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Preparation of chromium catalysts bearing bispyridylamine and its performance in ethylene oligomerization

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Abstract
A series of bispyridylamine ligands and chromium complexes designed for ethylene oligomerization have been synthesized, which was made up of both neutral organic ligand and inorganic anion. The compositions of these complexes have been fully characterized by spectroscopic and analytical methods. Catalysts (**Cr1**–**Cr4)** were evaluated in detail with methylaluminoxane (MAO) as an activator in the ethylene oligomerization. As a result, **Cr1** achieved a higher catalytic activity of 2.93×10^5g/(mol(Cr) h) and a higher selectivity of 55.34% toward the valuable C_8 compound using toluene as the solvent. The total selectivity to LAOs was 71.2%.

Introduction

Linear alpha olefins (LAOs) are of great importance, serving as intermediates and building blocks for the synthesis of various chemical products. According to the carbon chain length, olefins in the range C_4–C_{20} are used to produce polyethylene, synthetic lubricants, plasticizer, detergents and some co-polymers. Continually increasing demand for LAOs has led to a research interest in ethylene oligomerization technologies [1–3]. Complexes with late transition metals were widely applied to ethylene oligomerization as homogeneous catalysts, in which the most famous model initially developed by Brookhart et al. [4, 5] was based on 2, 6-bis(imino)pyridines. Among the transition metal complexes, chromium complexes supported by pincer ligands have always attracted more attention as the catalyst due to a wide range of applications spanning from hydrogenation of olefins to carbonyl compounds and carboxylic acid derivatives [6–11]. Chromium complexes are also potent catalysts to the shorter chain oligomerization reactions [12–14]. Indeed, chromium as a metal center has been dominated for ages in ethylene oligomerization [15]. Phillips catalyst is a typical example, producing 1-hexene and 1-octene [16, 17].

In addition, different ligand structures play a different role in controlling the catalytic performance and the product selectivity in ethylene oligomerization. Ligands such as N^N^N, N^N^O and C^N^C [18–20] determine the catalytic behavior via stabilizing a particular oxidation state. In order to improve the catalytic performances, N^N^N-cobalt catalysts have emerged, bearing cycloalkyl-fused pyridines [21]. Furthermore, systems based on bis(arylimino)pyridine pincer ligands were capable of generating either oligomers (mainly α-olefins) or highly linear polyethylene, depending on the steric properties of the N-aryl groups [12–14, 22, 23].

Herein, the synthesis of a new family of N^N^N-chromium catalysts bearing bispyridylamine ligands and their catalytic performance in ethylene oligomerization is reported. On activation with methylaluminoxane (MAO), good activities were observed for all the chromium complexes studied highly affording LAOs. Moreover, the effects of substituent pair ligands, Al/Cr molar ratio, reaction temperature, reaction pressure and the solvent types on their catalytic activities and selectivities have been investigated in detail.

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Experimental

Material and instrumentation

All manipulations of air- and moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene and tetrahydrofuran (THF) were refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 10 wt% in toluene) was bought from Sigma-Aldrich. 2-Phenoxyethylamine, 2-(2-methoxyphenoxy) ethylamine, 2-chloropyridine, 2-chloro-4-methylpyridine and $CrCl_3(THF)_3$ were purchased from Aladdin and used as received. Polymerization-grade ethylene was obtained from Daqing Summit Specially Gases (China). All other reagents were purchased from Tianjin Damao Chemical Reagent.

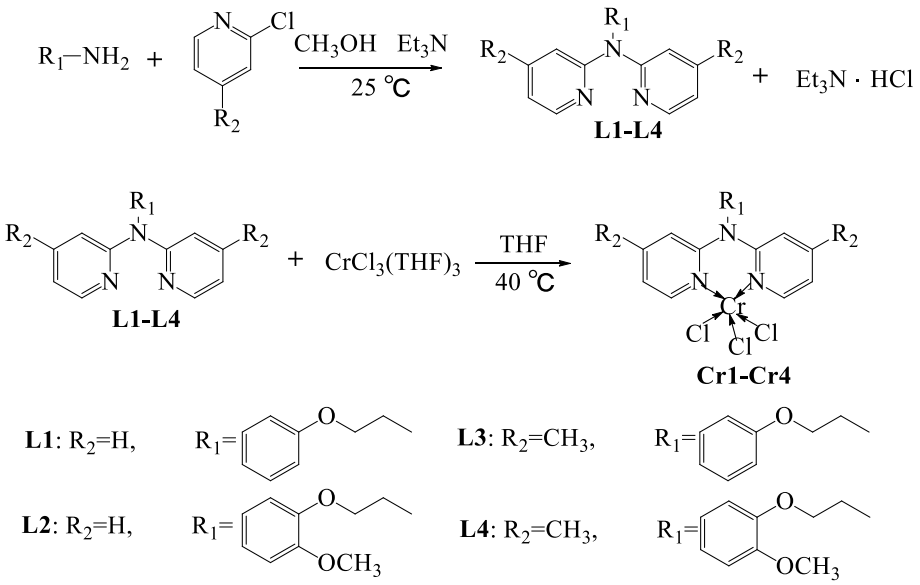
FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrophotometer from 4000 to 450 cm^{-1} using KBr pellets. MS data were collected from a micrOTOF-Q II mass spectrometer using electrospray ionization (ESI) as the ion source. ^1H NMR and ^{13}C NMR spectra were obtained using a Bruker DMX 400 MHz and 100 MHz instrument correspondingly at ambient temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed with a Foss-Heraeus 240 CHNO-Rapid Analyzer (Daqing Petrochemical Research Center). Gas chromatography (GC) analysis of oligomers was conducted on a Fuli GC 9720 using n-heptane as an internal standard, equipped with a flame ionization detector (FID) and a 50-m (0.2 mm id, 0.5 μm film thickness) HP-PONA column, operating at 50 °C for 5 min followed by heating at 10 °C min^{-1} until 140 °C and leaving for 0 min, then heating at 5 °C min^{-1} until 240 °C and leaving for 5 min, and 240 °C for sample injector.

Synthesis of ligands (L1–L4)

Proligands **L1**–**L4** were prepared as shown in Scheme 1.

Synthesis of *N*-(2-phenoxyethyl)-*N*-(pyridin-2-yl) pyridin-2-amine (L1)

A solution of 2-phenoxyethylamine (1.31 mL, 10 mmol) in methanol (10 mL) was added to a solution of triethylamine (Et_3N) (2.76 mL, 20 mmol) in methanol (10 mL) at 0 °C. A solution of 2-chloropyridine (3.80 mL, 40 mmol) in methanol (10 mL) was then added at 0 °C under N_2. After being stirred for 30 min, the reaction mixture was heated to 25 °C and stirred for 3 days. Then, the solvent was evaporated under reduced pressure to afford a yellow solid **L1** washed with methanol and dried under vacuum. Yield: 2.31 g (79%). FTIR data (KBr, pellet, cm^{-1}): υ 3335, 3057, 2922, 1573, 1436, 1243. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.94 (t, 2H, CH_2, J 47.8 Hz), 4.59 (t, 2H, CH_2), 6.85 (t, 2H, Py–H), 6.87 (d, 2H, Py–H, J 7.1 Hz), 7.15 (d, 2H, Ph–H), 7.26 (t, 1H, Ph–H), 7.54 (t, 2H, Ph–H), 7.57 (t, 2H, Py–H), 8.33 (d, 2H, Py–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 42.83, 67.63, 115.72, 116.79, 117.17, 121.13, 130.02, 137.32, 147.14, 157.30, 159.39. ESI–MS (m/z): 291.16 $[\mathbf{L1}+H]^+$. Anal. Calcd for $C_{18}H_{17}N_3O$ (Found) %: C, 74.23 (74.01); H, 5.84 (5.71); N, 14.43 (14.13).



Scheme 1 Synthetic routes of bispyridylamine ligands and chromium complexes

Synthesis of *N*-(2-(2-methoxyphenoxy) ethyl)-*N*-(pyridin-2-yl)pyridin-2-amine (L2)

This product was prepared by following a procedure similar to what was described above for **L1**, starting from 2-(2-methoxyphenoxy) ethylamine (1.50 mL, 10 mmol), 2-chloropyridine (3.80 mL, 40 mmol) and triethylamine (2.76 mL, 20 mmol). **L2** was obtained as a yellow oil. Yield: 2.43 g (76%). FTIR data (KBr, pellet, cm^{-1}): υ 3374, 3052, 2942, 1573, 1456, 1250. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.14 (*t*, 2H, CH_2), 3.59 (*s*, 3H, Ph-OCH_3), 3.75 (*t*, 2H, CH_2, *J* 5.2 Hz), 6.90 (*t*, 2H, Ph–H), 7.07 (*d*, 2H, Py–H), 7.25 (*d*, 2H, Ph–H), 7.26 (*t*, 1H, Ph–H), 7.32 (*t*, 2H, Ph–H), 7.34 (*d*, 2H, Ph–H), 7.37 (*t*, 2H, Py–H), 8.09 (*d*, 2H, Py–H, *J* 4.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 42.83, 56.83, 67.57, 85.28, 116.12, 116.65, 116.79, 117.17, 121.38, 122.22, 137.12, 147.14, 149.34, 151.71, 157.30. ESI–MS (*m*/*z*): 322.23 [**L2** + H]$^+$. Elemental Anal. Calcd for $C_{19}H_{19}N_3O_2$ (Found) %: C, 71.03 (70.89); H, 5.92 (5.68); N, 13.08 (12.86).

Synthesis of 4-methyl-*N*-(4-methylpyridin-2-yl)-*N*-(2-phenoxyethyl) pyridin-2-amine (L3)

This product was prepared by following a procedure similar to what was described above for **L1**, starting from 2-phenoxyethylamine (1.31 mL, 10 mmol), 2-chloro-4-methylpyridine (3.50 mL, 40 mmol) and triethylamine (2.76 mL, 20 mmol). **L3** was obtained as a yellow solid. Yield: 2.58 g (81%). FTIR data (KBr, pellet, cm^{-1}): υ 3284, 3052, 2948, 1592, 1417, 1276. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.33 (*s*, 6H, Py–CH_3), 3.66 (*t*, 2H, CH_2), 3.96 (*t*, 2H, CH_2), 6.86 (*d*, 2H, Py–H), 6.91 (*d*, 2H, Py–H), 6.98 (*d*, 2H, Ph–H, *J* 11.1 Hz), 7.07 (*t*, 1H, Ph–H), 7.24 (*t*, 2H, Ph–H), 8.18 (*d*, 2H, Py–H, *J* 5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.23, 42.83, 67.62, 114.48, 115.20, 115.72, 121.13, 130.02, 146.01, 152.19, 158.12, 159.39. ESI–MS (m/z): 321.16 [**L3** + H]$^+$. Anal. Calcd for $C_{20}H_{21}N_3O$ (Found) %: C, 75.24 (74.96); H, 6.58 (6.25); N, 13.17 (12.94).

Synthesis of *N*-(2-(2-methoxyphenoxy) ethyl)-4-methyl-*N*-(4-methylpyridin-2-yl)pyridine-2-amine (L4)

This product was prepared by following a procedure similar to what was described above for **L1**, starting from 2-(2-methoxyphenoxy) ethylamine (1.50 mL, 10 mmol), 2-chloro-4-methylpyridine (3.50 mL, 40 mmol) and triethylamine (2.76 mL, 20 mmol). **L4** was obtained as a yellow oil. Yield: 2.18 g (62%). FTIR data (KBr, pellet, cm^{-1}): υ 3302, 3058, 2955, 1649, 1431, 1241. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.40 (*s*, 6H, Py–CH_3), 2.75 (*t*, 2H, CH_2), 3.38 (*s*, 3H, Ph–OCH_3), 3.68 (*t*, 2H, CH_2), 7.23 (*s*, 2H, Py–H), 7.26 (*d*, 2H, Py–H), 7.32 (*d*, 2H, Ph–H, *J* 7.9 Hz), 7.66 (*t*, 2H, Ph–H), 7.68 (*t*, 2H, Ph–H), 7.70 (*d*, 2H, Ph–H), 8.40 (*d*, 2H, Py–H, *J* 19.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 21.23, 42.83, 56.83, 67.57, 114.48, 115.20, 116.12, 116.65, 121.38, 122.22, 146.00, 149.34, 151.71, 152.19, 158.12. ESI–MS (m/z): 350.35 [**L4** + H]$^+$. Anal. Calcd for $C_{21}H_{23}N_3O_2$ (Found) %: C, 72.21 (71.98); H, 6.59 (6.26); N, 12.03 (11.87).

Synthesis of chromium complexes (Cr1–Cr4)

The chromium complexes **Cr1**–**Cr4** were prepared as displayed in Scheme 1.

Synthesis of *N*-(2-phenoxyethyl)-*N*-(pyridin-2-yl) pyridin-2-amino chromium chloride (Cr1)

A solution of **L1** (0.32 g, 1 mmol) in THF (10 mL) was added to a solution of $CrCl_3(THF)_3$ (0.37 g, 1 mmol) in THF (10 mL). The mixture was stirred for 24 h at 40 °C under N_2, and then excess diethyl ether was poured into the mixture to precipitate the complex. The precipitate was collected by filtration, washed with diethyl ether and dried under vacuum to give the product **Cr1** as a green powder. Yield: 0.37 g (81%). FTIR data (KBr, pellet, cm^{-1}): υ 3308, 3082, 2979, 1641, 1436, 1147. ESI–MS (*m*/*z*): 450.96 [M + H]$^+$. Anal. Calcd for $C_{18}H_{17}N_3OCrCl_3$ (Found) %: C, 48.05 (47.86); H, 3.78 (3.46); N, 9.34 (9.02).

Synthesis of *N*-(2-(2-methoxyphenoxy) ethyl)-*N*-(pyridin-2-yl)pyridin-2-amino chromium chloride (Cr2)

In a manner similar to that described for **Cr1**, **Cr2** was isolated as a green powder. Yield: 0.46 g (95%). FTIR data (KBr, pellet, cm^{-1}): υ 3284, 3045, 2962, 1649, 1423, 1134. ESI–MS (*m*/*z*): 481.23 [M + H]$^+$. Anal. Calcd for $C_{19}H_{19}N_3O_2CrCl_3$ (Found) %: C, 47.55 (47.13); H, 3.96 (3.68); N, 8.76 (8.48).

Synthesis of 4-methyl-*N*-(4-methylpyridin-2-yl)-*N*-(2-phenoxyethyl)pyridin-2-amine chromium chloride (Cr3)

In a manner similar to that described for **Cr1**, **Cr3** was isolated as a green powder. Yield: 0.31 g (65%). FTIR data (KBr, pellet, cm^{-1}): υ 3308, 3076, 2966, 1566, 1436, 1140. ESI–MS (*m*/*z*): 479.34 [M + H]$^+$. Anal. Calcd for $C_{20}H_{21}N_3OCrCl_3$ (Found) %: C, 50.26 (50.01); H, 4.40 (4.18); N, 8.80 (8.68).

Synthesis of *N*-(2-(2-methoxyphenoxy) ethyl)-4-methyl-*N*-(4-methylpyridin-2-yl)pyridine-2-amine (Cr4)

In a manner similar to that described for **Cr1**, **Cr4** was isolated as a green powder. Yield: 0.33 g (65%). FTIR data (KBr, pellet, cm^{-1}): υ 3291, 3052, 2929, 1566, 1417, 1114. ESI–MS (*m*/*z*): 509.35 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}N_3O_2CrCl_3$ (Found) %: C, 49.66 (49.35); H, 4.53 (4.25); N, 8.28 (7.99).

General procedure for ethylene oligomerization

A 250-mL stainless steel autoclave equipped with mechanical stirring, internal temperature control and continuous feed of ethylene was employed for the reaction. The autoclave was placed under vacuum and replaced by ethylene for three times. When the desired reaction temperature was reached, a typical reaction was performed by introducing solvent, the proper amount of co-catalyst and the catalyst solution (the total volume was 50 mL). Then, the autoclave was immediately pressurized to the desired level, maintained at this level with constant feeding of ethylene. After the reaction was carried out for the required period, the reactor was cooled with water bath and the reaction solution was quenched with 10 wt% HCl in ethanol. The distribution of the oligomers was analyzed by GC when compared with the standard authentic samples.

Results and discussion

Characterization and synthesis of ligands and chromium complexes

Ligands **L1**–**L4** were readily synthesized by the substitution reaction of the corresponding primary amines and the corresponding pyridine compounds in refluxing methanol (Scheme 1). These ligands were characterized by FTIR, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and elemental analysis. In the FTIR spectra of the synthesized ligands (Supplementary Figure S1), the bands around 3302–3305 cm^{-1} were assigned to the –OH stretch due to the contaminate water in the KBr. The bands around 3052 cm^{-1} were due to the C-H of pyridine ring stretch vibration. The bands (C=N and C–N) of pyridine ring were observed at 1566–1649 cm^{-1} and 1243–1276 cm^{-1}, respectively. Bands at 1417–1456 cm^{-1} were assigned to pyridine rings. At room temperature, the ^{1}H NMR spectra of **L1**–**L4** in $CDCl_3$ exhibited resonances in the region where the protons on pyridine are attributed to δ 6.87–8.33 ppm (Supplementary Figure S2). The signals of methylene protons were 3.94–4.59 ppm (**L1**), 2.97–3.75 ppm (**L2**), 3.66–3.96 ppm (**L3**) and 2.75–3.68 ppm (**L4**). In addition, the proton signals in the range of 7.15–7.68 ppm were ascribed to the benzene ring. After substitution reaction with 2-chloro-4-methylpyridine, the signals of protons at 2.33–2.40 ppm belonged to the methyl of pyridine (**L3** and **L4**), respectively. Furthermore, the ^{13}C NMR data (L1–L4) are shown in Supplementary Figure S3.

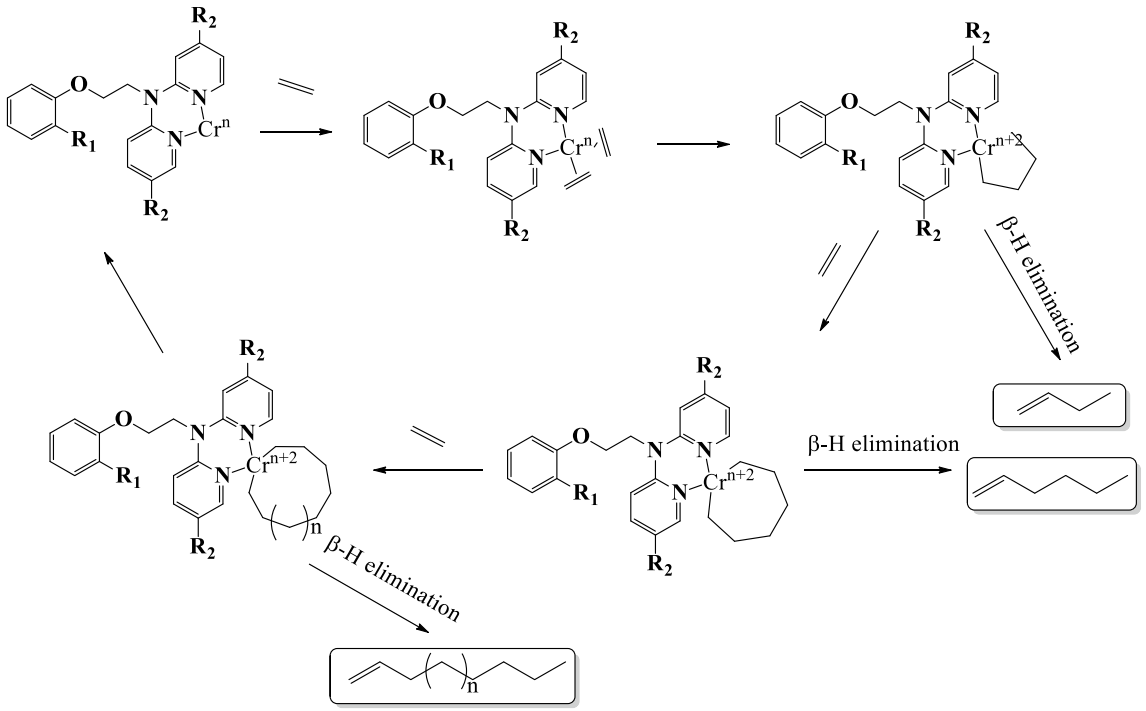
The reaction of $CrCl_3(THF)_3$ with ligands (**L1**–**L4**) in THF at 40 °C afforded the corresponding chromium complexes (**Cr1**–**Cr4**) isolated as green solids in moderate to good yields. The synthesized complexes were characterized by a combination of FTIR spectra and ESI–MS. From FTIR spectra of complexes (Supplementary Figure S1), we could know that the absorption peaks became broad and distinct. The band (C=N) is red-shifted from 1573 to 1553 cm^{-1} because the coordination between chromium ion and nitrogen atom saps the strength of double bond C=N and enhances the C–H bond bending vibration of carbon atom. In addition, the ESI–MS of **Cr1**–**Cr4** showed a molecular ion peak $[M+1]^+$ at m/z 450.96, 481.23, 479.34 and 509.35 (Supplementary Figure S4). Both 5- and 6-coordinated Cr(III) complexes are known [24–26], and our results of characterization consist of the 5-coordinated structure of Cr1–Cr4 proposed in Scheme 1.

Evaluation of the chromium complexes as catalysts for ethylene oligomerization reactions

After activation with MAO, the detailed selective ethylene oligomerization reaction of the complexes **Cr1**–**Cr4** was evaluated. Good catalytic activity and selectivity to 1-octene were shown. Various LAOs can be produced by inserting ethylene into the cationic chromium species, depending on the rates of chain propagation and chain transfer. Oxidative coupling of two ethylene molecules with the active catalytic metal gives a metallacycle intermediate. According to the currently accepted metallacycles mechanism, the postulated mechanism is shown in Scheme 2 [27–30].

Effect of N-substituent on catalytic activity and product selectivity

To explore the influence of the N-substituent on the catalytic activity and product selectivity, four catalysts were synthesized and the investigated results are listed in Table 1. As can be seen in Table 1, their catalytic activities showed the order **Cr1** > **Cr2** > **Cr4** > **Cr3**. Complexes **Cr1** and **Cr2** showed better activities than the corresponding analogous complexes **Cr3** and **Cr4**, which can be ascribed to detrimental effect due to the presence of an additional electron donating pyridine-based methyl group [31]. In addition, the chromium catalysts with more bulky steric hindrance showed higher selectivity to high carbon number olefins ($\geq C_8$), illustrating



Scheme 2 Postulated mechanism of ethylene oligomerization

Table 1 Effects of solvent and ligand types on catalytic activity and product selectivity

Entry	Solvent	Activity (10^5g/(mol(Cr) h))	Product selectivity (wt%)				α-olefins (wt%)
			C_4	C_6	C_8	C_{10}–C_{18}	
Cr1	Toluene	2.93	27.29	8.14	55.34	9.23	71.20
Cr1	Methylcyclohexane	2.52	41.27	48.84	6.94	2.95	46.02
Cr1	Cyclohexane	1.08	75.35	7.62	3.62	13.41	79.39
Cr2	Toluene	2.61	21.72	19.22	52.37	6.69	60.51
Cr2	Methylcyclohexane	2.15	29.88	57.03	8.74	4.35	88.78
Cr2	Cyclohexane	1.02	80.53	7.66	2.89	8.92	85.49
Cr3	Toluene	2.09	25.60	15.22	38.08	21.10	51.98
Cr3	Methylcyclohexane	1.16	32.27	29.17	14.80	23.76	50.52
Cr3	Cyclohexane	0.42	36.74	25.42	2.67	35.17	47.93
Cr4	Toluene	1.53	9.24	48.09	15.59	27.08	60.73
Cr4	Methylcyclohexane	1.45	22.55	55.29	11.48	10.68	55.42
Cr4	Cyclohexane	0.55	31.18	39.46	3.74	25.62	43.99

Reaction conditions: catalyst (5 μmol), *n*(Al)/*n*(Cr) (300), reaction temperature (50 °C), ethylene pressure (1.0 MPa), solvent (total volume: 50 mL) and reaction time (30 min)

the protection afforded to the active site by the sterically bulky substituent [32]. So, we chose **Cr1** as the next research catalyst at length [33, 34].

Effect of solvent on catalytic activity and product selectivity

Considering the effect of solvents on catalytic activity and product selectivity, three solvents (toluene, cyclohexane, and methylcyclohexane) were used to study with MAO as co-catalyst. The final results are displayed in Table 1. Under the same reaction conditions, the highest catalytic activity was observed in toluene compared with cyclohexane and methylcyclohexane, which could be due to the maximum polarity of toluene and the optimum solubility of chromium catalyst in toluene. On the other hand, the selectivity to C_8 was the highest with toluene as the solvent. The oligomers were mainly C_4 and C_6 in other solvent. As a result, we chose toluene as the solvent.

Effect of reaction temperature on catalytic activity and product selectivity

The effect of reaction temperature on catalytic activity and product selectivity is shown in Table 2. As we know from Table 2, the catalytic activity and product selectivity were strongly affected by reaction temperature. Elevating the reaction temperature from 20 °C to 60 °C, the catalytic activity increased initially with temperature and reached a maximum (2.98×10^5g/(mol(Cr) h)) around 40 °C. However, the selectivity to α-olefins and C_8 was higher at 50 °C than at 40 °C. As reaction temperature increased further from 40 °C to 60 °C, a sharp decrease in catalytic activity was observed, which was attributed to both the instability of the active species [35–37] and the lower solubility of ethylene in toluene at higher temperatures [38]. Moreover, higher temperatures resulted in higher rates of catalyst deactivation as well. The selectivity to C_8 showed the same tendency as the temperature-increasing activity at the expense of C_4 and C_6 due to a faster chain transfer and termination at higher temperatures.

Effect of ethylene pressure on catalytic activity and product selectivity

The effect of ethylene pressure on catalytic activity and product selectivity is shown in Table 3. From Table 3, we can know that the ethylene pressure played an important role in the catalytic activity and product selectivity. The catalytic activity first increased and then decreased with the increase in ethylene pressure, reaching a maximum (2.93×10^5g/(mol(Cr) h)) at 1.0 MPa. An elevated ethylene pressure led to an increase in the ethylene concentration in the solvent, leading to an increase in the chain propagation rate and thus inducing increased catalytic activity. But higher ethylene pressure made the active site distortion. The selectivity to C_4 and C_6 increased at the cost of C_8 with the increasing ethylene pressure, which may be due to the faster rates of β-H elimination than propagation in the oligomerization process.

Effect of Al/Cr molar ratio on catalytic activity and product selectivity

The effect of Al/Cr molar ratio on catalytic activity and product selectivity was investigated thoroughly, and the results are listed in Table 4. As shown in Table 4, typically the runs were performed in toluene under 1.0 MPa of ethylene pressure over 30 min with the molar ratio varied from 100 to 900. The optimum activity was observed as 2.93×10^5g/(mol(Cr) h) with a molar ratio of 300. The selectivity to C_8 was found to increase by more than half from 12.48 to 45.34 on changing the molar ratio from 100 to 300, which can be ascribed to increased chain propagation and active sites. On the contrary, the higher MAO could also interfere with the formation of the over-reduced chromium species and make the active species deactivated [39], indicating the decrease of catalytic activity and the selectivity to C_8.

Table 2 Effects of temperature on catalytic activity and product selectivity

Entry	Temperature (°C)	Activity (10^5g/(mol(Cr) h))	Product selectivity (wt%)				α-olefins (wt%)
			C_4	C_6	C_8	C_{10}–C_{18}	
1	20	1.67	32.06	12.01	52.30	3.63	70.08
2	30	2.36	29.04	9.74	58.04	3.18	72.06
3	40	2.98	24.78	17.16	51.60	6.46	53.86
4	50	2.93	27.29	8.14	55.34	9.23	71.20
5	60	2.14	45.79	14.23	33.01	6.97	59.87

Reaction conditions: catalyst (5 μmol), *n*(Al)/*n*(Cr) (300), ethylene pressure (1.0 MPa), solvent (toluene, 50 mL) and reaction time (30 min)

Table 3 Effects of ethylene pressure on catalytic activity and product selectivity

Entry	Pressure (MPa)	Activity (10^5g/(mol(Cr) h))	Product selectivity (wt%)				α-olefins (wt%)
			C_4	C_6	C_8	C_{10}–C_{18}	
1	0.5	1.13	40.79	15.31	19.11	24.79	63.53
2	1.0	2.93	27.29	8.14	55.34	9.23	71.20
3	1.5	1.89	42.22	15.29	32.09	10.40	67.13
4	2.0	1.77	24.39	27.99	25.85	21.77	41.94
5	2.5	1.32	61.78	13.99	15.58	8.65	76.17

Reaction conditions: catalyst (5 μmol), *n*(Al)/*n*(Cr) (300), reaction temperature (50 °C), solvent (toluene, 50 mL) and reaction time (30 min)

Table 4 Effects of Al/Cr molar radio on catalytic activity and product selectivity

Entry	N(Al)/n(Cr)	Activity (10^5g/(mol(Cr) h))	Product selectivity (wt%)				α-olefins (wt%)
			C_4	C_6	C_8	C_{10}–C_{18}	
1	100	1.52	61.17	14.37	12.48	11.98	73.67
2	300	2.93	27.29	8.14	55.34	9.23	71.20
3	500	2.12	63.55	9.96	19.99	6.50	80.95
4	700	1.56	68.99	15.01	13.39	2.61	80.24
5	900	1.51	66.76	12.34	11.73	9.17	77.39

Reaction conditions: catalyst (5 μmol), reaction temperature (50 °C), ethylene pressure (1.0 MPa), solvent (toluene, 50 mL) and reaction time (30 min)

Conclusion

A series of short-chain ligands were synthesized and characterized, to afford selective ethylene oligomerization chromium catalysts, producing the selectivity of 55.34% to C_8 and activity of 2.93×10^5g/(mol(Cr) h) with toluene as the solvent at the temperature of 50 °C, the ethylene pressure of 1.0 MPa and the molar ratio of 300. In this system, the effects of reaction temperature, ethylene pressure, Al/Cr molar ratio, solvents and the ligand types were investigated fully. The oligomerization results showed that **Cr1** had the highest selectivity and catalytic activity than **Cr2–Cr4** under the same conditions in most cases. The selectivity to LAOs could reach 71.2%.

Supporting information summary

The characterization data of short-chain ligands and chromium complexes are provided in supporting information.

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