Selectivity effects on *N,N,N'*-cobalt catalyzed ethylene dimerization/trimerization dictated through choice of aluminoxane co-catalyst

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ABSTRACT: The cobalt(II) chloride complexes, [2-(C₇H₄N₂H)-8-(ArN)C₁₀H₈N]CoCl₂ (Ar = 2,6-Me₂C₆H₃ **Co1**, 2,6-Et₂C₆H₃ **Co2**, 2,6-*i*-Pr₂C₆H₃ **Co3**, 2,4,6-Me₃C₆H₂ **Co4**, 2,6-Et₂-4-MeC₆H₂ **Co5**, 2,4,6-*t*-Bu₃C₆H₂ **Co6**), have each been prepared by a one-pot template reaction of 2-benzoimidazolyl-5,6,7-trihydroquinolin-8-one with the corresponding aniline in the presence of cobalt dichloride. The molecular structures of the methanol adducts, **Co1**(HOMe) and **Co4**(HOMe), reveal distorted octahedral geometries that self-assemble to form networks based on NH $\cdots$ Cl and OH $\cdots$ Cl intermolecular hydrogen bonding interactions. On activation with methylaluminoxane (MAO), all six cobalt complexes catalyzed ethylene dimerization with a high selectivity for 1-butene. By marked contrast, with modified methylaluminoxane (MMAO) products the result of ethylene dimerization and trimerization were observed with a bias towards the C₆ products (up to 49% 1-hexene). In general, the MMAO-promoted oligomerizations display higher catalytic activities with mesityl-containing **Co4** the stand-out performer [7.60 $\times$ 10⁵ g mol⁻¹(Co) h⁻¹ at 50 °C].

INTRODUCTION

Linear α -olefins such as 1-butene and 1-hexene are employed, among other things, as comonomers in the manufacture of linear low-density polyethylene (LLDPE). Selective routes to such short chain α -olefins *via* the selective dimerization and trimerization of ethylene are known and indeed operated industrially. With regard to dimerization, the AlphaButol process makes use of a homogeneous catalyst based on a combination of titanium tetrabutoxide and triethylaluminum,¹ while trimerization technology largely involves chromium catalysts some of which were originally disclosed by Union Carbide,² Chevron-Phillips³ and BP.⁴ In addition, other first row transition metal catalysts have been investigated for their effectiveness and selectivity in both transformations,⁵ though the use of cobalt is less well developed.⁶

Catalysts composed of bis(arylimino)pyridine-iron and cobalt complexes have shown promise for their development in this field as their less sterically demanding derivatives display a preference for ethylene oligomerization over polymerization.^{7,8} Indeed, alternative *N,N,N*-cobalt catalysts have emerged that favour the formation of shorter chain oligomers. Among them, cobalt precatalysts based on benzimidazole-substituted pyridylimines have shown a predilection towards dimers and trimers (Chart 1). Moreover, the nature of benzimidazole N-R substituent can influence the catalytic performance with alkylated precatalysts of type **A**^{8b} or **B**^{8c} proving less active than their protio-**C** counterpart.^{8a} On the other hand, substitution of the NH unit in **C** for an O atom in **D**,⁹ leads to an unusual switch between oligomerization and polymerization as a consequence of the temperature employed.

Chart 1. Developments in unsymmetrical *N,N,N'*-chelating ligands for cobalt(II) chlorides

In recent years, we have found that the introduction of controlled amounts of strain into a bis(imino)pyridine can have an effect on the performance of an ethylene polymerization catalyst. For example, sterically enhanced examples of cyclohexyl-fused **E**¹⁰ on suitable activation function effectively at 60 °C generating polyethylene waxes, while the corresponding bis(imino)pyridine-cobalt catalyst is much less productive under such high temperature operating conditions.¹¹ To explore whether a similar structural modification would have beneficial effects on an oligomerization catalyst, we report six examples of benzimidazole-containing **F** in which the steric and electronic properties of the N-aryl group have been systematically varied. An in-depth study is then conducted to determine the effects of the precatalyst structure, type and amount of co-catalyst and temperature on the selectivity of the ethylene oligomerization. Full synthetic and characterization details are additionally presented for the complexes.

RESULTS AND DISCUSSION

Synthesis and characterization of Co1 – Co6

The cobalt(II) chloride complexes, [2-(C₇H₄N₂H)-8-(ArN)C₁₀H₈N]CoCl₂ (Ar = 2,6-Me₂C₆H₃ **Co1**, 2,6-Et₂C₆H₃ **Co2**, 2,6-i-Pr₂C₆H₃ **Co3**, 2,4,6-Me₃C₆H₂ **Co4**,

2,6-Et₂-4-MeC₆H₂ **Co5**, 2,4,6-t-Bu₃C₆H₂ **Co6**), were obtained in reasonable yield (49 – 64%) by templating 2-benzoimidazol-6,7-dihydroquinolin-8 (5*H*)-one (**1**) with the corresponding aniline in the presence of cobalt dichloride in acetic acid at reflux (Scheme 1). Attempts to prepare the free ligands themselves by an acid catalyzed Schiff base condensation reaction of ketone **1** with the appropriate aniline proved unsuccessful. It is worthy of note that related one-pot template approaches have been applied elsewhere to synthesize similar species.¹² All six cobalt complexes have been characterized by IR spectroscopy as well as by elemental analysis. In addition, the adducts **Co1**(HOMe) and **Co4**(HOMe) have been the subject of single crystal X-ray diffraction studies.

Scheme 1. Template synthetic route to **Co1** – **Co6**

Single crystals of **Co1**(HOMe) and **Co4**(HOMe) suitable for the X-ray determinations were grown by layering diethyl ether onto a solution of the corresponding complex in a methanol/dichloromethane mixture. Perspective views are shown in Figures 1 and 2; selected bond lengths and angles are tabulated in Table 1. The structures of **Co1**(HOMe) and **Co4**(HOMe) are similar and will be discussed together. Each cobalt center is surrounded by two chlorides, one oxygen bound methanol and three nitrogen atoms belonging to the chelating 2-benzoimidazolyl-8-arylimino-5,6,7-trihydroquinoline (aryl = 2,6-Me₂Ph **Co1**, 2,4,6-Me₃Ph **Co4**)

to complete a geometry that can be best described as distorted octahedral.¹³ The methanol ligand occupies a site *trans* to Cl(1) [O(1)-Co(1)-Cl(1) 167.57(5) ° **Co1**, 166.49(5)° **Co4**], while Cl(2) is *trans* to the central nitrogen donor of the *mer*-configured tridentate ligand [N(2)-Co(1)-Cl(2) 178.49(4) ° **Co1**, 177.25(5)° **Co4**]; similar *N,N,N*-CoCl₂(HOMe) adducts have been structurally characterized previously.^{8c} Of the three cobalt-nitrogen distances, the one involving the central pyridine is the shortest [Co(1)-N(2) 2.0895(15) Å **Co1**, 2.0853(17) Å **Co4**] while the exterior nitrogen donors show some variation. In particular, the Co-N_{benzimidazole} distance is noticeably shorter [Co(1)-N(1) 2.1907(15) Å **Co1**, 2.1842(17) Å **Co4**] than the Co-N_{imine} distance [Co(1)-N(3) 2.2532(15) Å **Co1**, 2.2471(17) Å **Co4**], reflecting the superior donor properties of the benzimidazole-nitrogen. The Co-Cl bond distances also display some differences with Co(1)-Cl(1) (2.5600(9) Å **Co1**, 2.5576(7) Å **Co4**) notably longer than Co(1)-Cl(2) (2.2876(6) Å **Co1**, 2.2850(6) Å **Co4**), an observation that can be plausibly attributed to the variation in *trans*-donor. Within each 5-membered chelate ring the bite angles show some modest variation with that involving N_{benzimidazole} [N(1)-Co(1)-N(2) 75.41(6) ° **Co1**, 75.40(7)° **Co4**] slightly larger than that with N_{imine} [N(2)-Co(1)-N(3) 74.31(6) ° **Co1**, 74.43(6)° **Co4**], which presumably derives from the constraints of the 5-membered imidazole ring. The imine bond lengths [C(7)-N(3) 1.285(2) Å **Co1**, 1.280(3) Å **Co4**] are typical of this functionality while the N-aryl group is inclined almost orthogonally with respect to the imine vector. In each structure, the sp³-hybridized C(9) atom belonging to the trihydroquinoline unit is folded away from the plane of the neighboring unsaturated heterocycle with the result that it adopts a confirmation *cis* to the coordinated methanol. Due to the presence of both OH and NH groups within **Co1**(HOMe) and **Co4**(HOMe), an extensive intermolecular hydrogen bonding network is a feature of both structures (Figures 3 and S1). In particular, Cl(1) undergoes both Cl⋯HO and Cl⋯HN interactions with two different neighboring molecules

(N(4)⋯Cl(1) 3.127 Å Co1 3.140 Å **Co4**; O(1)⋯Cl(1) 3.131 Å, 3.187 Å) leading to a two dimensional array within the crystal structure.

Figure 1. ORTEP representation of **Co1(HOMe)** with the thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity

Figure 2. ORTEP representation of **Co4(HOMe)** with the thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity

Figure 3. NH⋯Cl and OH⋯Cl hydrogen-bonding interactions between neighboring molecules of

Co1(HOMe)**Table 1.** Selected bond lengths (Å) and angles (°) for **Co1(HOMe)** and **Co4(HOMe)**

	Co1	Co4
	Bond lengths	
Co(1)–N(1)	2.1907(15)	2.1842(17)
Co(1)–N(2)	2.0895(15)	2.0853(17)
Co(1)–N(3)	2.2532(15)	2.2471(17)
Co(1)–O(1)	2.2145(16)	2.2682(18)
Co(1)–Cl(1)	2.5600(9)	2.5576(7)
Co(1)–Cl(2)	2.2876(6)	2.2850(6)
N(1)–C(1)	1.323(2)	1.320(3)
N(3)–C(7)	1.285(2)	1.280(3)
N(4)–C(1)	1.355(2)	1.356(3)
	Bond angles	
N(1)–Co(1)–N(2)	75.40(6)	75.43(6)
N(1)–Co(1)–N(3)	149.50(5)	149.65(6)
N(2)–Co(1)–N(3)	74.31(6)	74.43(6)
N(1)–Co(1)–Cl(2)	105.77(4)	104.69(5)
N(2)–Co(1)–Cl(2)	178.49(4)	177.25(5)
N(3)–Co(1)–Cl(2)	104.46(4)	105.24(5)
N(1)–Co(1)–Cl(1)	87.36(4)	87.86(5)
N(2)–Co(1)–Cl(1)	85.31(5)	86.47(5)
N(3)–Co(1)–Cl(1)	93.67(4)	93.76(5)
Cl(2)–Co(1)–Cl(1)	95.68(3)	96.28(2)
O(1)–Co(1)–Cl(1)	167.57(5)	166.49(5)
O(1)–Co(1)–Cl(2)	95.10(5)	95.64(5)
O(1)–Co(1)–N(1)	83.77(6)	82.99(7)
O(1)–Co(1)–N(2)	84.05(6)	81.63(7)
O(1)–Co(1)–N(3)	89.62(6)	89.20(7)

The IR spectra of **Co1** – **Co6** reveal imine stretching frequencies in the range 1625 – 1618 cm^{-1} , which are characteristic of bound imine-nitrogen atoms; no absorption bands corresponding to complexed C=O groups or to free ketone **1** could be detected. In addition, the elemental analysis data confirmed complexes of composition LCoCl_2 .

Ethylene oligomerization

To explore the role of the co-catalyst, two separate oligomerization studies were performed with each precatalyst using either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) as the activator. Typically, the oligomerization runs were performed in toluene at 10 atm C₂H₄ over 30 minutes and any selectivity for dimerization, trimerization as well as specific α -olefins, assessed using gas chromatography (GC); the results of the two studies are gathered in Tables 2 and 3.

Table 2. Ethylene oligomerization using MAO as co-catalyst^[a]

Entry	Precatalyst	<i>T</i> [°C]	Al:Co	<i>t</i> [min]	Activity ^[b]	Oligomer Distribution ^[c] (%)	
						C ₄ /ΣC	α -C ₄
1	Co4	30	1000	30	0.49	100	94.1
2	Co4	40	1000	30	1.23	100	90.8
3	Co4	50	1000	30	0.90	100	85.1
4	Co4	60	1000	30	0.81	100	61.1
5	Co4	40	500	30	0.43	100	100
6	Co4	40	1500	30	0.61	100	84.2
7	Co4	40	2000	30	0.44	100	78.0
8	Co4	40	1000	5	3.17	100	100
9	Co4	40	1000	15	1.52	100	100
10	Co4	40	1000	45	1.06	100	80.5
11	Co4	40	1000	60	0.88	100	71.2
12 ^[d]	Co4	40	1000	30	0.46	100	91.9
13	Co1	40	1000	30	0.36	100	100
14	Co2	40	1000	30	0.53	100	100
15	Co3	40	1000	30	0.39	100	86.8
16	Co5	40	1000	30	0.77	100	90.6
17	Co6	40	1000	30	0.24	100	94.4

[a] General conditions: 3 μ mol of precatalyst, 10 atm C₂H₄, 100 mL of toluene; [b] $\times 10^5$ g $\cdot$ mol⁻¹ (Co) $\cdot$ h⁻¹; [c] Determined by GC and ΣC signifies the total amounts of oligomers; [d] 5 atm C₂H₄.

(a) Catalytic evaluation using MAO.

To allow an optimization of the conditions, **Co4** was selected as the test precatalyst and the effect of temperature, Al:Co molar ratio, run time and pressure were all investigated (entries 1 – 12, Table 2). Firstly, with the Al:Co molar ratio fixed at 1000, the run temperature was

increased from 30 to 60 °C and the activity in each case measured after 30 minutes (entries 1 – 4, Table 2). The optimum activity of $1.23 \times 10^5 \text{ g mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ for **Co4**/MAO was observed at 40 °C with a 100% selectivity for ethylene dimerization (C_4) with 1-butene being the major component (91%). Indeed, all runs resulted in solely C_4 formation with the selectivity for 1-butene decreasing as the temperature was raised.

Secondly, with the temperature maintained at 40 °C, the Al:Co molar ratio for **Co4**/MAO was increased from 500 to 2000 and the activity determined (entries 2, 5 – 7, Table 2). On comparison of the four runs, a molar ratio of 1000 resulted in a peak activity of $1.23 \times 10^5 \text{ g mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$. Once again, only products derived from ethylene dimerization could be detected with the selectivity for 1-butene reducing as the Al:Co molar was raised (*e.g.*, $\alpha\text{-C}_4$: 100% Al:Co = 500; 78% Al:Co = 2000). These decreases in 1-butene content with Al:Co ratio (entries 2, 5 – 7, Table 23) or reaction temperature can be attributed to the greater thermodynamic stability of internal olefins (*e.g.* 2-butene).

Thirdly, with the temperature and Al:Co molar ratio fixed at 40 °C and 1000, respectively, the runs using **Co4**/MAO were performed over 5, 15, 45 and 60 minutes. The highest activity of $3.17 \times 10^5 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ was observed after 5 minutes with 1-butene being the only product identifiable. However, this selectivity for 1-butene gradually decreased over time with only 71.2% selectivity noted after 60 minutes. With the pressure reduced to 5 bar C_2H_4 , no loss in selectivity for C_4 products was observed (92% 1-butene) but the activity dropped by more than half (entry 12, Table 2). Overall, these results highlight the importance of reaction temperature, Al:Co ratio and reaction time on influencing both the selectivity for 1-butene and the catalytic activity.

With the optimized conditions established as, temp = 40 °C, Al:Co = 1000, P_{C₂H₄} = 10 atm, the remaining five cobalt precatalysts were similarly screened. In terms of activity (range: 1.23 – 0.24 × 10⁵ g · mol⁻¹(Co)·h⁻¹), the six precatalysts were found to fall in the order: **Co4** > **Co5** > **Co2** > **Co3** ~ **Co1** > **Co6**. It would appear that both electronic and steric hindrance effects play a combined role on affecting performance with mesityl-containing **Co4** the most active and the 2,4,6-tri-*t*-butyl **Co6** the least. In particular, *para*-methyl **Co4** and **Co5** are more active than *para*-H **Co1**, **Co2** and **Co3** highlighting the importance of the electron donating *para*-substituent. On the other hand, the most sterically encumbered **Co6** likely impedes ethylene coordination leading to the lowest activity. It is noteworthy that the current systems generally display higher productivities when compared with other *N,N,N*-cobalt oligomerization precatalysts such as **A** – **D** (Chart 1).^{8,9} Nevertheless, all precatalysts, regardless of N-aryl substitution, gave solely C₄ products with selectivities for 1-butene of greater than 86.7% and indeed 100% for **Co1** and **Co2**.

Table 3. Ethylene oligomerization using MMAO as co-catalyst ^[a]

Entry	Precatalyst	<i>T</i> [°C]	Al:Co	<i>t</i> [min]	Activity ^[b]	Oligomer Distribution ^[c] (%)			
						C ₄ /ΣC	α-C ₄	C ₆ /ΣC	α-C ₆
1	Co4	30	1000	30	4.58	34.0	52.3	66.0	35.0
2	Co4	40	1000	30	4.96	17.3	64.8	82.7	40.3
3	Co4	50	1000	30	7.60	48.5	70.4	51.5	34.6
4	Co4	60	1000	30	4.50	21.4	66.1	78.6	35.1
5	Co4	70	1000	30	3.59	12.9	61.9	87.1	35.7
6	Co4	50	500	30	2.15	30.4	85.9	69.6	35.3
7	Co4	50	1500	30	7.14	15.0	61.6	85.0	35.3
8	Co4	50	2000	30	6.73	6.3	59.1	93.7	35.5
9	Co4	50	1000	5	26.3	16.5	58.0	83.5	35.5
10	Co4	50	1000	15	9.59	11.8	55.7	88.2	35.6
11	Co4	50	1000	45	5.91	8.2	68.7	91.8	35.5
12	Co4	50	1000	60	5.23	7.0	71.6	93.0	36.0
13 ^[d]	Co4	50	1000	30	6.00	16.0	63.7	84.0	34.9
14 ^[e]	Co4	50	1000	30	5.12	44.3	75.4	55.7	38.1
15	Co1	50	1000	30	4.76	9.8	57.7	90.2	36.4

16	Co2	50	1000	30	3.55	31.2	62.3	68.8	29.8
17	Co3	50	1000	30	5.28	9.0	47.3	91.0	49.2
18	Co5	50	1000	30	5.31	12.6	56.2	87.4	49.2
19	Co6	50	1000	30	5.64	17.1	62.8	82.9	37.3

[a] General conditions: 3 μmol of precatalyst, 10 atm C_2H_4 , 100 mL of toluene; [b] $10^5 \text{ g} \cdot \text{mol}^{-1} (\text{Co}) \cdot \text{h}^{-1}$; [c] Determined by GC and $\sum\text{C}$ signifies the total amounts of oligomers; [d] 5 atm C_2H_4 . [e] 100 mL of 1,2-xylene as solvent with the conditions otherwise the same as in entry 3.

(b) Catalytic evaluation using MMAO.

As with the MAO study, **Co4** was again used as the test precatalyst to establish the optimized conditions for the runs this time using MMAO as the co-catalyst. The effect of temperature was first explored with the Al:Co ratio set at 1000 (entries 1 – 5, Table 3). On increasing the temperature from 30 to 70 $^{\circ}\text{C}$, the highest activity of $7.60 \times 10^5 \text{ g} \cdot \text{mol}^{-1} (\text{Co}) \cdot \text{h}^{-1}$ was observed at 50 $^{\circ}\text{C}$ (entry 3, Table 3), which when compared with the MAO study represents not only a higher operating temperature but also a significantly higher activity (entry 2, Table 2). However, this higher activity is at the expense of poorer selectivity with products now the result of dimerization (C_4) and trimerization (C_6) evident ($\text{C}_4/\sum\text{C} = 48.5\%$, $\text{C}_6/\sum\text{C} = 51.5\%$). Moreover, as the temperature is raised the bias towards the C_6 products becomes more pronounced (70 $^{\circ}\text{C}$: $\text{C}_4/\sum\text{C} = 12.9\%$, $\text{C}_6/\sum\text{C} = 87.1\%$). With regard to the C_6 products, the selectivity towards 1-hexene remains relatively constant (*ca.* 35%) between 50 and 70 $^{\circ}\text{C}$, while at 40 $^{\circ}\text{C}$ a greater content of 1-hexene is apparent (up to 40%).

With the temperature of the run retained at 50 $^{\circ}\text{C}$, the Al:Co molar ratio was increased from 500 to 2000 (entries 3, 6 – 8). Examination of the data reveals the activity of **Co4**/MMAO reaches its highest value of $7.60 \times 10^5 \text{ g} \cdot \text{mol}^{-1} (\text{Co}) \cdot \text{h}^{-1}$ with an Al:Co molar ratio of 1000 with a gradual drop in the level as the ratio is increased to 2000 (entries 3, 6 –

8, Table 3). In terms of the oligomer distribution, the preference for C₆ products becomes more evident at higher molar ratios reaching a maximum of 93.7% at a ratio of 2000. However, the selectivity for 1-hexene remains constant at around 36% for all the Al:Co ratios highlighting the capacity of these cobalt catalysts to mediate isomerization to give 2-hexene as the major C₆ product.

The effect of time on activity of **Co4**/MMAO shows similar trends to that seen with MAO but with markedly higher activities observed over short run times. Indeed, the highest activity of $26.3 \times 10^5 \text{ g mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ of the entire study was seen after 5 minutes which equates to an eight fold increase when compared to that seen with MAO after the same time period. As the time elapses the activity slowly decreases reaching its lowest value of $5.23 \times 10^5 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ after 60 minutes which is still higher than seen with MAO after 5 minutes ($3.17 \times 10^5 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$, entry 8, Table 3). On the other hand, the bias towards the C₆ products increases with time with the amount of C₆ constituting 93.0% of the mixture after 60 minutes; the 1-hexene content however remains constant at around 36% over the various reaction times. Lowering the pressure from 10 to 5 atm C₂H₄, under otherwise identical conditions, saw the activity drop from 7.60 to $6.00 \times 10^5 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ with an increased preference for C₆ products at lower pressure (entries 3 and 13, Table 3). It is worth highlighting that no evidence of octenes could be detected in the GC. Indeed, we ran the oligomerizations in two different aromatic solvents namely toluene and 1,2-xylene to check for any solvent overlap (entry 3, Table 3 vs. entry 14, Table 3). In both of these runs no peaks corresponding to octenes could be observed. Notably, a slightly lower activity was observed in xylene when compared to toluene but the product distribution was nevertheless similar with hexenes being the major component (more details shows in Figures S2 and S3).

Using the optimal conditions established for **Co4**/MMAO (temp = 50 °C, Al:Co = 1000, $P_{C_2H_4}$ = 10 atm), **Co1** – **Co3** and **Co6** were additionally screened (entries 3, 15 – 19, Table 3). Inspection of the tabulated data reveals activities in the range $7.60 - 4.76 \times 10^5$ g $\cdot$ mol⁻¹(Co) $\cdot$ h⁻¹, with their relative values falling in the order: **Co4** > **Co6** > **Co2** > **Co5** > **Co3** > **Co1**. When compared with the results obtained with MAO, these MMAO-promoted systems are not only more active but reveal some variations in relative performance with the most sterically hindered system **Co6** now notably towards the top of the order rather than the bottom. Nevertheless, all precatalysts form predominantly products the result of ethylene trimerization rather than dimerization. In terms of the 1-hexene selectivity, some variation is observed between precatalysts with **Co3** and **Co5** affording 49% α -C₆ selectivity while **Co2** only 30%. Compared with previously reported *N,N,N*-cobalt oligomerization catalysts (*e.g.*, **A** – **D**, Chart 1), much higher overall catalytic activity is again a feature of the current systems. Moreover, unlike that observed with **A** - **D**, ethylene trimerization products have emerged as a major component of the oligomerization distribution. When compared with chromium-based catalysts bearing similar benzimidazole-containing multidentate ligands, the **Co**/MMAO-type catalysts described in this work show higher selectivity towards trimerization of ethylene and no evidence of polymeric fractions, a by-product that was a feature of these previous studies.¹⁴ On the other hand, when compared to the well-documented diphosphinoamine(PNP)-type chromium catalysts, the selectivity of the current catalysts for 1-hexene is noticeably less.¹⁵

In this investigation, the C₄/C₆ composition of short chain alkenes can be influenced by the alkylaluminum activator employed. With MAO, ethylene dimerization was achieved while with MMAO both dimers and trimers were observed. It would appear that the rapid

β -H elimination step that occurs under the activation with MAO is influenced by the structural features of the aluminoxane employed. With MMAO, it would seem plausible that the steric properties of the isobutyl groups belonging to this co-catalyst are somehow subtly affecting the active site leading to competitive ethylene trimerization.

CONCLUSIONS

Six examples of 2-benzoimidazolyl-8-arylimino-5,6,7-trihydroquinoline-cobalt(II) chloride complexes (**Co1** – **Co6**) have been successfully synthesized and fully characterized including in two cases by single crystal X-ray diffraction. On activation with either MAO or MMAO, the current systems exhibited higher catalytic activities for ethylene oligomerization when compared with previously reported *N,N,N*-cobalt precatalysts such as **A** – **D** (Chart 1).^{8,9} With MAO as co-catalyst, all the complexes were effective (activities up to $1.23 \times 10^5 \text{ g mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ for **Co4**) for selective ethylene dimerization (C_4) in which 1-butene accounted for the major isomer. By stark contrast, with MMAO as co-catalyst, products the result of ethylene dimerization (C_4) and trimerization (C_6) were obtained with the C_6 hydrocarbon constituting the major fraction with selectivities for 1-hexene up to 49% (with **Co3** and **Co5**). Moreover, these MMAO-promoted oligomerizations displayed a relatively higher activity (up to $7.60 \times 10^5 \text{ g mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ for **Co4**) despite the loss of selectivity for dimerization. It is unclear as to the origin of these variations in the C_4/C_6 product distribution that derive from the type of aluminoxane employed and hence will be the subject of further investigations.

EXPERIMENTAL SECTION

General Considerations All manipulations of air- and/or moisture-sensitive operations were undertaken in a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in n-heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. GC analyses were performed with a Varian CP-3800 gas chromatograph (Beijing, China) equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 mm film thickness) CP-Sil 5 CB column. The compound 2-(1H-benzoimidazol-2-yl)-6,7-dihydroquinolin-8(5H)-one (**1**) was prepared as described in the literature.¹⁶

Synthesis of [2-(C₇H₄N₂H)-8-(ArN)C₁₀H₈N]CoCl₂

(a) Ar = 2,6-Me₂C₆H₃ (**Co1**). A suspension of **1** (0.158 g, 0.60 mmol), 2,6-dimethylaniline (0.087 g, 0.72 mmol), cobalt dichloride (0.074 g, 0.57 mmol) in glacial acetic acid (10 mL) was stirred at reflux for 6 h affording a brown precipitate. On cooling to room temperature, the precipitate was collected by filtration, washed with diethyl ether (3 × 20 mL) and then dried under reduced pressure yielding **Co1** as a brown solid (0.160 g, 57%). FT-IR (KBr, cm⁻¹): 3031 (w), 2968 (w), 1625 (ν_{C=N}, m), 1591 (m), 1488 (w), 1462 (s), 1434 (w), 1423 (w), 1407 (w), 1377 (w), 1352 (w), 1318 (m), 1295 (m), 1263 (m), 1230 (m), 1198 (m),

1106 (m), 1069 (m), 1036 (m), 984 (m), 926 (m), 867 (m), 834 (m), 773 (s), 745 (s), 696 (m), 665 (m). Anal. calcd for $C_{24}H_{22}Cl_2CoN_4$: C, 58.08, H, 4.47, N, 11.29. Found: C, 58.46, H, 4.29, N, 10.98%.

(b) Ar = 2,6-Et₂C₆H₃ (**Co2**). Using a similar procedure and molar ratios as that described for **Co1**, **Co2** was obtained as a brown powder (0.190 g, 64%). FT-IR (KBr, cm⁻¹): 3142 (w), 3114 (w), 3064 (w), 2958 (m), 2930 (m), 2872 (m), 1624 (ν_{C=N}, m), 1590 (s), 1453 (s), 1405 (m), 1374 (m), 1323 (m), 1298 (m), 1261 (m), 1240 (m), 1223 (m), 1186 (m), 1145 (m), 1113 (w), 1093 (m), 1057 (m), 1040 (m), 1012 (w), 865 (m), 803 (m), 772 (s), 747 (s), 686 (m), 660 (m). Anal. calcd for $C_{26}H_{26}Cl_2CoN_4$: C, 59.56, H, 5.00, N, 10.68. Found: C, 59.87, H, 4.79, N, 10.36%.

(c) Ar = 2,6-i-Pr₂C₆H₃ (**Co3**). Using a similar procedure and molar ratios as that described for **Co1**, **Co3** was obtained as a brown powder (0.180 g, 57%). FT-IR (KBr, cm⁻¹): 3099 (w), 3068 (w), 2962 (s), 2928 (m), 2867 (m), 1618 (ν_{C=N}, m), 1590 (m), 1513 (w), 1462 (m), 1442 (m), 1410 (w), 1383 (m), 1359 (m), 1324 (m), 1300 (m), 1271 (m), 1252 (w), 1219 (m), 1184 (m), 1116 (m), 1047 (m), 929 (m), 838 (m), 801.0 (m), 774 (s), 747 (s), 698 (m), 665 (m), 654 (w). Anal. calcd for $C_{28}H_{30}Cl_2CoN_4$: C, 60.88, H, 5.47, N, 10.14. Found: C, 61.26, H, 5.25, N, 9.89%.

(d) Ar = 2,6-Et₂-4-MeC₆H₂ (**Co4**). Using a similar procedure and molar ratios as that described for **Co1**, **Co4** was obtained as a brown powder (0.180 g, 62%). FT-IR (KBr, cm⁻¹): 3058 (m), 2988 (w), 2948 (w), 2914 (w), 2863 (w), 1626 (ν_{C=N}, m), 1592 (s), 1461 (s), 1410 (w), 1376 (w), 1349 (m), 1319 (m), 1296 (m), 1269 (m), 1234 (m), 1214 (m), 1149 (m), 1037 (m), 858 (s), 834 (m), 765 (s), 747 (s), 709 (m), 666 (w). Anal. calcd for $C_{25}H_{24}Cl_2CoN_4$: C, 58.84, H, 4.74, N, 10.98. Found: C, 59.11, H, 4.49, N, 10.71%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**Co5**). Using a similar procedure and molar ratios as that described for **Co1**, **Co5** was obtained as a brown powder (0.150 g, 49%). FT-IR (KBr, cm⁻¹): 3142 (w), 2959 (m), 2928 (m), 2871 (m), 1627 (ν_{C=N}, m), 1590 (s), 1460 (s), 1435 (w), 1406 (m), 1375 (w), 1326 (m), 1299 (w), 1267 (m), 1210 (m), 1146 (m), 855 (s), 804 (m), 749 (s), 684 (m), 661 (m). Anal. calcd for C₂₇H₂₈Cl₂CoN₄: C, 60.23, H, 5.24, N, 10.41. Found: C, 60.61, H, 5.01, N, 10.13%.

(f) Ar = 2,4,6-t-Bu₃C₆H₂ (**Co6**). Using a similar procedure and molar ratios as that described for **Co1**, **Co6** was obtained as a brown powder (0.180 g, 50%). FT-IR (KBr, cm⁻¹): 3143 (w), 3112 (w), 3065 (w), 2957 (s), 2904 (w), 2868 (m), 1626 (ν_{C=N}, m), 1595 (s), 1489 (w), 1463 (w), 1434 (m), 1393 (m), 1357 (m), 1324 (m), 1297 (m), 1266 (m), 1238 (m), 1208 (s), 1148 (m), 1105 (m), 836 (s), 751 (s), 689 (w), 662 (m). Anal. calcd for C₃₄H₄₂Cl₂CoN₄: C, 64.15, H, 6.65, N, 8.80. Found: C, 64.48, H, 6.39, N, 8.72%.

X-ray crystallographic studies

Table 4. Crystal data and structure refinement details for **Co1**(HOMe) and **Co4**(HOMe)

	Co1 (HOMe)	Co4 (HOMe)
Formula	C ₂₅ H ₂₆ Cl ₂ CoN ₄ O	C ₂₆ H ₂₈ Cl ₂ CoN ₄ O
Formula weight	528.33	542.35
T (K)	173	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	6.8781(14)	7.0575(2)
b (Å)	20.363(4)	20.0029(6)
c (Å)	16.998(3)	17.2584(5)
α/°	90	90
β/°	93.68(3)	95.216(3)
γ/°	90	90
Volume/Å ³	2375.7(8)	2426.29(12)
Z	4	4
D _{calc} (g cm ⁻³)	1.474	1.482
μ/mm ⁻¹	0.973	0.955

F(000)	1088	1120
θ Range ($^{\circ}$)	4 - 54.966	4.072 - 54.958
Limiting indices	$-6 \leq h \leq 8$ $-26 \leq k \leq 24$ $-20 \leq l \leq 22$	$-9 \leq h \leq 8$ $-24 \leq k \leq 25$ $-22 \leq l \leq 22$
No. of rflns collected	15414	16612
No. unique rflns [R(int)]	5416 (0.0254)	5556 (0.0414)
Data/restraints/parameters	5416/0/305	5556/0/315
Goodness of fit on F^2	0.607	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0322$ $wR_2 = 0.0729$	$R_1 = 0.0465$ $wR_2 = 0.1202$
R indices (all data)	$R_1 = 0.0358$ $wR_2 = 0.0766$	$R_1 = 0.0535$ $wR_2 = 0.1272$
Largest diff peak and hole ($e \text{ \AA}^{-3}$)	0.34 and -0.24	and -0.30

Single crystals of **Co1**(HOMe) and **Co4**(HOMe) suitable for the X-ray diffraction studies were grown by slow diffusion of *n*-heptane into a solution of the corresponding complex in a mixture of methanol and dichloromethane at room temperature. Data collection for both X-ray determinations was carried out on a Rigaku MM007-HF Saturn 724 + CCD diffractometer with confocal mirror monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.¹⁷ Details of the X-ray structure determination and refinements are provided in Table 4.

Oligomerization of ethylene

General procedure. The ethylene oligomerizations were carried out in a 250 mL stainless steel autoclave equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. The autoclave was evacuated and refilled with ethylene three times.

Toluene (50 mL), the desired amount of co-catalyst (MAO or MMAO) and a solution of the precatalyst (**Co1** – **Co6**, 3 μmol) in toluene (50 mL) were successively added by syringe under an ethylene atmosphere taking the total volume of solvent to 100 mL. When the desired reaction temperature was reached, the stirring was commenced and the ethylene pressure increased to 10 atm and maintained at this level by a constant feed of ethylene. After 30 min, the reaction was stopped by cooling the reactor in an ice bath and the excess pressure then slowly released. A small amount of this cooled reaction solution was collected (*ca.* 1 mL) and 5% aqueous hydrogen chloride added to terminate the reaction. A sample of this mixture (0.02 μL) was then immediately injected into the GC instrument to determine the distribution of oligomers obtained. The mass of C₄ and C₆ was calculated based on the ratio of the corresponding peaks to the toluene peak in the gas chromatogram. Since the volume of the toluene (*n*) is fixed, the amount of butenes A (*n*₁) and hexenes B (*n*₂) can be determined (see Tables S1 and S2). Prior to the catalytic evaluations the retention times for 1-alkenes (1-butene and 1-hexene) and internal alkenes (2-butene, 2-hexene and 3-hexene) were established. The catalytic activity was based on the mass of all oligomers fractions obtained.

ASSOCIATED CONTENT

Supporting Information

The hydrogen-bonding interactions in the crystal structure (Figure S1), gas chromatograms (Figures S2 - S36), the approach to determining the catalytic activity and relative percentage of the products (Tables S1 and S2). Electronic Supplementary Information (ESI) available: CCDC 1871156 and 1871157 contains the supplementary crystallographic data for compounds **Co1**(MeOH),

Co4(MeOH). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Selectivity effects on *N,N,N'*-cobalt catalyzed ethylene dimerization/trimerization dictated through choice of aluminoxane co-catalyst