



2-Benzoxazolyl-6-(1-(arylimino)ethyl)pyridyl cobalt (II) chlorides: A temperature switch catalyst in oligomerization and polymerization of ethylene

Rong Gao^a, Kefeng Wang^a, Yan Li^a, Fosong Wang^a, Wen-Hua Sun^{a,*}, Carl Redshaw^b, Manfred Bochmann^b

^a Key laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK

ARTICLE INFO

Article history:

Received 28 February 2009

Received in revised form 25 May 2009

Accepted 27 May 2009

Available online 6 June 2009

Keywords:

Cobalt complexes

Temperature switch catalyst

Ethylene oligomerization

Ethylene polymerization

ABSTRACT

A series of cobalt (II) complexes ligated by 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines was synthesized and characterized by FT-IR spectroscopic and elemental analysis. The molecular structures of **Co1** (Ar = 2,6-Me₂C₆H₃), **Co2** (Ar = 2,6-Et₂C₆H₃) and **Co7** (Ar = 2,6-Br₂C₆H₃) were determined by single-crystal X-ray diffraction. Compounds **Co1** and **Co2** display a distorted trigonal-bipyramidal geometry, whereas complex **Co7** is a distorted square-pyramid. Upon activation with methylaluminoxane (MAO), all cobalt complexes showed reactivity towards ethylene. There was however an unexpected temperature dependence; whereas, at room temperature oligomerization was observed, giving 1-alkenes with high selectivities, at elevated temperatures polyethylene was produced. This unusual catalytic behavior of the new complexes was investigated in detail under various reaction parameters.

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1. Introduction

Iron and cobalt complexes based on bis(arylimino)pyridines are known as highly active catalysts for the polymerization of ethylene [1–3], and such systems are currently the focus of much research [4–10]. Bianchini, Erker and others [11–17] have investigated unsymmetrical systems in which one of the arylimino groups was replaced by an alkyl or aryl substituent. Complexes of this type have recently been reviewed [18–25]. Cobalt catalysts have attracted less attention than their iron counterparts because in general they show lower activities. On the other hand, cobalt complexes of 2,9-bis(1-(arylimino)ethyl)phenanthrolines [26] and 2-methyl-2,4-bis(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines [27,28] showed higher activities than their iron analogues. In line with the behavior of most polymerization catalysts, the molecular weights of the polyethylenes produced with these Co and Fe catalysts decrease with increasing reaction temperatures.

Since good activities were found for metal complexes bearing 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines [29–32], we decided to explore related 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridine ligands. Nickel complexes of these ligands show good to high catalytic activities for ethylene oligomerization [33,34]. On activation by MAO these cobalt catalysts showed an

unusual temperature dependence, whereby at room temperature ethylene oligomerization took place, whereas at elevated temperatures polyethylenes were produced. We report here the syntheses and characterization of these cobalt complexes and their catalytic behavior in ethylene oligomerization and polymerization.

2. Experimental

2.1. General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. The 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines (**L1–L7**) were prepared according to our reported procedure [34]. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corporation. Diethylaluminum chloride (Et₂AlCl, 1.7 M in toluene) was purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 300 MHz instrument at ambient temperature using TMS as an internal standard. FT-IR spectra were recorded on a PerkinElmer System 2000 FT-IR spectrometer. Elemental analyses were carried out using an HPMOD 1106 micro-analyzer. GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a

* Corresponding author. Tel.: +86 10 62557955; fax: +86 10 62618239.

E-mail address: whsun@iccas.ac.cn (W.-H. Sun).

Table 1
Crystal data and structure refinement details for **Co1**, **Co2** and **Co7**.

	Co1	Co2	Co7-CH₃OH
Formula	C ₄₄ H ₃₈ Cl ₄ Co ₂ N ₆ O ₂	C ₂₄ H ₂₃ Cl ₂ CoN ₃ O	C ₂₀ H ₁₃ Br ₂ Cl ₂ CoN ₃ O·CH ₃ OH
Formula weight	904.16	499.28	633.03
T (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P1	P2 ₁ /c	P2 ₁ /n
a (Å)	9.3733(19)	8.7814(18)	10.858(2)
b (Å)	9.5328(19)	15.155(3)	15.337(3)
c (Å)	11.674(2)	17.494(4)	13.744(2)
α (°)	92.97(3)	90	90
β (°)	99.60(3)	99.94(3)	101.06(3)
γ (°)	95.30(3)	90	90
V (Å ³)	1021.7(3)	2293.1(8)	2246.4(8)
Z	2	4	4
D _{calc} (Mg m ⁻³)	1.469	1.446	1.777
μ (mm ⁻¹)	1.118	1.003	4.575
F(000)	444	1028	1172
Crystal size (mm)	0.24 × 0.24 × 0.08	0.25 × 0.25 × 0.19	0.30 × 0.18 × 0.18
θ range (°)	1.77–27.38	2.35–27.48	2.01–27.44
Limiting indices	–12 ≤ h ≤ 12 –11 ≤ k ≤ 12 –15 ≤ l ≤ 15	–11 ≤ h ≤ 11 –19 ≤ k ≤ 19 –22 ≤ l ≤ 22	–14 ≤ h ≤ 14 –19 ≤ k ≤ 19 –17 ≤ l ≤ 17
No. of refinement collected	8390	10074	9818
No. of unique refinement	4609	5263	5124
Completeness to θ (%)	99.5 (θ = 27.38°)	99.9 (θ = 27.48°)	99.8 (θ = 27.44°)
Absorption correction	Multi-scan	Multi-scan	Multi-scan
No. of parameters	262	281	284
Goodness of fit on F ²	1.225	1.221	1.218
Final R indices (I > 2σ(I))	R1 = 0.0569 wR2 = 0.1296	R1 = 0.0578 wR2 = 0.1002	R1 = 0.0618 wR2 = 0.0844
R indices (all data)	R1 = 0.0746 wR2 = 0.1450	R1 = 0.0747 wR2 = 0.1052	R1 = 0.0911 wR2 = 0.0902
Largest difference peak and hole (e Å ⁻³)	0.614, –0.577	0.506, –0.465	0.546, –0.524

30 m (0.25 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yield of oligomers was calculated by referencing to the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. Selectivity for linear 1-alkenes was defined as (amount of linear 1-alkenes of all fractions)/(total amount of oligomer products) in percent.

2.2. Synthesis of cobalt complexes

General procedure. A solution of CoCl₂ in ethanol was added dropwise to a solution of the ligand in ethanol. The reaction mixture was stirred at room temperature for 12 h. The resulting precipitate was collected, washed with diethyl ether and dried in vacuum. All the complexes were prepared in high yield in this manner.

2.2.1. (E)-2,6-Dimethyl-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co1**)

Obtained as green powder in 90.8% yield. FT-IR (KBr; cm⁻¹): 3070 (w), 1616 (ν_{C=N}) (m), 1594 (w), 1570 (w), 1545 (m), 1469 (w), 1450 (m), 1375 (s), 1278 (s), 1214 (m), 1173 (w), 1095 (w), 1023 (w), 813 (w), 791 (w), 766 (s), 750 (w). Anal. Calcd. for C₂₂H₁₉Cl₂CoN₃O (471.24): C, 56.07; H, 4.06; N, 8.92. Found: C, 56.23; H, 4.12; N, 8.81.

2.2.2. (E)-2,6-Diethyl-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co2**)

Obtained as green powder in 91.3% yield. FT-IR (KBr; cm⁻¹): 2971 (m), 1614 (ν_{C=N}) (m), 1594 (w), 1570 (w), 1546 (m), 1449 (s), 1375 (s), 1276 (s), 1209 (w), 1195 (w), 1173 (w), 1102 (w), 1023 (w), 813 (w), 787 (s), 767 (s), 750 (w). Anal. Calcd. for C₂₄H₂₃Cl₂CoN₃O (499.30): C, 57.73; H, 4.64; N, 8.42. Found: C, 57.72; H, 4.79; N, 8.39.

2.2.3. (E)-2,6-Diisopropyl-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co3**)

Obtained as green powder in 85.8% yield. FT-IR (KBr; cm⁻¹): 3066 (w), 2962 (m), 2927 (w), 1613 (ν_{C=N}) (m), 1594 (w), 1548 (m), 1448 (m), 1373 (s), 1278 (s), 1193 (w), 1103 (w), 1022 (w), 817 (w), 789 (m), 762 (m), 749 (m). Anal. Calcd. for C₂₆H₂₇N₃Cl₂CoO (527.35): C, 59.22; H, 5.16; N, 7.97. Found: C, 59.13; H, 5.07; N, 7.96.

2.2.4. (E)-2,4,6-Trimethyl-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co4**)

Obtained as green powder in 77.0% yield. FT-IR (KBr; cm⁻¹): 3061 (w), 1610 (ν_{C=N}) (m), 1591 (w), 1540 (m), 1479 (m), 1447 (m), 1371 (m), 1290 (w), 1275 (s), 1218 (m), 1171 (m), 1101 (w), 1021 (w), 814 (w), 772 (s), 743 (w). Anal. Calcd. for C₂₃H₂₁Cl₂CoN₃O (485.27): C, 56.93; H, 4.36; N, 8.66. Found: C, 56.70; H, 4.42; N, 8.68.

2.2.5. (E)-4-Bromo-2,6-dimethyl-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co5**)

Obtained as green powder in 78.4% yield. FT-IR (KBr disk; cm⁻¹): 2911 (w), 1618 (ν_{C=N}) (m), 1595 (w), 1548 (m), 1453 (w), 1374 (m), 1276 (m), 1211 (s), 1023 (m), 995 (w), 865 (w), 772 (m). Anal. Calcd. for C₂₂H₁₈BrCl₂CoN₃O (550.14): C, 48.03; H, 3.30; N, 7.64. Found: C, 47.72; H, 3.35; N, 7.62.

2.2.6. (E)-2,6-Dichloro-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co6**)

Obtained as green powder in 90.8% yield. FT-IR (KBr; cm⁻¹): 3066 (w), 2962 (w), 2927 (w), 1617 (ν_{C=N}) (m), 1594 (w), 1545 (m), 1438 (s), 1376 (m), 1279 (s), 1176 (w), 1089 (w), 1023 (w), 812 (w), 771 (s), 748 (w). Anal. Calcd. for C₂₀H₁₃Cl₄CoN₃O (512.08): C, 46.91; H, 2.56; N, 8.21. Found: C, 46.73; H, 2.83; N, 8.13.

2.2.7. (E)-2,6-Dibromo-N-(1-(6-(benzo[d]oxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine CoCl₂ (**Co7**)

Obtained as green powder in 77.0% yield. FT-IR (KBr; cm⁻¹): 3049 (w), 1616 (ν_{C=N}) (m), 1594 (w), 1548 (m), 1449 (w), 1431 (s), 1374 (m), 1277 (s), 1229 (w), 1176 (w), 1099 (w), 1022 (w), 810 (w), 783 (m), 771 (s), 730 (m). Anal. Calcd. for C₂₀H₁₃Br₂Cl₂CoN₃O (600.98): C, 39.97; H, 2.18; N, 6.99. Found: C, 39.65; H, 2.25; N, 6.89.

2.3. Crystal structure determinations

Single-crystals of **Co1**, **Co2** and **Co7** suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into their methanol solutions. Single-crystal X-ray diffraction studies were carried out on a Rigaku RAXIS Rapid IP diffractometer using graphite 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 F². All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [35]. Crystal data and processing parameters for **Co1**, **Co2** and **Co7** are summarized in Table 1.

2.4. Oligomerization or/and polymerization of ethylene

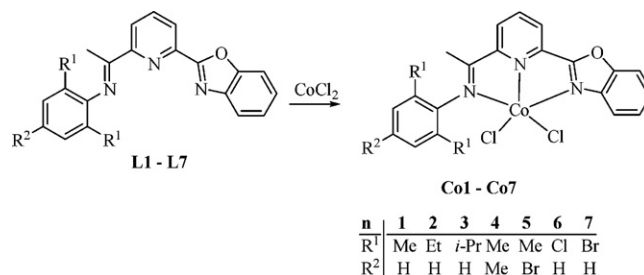
General procedure. Ethylene oligomerizations at 10 atm ethylene pressures were carried out in a 500 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. Toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, the ethylene pressure was increased to 10 atm, and maintained at this level by constant feeding of ethylene. After 30 min, the reaction was stopped by cooling the reactor on an ice bath before the excess pressure was released. A small amount of the reaction solution was collected, the reaction was terminated by the addition of 5% aqueous hydrogen chloride, and then this mixture was analyzed by gas chromatography (GC) to determine the distribution of oligomers obtained. The remaining reaction solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, and dried under vacuum at 60 °C to constant weight.

3. Results and discussion

3.1. Synthesis and characterization of cobalt complexes (**Co1–Co7**)

A series of 2-(2-benzoxazolyl)-6-(1-(arylimino)-ethyl)pyridine (**L1–L7**) ligands was prepared following previously reported procedures [34]. The cobalt complexes **Co1–Co7** were prepared by treating CoCl₂ with one equiv. of **L** in ethanol at room temperature (Scheme 1). The products were collected by filtration, washed with diethyl ether and dried under vacuum. The complexes are air-stable powders which were characterized by FT-infrared spectroscopy. The elemental analyses confirmed the composition LCoCl₂. The C=N stretching frequencies of **Co1–Co7** are shifted to lower values (1613–1616 cm⁻¹) compared to the free ligands.

Single crystals of **Co1**, **Co2** and **Co7** were grown from their methanol solutions layered with diethyl ether. The molecular structures were determined by X-ray diffraction. Selected bond lengths and angles are collected in Table 2. Fig. 1 shows the structures of **Co1** and **Co7**; they differ mainly in the orientation of the CoCl₂ moiety.



Scheme 1. Synthesis of complexes **Co1–Co7**.

Complexes **Co1** and **Co2** have essentially identical structures (for the ORTEP plot of **Co2** see the Supporting Information). The coordination geometry around the cobalt center is a distorted trigonal bipyramid, in which the pyridine-nitrogen (N(1)) and two chlorine atoms form the equatorial plane, while the cobalt atom lies slightly out of the equatorial plane by 0.0356 Å in **Co1** and 0.0203 Å in **Co2**. The axial positions are occupied by the other two nitrogen atoms N(2) and N(3). The N(2)–Co–N(3) moiety deviates significantly from linearity (**Co1**: N(2)–Co(1)–N(3) 147.28(1)°; **Co2**: 149.66(8)°). The equatorial planes of these two complexes are nearly perpendicular to the benzoxazole rings, with dihedral angles of 88.4° in **Co1** and 83.7° in **Co2**. The 2,6-dimethylphenyl substituent lies almost orthogonally to the plane N(3)–N(1)–N(2) (91.7° in **Co1** and 95.9° in **Co2**). Similar geometries are also observed in cobalt (II) complexes of 2-(benzimidazolyl)-6-iminopyridines [29,32], 2-imino-1,10-phenanthrolines [36,37], and 2-(benzimidazolyl)-1,10-phenanthrolines [38]. The steric effect of substituents at *ortho*-positions of the phenyl ring is reflected in the adjacent C–N bond lengths, i.e. the Co(1)–N(3) bond length of **Co1** (2.198(3) Å) is noticeably shorter than that of **Co2** (2.259(2) Å).

The structure of **Co7** is best described as a distorted square pyramid. The atoms N(1), N(2), N(3) and Cl(1) are almost coplanar, deviating only by 0.01 Å. The cobalt atom deviates from the N(1)–N(2)–N(3) plane by 0.1448 Å. The benzoxazole is almost coplanar with the pyridine ring, with a dihedral angle of 7.8°. The two Co–Cl bond lengths are substantially different, 2.3240(1) and 2.2523(1) Å, much larger than the bond length difference in **Co1** and **Co2** (0.02 Å). Clearly the introduction of electron-withdrawing substituents in the *ortho*-positions of the phenyl rings has a pronounced effect on the structure, and this is also likely to affect the catalytic activities.

Table 2
Selected bond lengths (Å) and angles (deg) for **Co1**, **Co2** and **Co7**.

	Co1	Co2	Co7
Bond lengths			
Co(1)–N(1)	2.080(3)	2.064(2)	2.089(4)
Co(1)–N(2)	2.218(3)	2.235(2)	2.179(4)
Co(1)–N(3)	2.198(3)	2.259(2)	2.194(4)
Co(1)–Cl(1)	2.2833(12)	2.2477(1)	2.2523(13)
Co(1)–Cl(2)	2.2439(12)	2.2671(9)	2.3240(13)
N(2)–C(6)	1.300(4)	1.297(3)	1.296(5)
N(2)–C(40)	1.397(4)	1.402(3)	1.397(5)
O(1)–C(6)	1.352(4)	1.350(3)	1.360(5)
N(3)–C(12)	1.285(4)	1.281(3)	1.297(5)
Bond angles			
N(1)–Co(1)–N(2)	74.99(11)	75.69(8)	75.10(14)
N(1)–Co(1)–N(3)	74.50(11)	74.19(8)	73.81(14)
N(2)–Co(1)–N(3)	147.28(1)	149.66(8)	144.46(14)
N(1)–Co(1)–Cl(1)	101.93(9)	129.98(7)	155.33(1)
N(2)–Co(1)–Cl(1)	92.46(8)	95.54(6)	100.78(1)
N(3)–Co(1)–Cl(1)	105.16(8)	100.92(7)	100.27(1)
Cl(1)–Co(1)–Cl(2)	118.28(5)	115.66(3)	111.10(5)
N(1)–Co(1)–Cl(2)	139.18(9)	114.17(7)	93.48(1)
N(2)–Co(1)–Cl(2)	95.46(8)	95.43(6)	92.88(1)
N(3)–Co(1)–Cl(2)	99.86(8)	100.07(7)	105.75(1)

Table 3
Oligomerization of ethylene with **Co1–Co7** at 20 °C.

Entry	Catalyst	Cocatalyst	Al/Co	Product mass (g)	Productivity ^a	Oligomer distribution (%) ^b		
						C ₄ /∑C	α-C ₄	C ₆ /∑C
1	Co1	MAO	1000	0.92	3.70	100	100% ^c	0
2	Co1	MMAO	1000	0.29	1.17	100	77.2	0
3	Co1	Et ₂ AlCl	200	–	–	–	–	–
4	Co2	MAO	1000	0.23	0.91	100	99.4	0
5	Co3	MAO	1000	0.17	0.68	98.8	99.0	1.2
6	Co4	MAO	1000	0.12	0.50	100	97.1	0
7	Co5	MAO	1000	0.28	1.12	96.7	93.2	3.3
8	Co6	MAO	1000	1.81	7.24	99.4	100% ^c	0.6
9	Co7	MAO	1000	1.88	7.52	100	100% ^c	0

Reaction conditions: 5 μmol Co; 10 atm ethylene; 30 min; 20 °C; 100 mL toluene.

^a In units of 10⁵ g (mol Co)⁻¹ h⁻¹.

^b Determined by GC; ∑C denotes the total amounts of oligomers.

^c No butene isomerization products could be detected.

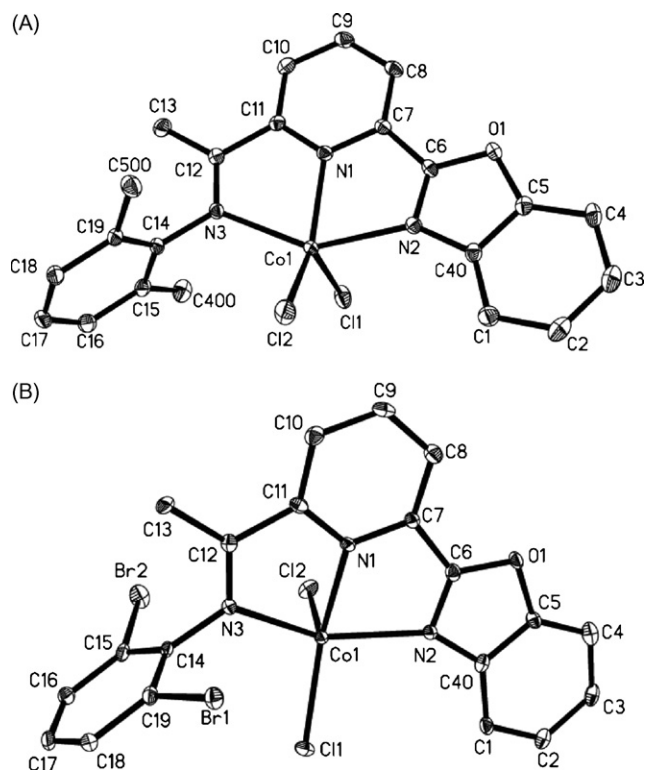


Fig. 1. Molecular structure of **Co1** (A) and **Co7** (B) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 4
Influence of the Al/Co ratio on the oligomerization of ethylene with **Co7**/MAO.

Entry	Al/Co	T (°C)	Product mass (g)	Activity ^a		Oligomer distribution (%) ^b		
				Oligomer	Polymer	C ₄ /∑C	α-C ₄	C ₆ /∑C
1	200	20	0.86	3.45	0	98.6	100% ^c	1.4
2	500	20	1.42	5.66	0	99.5	99.5	0.5
3	800	20	1.74	6.98	0	99.6	99.8	0.4
4	1000	20	1.88	7.52	0	100	100% ^c	0
5	1200	20	1.86	7.43	0	99.6	99.9	0.4
6	1500	20	0.70	2.78	0	99.7	99.7	0.3
7	1000	30	0.64	2.55	0	99.4	98.8	0.6
8	1000	40	0.22	0.14	0.72	94.8	100% ^c	5.2
9	1000	50	0.16	0.05	0.61	100	100% ^c	0

Conditions: 5 μmol **Co7**; 10 atm ethylene; 30 min; 100 mL toluene.

^a In units of 10⁵ g (mol Co)⁻¹ h⁻¹.

^b Determined by GC.

^c No butene isomerization products could be detected.

3.2. Reactions with ethylene

With methylaluminoxane (MAO) as activator under 10 atm of ethylene pressure, all the cobalt (II) complexes displayed moderate activities for the oligomerization of ethylene, with high selectivities for 1-alkenes (Table 3). Although MMAO or Et₂AlCl could also be used as cocatalyst, they give lower activities (entries 2, 3 in Table 3), hence further investigations were carried out using MAO as the cocatalyst.

As we had found previously with cobalt complexes of 2-(benzimidazolyl)-6-iminopyridines [29,32] and other ligands [28,37,38], **Co1–Co7** only produced ethylene dimers and trimers without polymeric by-products at 20 °C. The *N*-aryl substituents significantly affected the catalytic activities, and the ethylene oligomerization activities decreased in the order **Co7** ≈ **Co6** > **Co1** > **Co5** > **Co2** > **Co3** ≈ **Co4**. In general, electron-withdrawing substituents enhance catalyst activities, as do less bulky substituents. A possible explanation is that in late-transition metal catalytic systems, both bulkier and more electron-rich ligands weaken the interactions between the metal center and the incoming monomer and thereby retard the rate of ethylene insertion. The observed activity trends appear to be a superposition of electronic and steric factors. It is difficult to rationalize the steric influence of ligands; however, the electronic effects have been simulated and explained with the aid of computational studies that suggest a relationship of catalytic activity with the net charge of late-transition metal complexes [39–42].

The reaction parameters also affect the observed catalytic activities. For example, when the Al/Co molar ratio was increased from 200 to 1500, the activities of **Co7**/MAO initially increased and then decreased, with the optimum activity observed at an Al/Co molar ratio of 1000 (entry 4 in Table 4).

Table 5
Polymerization of ethylene with **Co1–Co7**/MAO at 40 °C.

Entry	Catalyst	Product mass (g)	Activity ^a		Oligomer distribution (%) ^b		PE mol. weight ^c	
			Oligomer	Polymer	C ₄ /Σ C	C ₆ /Σ C	M _w ^d	M _w /M _n
1	Co1	1.41	0	5.63	0	0	17.0	12
3	Co2	0.92	0	3.70	0	0	33.8	4.3
5	Co3	0.55	0	2.21	0	0	17.5	3.3
7	Co4	0.26	0	1.04	0	0	–	–
9	Co5	0.48	0	1.91	0	0	20.9	3.8
10	Co6	0.27	1.07	Trace	28.7	16.0	–	–
11	Co7	0.22	0.14	0.72	94.8	5.2	31.4	4.6

Conditions: 5 μmol Co; 1000 equiv. of MAO; 10 atm ethylene; 30 min; 40 °C; 100 mL toluene.

^a In units of 10⁵ g (mol Co)⁻¹ h⁻¹.

^b Determined by GC.

^c Determined by GPC.

^d In units of 10⁴ g mol⁻¹.

Rather unexpectedly, increasing the reaction temperature led to the formation of polyethylene (Table 5). At 40 °C under 10 atm of ethylene, the catalysts **Co1–Co5** solely produced polyethylenes, whereas **Co6** and **Co7** at 40 °C gave variable amounts of oligomers as well as polymers. The polyethylenes have moderate molecular weights in the order of (17–34) × 10⁴ g mol⁻¹. In all cases the polydispersities were rather broader than expected for single-site behavior.

Increasing the ethylene pressure from 10 to 30 atm over the temperature range of 40–60 °C led to an increase in catalytic activities (compare Table 6 with Table 5), and with **Co6** and **Co7** especially, the polymer molecular weight also increase significantly (Table 6, entries 9 and 10).

The origin of the change in catalytic behavior, i.e. formation of oligomers below 40 °C and of polymers above this threshold temperature, is as yet unknown. One possibility was the alkylation of the ligand framework. It did not prove possible to recover the ligand from the actual polymerization reactions. However, the following experiment was employed to check stabilities of the complex in the presence of MAO. A mixture of **Co3** with MAO (Al/Co=1000:1) was stirred at 60 °C for 30 min, followed by hydrolysis. From this mixture, the ligand 2,6-diisopropyl-N-(1-(6-(benzoxazol-2-yl)pyridin-2-yl)ethylidene)benzenamine was recovered in 76%, thus confirming that the ligand did not change on treatment with MAO or AlMe₃.

The catalytic activity of these cobalt systems is temperature dependent. The best activities were observed at 40 °C. The activities decreased with increasing reaction temperature even under 30 atm of ethylene, and at 70 °C precursor **Co1** had little activity.

Table 6
Polymerization of ethylene with **Co1–Co7**/MAO at 30 atm.

Entry	Catalyst	T (°C)	Product mass (g)	Activity ^a	PE mol. weight ^b	
					M _w ^c	M _w /M _n
1	Co1	40	2.19	21.9	55.5	4.3
2	Co1	50	1.32	13.2	26.5	3.9
3	Co1	60	1.20	12.0	21.0	3.6
4	Co1	70	Trace	Trace	–	–
5	Co2	40	0.42	4.2	124.2	2.8
6	Co3	40	0.34	3.4	110.0	4.4
7	Co4	40	0.46	4.6	70.1	4.0
8	Co5	40	0.76	7.6	43.4	2.5
9	Co6	40	0.41	4.1	124.0	7.6
10	Co7	40	0.43	4.3	214.6	7.0

Conditions: 2 μmol of Co; 1000 equiv. of MAO; 30 atm ethylene; 30 min; 40 mL toluene.

^a In units of 10⁵ g (mol Co)⁻¹ h⁻¹.

^b Determined by GPC.

^c In units of 10⁴ g mol⁻¹.

The most likely reason for this is more facile ligand transfer to Al and/or complex decomposition under such conditions.

4. Conclusion

The cobalt complexes bearing the unsymmetrical ligand 2-(benzoxazolyl)-6-(1-(arylimino)ethyl)pyridine give improved catalytic activities compared with the analogous 2-(benzimidazolyl)-6-aminopyridine complexes [29,32]. An ethylene oligomerization productivity of up to 7.5 × 10⁵ g (mol Co)⁻¹ h⁻¹ was found, with good selectivity for α-olefins. The activities increased with decreasing electron-donor strength of the ligands. However, increasing the reaction temperature to 40 °C led unexpectedly to the formation of polyethylene, with about the same order of productivity. This catalytic system is thus behaving as a temperature-switch catalyst for the oligomerization and polymerization of ethylene.

Supporting information available

All data for molecular structures of **Co1**, **Co2**, and **Co7** are provided in detail as supplementary material. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 721467 for **Co1**, 721468 for **Co2**, 721469 for **Co7**. Copy of this information is available free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgments

This work was supported by NSFC No. 20674089 and the Royal Society/NSFC (project IJP 2007/R3). We thank Dr. Steve Holding (RAPRA Technology, Shrewsbury, UK) for GPC measurements.

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