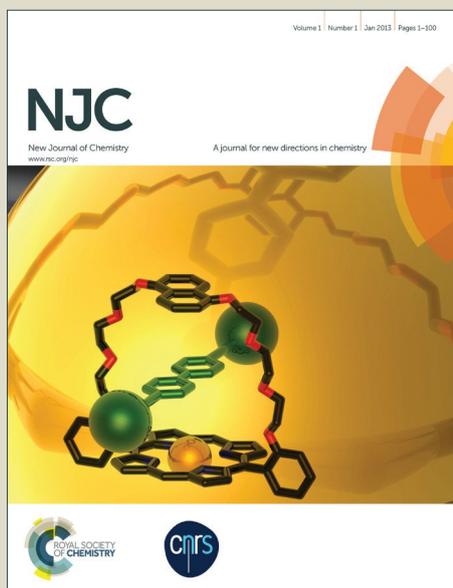


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Thermally stable and highly active cobalt precatalysts for vinyl-polyethylenes with narrow polydispersities: integrating fused-ring and imino-carbon protection into ligand design

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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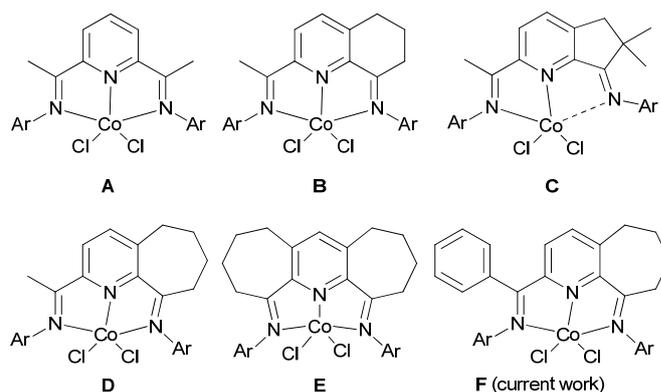
Abstract: A series of [2-(1-aryliminobenzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt chlorides (aryl = 2,6-Me₂Ph (**Co1**), 2,6-Et₂Ph (**Co2**), 2,6-*i*-Pr₂Ph (**Co3**), 2,4,6-Me₃Ph (**Co4**), 4-Me-2,6-Et₂Ph (**Co5**)), incorporating a fused seven-membered ring and an imino C-phenyl group, was synthesized and characterized. Upon activation with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), **Co1** – **Co5** all showed high activities toward ethylene polymerization with **Co4**/MAO system the highest (8.65 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹). Significantly, these systems exhibited good thermal stability (up to 80 °C) as well as long catalytic lifetimes. The polyethylenes obtained all contained vinyl end-groups as well as narrow polydispersities. These phenyl-modified cobalt precatalysts provide a functional system for generating a unique class of vinyl-polyethylenes due to their ease of preparation, high catalytic activities and thermally stable polymerization.

Introduction

The search for late-transition metal catalysts for ethylene polymerization is an area of keen current interest to both academic and industrial researchers.¹ In comparison to traditional Ziegler-Natta systems, a key advantage of late-transition metal catalysts is their ready tunability through straightforward ligand modification, which makes for easier and better control of the properties of the resultant polymers.² The last twenty years or so have seen a host of developments in the field,^{3,4} with two key milestones identifiable, viz., the α -diimine Ni(II) and Pd(II) catalysts⁵ and the bis(imino)pyridine Fe(II) and Co(II) catalysts.⁶ So far, there have been numerous studies dedicated to modifying the bis(imino)pyridine ligand framework, especially on varying the imino N-aryl group.⁶ By contrast, less research activity has been focused on changing substituents linked to the imino carbon atom.⁷

However, one drawback of the bis(imino)pyridine systems (e.g., **A**, Scheme 1) is their susceptibility to catalyst deactivation at higher operating temperatures. This may, in part, be attributed to degradation pathways involving

alkylation reactions of the catalyst by the alkylaluminium co-catalyst.⁸ Alternatively, the imino C-methyl groups can undergo deprotonation chemistry, providing a further route for catalyst deactivation.^{8a,9} To circumvent these unwanted side reactions, the introduction of a phenyl group at the imino carbon atom presents a potential means of inhibiting these pathways which in turn may improve the thermal stability of the catalyst.



Scheme 1. Ligand frameworks for active cobalt complex pre-catalysts

Elsewhere, our group has previously found that the fused ring-size plays a crucial role in controlling the catalytic activity and the properties of the resultant polyethylenes. Indeed cobalt catalysts based on a 2-(1-(arylimino)ethyl)-8-arylimino-5,6,7-trihydroquinolyl ligand set (**B**, Scheme 1), incorporating a six-membered ring, exhibit much higher activities and better thermal stability than the prototypical 2,6-bis(imino)pyridyl

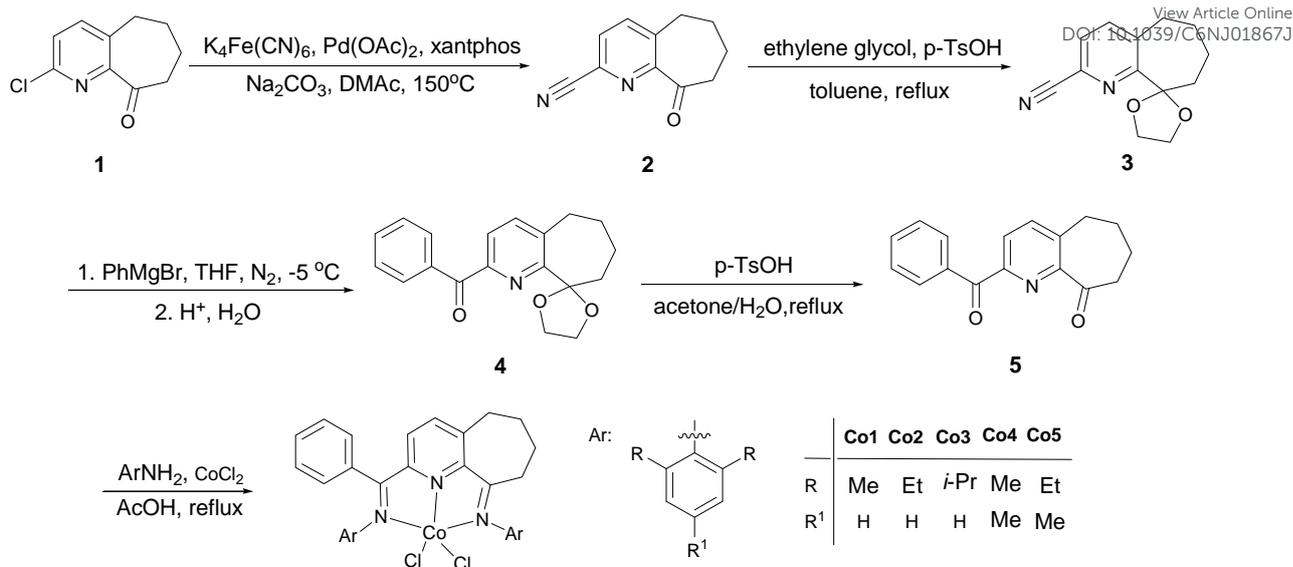
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† Appendix A. Supplementary material: CCDC 1476932 contains the supplementary crystallographic data for **Co3**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif



Scheme 2. Synthesis of organic compounds and their cobalt(II) complexes

cobalt complexes (**A**).¹⁰ On the other hand, contraction of the ring to a five-membered cyclopentane ring (**C**, Scheme 1), leads to much lower activities in ethylene polymerization;¹¹ an observation that can be attributed to inefficient imine-N coordination to the cobalt. Significantly however, the seven-membered ring system (**D**, Scheme 1) exhibits the highest activity among these cobalt systems, the longest catalyst lifetime and displays reasonable thermal stability.¹² Subsequent work has seen the development of alternative ligand sets incorporating two fused rings namely α,α' -dibenzylidene-2,3:5,6-bis(pentamethylene)pyridine¹³ (**E**, Scheme 1), their cobalt derivatives display high activity in ethylene polymerization.¹³

Herein, we are concerned with the synthesis of a new family of cobalt(II) chloride precatalysts bearing the unsymmetrical tridentate ligands of 2-(1-aryliminobenzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridines (**F**, Scheme 1), in which a single fused seven-membered ring and an imino C-phenyl group are incorporated into the ligand design. Five distinct members of the family are targeted in which the aryl substitution pattern has been systematically varied (aryl = 2,6-Me₂Ph, 2,6-Et₂Ph, 2,6-*i*-Pr₂Ph, 2,4,6-Me₃Ph, 4-Me-2,6-Et₂Ph); full characterization of all the complexes and organic precursor compounds are given. Moreover, a comprehensive ethylene polymerization screen is reported using both MAO and MMAO at different temperatures and pressures with a view to highlighting any effects of the ligand design on precatalyst performance and, above all, thermal stability of the catalyst itself. Furthermore, the resultant polyethylenes have been shown to contain vinyl chain-ends with narrow polydispersities, such materials¹⁴ are in high demand as new comonomers for long-chain branched polymers and coating materials.

Results and Discussion

Synthesis of 2-benzoylpyridyl-9-cycloheptanone (5). 2-Chloro-5,6,7,8-tetrahydrocyclohepta[b]pyridin-9-one (**1**), prepared according to the literature protocol,¹⁵ was reacted with 0.25 equivalents of potassium ferrocyanide for 8 hours in the presence of sodium carbonate as base and a catalytic amount of both Pd(OAc)₂ (5 mol%) and xantphos (Scheme 2).¹⁶ Following ketalization of the carbonyl group in carbonitrile compound (**2**) with ethylene glycol,¹⁷ the phenyl Grignard reagent was added dropwise into the solution of ketal (**3**) at low temperature.¹⁸ The resultant solution was then quenched and acidified with aqueous HCl to generate mono-ketone **4**. Deprotection of the ketal functionality in **4** under acidic conditions formed smoothly diketone 2-benzoylpyridyl-9-cycloheptanone (**5**).¹⁷ All new organic compounds, **2** - **5**, were characterized by FT-IR and NMR spectroscopy.

Synthesis and characterization of the cobalt complexes. As in previous work,¹³ we attempted to prepare the free bis-imino 2-(1-aryliminobenzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridine compounds, by condensation of diketone **5** with the corresponding aniline. However, these compounds were not stable and the yields were poor. Therefore, in order to avoid excessive consumption of **5** and maximize the yield, a one-pot template methodology was applied to synthesize the cobalt complexes based on approaches described in the literature.¹⁹ The template reaction of **5**, corresponding aniline and cobalt dichloride were carried out in boiling acetic acid for 6 hours to afford, after work-up, 2-(1-aryliminobenzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridylcobalt chlorides (aryl = 2,6-Me₂Ph (**Co1**), 2,6-Et₂Ph (**Co2**), 2,6-*i*-Pr₂Ph (**Co3**), 2,4,6-Me₃Ph (**Co4**), 4-Me-2,6-Et₂Ph (**Co5**)) in good yields (40.3%–91.0%, Scheme 2). The IR spectra of **Co1** – **Co5**

revealed stretching frequencies for the C=N bond in the range of 1608~1571 cm⁻¹, characteristic of bound imino-nitrogen atoms; no absorption corresponding to a complexed C=O bond or free diketone (**5**) was apparent. Additionally, the elemental analysis data confirmed the formulae of all the cobalt complexes.

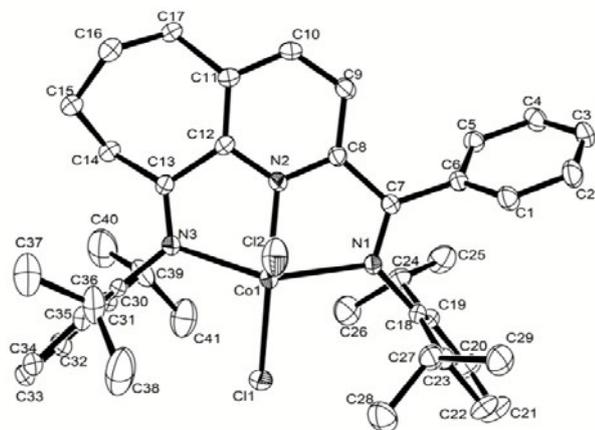


Figure 1. Molecular structure of compound **Co3** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (°) for **Co3**

Co3			
	Bond lengths, Å		Bond lengths, Å
	N(1)–C(7)		Co(1)–N(1)
	1.294(4)		2.194(2)
	N(3)–C(13)		Co(1)–N(2)
	1.269(5)		2.051(3)
	N(2)–C(8)		Co(1)–N(3)
	1.334(4)		2.198(3)
	N(2)–C(12)		Co(1)–Cl(1)
	1.326(4)		2.2343(11)
	C(7)–C(8)		Co(1)–Cl(2)
	1.486(4)		2.3251(12)
	C(12)–C(13)		
	1.494(5)		
	Bond angles, °		Bond angles, °
	N(1)–Co(1)–N(3)		C(7)–N(1)–Co(1)
	144.08(10)		113.2(2)
	N(1)–Co(1)–N(2)		C(18)–N(1)–Co(1)
	75.48(10)		126.04(19)
	N(3)–Co(1)–N(2)		C(13)–N(3)–Co(1)
	74.42(10)		114.0(2)
	N(1)–Co(1)–Cl(1)		C(30)–N(3)–Co(1)
	98.35(7)		124.0(2)
	N(3)–Co(1)–Cl(1)		N(1)–C(7)–C(8)
	98.80(8)		116.0(3)
	N(2)–Co(1)–Cl(1)		C(7)–C(8)–N(2)
	151.59(9)		114.0(3)
	N(1)–Co(1)–Cl(2)		C(8)–N(2)–C(12)
	95.94(7)		122.0(3)
	N(3)–Co(1)–Cl(2)		N(2)–C(12)–C(13)
	103.43(8)		112.1(3)
	N(2)–Co(1)–Cl(2)		C(12)–C(13)–N(3)
	90.45(9)		116.9(3)
	Cl(1)–Co(1)–Cl(2)		
	117.91(5)		

The **Co3** complex was also the subject of a single crystal X-ray diffraction study. Single crystals suitable for the study were grown by layering diethyl ether onto a solution of the complex in a methanol/dichloromethane mixture. The molecular structure is shown in Figure 1; selected bond lengths and angles of **Co3** are tabulated in Table 1. The coordination geometry of **Co3** can be best described as

distorted square-pyramidal, which is similar to related N,N,NCoCl₂ structures reported elsewhere.^{10,13} The basal plane is formed by the N_{pyridyl} atom, two N_{imino} atoms and one chloride atom (Cl1), while the other chloride Cl2 occupies the apical position. There is a deviation of 0.071 Å for Cl1 away from the basal plane. Since the cycloheptyl ring is more flexible than the cyclohexyl ring (see **B**, Scheme 1), an improved coordination between cobalt and N3 results. However, this has the consequent effect that sp³-hybridized C14 and C16 within the saturated ring distort 0.872 Å and 0.739 Å from the pyridyl plane, respectively. Furthermore, it can be seen that the central N_{pyridyl} atom is closer to the metal center than the exterior imino-nitrogen atoms (Co–N_{pyridyl} = 2.051(3) Å vs. Co–N_{imino} = 2.194(2) Å and 2.198(3) Å). Indeed, in comparison with the bond lengths in the [α,α'-bis(arylimino)-2,3,5,6-bis(pentamethylene)pyridyl]cobalt chlorides (Co–N_{pyridyl} = 2.082(3) Å),¹³ the Co–N_{pyridyl} bond is even shorter in **Co3**. It is likely that this improved coordination of the ligand will impact on the thermal stability of the cobalt catalyst (*vide infra*). On comparing **Co3** with **D**, similar bond distances are evident for the Co–N_{pyridyl} bond while some differences are apparent for the corresponding Co–N_{imino} distances. In **Co3** the Co–N_{imino} bond lengths are essentially identical (2.194(2) Å and 2.198(3) Å), while the bond lengths of the Co–N_{imino} display a deviation of 0.02 Å (2.197(5) Å and 2.175(5) Å) in **D**;¹² this difference might also influence the catalytic behavior of these pre-catalysts. The N-2,6-diisopropylphenyl groups lie almost orthogonal to the coordination plane with dihedral angles ranging from 84.32° and 89.86°.

Ethylene Polymerization

Ethylene Polymerization by Co1–Co5/MAO systems

In the first instance **Co4**, in combination with methylaluminoxane (MAO) as co-catalyst, was selected as the test catalyst system with a view to optimizing the polymerization parameters, such as reaction temperatures, Al/Co ratios and reaction times. The results obtained from the polymerization screen under ambient pressure using these set of variables are summarized in Table 2.

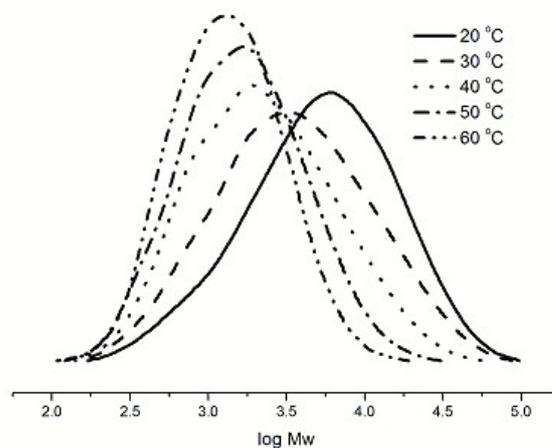


Figure 2. The GPC curves of polyethylene obtained at different temperatures using **Co4**/MAO (entries 1–5, Table 2)

Table 2. Polymerization results by Co1-Co5/MAO at ambient pressure of ethylene^aView Article Online
DOI: 10.1039/C6NJ01867J

Entry	Pre-cat	T(°C)	Al/Co	Polymer(g)	Activity ^b	T _m (°C) ^c	M _w /g·mol ^{-1d}	M _w /M _n ^d
1	Co4	20	1500	2.11	1.41	129.6	8750	3.2
2	Co4	30	1500	2.42	1.61	127.5	6373	3.3
3	Co4	40	1500	2.49	1.66	125.8	3856	2.8
4	Co4	50	1500	1.83	1.22	124.1	2478	2.2
5	Co4	60	1500	1.13	0.75	123.5	1826	1.9
6	Co4	40	1000	2.02	1.35	127.0	5482	3.2
7	Co4	40	2000	2.56	1.71	123.7	2294	2.1
8	Co4	40	2500	2.21	1.47	124.3	2145	2.0
9	Co4	40	3000	2.15	1.43	124.0	1917	2.0
10	Co4	40	3500	2.01	1.34	123.4	1843	1.9
11 ^e	Co4	40	2000	1.51	2.01	123.6	2098	2.0
12 ^f	Co4	40	2000	2.81	1.25	125.0	2943	2.4
13 ^g	Co4	40	2000	3.03	1.01	125.6	3365	2.5
14	Co1	40	2000	2.60	1.73	123.0	2283	2.2
15	Co2	40	2000	2.50	1.67	130.5	8533	2.5
16	Co3	40	2000	1.41	0.94	134.8	151949	2.3
17	Co5	40	2000	2.42	1.61	129.8	8494	2.2

^a General conditions: 3 μmol Co, 30 min, 30 mL toluene. ^b 10⁶ gPE·mol⁻¹(Co)·h⁻¹. ^c Determined by DSC. ^d Determined by GPC. ^e 15 min. ^f 45 min. ^g 60 min.

Firstly, the effect of reaction temperature on catalytic performance of Co4/MAO was probed by varying it between 20 °C and 60 °C (entries 1–5, Table 2). This indicated an optimal temperature of 40 °C with a catalytic activity of 1.66 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ (entry 3, Table 2) for polyethylene formation. The higher the temperature applied, the lower the molecular weight of the polymers obtained, which is consistent with the GPC curves shown in Figure 2. This observation may be due to the increased chain transfer taking place to alkylaluminium or an increased rate of chain termination occurring by β-H elimination at elevated temperature.^{1c,1d,20} Meanwhile the unimodal characteristics in the GPC curves (Figure 2) exhibited single-site active species operating in the polymerization process. In comparison with the results obtained at 40 °C, the lower temperature runs (entries 1 and 2, Table 2) resulted in a slight reduction in the activities while a dramatic drop occurred at higher temperatures (entries 4 and 5, Table 2), the latter observation probably due to partial decomposition of the active species and lower concentration of ethylene in toluene at higher temperature.²¹ Nevertheless, the activities were still up to 5 times higher than those observed using the imino C-methyl counterparts, [2-(1-(arylimino)ethyl)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (D, Scheme 1).¹²

Secondly, the polymerizations using Co4 were investigated at different MAO concentrations (Al/Co = 1000 to 3500), which showed the catalytic activity peaked at 1.71 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ with a Al/Co ratio of 2000 and then experienced a slight drop-off at higher ratios (entries 3, 6–10, Table 2). With a low molar ratio of Al/Co (1000),

polyethylenes with higher molecular weight (M_w = 5482 g·mol⁻¹) were formed while at a high ratio (3500) the M_w decreased to 1843 g·mol⁻¹; the latter likely due to the facile chain transfer at higher MAO concentrations.^{4b,4c} With regard to the lifetime of the active species, the highest activity of 2.01 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ was observed over the first 15 minute period of the run (entry 11, Table 2). On prolonging the reaction time (entries 7, 11–13, Table 2) the activities smoothly decreased, indicating there was no induction time in the catalytic reaction; similar observations were noted for their imino C-methyl counterparts (D, Scheme 1).¹² Furthermore, the molecular weights of the resultant polyethylenes gradually increased with the longer reaction times as borne out by changes in the GPC curves (Figure 3).

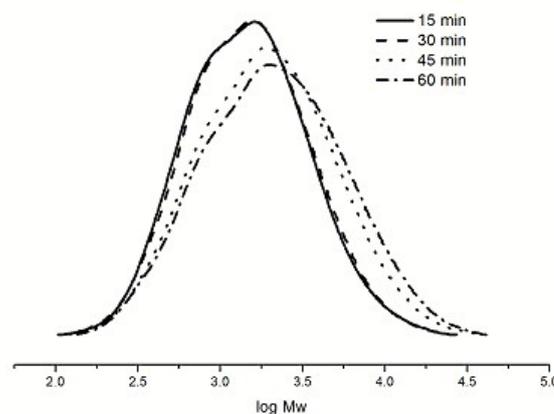


Figure 3. The GPC curves of the polyethylene at different reaction times using Co4/MAO (entries 7, 11–13, Table 2).

Using the optimum conditions (*viz.*, 40 °C, Al/Co = 2000 within 30 min) established for **Co4**/MAO, the other

derivatives, **Co1**, **Co2**, **Co3** and **Co5**, were also investigated as ethylene polymerization catalysts (entries 14–17, Table 2).

Table 3. Polymerization results by **Co1-Co5**/MAO at elevated pressure of ethylene^a

Entry	Pre-cat	T(°C)	Al/Co	Polymer(g)	Activity ^b	T _m (°C) ^c	M _w /g·mol ^{-1d}	M _w /M _n ^d
1	Co4	40	1500	3.84	2.56	127.7	5808	3.2
2	Co4	50	1500	8.32	5.55	127.2	5303	2.5
3	Co4	60	1500	9.18	6.12	127.5	5221	2.4
4	Co4	70	1500	7.95	5.30	127.5	5473	2.3
5	Co4	80	1500	2.77	1.85	127.4	4812	2.3
6	Co4	90	1500	0.53	0.35	126.8	3516	2.0
7	Co4	60	1000	8.77	5.85	127.5	5292	2.2
8	Co4	60	2000	10.86	7.24	127.7	4821	2.2
9	Co4	60	2500	12.98	8.65	127.8	4640	2.2
10	Co4	60	3000	12.03	8.02	127.0	4548	2.2
11 ^e	Co4	60	2500	7.09	14.18	126.8	4373	2.2
12 ^f	Co4	60	2500	9.76	9.76	127.0	4544	2.2
13 ^g	Co4	60	2500	14.75	6.56	127.7	4944	2.4
14 ^h	Co4	60	2500	15.67	5.22	128.4	5006	2.4
15 ⁱ	Co4	60	2500	9.76	6.51	127.5	4418	2.3
16	Co1	60	2500	12.23	8.15	127.1	4709	2.2
17	Co2	60	2500	9.29	6.19	130.8	14688	2.5
18	Co3	60	2500	8.49	5.66	133.7	113201	2.5
19	Co5	60	2500	9.57	6.38	130.7	12448	2.4

^a General conditions: 3 μmol Co, 30 min, 100 mL toluene, 10 atm ethylene. ^b 10⁶ gPE·mol⁻¹(Co)·h⁻¹·atm⁻¹. ^c Determined by DSC. ^d Determined by GPC. ^e 10min, ^f 20min, ^g 45min, ^h 60min, ⁱ 5 atm ethylene.

In all cases, high activities were observed with **Co1**/MAO the most active giving 1.73×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ (entry 14, Table 2). By inspection of the data recorded for all five precatalysts under the same conditions (entries 7, 14–17, Table 2), it is apparent that the activity of polymerization is susceptible to the nature of the *ortho* substituents on the N-aryl group as reported elsewhere.^{4,6} The less bulky methyl substituted complex **Co1** was more active than the bulkier ethyl- and isopropyl-substituted complexes (**Co2** and **Co3**). This is because the steric hindrance of the *ortho* substituents affects the rate of the ethylene monomer insertion as the ethylene monomer is more hindered in its approach to the metal center. When comparing **Co1** vs. **Co4** and **Co2** vs. **Co5**, respectively, the additional electron-donating methyl group in the N-aryl *para* position shows only modest effects on the activity with its presence, if anything, resulting in lowering of the activity.²²

As a further point, the steric bulk imparted by the *ortho* substituents of N-aryl group in **Co1-Co5** exhibited a significant effect on the properties of the polyethylenes. As has been observed in a number of previous reports,^{6,12,13} the presence of bulky groups in these cobalt catalysts leads to polymers with higher molecular weight. For example, the polymer obtained using 2,6-diisopropyl substituted complex **Co3** possesses the highest molecular weight ($M_w = 151.9$ Kg·mol⁻¹; entry 16, Table 2), which is far higher than that observed with

the diethyl substituted **Co2** ($M_w = 8.5$ Kg·mol⁻¹; entry 15, Table 2) and the dimethyl substituted **Co1** ($M_w = 2.3$ Kg·mol⁻¹; entry 14, Table 2).⁴ While the steric properties of the N-aryl group in these cobalt catalysts undoubtedly affect the molecular weights of these polyethylenes, it seems likely that the presence of the imino C-phenyl group is also influential.^{12,13}

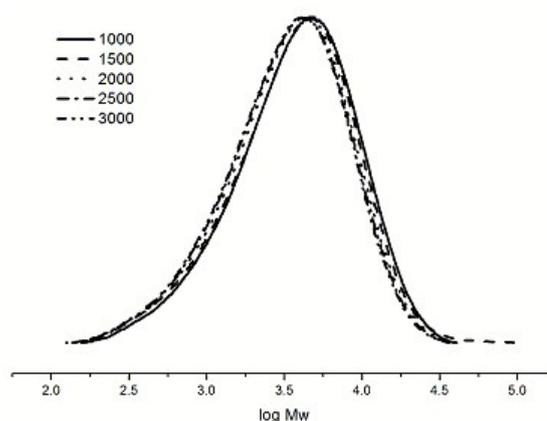


Figure 4. The GPC curves of the polyethylene at different Al/Co ratio using **Co4**/MAO (entries 3, 7–10, Table 3).

To further examine the thermal stability of the complexes, the ethylene polymerization screen was conducted at higher

ethylene pressure (*viz.*, 10 atm) and the optimal conditions were again established using **Co4** as the test precatalyst (Table 3). With the Al/Co ratio fixed at 1500, 60 °C was now identified as the temperature leading to the highest catalytic activity (entry 3, Table 3). The molar Al/Co ratio was then varied from 1000 to 3000 at 60 °C (entries 3, 7-10, Table 3), and the best activity of 8.65×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ was determined with a Al/Co ratio of 2500 (entry 9, Table 3). Notably, this good thermal-stability for **Co4**/MAO coupled with good catalytic performance is superior to that reported for both [2-(1-(arylimino)ethyl)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (**D**)¹² and [α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl]cobalt chlorides (**E**)¹³.

The GPC curves obtained for polyethylenes produced using **Co4**/MAO at different Al/Co ratios (Figure 4) indicate only gradual changes of molecular weight and similar molecular weight distributions. With regard to catalyst lifetime, the highest activity for **Co4** was observed over a 10 minute period with an activity of 14.18×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ (entry 11, Table 3). Even on extending the run time to 60 minutes, this system still maintained a good activity of 6.56×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ (entry 13, Table 3). For purposes of comparison, cobalt analogs **D**¹² and **E**,¹³ showed inferior lifetimes with the activity of **D** being 4.70×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ and **E** with 2.13×10^6 g(PE)·mol⁻¹(Co)·h⁻¹ under comparable conditions. Based on the optimised reactions conditions determined for **Co4**, complexes **Co1**, **Co2**, **Co3** and **Co5**, were also studied (entries 16–19, Table 3). On inspection of the data it is clear that high ethylene pressure significantly improves the catalytic activities and the thermal stability of the catalysts. A similar trend in catalytic activities was seen for analogs **D**¹² and **E**¹³. The dimethyl substituted complex **Co1** (8.15×10^6 g(PE)·mol⁻¹(Co)·h⁻¹, entry 16, Table 3) was again more active than **Co2** and **Co3** and complexes with bulkier substituents give higher molecular weights (113.2 Kg·mol⁻¹, entry 18, Table 3). However, the molecular weights of the polyethylenes obtained at 10 atm possessed less obvious variations compared with the PEs obtained under ambient ethylene pressure. As shown in Figure 5, the M_w for **Co1** and **Co4** were quite similar as is also the case for **Co2** and **Co5**, while **Co3** displayed a clear tendency to shift to high-molecular-weight fraction. Interestingly, the catalysts with *para*-methyl groups (**Co5** and **Co4**) performed with better activity than those without which was opposite to that observed at 1 atm ethylene pressure. This might be due to the *para*-methyl group being able to stabilize the active species at higher temperature.⁶¹ In general, the combination of high activity and good thermal stability of these cobalt systems exceeds that reported for previously documented cobalt catalysts,^{4,12} including [2-(1-(arylimino)ethyl)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (**D**),¹² [α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl]cobalt chlorides (**E**)¹³ and other fused-ring cobalt systems.^{6c,6f} Significantly, **Co4**/MAO even showed good activity at industrially significant temperatures of 80 °C (1.85×10^6 g(PE)·mol⁻¹(Co)·h⁻¹, entry 5, Table 3). The origin of the

enhanced performance characteristics is uncertain but it may be that the imino C-phenyl in these systems is preventing deprotonation in a way that could potentially occur for imino C-methyl counterpart **D** and hence stabilizing the catalyst at higher temperature.^{8a} In addition, the difference of Co-N_{imino} bond lengths between **D** and **Co3** (*vide supra*) might also affect the catalytic performances of these pre-catalysts. In all cases, the molecular weight distributions of the polyethylenes generally remained narrow and unimodal (PDIs = 1.9 – 2.4), and similar to those of their analogs **E**.¹³ The melting points of all the polymers were in the range 126.8 – 133.7 °C, consistent with highly linear materials.

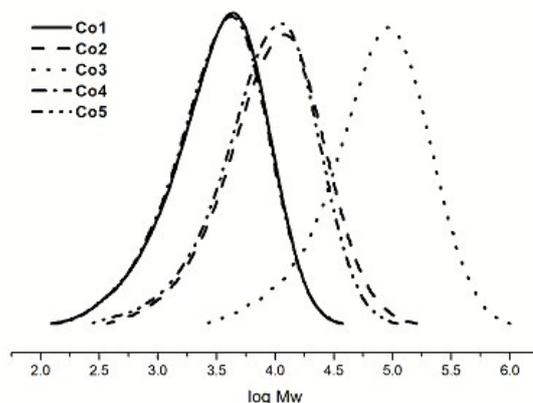


Figure 5. The GPC curves of polyethylene obtained by pre-catalysts **Co1** – **Co5** (entries 9, 16–19, Table 3)

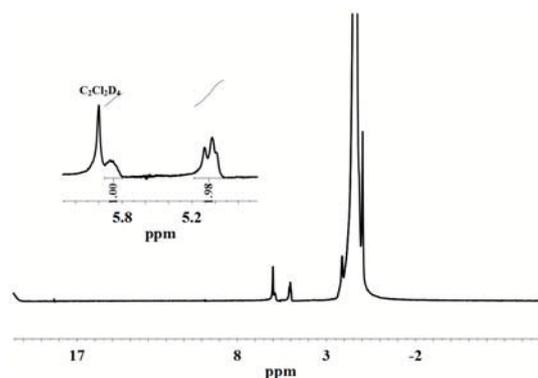


Figure 6. The ¹H-NMR spectrum of the polyethylene produced by **Co4**/MAO (entry 9, Table 3).

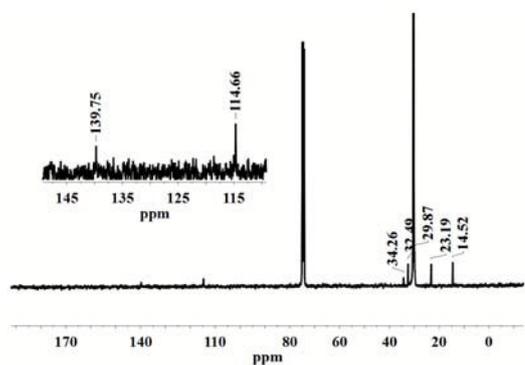


Figure 7. The ¹³C-NMR spectrum of the polyethylene produced by **Co4**/MAO (entry 9, Table 3).

Table 4. Polymerization results by **Co1–Co5**/MMAO at ambient pressure of ethylene^aView Article Online
DOI: 10.1039/C6NJ01867J

Entry	Pre-cat	T(°C)	Al/Co	Polymer(g)	Activity ^b	T _m (°C) ^c	M _w /Kg·mol ^{-1d}	M _w /M _n ^d
1	Co4	10	1500	1.89	1.26	132.1	14	2.2
2	Co4	20	1500	1.93	1.29	129.7	8.1	2.6
3	Co4	30	1500	2.08	1.39	128.5	6.8	2.8
4	Co4	40	1500	1.72	1.15	126.1	4.0	2.4
5	Co4	50	1500	1.50	1.00	127.3	3.4	2.3
6	Co4	30	1000	2.00	1.33	129.2	7.7	2.7
7	Co4	30	2000	2.18	1.45	127.3	5.0	2.5
8	Co4	30	2500	2.27	1.51	127.3	4.8	2.4
9	Co4	30	3000	2.08	1.39	125.8	4.0	2.4
10	Co4	30	3500	2.01	1.34	126.1	4.3	2.3
11	Co1	30	2500	2.42	1.61	127.6	5.1	2.4
12	Co2	30	2500	2.20	1.47	133.4	22	2.4
13	Co3	30	2500	1.59	1.06	136.2	220	2.5
14	Co5	30	2500	2.19	1.46	133.1	22	2.1

^a General conditions: 3 μmol Co, 30 min, 30 mL toluene. ^b 10⁶ gPE·mol⁻¹(Co)·h⁻¹·atm⁻¹. ^c Determined by DSC. ^d Determined by GPC.

To understand the microstructure of the polyethylenes obtained, a representative sample prepared using **Co4**/MAO at 60 °C was examined using ¹H NMR spectroscopy at 100 °C in deuterated 1,1,2,2-tetrachloroethane (C₂D₂Cl₄). The ¹H NMR spectrum (Figure 6) reveals a downfield multiplet at 5.90 ppm and an apparent triplet at 5.05 ppm, consistent with the polymer being mainly an α-olefin; no evidence for internal olefins could be detected. To corroborate this, the ¹³C NMR spectrum (Figure 7) revealed two single peaks existing between 140–110 ppm in agreement with the presence of a vinyl-group on the polyethylene. Furthermore, both the ¹H NMR and ¹³C NMR spectra showed that the PE samples were strictly linear.^{14,23} As a general comment, these highly linear, low molecular vinyl-polyethylenes are likely to be of high demand as new comonomers for long-chain branched polymers and coating materials.

Hence, a coordination-insertion mechanism allows chain propagation and β-hydrogen elimination facilitates chain termination to afford these vinyl-terminated linear polyethylenes (Scheme 3). We are currently interested in integrating the observed catalyst stability into a high temperature industrial process for generating polyethylenes of this type.

Ethylene Polymerization by **Co1–Co5**/MMAO Systems.

As a separate study we also examined the effect of using modified methylaluminoxane (MMAO) as the co-catalyst to activate **Co1 – Co5**. As before, the precatalyst **Co4** was employed to allow optimization of the reaction parameters; the results obtained at ambient ethylene pressure are tabulated in Table 4. With the Al/Co ratio fixed at 1500, the catalyst's activity was recorded in the 10 – 50 °C range and was found to peak at 1.39 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ at 30 °C (entries 1–5, Table 4). Notably, these values are five times higher than the activities of [α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl]cobalt chlorides (**E**) under comparable conditions.¹³

The molecular weights of the resultant polyethylenes obtained using **Co4**/MMAO decreased with an increase in the reaction temperature, consistent with the trend seen in the GPC curves (Figure 8) and attributable to facile chain transfer to alkylaluminium at higher temperature. When employing different molar ratios of Al/Co from 1000 to 3500, similar activities were observed (entries 3, 6–10, Table 4), with the activity showing a maximum of 1.51 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ at a Al/Co ratio of 2500 (entry 8, Table 4). Using these optimized conditions, the other cobalt precatalysts, **Co1**, **Co2**, **Co3** and **Co5**, were investigated for their polymerization behavior (entries 11–14, Table 4). In general, all the complexes showed the same order of activities as observed at 1 atm ethylene pressure: **Co1**[2,6-di(Me)] > **Co4**[2,4,6-

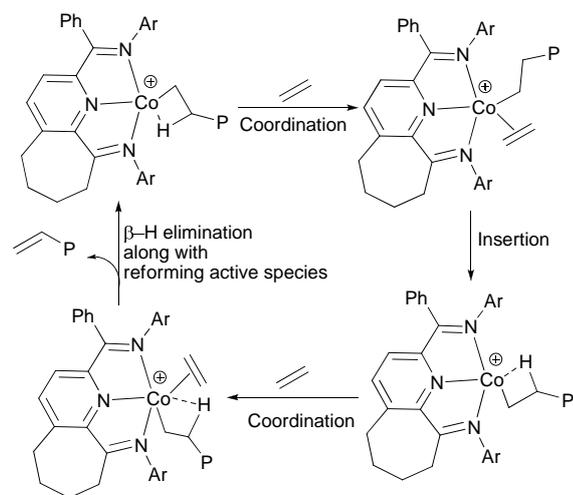
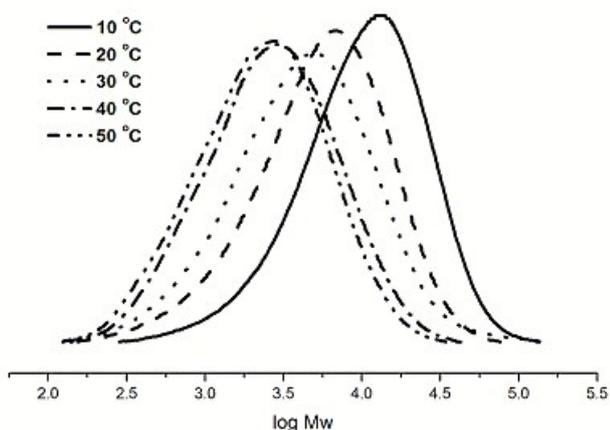
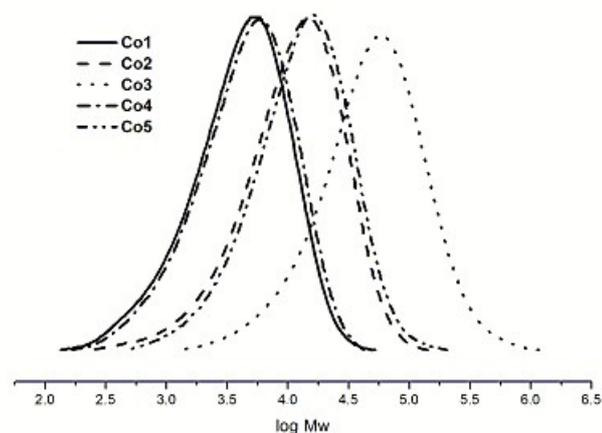
**Scheme 3.** Proposed mechanism for ethylene polymerization to vinyl-polyethylenes

Table 5. Polymerization results by Co1-Co5/MMAO at elevated pressure of ethylene^aView Article Online
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Entry	Pre-cat	T(°C)	Al/Co	Polymer(g)	Activity ^b	T _m (°C) ^c	M _w /g·mol ^{-1d}	M _w /M _n ^d
1	Co4	50	1500	2.93	1.95	129.0	6645	2.7
2	Co4	60	1500	3.86	2.57	127.3	6150	2.5
3	Co4	70	1500	5.14	3.43	129.6	6306	2.3
4	Co4	80	1500	0.98	0.65	126.8	4358	2.3
5	Co4	90	1500	0.18	0.12	129.4	8239	3.4
6	Co4	70	1000	3.75	2.50	128.6	6712	2.3
7	Co4	70	2000	4.38	2.92	128.0	5835	2.3
8	Co4	70	2500	4.05	2.70	128.6	5790	2.2
9 ^e	Co4	70	1500	2.80	1.87	127.9	5955	2.2
10	Co1	70	1500	4.18	2.79	128.2	5732	2.3
11	Co2	70	1500	4.01	2.67	131.0	15971	2.5
12	Co3	70	1500	1.77	1.18	134.4	76991	2.7
13	Co5	70	1500	4.43	2.95	131.3	18554	2.3

^a General conditions: 3 μmol Co, 30 min, 100 mL toluene. ^b 10⁶ gPE·mol⁻¹(Co)·h⁻¹·atm⁻¹, ^c Determined by DSC. ^d Determined by GPC. ^e 5atm.**Figure 8.** The GPC curves of polyethylene obtained at different temperatures using Co4/MMAO (entries 1–5, Table 4)**Figure 9.** The GPC curves of polyethylene obtained by pre-catalysts (entries 3, 10–13, Table 5)

tri(Me)] > Co2[2,6-di(Et)] > Co5[2,6-Et-4-Me] > Co3[2,6-di(*i*-Pr)], which is consistent with previous literature observations

for related N-aryl substitution patterns.^{6f} In comparison with the results obtained using MAO at 1 atm ethylene pressure, all the cobalt complexes revealed slightly lower activities while the polymers showed similar molecular weight distributions but higher molecular weights (up to 219.8 Kg·mol⁻¹, entry 13, Table 4). These variations are likely to stem from subtle differences in precatalyst activation between MMAO or MAO as well as counterion effects in the polymerization process. The *T_m* values of all the polymers generated were found to exceed 126.0 °C, indicative of high linearity for the polyethylene. It is noteworthy that linear PEs (wax) are in high demand as lubricants and colorants for plastics. As with the results obtained with MAO, higher molecular weight polyethylenes were obtained with the cobalt precatalysts bearing bulkier substituents: Co3 (220 Kg·mol⁻¹; entry 13, Table 4) > Co2 (22 Kg·mol⁻¹; entry 12, Table 4) > Co1 (5.1 Kg·mol⁻¹; entry 11, Table 4) and Co5 (22 Kg·mol⁻¹; entry 14, Table 4) > Co4 (4.8 Kg·mol⁻¹; entry 11, Table 4). In comparison with the polyethylenes obtained by [α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl] cobalt chlorides (E),¹³ the PDI values of polyethylenes herein are slightly broader (2.1–2.8) but still display unimodal feature consistent with semi-single site active species.

In order to investigate the effect of elevated pressure on catalytic performance and polymer properties, Co1 – Co5 were also screened at 10 atm. of ethylene in the presence of MMAO; the results are collected in Table 5. For Co4, the most optimal conditions were established at 70 °C with an Al/Co ratio of 1500 leading to an activity of 3.43 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹ (entry 3, Table 5). Under these conditions, Co1, Co2, Co3 and Co5, were also explored (entries 10–13, Table 5). All catalytic systems showed much better thermal stability and higher catalytic activities toward ethylene polymerization when compared with [2-(1-(arylimino)ethyl)-9-arylimino-5,6,7,8-tetrahydrocyclohepta [b]pyridyl]cobalt dichloride (D)¹² and α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)

pyridylcobalt chlorides (**E**)¹³. Once again this can be attributed to the presence of the imino C-phenyl group that prevents deprotonation at higher temperature.^{8a} In addition, the higher the ethylene pressure, the better the activities of polymerizations observed. With regard to the properties of the polyethylenes (entries 3, 10–13, Table 5), the GPC curves revealed a broad range of molecular weights spanning from thousands (**Co1**, 5.7 Kg·mol⁻¹, entry 10, Table 5) to tens of thousands (**Co3**, 77.0 Kg·mol⁻¹, entry 12, Table 5) with unimodal distributions (Figure 9). Moreover, the catalysts containing *para*-methyl groups were more active than those without, paralleling the trend seen using a MAO at 10 atm. which is also in line with thermal stability improvements imparted by *para* electron-donating substituents.⁶ⁱ The melting points of all resultant polymers were higher than 126.0 °C, suggesting highly linear polyethylenes. Though there was no direct evidence for enhancing the thermal stability of cobalt complexes by phenyl modification, the results of these new catalytic systems have convincingly demonstrated that cobalt complexes with preferable thermal stability can be obtained.

Conclusions

A series of [2-(1-aryliminobenzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt chlorides (**F**, Scheme 1: **Co1** – **Co5**) have been successfully synthesized and characterized. On activation with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), **Co1** – **Co5** all gave high activities toward ethylene polymerization with relatively narrow molecular distributions and unimodal features for the polymers. On comparison with previously reported [2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridyl]cobalt dichloride (**D**, Scheme 1) and [α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridyl]cobalt chlorides (**E**, Scheme 1), **Co1** – **Co5** all showed enhanced thermal stability and longer catalytic lifetimes. When the polymerization run is increased to a more industrially relevant temperature of 80 °C, **Co4**/MAO system still displays good activity (1.85 × 10⁶ g(PE)·mol⁻¹(Co)·h⁻¹). It is likely that this improved temperature stability can be attributed to the presence of the imino C-phenyl substituent present in all the cobalt complexes. In addition, the steric bulk of the *ortho* position on the N-aryl moiety plays an essential role in controlling the molecular weights of the polyethylenes. The molecular weight of the polymer obtained using **Co3** (up to 219.8 Kg·mol⁻¹) is over ten times higher than M_w using **Co1** and more than three times higher than M_w using **Co2**. Significantly, these new thermally stable cobalt complexes show considerable promise for producing vinyl-polyethylenes under industrially relevant conditions. Multiple applications are envisaged including as super-long chain α-olefins in copolymerization with ethylene or as a block for block-polymers through Click-reaction strategies and further functionalizations.²⁴ Subsequent investigations of these frameworks will focus on other core metals and further derivatives of the ligands.

Experimental Section

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DOI: 10.1039/C6NJ01867J

General Considerations. All manipulations of air- and/or moisture-sensitive operations were processed in a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (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 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. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distributions (MWD) of the polyethylenes were determined by a PL-GPC220 instrument at 150 °C, with 1,2,4-trichlorobenzene as the solvent. DSC traces and melting points of the polyethylenes were obtained from the second scanning run on Perkin-Elmer TA Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, about 3.0 mg of sample was heated to 160 °C at a rate of 20 °C/min and kept for 2 min at 160 °C and then cooled at a rate of 20 °C/min to -40 °C. NMR spectra of the polyethylene was recorded on a Bruker DMX 300 MHz instrument at 100 °C in deuterated 1,1,2,2-tetrachloroethane with TMS as an internal standard.

Synthesis of 9-oxo-5,6,7,8,9-pentahydrocyclohepta[b]pyridine-2-carbonitrile (2**).**¹⁶ A 150 mL three-necked flask was charged with 2-chloro-5,6,7,8-tetrahydrocyclohepta[b]pyridin-9-one (**1**, 7.6 g, 40 mmol), potassium ferrocyanide (4.4 g, 10 mmol, 0.25 equiv), sodium carbonate (4.2 g, 40 mmol, 1.0 equiv), Pd(OAc)₂ (0.3 g, 5 mol%), xantphos (0.7 g, 5 mol%) and dimethylacetamide (100 mL). The flask was evacuated and back-filled with nitrogen three times and then the reaction mixture stirred and heated at 150 °C using an oil bath. Monitoring of the reaction by GC revealed it was complete after 8 hours. On cooling to room temperature the mixture was diluted with dichloromethane (100 ml). The resulting slurry was filtered and the residue washed with more dichloromethane (3 × 20 mL). The solvent was removed under reduced pressure and then purified by silica gel chromatography affording **2** as a white solid (4.2 g, 56.5 %). ¹H-NMR (400 MHz; CDCl₃; TMS): δ 7.71 (m, 2H, Py), 2.96 (m, 2H, -CH₂-), 2.82(m, 2H, -CH₂-), 1.93 (m, 4H, 2 × -CH₂-). ¹³C NMR (100 MHz; CDCl₃; TMS): δ 202.8, 154.1, 138.9, 138.3, 129.8, 123.4, 116.6, 40.4, 31.4, 25.0, 21.7.

Synthesis of 9-oxo-5,6,7,8,9-pentahydrocyclohepta[b]pyridine-2-carbonitrile ethylene ketal (3**).**¹⁷ A mixture of **2** (8.0 g, 43 mmol), ethylene glycol (5.3 g, 2.0 equiv), *p*-TsOH (0.8 g, 10 % w/w) and toluene (300 mL) was stirred and heated to reflux for 8 h with azeotropic removal of water using a Dean-Stark apparatus and reflux condenser. On cooling to room temperature the solvent was removed and the residue purified by silica gel chromatography affording **3**

as a light yellow solid (8.0 g, 81.9 %). $^1\text{H-NMR}$ (400 MHz; CDCl_3 ; TMS): δ 7.54 (m, 2H, Py), 4.10 (t, $J = 3.0$ Hz, 2H, $-\text{CH}_2-$), 3.95 (t, $J = 2.7$ Hz, 2H, $-\text{CH}_2-$), 3.03 (m, 2H, $-\text{CH}_2-$), 2.04 (m, 4H, $2 \times -\text{CH}_2-$), 1.70 (m, 2H, $-\text{CH}_2-$). $^{13}\text{C NMR}$ (100 MHz; CDCl_3 ; TMS): δ 161.5, 141.7, 138.9, 129.7, 128.1, 117.6, 109.5, 64.9, 36.3, 34.5, 27.1, 25.5.

Synthesis of 2-benzoyl-5,6,7,8-tetrahydrocyclohepta[b]pyridin-9-one ethylene ketal (4).¹⁸ Under a nitrogen atmosphere, a solution of bromobenzene (15.7 g, 100 mmol) in dry THF (100 mL) was treated with magnesium (2.52 g, 105 mmol, 1.05 equiv). Once the formation of the Grignard reagent was complete, 50 mL of the solution was added by syringe to a solution of **3** (5.8 g, 25 mmol) in dry THF (100 mL) maintained at -5 °C. When no more starting material was present (checked by TLC), the reaction was quenched by the addition of water (10 mL) and then 3M HCl (10 mL). After stirring for 30 min, the organic layer was separated and extracted three times with dichloromethane. The aqueous layer was basified with saturated sodium bicarbonate and extracted twice with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography to afford **4** as a yellow solid (7.4 g, 95.8 %). $^1\text{H-NMR}$ (400 MHz; CDCl_3 ; TMS): δ 8.26 (m, 2H, Py), 7.93 (d, $J = 6.2$ Hz, 1H, Ph), 7.63 (d, $J = 6.2$ Hz, 1H, Ph), 7.57 (m, 1H, Ph), 7.46 (m, 2H, Ph), 4.07 (t, $J = 2.6$ Hz, 2H, $-\text{CH}_2-$), 3.96 (t, $J = 2.7$ Hz, 2H, $-\text{CH}_2-$), 3.04 (m, 2H, $-\text{CH}_2-$), 2.09-2.03 (m, 4H, $2 \times -\text{CH}_2-$), 1.75 (m, 2H, $-\text{CH}_2-$). $^{13}\text{C NMR}$ (100 MHz; CDCl_3 ; TMS): δ 192.8, 158.1, 151.3, 140.1, 139.3, 136.9, 132.6, 131.4, 127.8, 124.0, 110.0, 64.8, 36.7, 34.4, 27.3, 25.5.

Synthesis of 2-benzoyl-5,6,7,8-tetrahydrocyclohepta[b]pyridin-9-one (5).¹⁷ The ketal **4** (7.4 g, 24 mmol) was treated with *p*-TsOH (1.1 g, 15 % w/w) in mixture of acetone (75 mL) and water (75 mL) in a 250 mL flask. The mixture was stirred and heated to reflux for 6 h. On cooling to room temperature, the solvent was removed under reduced pressure and the aqueous layer extracted three times with dichloromethane. The combined organic layers were evaporated to give **5** as a light yellow solid (6.2 g, 97.7 %). $^1\text{H-NMR}$ (400 MHz; CDCl_3 ; TMS): δ 8.24 (m, 2H, Py), 8.10 (d, $J = 6.3$ Hz, 1H, Ph), 7.79 (d, $J = 6.3$ Hz, 1H, Ph), 7.60 (m, 1H, Ph), 7.50 (m, 2H, Ph), 3.01 (t, $J = 4.6$ Hz, 2H, $-\text{CH}_2-$), 2.83 (t, $J = 4.6$ Hz, 2H, $-\text{CH}_2-$), 2.00-1.92 (m, 4H, $2 \times -\text{CH}_2-$). $^{13}\text{C NMR}$ (100 MHz; CDCl_3 ; TMS): δ 204.1, 192.2, 154.5, 153.8, 138.9, 138.3, 136.0, 133.1, 131.5, 128.2, 126.3, 40.7, 31.4, 25.2, 21.9.

Synthesis of [2-(1-(2,6-dimethylphenylimino)benzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (Co1). A suspension of **5** (0.132 g, 0.5 mmol), 2,6-dimethylaniline (0.182 g, 1.5 mmol), cobalt dichloride (0.059 g, 0.45 mmol) in glacial acetic acid (10 mL) was refluxed 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 affording **Co1** as a brown solid (0.246 g, 91.0 %). FT-IR (KBr, cm^{-1}): 2973.8(w), 2937.4(m), 2918.3(m), 2860.8(m), 1608.4($\nu_{\text{C=N}}$, m), 1596.6(m), 1555.1(m), 1464.4(m), 1446.9(m), 1376.6(w), 1322.2(w), 1262.2(s), 1231.0(w),

1202.8(m), 1161.8(w), 1117.7(m), 1088.8(m), 1008.2(m), 967.6(w), 922.8(w), 876.3(w), 838.2(w), 765.0(vs), 702.2(s), 671.7(w). Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{Cl}_2\text{CoN}_3$: C, 65.90, H, 5.53, N, 6.99; Found: C, 65.63, H, 5.60, N, 6.96.

Synthesis of [2-(1-(2,6-diethylphenylimino)benzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (Co2). Using the similar procedure and molar ratios as that for described for **Co1**, **Co2** was obtained as a brown powder (0.215 g, 72.7 %). FT-IR (KBr, cm^{-1}): 3060.7(w), 2964.3(m), 2932.5(m), 2870.8(w), 1597.2($\nu_{\text{C=N}}$, m), 1565.6(s), 1446.8(vs), 1374.9(w), 1324.9(w), 1263.3(vs), 1194.2(m), 1113.9(s), 1006.7(m), 967.5(w), 862.9(w), 801.8(m), 772.4(s). Anal. Calcd for $\text{C}_{37}\text{H}_{41}\text{Cl}_2\text{CoN}_3$: C, 67.58, H, 6.28, N, 6.39; Found: C, 67.29, H, 6.10, N, 6.29.

Synthesis of [2-(1-(2,6-diisopropylphenylimino)benzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (Co3). Using the similar procedure and molar ratios as that for described for **Co1**, **Co3** was obtained as a brown powder (0.180 g, 56.0 %). FT-IR (KBr, cm^{-1}): 3059.7(w), 2963.7(s), 2866.3(m), 1571.1($\nu_{\text{C=N}}$, m), 1462.1(m), 1442.1(m), 1383.1(w), 1266.2(s), 1186.4(w), 1116.1(m), 1051.9(w), 1009.2(w), 941.1(w), 844.6(w), 769.0(vs). Anal. Calcd for $\text{C}_{41}\text{H}_{49}\text{Cl}_2\text{CoN}_3$: C, 69.00; H, 6.92; N, 5.89. Found: C, 68.53; H, 6.94; N, 5.72.

Synthesis of [2-(1-(mesitylimino)benzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (Co4). Using the similar procedure and molar ratios as that for described for **Co1**, **Co4** was obtained as a brown powder (0.213 g, 75.3 %). FT-IR (KBr, cm^{-1}): 3001.9(w), 2916.6(m), 2861.8(m), 1601.4($\nu_{\text{C=N}}$, m), 1559.8(m), 1473.8(m), 1447.2(s), 1378.6(w), 1305.9(w), 1263.6(s), 1214.1(m), 1180.2(w), 1156.5(w), 1114.9(m), 1033.7(w), 1008.6(m), 952.0(w), 854.9(s), 786.0(w), 701.9(vs). Anal. Calcd for $\text{C}_{35}\text{H}_{37}\text{Cl}_2\text{CoN}_3$: C, 66.78, H, 5.92, N, 6.67; Found: C, 66.31, H, 5.82, N, 6.58.

Synthesis of [2-(1-(2,6-diethyl-4-methylphenylimino)benzylidene)-9-arylimino-5,6,7,8-tetrahydrocyclohepta[b]pyridyl]cobalt dichloride (Co5). Using the similar procedure and molar ratios as that for described for **Co1**, **Co5** was obtained as a brown powder (0.124 g, 40.3 %). FT-IR (KBr, cm^{-1}): 3024.3(w), 2962.0(m), 2931.1(m), 2869.8(m), 1599.0($\nu_{\text{C=N}}$, m), 1563.7(m), 1454.9(vs), 1374.2(w), 1328.4(w), 1264.6(s), 1209.7(m), 1180.3(w), 1154.9(w), 1114.9(m), 1077.1(w), 1035.5(w), 1007.0(m), 971.8(w), 857.2(s), 790.4(m), 702.5(vs). Anal. Calcd for $\text{C}_{39}\text{H}_{45}\text{Cl}_2\text{CoN}_3$: C, 68.32, H, 6.62, N, 6.13; Found: C, 68.07, H, 6.50, N, 5.97.

Procedure for Ethylene Polymerization. Ethylene polymerization was 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 back-filled with ethylene three times. Once the reactor had reached the desired temperature, toluene and a toluene solution of the catalytic precursor and co-catalyst (total volume was 100 mL) were injected into the autoclave under an ethylene atmosphere. The ethylene pressure was then increased to the desired pressure and maintained with a constant feed of ethylene. On completion

of the run, the reactor was cooled with an ice-water bath and the excess ethylene vented. The resultant mixture was poured into HCl/ethanol solution, and the polymer collected and washed several times with ethanol and dried under reduced pressure.

Table 6. Crystal data and Structure Refinement for **Co3**.

Co3	
Cryst color	brown
Empirical formula	C ₄₁ H ₄₉ Cl ₂ CoN ₃
Formula weight	713.66
T (K)	173 (2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	P2(1)/n
a (Å)	9.1533(35)
b (Å)	23.7909(87)
c (Å)	18.2145(70)
α (°)	90.0000(0)
β (°)	97.1825(69)
γ (°)	90.0000(0)
v (Å ³)	3935.4(14)
Z	4
D _{calcd} (mgm ⁻³)	1.205
μ (mm ⁻¹)	0.602
F(000)	1508
cryst size (mm)	0.40×0.34×0.06
θ range (°)	2.05 - 25.00
limiting indices	-10 ≤ h ≤ 9 -28 ≤ k ≤ 28 -21 ≤ l ≤ 12
no. of rflns collected	13194
no. unique rflns [R(int)]	6857(0.0340)
completeness to θ (%)	99.0
Goodness of fit on F ²	1.096
Final R indices [I > 2σ(I)]	R1 = 0.0555 wR2 = 0.1271
R indices (all data)	R1 = 0.0638 wR2 = 0.1362
largest diff peak and hole (e Å ⁻³)	0.389 and -0.330

X-ray Crystallographic Studies. Single crystals of complex **Co3** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into the mixture of methanol and dichloromethane at room temperature. Data collection for **Co3** was carried out on Rigaku MM007-HF Saturn 724 + CCD diffractometer with confocal mirror monochromated Mo K α radiation ($\lambda = 0.71073$ 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.²⁵ The free solvents from the structure **Co3** were removed through the SQUEEZE option of the crystallographic program PLATON.²⁶ Details of the X-ray structure determinations and refinements are provided in Table 6.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. U1362204, 51473170, 21473160 and 21374123). GAS thanks the Chinese Academy of Sciences for a Visiting Scientist Fellowship.

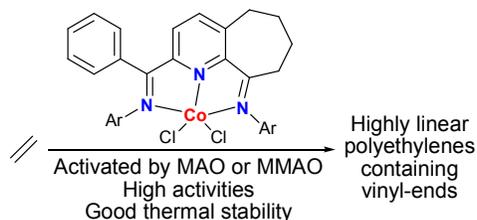
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View Article Online
DOI: 10.1039/C6NJ01867J

Thermally stable and highly active cobalt precatalysts for vinyl-polyethylenes with narrow polydispersities: integrating fused-ring and imino-carbon protection into ligand design

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The finely tuned cobalt complexes, upon activation with either MAO or MMAO, exhibited high activities up to 80 °C and produced the highly linear and vinyl-polyethylenes.