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Selectivity Effects on *N,N,N′*-Cobalt Catalyzed Ethylene Dimerization/Trimerization Dictated through Choice of Aluminoxane Cocatalyst

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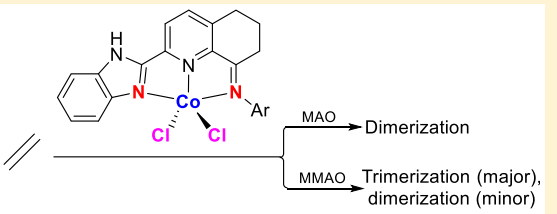
Supporting Information

ABSTRACT: The cobalt(II) chloride complexes, [2-($C_7H_4N_2H$)-8-(ArN)$C_{10}H_8N$]$CoCl_2$ (Ar = 2,6-$Me_2C_6H_3$ **Co1**; 2,6-$Et_2C_6H_3$ **Co2**; 2,6-*i*-$Pr_2C_6H_3$ **Co3**; 2,4,6-$Me_3C_6H_2$ **Co4**; 2,6-Et_2-4-MeC_6H_2 **Co5**; 2,4,6-*t*-$Bu_3C_6H_2$ **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···Cl and OH···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 toward the C_6 products (up to 49% 1-hexene). In general, the MMAO-promoted oligomerizations display higher catalytic activities with mesityl-containing **Co4** the stand-out performer [7.60×10^5 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-Phillips,[3] 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 favor the formation of shorter chain oligomers. Among them, cobalt precatalysts based on benzimidazole-substituted pyridylimines have shown a predilection toward dimers and trimers (Chart 1). Moreover, the nature of the 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.

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

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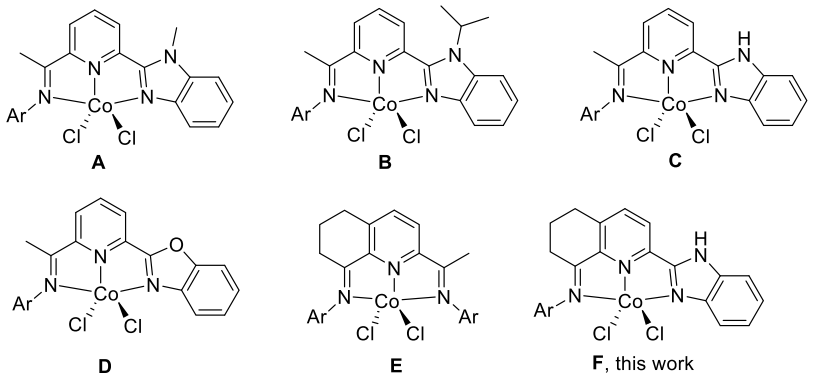
Chart 1. Developments in Unsymmetrical *N,N,N′*-Chelating Ligands for Cobalt(II) Chlorides

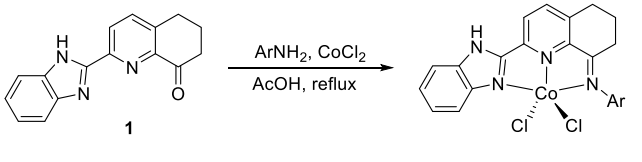


determine the effects of the precatalyst structure, type and amount of cocatalyst, and temperature on the selectivity of the ethylene oligomerization. Full synthetic and characterization details are additionally presented for the complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Co1−Co6. The cobalt(II) chloride complexes, [2-(C$_7$H$_4$N$_2$H)-8-(ArN)C$_{10}$H$_8$-N]CoCl$_2$ (Ar = 2,6-Me$_2$C$_6$H$_3$ **Co1**; 2,6-Et$_2$C$_6$H$_3$ **Co2**; 2,6-*i*-Pr$_2$C$_6$H$_3$ **Co3**; 2,4,6-Me$_3$C$_6$H$_2$ **Co4**; 2,6-Et$_2$-4-MeC$_6$H$_2$ **Co5**; 2,4,6-*t*-Bu$_3$C$_6$H$_2$ **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).

Scheme 1. Template Synthetic Route to Co1−Co6



	Co1	Co2	Co3	Co4	Co5	Co6
R^1	Me	Et	i-Pr	Me	Et	t-Bu
R^2	H	H	H	Me	Me	t-Bu
Yield (%)	57	64	57	62	49	50

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.

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-Me$_2$Ph **Co1**; 2,4,6-Me$_3$Ph **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*-CoCl$_2$(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−

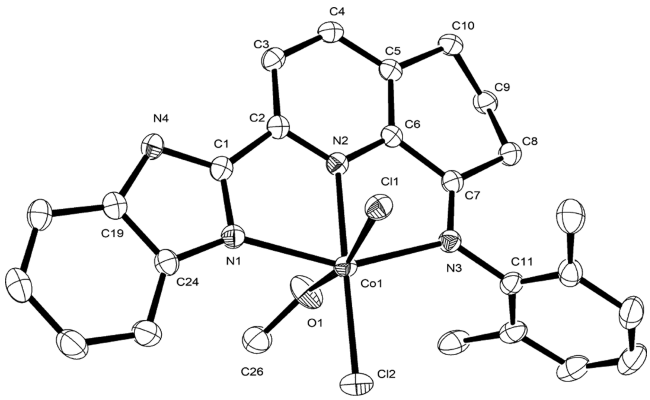


Figure 1. ORTEP representation of **Co1**(HOMe) with the thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity.

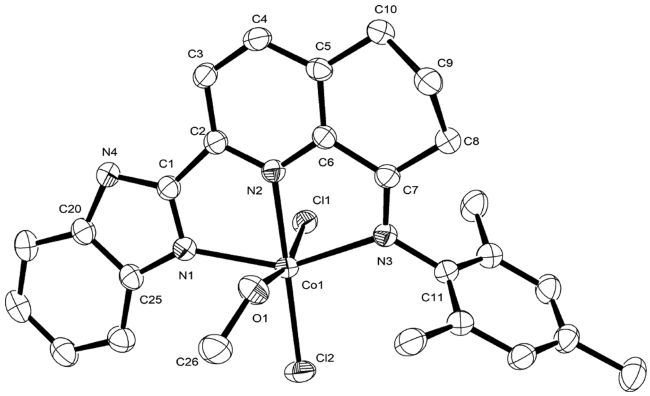


Figure 2. ORTEP representation of **Co4**(HOMe) with the thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) 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)

$N_{benzimidazole}$ 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 sp^3-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.

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 $LCoCl_2$.

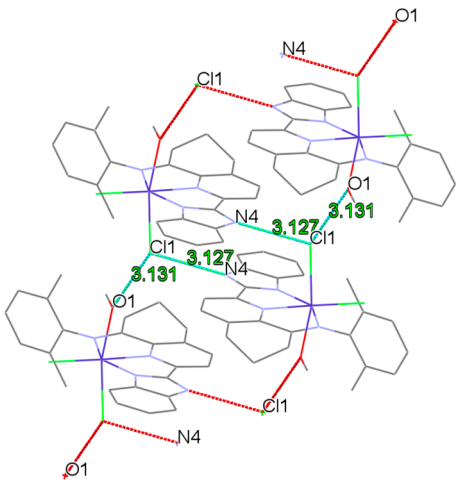

Figure 3. NH···Cl and OH···Cl hydrogen-bonding interactions between neighboring molecules of **Co1**(HOMe).

Ethylene Oligomerization. To explore the role of the cocatalyst, 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 C_2H_4 over 30 min 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.

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). First, 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 min (entries 1−4, Table 2). The optimum activity of 1.23×10^5 g·mol^{-1}(Co)·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.

Second, 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 1.23×10^5 g·mol^{-1}(Co)·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., α-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 2) or reaction temperature can be attributed to the greater thermodynamic stability of internal olefins (e.g., 2-butene).

Third, 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 min. The highest activity of 3.17×10^5 g·mol^{-1}(Co)·h^{-1} was observed after 5 min with 1-butene being the only product identifiable. However, this

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Table 2. Ethylene Oligomerization Using MAO as Cocatalyst[a]

entry	precatalyst	T [°C]	Al:Co	t [min]	activity[b]	oligomer distribution[c] (%)	
						$C_4/\sum C$	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 μmol of precatalyst, 10 atm C_2H_4, 100 mL of toluene. [b]$\times 10^5$ g·mol^{-1}(Co)·h^{-1}. [c]Determined by GC, and $\sum C$ signifies the total amounts of oligomers. [d]5 atm C_2H_4.

Table 3. Ethylene Oligomerization Using MMAO as Cocatalyst[a]

entry	precatalyst	T [°C]	Al:Co	t [min]	activity[b]	oligomer distribution[c] (%)			
						$C_4/\sum C$	α-C_4	$C_6/\sum C$	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 g·mol^{-1}(Co)·h^{-1}. [c]Determined by GC, and $\sum C$ 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.

selectivity for 1-butene gradually decreased over time with only 71.2% selectivity noted after 60 min. 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, $P_{C_2H_4}$ = 10 atm, the remaining five cobalt precatalysts were similarly screened. In terms of activity (range: 1.23−0.24 × 10^5 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,

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gave solely C_4 products with selectivities for 1-butene of greater than 86.7% and indeed 100% for **Co1** and **Co2**.

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 cocatalyst. 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 °C, the highest activity of 7.60×10^5 g·mol^{-1}(Co)·h^{-1} was observed at 50 °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 ($C_4/\sum C$ = 48.5%, $C_6/\sum C$ = 51.5%). Moreover, as the temperature is raised, the bias toward the C_6 products becomes more pronounced (70 °C: $C_4/\sum C$ = 12.9%, $C_6/\sum C$ = 87.1%). With regard to the C_6 products, the selectivity toward 1-hexene remains relatively constant (ca. 35%) between 50 and 70 °C, while, at 40 °C, a greater content of 1-hexene is apparent (up to 40%).

With the temperature of the run retained at 50 °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 7.60×10^5 g·mol^{-1}(Co)·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 C_6 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 C_6 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 26.3×10^5 g·mol^{-1}(Co)·h^{-1} of the entire study was seen after 5 min, which equates to an 8-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 5.23×10^5 g·mol^{-1}(Co)·h^{-1} after 60 min, which is still higher than that seen with MAO after 5 min (3.17×10^5 g·mol^{-1}(Co)·h^{-1}, entry 8, Table 3). On the other hand, the bias toward the C_6 products increases with time with the amount of C_6 constituting 93.0% of the mixture after 60 min; the 1-hexene content however remains constant at around 36% over the various reaction times. Lowering the pressure from 10 to 5 atm C_2H_4, under otherwise identical conditions, saw the activity drop from 7.60 to 6.00×10^5 g·mol^{-1}(Co)·h^{-1} with an increased preference for C_6 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 show 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·mol^{-1}(Co)·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 not only are more active but also reveal some variations in relative performance with the most sterically hindered system **Co6** now notably toward 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-C_6 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 toward trimerization of ethylene and no evidence of polymeric fractions, a byproduct 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 C_4/C_6 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 cocatalyst 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 cocatalyst, all the complexes were effective (activities up to 1.23×10^5 g·mol^{-1}(Co)·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 cocatalyst, 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 7.60×10^5 g·mol^{-1}(Co)·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.

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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 PerkinElmer 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-(1*H*-benzoimidazol-2-yl)-6,7-dihydroquinolin-8(5*H*)-one (**1**) was prepared as described in the literature.[16]

Synthesis of [2-($C_7H_4N_2H$)-8-(ArN)$C_{10}H_8N$]$CoCl_2$. *Ar = 2,6-$Me_2C_6H_3$ (**Co1**).* A suspension of **1** (0.158 g, 0.60 mmol), 2,6-dimethylaniline (0.087 g, 0.72 mmol), and 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 ($\nu_{C=N}$, 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%.

*Ar = 2,6-$Et_2C_6H_3$ (**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 ($\nu_{C=N}$, 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%.

*Ar = 2,6-i-$Pr_2C_6H_3$ (**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 ($\nu_{C=N}$, 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%.

*Ar = 2,6-Et_2-4-MeC_6H_2 (**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 ($\nu_{C=N}$, 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%.

*Ar = 2,6-Et_2-4-MeC_6H_2 (**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 ($\nu_{C=N}$, 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 $C_{27}H_{28}Cl_2CoN_4$: C, 60.23, H, 5.24, N, 10.41. Found: C, 60.61, H, 5.01, N, 10.13%.

*Ar = 2,4,6-t-$Bu_3C_6H_2$ (**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 ($\nu_{C=N}$, 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 $C_{34}H_{42}Cl_2CoN_4$: C, 64.15, H, 6.65, N, 8.80. Found: C, 64.48, H, 6.39, N, 8.72%.

X-ray Crystallographic Studies. 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−Kα radiation (λ = 0.71073 Å). 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.

Table 4. Crystal Data and Structure Refinement Details for Co1(HOMe) and Co4(HOMe)

	Co1-(HOMe)	**Co4**-(HOMe)
formula	$C_{25}H_{26}Cl_2CoN_4O$	$C_{26}H_{28}Cl_2CoN_4O$
formula weight	528.33	542.35
T (K)	173	173(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 (deg)	90	90
β (deg)	93.68(3)	95.216(3)
γ (deg)	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 (deg)	4−54.966	4.072−54.958
limiting indices	$-6 \le h \le 8$	$-9 \le h \le 8$
	$-26 \le k \le 24$	$-24 \le k \le 25$
	$-20 \le l \le 22$	$-22 \le l \le 22$
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	R_1 = 0.0465
	wR_2 = 0.0729	wR_2 = 0.1202
R indices (all data)	R_1 = 0.0358	R_1 = 0.0535
	wR_2 = 0.0766	wR_2 = 0.1272
largest diff peak and hole (e Å^{-3})	0.34 and −0.24	and −0.30

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 cocatalyst (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

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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 C_4 and C_6 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 Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00924.

The approach to determining the catalytic activity and relative percentage of the products (Tables S1 and S2), the hydrogen-bonding interactions in the crystal structure (Figure S1), and the gas chromatograms (Figures S2−S36) (PDF)

Accession Codes

CCDC 1871156 and 1871157 contain the supplementary crystallographic data for this paper. 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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