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The effect of *N*-aryl bisphosphineamine ligands on the selective ethylene tetramerization

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Abstract

Bisphosphineamine (PNP) ligands with various aryl substituents attached to the N atom of the ligand backbone were synthesized and tested together with $Cr(acac)_3$ as ethylene tetramerization catalysts. Activated by methylaluminoxane, the best ligand with 3,5-dimethylphenyl attached to N atom achieved selectivity as high as 86.13% (1-octene and 1-hexene) and catalytic activity up to 4.98×10^6 g/mol Cr h toward 1-octene. It was established that the increase of *m*-substitution steric bulk in the aryl skeleton led to a dramatic increase of catalytic activity. Interestingly, with the increase of steric bulk in the *o*-substitution of the aryl ring, the catalytic activity declined and the selectivity of the catalyst changed from predominant tetramerization to trimerization. It was concluded that fine tuning of the *N*-aryl moiety of the PNP ligand in molecular structure is essential for obtaining efficient catalysis of ethylene tetramerization.

Keywords: Linear α-olefins; Ethylene tetramerization; 1-Octene; Bisphosphineamine ligands

1. Introduction

Selective trimerization of ethylene to 1-hexene and selective tetramerization of ethylene to 1-octene are highly desirable because they would avoid the production of unwanted olefins that conventional transition metal oligomerization processes produce. The first process for the selective production of 1-hexene has been recently commercialized by Chevron Phillips in its 47,000 metric tonnes/year 1-hexene plant in Mesaieed, Qatar [1]. Selective ethylene tetramerization has seen tremendous advances in recent years with the advent of high activity catalysts based on bisphosphineamine (PNP) chromium catalyst reported by the laboratory of Sasol [2]. Following this discovery, a considerable amount of effort has been dedicated to investigate the nature of the active species [3–8], to design new catalysts based on these types of ligands [9–13], to optimize reaction conditions, to select solvents, to understand mechanism of ethylene tetramerization and to develop novel cocatalysts [14–21]. Changing the nitrogen substituent from methyl to isopropyl or related secondary carbon derivatives improves the performance of catalyst. More recently Killian et al. [9] reported that addition of sufficient steric bulk to the *N*-phenyl group via *ortho*-alkyl substitution increased the combined 1-hexene and 1-octene selectivity. In this article, new ligands were designed and synthesized with different aryl-substituents on N atom (Fig. 1). The effects of ligand structure on ethylene tetramerization have been probed in depth.

2. Experimental

2.1. Materials

Alkyl-substituted aniline and $Cr(acac)_3$ were purchased from Aldrich and used as received. Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (China). Methylaluminoxane (MAO) solution (1.4 mol/L) in toluene was purchased from Albemarle Corp. (USA). Cyclohexane, dichloromethane and ethanol were dehydrated and degassed before use. All other chemicals were obtained commercially and used as received.

2.2. Preparation and characterization of PNP ligand

PNP ligands were synthesized through the reaction between aryl-amine and diphenylphosphine chloride according to the

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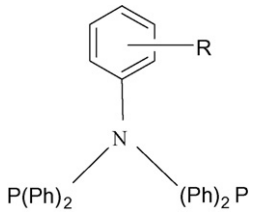

Fig. 1. The structure of diphosphinoamine ligands.

method described in the literature [18]. The results of analysis described in supporting information confirmed their structures.

2.3. Ethylene tetramerization

Ethylene tetramerization was processed in a 500 mL autoclave. After evacuation and flushing with nitrogen three times, then with ethylene two times, the autoclave was charged with 200 mL solvent and mechanically stirred under ambient ethylene atmosphere. When the desired reaction temperature was reached, quantitative MAO, PNP ligand, and $Cr(acac)_3$ were injected into the reactor. Typically 30 min later, the reaction solution was quickly cooled down to 20 °C and then quenched using ethanol/HCl (10 wt%). The catalytic activity was calculated from the increase of product mass.

2.4. Characterization of product

A small sample was washed by deionized water in order to remove alcohol, Cr(III), MAO and hydrochloric acid. The product was dried over anhydrous sodium carbonate and then analyzed by GC-MS using a HP-5890 with a HP-1 capillary column (30 m × 0.25 mm) and a HP-5971 mass spectroscopy. The sample was kept at 35 °C (10 min) and then heated at 10 °C/min until reaching 280 °C (remained for 10 min).

3. Results and discussion

Based on the reported results, a phenyl moiety seemed to be a suitable skeleton to probe the effect of substituents on the aryl groups which are in close vicinity to the *N* atom. This would provide the scope of optimizing the steric environment of the ligand with the aim of further enhancing catalyst activity and the selectivity to 1-octene.

3.1. Alkyl-substituted aryl PNP ligands

In order to maximize overall catalytic activity, we studied the influence of substituent position on catalytic activity and selectivity to 1-octene. The results of ethylene tetramerization are listed in Table 1. Different aryl substitution such as *ortho* (Entry 2) to *meta* (Entry 3) to *para* (Entry 4) gives out different productivity and selectivity of ethylene oligomerizaton. Aryl PNP ligand substituted by *meta*-methyl shows better catalytic activity than by *ortho* and *para* ones. The selectivities obtained with *para* are close to those obtained with the unsubstituted analogue (Entry 1). *ortho*-Substituted aryl ligand (Entry 2) gives poor activity, higher C_6 selectivities, higher by-products (including methylcyclopentane, methylenecyclopentane, C_{10} and higher fraction as well as solids) selectivities and lower 1-C_8 selectivities.

3.2. ortho-Substitute aryl PNP ligands

It was observed from Table 2 that increasing the bulk of 2-position substituent of the *N*-aryl moiety lead to the decrease of catalytic activity and the selectivity to 1-octene, and the increase of the selectivity to 1-hexene. The big sterically hindered ligands favored the formation of 1-hexene over 1-octene (selectivity toward 1-octene drops from 56.90% to 43.25% when substitute changes from 2-methyl to 2-isopropyl). This is consistent with the results reported by Killian et al. [8]. Further research showed that the catalyst exhibited the lowest catalytic productivity, the lowest selectivity to 1-octene when increasing the steric bulk of aryl-PNP ligands using *iso*-propyl substituents on the 2- and 6-positions of the *N*-aryl. Based on the above results, one may conclude that the changes of selectivity are primarily due to the variety of ligand steric hinderance. With the increase of *ortho*-substituent aryl steric bulky, the selectivity of the catalyst turned from predominant tetramerization to selective trimerization.

3.3. meta-Substitute aryl PNP ligands

We also investigated the effect of *N*-aryl's *meta*-substitutent on the catalytic behavior of ethylene tetramerization. The results

Table 1
Effects of methyl position in the *N*-aryl of ligand on catalytic activity and product selectivity[a]

Entry	R	Activity[b]	Product selectivity (wt%)							
			1-$C_4^=$	1-$C_6^=$	C_6H_{12}[c]	C_6H_{10}[d]	1-$C_8^=$	>1-C_{10}	1-$C_6^=$ + 1-$C_8^=$	PE
1	H	1.74	1.35	14.68	4.25	4.92	68.54	2.96	83.22	3.3
2	2-Methyl	1.42	1.62	23.71	5.11	5.59	56.9	2.27	80.61	4.8
3	3-Methyl	2.66	1.84	17.22	4.61	5.26	66.48	1.69	83.7	2.9
4	4-Methyl	2.09	1.54	15.35	4.89	5.08	69.25	1.79	84.6	2.1

[a] Reaction conditions: reaction temperature, 60 °C; ethylene pressure, 3.0 MPa; reaction time, 60 min.; solvent, cyclohexane; Cr(III)/PNP/MAO = 1:1:300.
[b] (10^6 g/mol Cr h).
[c] Methylcyclopentane.
[d] Methylenecyclopentane. 1-$C_8^=$ is the percentage 1-octene in the reaction mixture. Similarly this notation applies to the rest of the carbon fractions in the reaction mixture.

Table 2
Effects of 2-position substitutent in *N*-aryl ligand on catalytic activity and product selectivity[a]

Entry	R	Activity[b]	Product selectivity (wt%)							
			1-$C_4^=$	1-$C_6^=$	C_6H_{12}[c]	C_6H_{10}[d]	1-$C_8^=$	>1-C_{10}	1-$C_6^=$ + 1-$C_8^=$	PE
1	H	1.74	1.35	14.68	4.25	4.92	68.54	2.96	83.22	3.3
5	2-Methyl	1.42	1.62	23.71	5.11	5.59	56.90	2.27	80.61	4.8
6	2-Ethyl	1.22	0.91	29.41	3.84	4.07	53.6	2.07	83.01	6.1
7	2-Isopropyl	1.11	1.26	30.3	4.19	5.03	43.25	6.67	73.55	9.3
8	2,6-Diisopropyl	0.48	14.84	40.66	10.77	–	16.94	4.29	57.6	12.5

[a] Reaction conditions: reaction temperature, 60 °C; ethylene pressure, 3.0 MPa; reaction time, 60 min.; solvent, cyclohexane; Cr(III)/PNP/MAO = 1:1:300.
[b] (10^6 g/mol Cr h).
[c] Methylcyclopentane.
[d] Methylenecyclopentane.

Table 3
Effects of *meta*-substitute aryl PNP ligands on catalytic activity and product selectivity[a]

Entry	R	Activity[b]	Product selectivity (wt%)							
			1-$C_4^=$	1-$C_6^=$	C_6H_{12}[c]	C_6H_{10}[d]	1-$C_8^=$	>1-C_{10}	1-$C_6^=$ + 1-$C_8^=$	PE
1	H	1.74	1.35	14.68	4.25	4.92	68.54	2.96	83.22	3.3
9	3-Methyl	2.66	1.84	17.22	4.61	5.26	66.48	1.69	83.7	2.9
10	3-Ethyl	3.54	1.52	14.25	4.08	4.69	71.19	1.17	85.44	3.1
11	3,5-Dimethyl	4.98	1.62	13.16	4.76	5.41	70.97	0.58	86.13	1.5

[a] Reaction conditions: reaction temperature, 60 °C; reaction pressure, 3.0 MPa; reaction time, 60 min; solvent, cyclohexane; Cr(III)/PNP/MAO = 1:1:300(molar ratio).
[b] (10^6 g/mol Cr h).
[c] Methylcyclopentane.
[d] Methylenecyclopentane.

are shown in Table 3. It was found that the increase of *meta*-substituted *N*-aryl ligand size led to an increase in both catalytic activity and 1-octene selectivity. However, the selectivity to 1-hexene declined. The research results obtained by introducing two methyl groups (in the 3 and 5 positions) are consistent with the aforementioned trend. This unexpected behavior could be attributed to the steric considerations which play an important role in determining the reaction product selectivity.

4. Conclusions

The Cr catalyzed tetramerization of ethylene using PNP ligands with different aryl substituents attached to the N atom were systematic studied. The results showed that the oligomerization product selectivity is primarily dependent on the structure and size of aryl. It was revealed that addition of appropriate steric bulk to the *N*-aryl group via *meta*-alkyl substitution increased the productivity up to 4.98×10^6 g/mol Cr h. Addition of sufficient steric bulk to the *N*-aryl group via *ortho*-alkyl substitution decreased the catalytic activity, the selectivity of the catalyst changed from predominant tetramerization to trimerization. The fine tuning of the *N*-aryl moiety of the PNP ligand in molecular structure is essential for obtaining efficient tetramerization catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.10.009.

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