Ethylene tetramerization with a highly active and long-lifetime trinuclear diphenylphosphinoamine/Cr(III)/MAO catalyst

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The synthesis and characterization of a novel trinuclear diphosphinoamine ligand **2** are reported. The ligand combined with Cr(III), activated with methylaluminoxane, lead to highly active and long-lifetime catalytic systems for the tetramerization of ethylene to form 1-octene. The effects of reaction temperature, reaction pressure, molar ratio of Al/Cr and bis(diphenylphosphino)amine/Cr on the catalytic activity and product selectivity were studied. Compared with its mononuclear analogue **1**, ligand **2** showed a higher catalytic activity and longer lifetime for ethylene tetramerization in the presence of methylaluminoxane as cocatalyst. High molecular weight polyethylene was generated as a by-product with extremely broad molecular weight distributions.

ethylene tetramerization, 1-octene, trinuclear, diphenylphosphinoamine

In recent years there has been a substantial acceleration in research activity concerned with homogeneous transition metal catalysts for ethylene oligomerization and polymerization. Chromium catalysts play an important role in both of these processes [1–8]. Since the first report of ethylene tetramerization to form 1-octene using Cr-bis(diphenylphosphino)amine (PNP) catalysts [9], numerous studies have investigated the relationship between ligand structure and catalytic properties. These include investigations into various single-site PNP ligands, wherein alkyl [10–12], cycloalkyl [13], ether [14], thioether, pyridyl tethers [15] and aryl [16,17] substituents attached to the N or P atom of the ligand backbone were synthesized and evaluated. Several dual-site PNP ligands [12,18] and a triple-site [19] were also found to have moderate activity and selectivity toward 1-octene in ethylene tetramerization.

We were attracted by the potential for using chromium as an ethylene tetramerization active center because of its high catalytic activity and high selectivity to 1-octene. Here, we describe a new trinuclear PNP ligand that displays higher activity and a long lifetime for ethylene tetramerization to 1-octene.

1 Experimental

All manipulations of water and/or moisture sensitive compounds were performed by means of standard high-vacuum Schlenk techniques under a N_2 atmosphere. Toluene was refluxed and distilled from sodium/benzophenone under dry nitrogen. The ligand **1** was prepared according to a published procedure [9]. *Cis,cis*-1,3,5-cyclohexanetricarboxylic acid, diphenylphosphoryl azide(DPPA) and Cr(acac)$_3$ were purchased from Sigma-Aldrich(Pennsylvania, USA) and used as received. Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (Daqing, China). Methylaluminoxane (MAO) solution (1.4 mol/L) in toluene was purchased from Albemarle Corp. (Louisiana, USA). Cyclohexane, toluene and ethanol were dehydrated and de-

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gassed before use. All other chemicals were obtained commercially and used as received.

1.1 Preparation and characterization of the ligand

The synthesis method of trinuclear PNP ligand **2** is described in Figure 1. *Cis,cis*-1,3,5-triaminocyclohexane was prepared from commercially available *cis,cis*-1,3,5-cyclohexanetricarboxylic acid according to a procedure published previously [20]. Trinuclear PNP ligand **2** was synthesized through the reaction between *cis,cis*-1,3,5-triaminocyclohexane and diphenylphosphine chloride according to a method described in the literature [9].

(1) Preparation of *cis,cis*-1,3,5-triaminocyclohexane. *Cis,cis*-1,3,5-cyclohexanetricarboxylic acid (2.0 g, 9.2 mmol) was washed into a round-bottomed flask with toluene (75 mL) and Et3N (3.9 mL, 28 mmol) was added followed by DPPA (7.7 g, 28 mmol). The mixture was stirred for 0.5 h at room temperature and then refluxed for 0.5 h. Benzyl alcohol (3.34 g, 30.88 mmol) was added and the solution was refluxed for 18 h, during which a precipitate formed. After cooling to ambient temperature, the product was collected by vacuum filtration, washed with minimal cold toluene, and dried under vacuum to leave 2.47 g (75.8%). ^{1}H NMR(δ, CDCl$_3$, TMS): δ 7.37–7.20 (m, 5H), 5.0 (s, 2H), 3.39 (m, 1H), 1.90 (d, 1H). EI-MS (*m/z*) 532. Anal. Calcd. for C$_{30}$H$_{33}$N$_3$O$_6$ (%): C, 67.77; H, 6.27; N, 7.91. Found (%): C, 67.71; H, 6.25; N, 8.06. The CBZ groups were most efficiently cleaved by treatment of the solid directly with 33% HBr/HOAc. Shortly after a clear solution was achieved, a thick suspension formed, which was diluted with an equal volume of anhydrous ether to ease filtration. The product was collected and dried, providing the desired triamine as a solid. ^{1}H NMR (δ, CDCl$_3$, TMS): δ 0.83–0.95 (m, 3H), 1.00–1.40 (br, 6H), 1.90–2.06 (m, 3H), 2.70–2.85 (m, 3H).

(2) Preparation of trinuclear diphenylphosphinoamine.

To a solution of the bis(phenyl)phosphorus chloride (1.33 mL, 7.2 mmol) in dichloromethane (20 mL) and triethylamine (3.75 mL) at 0°C, *cis,cis*-1,3,5-triaminocyclohexane (0.155 g, 1.2 mmol) was added. It was stirred for 30 min and then the ice bath was removed. After stirring for a total of 14 h, the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallization in 65% yield. ^{1}H NMR (δ, CDCl$_3$, TMS): δ 1.46–1.55 (m, 3H), 2.69–2.78 (m, 3H), 2.85–2.93 (m, 3H), 6.82–7.65 (m, 60H). Anal. calcd. for C$_{78}$H$_{69}$N$_3$P$_6$ (%): C, 75.90; H, 5.63; N, 3.40. Found (%): C, 76.15; H, 5.41; N, 3.62. EI-MS (70 eV): *m/z* = 1233. Coordination of the ligand to the Cr(III) metal center was indicated by the immediate color change of the reaction mixture from pink to dark blue. Unfortunately, crystals suitable for X-ray structure determination were not obtained by recrystallization in CH$_2$Cl$_2$/hexane system. Because of the strong paramagnetic nature of the octahedral d3 Cr(III) center, complexes are silent in ^{31}P NMR and their ^{1}H and ^{13}C NMR spectra exhibited only broad signals that could not be exploited to establish their structure. Therefore, the complexes were primarily characterized by elemental analysis data.

1.2 Ethylene tetramerization

Ethylene tetramerization was processed in a 500 mL autoclave. After evacuation and flushing with nitrogen three times and then twice with ethylene, the autoclave was charged with 200 mL solvent and magnetically stirred under an ambient ethylene atmosphere. When the desired reaction temperature was established, the required amount of ligand, Cr(III) and MAO were injected into the reactor. Typically, 30 min later, the reaction solution was quickly cooled to 5°C and then quenched by adding HCl/ethanol (10 wt%). The catalytic activity was calculated based on the increase in product weight. The distribution of tetramerization product
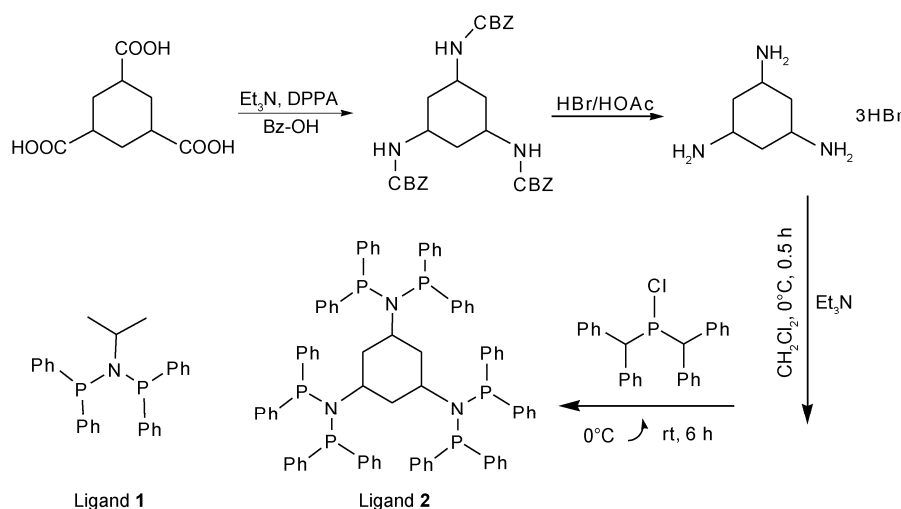

Figure 1 Synthesis of trinuclear PNP precatalyst **2**.

was analyzed by GC-MS, while the precipitated polymer was collected by filtration, washed with ethanol, dried under vacuum at 60°C to constant weight, weighed, and finally characterized.

1.3   Characterization of product

A small liquid sample was washed by deionized water to remove alcohol, MAO and hydrochloric acid. The organic layer was then dried over anhydrous sodium carbonate and analyzed by an HP-5890 GC-MS instrument equipped with an HP-1 capillary column (30 m × 0.25 mm) and an HP-5971 mass spectroscope, at 35°C (10 min) and then heated at 10°C/min until reaching 280°C (remaining for 10 min). The molecular weight and its distribution of polymers were determined by gel permeation chromatography (GPC) on a Waters Alliance GPCV2000 at 150°C with 1,2,4-trichlorobenzene as eluent. Melting points of polymers were measured on a Perkin-Elmer DSC-7 in the standard DSC run mode.

2   Results and discussion

2.1 The effect of reaction temperature on catalytic properties

As shown in Table 1, the catalytic activity and product distribution were strongly affected by reaction temperature. Elevating the reaction temperature from 30 to 70°C, the catalytic activity increased initially with temperature and reached a maximum around 40°C. As reaction temperature

increases from 40 to 70°C, a sharp decrease in productivity was observed. Higher temperatures can result in lower ethylene solubility and higher rates of catalyst deactivation, which can lead to reduced productivity. The results of the temperature study reveal considerable changes in the product distribution with temperature variation, showing an increasing trend in selectivity to 1-hexene and a decreasing trend in selectivity to 1-octene with increasing reaction temperature. In terms of the reaction mechanism [21], it can be concluded that at higher temperatures, the reductive elimination of 1-hexene is favored over β-hydride transfer to chromium. Noteworthy by-products of this reaction include methylcyclopentane and methylenecyclopentane (at an almost 1∶1 ratio). These cyclic by-products had the adverse effect of decreasing the total alpha selectivity and the loss of valuable ethylene feedstock led to further efforts aimed at reducing these unwanted products.

2.2   The effect of Al/Cr molar ratios on catalytic properties

The effect of the Al/Cr molar ratio on ethylene tetramerization was investigated in detail with ligand **2**, the results are listed in Table 2. A higher productivity was obtained at a ratio of 300. Decomposition of catalyst complex at higher MAO loading may explain the decrease in catalytic activity [22]. Contrary to the results reported previously [23], an increase in the Al/Cr molar ratio from 100 to 500 resulted in an increase in selectivity to 1-octene. The same results were found in the tetramerization of ethylene with triple-site diphosphinoamine (PNP)/Cr(III)/MAO[19].

Table 1   Effects of reaction temperature on catalytic activity and product distribution [a]

Entry	T (°C)	Activity (10^6 g mol^{-1}(cat) h^{-1})	Product selectivity (%)							
			1-C$_4^=$	1-C$_6^=$	C$_6$H$_{12}$[b]	C$_6$H$_{10}$[c]	1-C$_8^=$	1-C$_6^=$+1-C$_8^=$	>1-C$_{10}$	PE
1	30	1.19	1.39	24.21	3.84	4.33	61.8	86.01	3.52	0.91
2	40	2.46	0.98	32.47	3.26	2.45	52.7	85.17	3.31	4.83
3	50	1.70	0.77	33.24	2.37	2.78	50.7	83.94	3.35	6.79
4	60	1.65	1.26	35.38	3.37	3.63	46.4	81.78	4.68	6.54
5	70	1.10	1.42	37.90	3.23	3.45	40.7	78.6	7.11	6.19

a) Solvent: cyclohexane; reaction pressure: 2.0 MPa; **2**∶Cr(III)∶MAO=1∶3∶900; reaction time: 30 min. b) Methylcyclopentane. c) Methylenecyclopentane.

Table 2   Effects of Al/Cr molar ratio on catalytic activity and product distribution [a]

Entry	Al/Cr	Activity (10^6 g mol^{-1}(cat) h^{-1})	Product selectivity (%)							
			1-C$_4^=$	1-C$_6^=$	C$_6$H$_{12}$[b]	C$_6$H$_{10}$[c]	1-C$_8^=$	1-C$_6^=$+1-C$_8^=$	>1-C$_{10}$	PE
6	100	1.98	0.83	31.22	3.16	3.38	53.81	85.03	4.32	3.28
7	200	2.30	1.10	30.53	3.22	3.65	54.02	84.55	3.98	3.50
2	300	2.46	0.98	32.47	3.26	2.45	52.70	85.17	3.31	4.83
8	400	1.79	1.02	29.87	3.00	3.27	55.90	85.77	2.58	4.36
9	500	1.88	1.27	26.80	3.37	3.68	57.20	84.00	2.88	4.80

a) Solvent: cyclohexane; reaction pressure: 2.0 MPa; Cr(III)∶**2** =3∶1; reaction time: 30 min; reaction temperature: 40°C. b) Methylcyclopentane. c) Methylenecyclopentane.

2.3 The effect of reaction pressure on catalytic properties

The effects of reaction pressure on catalytic properties are shown in Table 3. An elevated ethylene pressure led to an increase in the ethylene concentration in the solvent, resulting in an increase in the chain propagation rate and thus inducing increased catalytic activity. The selectivity to 1-hexene decreased and the selectivity to 1-octene increased with increasing ethylene pressure. Changes in product distribution were in good agreement with the metallacycle mechanism proposed by Overett et al. [24]. This is indicative of a strong ethylene concentration influence on the product distribution in general and the formation of 1-octene in particular.

2.4 The dynamic behavior of the catalytic systems

The kinetic profiles of ethylene tetramerization using ligand **1**/Cr(III)/MAO and ligand **2**/Cr(III)/MAO were investigated by measuring the flow rate of ethylene into the reactor with a mass flowmeter. The effect of catalyst lifetime on catalytic activity is shown in Figure 2. The high ethylene flow rate during the first 4 min of reaction reflects the process of ethylene saturation in the solvent.

The rate profile of ligand **1** exhibits typical decay kinetics, with a very high initial rate followed by a rapid decay. The attenuation rate of the catalytic activity of ligand **1** was

much faster than that of ligand **2**. The catalytic activity of ligand **2** was found to remain constant up to 60 min, followed by a laggard attenuation. Hence, ligand **2** exhibited much higher catalytic activity than ligand **1** with polymerization time, which indicates that the trinuclear can restrain the chromium catalytic active center from deactivation [22].

2.5 Characterization of polyethylene

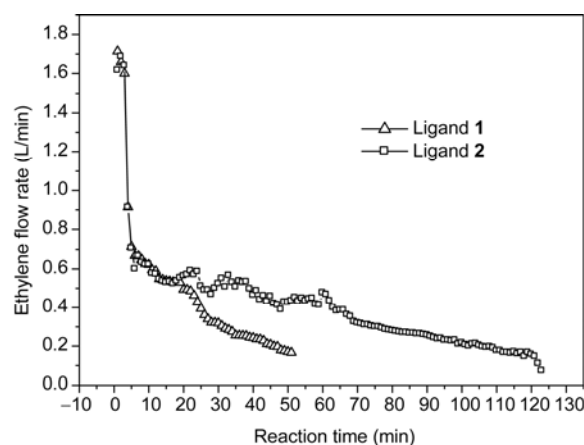Noteworthy by products of this reaction include polyeth-

Figure 2 Kinetic profiles of ethylene tetramerization using ligands **1** and **2** with Cr(III) and MAO. Reaction pressure: 3.0 MPa; reaction temperature: 40°C; Al/Cr ratio: 300.

Table 3 Effects of reaction pressure on catalytic activity and product distribution [a]

Entry	P (MPa)	Activity (10^6 g mol^{-1} (cat) h^{-1})	Product selectivity (%)							
			1-C$_4^=$	1-C$_6^=$	C$_6$H$_{12}$[b]	C$_6$H$_{10}$[c]	1-C$_8^=$	1-C$_6^=$+1-C$_8^=$	>1-C$_{10}$	PE
2	2.0	2.46	0.98	32.47	3.26	2.45	52.7	85.17	3.31	4.83
10	3.0	4.79	1.08	26.94	3.08	3.00	57.7	84.64	3.20	5.00
11	4.0	9.45	0.99	24.99	2.91	3.24	58.8	83.79	3.78	5.29

a) Solvent: cyclohexane; **2**∶Cr(III)∶MAO=1∶3∶900; reaction time: 30 min; reaction temperature: 40°C. b) Methylcyclopentane. c) Methylenecyclopentane.

Table 4 Characterization of polyethylenes

Entry	T (°C)	Al/Cr	PNP/Cr	P (MPa)	T_m (°C)	$M_w \times 10^4$	M_n	M_w/M_n
1	30	300	1.0	2.0	130.20	46.5	5251	88.61
2	40	300	1.0	2.0	131.03	35.3	4693	75.13
3	50	300	1.0	2.0	130.87	25.8	3430	75.11
4	60	300	1.0	2.0	130.21	24.5	6192	73.36
5	70	300	1.0	2.0	129.87	17.5	1496	117.14
6	40	100	1.0	2.0	–	–	–	–
7	40	200	1.0	2.0	130.37	32.9	4010	82.05
2	40	300	1.0	2.0	131.03	35.3	4693	75.13
8	40	400	1.0	2.0	131.20	40.9	5439	75.20
9	40	500	1.0	2.0	129.37	41.9	5552	75.51
2	40	300	1.0	2.0	131.03	35.3	4693	75.13
10	40	300	1.0	3.0	132.37	37.6	4612	81.55
11	40	300	1.0	4.0	132.37	36.0	3456	104.11

ylene (PE). This phenomenon not only poses an undesired pathway for ethylene transformation, but in a continuous polymer formation process, would lead to uncontrollable reactor fouling, preventing proper reaction heat removal and ultimately leading to the shut-down of the process. A somewhat increased polymer formation compared to its mononuclear ligand **1**. The polymeric fraction can be ascribed most probably to the very low solubility of the trinuclear complex in cyclohexane solvents. As shown from Table 4, the polymer produced was found to be high molecular weight polyethylene with an average molecular weight distribution larger than 70. The melting points (T_m) of the resultant PEs revealed that only one melting peak appeared and the melting temperature was at about 130°C for each product.

The molecular weights of the resulting polymers decreased with increasing reaction temperature. The molecular weight of resulting polymers increased with increasing Al/Cr molar ratio. This result is in disagreement with that reported for Fe(II), Co(II) and Cr(III) catalysts [25,26]. The molecular weights of the resulting polymers increased with increasing Al/Cr ratio, so there is probably no chain transfer to aluminum in the **2**/Cr(III)/MAO catalytic system for the tetramerization of ethylene.

High temperature ^{13}C NMR spectroscopy for the PE sample listed in entry 3 of Table 4 was also performed (Figure 3). The NMR spectrum of polyethylene presented in Figure 3 is in good agreement with a highly linear polyethylene.

3　Conclusion

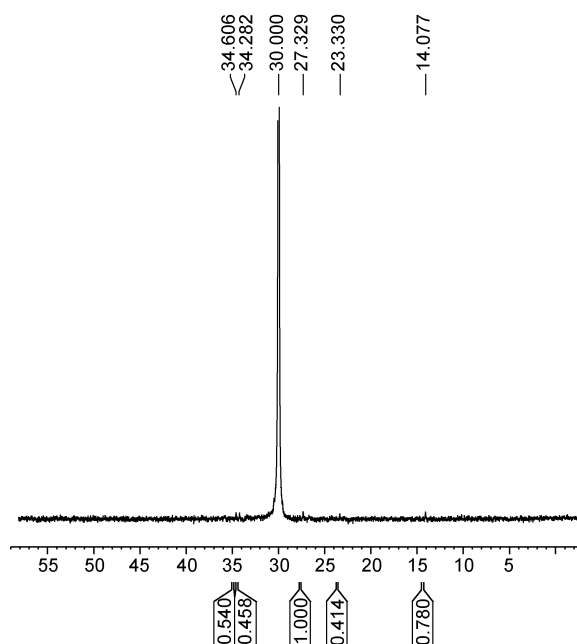A novel trinuclear diphosphinoamine ligand was synthesiz-

ed and characterized. The ligand combined with Cr(III) and activated with methylaluminoxane (MAO), produced highly active and long-lifetime catalytic systems for the tetramerization of ethylene to 1-octene. High molecular weight polyethylene was generated as by-product with extremely broad molecular weight distributions. The molecular weights of the resulting polymers increased with increasing Al/Cr ratio. There was probably no chain transfer to aluminum in the **2**/Cr(III)/MAO catalytic system for the tetramerization of ethylene.

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Figure 3　^{13}C NMR spectra of PE byproducts.

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