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Polymerizations of methyl methacrylate and *rac*-lactide by 4-coordinate cobalt(II) complexes supported by N'-substituted N,N',N-bis((1H-pyrazol-1-yl)methyl)amine derivatives

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Abstract

The novel complexes $[L_nCoCl_2]$ ($L_n = L_A - L_H$), containing the N,N-chelating ligands N,N-bis((1H-pyrazol-1-yl)methyl)aniline (LA), N,N-bis((3,5-dimethyl-1H-pyrazol-1yl)-3,5-dimethylaniline (L_B), N,N-bis((1H-pyrazol-1-yl)methyl)-3,5-dimethylaniline (L_C), *N*,*N*-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-3,5-dimethylaniline N,N-bis((1H- $(\mathbf{L}_{\mathbf{D}}),$ pyrazol-1-yl)methyl)-4-methoxyaniline N,N-bis((3,5-dimethyl-1H-pyrazol-1- $(\mathbf{L}_{\mathbf{E}}),$ vl)methyl)-4-methoxyaniline (L_F), N,N-bis((1H-pyrazol-1-yl)methyl)-4-fluoroaniline (L_G) N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-4-fluoroaniline (L_H), and have been synthesized and structurally characterized. The molecular structures of these Co(II) complexes showed a distorted tetrahedral geometry. No interaction exists between the Namine atom and the Co(II) centre in the $[L_nCoCl_2]$ complexes, thus resulting in the formation of an eight membered chelate ring. [L_DCoCl₂] exhibited the highest catalytic activity $(4.02 \times 10^4 \text{ g})$ PMMA/molCo h) for the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) at 60 °C and yielded poly(methylmethacrylate) (PMMA) with high molecular weight (M_w) (10.5 × 10⁵ g/mol). Syndiotactic enriched PMMA was obtained with T_e in range 123-130 °C. The MMA polymerization activity of the complexes in the current study should not be solely considered as a function of the total steric hindrance from the ligands around the metal center. The dimethyl derivatives $[L_nCoMe_2]$ (L_n = $L_A - L_H$), generated in situ, effectively polymerized rac-lactide (rac-LA) and yielded polylactide (PLA) with good number-average molecular weights and narrower polydispersity indices (PDIs). The electronic density around the metal center in these dimethyl cobalt initiators seemed to enhance the activity, while the stereoselectivity is negatively affected. Thus, the presence or absence of a methyl group in the pyrazole ring moiety influences not only the activity of the Co(II) complexes in the MMA polymerization, but also the stereoselectivity of the Co(II) initiators in the ROP of rac-LA.

Keywords: 4-coordinate cobalt(II) complex, *N*,*N*-bis((1H-pyrazol-1-yl)methyl)aniline, syndiotactic poly(methylmethacrylate), heterotactic polylactide

1. Introduction

Pyrazoles have been extensively studied as N-donor ligands to metals since the first review of pyrazole-derived ligands in 1972 [1]. Pyrazole-based ligands are attractive due to their efficient synthesis and various modifications on the linker unit of two or three pyrazole moieties [2,3]. Since the pioneering work of Driessen in 1982 [4], *N*-substituted pyrazolyl amines based ligands and their transition metal complexes, due to their structural stability, diverse coordination modes and catalytic efficacy, have found profound applicability as supramolecules for metal-organic frames (MOF) [5], catalysts for organic transformations [6], biological agents [7], cancer sensors and as hydrolysis and oxidation agents [8].

More recently, *N*-substituted pyrazolyl amines ligated to a variety of late transition metals, such as Ru(II), Pt(II), Pd(II), Rh(I), Co(II) and Zn(II), have revealed various useful catalytic properties in olefin [9] and methyl methacrylate (MMA) polymerizations [10]. Early transition metal complexes generally cannot tolerate polar functional groups owing to the highly electron-deficient nature of the metal center. To overcome this drawback, late transition metal complexes were developed which proved to be better candidates for polymerization of a polar monomer in controlled fashion, due to their less oxophilic nature [11,12].

As a part of our ongoing research towards stereoselective MMA and *rac*-lactide (*rac*-LA) polymerization, we have recently investigated a variety of late transition metal complexes, including Co(II), Zn(II), Pd(II), Cd(II) and Cu(II) with *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline and its derivatives, which exhibit diverse coordination modes with high

activities and mediocre stereoselectivities [13,14]. These results and the potential merit of *N*-substituted pyrazolyl amine based ligands, that show fine tuning of the reactivity of the metal centre to which they are bound, prompted us to explore the complexing properties of *N*,*N'*,*N*-bis((1H-pyrazol-1-yl)methyl)amine ligands to the Co(II) centre and its catalytic capabilities. Further, the influence of substituents on the aniline and pyrazole moieties on the catalytic activity in both methyl methacrylate and *rac*-LA polymerization is also discussed.

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2. Experimental

2.1. Materials

1H-pyrazole, 3,5-dimethylpyrazole, para-formaldehyde, aniline, 3,5-dimethylaniline, p-anisidine, 4-fluoroaniline, magnesium sulfate (MgSO₄), molecular sieve (0.4 nm), [CoCl₂·6H₂O] and methyl methacrylate (MMA) were purchased from Sigma-Aldrich (St. Louis, MO) and anhydrous solvents, such as CH₂Cl₂, anhydrous EtOH, acetonitrile, hexane, diethyl ether (Et₂O) and DMF, were purchased from Aldrich and Merck (Darmstadt, Germany) and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation (Tokyo, Japan) as 5.90 % aluminum (by weight) in a toluene solution and used without further purification.

2.2. Physical measurements

Elemental analyses (C, H, N) of the synthesized ligands and their corresponding metal complexes were performed on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ¹H (operating at 500 MHz) and ¹³C (operating at 125 MHz) NMR spectra were recorded on an Avance Digital 500 NMR spectrometer (Bruker, Billerica, MA); chemical shifts were recorded in ppm units (δ) relative to SiMe₄ as an internal standard. Infrared (IR)

spectra were recorded on a Bruker FT/IR-Alpha spectrophotometer (neat solid or neat liquid) and the data were reported in reciprocal centimeters (cm⁻¹). The molecular weights and molecular weight distributions of the obtained poly(methyl methacrylate) (PMMA) were determined using gel permeation chromatography (GPC) (THF, Alliance e2695; Waters Corp., Milford, MA). The glass transition temperature (T_g) was determined using a thermal JUSCE analyzer (Q2000; TA Instruments, New Castle, DE).

2.3. Synthetic procedures

2.3.1. Preparation of the ligands

1H-pyrazolyl-1-methanol and 3,5-dimethyl-1H-pyrazolyl-1-methanol as starting materials were prepared according to the reported method [15]. The syntheses of the ligands L_A , L_B , L_C , L_E and L_G were carried out as reported previously [13a, 13d, 14c, 16c].

2.3.1.1. N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-3,5-dimethylaniline (L_D)

A CH₂Cl₂ solution (50.0 mL) of 3,5-dimethylaniline (2.00 mL, 16.0 mmol) and molecular sieves (20.0 g, 0.4 nm) were slowly added to a CH₂Cl₂ (50.0 mL) solution of 3,5dimethylpyrazole-1-methanol (4.05 g, 32.1 mmol). The reaction solution was stirred at ambient temperature for 120 h and the molecular sieves were filtered off. The reaction solvent was removed under reduced pressure to give a yellow solid, which was recrystallized in CH₂Cl₂ at -78 °C (3.80 g, 70.3 %). Analysis calculated for C₂₀H₂₇N₅ (%): C, 71.2; H, 8.06; N, 20.8. Found: C, 71.5; H, 8.14; N, 20.3. ¹H NMR (CDCl₃, 500 MHz) δ, ppm: 6.65 (s, 2H, o-NC₆H₃(CH₃)₂-), 6.62 (s, 1H, p-NC₆H₃(CH₃)₂-), 5.74 (s, 2H, -N=C(CH₃)-CH=C(CH₃)-N-), 5.47 (s, 4H, -N-CH₂-N-), 2.23 (s, 6H, -NC₆H₃(CH₃)₂), 2.21 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-), 2.06 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-). ¹³C-NMR (CDCl₃, 125 MHz) δ, ppm: 147.62

(s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 146.39 (s, 1C, *ipso*-NC₆H₃(CH₃)₂-), 139.47 (s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 138.50 (s, 2C, *m*-NC₆H₃(CH₃)₂-), 124.35 (d, 1C, J = 155 Hz, *p*-NC₆H₃(CH₃)₂-), 118.47 (d, 2C, J = 156 Hz, *o*-NC₆H₃(CH₃)₂-), 105.62 (d, 2C, J = 172 Hz, *-*N=C(CH₃)-CH=C(CH₃)-N-), 64.21 (t, 2C, J = 151 Hz, -N-CH₂-N-), 21.39 (q, 2C, J = 126 Hz, -NC₆H₃(CH₃)₂-), 13.55 (q, 2C, J = 127 Hz, -N=C(CH₃)-CH=C(CH₃)-N-), 10.94 (q, 2C, J = 129 Hz, -N=C(CH₃)-CH=C(CH₃)-N-). IR (solid neat; cm⁻¹): 2996 (w), 2977 (w), 2912 (w), 1602 (m), 1549 (m), 1451 (m), 1336 (m), 1279 (m), 1238 (m), 1196 (s), 1028 (m), 960 (m), 885 (m), 812 (m), 773 (s), 685 (w), 623 (w).

2.3.1.2. N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-4-methoxylaniline (L_F)

An analogous method as described for L_D was used to synthesize L_F , except utilizing *p*-anisidine (2.00 g, 16.2 mmol), molecular sieve (20.0 g, 0.4 nm) and 3,5-dimethylpyrazole-1-methanol (4.10 g, 32.5 mmol) in CH₂Cl₂ (50.0 mL). The final ligand was obtained as a brown solid (4.33 g, 78.6 %). Analysis calculated for $C_{19}H_{25}N_5O$ (%): C, 67.2; H, 7.42; N, 20.6. Found: C, 67.1; H, 7.47; N, 20.1. ¹H NMR (CDCl₃, 500 MHz) δ , ppm: 6.83 (d, 2H, *J* = 8.9 Hz, *p*-NC₆H₄-OCH₃), 6.74 (d, 2H, *J* = 8.8 Hz, *o*-NC₆H₄-OCH₃), 5.71 (s, 2H, -N=C(CH₃)-CH=C(CH₃)-N-), 5.38 (s, 4H, -N-CH₂-N-), 3.74 (s, 3H, -NC₆H₄-OCH₃), 2.20 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-), 1.93 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-). ¹³C NMR (CDCl₃, 125 MHz) δ , ppm: 156.60 (s, 1C, *p*-NC₆H₄-OCH₃), 147.70 (s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 139.65 (s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 139.35 (s, 1C, *ipso*-NC₆H₄-OCH₃), 125.45 (d, 2C, *J* = 159 Hz, *o*-NC₆H₄-OCH₃), 114.27 (d, 2C, *J* = 160 Hz, *m*-NC₆H₄-OCH₃), 105.47 (d, 2C, *J* = 173 Hz, -N=C(CH₃)-CH=C(CH₃)-N-), 65.72 (t, 2C, *J* = 151 Hz, -N-CH₂-N-), 55.33 (q, 1C, *J* = 143 Hz, *o*-NC₆H₄-OCH₃), 13.58 (q, 2C, *J* = 127 Hz, -N=C(CH₃)-CH=C(CH₃)-N-), 10.78 (q, 2C, *J* = 128 Hz, -N=C(CH₃)-CH=C(CH₃)-N-). IR (solid neat; cm⁻¹): 2970 (w), 2918 (w), 2836 (w), 1553 (m), 1511 (s), 1419 (m), 1286 (w), 1242 (s), 1179 (s), 1116 (m), 1030 (s),

932 (w), 776 (s), 689 (w), 623 (w), 571 (m).

2.3.1.3. N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-4-fluoroaniline (L_H)

An analogous method as described for L_D was used to synthesize L_H , except utilizing 4-fluoroaniline (2.00 mL, 21.1 mmol) and 3,5-dimethylpyrazole-1-methanol (5.33 g, 42.2 mmol) in CH₂Cl₂. The final product was obtained as a white solid by recrystallization from hexane (5.86 g, 86.8 %). Analysis calculated for C₁₈H₂₂N₃F (%): C, 66.0; H, 6.77; N, 21.4. Found: C, 65.8; H, 6.89; N, 21.8. ¹H NMR (DMSO, 500 MHz) δ , ppm: 6.93 (s, 2H, *p*-NC₆H₄-F), 6.91 (d, 2H, *J* = 2.0 Hz, *o*-NC₆H₄-F), 5.74 (s, 2H, -N=C(CH₃)-CH=C(CH₃)-N-), 5.41 (s, 4H, -N-CH₂-N), 2.20 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-), 1.99 (s, 6H, -N=C(CH₃)-CH=C(CH₃)-N-). ¹³C-NMR (DMSO, 125 MHz) δ , ppm: 160.41 158.48 (s, 2C, *p*-NC₆H₄-F), 147.89 (s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 142.44 (s, 2C, *ipso*-NC₆H₄-F), 139.54 (s, 2C, -N=C(CH₃)-CH=C(CH₃)-N-), 124.57 (d, 2C, *J* = 161 Hz, *m*-NC₆H₄-F), 115.73 (d, 1C, *J* = 163 Hz, *o*-NC₆H₄-F), 105.68 (d, 2C, *J* = 172 Hz, -N=C(CH₃)-CH=C(CH₃)-N-), 10.82 (q, 2C, *J* = 128 Hz, -N=C(CH₃)-CH=C(CH₃)-N-). IR (solid neat; cm⁻¹): 2975 (w), 2950 (w), 2915 (w), 1550 (m), 1512 (m), 1454 (m), 1360 (m), 1252 (m), 1191 (s), 1021 (m), 951 (m), 813 (s), 773 (s), 713 (w), 683 (w), 621 (w).

2.3.2. Preparation of the Co(II) complexes

The synthesis of complexes $[L_ACoCl_2]$ and $[L_BCoCl_2]$ was carried out as reported previously [13b,16d].

2.3.2.1. [N,N-bis((1H-pyrazol-1-yl)methyl)-3,5-dimethylaniline]cobalt(II) chloride ([L_cCoCl₂])

A solution of L_C (1.00 g, 3.55 mmol) in anhydrous EtOH (15.0 mL) was slowly added to solution of [CoCl₂·6H₂O] (0.850 g, 3.55 mmol) in anhydrous EtOH (15.0 mL). Precipitation of a blue solid occurred while stirring at 25 °C for 24 h. The blue powder was filtered and washed with cold EtOH (20.0 mL × 3), followed by washing with hexane (20.0 mL × 3) to get the final product (1.31 g, 89.7 %). Analysis calculated for C₁₆H₁₉Cl₂N₅Co (%): C, 46.7; H, 4.66; N, 17.0. Found: C, 46.6; H, 4.63; N, 17.2. IR (solid neat; cm⁻¹): 3495 (w), 3102 (w), 1593 (w), 1511 (w), 1459 (w), 1404 (m), 1266 (m), 1148 (m), 1065 (s), 991 (w), 850 (w), 819 (w), 783 (s), 702 (m), 611 (m).

2.3.2.2. [N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-3,5-dimethylaniline]cobalt(II) chloride ([L_DCoCl₂])

An analogous method as described for [L_CCoCl_2] was used, except utilizing L_D (1.00 g, 2.96 mmol) and [$CoCl_2 \cdot 6H_2O$] (0.710 g, 2.96 mmol) in anhydrous EtOH, giving a blue solid as the final product (0.770 g, 55.8 %). Analysis calculated for $C_{20}H_{27}Cl_2N_5Co$ (%): C, 51.4; H, 5.82, N, 15.0. Found: C, 51.7; H, 5.84; N, 14.7. IR (solid neat; cm⁻¹): 2915 (w), 1592 (w), 1554 (m), 1463 (m), 1420 (w), 1374 (m), 1282 (m), 1227 (w), 1157 (m), 1121 (m), 1046 (m), 957 (m), 850 (m), 797 (s), 726 (w), 694 (s).

2.3.3.3 [N,N-bis((1H-pyrazol-1-yl)methyl)-4-methoxyaniline[cobalt(II) chloride ([L_ECoCl_2]) An analogous method as described for [L_CCoCl_2] was used, except utilizing L_E (1.00 g, 3.53 mmol) and [CoCl₂·6H₂O] (0.84 g, 3.53 mmol) in anhydrous EtOH, giving a blue powder as the final product (1.25 g, 85.9 %). Analysis calculated for C₁₅H₁₇Cl₂N₅OCo (%): C, 43.6; H, 4.15; N, 17.0. Found: C, 43.9; H, 4.15; N, 16.6. IR (solid neat; cm⁻¹): 3111 (w), 1609 (w), 1513 (s), 1463 (m), 1408 (m), 1312 (m), 1283 (m), 1244 (m), 1190 (s), 1166 (m), 1098 (s), 1028 (m), 998 (m), 958 (m), 915 (m), 841 (m), 809 (w), 772 (s), 741 (m), 693 (m), 642

(w), 611 (s), 574(s)

2.3.3.4. [N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-4-methoxyanilin] cobalt(II) chloride ([L_FCoCl₂])

An analogous method as described for [L_CCoCl₂] was used, except utilizing L_F (1.00 g, 2.95 mmol) and [CoCl₂·6H₂O] (0.700 g, 2.95 mmol) in anhydrous EtOH, giving a blue crystalline solid as the final product (1.07 g, 82.5 %). Analysis calculated for $C_{19}H_{25}Cl_2N_5OCo$ (%): C, 48.6; H, 5.37; N, 14.9. Found: C, 48.2; H, 5.36; N, 15.0. IR (solid neat; cm⁻¹): 2995 (w), 2924 (w), 2829 (w), 1606 (w), 1585 (w), 1554 (m), 1510 (m), 1463 (m), 1423 (m), 1376 (m), 1350 (m), 1299 (m), 1243 (s), 1206 (m), 1170 (m), 1118 (m), 1035 (s), 935 (m), 835 (m), 798 (s), 742 (m), 702 (s), 632 (m), 567 (s)

2.3.3.5. [N,N-bis((1H-pyrazol-1-yl)methyl)-4-fluoroaniline]cobalt(II) chloride ([L_GCoCl_2])

An analogous method as described for [L_CCoCl_2] was used, except utilizing L_G (1.00 g, 3.69 mmol) and [$CoCl_2 \cdot 6H_2O$] (0.880 g, 3.69 mmol) in anhydrous EtOH, giving a blue powder as the final product (1.31 g, 88.4 %). Analysis calculated for $C_{14}H_{14}Cl_2N_5FCo$ (%): C, 41.9; H, 3.52; N, 17.5. Found: C, 41.9; H, 3.59; N, 17.6. IR (solid neat; cm⁻¹): 3127 (w), 2358 (w), 1638 (w), 1611 (w), 1512 (m), 1456 (m), 1401 (w), 1316 (m), 1282 (m), 1226 (s), 1160 (m), 1101 (m), 1066 (s), 1014 (w), 991 (m), 923 (w), 903 (w), 831 (s), 761 (s), 717 (m), 644 (m), 606 (s), 564 (m)

2.3.3.6. [N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)-4-fluoroaniline]cobalt(II) chloride ([L_HCoCl₂])

An analogous method as described for $[L_C CoCl_2]$ was used, except utilizing L_H (1.00 g, 3.05 mmol) and $[CoCl_2 \cdot 6H_2O]$ (0.730 g, 3.05 mmol) in anhydrous EtOH, to get the final

product (1.30 g, 92.9 %). Analysis calculated for $C_{18}H_{22}Cl_2N_5FCo$, CH_2Cl_2 (%): C, 42.1; H, 4.46; N, 12.9. Found: C, 42.1; H, 4.50; N, 13.4. IR (solid neat; cm⁻¹): 3008 (w), 2865 (w), 1552 (m), 1508 (s), 1458 (m), 1383 (m), 1344 (m), 1304 (m), 1255 (m), 1230 (m), 1210 (m), 1175 (s), 1160 (m), 1120 (s), 1045 (m), 1010 (m), 987 (m), 936 (m), 841 (m), 821 (s), 803 (s), 749 (m), 717 (m), 688 (m), 631 (m).

C

2.4. Catalytic activities for MMA polymerization

The methyl methacrylate (MMA) was extracted with 10% NaOH, washed with water, dried over MgSO₄ and distilled over CaH₂ under reduced pressure before use. In a Schenk flask, the synthesized complex (15.0 µmol, 5.70 mg for [L_ACoCl₂], 6.60 mg for [L_BCoCl₂], 6.20 mg for [L_CCoCl₂], 7.00 mg for [L_DCoCl₂], 6.20 mg for [L_ECoCl₂], 7.00 mg for [L_FCoCl₂], 6.00 mg for [L_GCoCl₂] and 8.20 mg for [L_HCoCl₂]) was dissolved in dried toluene (10.0 mL), followed by the addition of MMAO (5.90 wt% in toluene 3.80 mL, 7.50 mmol and $[MMAO]_0/[catalyst]_0=500)$ as a co-catalyst. The solution was mixed by stirring for 20 min at a temperature of 60 °C. MMA (5.00 mL, 47.1 mmol and [MMA]₀/[catalyst]₀= 3100) was slowly added to the above reaction solution and stirred for 2 h at 60 °C to obtain a viscous solution. Methanol (2.00 mL) was added to terminate the polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL) to precipitate PMMA from the toluene solution and HCl (5.00 mL, 35.0 %) was injected to remove the remaining co-catalyst (MMAO). White PMMA was obtained by filtration, washed with MeOH (250 mL \times 2) and dried under vacuum at 60 °C for 12 h. The polymers were isolated as white solids and characterized by GPC in THF using standard polystyrene as the reference. Three polymer trials were conducted to confirm the activities of the synthesized complexes at 60 °C. The temperature of the polymerization was optimized by previous work between 0, 25, 50 and 60

°C [17].

2.5. Typical procedure for ROP of rac-lactide

In a general polymerization reaction for *rac*-LA with the dimethyl cobalt initiators, the catalyst species were generated as follows. The dichloro cobalt complexes (0.500 mmol) and dried THF (7.40 mL) were added to a 100 mL Schlenk flask under an argon atmosphere. To this solution MeLi (1.00 mmol, 0.63 mL of a 1.6 M solution in Et₂O) was added dropwise at -78 °C to generate the *in situ* dimethyl Co(II) species, [L_nCOMe₂] (L_n = L_A – L_H). After being stirred for 2 h at room temperature, the resulting THF solution of the dimethyl Co(II) complexes, i.e. [L_nCOMe₂] (Ln = L_A – L_H), was used as an initiator for the ROP of *rac*-LA. The general procedure for the polymerization reaction was as follows. A Schlenk flask (100 mL) was charged with *rac*-LA (0.901 g, 6.25 mmol) under an argon atmosphere and 5.00 mL of dried CH₂Cl₂ was added. The polymerization was initiated by the slow addition of the catalyst solution (1.00 mL, 0.0625 mmol) *via* a syringe under argon at -50 °C. The reaction mixture was stirred for the allotted time and the polymerisation reactions were quenched using H₂O (1.00 mL). Hexane (2.00 mL) was then added to precipitate the polymer. ¹H NMR (CDCl₃, 400 MHz) for the obtained polymer, δ , ppm: 5.13-5.20 (m, 1H), 1.51-1.63 (m, 3H).

2.6. X-ray crystallographic studies

Crystals suitable for an X-ray study of the synthesized Co(II) complexes were obtained by layering hexane on a CH₂Cl₂ solution or by Et₂O diffusion into a DMF solution. X-ray quality single crystals of some cobalt complexes were coated with paratone-*N* oil and the diffraction data were measured at 100(2) K with synchrotron radiation ($\lambda = 0.610$ Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator

(DCM) at the Pohang Accelerator Laboratory, Korea. The BL2DSMDC program was used for data collection (detector distance is 63 mm, omega scan; $\Delta \omega = 1^{\circ}$, exposure time is 1 s per frame) and HKL3000sm (Ver. 703r) was used for cell refinement, reduction and absorption corrections. The structures were solved by direct methods and refined by full-matrix leastsquares refinement using the SHELXS-2014 and SHELXL-2016 computer programs.

The crystals of the other cobalt complexes were picked up with paratone oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation source under a nitrogen cold stream (200(2) K). Data collection and integration were performed with SMART and SAINT-Plus software packages [18]. Multi-scan absorption corrections based on equivalent reflections were applied by SADABS [19]. The structures were solved by direct methods and refined using a full-matrix least-squares method on F² using SHELXTL [20]. Structural refinement and crystallographic data for [L_nCoCl₂] (L_n= L_C – L_H) are presented in Table 1.

3. Results and discussion

3.1. Synthesis and chemical properties

The ligands were obtained in a single step from the substituted aniline and 1Hpyrazolyl-1-methanol or 3,5-dimethylpyrazol-1-methanol in CH₂Cl₂ or MeCN, as described in the literature [13,14c,16c]. The corresponding [L_nCoCl_2] ($L_n = L_A - L_H$) complexes were obtained (approximately 82 ~ 93 % yields) by direct ligation of the metal starting materials with the ligands in a 1:1 ratio in dried EtOH (Scheme 1). The synthesized complexes [L_nCoCl_2] ($L_n = L_A - L_H$) were characterized using IR spectra and elemental analysis data. Owing to the paramagnetic nature of the Co(II) complexes, we were unable to study the synthesized complexes *via* NMR spectroscopy. However, a comparison of the IR spectra of

the ligands with those of the complexes was performed in the C–H stretching region. For instance, characteristic C–H peaks for the L_D , L_F and L_G free ligands in the IR spectra were observed at 2996, 2970 and 2975 cm⁻¹, while the C–H stretching bands appeared at 3019, 3115 and 3016 cm⁻¹, respectively in their corresponding Co(II) complexes. All the synthesized complexes were stable towards oxygen and moisture.

3.2. Description of the molecular structures

Crystals suitable for the X-ray study of the Co(II) complexes were obtained by layering hexane on CH₂Cl₂ solutions of the cobalt complexes. The molecular structures of $[L_nCoCl_2]$ $(L_n = L_C - L_H)$, with 30 % probability level, are illustrated in Figs. 2-7, respectively. Selected bond lengths and angles are described in Table 2.

Among the synthesized Co(II) complexes, $[\mathbf{L}_{C}\mathbf{CoCl_2}]$, $[\mathbf{L}_{P}\mathbf{CoCl_2}]$, $[\mathbf{L}_{F}\mathbf{CoCl_2}]$, and $[\mathbf{L}_{H}\mathbf{CoCl_2}]$ crystallized in the monoclinic system with *Cc*, *P2*₁/*c* and *P2*₁/*n* space groups. $[\mathbf{L}_{E}\mathbf{CoCl_2}]$ and $[\mathbf{L}_{G}\mathbf{CoCl_2}]$ crystallized in the triclinic system with the *P-1* space group. The central cobalt atom was bonded to the *N'*-aromatic group substituted *N*,*N'*,*N*-bis((1H-pyrazol-1-yl)methyl)amine framework *via* the N atoms of the pyrazole moiety in a bidentate binding mode, resulting in a distorted tetrahedral geometry. No interaction between the N_{amine} atom and the cobalt metal center exists in the 4-coordinate $[\mathbf{L}_{n}\mathbf{CoCl_2}]$ ($\mathbf{L}_{n} = \mathbf{L}_{C} - \mathbf{L}_{H}$) complexes, resulting in an eight membered chelate ring [13b,14c], which is in contrast to our previously reported Co(II) complexes with a similar ligand architecture (*N'-non* aromatic group substituted *N*,*N'*,*N*-bis((1H-pyrazol-1-yl)methyl)amine framework), where a 5-coordinate distorted trigonal bipyramid geometry resulted *via* an N_{amine} atom and cobalt centre coordinative interaction [14b,14c,21].

The average Co-N_{pyrazole} bond lengths in [L_nCoCl₂] (L_n = L_C - L_H) lie in the expected range, 2.000(6)-2.0421(1) Å, as found in similar reported complexes [11a,b,12c]. It is

observed that the Co-N_{pyrazole} bond length in $[L_DCoCl_2]$, $[L_FCoCl_2]$ and $[L_HCoCl_2]$ is about 0.012-0.038 Å longer compared to those in $[L_CCoCl_2]$, $[L_ECoCl_2]$ and $[L_GCoCl_2]$. The difference in the steric environment provided by two methyl groups of the pyrazole ring might be responsible for this increase in the bond lengths. Similarly, all the Co-Cl bond lengths lie in the accepted range, i.e. 2.229(5)-2.251(1) Å, of the reported Co(II) pyrazole amine complexes [11b].

The Cl_{terminal}-Co-Cl_{terminal} and N_{pyrazole}-Co-N_{pyrazole} angles of [L_nCoCl₂] (L_n = L_C - L_H) are in the range 108.4(7)-117.1(2) and 107.8(2)-114.7(2)°, respectively. The N_{pyrazole}-Co-N_{pyrazole} angles in the [L_CCoCl₂], [L_DCoCl₂], [L_FCoCl₂], [L_GCoCl₂] and [L_HCoCl₂] complexes show almost ideal tetrahedral angles (109.0°), although those of the $[L_E CoCl_2]$ complex are approximately 5° larger (Table 2). A useful index for tetrahedral geometries of 4-coordinate complexes is the τ_4 value (for a perfect T_d , τ_4 is given 1.00 and 0 for a perfect square plane, D_{4h} [22a], which is calculated by R. P. Houser et al. who modified the equation of τ_5 (for the geometry of 5-coordinate complexes) and is introduced by A.W. Addition, J. Reedijk and coworkers [22b]. In addition, the THCDA/100 index suggests useful analysis of the tetrahedral and the trigonal pyramidal extremes [22c,d,e]. For instance, a value of 1.00 for the THC_{DA}/100 index represents a perfect tetrahedral geometry, while a value of 0 is for a perfect trigonal pyramidal geometry. Further, the FCGP/100 index is applied to the tetrahedral geometry of main group complexes [22f]. Table 3 shows the 4-coordinate geometry indices for the Co(II) complexes with N'-substituted N,N',N-bis((1H-pyrazol-1-yl)methyl)amine derivatives. The τ_4 values of all the [L_nCoCl₂] (L_n = L_A - L_H) complexes, except the complex [L_GCoCl₂], fall in the range 0.922 to 0.945, indicated a distortion of the tetrahedral geometry. Note, the τ_4 values of 5-coordinated trigonal bipyramidal Co(II) complexes with a similar ligand system are between 0.833 and 0.891. These Co(II) complexes have an interaction between the nitrogen atom of the amine moiety and the cobalt metal center (the bond lengths

are from 2.522(6) to 2.382(2) Å, indicating a solid covalent bond) [14,21]. The calculated bond distance between the nitrogen atom of the amine moiety and the cobalt metal center in [L_GCoCl₂] is 2.653 Å and obviously there is a significant interaction to give a τ_4 value of a trigonal bipyramidal geometry, 0.871. In contrast, the calculated bond distances between the nitrogen atom of the amine moiety and the cobalt metal center in [L_nCoCl₂] (L_n = L_A – L_F and L_H) were from 3.909 to 3.298 Å, indicating that there no interaction between these atoms, thus giving a distorted tetrahedral geometry around the metal center. Another interesting feature is that the complexes with methyl substituents at the pyrazolyl moiety, [L_nCoCl₂] (L_n= L_B, L_D, L_F and L_H), are found to have more distorted tetrahedrality than the complexes with *non*-methyl substituents at the pyrazolyl moiety, [L_nCoCl₂] (L_n= L_A, L_C, L_E and L_G), as judged by the τ_4 values.

To find the effect of *N*'-substitution on the tetrahedrality of the complexes, we have calculated the tilt angle between the *N*-aromatic ring on the amine moiety and the plane of the *N*,*N*-bispyrazole ring. For example, the tilt angle between the *N*'-aromatic ring on the amine moiety defined by the plane of yz and the xz plane of the *N*,*N*-bis pyrazole ring (containing the metallacyclic ring residue) in [L_DCoCl₂] and [L_HCoCl₂] was perpendicular (90°). It is found that the complexes with methyl substituents at the pyrazolyl moiety, [L_nCoCl₂] (L_n= L_B, L_D, L_F and L_H; tilt angles 9, 0, 8 and 0°, respectively), are found to have less tilt angles than the complexes with *non*-methyl substituents at the pyrazolyl moiety, [L_nCoCl₂] (L_n= L_A, L_C, L_E and L_G; tilt angles 43, 38, 15 and 30°, respectively). Similarly, it has been found that the orientation of the phenyl moiety is slightly affected by the substituents of the pyrazolyl rings, as exhibited by our previously reported complexes where the orientation of the cyclopentyl unit with respect to the plane of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole ring is slightly affected by the substituents of the pyrazole moieties [21]. The orientation of the plane of the pyrazole ring is slightly affected by the pyrazole is slightly affected by the pyrazole is slightly affected by the pyrazole is tilted towards one side with respect to the plane of the pyrazole ring is

the methyl substituted pyrazole rings in [L_nCoCl_2] ($L_n = L_A - L_H$) by 0-90°. However, the observed angles are not significantly affected by the substituents attached to the *N*'-aromatic phenyl ring (-H, -CH₃, -OCH₃, -F). Further, the tilt angle between the *N*'-aromatic ring on the amine moiety and the plane of the *N*,*N*-bispyrazole ring was not significantly related to the τ_4 values of the complexes.

3.3. Methyl methacrylate (MMA) polymerization

Isotactic PMMA, produced through radical processes commercially, has a T_g value around 65 °C [23]. Thus, non-radical mediated polymerization of MMA by coordination complexes is of recent interest to achieve PMMA with a high T_g value and hence improved properties. As a part of the ongoing research in our group, targeted towards the synthesis of pyrazolyl based initiators in stereoselective polymerization of MMA, the catalytic capabilities of the *N*,*N'*,*N*-bis((1H-pyrazol-1-yl)methyl)amine based Co(II) complexes were tested for polymerization in the presence of modified methylaluminoxane (MMAO) at 60 °C. All the synthesized complexes were found to be efficient initiators, yielding PMMA with glass transition temperatures (T_g) of 127-135 °C [24-26]. The polymers were isolated as white polymeric materials and characterized by GPC in THF using standard polystyrene as a reference. The resulting polymer characteristics are summarized in Table 4.

To see the ligand effect on the metal complexes, a blank polymerization of methyl methacrylate (MMA) was processed with the starting material $[CoCl_2]/MMAO$ or solely with MMAO under the same experimental conditions. It is evident from the polymerization data (Table 4) that $[CoCl_2]$ exhibited slightly higher activity compared to $[L_ACoCl_2]$ and $[L_GCoCl_2]$, yielding PMMA with comparable molecular weights. However, the remaining Co(II) complexes showed not only better activities, but also exhibited better

stereoselectivities and yielded PMMA with high molecular weights compared to the starting material [CoCl₂]. The mediocre activities of our current system can be attributed to their low solubility in the polymerization media. It is apparent that the complexes with methyl substituents at the pyrazolyl moiety are found to have more enhanced solubility than the complexes with the *non*-methyl substituents at the pyrazolyl moiety in the organic solvents. Thus, [L_nCoCl₂] (L_n= L_B, L_D, L_F and L_H), which have 3,5-dimethyl substituents at the pyrazolyl residue, gave better activity for the polymerization of methylmethacrylate than the corresponding [L_nCoCl₂] complexes (L_n= L_A, L_C, L_E and L_G) having a 1-H-pyrazole moiety (Table 4).

Similarly, no appreciable amount of PMMA resulted with the dichloro Co(II) complexes in the absence of MMAO. In the case of using $[L_nCoCl_2]$ ($L_n = L_A - L_H$) for MMA polymerization, $[L_DCoCl_2]$ exhibited the highest catalytic activity (4.02 × 10⁴ g/mol Co h) with high molecular weights (10.5 × 10⁵ g/mol).

In a previous study, the higher activity was attributed to steric hindrance provided by the methyl substituents attached to the pyrazole moiety [14,16c]. The catalytic activities of initiators bearing methyl substituents attached to the pyrazole moiety exhibited higher activities compared to their counterparts without methyl substituents on the pyrazole moiety (Table 4). Thus, this enhance activity of the Co(II) complexes containing two methyl substituents on the pyrazole ring might be due to greater electron density and local steric hindrances around the metal center, as shown previously by the *N*,*N*-bis(1H-pyrazolyl-1methyl)aniline Co(II) system [11a]. Further, the catalytic activity can also be enhanced with better solubility of the initiators with methyl substituents on the phenyl as well the pyrazolyl ring in polymerization. These observations are in contrast to the previous report [21b] where the bulky substituents at the pyrazole moiety negatively affect the MMA activation, probably the steric bulk around the metal center depresses the monomer approach to the metal sites.

Interestingly, the aniline substituents have no significant influence on the MMA polymerization in this [L_nCoCl₂] ($L_n = L_A - L_H$) system, in which is difficult to observe the steric and electronic effects by N'-aromatic substitution (aniline moiety). Thus, to evaluate the total steric hindrance of the bulky ligands towards metal center, it can be predicted and quantitatively calculated by comparison through a topographic steric map of the Co(II) complexes by use of the program "SambVca" [27]. Figure 7 shows a ball and stick model, space-filling mode and a topographic steric map of $[L_nCoCl_2]$ ($L_n = L_A - L_H$) for presenting the bulky ligands. Note that steric hindrance of $[L_nCoCl_2]$ ($L_n = L_B$, L_D , L_F and L_H) which have 3,5-dimethyl substituents at the pyrazolyl residue is bigger than that of the corresponding $[L_nCoCl_2]$ ($L_n = L_A$, L_C , L_E and L_G) complexes, having a 1-H-pyrazole moiety, by judging the buried volume % of the ligands in Fig. 7. Moreover, the more sterically hindered [L_nCoCl_2] ($L_n = L_B$, L_D , L_F and L_H) has more open reaction space for the monomer MMA to approach the metal center in the directions of north and south in the steric map than the less sterically hindered [L_nCoCl_2] ($L_n = L_B$, L_D , L_F and L_H). Thus, it may be reasonable to interpret that the more sterically hindered [L_nCoCl_2] ($L_n = L_B$, L_D , L_F and L_H), which has 3,5dimethyl substituents at the pyrazolyl residue, gives higher activity for the polymerization of methylmethacrylate than the corresponding the less sterically hindered $[L_nCoCl_2]$ ($L_n = L_A$, L_C, L_E and L_G), having the 1-H-pyrazole moiety. However, only considering the total steric factor from the topographic steric map of $[L_nCoCl_2]$ ($L_n = L_A - L_H$), no relationship was found between the total steric factor of ligands and the activity for the MMA polymerization of the Co(II) complexes. Finally, both the steric and electronic effects of the catalysts are carefully considered to correlate the polymerization activity and the structure of the complexes. Further, the solubility of the complexes or active species in the polymerization solvent also substantially influences the polymerization activity.

The behavior of the Co(II) system under investigation as compared with that of the

previously reported *N*,*N*-bis{(1-pyrazolyl)methyl}aniline Co(II)/MMAO system yielded PMMA with high molecular weights and narrow PDIs with improved syndiotactic enchainment and a higher T_g value of 60 °C [11b]. Similarly, in comparison with our previously reported 5-coordinated Co(II) complexes bearing *N*,*N*-bis((1H-pyrazol-1yl)methyl)cyclopentanamine and *N*,*N*-bis((3,5-dimethyl-1H-pyrazol-1yl)methyl)cyclopentanamine [21], the current catalytic system exhibited comparable activities and stereoselectivities, yielding PMMA with a higher molecular weight (11.5 × 10^5 g/mol) and T_g value (Table 4).

The tacticity of PMMA was analyzed by ¹H NMR spectroscopy. The tacticity of PMMA can be identified as syndiotactic (rr, 0.85 ppm), heterotactic (mr, 1.02 ppm) and isotactic (mm, 1.21 ppm) [28,29]. The syndiotacticity of the resultant PMMA ranged from 0.67 to 0.70, and was similar for all the $[L_n CoCl_2]$ complexes used, regardless of the aniline substituents. Although the moderate syndiotacticity was not sufficient to confer a mechanism of the coordination polymerisation, a steric effect was not clearly seen for $[L_nCoCl_2]$ ($L_n = L_A$ - L_H) during the MMA polymerisation. From this data, it is also evident that the syndiotacticity was not affected by variation of the substituents on aniline as well as the pyrazole ring. Moreover, the molecular weights of the resultant PMMAs and the molecular weight distributions are also not significantly influenced by the substituents on the ligand framework. It can be concluded that the ligand architecture in the current study has made no dramatic effect on the activity of resultant PMMA as the activity, in some cases, is essentially the same both for the synthesized cobalt complexes and the starting material. The MMA polymerization activity of the complexes in the current study should be considered as a function of steric bulk in the local part of the ligand around the metal center. Further modification of the ligand architecture to improve the catalytic performance and the resultant stereo-control of the MMA polymerization are presently on-going in our laboratory.

3.4. rac-LA polymerization

The ring opening polymerization of *rac*-LA was effectively initiated by the dimethyl derivatives $[L_nCoMe_2]$ ($L_n = L_A - L_H$), yielding PLAs with high molecular weights and narrow molecular weight distributions (Mw/Mn = 1.04-1.24) at -50 °C in CH₂Cl₂. The active catalytic species were generated *in situ*, by treating the dichloro cobalt complexes [L_nCoCl_2] ($L_n = L_A - L_H$) with two equivalents of MeLi in THF. The representative polymerization data are tabulated in Table 5. Complete conversion of *rac*-LA to PLA was confirmed by the absence of monomer signals in the ¹H NMR spectra. The number average molecular weights (M_n) were determined based on end-group analysis of the ¹H NMR spectra and by GPC in THF relative to polystyrene standards. The M_n determined from the ¹H NMR spectra of the obtained PLA and those determined by GPC were almost identical to the M_n (corrected using the Mark–Howink factor of 0.58) [30] value obtained from the monomer to initiator ratio. The narrower polydispersities (1.14-1.31) indicate that the polymerisation is well controlled with a single reaction site provided by these dimethyl cobalt complexes. No activity has been exhibited by the dichloro complexes [L_nCoCl_2] ($L_n = L_A - L_H$) screened for the ROP of *rac*-LA under same experimental conditions.

The polymerization data revealed that the Co(II) complexes effectively polymerized the ROP of *rac*-LA (Table 5) with 100% conversion. In a previous study, complexes with more sterically demanding ligands are more active towards lactide polymerization, which might be due to the enhanced electron density on the metal center. However, previously reported systems where sterically hindered groups tend to block the coordination/insertion of the incoming monomer, there is an adverse effect on the catalytic activity [31,32]. These result indicated that there is no corelaton of the steric and electronic factors to the activity for the ROP of *rac*-LA. Note, these dimethyl Co(II) complexes exhibited higher activities with

better polymerization control and comparable stereoselectivities as compared to the dimethyl Zn(II) complexes reported by our group [33] (Table 5).

The ¹H NMR spectra showed peaks for the methane protons of $-CH(CH_3)(OH)$ at δ 2.90 ppm and the signals for $-C(=O)CH_3$ at the other terminus overlapped with those of the PLA backbone. A coordination insertion mechanism [34-36] for the ROP of *rac*-LA can be anticipated where initially LA is coordinated to the Co(II) center to yield a 5-coordinated intermediate, followed by the cleavage of the acyl-oxygen bond, opening the monomer ring. Further, another molecule of *rac*-LA undergoes ring opening by coordinating to the Co(II) center in similar manner. The following addition of LA produces hetero-enriched PLA.

The stereo-selectivity of PLA is slightly affected by the structure of the ligand framework attached to central metal atom during the polymerization process. Microstructural analysis of the obtained PLA was performed by inspecting the methane proton region of the homo-decoupled ¹H NMR spectra and the P_r values were calculated with the equation $P_r =$ $2I_1/(I_1 + I_2)$ where $I_1 = (sis + sii)$ and $I_2 = (iis + iii + isi)$ [37-39]. It is clear from the polymerization data that all the complexes exhibited a preference for heterotactic enchainment (Table 5). It has been observed that among the synthesized Co(II) complexes enhancing the steric hindrance on the pyrazole moiety leads to an increased heterotacticity, i.e. $[L_nCoCl_2]$ ($L_n = L_B$, L_D , L_F and L_H) (the highest $P_r = 0.85$, Table 5, entry 7) compared to $[L_nCoCl_2]$ ($L_n = L_A$, L_B , L_C and L_D) (the lowest $P_r = 0.78$, Table 5, entry 1), indicating that the larger steric hindrance might probably impede the regularity of monomer insertion [32,33b].

The polymerization results showed that the catalytic activities of these dimethyl complexes were not affected by the steric hindrance provided by the ligand framework around the metal center. The increase in the steric bulk and the electronic effect due to the methyl substituents on the pyrazole moiety around the metal center have a positive effect,

resulting in better stereoselectivities. However, the substituents on aniline moiety do not exert an influence on the activity and stereoselectivity towards the ROP of *rac*-LA. More investigations are ongoing to fully describe the role of the current catalytic system and the mechanism of the ROP of *rac*-LA.

4. Conclusion

In summary, we have investigated the synthesis and X-ray crystallographic structures of $[L_nCoCl_2]$ ($L_n = L_A - L_H$), which were prepared by the reaction of the corresponding metal starting materials and N,N',N-bis((1H-pyrazol-1-yl)methyl)amine derivatives in high yield and purity. The molecular structures of the 4-coordinated Co(II) complexes were found to be distorted tetrahedral, obtained via coordination of the N_{pyrazole} atoms to the metallic center. [L_DCoCl₂] exhited highest catalytic activity and yielded high molecular weight syndiotactic PMMA with slightly broader PDIs. The MMA polymerization activity of the complexes in the current study should not be considered as a function of the total steric encumbrance in the ligand around the metal center. However, local steric hindrance and the electronic effect of the methyl substituents on the pyrazole moiety enhanced the activity of MMA polymerization compared to the corresponding complex with non-methyl substitution on the pyrazole moiety. Moreover, the syndiotacticity was not affected much by the substituents of the pyrazole and aniline moieties. The dimethyl derivatives of the synthesized complexes effectively polymerized rac-LA and yielded heterotactic PLA. The presence or absence of a methyl group in the pyrazole influences not only the solubility of the complexes but also does have some electronic influence, which in turn has an influence on the activity of the Co(II) complexes in the MMA polymerization and on the stereoselectivity of the Co(II) initiators in the ROP of rac-LA.

Supplementary materials

CCDC 1579005-157010 contains the supplementary crystallographic data for complexes $[L_CCoCl_2]-[L_HCoCl_2]$. These data can be obtained free of charge *via* <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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Acceleration



Scheme 1. Synthetic route to the ligands and their corresponding Co(II) complexes $[L_nCoCl_2]$ $(L_n = L_A - L_H)$.

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	[L _C CoCl ₂]	[L _D CoCl ₂]	[L _E CoCl ₂]	[L _F ZnCl ₂]	[L _G CoCl ₂]	[L _H CoCl ₂]
mpirical formula	C ₁₆ H ₁₉ Cl ₂ N ₅ Co, CH ₂ Cl ₂	$C_{20}H_{27}Cl_2N_5Co$	$C_{15}H_{17}Cl_2CoN_5O_1$	$C_{19}H_{25}Cl_2N_5CoO$	$C_{14}H_{14}Cl_2N_5CoF$	C ₁₈ H ₂₂ Cl ₂ N ₅ CoF, CH ₂ Cl ₂
ormula weight	496.12	467.29	413.17	469.27	401.13	542.16
emperature (K)	200(2)	100(2)	200(2)	100(2)	200(2)	100(2)
vavelength (Å)	0.71073	0.610	0.71073	0.610	0.71073	0.610
rystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
pace group	Cc	$P2_{1}/c$	P-1	$P2_{1}/n$	P-1	$P2_{1}/n$
nit cell dimensions						
(Å)	13.6758(2)	12.891(3)	8.5385(9)	19.411(4)	7.1932(7)	8.3130(2)
(Å)	19.180(2)	15.504(3)	13.5955(2)	12.463(3)	10.2051(9)	15.881(3)
(Å)	8.6605(1)	13.943(3)	15.8732(2)	19.504(4)	12.8954(1)	18.312(4)
(°)	90	90	84.027(2)	90	101.366(2)	90
(°)	99.607(2)	114.04(3)	84.864(2)	114.76(3)	103.410(2)	102.64(3)
°)	90	90	86.870(2)	90	108.419(2)	90
olume (Å ³), Z	2239.8(4), 4	2545.0(1), 4	1823.4(3), 2	4284.5(2), 8	835.31(1), 2	2358.9(9), 4
ensity (calculated) (Mg/m ³)	1.471	1.220	1.505	1.455	1.595	1.527
bsorption coefficient (mm ⁻¹)	1.255	0.588	1.246	0.701	1.361	0.786
(000)	1012	972	844	1944	406	1108
rystal size (mm ³)	$0.32 \times 0.22 \times 0.18$	$0.100 \times 0.050 \times 0.030$	$0.26 \times 0.24 \times 0.23$	$0.200 \times 0.050 \times 0.030$	$0.38 \times 0.17 \times 0.12$	$0.150\times0.050\times0.030$
heta range for data collection (°)	1.85 to 28.31	1.776 to 25.999	1.29 to 27.02	1.666 to 27.999	2.20 to 28.28	1.472 to 28.000
dex ranges	$-12 \le h \le 18, -25 \le k \le 23,$	$-18 \le h \le 18, -21 \le k \le 22,$	$-10 \le h \le 10, -17 \le k \le 12,$	$-29 \le h \le 29, -19 \le k \le 19,$	$-9 \le h \le 9, -13 \le k \le 13,$	$-12 \le h \le 12, -24 \le k \le 24,$
	$-11 \le l \le 11$	$-20 \le l \le 20$	$-20 \le l \le 20$	$-30 \le 1 \le 30$	$-17 \le l \le 11$	$-28 \le l \le 28$
eflections collected	8180	27619	12485	57036	6093	32367
		5	29			
	C					

Table 1. Crystal data and structural refinement for $[L_nCoCl_2]$ $(L_n = L_C - L_H)$.

dependent reflec	ent reflections $4658 [R(int) = 0.0401]$ 7891 [R(int) = 0.0401]		7891 [R(int) = 0.02	283]	7900 [R(i	nt) = 0.0537]	16343 [R(int) = 0.0385]	4086 [R(int) = 0.0	0235]	8940 [R((int) = 0.0429]		
ompleteness to th	eness to theta = 28.30° 99.5 % 99.9 %		99.9 %		99.4 %		99.9 %		98.5 %			99.9 %			
bsorption correct	ion	None Empirical			None		Empirical		None			Empirical			
efinement metho	d	Full-matrix lea	st-squares	Full-matrix least-	squares	Full-matr	ix least-squares	Full-matrix	least-squares	Full-matr	rix least	-squares	Full-mat	rix least-squares of	m
		on F ²		on F^2		on F ²		on F ²		on F ²			F^2		
ata / restraints / p	parameters	4658 / 2 / 246		7891 / 0 / 259		7900 / 0 /	435	16343 / 0 / 5	15	4086 / 0 /	/ 208		8940 / 1	/ 280	
oodness-of-fit on	F^2	1.047		1.065		1.170		1.040		1.193			1.058		
nal R indices [I>	2sigma(I)]	$R_1 = 0.0510, wR$	2=	$R_1 = 0.0278, wR_2 =$:	$R_1 = 0.06$	31, $wR_2 =$	$R_1 = 0.0366,$	$wR_2 =$	$\mathbf{R}_1 = 0$).0565,	$wR_2 =$	$R_1 = 0.04$	414, $wR_2 =$	
		0.1118		0.0762		0.1338		0.0941		0.1010			0.1137		
indices (all data))	$R_1 = 0.0897, wR$	₂ =	$R_1 = 0.0312, wR_2 =$:	$R_1 = 0.11$	90, $wR_2 =$	$R_1 = 0.0486,$	$wR_2 =$	$R_1 = 0$	0.1054,	$wR_2 =$	$R_1 = 0.02$	528, $wR_2 =$	
		0.1663		0.0777		0.2148		0.0978		0.1693			0.1190		
argest diff. peak a	and hole (e Å ⁻³)	0.686 and -0.896	5	0.376 and -0.882		0.866 and	-1.052	1.044 and -1.	337	1.136 and	d -1.794		1.258 an	d -1.384	
	Table 2. Sele	ected bond leng	ths (Å) ar	nd angles (°) of [I	L _n CoCl	$_{2}](L_{n}=L$	$L_{\rm C}-L_{\rm H}$).								
[L _C C	oCl ₂]	[L _D C	oCl ₂]	[L _F	CoCl ₂]		[L _F Co	Cl ₂]	[I	GCoCl ₂]			[L _H C	oCl ₂]	
						Bond len	gths (Å)								
Co(1)-N(1)	2.000(6)	Co(1)-N(5)	2.0382	(9) $Co(1)-N(1)$	2.0	018(5)	Co(1)-N(5)	2.0295(1)	Co(1)-N(1)	2.0)16(5)	Co(1)-	N(1)	2.0293(1)	
Co(1)-N(4)	2.009(6)	Co(1)-N(1)	2.0397	(1) $Co(1)-N(4)$	2.0	018(5)	Co(1)-N(1)	2.0298(1)	Co(1)-N(4)	2.0)27(5)	Co(1)-	N(5)	2.0421(1)	
Co(1)-Cl(2)	2.2348(2)	Co(1)-Cl(2)	2.2375	(6) $Co(1)-Cl(1)$	2.2	236(2)	Co(1)-Cl(1)	2.2299(5)	Co(1)-Cl(1)	2.2	2510(2)	Co(1)-	Cl(2)	2.2447(6)	
Co(1)-Cl(1)	2.251(2)	Co(1)-Cl(1)	2.2437	(5) $Co(1)-Cl(2)$	2.2	2390(2)	Co(1)-Cl(2)	2.2517(6)	Co(1)-Cl(2)	2.2	2995(2)	Co(1)-	Cl(1)	2.2487(6)	
N(1)-C(1)	1.323(9)	N(1)-C(2)	1.3449	(1) $N(1)-C(1)$	1.	330(8)	N(1)-C(2)	1.3425(2)	N(1)-C(1)	1.3	328(7)	N(1)-C	(2)	1.3434(2)	
N(1)-N(2)	1.360(7)	N(1)-N(2)	1.3742	(1) N(1)-N(2)	1.3	352(6)	N(1)-N(2)	1.3785(2)	N(1)-N(2)	1.3	353(6)	N(1)-N	(2)	1.3732(2)	
N(2)-C(3)	1.351(8)	N(2)-C(4)	1.3588	(1) $N(2)-C(3)$	1.3	339(8)	N(2)-C(4)	1.3565(2)	N(2)-C(3)	1.3	338(7)	N(2)-C	2(4)	1.356(2)	
N(2)-C(4)	1.460(9)	N(2)-C(6)	1.4643	(1) $N(2)-C(4)$	1.4	455(8)	N(2)-C(6)	1.4688(2)	N(2)-C(4)	1.4	157(7)	N(2)-C	2(6)	1.4507(2)	
N(5)-C(9)	1.408(8)	N(3)-C(13)	1.4251	(1) $N(5)-C(9)$	1.4	441(8)	N(3)-C(13)	1.4361(2)	N(5)-C(9)	1.4	450(7)	N(3)-C	(13)	1.4309(2)	
						3	0								
			\mathbf{O}												

Bond angles (°)											
N(1)-Co(1)-N(4)	107.8(2)	N(5)-Co(1)-N(1)	109.92(4)	N(1)-Co(1)-N(4)	114.7(2)	N(5)-Co(1)-N(1)	109.23(5)	N(1)-Co(1)-N(4)	109.0(2)	N(1)-Co(1)-N(5)	111.00(5)
N(1)-Co(1)-Cl(2)	103.94(2)	N(5)-Co(1)-Cl(2)	111.50(3)	N(1)-Co(1)-Cl(1)	106.65(2)	N(5)-Co(1)-Cl(1)	102.85(4)	N(1)-Co(1)-Cl(1)	119.94(2)	N(1)-Co(1)-Cl(2)	113.77(4)
N(4)-Co(1)-Cl(2)	108.80(2)	N(1)-Co(1)-Cl(2)	106.74(3)	N(4)-Co(1)-Cl(1)	110.50(2)	N(1)-Co(1)-Cl(1)	114.01(4)	N(4)-Co(1)-Cl(1)	117.23(2)	N(5)-Co(1)-Cl(2)	106.92(5)
N(1)-Co(1)-Cl(1)	111.63(2)	N(5)-Co(1)-Cl(1)	105.02(3)	N(1)-Co(1)-Cl(2)	105.59(2)	N(5)-Co(1)-Cl(2)	112.73(4)	N(1)-Co(1)-Cl(2)	100.91(2)	N(1)-Co(1)-Cl(1)	104.54(4)
N(4)-Co(1)-Cl(1)	108.23(2)	N(1)-Co(1)-Cl(1)	106.43(3)	N(4)-Co(1)-Cl(2)	104.28(2)	N(1)-Co(1)-Cl(2)	102.68(4)	N(4)-Co(1)-Cl(2)	97.53(2)	N(5)-Co(1)-Cl(1)	107.41(4)
Cl(2)-Co(1)-Cl(1)	116.15(9)	Cl(2)-Co(1)-Cl(1)	117.055(2)	Cl(1)-Co(1)-Cl(2)	115.25(8)	Cl(1)-Co(1)-Cl(2)	115.53(2)	Cl(1)-Co(1)-Cl(2)	108.40(7)	Cl(2)-Co(1)-Cl(1)	113.106(2)
C(1)-N(1)-N(2)	106.1(6)	C(2)-N(1)-N(2)	105.91(9)	C(1)-N(1)-N(2)	106.2(5)	C(2)-N(1)-N(2)	105.96(1)	C(1)-N(1)-N(2)	106.1(5)	C(2)-N(1)-N(2)	105.26(1)
C(1)-N(1)-Co(1)	127.7(5)	C(2)-N(1)-Co(1)	123.91(8)	C(1)-N(1)-Co(1)	128.7(4)	C(2)-N(1)-Co(1)	127.75(9)	C(1)-N(1)-Co(1)	131.0(4)	C(2)-N(1)-Co(1)	131.21(1)
N(2)-N(1)-Co(1)	125.7(4)	N(2)-N(1)-Co(1)	129.93(7)	N(2)-N(1)-Co(1)	124.8(4)	N(2)-N(1)-Co(1)	125.16(9)	N(2)-N(1)-Co(1)	122.9(4)	N(2)-N(1)-Co(1)	123.14(9)
C(3)-N(2)-N(1)	109.4(6)	C(4)-N(2)-N(1)	110.87(9)	C(3)-N(2)-N(1)	109.9(5)	C(4)-N(2)-N(1)	110.72(1)	C(3)-N(2)-N(1)	110.7(5)	C(4)-N(2)-N(1)	111.14(1)

Table 3. Four-coordinate geometry indices for $[L_nCoCl_2]$ ($L_n = L_A - L_H$) and representative examples from the literature.

Complexes	Geometry	${ au_4}^a$	<i>THC_{DA}/100</i> ^b	FCGP/100 ^c	Bond distance (Å) ^d	References
Tetrahedral (T _d)	Tetrahedral	1.00	1.00	0.00	-	[22a]
[L _A CoCl ₂]	Tetrahedral	0.926	0.729	0.166	3.664	[13a, b] ^e
[L _B CoCl ₂]	Tetrahedral	0.945	0.806	0.0220	3.419	[4b, 13a] ^f
[L _C CoCl ₂]	Tetrahedral	0.938	0.800	0.0951	3.522	This work
[L _D CoCl ₂]	Tetrahedral	0.932	0.775	0.101	3.878	This work
[L _E CoCl ₂]	Tetrahedral	0.922	0.734	0.0636	3.298	This work
[L _F CoCl ₂]	Tetrahedral	0.925	0.694	0.0700	3.870	This work
[L _G CoCl ₂]	Tetrahedral	0.871	0.552	0.389	2.653	This work
[L _H CoCl ₂]	Tetrahedral	0.944	0.789	0.0647	3.909	This work
[(N,N-bis((1H-pyrazol-1-yl)methyl)-N-(cyclohexylmethanamine)CoCl ₂]	Tetrahedral	0.935	0.766	0.0943	2.466	[14c]
$[(N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-diethylbenzeneamine)CoCl_2] = [L_ICoCl_2]$	Tetrahedral	0.887	0.651	0.0436	3.437	[14c]
$[(N,N-bis((1H-pyrazol-1-yl)methyl)-4-bromobenzeneamine)CoCl_2] = [L_JCoCl_2]$	Tetrahedral	0.915	0.739	0.0365	3.292	[14c]
[(N,N-bis((1H-pyrazol-1-yl)methyl)cyclopentanamine)CoCl ₂]	Trigonal bipyramidal	0.833	0.391	0.521	2.425(4)	[21a]
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[(N,N-bis((3,5H-dimethylpyrazol-1-yl)methyl)cyclopentanamine)CoCl ₂]	Trigonal bipyramidal	0.869	0.458	0.482	2.388(2)	[21a]
[(N,N-bis((1H-pyrazol-1-yl)methyl)-3-methoxypropan-1-amine)CoCl ₂]	Trigonal bipyramidal	0.883	0.890	0.359	2.522(6)	[21b]
[(<i>N</i> , <i>N</i> -bis((3,5H-dimethylpyrazol-1-yl)methyl)-3-methoxypropan-1-amine)CoCl ₂]	Trigonal bipyramidal	0.881	0.498	0.445	2.382(2)	[21b]
[(N,N-bis((1H-pyrazol-1-yl)methyl)cyclohexanamine)CoCl ₂]	Trigonal bipyramidal	0.891	0.402	0.484	2.466(4)	[14c]
[(N,N-bis((1H-pyrazol-1-yl)methyl)(furan-2-yl)methanimine)CoCl ₂]	Trigonal bipyramidal	0.848	0.466	0.468	2.507(4)	[14c]
[(N,N-bis((1H-pyrazol-1-yl)methyl)-2-methoxyethanamine)CoCl ₂]	Trigonal bipyramidal	0.853	0.477	0.465	2.514(4)	[14c]
[(N,N-bis((1H-pyrazol-1-yl)methyl)-3-(methylthio)propan-1-amine)CoCl ₂]	Trigonal bipyramidal	0.883	0.559	0.395	2.522(6)	[14c]
Square planar (D _{4h})	Square Planar	0.00	-1.43	-0.40	-	[22a]
Trigonal pyramidal (C _{3v})	Trigonal pyramidal	0.850	0.00	1.00	-	[22c,d,e]

^a See reference [22a]. ^b See reference [22c,d,e]. ^c See reference [22f]. ^d Assume that the geometry of $[L_nCoCl_2](L_n = L_A - L_H)$ is 5-coordinated, the bond distance for coordinative interaction between the nitrogen atom of the aniline moiety and the cobalt metal centre. See the reference [22b] to get the τ_5 value for trigonal bipyramidal geometry. ^e Four-coordinate geometry indices of $[L_ACoCl_2]$ are calculated using the CIF file of $[L_AZnCl_2]$. ^f Although the molecular structure of $[L_BCoCl_2]$ is reported in the literature [4b], its CIF file is not available. Four-coordinate geometry indices of $[L_BCoCl_2]$ are calculated using the CIF file of $[L_BZnCl_2]$.

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Table 4. MMA polymerization by $[L_nCoCl_2]$ ($L_n = L_A - L_H$) in the presence of MMAO.



		Yield ^b	Activity ^c	$\mathbf{T_g}^d$	r	Facticity	v (%)	M _w ^e	£
Entry	Catalyst ^a	(%)	× 10 ⁴ (g/molcat h)	(°C)	mm	mr	rr	× 10 ⁵ (g/mol)	M_w/M_n^J
1	[CoCl ₂] ^g	17.4	2.72	125	7.70	24.6	51.9	8.15	1.97
2	MMAO ^h	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
3	[L _A CoCl ₂]	15.8	2.46	125	7.32	23.0	69.7	8.78	2.50
4	[L _B CoCl ₂]	23.1	3.60	124	7.09	25.3	67.6	10.1	2.59
5	[L _C CoCl ₂]	19.7	3.07	125	7.32	24.9	69.8	9.92	2.57
6	[L _D CoCl ₂]	28.8	4.02	125	6.79	23.9	70.3	10.5	2.54
7	[L _E CoCl ₂]	22.0	3.44	124	7.23	25.0	68.2	10.4	2.49
8	[L _F CoCl ₂]	23.9	3.72	123	7.02	24.8	68.2	10.2	2.59
9	[L _G CoCl ₂]	15.5	2.42	123	7.56	24.3	68.1	10.5	2.57
10	[L _H CoCl ₂]	24.5	3.82	125	7.11	24.5	68.4	10.6	2.55
11	[L _I CoCl ₂] ⁱ	23.9	3.73	123	6.49	22.7	70.8	9.03	1.90
12	[L _J CoCl ₂] ⁱ	20.5	3.20	129	7.29	21.8	70.8	11.8	1.68

^{*a*} $[M(II) \text{ catalyst}]_0 = 15 \ \mu\text{mol}, \ [MMA]_0 / [MMAO]_0 / [Co(II) \text{ catalyst}]_0 = 3100:500:1, \ \text{Temp} = 60 \ ^\circ\text{C}, \ \text{time} = 2 \ \text{h}.$

^b Yield defined as (mass of dried polymer recovered)/(mass of monomer used).

^c Activity is (g PMMA)/(molcat h).

 d T_g is the glass transition temperature determined using a thermal analyzer.

^{*e*} Determined using gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.

^f M_n refers to the number average of molecular weights of PMMA.

^g This is a blank polymerization in which anhydrous [CoCl₂] was also activated by MMAO.

^h This is a blank polymerization which was done solely by MMAO.

^{*i*} Data of polymerization came from the reference [14c].



Table 5. Polymerization of *rac*-lactide with *in situ* generated $[L_nCoMe_2]$ ($L_n = L_A - L_H$).

Entry	Catalyst ^a	Conv. ^b (%)	$M_n^{\rm c}$ (g/mol) $\times 10^3$ (calcd.)	$M_n^{\rm d}$ (g/mol) $\times 10^3$ (GPC)	PDI ^e	$P_r^{\rm f}$
1	MeLi	85	12.25	3.88	1.14	0.67
2	[L _A CoMe ₂]	97	13.98	9.27	1.16	0.78
3	[L _B CoMe ₂]	100	14.41	10.71	1.15	0.83
4	[L _C CoMe ₂]	100	14.41	7.25	1.11	0.80
5	[L _D CoMe ₂]	100	14.41	7.39	1.13	0.81
6	[L _E CoMe ₂]	100	14.41	8.52	1.15	0.80
7	[L _F CoMe ₂]	100	14.41	7.23	1.21	0.85
8	[L _G CoMe ₂]	100	14.41	10.25	1.31	0.83
9	[L _H CoMe ₂]	100	14.41	8.85	1.20	0.83

^a Conditions: [Initiator] = 0.0625 mmol, [*rac*-LA]/[Initiator] = 100, 5.0 mL of solvent (CH₂Cl₂), time = 2 h, temp = -50 °C.

^b Monomer conversion (%) (quantitative disappearance of monomer) determined by ¹H NMR spectroscopy.

^c Calculated from ([molecular weight of *rac*-LA] × [mol concentration of used *rac*-LA]/[mol concentration of initiator])× (conversion).

^d Experimental values (corrected using the Mark-Houwink factor of 0.58) [30].

^e Determined by gel permeation chromatography in THF, relative to the polystyrene standard.

^f Probability of heterotactic enchainment (P_r) were calculated on the basis of homonuclear decoupled ¹H NMR spectra according to the literature [37-39].



Fig.1. ORTEP drawing of $[L_CCoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.



Fig. 2. ORTEP drawing of $[L_DCoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing of $[L_E CoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP drawing of $[L_FCoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.



Fig.5. ORTEP drawing of $[L_GCoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.



Fig.6. ORTEP drawing of $[L_HCoCl_2]$ with thermal ellipsoids at 30% probability. All hydrogen atoms and the water molecule are omitted for clarity.









Fig. 7. Ball and stick models, space-filling models and topographic steric maps of $[L_nCoCl_2]$ ($L_n = L_A - L_H$) for presenting sterically bulky ligands. CIF files of $[L_ACoCl_2]$ and $[L_BCoCl_2]$ were not available for the calculation of the steric hindrance. Varied volumes of the ligands in the tetrahedral $[L_ACoCl_2]$ and $[L_BCoCl_2]$ complexes were calculated using the CIF files of the tetrahedral $[L_AZnCl_2]$ and $[L_BZnCl_2]$ complexes, respectively [13a] since the metal center is omitted during the calculations.

Graphical Abstract (Pictorial)

