Supplementary Information

"Monometallic and Heterobimetallic Azanickellacycles as Ethylene Polymerization Catalysts"

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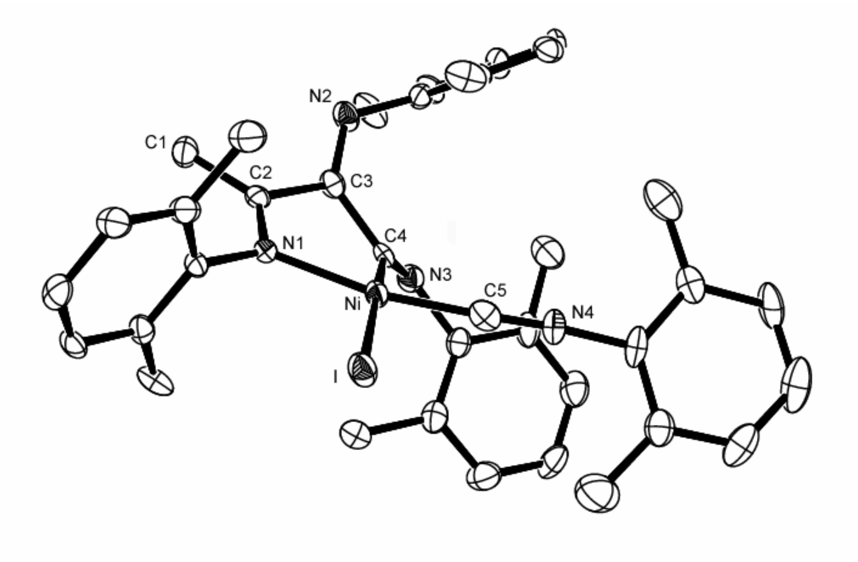
I. Preparation of Nickel Complexes.

Ni(CN-2,6-xylyl)$_4$

To a solution of Ni(COD)$_2$[1] (5.8 g, 21.2 mmol) in benzene (50 mL) was added a solution of 2,6-xylylisocyanide (11.1 g, 85.2 mmol) in benzene (100mL), and the mixture was stirred at room temperature for 2 h, and the resulting solution was concentrated *in vacuo*. The obtained pale yellow residue was washed with hexane three times (in total 150 mL). The crude product (9.39 g) was used for further reaction without any purification. ^{1}H NMR (395 MHz, CDCl$_3$): δ7.31-6.51 (br,12H), 2.88-2.00 (br,24H).

Iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel(II)(**1**)

To a benzene solution (100 mL) of Ni(CN-2,6-xylyl)$_4$ (9.39 g, 16.1 mmol) synthesized by the above procedure was added methyl iodide (6.6 mL, 106 mmol). After heating under reflux for 24 h, the reaction mixture was concentrated *in vacuo*, and the brown residue was washed with hexane (250 mL). Purification by recrystallization from dichloromethane/hexane gave the desired complex **1** in 95% yield (11.1 g) as brown platelets. m.p. 141 °C (dec.). IR: $\nu_{C\equiv N}$ 2161 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.15 (s, 3H), 7.02 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 2H), 6.54 (t, *J* = 7.8 Hz, 1H), 2.36 (s, 6H), 2.24 (s, 6H), 2.20 (s, 3H), 2.06 (s, 6H), 1.92 (s, 6H). ^{1}H NMR (600 MHz, C$_6$D$_6$): δ6.97-6.96 (m, 5H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 2H), 6.48 (t, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 2H), 2.32 (s, 6H), 2.29 (s, 6H), 2.09 (s, 6H), 1.95 (s, 6H). ^{13}C NMR (600 MHz, CDCl$_3$): δ 185.83, 178.73, 164.16, 148.99, 148.14, 146.34, 134.35, 129.00, 128.71, 128.55, 128.33, 128.20, 127.67, 127.51, 127.32, 127.18, 125.78, 124.12, 123.67, 123.56, 19.15, 18.92, 18.56, 18.55, 17.14. ^{13}C NMR (600 MHz, C$_6$D$_6$): δ 188.70, 178.95, 165.12, 150.06, 148.96, 146.81, 134.59, 128.90, 128.73, 128.54, 128.29, 128.09, 127.92, 127.51, 127.31, 127.22, 126.26, 124.48, 123.98, 123.83, 19.32, 19.26, 18.87, 18.61, 16.73. Anal. Calcd for $C_{37}H_{39}N_4I_1Ni$: C, 61.27; H, 5.42; N, 7.72%. Found: C, 61.48; H, 5.44; N, 7.61%.



Selected bond lengths (Å), and torsion angles (deg):

Ni-I	2.5770(8)
Ni-N1	1.969(4)
Ni-C4	1.906(5)
Ni-C5	1.821(5)
C5-N4	1.159(6)
C2 -N1	1.317(8)
C3-N2	1.274(8)
C4-N3	1.255(6)
C1-C2-C3-N2	32.5(7)

Molecular structure of **1** in the crystal (ellipsoids represent 50% probability; hydrogen atoms are omitted for clarity).

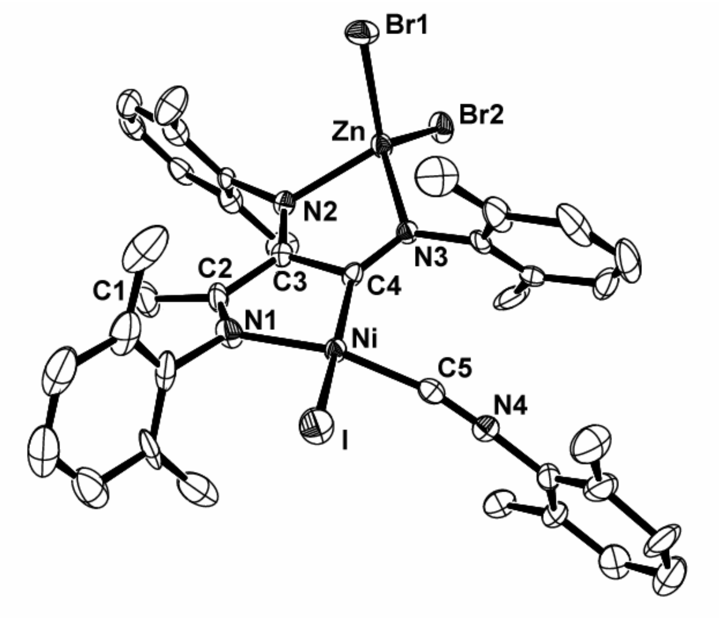
Empirical Formula	$C_{37}H_{39}IN_4Ni$	Z value	8
Formula Weight	725.35	D_{calc}	1.434 g/cm^3
Crystal Color, Habit	colorless, prism	F_{000}	2960.00
Crystal Dimensions	0.24 x 0.08 x 0.06 mm	Reflection/Parameter Ratio	17.85
Crystal System	monoclinic	Residuals: R (All reflections)	0.092
Lattice Type	C-centered	Residuals: R1 ($I>2.00\sigma(I)$)	0.042
Lattice Parameters	a = 29.374(9) Å	Residuals: wR2 (All reflections)	0.111
	b = 14.767(4) Å	Goodness of Fit Indicator	1.000
	c = 17.319(5) Å	Max Shift/Error in Final Cycle	0.000
	β = 116.5987(11) ^{o}	Maximum peak in Final Diff. Map	1.06 e$^-$/Å^3
	V = 6717.6(33) Å^3	Minimum peak in Final Diff. Map	-0.98 e$^-$/Å^3
Space Group	C2/c (#15)		

II Preparation of the Heterobimetallic (or Homobimetallic) Complexes of Ni-Zn(2a), Ni-Co(2b), Ni-Fe(2c) and Ni-Ni(2d).

The following complexes were generally prepared by treatment of the azanicklellacyclopentane complex **1** and a MBr_2 precursor (M = Zn, Co, Fe, and Ni) as described below. For the polymerization, the crude complex was used without further purification. As representatives, isolation of two of these complexes, the diamagnetic Ni-Zn complex **2a** and the paramagnetic Ni-Co complex **2b**, was carried out and subjected to characterization, which evidenced the structures of heterobimetallic catalysts presented in this paper.

[Iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel(II)] dibromozinc(II) (**2a**)

To a solution of $ZnBr_2$ (0.17 g, 0.73 mmol) in EtOH (10 mL) was added a solution of **1** (0.53 g, 0.73 mmol) in CH_2Cl_2 (10 mL). After it was stirred at room temperature for 24 h, the reaction mixture was concentrated under a reduced pressure. The crude product was used for the ethylene polymerization without further purification. For the characterization of the product, purification by recrystallization from dichloromethane/hexane gave the desired complex **2a** in 77% yield (0.54 g) as brown platelets. m.p. 139 ^{o}C (dec.). IR: $\nu_{C\equiv N}$. 2165 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17-7.11 (br m, 6H), 6.98 (br t, *J* = 7.8 Hz, 1H), 6.96 (br d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.50 (t, *J* = 7.2 Hz, 1H), 2.69 (s, 6H), 2.47 (s, 6H), 2.34 (s, 6H), 2.24 (s, 6H), 1.45 (s, 3H). ^{13}C NMR (600 MHz, $CDCl_3$): δ 176.19, 167.88, 148.13, 142.71, 133.66, 129.40, 129.32, 129.18, 128.77, 128.65, 128.61, 128.39, 128.20, 128.11, 127.86, 127.71, 127.63, 127,55, 127.21, 127.16, 20.77, 19.99, 19.42, 19.17, 18.52. Anal. Calcd for $C_{37}H_{39}Br_2N_4I_1Ni_1Zn_1$: C, 46.75; H, 4.53; N, 5.89%. Found: C, 46.45; H, 4.53; N, 5.68%.



Selected bond lengths (Å), and torsion angles (deg):

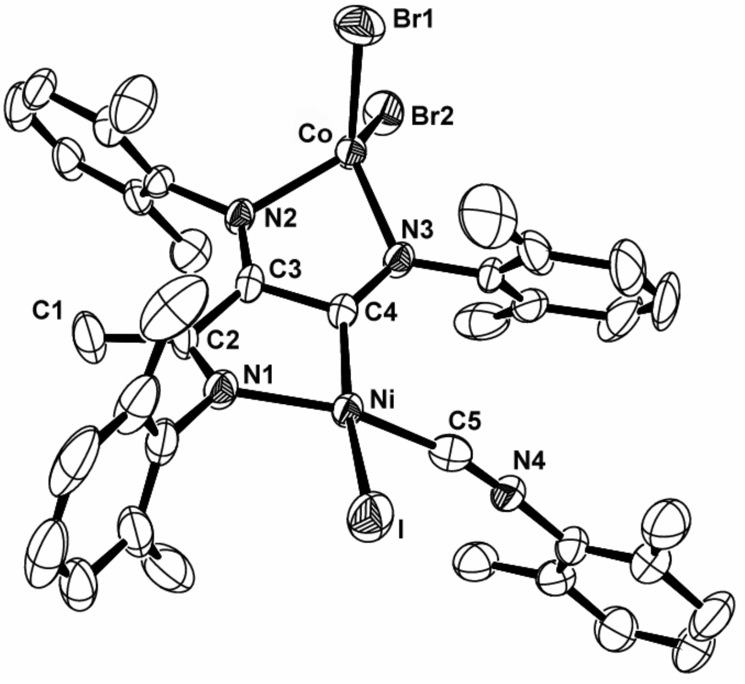
Ni-I	2.481(1)
Ni-N1	1.941(8)
Ni-C4	1.863(8)
Ni-C5	1.824(9)
C5-N4	1.16(1)
C2 -N1	1.27(1)
C3-N2	1.28(1)
C4-N3	1.29(1)
C1-C2-C3-N2	18(1)

Molecular structure of **2a** in the crystal (ellipsoids represent 50% probability; hydrogen atoms and CH_2Cl_2 are omitted for clarity).

Empirical Formula	$C_{37}H_{39}Br_2IN_4NiZn \cdot CH_2Cl_2$	Space Group	$P2_1/c$ (#14)
Formula Weight	1035.47	Z value	4
Crystal Color, Habit	brown, chip	D_{calc}	1.728 g/cm^3
Crystal Dimensions	0.15 X 0.10 X 0.05 mm	F_{000}	2048.00
Crystal System	monoclinic	Residuals: R1 (I>3.00σ(I))	0.055
Lattice Type	Primitive	Residuals: wR2 (I>3.00σ(I))	0.161
Lattice Parameters	a = 15.091(2) Å	Goodness of Fit Indicator	1.004
	b = 11.585(2) Å	Max Shift/Error in Final Cycle	0.000
	c = 22.938(4) Å	Maximum peak in Final Diff. Map	3.52 e$^-$/Å^3
	β = 97.1574(8) ^{o}	Minimum peak in Final Diff. Map	-1.48 e$^-$/Å^3
	V = 3979.1(11) Å^3		

[Iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel(II)] dibromocobalt(II) (**2b**)

Complex **1** (240 mg, 0.33 mmol) and $CoBr_2$ (72 mg, 0.33 mmol) were dissolved in a mixture of benzene (20 mL) and THF (5 mL). The mixture was stirred at room temperature for 24 h, the reaction mixture was concentrated *in vacuo.* The product was for polymerization without further purification. The heterobimetallic complex can be isolated by recrystallization from dichloromethane/hexane as black crystals. m.p. 193 ^{o}C (dec.). IR: $\nu_{C\equiv N}$.2159 cm^{-1}. Anal. Calcd for $C_{37}H_{39}Br_2Co_1N_4I_1Ni_1$□$CH_2Cl_2$: C, 44.35; H, 4.02; N, 5.44%. Found: C, 44.59; H, 3.99; N, 5.47%.



Selected bond lengths (Å), and torsion angles (deg):

Ni-I	2.493(1)
Ni-N1	1.918(7)
Ni-C4	1.863(7)
Ni-C5	1.821(8)
C5-N4	1.17(1)
C2 -N1	1.30(1)
C3-N2	1.28(1)
C4-N3	1.288(9)
C1-C2-C3-N2	16(1)

Molecular structure of **2a** in the crystal (ellipsoids represent 50% probability; hydrogen atoms and CH_2Cl_2 are omitted for clarity).

Empirical Formula	$C_{37}H_{39}N_4Br_2CoINi \cdot CH_2Cl_2$	Z value	4
Formula Weight	1029.02	D_{calc}	1.692 g/cm^3
Crystal Color, Habit	black, platelet	F_{000}	2036.00
Crystal Dimensions	0.50 x 0.50 x 0.03 mm	Reflection/Parameter Ratio	19.95
Crystal System	monoclinic	Residuals: R (All reflections)	0.109
Lattice Type	Primitive	Residuals: R1 (I>2.00σ(I))	0.069
Lattice Parameters	a = 15.211(1) Å	Residuals: wR2 (All reflections)	0.225
	b = 11.6798(8) Å	Goodness of Fit Indicator	1.048
	c = 22.888(2) Å	Max Shift/Error in Final Cycle	0.002
	β = 96.590(2) ^{o}	Maximum peak in Final Diff. Map	1.66 e$^-$/Å^3
	V = 4039.5(5) Å^3	Minimum peak in Final Diff. Map	-2.09 e$^-$/Å^3
Space Group	$P2_1/c$ (#14)		

[Iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel(II)] dibromoiron(II) (**2c**)

To a solution of **1** (220 mg, 0.31 mmol) in benzene (20 mL) was added a solution of $FeBr_2$ (66 mg, 0.31 mmol) in THF (5 mL). After it was refluxed for 3 h, the reaction mixture was concentrated *in vacuo*. Then the residue was dissolved in CH_2Cl_2 (20 mL), and this solution was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure, and the crude product was used for the ethylene polymerization without further purification.

[Iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel(II)] dibromonickel(II) (**2d**)

Complex **1** (131 g, 0.18 mmol) and $NiBr_2$(dme) (56 mg, 0.18 mmol) were dissolved in benzene (20 mL). After it was refluxed for 5 h, the reaction mixture was concentrated *in vacuo*, and the crude product was used for the ethylene polymerization without further purification.

III A Representative example of Ethylene Polymerization.

To a solution of the nickel complex **1** (4 μmol) in toluene (20 mL) was added a 7.9 wt% solution of MAO (TOSOH. Co. Ltd) in toluene (0.8 mmol, 0.68 mL), and the resultant mixture was stirred at ambient temperature for 30 min. A part of the resulting catalyst/cocatalyst solution (5mL) was loaded into a 100 mL stainless steel autoclave, and ethylene was introduced (0.8 MPa) at room temperature. A continuous supply of ethylene kept the gas pressure at 0.8 MPa during the reaction for 20 min. The polymerization was terminated by the release of ethylene and subsequent addition of methanol (10 mL). The resultant suspension was added to a mixture of methanol (240 mL) and concentrated HCl (12 mL) to remove the aluminum residue. Precipitated polyethylene was isolated by filtration, washed with methanol, and dried *in vacuo* for 12 h.

IV ^{13}C NMR analysis of polyethylene (a typical example)

1. The chart from the literature,2) in which complete characterization of polymer branching was performed.

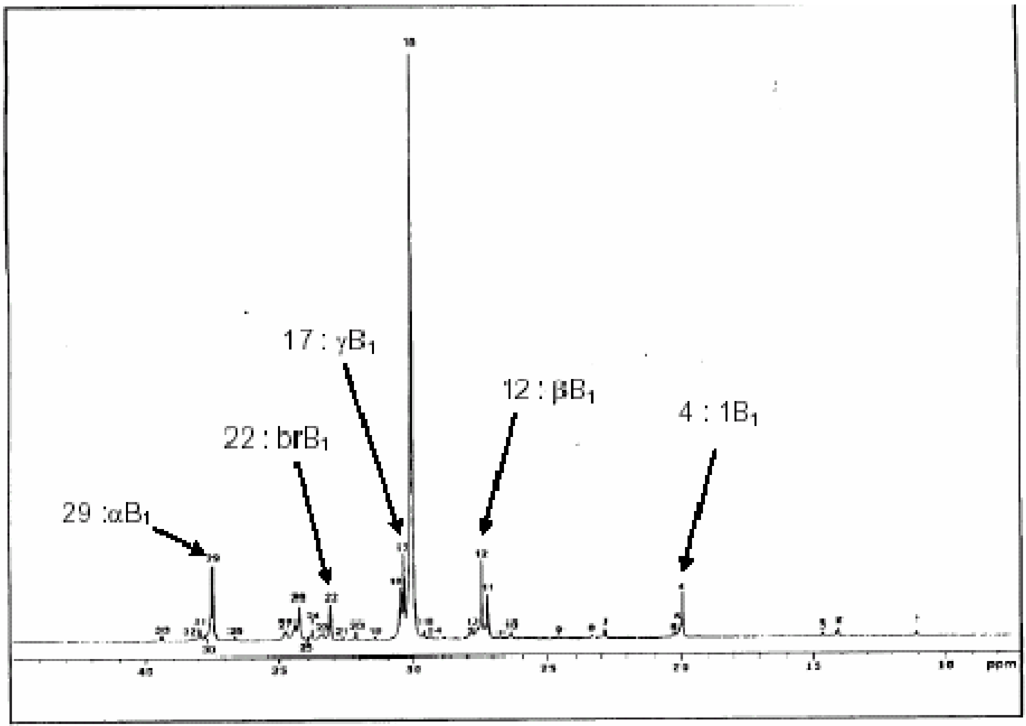
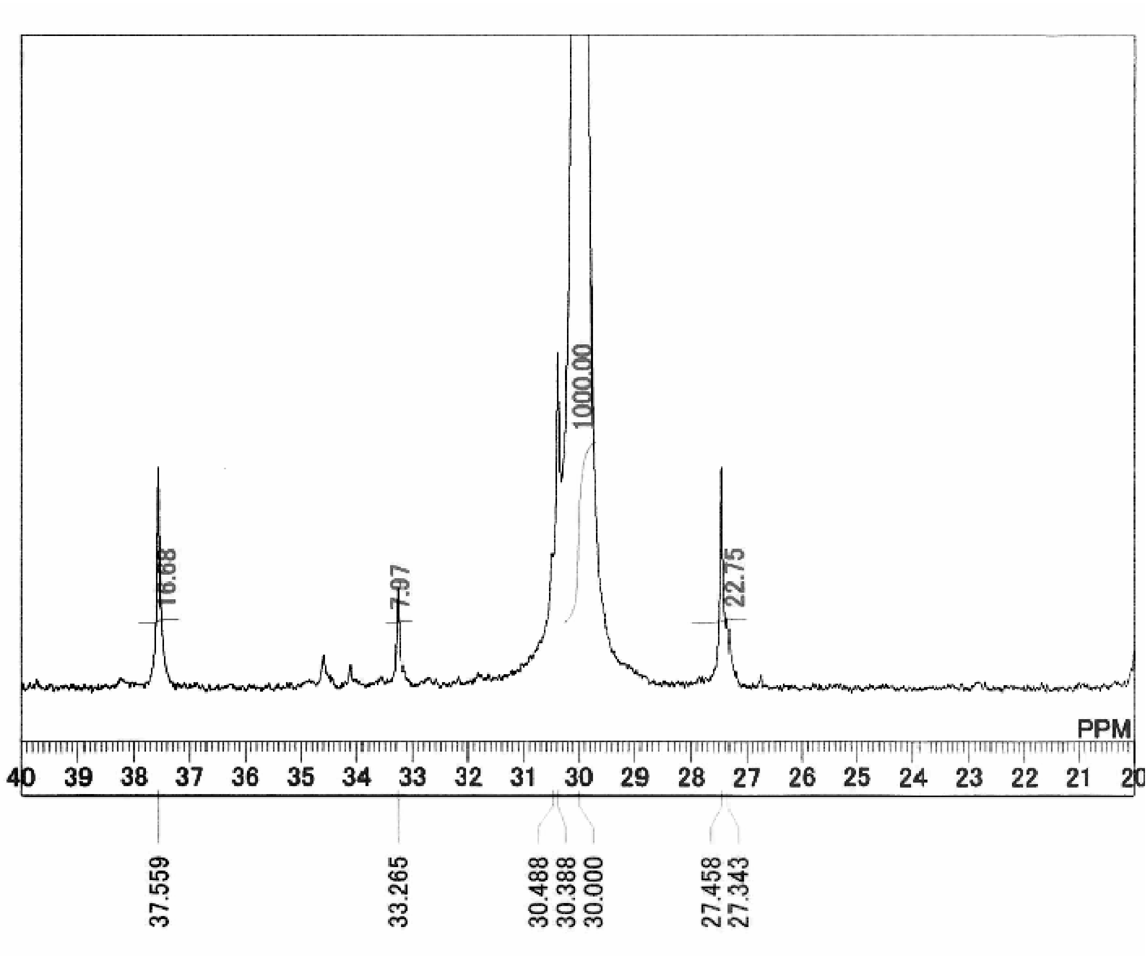


Figure 2. ^{13}C NMR spectrum of polyethylene synthesized at the following polymerization conditions: 20 °C, P_E = 1 atm, Al/Ni = 100, solvent = PhCl. Peaks marked with an asterisk were not assigned.

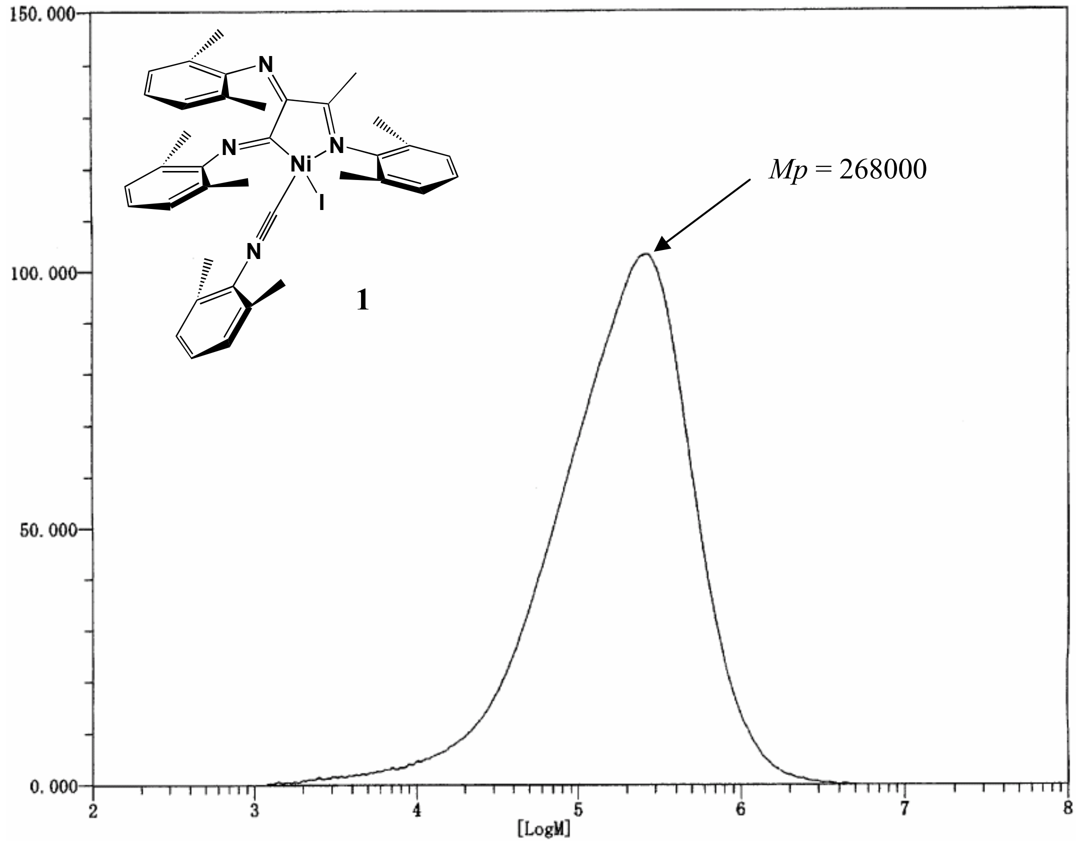
2. The ^{13}C NMR chart of polyethylene formed by the experiment show in Table1; entry1.

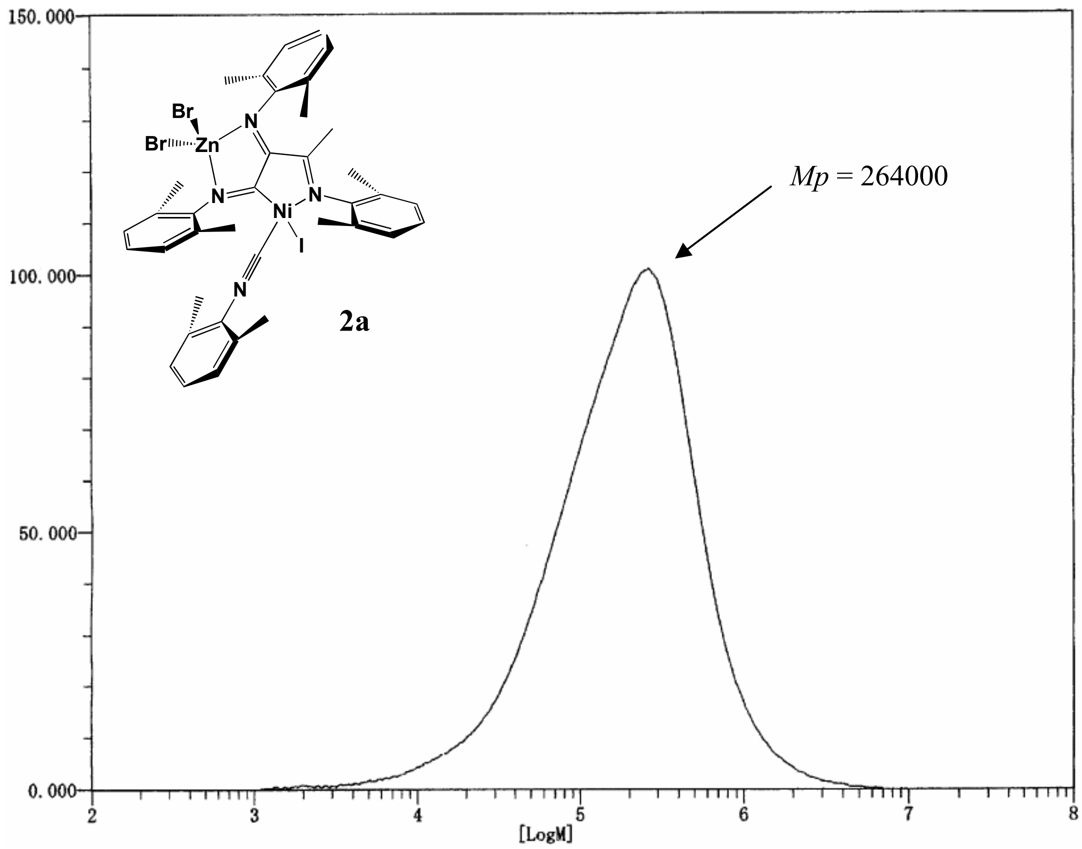


1) R. A. Schunn, *Inorg. Synth.*, 1974, **15**, 5.
2) G. B. Galland, *Macromolecules*, 1999, **32**, 1620.

V GPC profiles

Molecular weights of the formed polyethylene were determined by gel permeation chromatography (TOSOH HLC-8121GPC/HT) using 1,2,4-terachlorobenzene as a solvent at 140 °C. The *Mw*, *Mw/Mn* and *Mp* were calculated by a software package included in the GPC equipment.





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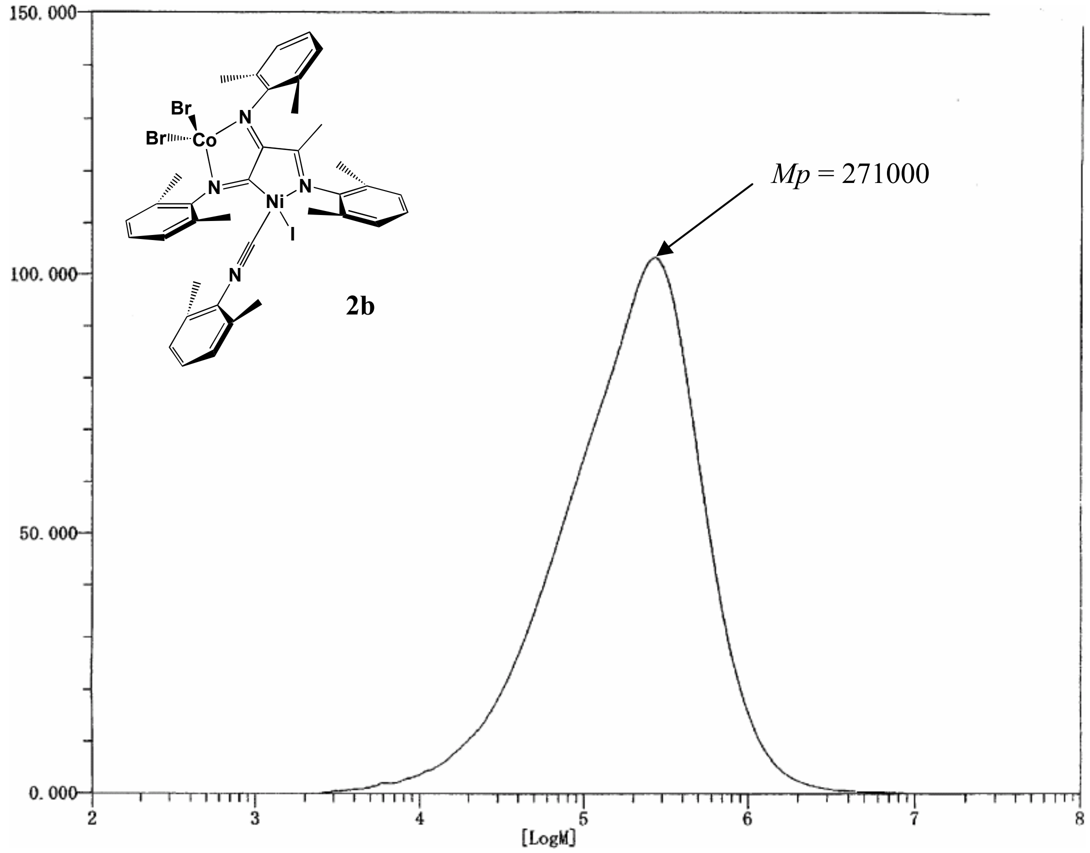
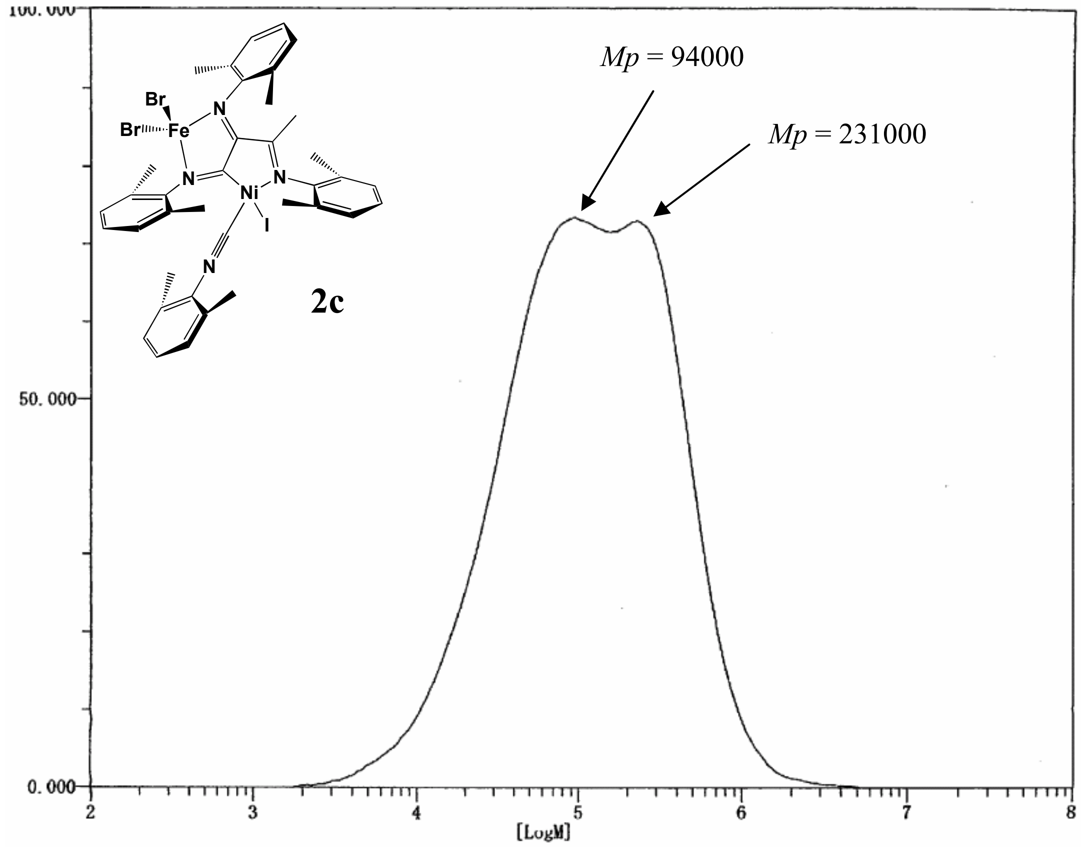


Mp = 271000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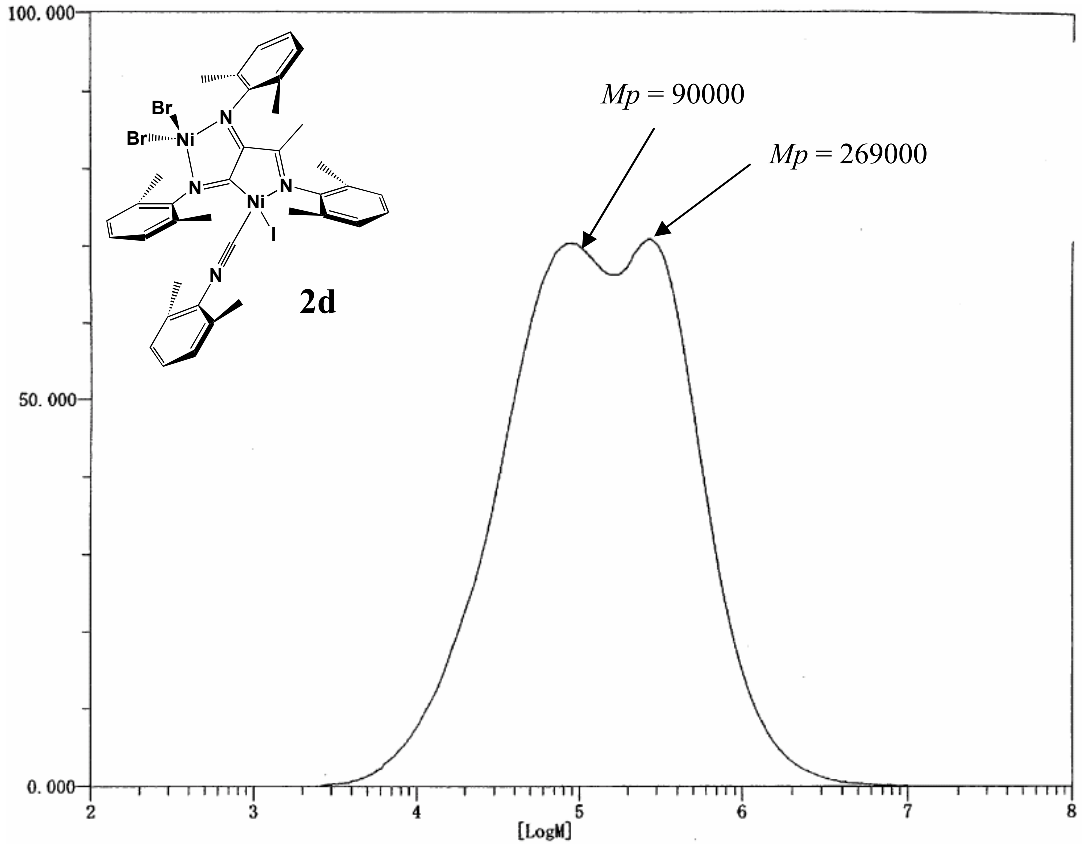
50.000
0.000
Br
Br
Fe
N
N
N
Ni
I
N
2c
Mp = 94000
Mp = 231000
2
3
4
5
6
7
8
[LogM]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Br
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N
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I
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2
3
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5
6
7
8
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