Ultra-low-molecular-weight PE wax using a cyclohexyl-fused bis(imino)pyridinecobalt catalyst functionalized with a remote *para*-phenyl group

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1. Additional ethylene polymerization runs

Run	Precat.	Mass of PE (g)	Activity ^b	$M_{ m w}$ °	$M_{ m w}/M_{ m n}$ °	$T_{\rm m}^{~\rm d}$
1	Co1'	6.34	6.34	0.524	1.4	62.56
2	Co2'	5.92	5.92	1.09	1.8	103.33

Table S1 Catalytic evaluation of **Co1'** and **Co2'** for ethylene polymerization following activation with MAO ^a

^a General conditions: MAO as activator, 2 μ mol of pre-cat., temp. = 40 °C, Al/Co = 2750, 100 mL of toluene, 10 atm of ethylene pressure, 30 min for reaction time; ^b Activity in unit of 10⁶ g (PE) mol⁻¹ (Co) h⁻¹; ^c Values in unit of kg mol⁻¹ via GPC; ^d Values in unit of °C via DSC, broad peak.



Figure S1 GPC trace of the PE generated using Co1'/MAO (run 1, Table S1)



Figure S2 GPC trace of the PE generated using Co2'/MAO (run 2, Table S1)

2. ¹H NMR and ¹³C NMR spectra of compounds 2 and 3



Figure S3 ¹H NMR spectrum of 2; recorded in CDCl₃ at room temperature





Figure S4 ¹³C NMR spectrum of compound 2; recorded in CDCl₃ at room temperature



Figure S5 ¹H NMR spectrum of compound 3; recorded in CDCl₃ at room temperature



Figure S6 ¹³C NMR spectrum of compound 3; recorded in CDCl₃ at room temperature

3. ESI-MS of Co1–Co5



Figure S7 ESI-MS of Co1.



ESI(P),Co-2,20250109

1000.0 m/z

ESI(P),Co-3,20250109



Figure S9 ESI-MS of Co3.

Analysis Info Analysis Name D:\Data\ESI\S 1/9/2025 10:28:09 AN Sample Name Co-4 solariX n Parameter Mode Single MS Positive Low Mass 57.7 m/z Acquisition Para Acquisition Mode 5 ed Scans Polarity Broadba 1000.0 m/z intens. ×10⁹ 0.8 0.6 643.26011 1+ 0.4 0.2 0.0 x10⁹ 1.2 1.0 0.8-0.6 0.4 Co-4_000001.d: +MS Meas.m/z # Ion Formula Score m/z err [ppm] Mean err [ppm] mSigma rdb e Conf 619.215675 1 C37H39CICoN3 100.00 619.215897 -0.4 1.1 39.9 19.5 even N-Rul

ESI(P),Co-4,20250109

Figure S10 ESI-MS of Co4.



ESI(P),Co-5,20250109

Figure S11 ESI-MS of Co5.

4. GPC traces of the polyethylene samples



Figure S12 For Co1/MMAO: (a) GPC traces of the polyethylene generated at various run temperatures; (b) Plots of catalytic activity and M_w as a function of run temperature.



Figure S13 For Co1/MMAO: (a) GPC traces of the polyethylene generated at different Al/Co molar ratios; (b) Plots of catalytic activity and molecular weight (M_w) as a function of Al/Co molar ratio.



Figure S14 For Co1/MMAO: (a) GPC traces of the polyethylene generated over different reaction times; (b) Plots of catalytic activity and M_w as a function of reaction time.

5. ¹H NMR and ¹³C NMR spectra of selected polymers



Figure S15 ¹H NMR spectrum of the polyethylene obtained using Co2/MAO (run 2, Table 3); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S16 ¹H NMR spectrum of the polyethylene obtained using Co3/MAO (run 3, Table 3); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S17 ¹H NMR spectrum of the polyethylene obtained using Co4/MAO (run 4, Table 3); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S18 ¹H NMR spectrum of the polyethylene obtained using Co5/MAO (run 5, Table 3); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S19 ¹H NMR spectrum of the polyethylene obtained using Co1/MMAO (run 1, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S20 ¹H NMR spectrum of the polyethylene obtained using Co2/MMAO (run 2, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S21 ¹H NMR spectrum of the polyethylene obtained using Co3/MMAO (run 3, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S22 ¹H NMR spectrum of the polyethylene obtained using Co4/MMAO (run 4, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S23 ¹H NMR spectrum of the polyethylene obtained using Co5/MMAO (run 5, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .



Figure S24 ¹³C NMR spectrum of the polyethylene obtained using Co1/MMAO (run 1, Table 5); recorded at 100 °C in 1,1,2,2,-tetrachloroethane- d_2 .

6. Calculation method used to determine the percentage of vinyl chain ends and M_n -NMR

Chain A
$$H_a \xrightarrow{H_b} H_c \xrightarrow{H_d} H_e$$

Chain B $H_e \xrightarrow{H_d} H_e$

Figure S25 Linear PE chain composition based on unsaturated chain A and saturated chain B.

It has been reported for iron and cobalt ethylene polymerization catalysis that there are three different chain transfer pathways (namely β -H transfer to monomer, β -H elimination and chain transfer to aluminum) which can generate linear polyethylene based on partially unsaturated chain ends (chain **A**, Figure S25) and/or fully saturated chain ends (chain **B**, Figure S25)^{1,2}.

To calculate the vinyl end chain content, the moles of chain **A** is set as *x* and as *y* for chain **B**, while the integral of signal H_b in the ¹H NMR spectrum is set as *I*(b) and *I*(e) for signal H_e .

The equation can be obtained as:
$$\frac{I(b)}{I(e)} = \frac{2x}{3x + 6y}$$
(1).

From Figures 7 and Figures S12–S20, I(b) can be set as 2, then equation (1) can be transformed

$$\frac{x}{to:} \frac{x}{y} = \frac{6}{l(e) - 3}$$
 (2). $(x + y = 1)$

Therefore, the percentage of chain **A** can be calculated as: $x = \frac{6}{3 + I(e)}$ (3).

Meanwhile, the vinyl chain end ratio can be obtained from the integrals of the corresponding signals in the ¹³C NMR spectrum. Thus, the ¹³C NMR integral (Figure 8) of C_b is set at 1.0 and C_h is set at *I*(h).

The equation can be obtained as:
$$\frac{1}{I(h)} = \frac{x}{x+2y}$$
 (4).

$$(x+y=1)$$

Hence, the vinyl chain end ratio can be calculated as: $x = \frac{2}{I(h) + 1}$ (5).

For calculating the number-averaged molecular weight using NMR spectroscopy (M_n -NMR), it is assumed that the average carbon number (Z) of the unsaturated and saturated polymers is equal because the polymers show narrow polydispersity on the basis of the GPC results.

The intensity of the ¹H NMR signal H_d in chain **A** is set as *A* and *B* in chain **B**, and the total intensity of H_d is set at *I*(d). By counting the carbon numbers of the polymer chain (for chain A, there are 4 carbons except carbons linked to H_d ; for chain B, there are 2 carbons except carbons linked to H_d ; here are 2 carbons except carbons linked to H_d), the equation can be obtained as:

$$4 + \frac{A}{2} = Z \qquad (6); \qquad 2 + \frac{B \times \frac{3}{I(e) - 3}}{2} = Z \qquad (7); \qquad A + B = I(d)$$
(8).

. .

By combining equations (6) and (7):
$$B = \frac{(4 + I(d)) \times (I(e) - 3)}{I(e)}$$
(9).

Then the average carbon number (Z) can be calculated through equations (6), (8) and (9). The M_n -NMR of the polyethylene is then calculated by multiplying the molecular weight (14 g/mol) of -CH₂- repeat unit with the average carbon number (Z).

Table S2 Results of the calculations used to determine the percentage vinyl chain ends, average carbon number and M_n -NMR.^a

PE source	Catalyst	Vinyl chain end (%) Average carbon		M _n -NMR (g/mol)
	system		number	
Run 1, Table 3	Co1/MAO	96	45.83	642
Run 2, Table 3	Co2/MAO	93	65.53	917

Run 3, Table 3	Co3/MAO	73	116.93	1637
Run 4, Table 3	Co4/MAO	95	45.85	642
Run 5, Table 3	Co5/MAO	94	68.52	959
Run 1, Table 5	Co1/MMAO	95	47.11	660
Run 2, Table 5	Co2/MMAO	93	71.37	999
Run 3, Table 5	Co3/MMAO	82	152.31	2132
Run 4, Table 5	Co4/MMAO	97	44.73	626
Run 5, Table 5	Co5/MMAO	94	72.50	1015

^a The calculation method is described above, polymer samples are given in Tables 3 and 5.

7. Crystal refinement data

Identification code	Co3	Co4
CCDC number	2441077	2441078
Empirical formula	$C_{43}H_{51}Cl_2CoN_3$	$C_{37}H_{39}Cl_2CoN_3$
Formula weight	739.69	655.54
Temperature/K	170(2)	169.99(10)
Crystal system	tetragonal	orthorhombic
Space group	I-42d	Fdd2
a/Å	22.7671(8)	33.7269(6)
b/Å	22.7671(8)	32.7780(6)
c/Å	14.8686(7)	14.0568(3)
a/°	90	90
β/°	90	90
$\gamma/^{\circ}$	90	90
Volume/Å ³	7707.0(7)	15539.8(5)
Ζ	8	16
$ ho_{calc}g/cm^3$	1.275	1.121
μ/mm^{-1}	5.013	4.916
F(000)	3128.0	5488.0
Crystal size/mm ³	$0.15\times0.1\times0.08$	0.3 imes 0.2 imes 0.15
Radiation	Cu Kα (λ = 1.54184)	$Cu K\alpha (\lambda = 1.54184)$
2 Θ range for data collection/°	7.1 to 152.63	7.328 to 155.224
T., 1	$-25 \leq h \leq 28, -28 \leq k \leq 23, +$	- $-41 \le h \le 37, -41 \le k \le 40, -$
index ranges	$7 \le l \le 18$	$16 \leq l \leq 17$
Reflections collected	11391	13794

Table S3 Crystal data and structure refinements for Co3 and Co4.

Independent reflections	$3703 [R_{int} = 0.0485, R_{sigma} = 6154 [Rint = 0.0329, Rsigma$			
Independent reflections	0.0466]	= 0.0398]		
Data/restraints/parameters	3703/0/228	6154/383/437		
Goodness-of-fit on F ²	0.797	1.052		
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0627, wR_2 = 0.1856$	R1 = 0.0661, wR2 = 0.1870		
Final R indexes [all data]	$R_1 = 0.0784, wR_2 = 0.2072$	R1 = 0.0715, wR2 = 0.1925		
Largest diff. peak/hole / e Å-3	0.71/-0.57	0.31/-0.35		
Flack parameter	0.004(5)	0.062(7)		

8. Epoxidation method

Scheme S1 Synthetic route to the epoxidized chain-end polyethylene, PE-epoxy.

The selected polymer (2.00 g, obtained using Co1/MAO, run 1, Table 3) and *m*-chloroperoxybenzoic acid (3.00 g, 0.0174 mol) were dissolved in toluene (50 mL) at 80 °C, and the mixture stirred and heated to reflux for 18 h. After cooling to room temperature, a yellow suspension was obtained and excess methanol (50 mL) was added to induce the formation of a white precipitation. PE-epoxy was obtained as a white powder following filtration and washing with methanol (x3) (1.767 g, 88%).

References

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