Inorganic Chemistry Communications 14 (2011) 189–193

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis, characterization, and MMA polymerization activity of tetrahedral Co (II) complex bearing *N, N*-bis(1-pyrazolyl)methyl ligand based on aniline moiety

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ARTICLE INFO

Article history:
Received 14 September 2010
Accepted 21 October 2010
Available online 28 October 2010

Keywords:
N,N-bis(1-H-Pyrazole-1-yl)
Tetrahedral Co (II) complex
Methyl methacrylate
PMMA

ABSTRACT

A new series of air-stable Co(II) complexes, [bpmaL1]$CoCl_2$ (**1a**), [bpmaL2]$CoCl_2$ (**2a**), [bpmaL3]$CoCl_2$ (**3a**), and [bpmaL4]$CoCl_2$ (**4a**), where, for example, [bpmaL1 = *N*,*N*-bis{(1-pyrazolyl)methyl}aniline], has been synthesized. X-ray crystallography of **2a** indicated that it has a dipper-type structure in which the aniline moiety plays the role of the handle with a tetrahedral cobalt located at the edge with an eight-membered chelate ring formation. However, there is no indication that the metal is coordinated to the nitrogen of the aniline group. Moreover, complexes showed the highest catalytic activity in the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) with an activity of 1.14×10^6 g PMMA/mol-Co·h at 60 °C and syndiotacticity of PMMA, characterized by ^{13}C NMR spectroscopy, which value was *ca.* 0.57.

Late transition metal complexes with *N*,*N*-chelate ligands [1] have attracted considerable attention due to their catalytic actions since the pioneering studies of Keim and Fink [2] and Brookhart et al. reported the discovery of α-diimine complexes of Ni (II) and Pd (II) catalysts for the polymerization or oligomerization of α-olefins [3–5]. Subsequently, several structural variations of diimines have also been reported allowing adjustment of the steric and electronic properties of the *N*,*N*-chelate ligands. These include β-diimines and analogs the Ni(II) and Pd(II) complexes of which usually exhibit lower catalytic activities than the α-diimine complexes [6]. Specifically, the highly active 2,6-bis(imino)pyridines initially discovered independently by the groups of Brookhart and Gibson [7–11] are well known cobalt and iron systems [12–16]. A further modification involves appending a donor side arm to construct tridentate chelating ligands, such as [*N*,*O*], [*N*,*N*,*N*], and [*N*,*N*,*O*] ligands [17,18].

Moreover, despite many reports on nitrogen-based metal complexes [19,20], little is known about pyrazole-based ligand late transition metal complexes as catalysts for olefin polymerization [21–24] and methyl methacrylate polymerization,[25–27] in comparison with early transition metal complexes [20,28–31]. In particular, pyrazoles, which are among the fundamental heterocycles, have been extensively used as N-donor ligands to metals since the first review of pyrazole-derived ligands in 1972 [32–34]. Pyrazoles and their derivatives are attractive ligands because their steric and electronic properties can be fine-tuned by the appropriate choice of substitutions on the 2-N, 3-C, 4-C, and 5-C atoms of pyrazole [35–38]. The range of pyrazoles enables optimization of the electrophilic properties of transition metal complexes of pyrazoles and their derivatives for use as catalysts for olefin polymerization. Thus, many pyrazoles and their transition metal complexes in different oxidation states have been isolated and structurally characterized, because of their diverse potential applications, including roles as industrial catalysts, such as in olefin oligomerization or polymerization [39,40], as bioinorganic materials in pharmaceutical preparations [41–45], and as metal ion extractants [46].

These interesting features prompted us to explore the present system involving the *N*,*N*-bispyrazolylmethyl ligand, based on an aniline moiety [47,48] and their Co complexes to investigate the steric and electronic influence of substituents on the aniline ring in formation of complex and catalytic activity in both α-olefin and methyl methacrylate polymerization.

Ligands [bpmaL1 - bpmaL4], were prepared in facile forms with high yields by dehydration of the alcoholic moiety of 1*H*-pyrazole-1-yl methanol,{R. Hüttel, 1952 #348} which readily undergoes sublimation, with aniline or substituted anilines, such as 2,6-diispropylaniline and 2,4,6-trimethylaniline. Solid ligands [bpmaL2–bpmaL4] and liquid ligand [bpmaL1] were very hydroscopic, with decomposition to the starting materials at certain time periods [49]. Synthesis of bidentate [*N*,*N*]-cobalt (II) dichloride complexes, **1a**–**4a** was straightforward by reaction of the cobalt metal halide, *i.e.*, $CoCl_2 \cdot 6H_2O$ with the corresponding ligands [bpmaL1–bpmaL4], to give them in high yield and high purity (Scheme 1) [50]. The bulkiness of the aniline moiety had no effect on the synthesis of ligands or complexes. Ligands and their Co complexes were characterized using various spectroscopic techniques, such as NMR with ^1H-^1H COSY and ^{13}C-^1H HMQC, IR, elemental analysis, and UV/Vis spectroscopy. All Co(II) complexes

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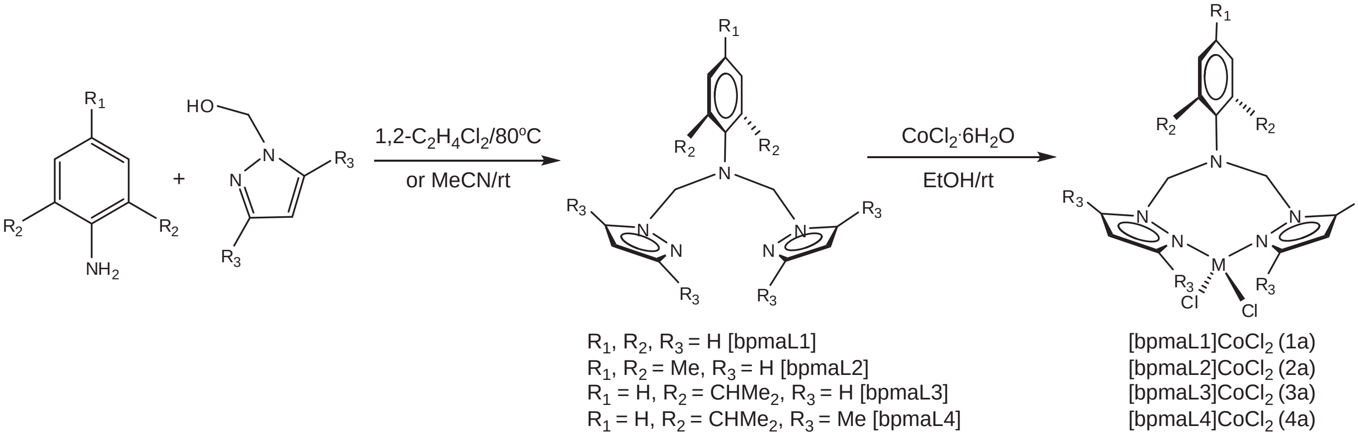
doi:10.1016/j.inoche.2010.10.019



Scheme 1. Synthesis of [bpmaL]$CoCl_2$.

were deeply colored, ranging from dark blue to sky blue, were stable to both heat and moisture, and were paramagnetic, preventing useful NMR analysis. The complex **2a** was further characterized by X-ray crystallography. A single crystal of **2a** was obtained by slow evaporation of the compound in toluene at room temperature. X-ray crystallography of complex **2a** indicated that it has a dipper-type structure in which the aniline moiety played the role of the handle with the tetrahedral cobalt located at the edge [51]. The ORTEP representation of complex **2a** with the atom labeling for non-hydrogen atoms with some selected bond angles and bond lengths is shown in Fig. 1. The metal center is bonded to the ligand through the nitrogen atoms of the pyrazolyl moiety in a bidentate manner, forming an eight-membered chelate ring. The geometry around the [CoN_2Cl_2] core has a slightly distorted tetrahedral configuration. Geometric distortion from ideal angles can be explained by the need to accommodate the bulky eight-membered chelate ring. Such eight-membered chelate rings are rare, primarily because of the destabilization caused by non-bonding interactions within the eight-membered ring due to unfavorable torsion angles imposed by the ring size. The flexibility within the pyrazolyl backbone, the presence of suitably positioned sterically demanding substituents, and heteroatoms probably contribute to the stability of the eight-membered chelate ring. The bond length between Co–N(1) and Co–N(5) are mutually equal and comparable to similar [*N*,*N*-bis{(3,5-dimethylpyrazol-1-ylmethyl}aminobenzene]Co(II) complexes [51]. Although the distance of N(3)–Co(1) was 3.482 (4) in complex **2a** was shorter by *ca.* 0.4 Å than that in the comparable [*N*,*N*-bis{(3,5-dimethylpyrazol-1-ylmethyl}aminobenzene] Co(II) complex, there was no indication of bond formation between the cobalt ion and the nitrogen of the aniline moiety [52,53]. For comparison, the bond distance between the cobalt ion and the nitrogen of the pyridine was 2.051(3) Å in the pentacoordinate-distorted square pyramidal bis(imino)pyridine-Co(II) complex [54,55]. The bite angle of N(5)-Co(1)-N(1) is 107.69(14)° and is slightly smaller than the ideal tetrahedral angle. The Co–Cl bond lengths are similar and comparable to the other tetrahedral cobalt (II) complexes with a chromophore group [$CoCl_2N_2$]. The ligand–metal–ligand angle differed from the ideal value of 109.5°, varying between 116.14(6)° [Cl(1)-Co-Cl(2)] and 110.50(12)° [N(1)-Co-Cl(2)], showing a slightly distorted tetrahedral configuration.

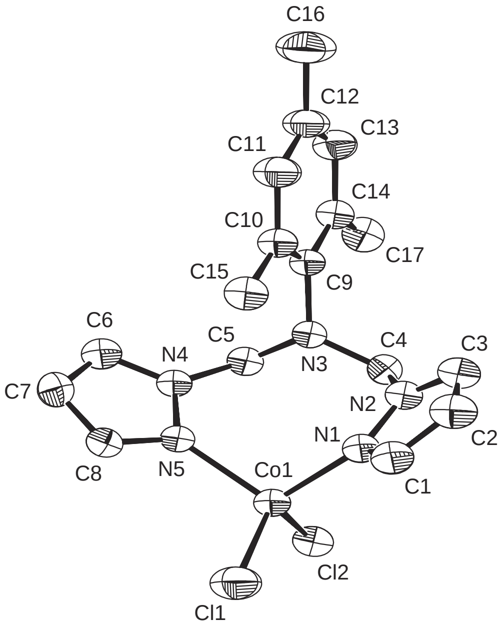


Fig. 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (°) are Co(1)-N(5) 2.011 (4), N(4)-C(6) 1.334 (5), Co(1)-Cl(2) 2.228 (1), N(5)-C(8) 1.337 (6), Co(1)-N(3) 3.482 (4), N(4)-N(5) 1.348 (5), N(2)-C(4) 1.454 (6), C(1)-C(2) 1.377 (8), N(3)-C(5) 1.424 (6), C(2)-C(3) 1.356 (9), N(3)-C(9) 1.438 (5), C(6)-C(7) 1.337 (7), N(5)-Co(1)-N(1) 107.69 (14), N(5)-N(4)-C(5) 121.34 (4), N(1)-Co(1)-Cl(2) 110.50 (12), Cl(2)-Co(1)-Cl(1) 118.4 (4), N(1)-Co(1)-Cl(1) 105.29 (12), C(5)-N(3)-C(9) 118.69(5), N(5)-Co(1)-N(3) 61.54 (12), C(1)-N(1)-Co(1) 105.0 (5), N(4)-N(5)-Co(1) 126.73 (3), C(3)-C(2)-C(1) 120.0(3), Cl(2)-Co(1)-N(3) 89.25 (7), N(2)-C(3)-C(2) 109.5 (5), N(2)-N(1)-Co(1) 126.63 (3), N(3)-C(4)-N(2) 114.5 (4).

The electronic absorption spectra of ligands and Co complexes in toluene appear to be mainly of an intraligand character (Fig. 2). For example, ligand [bpmaL1] showed two absorption bands at $\lambda_1 = 267$ nm and $\lambda_2 = 284$ nm with molar absorption coefficients of 3604 $cm^{-1}\,M^{-1}$ and 5174 $cm^{-1}\,M^{-1}$, respectively, which were attributed to π–π* interactions of the aniline and pyrazolyl moiety. The absorption spectra of cobalt complex **1a** showed 3 bands at almost $\lambda_1 = 262$ nm, $\lambda_2 = 285$ nm, and $\lambda_3 = 608$ nm with molar absorption coefficients of 10155 $cm^{-1}\,M^{-1}$, 15074 $cm^{-1}\,M^{-1}$, and 263 $cm^{-1}\,M^{-1}$, respectively. The absorption band of the pyrazole moiety showed a slight blue shift, due to coordination of the pyrazole to the cobalt metal, while the absorption band of the aniline moiety was very similar to that of the ligand, indicating that the aniline moiety did not affect coordination to the cobalt ion. Moreover, it was concluded from the spectra that the substituents on the aniline moiety (*i.e.* methyl and isopropyl groups) had no effect on λ_{max} or the intensity of the absorption band. The spectra of the complexes showed distinct d–d transitions, which may be assigned to the transition from $^4A_2$ to $^4T_1$ (*p*) [56].

The chemical properties paralleled those of Brookhart and Gibson's N-arylbis(amino)pyridyl Co and Fe complexes, which are known to be pentacoordinated complexes. However, tetrahedral Co complexes **1a**–**4a** were very inert to ethylene polymerization or

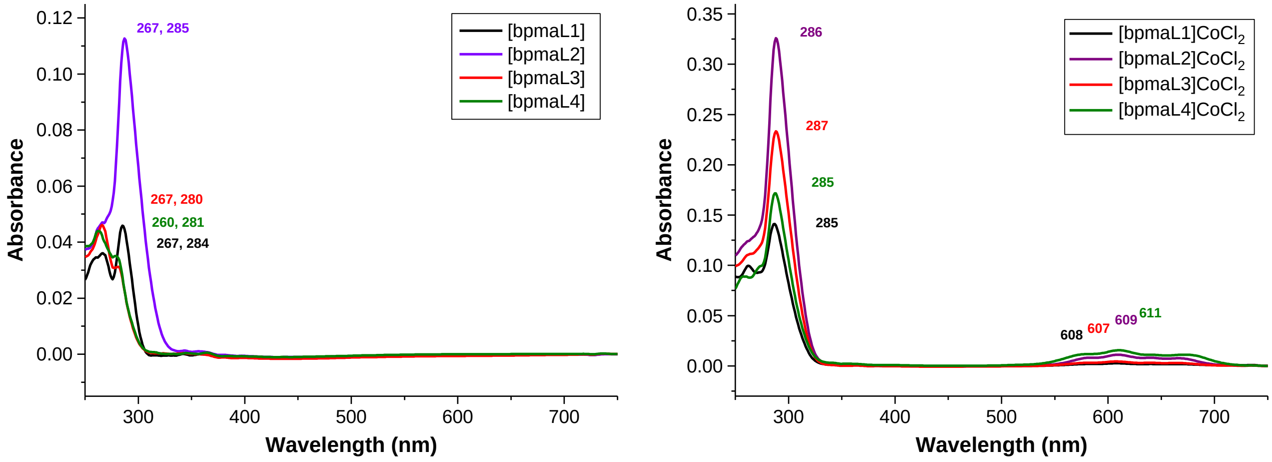


Fig. 2. UV absorption spectra of ligands [bpmaL] and complexes [bpmaL]CoCl$_2$.

ethylene and 1-octene copolymerization even at an ethylene pressure of 30 bar in toluene media at various temperatures, unlike bis(imino) pyridine-Co(II) complex, which shows high catalytic activity for ethylene polymerization and α-olefin oligomerization. To confirm the catalytic inertness for olefin oligomerization, dimerization of 1-octene in toluene was also attempted at 30 °C and 80 °C with no noticeable result. As the tetrahedral benzo[b]thiophen-2-yl-substituted (imino) pyridine-Co(II) complexes [57] were reported to have catalytic activity for oligomerization of ethylene to linear α-olefins, it would not be appropriate to attribute the lack of catalytic activity of precursor complexes **1a**–**4a** to their structural properties. Additionally, no catalytic activity for olefin polymerization was demonstrated indirectly, by the failure of bis-hydrocarbyl substituted Co derivative synthesis. Although alkyl derivatives of the complex cobalt (II) amidodiphosphine halide are known to be stable [58], the synthesis of dihydrocarbyl derivatives of the complex **1a–4a** by changing the polarity of reagents and solvents at various temperatures was unsuccessful. The reactions were either unreactive in less polar environments or decomposed in more polar surroundings. However, all complexes could be activated with MMAO to polymerize methyl methacrylate (MMA) to give PMMA with T_g from 110 °C to 120 °C [59–62]. The results of polymerization, including the influence of temperature and tacticity, are summarized in Table 1 [63]. To confirm the catalytic activity of MMA polymerization, blank polymerization of MMA was performed with starting Co complex, $CoCl_2 \cdot 6H_2O$, and MMAO themselves at the given temperature. The activity of **4a** (1.14×10^6 g/mol-Co·h) was highest, while those of **2a** (8.00×10^5 g/mol-Co·h) and **3a** (6.73×10^5 g/mol-Co·h) were only moderate and that of **1a** (6.17×10^4 g/mol-Co·h) was the lowest at 60 °C. These observations indicated that the bulkier the substituents on the aniline moiety – especially the pyrazole ring – making a crowded environment around the Co metal center, the higher the catalytic activity for MMA polymerization. In contrast, high molecular weight (1.13×10^6 g/mol) and narrow polydispersity index (PDI = 1.75) were achieved with the catalyst **1a** at 60 °C. Moreover, with increasing polymerization temperature, the catalytic activity was markedly increased for the precatalyst complex **4a**. Although syndiotacticity of PMMA, which was calculated by ^{13}C NMR of PMMA in $CDCl_3$ at 50 °C, increased as the polymerization temperature increased when using catalyst **4a**, any syndiotacticity correlation with the structural relationship of complexes was obscure [64]. The highest syndiotacticity of 57% was achieved with catalyst **4a** at $T_p = 50$ °C.

Further detailed analyses of MMA polymerization, including analysis of tacticity, the catalyst structure relationship, and mechanistic aspects of active species are currently underway in our laboratory.

Acknowledgments

Thanks are due to Dr. Yeon Kyu Lee from Instrumental Analysis Center (IAC) facility at Yeungnam University for technical support. This research was supported by Basic Science Research Programs

Table 1
Polymerization of MMA by [bpmaL]CoCl$_2$ in the presence of MMAO.

Entry	Catalyst[a]	Temp.	Yield[b]	Activity[c]	T_g	Tacticity			M_w[d]	M_w/M_n
		(°C)	(g)	(g/mol-Co·h) × 10^5	(°C)	%mm	%mr	%rr	(g/mol) × 10^5	
1	$CoCl_2 \cdot 6H_2O$[e]	60	0.80	0.266	116.54	4.72	8.46	86.82	10.9	1.82
2	MMAO[f]	60	0.42	0.140	119.61	37.20	10.92	51.88	6.78	2.09
3	[bpmaL4]CoCl$_2$	0	0.21	0.07	118.35	93.64	3.81	2.55	0.64	2.41
4	[bpmaL4]CoCl$_2$	25	0.21	0.07	118.13	60.86	39.06	0.08	1.94	2.35
5	[bpmaL4]CoCl$_2$	40	0.67	0.223	115.59	64.63	32.47	2.90	0.90	1.47
6	[bpmaL4]CoCl$_2$	50	1.20	0.400	117.78	39.85	12.16	47.99	13.4	1.62
7	[bpmaL4]CoCl$_2$	60	3.43	1.143	109.91	41.35	2.84	55.81	9.67	2.31
8	[bpmaL3]CoCl$_2$	60	2.02	0.673	118.80	45.93	52.47	1.59	0.40	3.11
9	[bpmaL2]CoCl$_2$	60	2.40	0.800	117.68	47.62	43.11	9.27	10.6	2.32
10	[bpmaL1]CoCl$_2$	60	1.85	0.617	121.41	55.94	27.08	16.98	11.3	1.75

[a] $[Co (II) catalyst]_0 = 15$ μmol, and $[MMA]_0/[MMAO]_0/[Co (II) catalyst]_0 = 3100:500:1$.
[b] Yield defined a mass of dried polymer recovered/mass of monomer used.
[c] Activity is g of PMMA/(mol-Co·h).
[d] Determined by GPC eluted with THF at room temperature by filtration with polystyrene calibration.
[e] It is a blank polymerization in which $CoCl_2 \cdot 6H_2O$ was also activated by MMAO.
[f] It is a blank polymerization which was done solely by MMAO.

through the National Research Foundation of Korea (NRF), funded by the Ministry of the Education, Science, and Technology (Grant No. 2009-0075742).

Appendix A. Supplementary material

The supplementary crystallographic data for **2a** can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.10.019.

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[50] Representative synthesis of N,N-Bis{(1-H-Pyrazole-1-yl)methyl}-2,4,6-trimethylaniline, [bpmaL2]: 2,4,6-trimethylaniline (3.12 mL, 22.2 mmol) was added slowly to (1-H-Pyrazole-1-yl)methanol (4.35 g, 44.3 mmol) solution in 1,2-dichloroethane (150 mL). The reaction solution was dried over $MgSO_4$ after stirring the reaction mixture at 80 °C for 36 hours. The filtrate solvent was removed under reduced pressure to give pale yellow residue, which was recrystalized in hexane as a yellow solid (5.90 g, 90.1%). m.p = 71-72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 ([-$(N_2C_3H_3)_2$-], d, 2 H, J = 0.15 Hz), 7.32 ([-$(N_2C_3H_3)_2$-], d, 2 H, J = 0.15 Hz), 6.82 ([$C_6H_2(CH_3)_3$ N-], s, 2 H), 6.25 ([-$(N_2C_3H_3)_2$-], t, 2 H, J = 0.38 Hz), 5.40 ([-N $(CH_2)_2$-], s, 4 H), 2.23 ([$C_6H_2(CH_3)_3$ N-], s, 3 H), 1.75 ([$C_6H_2(CH_3)_3$ N-], s, 6 H). ^{13}C NMR ($CDCl_3$, 400 MHz) : δ 140.86 ([$C_6H_2(CH_3)_3$ N-], s, 1 C), 139.86 ([-$(N_2C_3H_3)_2$-], d, 2 C, J = 185 Hz), 136.82 ([$C_6H_2(CH_3)_3$ N-], s, 2 C), 136.27 ([$C_6H_2(CH_3)_3$ N-], s, 1 C), 129.54 ([$C_6H_2(CH_3)_3$ N-], d, 2 C, J = 155 Hz), 129.21 ([-$(N_2C_3H_3)_2$-], d, 2 C, J = 186 Hz), 105.95 ([-$(N_2C_3H_3)_2$-], d, 2 C, J = 176 Hz), 68.25 ([-N$(CH_2)_2$], t, 2 C, J = 150 Hz), 20.78 ([$C_6H_2(CH_3)_3$ N-], q, 1 C, J = 126 Hz), 17.66 ([$C_6H_2(CH_3)_3$ N-], q, 2 C, J = 127 Hz). UV-vis (Toluene)/nm 267 (ε/cm^{-1} M^{-1} 4704), 285 (ε/cm^{-1} M^{-1} 12327). Analysis calculated for $C_{17}H_{21}N_5$: C, 69.12; H, 7.17; N, 23.71%. Found: C, 68.83; H, 7.44; N, 23.89%. IR (solid neat/cm^{-1}): 1603 (w), 1509 (m), 1485 (m), 1444 (w), 1420 (w), 1395 (m), 1360 (w), 1349 (w), 1323 (w), 1286 (m), 1260 (m), 1202 (m), 1187 (m), 1152 (s), 1099 (w), 1085 (s), 1042 (s), 966 (m), 954 (m), 943 (w), 917 (w), 891 (w), 867 (w), 851 (w), 790 (m), 753 (s), 732 (s), 701 (m), 652 (m), 616 (s), 589 (s). Representative synthesis of **2a**: A solution of [bpmaL2] (2.00 g, 6.77 mmol) in dried ethanol (50 mL) was added to a solution of $CoCl_2 \cdot 6H_2O$ (1.61 g, 6.77 mmol) in dried ethanol (50 mL) at room temperature. A dark blue solid was precipitated after stirring at room temperature for 24 h. The solid was filtered and washed with fresh cold ethanol (30 mL × 3), followed by washing with hexane (30 mL × 2), to give a sky blue-colored crystalline solid (2.65 g, 92.0%). m.p = 207-208 °C. UV-vis (Toluene)/nm 262 (ε/cm^{-1} M^{-1} 12573), 286 (ε/cm^{-1} M^{-1} 34372), 609 (ε/cm^{-1} M^{-1} 1111). Analysis calculated for $C_{17}H_{21}Cl_2CoN_5$: C, 48.02; H, 4.98; N, 16.47%. Found: C, 47.45; H, 4.95; N, 16.32%. IR (solid neat/cm^{-1}): 1453 (w), 1405 (m), 1321 (w), 1302 (m), 1250 (m), 1206 (w), 1190 (m),1169 (s), 1158 (m), 1100 (w), 1083 (w), 1064 (s), 991 (w), 975 (m), 941 (w), 921 (w), 907 (w), 878 (w), 847 (m), 815 (w), 765 (s), 735 (s), 687 (w), 675 (w), 644 (m), 608 (s), 588 (s), 555 (s).

[51] Crystallographic data for **2a**: C17H21Cl2N5Co, M = 235.64, T = 293(2) K, Wavelength 0.71073 Å, Crystal size 0.40 × 0.35 × 0.20 mm, Triclinic, P$\bar{1}$, a = 12.4569(8)Å, b = 13.2915(8) Å, c = 15.1502(14) Å, U = 2295.6(3) Å3, Z = 8, Dc = 1.364 Mg/m3, μ (λ = 0.71073 Å) = 0.996 mm-1, F(000) = 976, Reflections collected 9229, Independent reflections 8526 [R(int) = 0.0111], Reflections observed (>2σ) 4959, Data Completeness 0.993, Refinement method, Full-matrix least-squares on F@2, Data / restraints / parameters, 8536 / 0 / 258, Goodness-of-fit on F@2, 1.049, Final R indices [I>2σ (I)], R1 = 0.0491, wR2 = 0.1572, R indices (all data), R1 = 0.1040, wR2 = 0.1681. Theta range for data collection 1.64° to 25.55° Index ranges -15 ≤ h ≤ 14, -16 ≤ k ≤ 0, -18 ≤ l ≤ 18, Largest diff. peak and hole 0.595 and -0.358 e. Å-3. An X-ray-quality single crystal was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections (10° < θ < 13°). Intensity data were collected with a θ range of 1.83° to 25.46° in ω/2θ scan mode. Three standard reflections were monitored every 1 h during data collection. The data were corrected for Lorentz polarization effects and decay. Empirical absorption corrections with χ-scans were applied to the data. The structure was solved using the Patterson method and refined by the full-matrix least-squares techniques on F using SHELX-97 and SHELX-97 program packages. The positions of all non-hydrogen atoms were refined geometrically using a riding model correction with fixed isotropic thermal factors. The final cycle of refinement converged with R_1 = 0.1040 and wR_2 = 0.1681.

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[64] Representative polymerization procedure of MMA: Methyl methacrylate (MMA) was extracted with 10% sodium hydroxide, washed with water, dried over magnesium sulfate, and distilled over calcium hydride under reduced pressure before use. To a 100-mL Schlenk flask containing [bpmaL]CoCl2 (5.8 mg, 15.0 μmol) in toluene (1 mL) was added MMAO (modified methylaluminoxane, 6.9 wt% in toluene, 3.25 mL, [MMAO]0/[Catalyst]0 = 500) under a dry argon atmosphere. After the mixture had been stirred at room temperature for 10 min, it was transferred into MMA (5.0 mL, 47.0 mmol, [MMA]0/[Co (II) catalyst]0 = 3100). Then, the reaction flask was immersed in an oil bath at 60 °C and stirred for 2 h. The resulting polymer was precipitated in methanol (400 mL) and HCl (3 mL) was added with stirring for 10 min. The polymer was filtered and washed with methanol (400 mL × 3) to give PMMA, which was vacuum-dried at 60 °C. Additionally, polymerization was examined at different temperatures (0 °C, 25 °C, 40 °C, 50 °C) with **4a**.