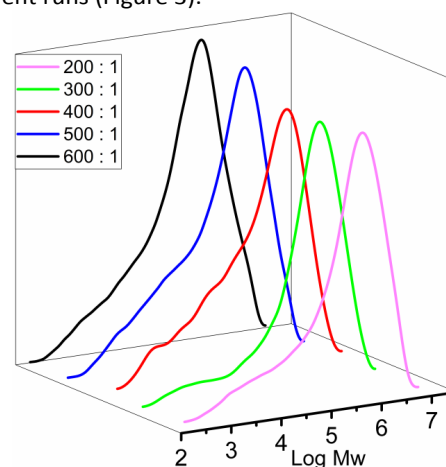

Figure 3 GPC curves for the polyethylenes obtained using **Cr4**/Et_2AlCl with various Al/Cr ratios (entries 1–5, Table 3).
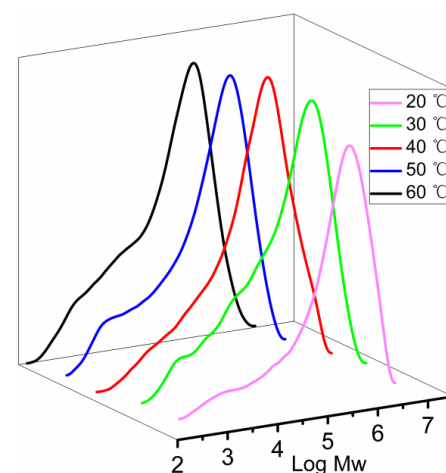

Figure 4 GPC curves for the polyethylenes obtained using **Cr4**/Et_2AlCl at different reaction temperatures (entries 3 and 6–9, Table 3).

Secondly, a variable temperature study was conducted in which the Al/Cr ratio was fixed at 400. On raising the reaction temperature from 20 to 60 °C (entries 3 and 6–9, Table 3), the best activity of 3.00 × 10^5 g of PE (mol of Cr)-1 h-1 was observed at 20 °C (entry 6, Table 3), after which the activity steadily decreased reaching a minimum of 0.60 × 10^5 g of PE (mol of Cr)-1 h-1 at 60 °C (entry 9, Table 3). As a result of the deactivation of the active species occurring at the higher temperatures, the polyethylenes with greatest molecular weight were produced at the lower reaction temperature. This

trend is depicted in the GPC curves for the four runs in which the molecular weight decreases from 1189.6 to 454.6 Kg·mol^{-1} as the temperature was increased from 20 to 60 °C (Figure 4).

Thirdly, to explore the lifetime of the **Cr4**/Et$_2$AlCl catalyst, the runs were performed over 15, 30, 45 and 60 minutes with the temperature set at 20 °C and the Al/Cr ratio at 400 (entries 6 and 10–12, Table 3). The best activity of 4.13 × 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1} was achieved over 15 minutes after which the activity gradually decreased reaching its lowest value of 2.27 ×

10^5 g of PE (mol of Cr)$^{-1}$ h^{-1} after 60 minutes. This observation would suggest that the active species formed quickly after the addition of Et$_2$AlCl and underwent gradual deactivation over time. On the other hand, the molecular weight of the polymers slightly increased over time while the molecular weight distribution showed some narrowing (Figure 5). Notably, catalytic runs performed at lower ethylene pressure (5 or 1 atmospheres) led to a marked decrease in activity (entries 6 and 13–14, Table 3).

Table 3 Catalytic screening of **Cr1 – Cr5** with Et$_2$AlCl as co-catalyst ^{a}

Entry	Pre-catalyst	T (°C)	t (min)	Al/Cr	PE (g)	Activity ^{b}	M_W ^{c}	M_W/M_n ^{c}	T_m ^{d} (°C)
1	**Cr4**	30	30	200	0.09	0.60	1068.3	36.1	133.1
2	**Cr4**	30	30	300	0.28	1.87	905.2	38.8	133.9
3	**Cr4**	30	30	400	0.37	2.47	799.8	39.3	135.0
4	**Cr4**	30	30	500	0.24	1.60	754.0	37.0	134.5
5	**Cr4**	30	30	600	0.19	1.27	670.1	35.3	134.5
6	**Cr4**	20	30	400	0.45	3.00	1189.6	30.9	134.7
7	**Cr4**	40	30	400	0.22	1.47	675.7	33.3	134.9
8	**Cr4**	50	30	400	0.11	0.73	586.7	37.7	128.7
9	**Cr4**	60	30	400	0.09	0.60	454.6	31.8	132.1
10	**Cr4**	20	15	400	0.31	4.13	646.0	39.4	134.7
11	**Cr4**	20	45	400	0.57	2.53	843.4	36.0	134.7
12	**Cr4**	20	60	400	0.68	2.27	924.2	31.1	135.1
13^e	**Cr4**	20	30	400	0.21	1.40	639.1	37.1	135.0
14^f	**Cr4**	20	30	400	trace	trace	-	-	-
15	**Cr1**	20	30	400	0.32	2.13	691.2	15.2	134.7
16	**Cr2**	20	30	400	0.31	2.07	630.3	31.5	134.9
17	**Cr3**	20	30	400	0.26	1.73	924.9	29.5	135.5
18	**Cr5**	20	30	400	0.30	2.00	645.9	39.4	134.4

^{a} Conditions: 3.0 μmol of **Cr**, 100 mL toluene for 10 atm ethylene; ^{b} 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}, ^{c} M_W: Kg·mol^{-1}, M_W and M_W/M_n determined by GPC; ^{d} Determined by DSC, ^{e} 5 atm, ^{f} 1 atm.
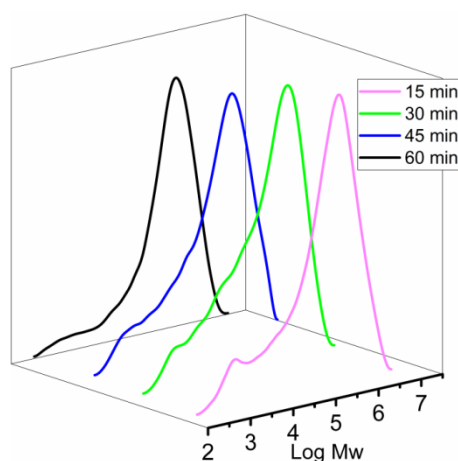

Figure 5 GPC curves for the polyethylenes obtained using **Cr4**/Et$_2$AlCl at different reaction times (entries 6 and 10–12, Table 3).

With the optimum conditions established [Al/Cr ratio of 400, reaction temperature of 20 °C and a polymerization run time of 30 minutes], the four other chromium pre-catalysts, **Cr1**, **Cr2**, **Cr3** and **Cr5**, were screened (entries 6, 15–18, Table 3). In comparison with **Cr4**, **Cr1 – Cr3** and **Cr5** exhibited lower activities (range: 1.73 – 2.13 x 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}), generating broad molecular weight distributions with molecular weights between 924.9 and 630.3 Kg·mol^{-1}. Two key

trends in catalytic activity can be identified: **Cr4** [2,4,6-tri(Me)] > **Cr5** [2,6-di(Et)-4-Me] and **Cr1** [2,4-di(Me)] > **Cr2** [2,6-di(Et)] > **Cr3** [2,6-di(^{i}Pr)]. It would appear that the steric properties of the *ortho*-substituents of the *N*-aryl rings influence the catalytic activity with the more bulky groups leading to lower polymerization rates which can be attributed to increased hindrance to ethylene coordination and insertion.[14]

In general, the melting temperatures (T_m) of the polyethylenes obtained (entries 1-18, Table 3) were higher than 130 °C (entry 8 the exception at 128.7 °C), consistent with highly linear material. To lend support to this observation a sample of the polyethylene obtained at 20 °C (entry 6, Table 3)
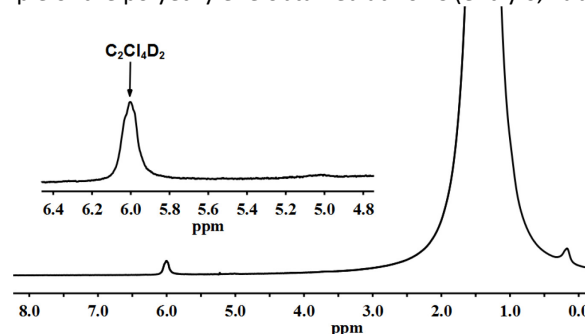

Figure 6 ^{1}H NMR spectrum of the polyethylene obtained using **Cr4**/Et$_2$AlCl at 20 °C with 1,1,2,2-tetrachloroethane-d_2 as solvent (entry 6, Table 3).

Figure 7 ^{13}C NMR spectrum of the polyethylene obtained using **Cr4**/Et$_2$AlCl at 20 °C with 1,1,2,2-tetrachloroethane-d_2 as solvent (entry 6, Table 3).

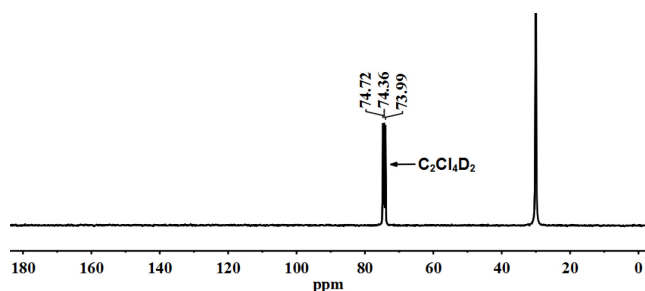was subject to a high-temperature ^{1}H NMR and ^{13}C NMR spectroscopic study (recorded in 1,1,2,2-tetrachloroethane-d_2 at 100 °C). The presence of singlet resonances in both the ^{1}H NMR spectrum (at δ 0.97, Figure 6) and the ^{13}C NMR spectrum (at δ 30.0, Figure 7) is characteristic with high linearity polyethylene.

Catalytic evaluation with Cr1–Cr5/MMAO

As with the study using Et$_2$AlCl, **Cr4** was used as the test pre-catalyst this time with MMAO as the co-catalyst. Optimization of the reaction conditions was again performed in regard to the reaction temperature, the Al/Cr ratio and reaction time (Table 4).

Table 4 Catalytic screening of **Cr1 – Cr5** with MMAO as co-catalyst[a]								
Entry	Pre-catalyst	T (°C)	t (min)	Al/Cr	PE (g)	Activity [b]	M_W [c]	M_W/M_n [c]	T_m [d] (°C)
1	**Cr4**	30	30	2000	0.56	3.73	20.0	22.5	127.2
2	**Cr4**	40	30	2000	1.25	8.33	14.9	14.9	125.9
3	**Cr4**	50	30	2000	3.01	20.07	8.3	3.5	129.4
4	**Cr4**	60	30	2000	6.83	45.53	4.6	5.9	122.6
5	**Cr4**	70	30	2000	17.81	118.73	3.0	2.0	117.1
6	**Cr4**	80	30	2000	22.33	148.87	2.0	1.8	116.5
7	**Cr4**	90	30	2000	14.81	98.73	1.6	1.6	115.1
8	**Cr4**	100	30	2000	6.65	44.33	1.3	1.5	113.9
9	**Cr4**	80	30	1500	12.99	86.60	2.9	2.1	122.6
10	**Cr4**	80	30	1750	20.82	138.81	2.2	1.8	120.9
11	**Cr4**	80	30	2250	21.09	140.60	1.6	1.6	123.9
12	**Cr4**	80	30	2500	15.06	100.42	1.3	1.6	114.1
13	**Cr4**	80	15	2000	12.02	160.27	1.6	1.7	111.2
14	**Cr4**	80	45	2000	26.35	117.11	2.4	1.9	114.8
15	**Cr4**	80	60	2000	28.73	95.77	2.9	1.9	116.1
16 [e]	**Cr4**	80	30	2000	7.23	48.20	1.2	1.4	108.4
17 [f]	**Cr4**	80	30	2000	trace	trace	-	-	-
18	**Cr1**	80	30	2000	19.97	133.13	2.1	1.8	122.6
19	**Cr2**	80	30	2000	10.22	68.13	2.0	1.6	122.5
20	**Cr3**	80	30	2000	15.10	100.67	3.0	2.0	127.3
21	**Cr5**	80	30	2000	12.39	82.61	2.7	2.0	121.1

[a] Conditions: 3.0 µmol of **Cr**, 100 mL toluene for 10 atm ethylene; [b] 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}, [c] M_W: Kg·mol^{-1}, M_W and M_W/M_n determined by GPC; [d] Determined by DSC, [e] 5 atm, [f] 1 atm.

Firstly, with the Al/Cr ratio fixed at 2000, the reaction temperature for the run was varied between 30 and 80 °C (entries 1–6, Table 4). The activities were found to increase quite sharply with temperature reaching a maximum at 80 °C of 148.87 × 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}. On further raising the reaction temperature to 100 °C (entry 8, Table 4), the activity decreased but nevertheless revealed a good level of 44.33 × 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}. It is worth highlighting that these **Cr4**/MMAO systems display superior thermal stability when compared with the **Cr4**/Et$_2$AlCl system discussed earlier. With regard to the properties of the polyethylenes, lower molecular weights were generated at higher reaction temperature, a feature that can be attributed to fast decomposition of the active species at elevated temperature. Raising the reaction temperature from 30 to 100 °C, the molecular weights of resultant polyethylenes decreased sharply from 20.0 to 1.3 Kg mol^{-1} (entries 1–8, Table 4); this trend is illustrated in Figure 8. Furthermore with the reaction temperature at 70 °C or above, the polyethylenes exhibited narrow molecular weight

distributions (1.5–2.0) in agreement with single site species being generated at elevated reaction temperature.
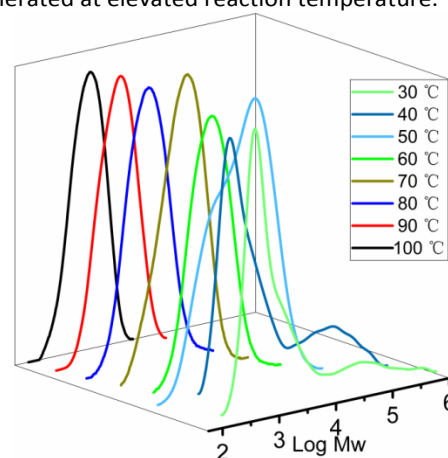

Figure 8 GPC curves for the polyethylenes obtained using **Cr4**/MMAO at different reaction temperatures (entries 1–8, Table 4).

Secondly, with the temperature set at 80 °C, the Al/Cr molar ratio was adjusted from 1500 to 2500 using **Cr4**/MMAO (entries 6, 9–12, Table 4). Inspection of the data reveals the best activity to be achieved at a ratio of 2000. Another key observation is that the molecular weight of the polymer decreases as the ratio of MMAO increases, this variation can be attributed to more facile chain transfer from chromium to aluminium,[13] generating polyethylenes of lower molecular weight and slightly different molecular weight distributions. This trend is further highlighted by the GPC curves for the five runs (Figure 9), which clearly shows that molecular weights decrease from 2.9 to 1.3 Kg·mol^{-1} as the Al/Cr ratio is increased 1500 to 2500.
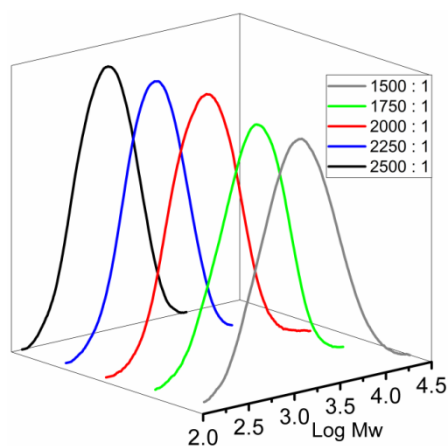

Figure 9 GPC curves for the polyethylenes obtained using **Cr4**/MMAO system with various Al/Cr ratios (entries 6, 9–12, Table 4).
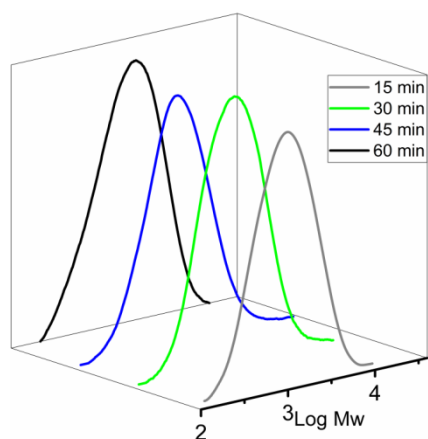

Figure 10 GPC curves for the polyethylenes obtained using **Cr4**/MMAO system at different reaction times (entries 6 and 13–15, Table 4)

Thirdly, a lifetime study was conducted over 15 to 60 minutes using **Cr4**/MMAO with the temperature maintained at 80 °C and the Al/Cr ratio at 2000. The highest activity was achieved after 15 minutes and then gradually decreased as the reaction time was extended to 60 minutes (entries 6 and 13–15, Table 4). As with the study involving Et$_2$AlCl, this would suggest that the active species was formed quickly and then became gradually deactivated over time. Moreover, the molecular weights of the polyethylenes were found to slightly increase over longer reaction times (Figure 10).

Finally, the remaining chromium pre-catalysts, **Cr1**, **Cr2**, **Cr3** and **Cr5**, were evaluated using the optimized conditions identified for **Cr4** namely, an Al/Cr ratio of 2000, a reaction temperature of 80 °C and a 30 minute run time. In general, good activities were observed for all of these systems (range: 68.13 – 133.13 x 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}), albeit lower than that seen with **Cr4** (148.87 x 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}). With respect to the relative order of activities (entries 6 and 18–21, Table 4), these follow: **Cr4** [2,4,6-tri(Me)] > **Cr1** [2,6-di(Me)] > **Cr3** [2,6-di(^{i}Pr)] > **Cr5** [2,6-di(Et)-4-Me] > **Cr2** [2,6-di(Et)]. Clearly both steric and electronic effects imparted by the ligand influence catalytic performance.

To investigate the microstructural properties of the polymers obtained both DSC and high-temperature ^{1}H NMR and ^{13}C NMR spectroscopic measurements were recorded. Generally, the T_m values of the materials obtained using **Cr1** – **Cr5** under comparable conditions [entries 6, 18–21, Table 4] were higher than 116 °C supportive of highly linear microstructures. In the case of the polyethylene obtained using **Cr4** (entry 6, Table 4), the ^{1}H NMR spectrum [recorded at 100 °C in 1,1,2,2-tetrachloroethane-d_2] revealed a singlet of high intensity at around δ 0.97, confirming the linearity of the material. In addition, signals at δ 5.90 and at δ 5.00 integrating to 1 and 2, respectively, are characteristic of a vinyl end-group (–CH=CH$_2$) (Figure 11). The presence of the latter functional group implies that β-hydride elimination has occurred during termination of the polymerization.[10d,11b,15] This vinylic assignment is further corroborated in the ^{13}C NMR spectrum with peaks at δ 114.7 and δ 139.9, while a single peak of high intensity observed around δ = 30.0 lends more support to the high linearity of the polyethylene (Figure 12).[10d,11b,15]
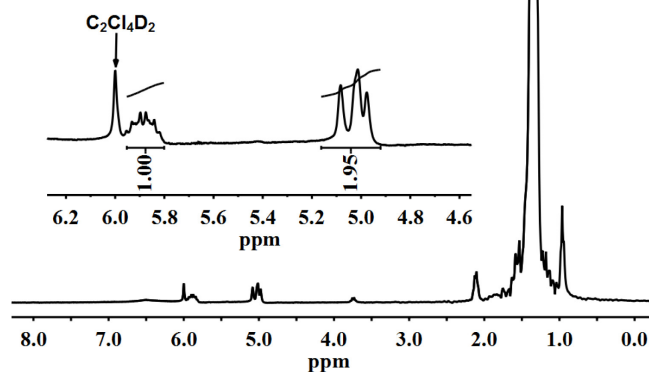

Figure 11 ^{1}H NMR spectrum of the polyethylene obtained using **Cr4**/MMAO at 80 °C with 1,1,2,2-tetrachloroethane-d_2 as solvent (entry 6, in Table 4).

It is worth emphasizing that the polyethylenes generated using **Cr1** – **Cr5**/MMAO display relatively low molecular weights (2.0 – 3.0 Kg·mol^{-1}) and narrow molecular weight distributions (1.6–2.0), in stark contrast to the HDPE obtained using **Cr1** – **Cr5**/Et$_2$AlCl. Such properties are characteristic of polyethylene waxes. In comparison with commercial metallocene or Ziegler-Natta processes for producing polyethylene waxes, the current catalytic system offers an economically viable method of producing such materials without using hydrogen to control the molecular weight and molecular weight distribution. Furthermore, considering the

highly exothermic nature of ethylene polymerization process, a critical factor in an industrial application is to maintain good activity within the temperature range 80 – 100 °C. Pleasingly, the current system exhibits high activity and exceptional thermal stability, with the highest activity (148.87 × 10^5 g of PE (mol of Cr)$^{-1}$ h^{-1}) achieved at a temperature of 80 °C. Therefore, we view **Cr1 – Cr5**/MMAO as showing great promise for potential industrial applications requiring low molecular weight highly linear polyethylene waxes with vinyl end-groups.
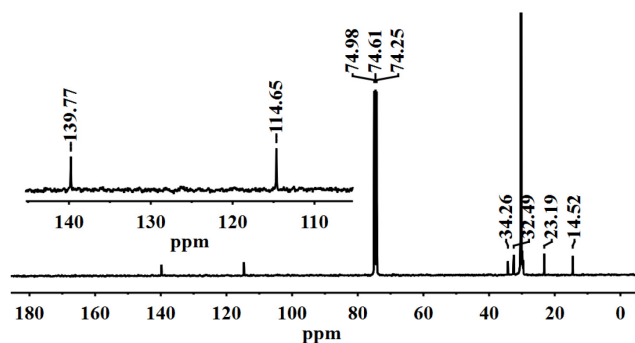

Figure 12 ^{13}C NMR spectrum of the polyethylenes obtained using **Cr4**/MMAO at 80 °C with 1,1,2,2-tetrachloroethane-d_2 as solvent (entry 6, in Table 4).

Conclusions

A one-pot template approach has been successfully employed to prepare α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridinechromium(III) chloride complexes, **Cr1 – Cr5**, in good yields. On activation with Et$_2$AlCl, all the complexes exhibited good activities in ethylene polymerization, producing highly linear polyethylene with high molecular weights and broad molecular weight distributions. By contrast, with MMAO as co-catalyst, significantly higher activities and enhanced thermal stability were notable features, resulting in highly linear polyethylene waxes displaying lower molecular weights and containing vinyl end-groups (–CH=CH$_2$). Correlations between reaction conditions, as well as steric/electronic properties of the *N*-aryl groups, with the properties of the resultant polyethylenes have been thoroughly investigated.

Experimental Section

General Consideration

All manipulations involving air- and moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Diethylaluminium chloride (Et$_2$AlCl, 1.17 M in toluene), dimethylaluminium chloride (Me$_2$AlCl, 1.00 M in toluene) and ethylaluminium sesquichloride (EASC, 0.87 M in toluene) were purchased from Acros Chemicals. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 2.00 M in *n*-heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing

Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weight and molecular weight distributions (MWD) of the polyethylenes were determined using a PL-GPC220 instrument at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The melting points of the polyethylenes were measured from the fourth scanning run on a Perkin-Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 5.0 mg was heated to 140 °C at a rate of 20 °C /min and kept for 2 min at 140 °C to remove the thermal history and then cooled at a rate of 20 °C /min to −40 °C. The ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 100 °C in deuterated 1,1,2,2-tetrachloroethane-d_2 with TMS as an internal standard. α,α'-Dioxo-2,3:5,6-bis(pentamethylene) pyridine was made by our literature method.[10f,11a,16]

Synthesis of Cr1 – Cr5

Cr1. A suspension of α,α'-dioxo-2,3:5,6-bis(pentamethylene) pyridine (0.243 g, 1.0 mmol), 2,6-dimethylaniline (0.484 g, 4.0 mmol) and CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol) in glacial acetic acid (10 mL) were stirred and heated to reflux for 3 h. The resulting solution was cooled to room temperature and the solid precipitated by adding diethyl ether (10 mL) before being collected by filtration. The solid was then re-dissolved in methanol and precipitated again by adding diethyl ether. Further filtration and drying under reduced pressure afforded **Cr1** as a dark green powder (0.385 g, 63%). FT-IR (cm^{-1}): 3007 (w), 2971 (w), 2831 (w), 1614 (m, $v_{C=N}$), 1581 (s), 1462 (s), 1393 (w), 1300 (w), 1211 (m), 1157 (w), 1095 (w), 776 (vs), 680 (w). Anal. Calc for C$_{31}$H$_{35}$N$_3$CrCl$_3$ (607.98): C, 61.24; H, 5.80; N, 6.91%. Found: C, 61.06; H, 5.97; N, 7.06%.

Cr2. Based on a one-pot procedure similar to that described for **Cr1**, using α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine (0.243 g, 1.0 mmol), 2,6-diethylaniline (0.596 g, 4.0 mmol) and CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol), **Cr2** could be isolated as a dark green powder (0.492 g, 74%). FT-IR (cm^{-1}): 2967 (w), 2930 (w), 1610 (m, $v_{C=N}$), 1451 (s), 1378 (w), 1252 (w), 1048 (w), 958 (w), 847 (w), 769 (w), 657 (m). Anal. Calc for C$_{35}$H$_{43}$N$_3$CrCl$_3$ (664.09): C, 63.30; H, 6.53; N, 6.33%. Found: C, 63.13; H, 6.56; N, 6.12%.

Cr3. Based on a one-pot procedure similar to that described for **Cr1**, using α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine (0.243 g, 1.0 mmol), 2,6-diisopropylaniline (0.708 g, 4.0 mmol) and CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol), **Cr3** could be isolated as a dark green powder (0.479 g, 67%). FT-IR (cm^{-1}): 2950 (w), 2866 (w), 1615 (m, $v_{C=N}$), 1542 (w), 1453 (s), 1382 (w), 1359 (w), 1255 (m), 1182 (m), 1048 (w), 821 (w), 771 (s), 659 (s). Anal. Calc for C$_{39}$H$_{51}$N$_3$CrCl$_3$ (720.20): C, 65.04; H, 7.14; N, 5.83%. Found: C, 64.89; H, 7.00; N, 5.74%.

Cr4. Based on a one-pot procedure similar to that described for **Cr1**, using α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine

(0.243 g, 1.0 mmol), 2,4,6-trimethylaniline (0.540 g, 1.0 mmol) and CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol), **Cr4** could be isolated as a dark green powder (0.408 g, 64%). FT-IR (cm^{-1}): 2920 (w), 2866 (w), 1612 (m, $v_{C=N}$), 1592 (m), 1515 (m), 1450 (s), 1384 (w), 1259 (m), 1206 (w), 1140 (w), 1108 (w), 1033 (m), 855 (s), 742 (m). Anal. Calc for C$_{33}$H$_{39}$N$_3$CrCl$_3$ (636.04): C, 62.32; H, 6.18; N, 6.61%. Found: C, 61.98; H, 6.21; N, 6.48%.

Cr5. Based on a one-pot procedure similar to that described for **Cr1**, using α,α'-dioxo-2,3:5,6-bis(pentamethylene)pyridine (0.243 g, 1.0 mmol), 2,6-diethyl-4-methylaniline (0.652 g, 4.0 mmol) and CrCl$_3$·6H$_2$O (0.266 g, 1.0 mmol), **Cr5** could be isolated as a dark green powder (0.485 g, 70%). FT-IR (cm^{-1}): 2970 (w), 2830 (w), 1606 (m, $v_{C=N}$), 1551 (w), 1449 (s), 1366 (w), 1258 (m), 1166 (w), 1143 (w), 958 (w), 861 (s), 776 (m). Anal. Calc for C$_{37}$H$_{47}$N$_3$CrCl$_3$ (692.14): C, 64.21; H, 6.84; N, 6.07%. Found: C, 64.01; H, 6.92; N, 6.00%.

Ethylene Polymerization

Ethylene polymerization at 1 atm ethylene pressure Cr4 (1.9 mg, 3.0 µmol) was added to the Schlenk vessel, equipped with stir bar, followed by freshly distilled toluene (100 mL). The required amount of co-catalyst, Et$_2$AlCl (1.0 mL, 1.2 mmol) or MMAO (3.0 mL, 6 mmol), was then added by syringe. The reaction mixture was stirred at 1 atm of ethylene pressure at 20 ℃ (for **Cr4**/Et$_2$AlCl system) or 80 ℃ (for **Cr4**/MMAO system). After 30 min, the reaction was quenched with 10% hydrochloric acid in ethanol. The polymer was washed with ethanol, then dried under reduced pressure at 60 ℃ and weighed.

Ethylene polymerization at 5/10 atm ethylene pressure The higher pressure polymerization runs were carried out in stainless steel autoclave (0.25 L) equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. At the designated reaction temperature, freshly distilled toluene (30 mL) was injected into the autoclave, followed by the complex (3.0 µmol) dissolved in toluene (50 mL). The required amount of co-catalyst was then injected and finally more toluene (20 mL) introduced. The autoclave was immediately pressurized to the desired ethylene pressure and the stirring commenced. After the required reaction time, the ethylene pressure was vented, the polymer washed with ethanol and then dried under reduced pressure at 60 ℃ and weighed.

X-Ray Structure Determination

Single-crystal X-ray diffraction study for **Cr1** and **Cr4** were conducted on a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K, and cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the Olex2 1.2 package.[17] Crystal data and

processing parameters for **Cr1** and **Cr4** are summarized in Table 5.

Table 5 Crystal data and structure refinement for **Cr1** and **Cr4**

Complex	Cr1	Cr4·2CH$_2$Cl$_2$
Empirical formula	C$_{31}$H$_{35}$Cl$_3$CrN$_3$	C$_{35}$H$_{43}$Cl$_7$CrN$_3$
Formula weight	607.97	805.92
Temperature/ K	173.1500	173.1500
Wavelength/ Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
space group	P2$_1$/n	P2$_1$/c
a/Å	13.671 (3)	16.544 (3)
b/Å	13.380 (3)	12.665 (3)
c/Å	16.481 (3)	18.291 (4)
Alpha/°	90.00	90
Beta/°	105.28 (3)	95.51 (3)
Gamma/°	90.00	90
Volume/Å^3	2908.0 (10)	3814.9 (13)
Z	4	4
D_{calcd}/ (g cm^{-3})	1.389	1.4031
μ/mm^{-1}	0.695	0.819
F(000)	1268.0	1673.9
Crystal size /mm	0.416 × 0.342 × 0.218	0.807 × 0.269 × 0.068
2ϑ range /°	3.46 to 55.02	3.92 to 54.94
Limiting indices	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -19 ≤ l ≤ 21	-21 ≤ h ≤ 21, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23
No. of rflns collected	30864	41032
No. unique rflns [R(int)]	6649 [R$_{int}$ = 0.0422]	8697 [R$_{int}$ = 0.0419]
Completeness to ϑ	99.2%	99.6%
Data/restraints/parameters	6649/0/347	8697/0/420
Goodness of fit on F^2	1.165	1.036
Final R indices [$I>2\Sigma(I)$]	R$_1$ = 0.0512, wR$_2$ = 0.1163	R$_1$ = 0.0689, wR$_2$ = 0.1911
R indices (all data)	R$_1$ = 0.0552, wR$_2$ = 0.1189	R$_1$ = 0.0730, wR$_2$ = 0.2024
Largest diff. peak and hole (e Å^{-3})	0.59/-0.33	3.00/-1.35

Acknowledgements

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