

Review

# The effect of halide and the coordination geometry of chromium center in homogeneous catalyst system for ethylene trimerization

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## Abstract

In homogeneous chromium-based catalyst system [Cr(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/halide], the effect of halide compound to 1-hexene formation selectivity and catalytic activity was investigated. The comparative studies showed that the promotion effect of a chloride was much better than that of a corresponding fluoride or bromide and the best kind of halides is multi-chloro compound which shows significant promotion effect to assist chromium center to achieve high 1-hexene formation selectivity and highly catalytic activity. In catalyst system, facial coordination geometry of chromium center is much more favorable for ethylene trimerization than meridional coordination geometry. The effect of halide could be interpreted well from the stabilization on facial geometry of chromium complex through the coordination of halo group with chromium center in some specific ways. Under the guide of the roles proposed on halide component, a new catalyst system [Cr(2-ethylhexanoate)<sub>3</sub>/2,5-dimethylpyrrole/AlEt<sub>3</sub>/2-fluoro-6-chloro- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trichlorotoluene] was developed successfully, demonstrating both high 1-hexene formation selectivity and highly catalytic activity.

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**Keywords:** Ethylene; 1-Hexene; Chromium; Trimerization; Chloride

## 1. Introduction

The properties of linear low density polyethylene (LLDPE) prepared by using 1-hexene as comonomer [1–5] is much superior to the properties of LLDPE prepared by using 1-butene as comonomer, resulting in the development of high quality LLDPE largely based on the development of 1-hexene production. It is well known that the conventional ethylene oligomerization processes, such as Shell Higher Olefins Process by using nickel/phosphine catalyst [6], generally produce  $\alpha$ -alkenes with a broad Schulz–Flory distribution from which pure 1-hexene has to be separated by fractional distillation, therefore the ethylene selective trimerization process has much more economic significance to produce 1-hexene. So highly efficient and selective catalyst for ethylene trimerization to 1-hexene has attracted extensive interests and attention during the past decade.

Early in 1977, Union Carbide researchers, Manyik et al. [7], reported the first selective trimerization of ethylene to

1-hexene, which was then found to be an oligomeric by-product in ethylene polymerization catalyzed by homogeneous chromium-based catalyst system [chromium(III) tris(2-ethylhexanoate)/hydrolyzed tri-isobutylaluminum (TIBA)]. Soon after, Briggs [8,9] developed this catalyst system by introducing a donor ligand selected from dimethoxyethane, monoglyme, diglyme, triglyme and *o*-dimethoxybenzene, into a different type catalyst system [chromium(III) tris(2-ethylhexanoate)/donor ligand/hydrolysed tri-isobutylaluminum] which produces 1-hexene as majority product with 1-hexene formation selectivity values up to 74%, at the same time only a small amount of polyethylene is formed. Based on this interesting finding, Phillips Petroleum Company [10–19], Mitsubishi Chemical Corporation [20–24] and Sumitomo Chemical Company [25–27] have developed some catalyst systems for ethylene trimerization to 1-hexene by utilizing pyrrole or 2,5-dimethylpyrrole (DMP) as ligand. Particularly, the four-membered catalyst systems with halide compound having specific structure as promoters [23,24,26,27], such as catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/CCl<sub>4</sub>], have significantly improved catalytic activity and 1-hexene

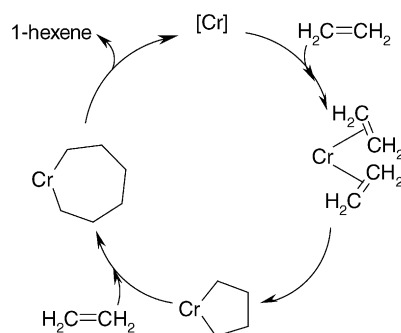
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formation selectivity with values over 90%, comparing with the corresponding three-membered catalyst system without halide promoter. Some chromium-based solid catalysts are also prepared and studied by supporting chromium(III) catalyst system on inorganic materials selected from silica [28], aluminophosphate and alumina [14,15] as supports. Recent advances on ethylene trimerization catalysts revealed that chromium(III) complexes of tridentate [29–36] ligands, in particular the tridentate ligands having tripod structure [31,34], are highly active and selective catalysts for ethylene trimerization to 1-hexene under the activation of methyl aluminoxane (MAO). Meanwhile, some ethylene trimerization catalysts based on titanium [37] and tantalum [38,39] have been developed, although generally displaying lower catalytic activity and selectivity than chromium-based catalyst system.

Among all the chromium-based catalyst systems reported up to now, from industrial view, the most notable catalyst system is the four-membered catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/ $\text{AlEt}_3$ /halide compound] because of its three strong points: (1) the four-membered catalyst system has high selectivity and highly catalytic activity for ethylene trimerization to 1-hexene; (2) the ligand, pyrrole or 2,5-dimethylpyrrole, is much simpler and cheaper than tridentate ligands; (3)  $\text{AlEt}_3$  is much cheaper and more readily available than methyl aluminoxane (MAO) which is the essential cocatalyst for chromium/(tridentate ligand) catalyst. Therefore it is necessary to study this four-membered catalyst system intensively and systematically in order to accelerate the step for industrialization.

Among the four-membered catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/ $\text{AlEt}_3$ /halide compound], the halide promoter plays an important role to assist chromium center to achieve high 1-hexene formation selectivity and highly catalytic activity. Although generally most halides could improve the catalytic activity and selectivity, so far, only a few of them were found to improve both 1-hexene formation selectivity and catalytic activity markedly, such as  $\text{CHCl}_2\text{CHCl}_2$ ,  $\text{CCl}_3\text{CCl}_3$  and  $\text{CCl}_4$ . Therefore it is important to screen more halides to optimize the halide promoter to form new four-membered catalyst system having both high 1-hexene formation selectivity and highly catalytic activity.

In order to interpret the high 1-hexene formation selectivity of chromium-based catalyst system, Briggs [8] proposed a unique catalytic 1-hexene formation cycle (see Scheme 1) involving a chromacyclopentane intermediate and a chromacycloheptane intermediate, which have not been defined yet. While a chromacycloheptane [40] complex was prepared as a model compound to support the chromacycloheptane intermediate containing catalytic mechanism. However, it did not demonstrate the selective ethylene trimerization activity probably due to the rigidity and stability of the chromacycloheptane compound with the specific amino-substituted cyclopentadienyl ligand, but



Scheme 1. Catalytic cycle for ethylene trimerization proposed by Briggs.

showed efficient ethylene polymerization activity under mild conditions.

Based on the proposed catalytic cycle for ethylene trimerization shown in Scheme 1, recently, Yang et al. [41] studied the promotion effect of chloro compound to 1-hexene formation selectivity and catalytic activity in homogeneous [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/ $\text{AlEt}_3$ /chloro compound] catalyst system. They proposed that 1-hexene formation selectivity enhancement of chloro compound was due to the coordination of chloro group with chromium center in chromacyclopentane intermediate, thus chloro compounds could prevent the coordination of 1-hexene with chromium center, by this way the decene selectivity decreased, which resulted in the significant increase of the 1-hexene formation selectivity, but this could not interpret why the 1-butene selectivity is also decreased besides the decrease of decene selectivity when halide compound is used. Furthermore, in most cases, 1-butene selectivity is even lower than decene selectivity. More importantly, along with this consideration, chloro group can also prevent the coordination of ethylene with chromium center in chromacyclopentane intermediate to produce chromacycloheptane by ring expansion, obviously this should cause the decrease of catalytic activity, but actually, some chloro compounds could increase the catalytic activity significantly. In order to interpret the promotion effect of chlorides on catalytic activity, they further proposed some specific interaction modes of chloro groups with dimeric  $\text{AlEt}_3$ , which is transferred by chloro groups to monomeric  $\text{AlEt}_3$  for the facile formation of active species in the catalytic system. Even if this proposal could interpret why 2,2-dichloropropane has higher promotion effect on catalytic activity than 1,2-dichloroethane, it could not interpret why multi-chloro compounds, such as 1,1,2,2-tetrachloroethane, hexachloroethane and tetrachloromethane, have much higher promotion effect on catalytic activity. Therefore it is more reasonable to interpret the promotion effect of chloro compound on both 1-hexene formation selectivity and catalytic activity from the interaction of chloro compound with chromium center.

In this paper, we propose a new interpretation to account for the significant promotion effect of multi-chloro compound for both 1-hexene formation selectivity and catalytic

activity from the coordination geometry of chromium center and its coordination fashions with chloro compound possibly forming some specific molecular complexes. Under the guide of the roles proposed on halide component, we found that 2-chloro-6-fluoro- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trichlorotoluene showed significant promotion effect for both 1-hexene formation selectivity and catalytic activity, thus a new catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AIEt<sub>3</sub>/2-chloro-6-fluoro- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trichlorotoluene] is formed with 1-hexene formation selectivity up to 92.1% and catalytic activity up to 243.8 kg 1-hexene/(g Cr.h).

## 2. Experimental

### 2.1. General considerations

All manipulations involving air-sensitive materials were carried out in a dry nitrogen atmosphere glovebox or using standard Schlenk line techniques under an atmosphere of dry nitrogen. Chromium(III) tris(2-ethylhexanoate) [abbreviation: Cr(2EH)<sub>3</sub>] was prepared according to a patent method [42]. AIEt<sub>3</sub> was purchased from Aldrich and was diluted to a heptane solution of 1 mmol/ml before use. 2,5-dimethylpyrrole was purchased from Aldrich. All the other normal chemicals involving pyrrole, heptane and halides were purchased from Beijing Chemical Corporation, all the normal chemicals were dried with 4 Å molecular sieves until water content was below 2 ppm. The purity of ethylene is above 99.99% with either O<sub>2</sub> content or water content below 1 ppm. The trimerization product was analyzed with gas chromatography using SE-52 30 m capillary column on HP5890II GC instrument.

### 2.2. General procedure for ethylene trimerization

The ethylene trimerization was performed in a 200 ml stainless-steel autoclave equipped with a magnetic drive

stirrer, a thermocouple, a pressure meter, a gas inlet, a gas outlet port and a liquid inlet chamber. Before reaction the autoclave was dried by heating at 100 °C under vacuum for 2 h. Meanwhile the autoclave was swept with dry nitrogen at least three times. After cooled to room temperature, the autoclave was swept with ethylene three times, then a mixture containing desired amount of pyrrole or 2,5-dimethylpyrrole, AIEt<sub>3</sub>, halide and *n*-heptane was forced into through liquid injection chamber, immediately 1.0 MPa ethylene was pressurized into. The autoclave was then allowed to be heated to 100 °C, at this point the *n*-heptane solution of desired chromium(III) tris(2-ethylhexanoate) was pressed into with 5.0 MPa ethylene. The ethylene trimerization was initiated immediately. After the trimerization was prolonged for 1 h, the autoclave was cooled down in ice water, vented and opened. The gas portion product and liquid portion product were analyzed with GC.

## 3. Results and discussion

### 3.1. Studies on the effect of halides of different types in ethylene trimerization

Based on the four-membered homogeneous chromium catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AIEt<sub>3</sub>/halide compound], in order to investigate the roles of halide compound, the effect of halides of three types on 1-hexene formation selectivity and catalytic activity of chromium catalyst was investigated, involving two fluorides, seven chlorides and one bromide. The results are shown in Table 1.

From Table 1, it can be concluded that all of the 10 halides can improve the 1-hexene formation selectivity and catalytic activity, although the improvement capacity of different halides varies in a wide range. In general, the improvement capacity of a chloride on the 1-hexene formation selectivity and catalytic activity is much better than that of a corresponding fluoride or bromide. For example,

Table 1  
The effect of halides on ethylene trimerization

Entry	Halide compound	Halide/Cr ( <i>n</i> )	Selectivity (wt.%)					Activity (kg 1-hexene/(g Cr.h))
			C <sub>4</sub> <sup>=</sup>	C <sub>6</sub> <sup>=</sup>	C <sub>8</sub> <sup>=</sup>	C <sub>10</sub> <sup>=</sup>	C <sub>12+</sub> <sup>=</sup>	
1	None	0	20.5	48.5	3.0	24.2	3.8	34.9
2	1-Fluorononane	10	19.0	57.3	5.7	15.7	3.0	40.5
3	1-Chlorobutane	10	4.8	78.0	1.2	13.5	2.5	60.8
4	1-Bromobutane	10	3.0	70.6	4.4	10.8	11.2	44.3
5	2,2-Dichloropropane	10	2.3	86.0	0.5	10.0	1.2	71.6
6	1,1,2,2-Tetrachloroethane (TCE)	10	0.5	91.0	0.4	7.6	0.5	186.7
7	Hexachloroethane (HCE)	10	0.4	95.0	0.4	4.0	0.2	161.5
8	$\alpha$ , $\alpha$ , $\alpha$ -Trifluorotoluene	10	20.1	60.2	1.4	13.0	5.3	48.6
9	$\alpha$ , $\alpha$ , $\alpha$ -Trichlorotoluene	10	8.2	80.0	1.1	9.1	1.6	136.2
10	Tetrachloromethane (TCM)	10	1.2	90.5	0.2	8.1	0.5	128.3
11	Tetrachlorogermanium	5	0.8	92.5	0.5	5.9	0.8	79.6

Reaction conditions: the trimerization was performed at 100 °C under 5.0 MPa ethylene pressure for 1 h using 80 ml *n*-heptane as solvent. In situ catalyst preparation was performed under ethylene ambience. Cr(2EH)<sub>3</sub>/2,5-DMP/AIEt<sub>3</sub> = 1:5:100 (molar ratio).

both the 1-hexene formation selectivity and catalytic activity of the catalyst system containing 1-chlorobutane (entry 3, 78.0%, 60.8 kg 1-hexene/(g Cr.h)) are better than the 1-hexene formation selectivity and catalytic activity of the catalyst system containing 1-fluorononane (entry 2, 57.3%, 40.5 kg 1-hexene/(g Cr.h)) or the 1-hexene formation selectivity and catalytic activity of the catalyst system containing 1-bromobutane (entry 4, 70.6%, 44.3 kg 1-hexene/(g Cr.h)); both the 1-hexene formation selectivity and catalytic activity of the catalyst system containing  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trichlorotoluene (entry 9, 80.0%, 136.2 kg 1-hexene/(g Cr.h)) are better than the 1-hexene formation selectivity and catalytic activity of the catalyst system containing  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trifluorotoluene (entry 8, 60.2%, 48.6 kg 1-hexene/(g Cr.h)). Together considering that the coordination ability of chloro group with chromium center might be stronger than the coordination ability of fluoro group but weaker than the coordination ability of bromo group [43], it might be suggested that the best improvement effect of chloride on both the 1-hexene formation selectivity and catalytic activity among the three type halides, is due to the suitable coordination ability with chromium center. By comparing the number of chloro substitutions contained in chloride molecule, it can be found that the improvements on both 1-hexene formation selectivity and catalytic activity of the catalyst system containing multi-chloro chloride are much higher than the 1-hexene formation selectivity and catalytic activity of the catalyst system containing mono-chloro chloride or di-chloro chloride. This effect might be due to the coordination geometry of multi-chloride halide with chromium center and will be discussed later in this paper. Among all the 10 halides, only 1,1,2,2-tetrachloroethane (entry 6), hexachloroethane (entry 7) and tetrachloromethane (entry 10) can improve both the 1-hexene formation selectivity and catalytic activity significantly.

### 3.2. Studies on the effect of halide/Cr molar ratio in ethylene trimerization

For homogeneous chromium-based catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/hexachloroethane], the halide/Cr molar ratio has significant effect on both 1-hexene formation selectivity and cat-

alytic activity. The results of studies on hexachloroethane/chromium molar ratio from 0 to 30 are listed in Table 2.

Table 2 shows clearly that, for the effect of HCE/Cr molar ratio on 1-hexene formation selectivity, with the increasing of HCE/Cr molar ratio from 0 to 10, the 1-hexene formation selectivity is increased quickly from 48.5% (entry 1) to 95.0% (entry 6), further increase on HCE/Cr molar ratio from 10 to 30 resulted in a little lose of 1-hexene formation selectivity which is decreased from 95.0% (entry 6) to 92.8% (entry 7); for the effect of HCE/Cr molar ratio on catalytic activity, with the increasing of HCE/Cr molar ratio from 0 to 6, the catalytic activity is increased more quickly from 34.9 kg 1-hexene/(g Cr.h) (entry 1) to 230.9 kg 1-hexene/(g Cr.h) (entry 4), but further increase on HCE/Cr molar ratio from 6 to 30 resulted in a dramatic loss of catalytic activity which is decreased quickly from 230.9 kg 1-hexene/(g Cr.h) (entry 4) to 82.1 kg 1-hexene/(g Cr.h) (entry 7).

### 3.3. Studies on ligand/Cr molar ratio in ethylene trimerization

The ligand/Cr molar ratio has also significant effect on 1-hexene formation selectivity and catalytic activity in chromium-catalyzed ethylene trimerization. The results are shown in Table 3.

Table 3 shows clearly that, without halide compound, when ligand/Cr molar ratio is at 3, the peak values for both the 1-hexene formation selectivity and catalytic activity are achieved (entry 2, 58.3%, 34.1 kg 1-hexene/(g Cr.h)), further increase on ligand/Cr molar ratio to 5 resulted in an evident decrease of both 1-hexene formation selectivity and catalytic activity (entry 3, 38.8%, 18.1 kg 1-hexene/(g Cr.h)); for the catalyst system containing hexachloroethane which is six molar times of chromium center, when ligand/Cr molar ratio is increased to 3, both the 1-hexene formation selectivity and catalytic activity reach high values (entry 5, 90.1%, 216.2 kg 1-hexene/(g Cr.h)). But within the subsequent increase of ligand/Cr molar ratio from 3 to 8, the 1-hexene formation selectivity and catalytic activity have relatively stable values (entry 5, 6, 7). This result will be interpreted in the following discussions.

Table 2  
The effect of hexachloroethane (HCE)/chromium molar ratio in ethylene trimerization

Entry	HCE/Cr ( <i>n</i> )	Selectivity (wt.%)					Activity (kg 1-hexene/(g Cr.h))
		C <sub>4</sub> =	C <sub>6</sub> =	C <sub>8</sub> =	C <sub>10</sub> =	C <sub>12+</sub> =	
1	0	20.5	48.5	3.0	24.2	3.8	34.9
2	2	9.7	78.0	1.4	9.5	0.4	136.5
3	4	5.4	83.9	1.4	8.8	1.0	184.7
4	6	2.0	92.3	0.9	5.3	0.0	230.9
5	8	0.8	93.2	0.4	5.4	0.2	214.4
6	10	0.4	95.0	0.4	4.0	0.2	161.5
7	30	1.0	92.8	0.3	5.8	0.1	82.1

Reaction conditions: the trimerization was performed at 100 °C under 5.0 MPa ethylene pressure for 1 h using 80 ml *n*-heptane as solvent. In situ catalyst preparation was performed under ethylene ambience. Cr(2EH)<sub>3</sub>/2,5-DMP/AlEt<sub>3</sub> = 1:5:100 (molar ratio).

Table 3  
The effect of ligand/Cr molar ratio in ethylene trimerization

Entry	Ligand/Cr (n)	HCE/Cr (n)	Selectivity (wt.%)					Activity (kg 1-hexene/(g Cr.h))
			C <sub>4</sub> =	C <sub>6</sub> =	C <sub>8</sub> =	C <sub>10</sub> =	C <sub>12+</sub> =	
1	1	0	56.1	24.1	5.2	7.5	7.1	2.4
2	3	0	17.7	58.3	1.8	21.0	1.2	34.1
3	5	0	48.0	38.8	2.9	5.2	5.1	18.1
4	1	6	8.0	76.0	0.8	14.0	1.2	83.6
5	3	6	1.2	90.1	0.6	6.3	1.8	216.2
6	5	6	2.0	92.3	0.4	5.3	0.0	230.9
7	8	6	4.5	91.4	0.3	3.7	0.1	221.2

Reaction conditions: the trimerization was performed at 100 °C under 5.0 MPa ethylene pressure for 1 h using 80 ml *n*-heptane as solvent. In situ catalyst preparation was performed under ethylene ambience. For entries 1–3, the ligand is pyrrole and Cr(2EH)<sub>3</sub>/AlEt<sub>3</sub>=1:60 (molar ratio); For entries 4–7, the ligand is 2,5-DMP, Cr(2EH)<sub>3</sub>/AlEt<sub>3</sub>/C<sub>2</sub>Cl<sub>6</sub> = 1:100:6 (molar ratio).

### 3.4. The roles of halide compound and the coordination geometry of chromium center

To account for the high 1-hexene formation selectivity, Briggs [8] has proposed a unique catalytic mechanism (see Scheme 1). The key of this mechanism is the two active species, chromacyclopentane intermediate and chromacycloheptane intermediate, which have not been defined up to now. Although a chromacycloheptane complex was prepared by Emrich et al. as a model compound [40] to support this unique mechanism. However, this model compound did not demonstrate the selective ethylene trimerization activity, but showed efficient ethylene polymerization activity under mild conditions.

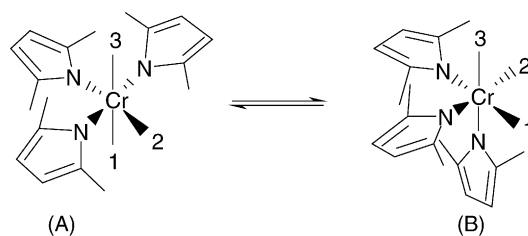
Based on the mechanism proposed by Briggs [8], Yang et al. [41] proposed that 1-hexene formation selectivity enhancement of chloro compound is due to the coordination of chloro group with chromium center in chromacyclopentane intermediate, thus chloro compounds could prevent the coordination of 1-hexene with chromium center, by this way the decene selectivity decreased, which resulted in the significant increase of the 1-hexene formation selectivity. But this could not interpret why the 1-butene selectivity is also decreased besides the decrease of decene selectivity when halide compound is used (see Tables 1 and 2). Furthermore, in most cases, 1-butene selectivity is even lower than decene selectivity. More importantly, along with this consideration, chloro group can also prevent the coordination of ethylene with chromium center in chromacyclopentane intermediate to produce chromacycloheptane by ring expansion, obviously this should cause the decrease of catalytic activity, but actually, some chloro compounds could increase the catalytic activity significantly. In order to interpret the promotion effect of chlorides on catalytic activity, Yang et al. [41] further proposed some specific interaction modes of chloro groups with dimeric AlEt<sub>3</sub>, which is transferred by chloro groups to monomeric AlEt<sub>3</sub> for the facile formation of active species in the catalytic system. Even though this proposal could interpret why 2,2-dichloropropane has higher promotion effect on catalytic activity than 1,2-dichloroethane, it could not interpret why multi-chloro compounds, such

as 1,1,2,2-tetrachloroethane, hexachloroethane and tetrachloromethane, have much higher promotion effect on catalytic activity. Therefore it is more reasonable to interpret the promotion effect of chloro compound on both 1-hexene formation selectivity and catalytic activity from the interaction of chloro compound with chromium center.

It is well known that halo-bridges are widely exist in metallic halides, and this kind of halo-bridges play an important role on the basic properties of the corresponding metallic halide. In order to elucidate the effects of the halide compound in the four-membered catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/halide compound], we suggest that the effects of halide compound in ethylene trimerization are arisen by coordination with chromium center to regulate the coordination fashion of chromium species and to make the coordination geometry of chromium center more suitable for ethylene trimerization.

Although the active intermediate of chromium-based catalyst system in ethylene trimerization has not been defined, it is believed that the chromium center is octahedrally six-coordinated, three of which are occupied by donor ligands, the other three coordination sites are provided for ethylene trimerization [32,33,36]. Therefore chromium center has two coordination fashions, one is meridional coordination fashion, another is facial coordination fashion, which can be converted to each other (Scheme 2).

When tridentate ligands having tripod structure are used instead of 2,5-dimethylpyrrole, only complex in facial coordination fashion is formed, catalytic studies showed that this kind of catalyst demonstrated high 1-hexene formation



Scheme 2. Meridional fashion (A) and facial fashion (B) of chromium species.

selectivity and highly catalytic activity for ethylene trimerization without the assist of halide [31,34]. For some conformationally flexible tridentate ligands, although some catalyst precursors of tridentate ligands is in meridional fashion, it is believed that in the active catalyst species, the ligand is coordinated with chromium center in a facial coordination geometry [32,33] because of the flexibility of the tridentate ligand. When planar conformationally restricted tridentate ligand is used, such as 2,6-bis(imino)pyridyl ligand, only [2,6-bis(imino)pyridyl]CrCl<sub>3</sub> complex in meridional coordination fashion is formed. In this case, chromium catalyst showed no ethylene trimerization activity, but demonstrated highly catalytic activity for ethylene polymerization [44]. Therefore here we propose that chromium species in facial coordination geometry is much more favorable for ethylene trimerization than chromium species in meridional coordination geometry.

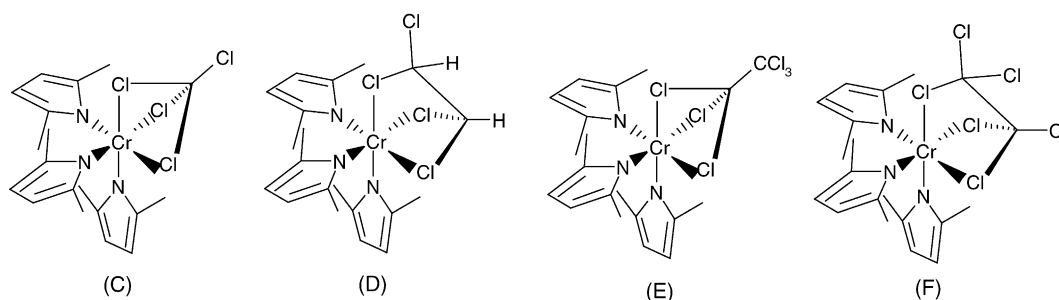
For the catalyst systems studied in this paper, only 0.2–0.5% polymer was produced. Because the route to form polymer is different from the route to form 1-hexene, it might suggest that, in catalyst system with halide compound, the number of chromium species in meridional fashion (A) is less than the number of chromium species in facial fashion (B), and its catalytic activity for ethylene polymerization was low.

Comparing the modular structure between meridional coordination fashion (A) and facial coordination fashion (B) revealed that the special steric hindrance among the three 2,5-dimethylpyrrole ligands in meridional fashion (A) is much lower than the special steric hindrance among the three 2,5-dimethylpyrrole ligands in facial fashion (B), resulting in meridional fashion (A) in lower energy state and more stable than facial fashion (B), therefore it is possible that the number of chromium species in meridional fashion (A) is more than the number in facial fashion (B) in a homogeneous catalyst system without halide compound. In meridional fashion (A), the coordination site 1 or site 3 of chromium center is screened by three methyl groups from three 2,5-dimethylpyrrole ligands, only coordination site 2 is exposed and could easily be coordinated with halo group or ethylene. However, in facial fashion (B), all of the three coordination sites 1–3 are exposed and could easily be coordinated with halo group or ethylene. In general, either

meridional fashion (A) or facial fashion (B) could be stabilized by coordination with halo group or ethylene, furthermore, facial fashion (B) could be stabilized in larger extent than meridional fashion (A) because facial fashion (B) has three coordination sites to be exposed and easily to be coordinated. So under the stabilization of halide, the number of chromium species in facial fashion (B) would be increased while the number of chromium species in meridional fashion (A) would be decreased. All the 10 halides in Table 1 could stabilize facial fashion (B) by coordination of halo group with chromium center, therefore all the 10 halides could increase the 1-hexene formation selectivity. The coordination of halo group with chromium center should be reversible and halo group could easily be replaced by ethylene for trimerization. The result in Table 1 might suggest that the coordination of chloro group with chromium center is most suitable among three halo groups. The coordination of fluoro group with chromium center might be too weak, while the coordination of bromo group with chromium center might be too strong and the catalyst is poisoned slightly comparing with chloride. This also might be the reason when sulfur and triphenylphosphine [41] were used, the 1-hexene formation selectivity was increased efficiently, but the catalytic activity was decreased slightly.

Comparing with mono-chloro and di-chloro compounds, multi-chloro compound has more opportunities to coordinate with chromium center, particularly multi-chloro compound could occupy the three coordination sites 1–3 in facial fashion (B) which is to be stabilized more efficiently. This might be the reason why multi-chloro compounds could improve both the 1-hexene formation selectivity and catalytic activity more significantly.

The possible coordination structures of tetrachloromethane, 1,1,2,2-tetrachloroethane and hexachloroethane with chromium center in facial fashion (B) are shown in Scheme 3. Considering the coordination structure between chlorides and chromium center, tetrachloromethane could coordinate with chromium through three chloro-bridged four-membered rings to form possible molecular complex (C). In a similar way, 1,1,2,2-tetrachloroethane could coordinate with chromium through one chloro-bridged four-membered ring and two chloro-bridged five-membered rings to form possible molecular complex (D). The structural



Scheme 3. Possible coordination structure of chromium with tetrachloromethane (C), 1,1,2,2-tetrachloroethane (D) and hexachloroethane (E) (F).

Table 4  
Mathematical permutation and combination result from facial geometry chromium species

Coordination site			Estimated product	Product ratio
1	2	3		
CD <sub>2</sub> CD <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	C <sub>6</sub> D <sub>12</sub>	1
CD <sub>2</sub> CD <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> D <sub>8</sub> H <sub>4</sub>	3
CD <sub>2</sub> CD <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	C <sub>6</sub> D <sub>8</sub> H <sub>4</sub>	
CH <sub>2</sub> CH <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	C <sub>6</sub> D <sub>8</sub> H <sub>4</sub>	
CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	C <sub>6</sub> D <sub>4</sub> H <sub>8</sub>	3
CH <sub>2</sub> CH <sub>2</sub>	CD <sub>2</sub> CD <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> D <sub>4</sub> H <sub>8</sub>	
CD <sub>2</sub> CD <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> D <sub>4</sub> H <sub>8</sub>	
CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>12</sub>	1

difference between (C) and (D) might be the reason why 1,1,2,2-tetrachloroethane has better improvement on catalytic activity than tetrachloromethane, although these two chlorides have the same number of chloro groups in molecular structure.

Hexachloroethane could coordinate with chromium in two ways to form possible molecular complexes (E) and (F). For coordination structure, complex (E) is close to (C), complex (F) is close to (D). Because hexachloroethane has the most opportunities to coordinate with chromium center, it shows the best improvement effect on both 1-hexene formation selectivity and catalytic activity among the 10 halides in Table 1.

Recently, Agapie et al. [36], reported that trimerization of a 1:1 mixture of C<sub>2</sub>D<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> catalyzed by chromium catalyst produced only C<sub>6</sub>D<sub>12</sub>, C<sub>6</sub>D<sub>8</sub>H<sub>4</sub>, C<sub>6</sub>D<sub>4</sub>H<sub>8</sub> and C<sub>6</sub>H<sub>12</sub> in a 1:3:3:1 ratio. Interestingly, this ratio is consistent with the mathematical permutation and combination result from the three coordination sites of facial fashion (B) in Scheme 2 (see Table 4). This consistency may suggest that, every three ethylene molecules are coordinated with the three coordination sites 1–3 in facial geometry, and are converted to 1-hexene through a certain specific route. While the exact nature of the active catalytic species and the detailed mechanism of ethylene trimerization are not defined, therefore still remain to be elucidated through further research.

### 3.5. Interpretation to the effect of hexachloroethane (HCE)/Cr molar ratio and the effect of ligand/Cr molar ratio in ethylene trimerization

With the roles of halide in ethylene trimerization proposed in Section 3.4, the effect of hexachloroethane (HCE)/Cr molar ratio (see Table 2) and the effect of ligand/Cr molar ratio (see Table 3) in ethylene trimerization can be interpreted well.

Hexachloroethane could stabilize facial coordination fashion (B) of chromium center (see Scheme 2) through coordination with chromium center to form possible molecular structures (E) and (F) (see Scheme 3), therefore hexachloroethane could enhance 1-hexene formation selectivity and catalytic activity significantly. In Table 2, when HCE/Cr

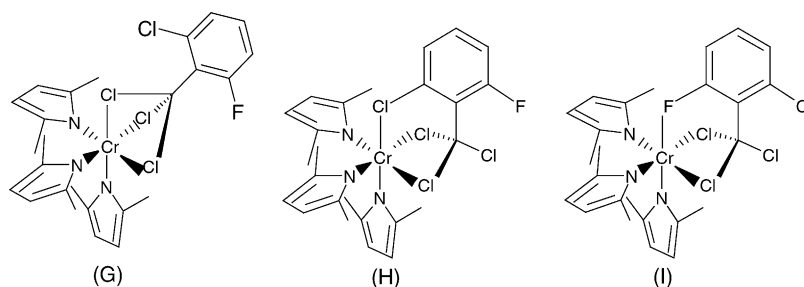
molar ratio was increased from 0 to 6, 1-hexene formation selectivity was increased quickly from 48.5 to 92.3%. Because when HCE/Cr molar ratio was at 6, the amount of hexachloroethane was enough to stabilize facial coordination fashion (B) to assist chromium center to achieve high 1-hexene formation selectivity, further increase of HCE/Cr molar ratio from 6 to 30 showed no evident effect on 1-hexene formation selectivity, which remained a relatively stable value. Meanwhile, when HCE/Cr molar ratio was increased from 0 to 6, the catalytic activity was increased more quickly from 34.9 to 230.9 kg 1-hexene/(g Cr.h). Because too much hexachloroethane could prevent the coordination of ethylene with chromium center, further increase on HCE/Cr molar ratio from 6 to 30 resulted in dramatic decrease of catalytic activity, which is decreased quickly from 230.9 to 82.1 kg 1-hexene/(g Cr.h). So the effect of HCE/Cr molar ratio in ethylene trimerization is interpreted well.

In Table 3, without halide compound, the peak values of 1-hexene formation selectivity and catalytic activity were achieved when ligand/Cr molar ratio was at 3, more ligand will occupy the coordination sites 1–3 in facial fashion (B) (see Scheme 2) to make the catalyst being deactivated. Therefore when ligand/Cr molar ratio was increased from 3 to 5, both 1-hexene formation selectivity and catalytic activity were decreased. Hexachloroethane could coordinate with chromium center to form possible molecular complexes (E) and (F), therefore it can prevent excess ligand to coordinate with chromium center on coordination sites 1–3, so further increase on ligand/Cr molar ratio from 3 to 8 caused no evident effect on both 1-hexene formation selectivity and catalytic activity, which remained relatively stable values. Therefore the effect of ligand/Cr molar ratio in ethylene trimerization is interpreted well.

### 3.6. The development of new catalyst system by using ortho-halo- $\alpha$ , $\alpha$ , $\alpha$ -trihalotoluene as promoter

Under the guide of the roles of halide compound proposed in Section 3.4, we thought of ortho-halo- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trihalotoluene which may form molecular coordination complexes in a similar but different way comparing with hexachloroethane (see Scheme 4) therefore it could be potential efficient promoter for chromium-catalyzed ethylene trimerization, which was proved to be correct by ethylene trimerization results. The corresponding four-membered chromium-based catalyst system has high 1-hexene formation selectivity and catalytic activity (Table 5).

Table 5 shows clearly that all the four o-halo- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trihalotoluene halides demonstrate efficient promotion effect on both 1-hexene formation selectivity and catalytic activity. When fluoro groups are replaced by chloro groups gradually from 2-fluoro- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trifluorotoluene (entry 2) to 2-chloro- $\alpha$ ,  $\alpha$ ,  $\alpha$ -trichlorotoluene (entry 4), both the 1-hexene formation selectivity and catalytic activity were increased quickly, indicating that the effect of a chloride is better than the effect of a corresponding fluoride.

Scheme 4. Possible molecular complexes of chromium with 2-fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene.Table 5  
Ethylene trimerization results with *o*-halo- $\alpha, \alpha, \alpha$ -trihalotoluene containing catalyst system

Entry	Halides	Selectivity (wt.%)					Activity (kg 1-hexene/(g Cr.h))
		C <sub>4</sub> <sup>=</sup>	C <sub>6</sub> <sup>=</sup>	C <sub>8</sub> <sup>=</sup>	C <sub>10</sub> <sup>=</sup>	C <sub>12+</sub> <sup>=</sup>	
1	None	20.5	48.5	3.0	24.2	3.8	34.9
2	2-Fluoro- $\alpha, \alpha, \alpha$ -trifluorotoluene	26.0	62.9	2.1	9.0	0.0	64.0
3	2-Fluoro- $\alpha, \alpha, \alpha$ -trichlorotoluene	1.3	85.8	0.7	10.4	1.8	140.7
4	2-Chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene	0.5	88.5	0.4	10.2	0.4	146.7
5	2-Fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene(FCTCT)	1.0	92.1	0.3	5.0	1.6	243.8
6	Hexachloroethane (HCE)	0.4	95.0	0.4	4.0	0.2	161.5

Reaction conditions: the trimerization was performed at 100 °C under 5.0 MPa ethylene pressure for 1 h using 80 ml *n*-heptane as solvent. In situ catalyst preparation was performed under ethylene ambience. Cr(2EH)<sub>3</sub>/2,5-DMP/AlEt<sub>3</sub>/halide = 1:5:100:10 (molar ratio).

This result is consistent with that deduced from Table 1. Among the four halides in Table 5, 2-fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene (FCTCT) is the best one for both 1-hexene formation selectivity and catalytic activity (entry 5, 92.1%, 243.8 kg 1-hexene/(g Cr.h)) because it has most opportunities to coordinate with chromium center (see Scheme 4). Comparing with the catalyst system containing hexachloroethane, which is the best halide found by other researchers (entry 6, 95.0%, 161.5 kg 1-hexene/(g Cr.h)), the catalyst system containing 2-fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene shows only slightly lower 1-hexene formation selectivity, but much higher catalytic activity, may be due to the structural difference between the possible molecular complexes of this two halides with chromium center (Schemes 3 and 4). The main structural difference is that the molecular complex (H) of 2-fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene has two chloro-bridged six-membered rings, while the molecular complex (F) of hexachloroethane has two chloro-bridged five-membered rings. In summary, a highly efficient catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/FCTCT] was developed successfully.

#### 4. Conclusions

In the homogeneous chromium-based catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/halide compound], suitable halide compound could significantly enhance the 1-hexene formation selectivity and catalytic activity in ethylene trimerization. The comparative

studies showed that the promotion effect of a chloride is much better than that of a corresponding fluoride or bromide; and the best kind of halide is multi-chloro compound which shows significant promotion effect to assist chromium center to achieve high 1-hexene formation selectivity and highly catalytic activity. In catalyst system, facial coordination geometry of chromium complex is much more favorable for ethylene trimerization than meridional coordination geometry. The effect of halide compound can be interpreted well from the stabilization on facial geometry complex through the coordination of halo group with chromium center in some specific ways. Under the guide of the roles proposed on halide component in ethylene trimerization, a new catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethylpyrrole/AlEt<sub>3</sub>/2-fluoro-6-chloro- $\alpha, \alpha, \alpha$ -trichlorotoluene] having both high 1-hexene formation selectivity and highly catalytic activity, was developed successfully.

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