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Communication

Heteroscorpionate bis-pyrazolyl ligands in Cr(III)-catalyzed ethylene oligomerization

Mingfang Zheng [a], Hongfei Wu [a], Xuejun Zhang [b], Jun Zhang [b, *]

[a] Yanshan Branch, Beijing Research Institute of Chemical Industry, SINOPEC, Beijing 102500, China
[b] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237, China

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ABSTRACT

We have investigated Cr(III) catalysts supported by the bis-pyrazoyl ligands containing a range of appendices from heteroaryl groups, such as quinolinyl, furanyl, and thiopheneyl, to hydroxy-containing groups such as carboxyl and hydroxyl. These catalysts, upon activation with MAO, are active for ethylene oligomerization. The Cr precatalyst supported by the bis-pyrazolyl ligand with thiopheneyl achieved a activity of 29.8 kg/(g Cr/h) with a total selectivity of 58.5% toward 1-hexene and 1-octene. The complexation reaction of carboxyl-containing ligand with $Cr(THF)_3Cl_3$ gave an acetoxychromium(III) chloride through the HCl elimination.

1. Introduction

Over the last two decades, to meet high growth in the end-user applications industry for 1-hexene and 1-octene, the selective ethylene tri- and tetramerization have been paid a great deal of attention from both the academic and industrial communities [1]. Since this was first observed with Cr catalysts in 1977 [2], only a few highly active and selective catalysts for ethylene trimerization have been established [3], including the Phillips pyrrolide [3a,3b], the BP diphosphinoamine [3c], and the Sasol mixed heteroatomic systems [3d]. Other diphosphine ligands [4] and P,N-ligands [5] were also been developed to support the Cr-based ethylene trimerization catalysts. In 2004, the researchers from Sasol first reported a Cr-based ethylene tetramerization catalyst by modification of the BP diphosphinoamine (PNP) ligand, giving an 1-octene selectivity up to 70% [6]. Stimulated by the results, an ever increasing number of publications and patents have been reported for the selective ethylene tri- and tetramerization, among which a variety of new ligands have been developed for this purpose [7].

The novel PNPNHP ligands bearing a protic nitrogen linked to the nitrogen backbone of the typical PNP ligands have been found to be efficient to support Cr catalysts in ethylene trimerization when using alkylaluminium as cocatalysts, probably due to the presence of a reactive protic nitrogen, which could react with the alkylaluminium activator [8]. The concept was also extended to the use of hydroxy moieties with other phosphine ligands [9]. In 2008, one of us, Hor, and Braunstein et al. have developed Cr(III) catalytic systems supported by either heteroscorpionate pyrazolyl ligands of the type **A** (X = O, S, NR′) with [NNO], [NNS], or [NNN] donor sets or those of the type **B** bearing a third donor group altered between pyrazolyl, pyridyl and imidazolyl (Fig. 1), exhibiting excellent selectivity (up to 98 wt%) for ethylene trimerization [10]. As part of our long-standing interest in the design and synthesis of new ligands for selective ethylene oligomerization catalysis, we have recently developed asymmetric carbon-bridged diphosphine ligands [11] and a family of asymmetric PNPO ligands bearing a phenol moiety [12] for supporting the Cr catalysts. Herein, we present further the structural adaptation of the bis-pyrazoyl motif through the introduction of a range of appendices, from heteroaryl groups, such as quinolinyl, furanyl, and thiopheneyl, to hydroxy-containing groups such as carboxyl and hydroxyl (**C** and **D**, Fig. 1). The bis-pyrazoyl ligands of type **C** are first reported. The effect of the ligands on ethylene trimerization is demonstrated. Isolation of an acetoxychromium chloride ligated by the bis-pyrazoyl motif through the HCl elimination is also presented.

* Corresponding author.
E-mail address: zhangj@ecust.edu.cn (J. Zhang).

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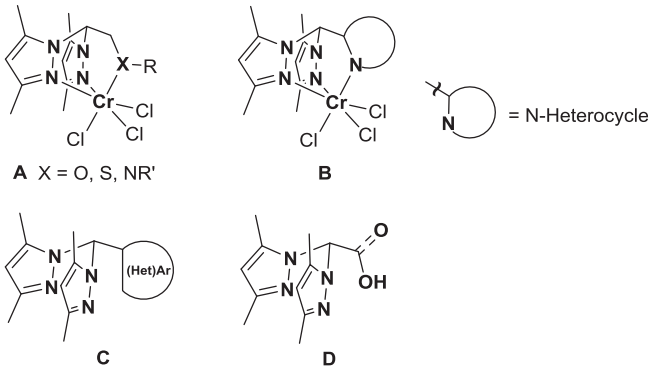


Fig. 1. Selected bis-pyrazolyl ligands for selective ethylene oligomerization.

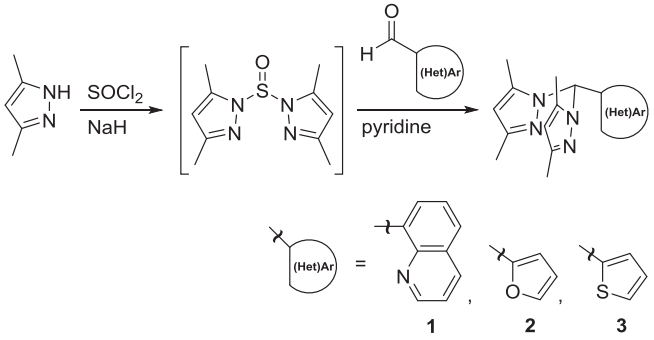
2. Results and discussion

Avoiding the use of dangerous phosgene, we have synthesized the new ligands **1**~**3** in 39–75% yields, by a modified method [13], from a condensation reaction of the corresponding aldehydes with $(Pz')_2S{=}O$ (from thionyl chloride) (Scheme 1). The hydroxy-containing ligands **4**~**6** and were known compounds and prepared by the literature methods [14–16]. For comparison, the ligand **7** having a third ester donor was also synthesized according to the known procedure [17] (Fig. 2).

The ligands **1**~**7** were examined for ethylene oligomerization in conjunction with chromium source upon activation with MAO, and the results are summarized in Table 1.

At 35 bar ethylene and 60 °C and in the presence of 600 M excess of MAO, all of the Cr precatalysts supported by the dipyrazolyl ligands (**1**~**7**) were reactive in ethylene oligomerization reaction. Among the ligands **1**~**3** bearing a third heteroaryl groups, **3** having a thiopheneyl group achieved better result, exhibiting the highest activity with a 55.4% total selectivity toward 1-hexene and 1-octene (Table 1, entries 1–3). Furanyl-containing **2** achieved a highest total selectivity of up to 68% toward 1-hexene and 1-octene, but gave a low activity (Table 1, entry 2). It is notable that the Cr catalysts supported by the ligands **1**~**3** show much lower selectivities toward ethylene oligomerization than those bipyrazolyl Cr catalysts bearing a pyrazolyl, pyridyl, or imidazolyl group, which implies subtle differences in the ligand structure dramatically influences the catalytic behavior.

Compared with the hydroxy-containing ligand **5**, the carboxyl-containing ligand **4** exhibited higher activity and similar selectivity toward 1-hexene and 1-octene (Table 1, entries 4 and 5). Introduction of two phenyl groups in the hydroxy-containing **5** resulted in a dramatic decrease in activity (Table 1, entry 6). Disappointedly, upon activation with triethylaluminium either the



Scheme 1. Synthesis of bis-pyrazolyl ligands **1**~**3**.

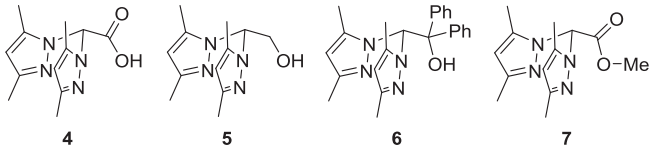


Fig. 2. Selected bis-pyrazolyl ligands **4**~**7**.

carboxyl-containing **4** or the hydroxy-containing **5** and **6** didn't show reactivity toward ethylene oligomerization, although all of them have a reactive hydroxyl group. Compared with the carboxyl-containing ligand **4**, the catalyst supported by the ester-containing ligand **7** showed lower activity and similar selectivity (Table 1, entries 4 and 7).

Ligand **3** having a thiopheneyl group achieved the highest activity with a considerable total selectivity toward 1-hexene and 1-octene, and were then selected for further investigation under different reaction condition to improve the catalyst performance. Increasing the Al/Cr molar ratio from 600 to 800 enhanced the activity and produced slight more total selectivity toward 1-hexene and 1-octene, with a similar amount of polymer formed (Table 1, entries 3 and 8). Increasing temperature from 60 °C to 80 °C led to a slight increase in activity and a decrease in selectivity toward either 1-hexene or 1-octene (Table 1, entries 3 and 9). Same trend was also observed when keeping the reaction temperature at 80 °C and increasing the Al/Cr molar ratio from 600 to 800 (Table 1, entries 3 and 10).

In order to establish the coordination mode of the heteroscorpionate ligands, the complexation reaction of carboxyl-containing **4** with $Cr(THF)_3Cl_3$ has been exploitation. The reaction of **4** with $Cr(THF)_3Cl_3$ and followed treatment with DMSO led to a Cr complex **8** (Scheme 2). Single crystals, suitable for X-ray diffraction study, were obtained by slow evaporation of a DMSO solution of **8**, and the structure is illustrated in Fig. 3, which revealed a HCl elimination occurred during the complexation reaction. Complex **8** displays a distorted-octahedral geometry, with the Cr atom facially capped by the anionic tridentate heteroscorpionate ligand and with coordination of all three donor atoms.

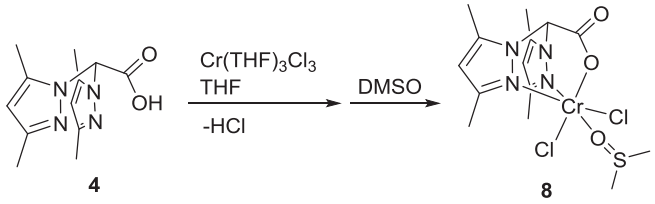
In the previous work of one of our group, treatment of a related tris(pyrazolyl)methane Cr(III) complex **9** with AlMe3 resulted ultimately in reduction to a Cr(II) complex **10** and cation formation (Scheme 3). The Cr(II) complex, **10**, was likely formed through the methyl-chromium(III) intermediate **11**, a methylation product obtained from the reaction of **9** with MAO.

The selective formation of 1-hexene and 1-octene using the Cr catalysts supported by the bis-pyrazolyl ligands **1**~**7** could be explained by the commonly accepted metallacycle mechanism [1a] (Scheme 4). Based on the previous observation of the formation of related Cr intermediates **10** and **11**, we speculate that upon the activation of MAO, the Cr catalyst supported by the bis-pyrazolyl ligand underwent methylation, followed by reduction, and generating a Cr active intermediate I (Scheme 4). Active Cr species **I** coordinates with two ethylene molecules, and undergoes oxidative coupling of them to produce a metallacyclopentane complex **III**. Insertion of further ethylene into the metallacyclopentane **III** produces larger ring metallacycles. At any point, decomposition of the metallacycle occurs via the formation of a chromium alkenyl hydride species, which undergoes reductive elimination to product the corresponding linear α-olefins and the active catalytic species **I** again. The selectivity of the transformation is controlled by relative stability of the different sized metallacycles, which is dramatically influenced by the supportive ligand.

Table 1
Ethylene oligomerization with dipyrazolyl ligands **1**~**7** in conjunction with chromium source and MAO.[a]

Entry (Lig.)	Activity (kg/g Cr/h)	Oligomer distribution 1-olefins (wt%)				PE (wt%)[c]
		C_6 (wt%)[b]	C_8 (wt%)[b]	C_{10} (wt%)[b]	C_{12} (wt%)[b]	
1 (**1**)	15.7	33.8	26.7	17.3	10.9	22.5
2 (**2**)	6.6	39.0	29.0	17.4	9.0	40.7
3 (**3**)	19.0	30.1	25.3	17.7	11.4	21.1
4 (**4**)	18.1	33.8	24.6	16.2	10.5	19.7
5 (**5**)	12.0	30.2	28.3	19.0	11.7	31.0
6 (**6**)	3.7	40.5	29.0	15.6	8.2	40.1
7 (**7**)	14.1	30.7	26.7	18.3	11.2	39.5
8 (**3**)[d]	29.8	33.8	24.7	16.3	10.6	19.7
9 (**3**)[e]	19.8	21.4	22.7	18.9	14.5	25.1
10 (**3**)[d,e]	22.1	18.3	19.5	16.8	13.0	23.1

[a] Conditions: 10 μmol $Cr(THF)_3Cl_3$, 1.0 equiv ligand, 600 equiv. MAO, 35 bar of ethylene, 25 mL toluene, 60 °C, 30 min.
[b] wt % of liquid products (oligomers).
[c] wt % of total product (oligomers + polymer).
[d] 800 equiv. MAO.
[e] 80 °C.



Scheme 2. Synthesis of bis-pyrazolyl Cr complex **8**.

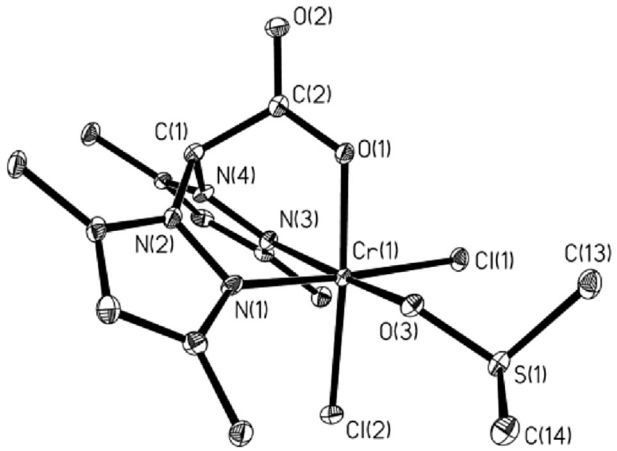
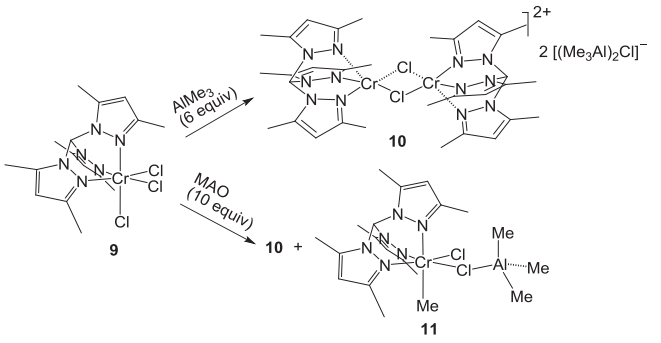


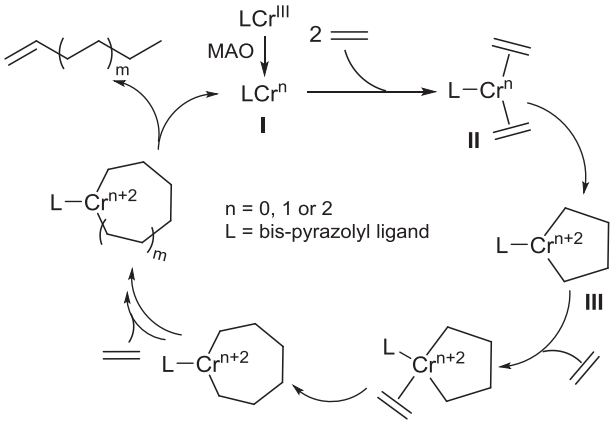
Fig. 3. Molecular structure of **8** with 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)–O(3) 1.976(3); Cr(1)–O(1) 1.988(3); Cr(1)–N(1) 2.076(3); Cr(1)–N(3) 2.078(3); Cr(1)–Cl(1) 2.3041(12); Cr(1)–Cl(2) 2.3132(11); O(3)-Cr(1)-N(1) 85.36(12); O(1)-Cr(1)-N(1) 85.12(13); O(3)-Cr(1)-N(3) 171.07(12); O(1)-Cr(1)-N(3) 85.03(12); N(1)-Cr(1)-N(3) 87.64(13); O(1)-Cr(1)-Cl(1) 90.11(9); N(1)-Cr(1)-Cl(1) 174.48(10); N(3)-Cr(1)-Cl(1) 94.73(10).

3. Conclusion

In summary, Cr(III) catalysts supported by the bis-pyrazoyl ligands having a third quinolinyl, furanyl, thiopheneyl, carboxyl, hydroxyl, or ester group, which, upon activation with MAO, are active for ethylene oligomerization. The catalyst with thiopheneyl-containing ligand **3** achieved a activity of 29.8 kg/(g Cr/h) with a total selectivity of 58.5% toward 1-hexene and 1-octene. The complexation reaction of carboxyl-containing **4** with $Cr(THF)_3Cl_3$ gave an acetoxychromium complex through the HCl elimination.



Scheme 3. Reaction of the related tris(pyrazolyl)methane Cr(III) complex **9** with $AlMe_3$ or MAO. See Ref. 10b.



Scheme 4. Proposed mechanism for the selective ethylene oligomerization via a metallacycle mechanism.

4. Experimental

4.1. General information

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. MMAO-3A (modified methylaluminoxane) (7 wt % in heptane solution) was purchased from Akzo-Nobel. NMR spectra were recorded by using a

Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Mass spectra were recorded on the HP-5989 instrument by EI methods. Quantitative gas chromatographic analysis of the products of oligomerization was performed on an Agilent 6890 Series GC instrument with a J&W DB-1 column working at 36 °C for 10 min and then heating at 10 °C min^{-1} until 250 °C. ^{n}Nonane was used as an internal standard. Ligands **4**~**7** are known compounds, and were prepared according to modified literature methods, respectively [14–17].

4.2. 8-(Bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl)quinolone (**1**)

In a representative procedure, 3,5-dimethylpyrazole (2.8 g, 30 mmol) was added at 0 °C to a stirred suspension of sodium hydride (1.2 g, 30 mmol) in tetrahydrofuran (30 mL). Stirring was continued for 30 min sulfurous dichloride (1 mL, 14.9 mmol) was added in one portion via syringe, and the resulting mixture was allowed to warm to room temperature. After treatment with 8-quinolinecarboxaldehyde (2.35 g, 14.9 mmol) and pyridine (1.2 g, 15 mmol), the reaction mixture was kept at the reflux temperature for 12 h. Water was added and the aqueous phase extracted into dichloromethane. The combined organic extracts were dried over magnesium sulphate and filtered, and the filtrate was evaporated to dryness under a vacuum. The crude product was purified by column chromatography (silica gel; hexane/EtOAc1:1) to afford **1** (3.5 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.83$ (s, 1H), 8.72 (s, 1H), 8.13 (d, $J = 8$ Hz, 1H), 7.81 (d, $J = 8$ Hz, 1H), 7.62 (d, $J = 6.8$ Hz, 1H), 7.53 (d, $J = 7.2$ Hz, 1H), 7.35–7.38 (m, 1H), 5.84 (s, 2H), 2.23 (s, 6H), 2.18 (s, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = 149.9, 148.0, 145.2, 139.9, 136.0, 134.4, 129.4, 128.6, 127.9, 126.2, 121.1, 106.1, 68.2, 13.9, 11.2$. HRMS (EI): m/z $[M]^+$ calcd for $C_{20}H_{21}N_5^+$: 331.1797, found: 331.1800.

4.3. 1,1′-(furan-2-ylmethylene)bis(3,5-dimethyl-1H-pyrazole) (**2**)

Ligand **2** has been prepared similarly to **1** with a yield of 75%, starting from 3,5-dimethylpyrazole (2.8 g, 30 mmol), sodium hydride(1.2 g, 30 mmol), sulfurous dichloride (1 mL, 14.9 mmol), 2-furanaldehyde (1.44 g, 14.9 mmol), and pyridine (1.2 g, 15 mmol), tetrahydrofuran (30 mL). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (s, 1H), 7.45 (s, 1H), 6.38 (s, 1H), 6.20 (s, 1H), 5.83 (s, 2H), 2.22 (s, 6H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 148.5, 148.2, 143.0, 140.7, 111.7, 110.6, 106.9, 69.1, 13.7, 11.1$. HRMS (EI): m/z $[M]^+$ calcd for $C_{15}H_{18}N_4O^+$: 270.1481, found: 270.1484.

4.4. 1,1′-(thiophen-2-ylmethylene)bis(3,5-dimethyl-1H-pyrazole) (**3**)

Ligand **3** has been prepared similarly to **1** with a yield of 39%, starting from 3,5-dimethylpyrazole (2.8 g, 30 mmol), sodium hydride (1.2 g, 30 mmol), sulfurous dichloride (1 mL, 14.9 mmol), 2-thiophenaldehyde (1.68 g, 14.9 mmol), and pyridine (1.2 g. 15 mmol), tetrahydrofuran (30 mL). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$ (s, 1H), 7.33 (s, 1H), 6.95 (s, 1H), 6.78 (s, 1H), 5.84 (s, 2H), 2.26 (s, 6H), 2.20 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 148.3, 140.7, 139.2, 127.3, 126.8, 126.5, 107.1, 71.1, 13.7, 11.7$. HRMS (EI): m/z $[M]^+$ calcd for $C_{15}H_{18}N_4S^+$: 286.1252, found: 286.1257.

4.5. Synthesis of Cr complex **8**

To a solution of ligand **4** (0.112 g, 0.45 mmol) in dry THF (10 mL) was added $Cr(THF)_3Cl_3$ (0.167 g, 0.45 mmol), producing a light green precipitate. The resulting mixture was stirred at r.t. for 8 h. The solvent was evaporated to dryness, and the residue was crystallized in DMSO to give Cr complex **8** (0.131 g, 65%). Anal. Calcd for $C_{14}H_{21}Cl_2CrN_4O_3S$ (%): C, 37.51; H, 4.72; N, 12.50. Found: C, 37.90; H, 4.35; N, 13.01.

4.6. Oligomerization of ethylene

A 120 mL stainless steel reactor was dried at 120 °C for 3 h under vacuum, and then cooled down to the desired reaction temperature. The precatalysts and co-catalysts (MAO) were combined in a Schlenk vessel in the ratios indicated in Table 1. The resultant mixture was stirred for 1 min and immediately transferred to the reactor. Then the reactor was immediately pressurized. After the specified reaction time, the reaction was stopped by shutting in the ethylene feed, cooling the system at 0 °C, depressurizing, and quenched by addition of 30 mL of 10% aq. HCl. A small sample of the upper-layer solution was filtered through a layer of Celite and analysed by GC using nonane as the internal standard. The individual oligomerization products were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric products. The solid products were suspended in 10% aq. HCl and stirred for 24 h, dried under reduced pressure and weighed.

Acknowledgments

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Supplementary data

CCDC 1017399 contained the supplementary crystallographic data for **8**. This data could be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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