

Controlled vinyl-addition-type polymerization of norbornene initiated by several cobalt complexes having substituted terpyridine ligands

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Abstract

A series of cobalt(II) complexes having terpyridine derivatives such as 2,2':6',2''-terpyridine (**1**), 4,4',4''-*t*-Bu₃-2,2':6',2''-terpyridine (**2**), 5,5''-Me₂-2,2':6',2''-terpyridine (**3**), 6,6''-Me₂-2,2':6',2''-terpyridine (**4**) and 6,6''-(3,5-Me₂C₆H₃)₂-2,2':6',2''-terpyridine (**5**) was synthesized. The structures of **1**, **3**, and **4** were confirmed by X-ray crystallography. The coordination sphere around the cobalt center in **1** can be described as pseudo square pyramidal. On the other hand, complex **4** has pseudo trigonal bipyramidal structure. Upon activation with d-MAO (dried-methylaluminumoxane), these complexes showed high activities for the polymerization of norbornene (NBE). In particular, polymerization of NBE with **4**/d-MAO system at room temperature resulted in quantitative yield within several hours to give the polymers with relatively narrow molecular weight distributions and controlled molecular weight. The polymerizations of NBE with these cobalt catalyst systems proceeded in vinyl addition polymerization, which was confirmed by ¹H NMR spectra of the resulting polymers.

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Keywords: Cobalt; Terpyridine; Norbornene; Polymerization

1. Introduction

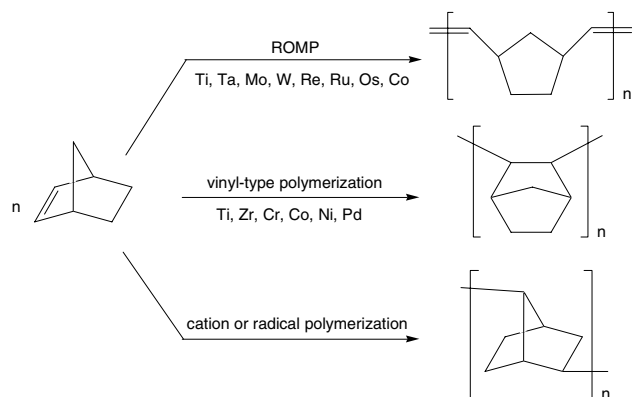
Group 4 transition metal complexes have been extensively studied as precursors of the homogeneous catalysts for olefin polymerization [1,2]. On the other hand, several new late transition metal-based non-metallocene complexes have recently emerged as potentially useful single site catalysts for olefin polymerization. A significant development in late transition metal polymerization catalyst technology was reported by Brookhart and co-workers who showed that the catalysts based on nickel and palladium could be used to access a range of linear and branched polyethylenes [3]. Iron(II) and cobalt(II) complexes with tridentate bis(imino)pyridine ligands also have a potential for producing a much broader range of polyolefinic materials at low cost [4]. We have been interested in terpyridine type ligands due to their

similar coordination geometry to bis(imino)pyridine and their extended conjugation system. Our preliminary studies on the polymerization of ethylene by terpyridine complexes of several late transition metals revealed that their activities for the ethylene polymerization were rather low. In the course of this study, we found that terpyridine cobalt complexes were very effective for the vinyl-type polymerization of norbornene (NBE).

Great interest lies in its polymerization mechanism including ring-opening metathesis polymerization (ROMP), vinyl addition polymerization, and radical polymerization, which are controlled by metal of catalyst center or cocatalyst (Scheme 1). Polymers obtained by ROMP and vinyl addition are useful as high oil-absorbing materials, shape-memory resin, and optical materials. In the case of polymerization of NBE with cobalt carboxylate complex, ROMP proceeds upon activation with alkylaluminum compounds, while vinyl addition polymerization proceeds in combination with MAO [5]. In the field of *vinyl-type* polymerization of NBE, living polymerization has not yet been achieved,

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Scheme 1.

while living ring-opening metathesis polymerization has already been widely known [6].

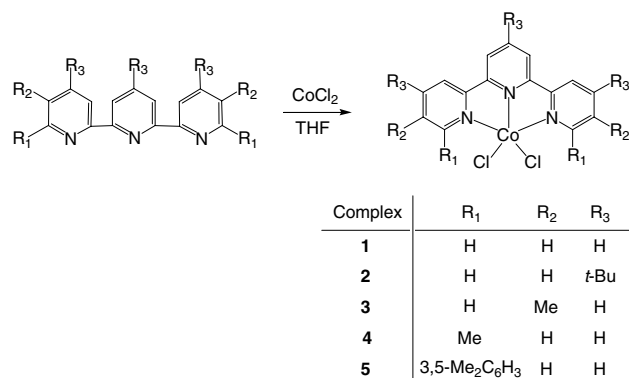
In this study, we synthesized a series of cobalt(II) complexes having terpyridine derivatives, and examined catalytic activity for the polymerization of NBE to give the polymers with controlled molecular weight and relatively narrow molecular weight distributions.

2. Results and discussion

2.1. Syntheses and structures of cobalt(II) complexes

A series of cobalt(II) complexes **1–5** having terpyridine (Tpy) derivatives as tridentate *N*-donor ligands was synthesized by the reaction of CoCl_2 with a stoichiometric amount of terpyridines at room temperature in good yield (Scheme 2).

Harris et al. reported the crystal properties of $\text{CoCl}_2(\text{terpyridine})$ **1**. However only the space group and cell parameters were described in their paper [7]. Thus, we performed the X-ray crystallography of **1** to compare with other new substituted terpyridine complexes. Fig. 1 shows the molecular structure of **1**. The selected bond distances and angles are summarized in Table 1. The



Scheme 2.

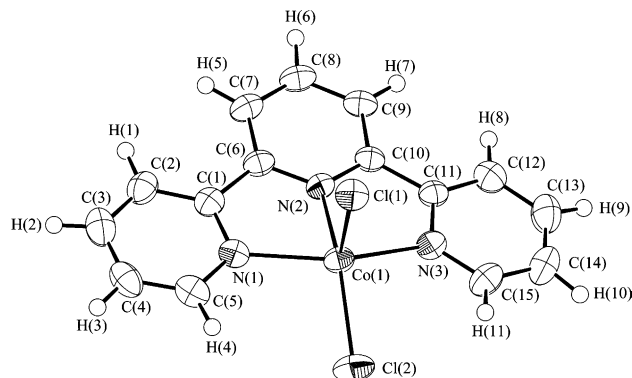


Fig. 1. Molecular structure of **1**. Thermal ellipsoids are the 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°)

	Complex 1	Complex 3	Complex 4
<i>Bond lengths</i>			
Co–N(1)	2.143(2)	2.164(2)	2.207(2)
Co–N(2)	2.069(2)	2.070(2)	2.029(2)
Co–N(3)	2.159(2)	2.156(2)	2.2192(2)
Co–Cl(1)	2.3171(8)	2.2895(9)	2.2960(9)
Co–Cl(2)	2.2815(8)	2.2808(9)	2.2921(8)
<i>Bond angles</i>			
Cl(1)–Co–Cl(2)	110.42(3)	115.13(4)	125.48(3)
Cl(1)–Co–N(1)	96.12(7)	97.33(7)	96.54(7)
Cl(1)–Co–N(2)	98.87(7)	100.12(7)	111.82(7)
Cl(1)–Co–N(3)	101.76(7)	101.53(7)	95.85(7)
Cl(2)–Co–N(1)	101.31(7)	96.59(7)	96.27(7)
Cl(2)–Co–N(2)	150.70(7)	144.61(7)	122.70(7)
Cl(2)–Co–N(3)	97.15(7)	98.81(7)	95.29(7)
N(1)–Co–N(2)	75.77(9)	75.03(9)	76.81(9)
N(1)–Co–N(3)	147.90(9)	147.65(9)	153.65(9)
N(2)–Co–N(3)	75.29(9)	75.94(9)	77.01(9)

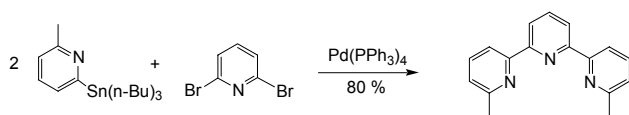
Complex **1** has mononuclear pseudo square pyramidal geometry, in which Cl(1) occupies an apical position. The Cl(1)–Co–N(2) and Cl(2)–Co–N(2) angles are 98.87(7)° and 150.70(7)°, respectively. The Co–N(1) and Co–N(3) bond lengths [2.143(2) and 2.159(2) Å] are longer than Co–N(2) [2.069(2) Å].

In order to elucidate the effects of the substituents, we systematically synthesized a series of new cobalt complexes having various substituted terpyridine ligands. A cobalt complex having a commercially available 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine, $\text{CoCl}_2(4,4',4''\text{-tri-}t\text{-butyl-2,2':6',2''-terpyridine})$ **2**, was obtained as a gray powder in 80% yield.

5,5''-Dimethyl-2,2':6',2''-terpyridine (5,5''-Me₂Tpy) was prepared according to the literature [8], in which 6,6''-dimethyl-2,2':6',2''-terpyridine (6,6''-Me₂Tpy) could not be synthesized in the same manner to that for 5,5''-Me₂Tpy, but obtained from the reaction of 2,6-bis(trimethyltin)pyridine and 2-bromo-6-methylpyridine in 43% yield. Here, we succeeded in the preparation of

the 6,6''-Me₂Tpy as a Stille-type coupling [9] of 2-tributyltin-6-methylpyridine and 2,6-dibromopyridine in 80% yield (Scheme 3).

Cobalt complexes having dimethylterpyridine ligands, CoCl₂(5,5''-Me₂Tpy) **3** and CoCl₂(6,6''-Me₂Tpy) **4**, were obtained as a green powder in 99% and 82% yield, respectively. Single crystals of **3** and **4** suitable for X-ray diffraction studies were obtained by recrystallizations from CH₂Cl₂/hexane. The molecular structures of these complexes are shown in Figs. 2 and 3. The selected bond distances and angles are included in Table 1. In sharp contrast to the pseudo square pyramidal geometry of **1**, the geometry of **4** can be described as pseudo trigonal bipyramidal in which N(1) and N(3) are located at apical positions. The complex **3** has an intermediate geometry between square pyramidal and trigonal bipyramidal. The Cl(1)–Co–N(2) and Cl(2)–Co–N(2) angles are 100.12(7)° and 144.61(7)° in **3**, 111.82(7)° and 122.70(7)° in **4**, respectively. The differ-



Scheme 3.

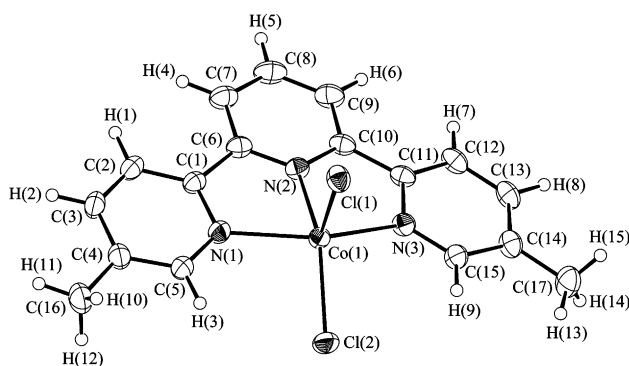


Fig. 2. Molecular structure of **3**. Thermal ellipsoids are the 50% probability level.

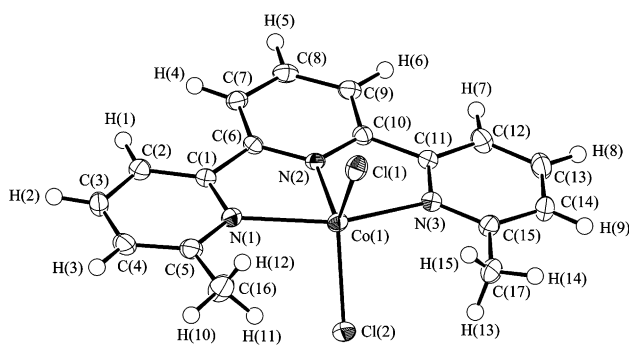


Fig. 3. Molecular structure of **4**. Thermal ellipsoids are the 50% probability level.

ence between the two of N(2)–Co–Cl angles are 44.49° in **3** and 51.83° in **1**, while only 10.88° in **4**. The coordination sphere around the metal in **4** is restricted to have pseudo trigonal bipyramidal structure due to the steric hindrance of 6- and 6''-methyl groups on the terpyridine ligand. The methyl substitutions at 5- and 5''-positions in **3** also affect the coordination geometry, although the effect is weaker than those at 6- and 6''-positions in **4**. The tendencies of Co–N bonds distances of **3** and **4** are similar to **1**: Co–N(2) bond lengths are shorter than Co–N(1) and Co–N(3) lengths.

We have recently developed terpyridine derivatives having bulky substituents at 6- and 6''-positions [10]. In this study, CoCl₂[6,6''-(3,5-Me₂C₆H₃)₂-2,2':6',2''-terpyridine] **5** was synthesized. Complex **5** was characterized by elemental analysis.

A cobalt(II) complex bearing 2,6-bis(imino)pyridine type tridentate N-donor ligand, CoCl₂{2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine} **6**, was prepared according to the literature [11] for comparison of catalytic properties with those of terpyridine complexes.

2.2. Polymerizations of norbornene

The catalyses of these cobalt complexes **1–6** for the polymerization of NBE were investigated in the presence of aluminum cocatalyst. Without cocatalyst, these complexes showed no catalytic activity. The complexes **1–5** showed very low activities (~5% yield) for polymerization of NBE upon activation with MMAO. Thus, we used d-MAO as a cocatalyst for these cobalt complexes. d-MAO was prepared by drying ordinary MAO (toluene solution) in vacuo at 40 °C to remove toluene and AlMe₃ and used as a solution in chlorobenzene.

Table 2 summarized the polymerization of NBE by the cobalt complexes **1–5** activated with d-MAO. In combination with d-MAO, catalytic activities of these complexes were drastically increased compared to the MMAO systems and the polymerization of NBE with these cobalt catalyst systems proceeded in vinyl addition polymerization, which was confirmed by ¹H NMR spectra of the resulting polymers (Fig. 4). In particular, polymerization of NBE with **4**/d-MAO system at room temperature resulted in quantitative yield within 3 h while other systems required more than 12 h to achieve complete consumption of the monomer. On the other hand, the molecular weight distributions (MWD) of poly(NBE) obtained by **1** or **2** were found to be relatively narrow (*M_w*/*M_n* ~ 1.2). With increasing the steric hindrance around cobalt center, the polymer yield decreased. The complex **5** having large substituents at 6- and 6''-positions of terpyridine, showed the lowest activity among these terpyridine systems. Similarly, the 2,6-diisopropylphenyl groups of bis(imino)pyridine ligand in **6**, which were necessary for inhibition of β-H elimination to proceed high polymerization of ethylene,

Table 2
Polymerization of Norbornene with cobalt complexes/d-MAO systems

Complex	Time (h)	Yield (%)	$M_n \times 10^{-4a}$	M_w/M_n^a
1	3	62	4.1	1.66
	12	>99	6.0	1.22
2	3	30	3.2	1.87
	12	>99	6.4	1.21
3	3	60	5.1	1.38
	12	94	7.9	1.33
4	3	>99	3.2	1.61
	12	>99	4.5	1.36
5	3	41	4.6	1.70
	12	88	4.2	1.49
6 CoCl ₂	3	17	6.1	1.59
	12	38	7.7	1.36
– ^b	3	Trace		

Conditions; Cat. = 0.02 mmol, Cocat. = d-MAO, [Al]/[Co] = 100 mol/mol, [NBE]₀/[Co] = 214 mol/mol, Solvent = 5 ml of chlorobenzene, Temp. = r.t.

^a Determined by GPC calibrated with standard polystyrenes at 40 °C, eluent CHCl₃.

^b Without cobalt complex.

were not suitable for polymerization of NBE. Thus the polymer yield was distinctly low in 6/d-MAO system.

In spite of the steric hindrance of the methyl groups at 6- and 6''-positions of terpyridine group, the complex 4 was most active among these cobalt systems. Fig. 5 shows space filling models of complexes 1, 3, and 4. The 6,6''-methyl groups exist close to the metal center, and this should prevent association of d-MAO anions with cationic species. Thus the loose ionic pair would be formed which is favorable for coordination and insertion of norbornene monomer. Moreover, the complex 4 has pseudo trigonal bipyramidal structure. If the coordination sphere is maintained in polymerization system, both the coordination sites for NBE and growing

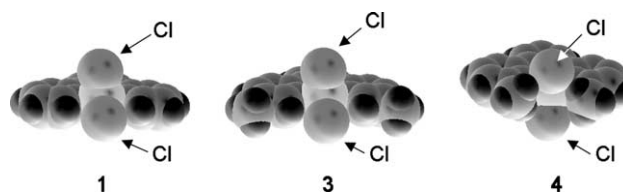


Fig. 5. Space filling models of 1, 3, and 4. Calculated by Crystal-Structure 3.10.

polymer chain could be situated at two equivalent equatorial positions. As a consequence, 4/d-MAO system becomes active than 3/d-MAO in which one pseudo axial position would be located close to crowded terpyridine plane. In the case of 1/d-MAO and 2/d-MAO systems, d-MAO anions could more strongly tie to the cobalt cation so that the growing rate of poly(NBE) might be slowed down and a chain transfer reaction should be hindered to give polymers with relatively narrow MWD.

Table 3 shows the effect of [NBE]₀/[Co] ratio on the polymerization of NBE with 4/d-MAO system. Polymer yields were decreased in the polymerizations for 3 h under the high [NBE]₀/[Co] ratio, while the polymerizations for 12 h afforded polymers in good yield even under high [NBE]₀/[Co] ratio. Increasing of the [NBE]₀/[Co] ratio resulted in an increase of number average molecular weights (M_n) of PNBE. The molecular weight distributions of these polymers remained relatively narrow (< 2) and M_n were close to the theoretical value calculated from feed [NBE]₀/[Co] ratio, especially the polymerization under [NBE]₀/[Co] ratio of 1170 mol/mol. These results indicate that this polymerization system has a potential to proceed the living polymerization.

The introduction of bulkier alkyl groups into terpyridine is now under investigation.

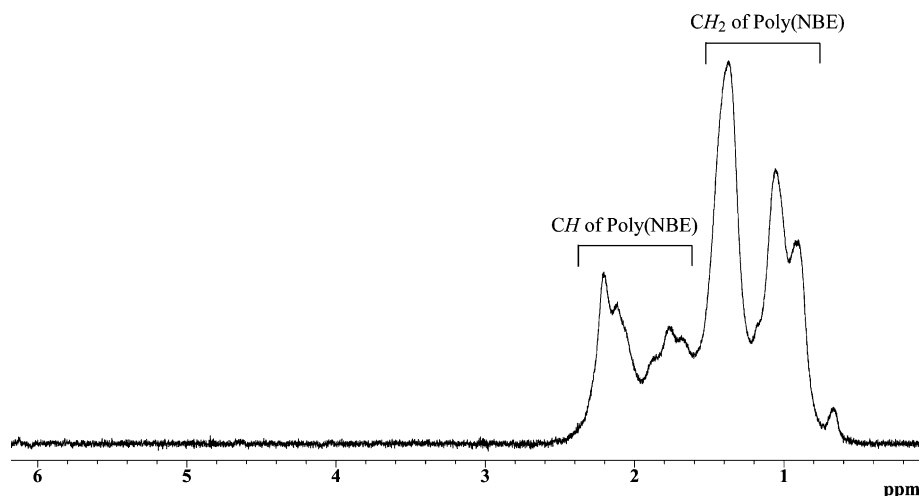


Fig. 4. ¹H NMR spectrum of poly(NBE) obtained with 4/d-MAO shown in Table 2 (polymerization time = 12 h).

Table 3
Effect of monomer ratio on the polymerization of NBE with 4/d-MAO system

[NBE] ₀ /[Co] [mol]/[mol]	$M_{n(\text{calcd.})} \times 10^{-4}$	3 h			12 h		
		Yield (%)	$M_{n(\text{found})} \times 10^{-4a}$	M_w/M_n^a	Yield (%)	$M_{n(\text{found})} \times 10^{-4a}$	M_w/M_n^a
117	1.1	>99	3.3	1.63	>99	4.0	1.42
214	2.0	>99	3.2	1.61	>99	4.5	1.36
351	3.3	86	6.5	1.54	95	5.9	1.94
468	4.4	88	8.7	1.74	95	9.1	1.73
819	7.7	75	10.4	1.66	98	10.7	1.73
1170	11.0	48	14.6	1.69	85	13.8	1.70

Conditions: Cat. = 0.02 mmol, Cocat. = d-MAO, [Al]/[Co] = 100 mol/mol, Solvent = 5 ml of chlorobenzene, Temp. = r.t.

^a Determined by GPC calibrated with standard polystyrenes at 40 °C, eluent CHCl₃.

3. Conclusion

A series of cobalt(II) complexes having terpyridine ligands such as CoCl₂(Tpy) (**1**), CoC₂(4,4',4''-*t*-Bu₃-Tpy) (**2**), CoCl₂(5,5''-Me₂Tpy) (**3**), CoCl₂(6,6''-Me₂Tpy) (**4**) and CoCl₂[6,6''-(3,5-Me₂C₆H₃)₂-Tpy] (**5**) was synthesized. The structures of **1**, **3**, and **4** were confirmed by X-ray crystallography and complex **4** had pseudo trigonal bipyramidal structure. Upon activation with d-MAO, these complexes showed high activities for the polymerization of norbornene (NBE). In particular, the polymerization of NBE with 4/d-MAO system at room temperature resulted in quantitative yield. The molecular weights of the polymers were controllable by the feed [NBE]₀/[Co] ratio and the resulting molecular weight distributions were relatively narrow. As far as we know this is the first example of controlled vinyl-type polymerization of NBE with cobalt complexes.

4. Experimental

4.1. General considerations

All operations were performed under argon by using standard Schlenk techniques. ¹H NMR spectra were recorded on a JEOL JNM-LA-400 spectrometer (400 MHz), and chemical shifts were calibrated with residual chloroform ($\delta = 7.26$ ppm) in CDCl₃. ¹H NMR spectra of poly(NBE)s were measured using a mixture of *o*-dichlorobenzene and benzene-*d*₆ (4:1) as a solvent at 100 °C. Elemental analyses of the cobalt complexes were carried out on a Perkin Elmer 2400 series II CHN/O analyzer after sealing the sample in a tin foil under argon. Gel permeation chromatographic (GPC) analyses of PNBE were run on a Tosoh model SC-8010 instrument (RI 8020 detector) with the TSK gel columns G1000, G2500, G4000, and G7000 in chloroform at 40 °C. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were determined with reference to a calibration curve plotted with standard polystyrene.

4.2. Materials

Tetrahydrofuran (THF) was dried over Na–K alloy and distilled before use. CoCl₂, 2,6-dibromopyridine, and norbornene were purchased from Kanto Chemical Co. 2,2':6',2''-terpyridine and 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine were purchased from Aldrich Chemical Company Inc. NBE was dried over CaH₂ and then over a dried molecular sieve 4A. MAO (methylaluminoxane) and MMAO (modified MAO) were supplied by Tosoh Fine Chemistry, Co. and used without further purification.

4.3. Synthesis of CoCl₂(4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine) (**2**)

A mixture of CoCl₂ (0.50 g, 3.90 mmol), 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine (1.57 g, 3.90 mmol), and 45 ml of THF was placed in a 100 ml two neck round flask. The mixture was stirred for 12 h at 25 °C, resulting in the formation of a green suspension. The green precipitates were collected by centrifugation and washed with THF followed by drying in vacuo. CoCl₂(4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine) (**2**) was obtained as a green powder. Yield: 80% (1.65 g, 3.10 mmol). Anal. Calcd. for C₂₇H₃₅N₃CoCl₂: C, 61.02; H, 6.64; N, 7.91. Found: C, 61.39; H, 6.92; N, 8.62%.

4.4. Synthesis of CoCl₂(5,5''-dimethyl-2,2':6',2''-terpyridine) (**3**)

A mixture of CoCl₂ (0.30 g, 2.20 mmol), 5,5''-dimethyl-2,2':6',2''-terpyridine (0.61 g, 2.20), and 45 ml of THF was placed in a 100 ml two neck round flask. The mixture was stirred for 12 h at 25 °C, resulting in the formation of a green suspension. The green precipitates were collected by centrifugation and washed with THF followed by drying in vacuo. CoCl₂(5,5''-dimethyl-2,2':6',2''-terpyridine) (**3**) was obtained as a green powder. Yield: 99% (0.84 g, 2.16 mmol). Anal. Calcd. for C₂₇H₃₅N₃CoCl₂: C, 52.20; H, 3.87; N, 10.74. Found: C, 50.71; H, 3.86; N, 10.61%.

4.5. Synthesis of 6,6''-dimethyl-2,2':6',2''-terpyridine

A mixture of 6-methyl-2-tributylstannylpyridine (30.5 g, 80.1 mmol), 2,6-dibromopyridine (8.1 g, 34.2 mmol), and tetrakis(triphenylphosphine)palladium (2.4 g, 2.0 mmol) was refluxed for 4 days in absolute toluene (150 ml). After removal of the solvent, the black residue was treated with aq. HCl solution (3 × 30 ml, 6 M). The suspension was extracted with CH₂Cl₂, and the organic phase was washed again with aqueous HCl. The aqueous solution was added dropwise into aqueous ammonia (250 ml, 10%). The precipitates were filtered, dissolved in CH₂Cl₂, treated with activated carbon, and dried over MgSO₄. The solvent was removed in vacuo to give 6,6''-dimethyl-2,2':6',2''-terpyridine as a white powder. Yield: 80% (7.1 g, 27.2 mol). Anal. Calcd. for C₂₇H₃₅N₃: C, 78.13; H, 5.79; N, 16.08. Found: C, 78.05; H, 5.78; N, 16.02%.

4.6. Synthesis of CoCl₂(6,6''-dimethyl-2,2':6',2''-terpyridine) (4)

A mixture of CoCl₂ (0.3 g, 2.3 mmol), 6,6''-dimethyl-2,2':6',2''-terpyridine (0.6 g, 2.3 mmol), and 45 ml of THF was placed in a 100 ml two neck round flask. The mixture was stirred for 12 h at 25 °C, resulting in the formation of a green suspension. The green precipitates

were collected by centrifugation and washed with THF followed by drying in vacuo. CoCl₂(6,6''-dimethyl-2,2':6',2''-terpyridine) (4) was obtained as a green powder. Yield: 82% (0.74 g, 1.9 mmol). Anal. Calcd. for C₂₇H₃₅N₃CoCl₂: C, 52.20; H, 3.87; N, 10.74. Found: C, 52.04; H, 3.84; N, 10.68%.

4.7. Synthesis of CoCl₂[6,6''-(3,5-Me₂C₆H₃)-2,2':6',2''-terpyridine] (5)

A mixture of CoCl₂ (0.2 g, 2.0 mmol), 6,6''-(3,5-Me₂C₆H₃)-2,2':6',2''-terpyridine (0.9 g, 2.0 mmol), and 45 ml of THF was placed in a 100 ml two neck round flask, and stirred for 12 h at 25 °C, resulting in the formation of a green suspension. The green precipitates were collected by centrifugation and washed with THF followed by drying in vacuo. CoCl₂[6,6''-(3,5-Me₂Ph)-2,2':6',2''-terpyridine] (5) was obtained as a green powder. Yield: 28% (0.31 g, 0.6 mmol). Anal. Calcd. for C₃₁H₂₇N₃CoCl₂: C, 65.16; H, 4.76; N, 7.35. Found: C, 65.17; H, 5.33; N, 7.08%.

4.8. Polymerization of norbornene

A solution of d-MAO in chlorobenzene (1.2 ml, 4 M) was added to a solution of cobalt complex (0.02 mmol) in chlorobenzene (5 ml) at ambient temperature or 0 °C

Table 4
Crystal data and data collection parameters

	Complex 1	Complex 3	Complex 4
Empirical formula	C ₁₅ H ₁₁ N ₃ CoCl ₂	C ₁₇ H ₁₅ N ₃ CoCl ₂	C ₁₇ H ₁₅ N ₃ CoCl ₂
Formula weight	363.11	391.16	391.16
Temperature/°C	23	23	-150
Color	Green	Green	Green
Crystal dimensions/mm	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.10	0.15 × 0.10 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₁ / <i>c</i> (#14)	<i>P</i> ₁ / <i>n</i> (#14)	<i>P</i> ₁ / <i>c</i> (#14)
<i>a</i> /Å	10.8405(3)	9.9660(2)	7.353(1)
<i>b</i> /Å	8.2395(3)	14.5933(3)	17.489(2)
<i>c</i> /Å	16.1844(6)	11.6216(3)	12.718(1)
<i>α</i> /°	90	90	90
<i>β</i> /°	95.043(1)	103.2871(7)	102.360(5)
<i>γ</i> /°	90	90	90
<i>V</i> /Å ³	1440.00(8)	1644.96(6)	1597.6(4)
<i>Z</i>	4	4	4
<i>D</i> _{calc} /g cm ⁻³	1.675	1.579	1.626
<i>μ</i> (Mo Kα)/cm ⁻¹	15.57	13.69	14.095
Diffractometer	Rigaku RAXIS-RAPID	Rigaku RAXIS-RAPID	Rigaku RAXIS-RAPID
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
2θ _{max} /°	54.9	55.0	55.0
Number of measured reflections	3541	15381	15219
Number of unique reflections	3307	3734	3675
Number of variables	236	270	270
<i>R</i> ₁ ^a	0.090	0.044	0.041
<i>wR</i> ₂ ^b	0.170	0.090	0.111
GOF	1.02	1.09	1.14

^a *R*₁ = ∑ ||*F*₀ - |*F*_c|| / ∑ |*F*₀|, for all *I* > 2σ(*I*).

^b *wR*₂ = [∑ (w(*F*₀² - *F*_c²)) / ∑ w(*F*₀²)]^{1/2}.

and maintained for 5 min. A prescribed amount of NBE solution in chlorobenzene was added at room temperature to start polymerization. The reaction mixture was stirred for a given period. The polymerization mixture was quenched with a large amount of methanol/hydrochloric acid mixture. The precipitated polymers were collected by centrifugation and dried in vacuo. The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC).

4.9. X-ray structure determination

Single crystals of **1**, **3** and **4** suitable for X-ray diffraction were mounted in a cryoloop. Measurements of these crystals were made on a Rigaku RAXIS RAPID Imaging Plate for data collection using Mo K α radiation. Crystal data and data collection parameters of these complexes are summarized in Table 4. Indexing was performed from three oscillations which were exposed for 3.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.10 mm pixel mode. A linear absorption coefficient, μ , was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELX-86 [12] for **1**, SHELX-97 [13] for **3** and **4**), and expanded using Fourier techniques (DIRDIF99) [14]. The data were refined by the full-matrix least-square method. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms for each complex were refined using the riding model. The final cycle of full-matrix least-squares refinements was performed on F^2 . All calculations were performed using the CrystalStructure [15,16] crystallographic software package except for refinement, which was performed using SHELXL-97 [13].

5. Supplementary material

Crystallographic data for the structural analysis of **1**, **3**, and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 210854 for $\text{CoCl}_2(2,2':6',2'')\text{-terpyridine}$ (**1**), No. 210855 for $\text{CoCl}_2(5,5''\text{-Me}_2\text{-}2,2':6',2'')\text{-terpyridine}$ (**3**), and No. 210856 for $\text{CoCl}_2(6,6''\text{-Me}_2\text{-}2,2':6',2'')\text{-terpyridine}$ (**4**), respectively. Copies of these information may be

obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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