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### FULL PAPER



# Zinc (II), palladium (II) and cadmium (II) complexes containing 4-methoxy-*N*-(pyridin-2-ylmethylene) aniline derivatives: Synthesis, characterization and methyl methacrylate polymerization

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### Funding information

Ministry of Education, Science, and Technology (MEST), Grant/Award Number: 2017R1A2B4002100 A series of Zn (II), Pd (II) and Cd (II) complexes,  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2), containing 4-methoxy-N-(pyridin-2-ylmethylene) aniline (L-a), 4-methoxy-N-(pyridin-2-ylmethyl) aniline (L-b) and 4-methoxy-N-methyl-N-(pyridin-2-ylmethyl) aniline (L-c) have been synthesized and characterized. The X-ray crystal structures of Pd (II) complexes [L<sub>1</sub>PdCl<sub>2</sub>] (L = L-b and L-c) revealed distorted square planar geometries obtained via coordinative interaction of the nitrogen atoms of pyridine and amine moieties and two chloro ligands. The geometry around Zn (II) center in [(L-a)ZnCl<sub>2</sub>] and [(L-c)ZnCl<sub>2</sub>] can be best described as distorted tetrahedral, whereas [(L-b)<sub>2</sub>ZnCl<sub>2</sub>] and [(L-b)<sub>2</sub>CdBr<sub>2</sub>] achieved 6-coordinated octahedral geometries around Zn and Cd centers through 2-equivalent ligands, respectively. In addition, a dimeric  $[(L-c)Cd(\mu-Br)Br]_2$  complex exhibited typical 5-coordinated trigonal bipyramidal geometry around Cd center. The polymerization of methyl methacrylate in the presence of modified methylaluminoxane was evaluated by all the synthesized complexes at 60°C. Among these complexes, [(L-b)PdCl<sub>2</sub>] showed the highest catalytic activity  $[3.80 \times 10^4$  g poly (methyl methacrylate) (PMMA)/mol Pd hr<sup>-1</sup>], yielding high molecular weight  $(9.12 \times 10^5 \text{ g mol}^{-1})$  PMMA. Syndio-enriched PMMA (characterized using <sup>1</sup>H-NMR spectroscopy) of about 0.68 was obtained with  $T_{\rm g}$  in the range 120–128°C. Unlike imine and amine moieties, the introduction of N-methyl moiety has an adverse effect on the catalytic activity, but the syndiotacticity remained unaffected.

### KEYWORDS

4-methoxy-*N*-methyl-*N*-(pyridin-2-ylmethyl) aniline, 4-methoxy-*N*-(pyridin-2-ylmethyl) aniline, 4-methoxy-*N*-(pyridin-2-ylmethylene) aniline, methyl methacrylate polymerization, molecular structures

# **1** | INTRODUCTION

 and *N*-methyl-1-(pyridin-2-yl) methanamine<sup>[8,9]</sup> moieties have been broadly researched owing to their diverse coordination geometries ranging from bidentate<sup>[10-12]</sup> to polydentate coordination modes.<sup>[13-15]</sup> In addition, the steric and electronic properties can be easily modified by appropriate variation on *N*-donors of pyridinylmethanimine moiety, and resulted in stable complexes with a variety of transition or inner transition metals.<sup>[16,17]</sup> These metal complexes have found a wide range of applications in various fields, such as synthesis and spectroscopic studies,<sup>[18]</sup> as catalysts for transfer hydrogenation of ketones,<sup>[19]</sup> oxidation,<sup>[20]</sup> supramolecular metal–organic frameworks,<sup>[21]</sup> olefin polymerization,<sup>[22]</sup>  $\varepsilon$ -caprolactone<sup>[23]</sup> and methyl methacrylate (MMA) polymerization.<sup>[24,25]</sup>

On the other hand, the metal-mediated poly (methyl methacrylate) (PMMA) polymerization is of growing interest both in industry and academia due to its significant optical properties.<sup>[26-30]</sup> The optical properties of PMMA are far improved with high  $T_g$ , which in turn depend on tacticity of PMMA, i.e.  $T_g$  of isotactic PMMA is about 65°C, whereas syndiotactic PMMA<sup>[31]</sup> exhibits  $T_g$  about 140°C. That is why many attempts aiming to increase the syndiotacticity of PMMA were planned.

Recently, we have studied Zn (II), Cd (II), Co (II), Pt (II) and Pd (II) complexes with N,N-di(2-picolyl) amine, 2iminomethylpyridine, N-methyl-N-((pyridin-2-yl)methyl) cyclohexanamine, N-(pyridin-2-ylmethyl) aniline and N, N-di(2-picolyl) cycloalkylamine ligands in MMA polymerization with promising results,<sup>[25,32-38]</sup> as a slight difference in ligand architecture is able to influence the stereoregular outcomes during polymerization reactions. Thus, suitable ligand architecture around the metal center is vital for achieving a high degree of polymerization as these complexes/initiators regulate various steps involved in polymerization.<sup>[39-43]</sup> Our current findings demonstrate the synthesis, X-ray structures of Zn (II), Pd (II) and Cd (II) complexes ligated to 4-methoxy-N-(pyridin-2-ylmethylene) aniline derivatives and their catalytic efficiency for MMA polymerization. Moreover, the electronic and steric effect from slight variation of N atom substituents on the catalytic efficacy of stereoregulated MMA polymerization is especially discussed.

### 2 | EXPERIMENTAL

# 2.1 | Physical measurements and instrumentations

 $PdCl_2$  was purchased from Kojima Chemicals, and  $[Pd (MeCN)_2Cl_2]$  was prepared according to the literature method.<sup>[44]</sup> [ZnCl\_2], [CdBr\_2·4H\_2O], NaBH\_4, CH\_3I, 2-pyridinecarboxaldehyde, 4-methoxyaniline, magnesium sulfate (MgSO<sub>4</sub>) and MMA were purchased from Aldrich. Anhydrous solvents such as acetonitrile (CH<sub>3</sub>CN), ethanol (EtOH), dimethylformamide (DMF), diethyl ether

(Et<sub>2</sub>O) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were purchased from Merck, and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Fine Chemicals as 5.90% weight aluminum of a toluene solution and used without further purification. Ligands  $\mathbf{L}$ - $\mathbf{a}$ ,<sup>[45]</sup>  $\mathbf{L}$ - $\mathbf{b}$ <sup>[46]</sup> and  $\mathbf{L}$ - $\mathbf{c}$ <sup>[47]</sup> have been prepared by literature methods. Complexes [(L-a)PdCl<sub>2</sub>],<sup>[48]</sup> [(La) $ZnCl_2$ ],<sup>[49]</sup>  $([(L-a)Cd(\mu-Br)Br]_2^{[50]})$ and [(L-b) **PdCl**<sub>2</sub>**l**<sup>[46]</sup> have been synthesized as described previously. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) spectra were recorded on a Bruker Avance Digital 500 NMR spectrometer; chemical shifts were reported in ppm units ( $\delta$ ) relative to SiMe<sub>4</sub> as the internal standard. Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters  $(cm^{-1})$ . The molecular weights  $(M_{\rm p})$  and molecular weight distribution [polydispersity] indexes (PDIs)] of the obtained PMMA were carried out using gel permeation chromatography (GPC; in THF, Alliance e2695; Waters, Milford, MA, USA). Glass transition temperature  $(T_{\alpha})$  was determined using a thermal analyzer (DSC 4000; PerkinElmer).

# 2.2 | Preparation of Pd (II), Zn (II) and Cd (II) complexes

### 2.2.1 | 4-methoxy-*N*-(pyridin-2-ylmethyl) anilinezinc (II) chloride, [(L-b)<sub>2</sub>ZnCl<sub>2</sub>]

[L-b] (0.401 g, 1.87 mmol) solution in EtOH (10.0 mL) was treated with  $ZnCl_2$  (0.127 g, 0.935 mmol) solution in EtOH (10.0 mL) at ambient temperature. The resultant precipitate was filtered and washed with cold EtOH and Et<sub>2</sub>O to give white crystalline solid as final product (0.422 g, 79.9%). X-ray crystallographies were obtained from Et<sub>2</sub>O (5.00 mL) diffusion into acetone solution (3.00 mL). X-ray quality crystals for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>] were obtained from slow diffusion of Et<sub>2</sub>O (10.0 mL) into DMF solution (5.00 mL) of [(L-b)<sub>2</sub>ZnCl<sub>2</sub>]. Analysis calculated for C<sub>26</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn (%): C, 55.3; H, 5.00; N, 9.92. Found: C, 55.3; H, 5.02; N, 9.81. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ , ppm): 8.53 (ddd, 1H, J = 4.88Hz, -N=C-CH=CH-CH=CH-), 7.75 (td, 1H, J = 7.63 Hz, -N=C-CH=CH-CH=CH-), 7.38 (d, 1H, J = 7.93 Hz, -N=C-CH=CH-CH=CH-), 7.26 (ddd, 1H, J= 7.32 Hz, -N=C-CH=CH-CH=CH-), 6.69 (d, 2H, J= 9.00 Hz,  $-CH_3OC_6H_4$ -), 6.55 (d, 2H, J = 8.85 Hz,  $-CH_{3-2}$  $OC_6H_4$ -), 5.95 (t, 1H, J = 6.10 Hz,  $-NH-CH_2-NC_5H_4$ -), 4.31 (d, 2H, J = 6.10 Hz,  $-NH-CH_2-NC_5H_4-$ ), 3.61 (s, 3H, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, δ,

ppm): 159.60 (s, 1C, ipso-N=C-CH=CH-CH=CH-), 151.45 (s, 1C,  $ipso-CH_3OC_6H_4-$ ), 148.67 (d, 1C, J =178.93 Hz, -N=C-CH=CH-CH=CH-), 142.19 (s, 1C,  $ipso-CH_3OC_6H_4-$ ), 137.26 (d, 1C, J = 163.49 Hz, -N=C-CH=CH-CH=CH-), 122.28 (d, 1C, J = 164.40 Hz, -[(L-c)PdCl<sub>2</sub>] was pre

178.93 Hz, -N=C-CH=CH-CH=CH-), 142.19 (s, 1C, *ipso*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 137.26 (d, 1C, J = 163.49 Hz, -N=C-CH=CH-CH=CH-), 122.28 (d, 1C, J = 164.40 Hz, -N=C-CH=CH-CH=CH-), 121.55 (d, 1C, J = 163.49Hz, -N=C-CH=CH-CH=CH-), 114.54 (d, 2C, J =158.95 Hz, *m*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 114.25 (d, 2C, J = 158.04Hz, o-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 55.29 (q, 1C, J = 143.51 Hz,  $-CH_3OC_6H_4-)$ , 49.58 (t, 1C, J = 135.33 Hz,  $-CH_2-$ NC<sub>5</sub>H<sub>4</sub>-). IR (solid neat; cm<sup>-1</sup>): 3240 (w), 2994 (w), 2913 (w), 2838 (w), 1603 (m), 1570 (w), 1508 (s), 1440 (m), 1307 (w), 1241 (s), 1215 (m), 1183 (m), 1072 (m), 1008 (s), 904 (m), 853 (s), 816 (m), 761 (s), 730 (m), 642 (w).

### 2.2.2 | 4-Methoxy-*N*-(pyridin-2-ylmethyl) anilinecadmium (II) bromide ([(Lb)<sub>2</sub>CdBr<sub>2</sub>])

[(L-b)<sub>2</sub>CdBr<sub>2</sub>] was prepared according to a similar procedure as described for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>], except utilizing [L**b**] (0.401 g, 1.87 mmol) and CdBr<sub>2</sub>·4H<sub>2</sub>O (0.322 g, 0.935 mmol) to give a white solid (0.605 g, 92.3%). X-ray quality crystals for [(L-b)<sub>2</sub>CdBr<sub>2</sub>] were obtained from slow diffusion of Et<sub>2</sub>O (10.0 mL) into DMF solution (5.00 mL) of  $[(L-b)_2CdBr_2]$ . Analysis calculated for  $C_{26}H_{28}Br_2CdN_4O_2$ (%): C, 44.6; H, 4.03; N, 8.00. Found: C, 45.0; H, 4.01; N, 7.98. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ , ppm): 8.53 (ddd, 1H, J = 4.88 Hz, -N=C-CH=CH-CH=CH-), 7.76 (td, 1H, J = 7.63 Hz, -N=C-CH=CH-CH=CH-), 7.39 (d, 1H, J = 7.78 Hz, -N=C-CH=CH-CH=CH-), 7.27 (ddd, 1H, J = 7.32 Hz, -N=C-CH=CH-CH=CH-), 6.69 (d, 2H, J = 9.00 Hz,  $-CH_3OC_6H_4-$ ), 6.57 (d, 2H, J = 9.00 Hz,  $-CH_3OC_6H_4-$ ), 5.93 (t, 1H, J = 5.65 Hz,  $-NH-CH_2 NC_5H_4-$ ), 4.30 (d, 2H, J = 5.80 Hz,  $-NH-CH_2-NC_5H_4-$ ), 3.61 (s, 3H, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 125 MHz, δ, ppm): 159.15 (s, 1C, ipso-N=C-CH=CH-CH=CH-), 151.76 (s, 1C, ipso-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 148.70 (d, 1C, J = 178.93 Hz, -N=C-CH=CH-CH=CH-), 142.04 (s, 1C, *ipso*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 137.36 (d, 1C, J = 163.49 Hz, -N=C-CH=CH-CH=CH-), 122.38 (d, 1C, J=165.30 Hz, -N=C-CH=CH-CH=CH-), 121.81 (d, 1C, J=163.49 Hz, -N=C-CH=CH-CH=CH-), 114.85 (d, 2C, J = 158.04 Hz, m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 114.41 (d, 2C, J = 158.04Hz,  $o-CH_3OC_6H_4-$ ), 55.27 (q, 1C, J = 142.60 Hz,  $-CH_3OC_6H_4-$ ), 49.76 (t, 1C, J = 136.24 Hz,  $-CH_2-$ NC<sub>5</sub>H<sub>4</sub>-). IR (solid neat; cm<sup>-1</sup>): 3235 (w), 2989 (w), 2960 (w), 2907 (w), 2836 (w), 1600 (m), 1507 (s), 1462 (s), 1438 (m), 1240 (s), 1181 (m), 1149 (m), 1118 (w), 1071 (w), 1033 (w), 1000 (m), 964 (w), 895 (m), 845 (s), 763 (s).

# 2.2.3 | 4-Methoxy-*N*-methyl-*N*-(pyridin-2ylmethyl) anilinepalladium (II) chloride ([(L-c)PdCl<sub>2</sub>])

[(L-c)PdCl<sub>2</sub>] was prepared according to a similar procedure as described for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>], except utilizing [Lc] (0.400 g, 1.75 mmol) and [Pd (MeCN)<sub>2</sub>Cl<sub>2</sub>] (0.454 g, 1.75 mmol) in acetonitrile (50.0 mL) to give an orange solid (0.603 g, 84.9%). X-ray quality crystals for [(L-c)  $PdCl_2$ ] were obtained from slow diffusion of  $Et_2O$  (10.0 mL) into DMF solution (5.00 mL) of [(L-c)PdCl<sub>2</sub>]. Analysis calculated for C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>OPd (%): C, 41.5; H, 3.98; N, 6.91. Found: C, 41.9; H, 3.99; N, 6.91. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ , ppm): 8.65 (dd, 1H, J = 5.80 Hz, -N=C-CH=CH-CH=CH-), 8.11 (td, 1H, J = 7.63 Hz, -N=C-CH=CH-CH=CH-), 7.85-7.80 (m, 3H, -N=C-CH=CH-CH=CH-,  $-CH_3OC_6H_4$ -), 7.49 (t, 1H, J = 6.26Hz, -N=C-CH=CH-CH=CH-), 6.91 (d, 2H, J=9.16 Hz,  $-CH_3OC_6H_4$ -), 5.21 (d, 1H, J = 16.02 Hz,  $-NCH_3$ - $CH_2-NC_5H_4-$ ), 4.89 (d, 1H, J = 16.17 Hz,  $-NCH_3-CH_2-$ NC<sub>5</sub>H<sub>4</sub>-), 3.71 (s, 3H, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 3.07 (s, 3H, -NCH<sub>3</sub>-CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz, δ, ppm): 160.07 (s, 1C, ipso-N=C-CH=CH-CH=CH-), 157.56 (s, 1C, *ipso*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 149.27 (d, 1C, J =188.01 Hz, -N=C-CH=CH-CH=CH-), 142.72 (s, 1C, *ipso*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 140.65 (d, 1C, J = 168.03 Hz, -N=C-CH=CH-CH=CH-), 124.18 (d, 1C, J = 171.66 Hz, -N=C-CH=CH-CH=CH-), 123.44 (d, 2C, J = 160.76 Hz,  $o-CH_3OC_6H_4-$ ), 122.78 (d, 1C, J = 171.66 Hz, -N=C-CH=CH-CH=CH-), 114.38 (d, 2C, J = 162.58 Hz, m- $CH_3OC_6H_4-$ ), 67.45 (t, 1C, J = 141.69 Hz,  $-NCH_3-CH_2-$ NC<sub>5</sub>H<sub>4</sub>-), 55.36 (q, 1C, J = 144.41 Hz, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 54.54 (q, 1C, J = 141.69 Hz,  $-NCH_3-CH_2-NC_5H_4-$ ). IR (solid neat; cm<sup>-1</sup>): 3108 (w), 3069 (w), 3054 (w), 3034 (w), 3001 (w), 2940 (w), 2830 (w), 1608 (m), 1509 (m), 1250 (s), 1185 (m), 1034 (s), 995 (w), 947 (m), 829 (w), 806 (s), 774 (m), 736 (s), 693 (m), 575 (w).

## 2.2.4 | 4-Methoxy-*N*-methyl-*N*-(pyridin-2ylmethyl) anilinezinc (II) chloride ([(L-c) ZnCl<sub>2</sub>])

**[(L-c)ZnCl<sub>2</sub>]** was prepared according to a similar procedure as described for **[(L-b)<sub>2</sub>ZnCl<sub>2</sub>]**, except utilizing **[Lc]** (0.400 g, 1.75 mmol) and **[ZnCl<sub>2</sub>]** (0.239 g, 1.75 mmol) to give a beige solid (0.429 g, 67.2%). X-ray quality crystals for **[(L-c)ZnCl<sub>2</sub>]** were obtained from layering of hexane (3.00 mL) on the chloroform solution (2.00 mL) of **[(Lc)ZnCl<sub>2</sub>]**. Analysis calculated for C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>OZn (%): C, 46.1; H, 4.42; N, 7.68. Found: C, 46.5; H, 4.43; N, 7.59. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 500 MHz,  $\delta$ , ppm): 8.52 (ddd, 1H, *J* = 4.73 Hz, -N=C-CH=CH-CH=CH-), 7.70 (td, 4 of 15 WILEY Organometallic Chemistry

1H, J = 7.78 Hz, -N=C-CH=CH-CH=CH-), 7.23 (ddd, 1H, J = 7.48 Hz, -N=C-CH=CH-CH=CH-), 7.15 (d, 1H, J = 7.78 Hz, -N=C-CH=CH-CH=CH-), 6.76 (d, 2H, J = 9.16 Hz,  $-CH_3OC_6H_4-$ ), 6.66 (d, 2H, J = 9.16 Hz, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 4.53 (s, 2H, -NCH<sub>3</sub>-CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-), 3.63 (s, 3H, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 3.00 (s, 3H, -NCH<sub>3</sub>-CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>–). <sup>13</sup>C-NMR (DMSO- $d_6$ , 125 MHz,  $\delta$ , ppm): 159.28 (s, 1C, ipso-N=C-CH=CH-CH=CH-), 151.16 (s, 1C, *ipso*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 149.17 (d, 1C, J = 178.02 Hz, -N=C-CH=CH-CH=CH-), 143.60 (s, 1C, ipso- $CH_3OC_6H_4-$ ), 137.10 (d, 1C, J = 162.58 Hz, -N=C-CH=CH-CH=CH-), 122.23 (d, 1C, J = 165.30 Hz, -N=C-CH=CH-CH=CH-), 121.39 (d, 1C, J = 163.49 Hz, -N=C-CH=CH-CH=CH-), 114.62 (d, 2C, J=158.95 Hz, 0-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 113.81 (d, 2C, J = 158.04 Hz, m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 58.46 (t, 1C, J = 136.24 Hz, -NCH<sub>3</sub>-CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-), 55.32 (q, 1C, J = 143.51 Hz, -CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 39.74 (q, 1C, J = 135.33 Hz,  $-NCH_3-CH_2-NC_5H_4-$ ). IR (solid neat; cm<sup>-1</sup>): 3077 (w), 3023 (w), 2988 (w), 2950 (w), 2927 (w), 2906 (w), 2833 (w), 1606 (m), 1572 (w), 1512 (s), 1442 (m), 1302 (m), 1253 (m), 1028 (s), 918 (m), 837 (s), 766 (m), 752 (m), 650 (w), 569 (m).

### 2.2.5 | 4-Methoxy-*N*-methyl-*N*-(pyridin-2ylmethyl) anilinecadmium (II) bromide ([(L-c)cd(μ-Br)Br]<sub>2</sub>)

 $[(L-c)Cd(\mu-Br)Br]_2$  was prepared according to a similar procedure as described for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>], except utilizing [L-c] (0.400 g, 1.75 mmol) and [CdBr<sub>2</sub>·4H<sub>2</sub>O] (0.602 g, 1.75 mmol) in anhydrous EtOH to give a beige solid (1.17 g, 66.8%). X-ray quality crystals for  $[(L-c)Cd(\mu-Br)]$  $\mathbf{Br}_{2}$  were obtained from slow diffusion of  $\mathbf{Et}_{2}\mathbf{O}$  (5.00) mL) into acetone solution (3.00 mL) of  $[(L-c)Cd(\mu-Br)]$ **Br**]<sub>2</sub>. Analysis calculated for  $C_{28}H_{32}Br_4Cd_2N_4O_2$  (%): C, 33.6; H, 3.22; N, 5.60. Found: C, 34.0; H, 3.29; N, 5.60. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ , ppm): 8.53 (ddd, 1H, J = 4.88 Hz, -N = C - CH = CH - CH = CH - ), 7.72 (td, 1H, J = 7.63 Hz, -N=C-CH=CH-CH=CH-), 7.25 (ddd, 1H, J = 7.32 Hz, -N=C-CH=CH-CH=CH-), 7.18 (d, 1H, J =7.78 Hz, -N=C-CH=CH-CH=CH-), 6.76 (d, 2H, J=9.31 Hz,  $-CH_3OC_6H_4-$ ), 6.70 (d, 2H, J = 9.31 Hz,  $-CH_{3-}$  $OC_6H_4$ -), 4.52 (s, 2H, -NCH<sub>3</sub>-CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-), 3.63 (s, 3H,  $-CH_3OC_6H_4$ -), 2.98 (s, 3H,  $-NCH_3-CH_2-NC_5H_4$ -). <sup>13</sup>C-NMR (DMSO- $d_6$ , 125 MHz,  $\delta$ , ppm): 158.83 (s, 1C, ipso-N=C-CH=CH-CH=CH-), 151.46 (s, 1C, ipso- $CH_3OC_6H_4-$ ), 149.15 (d, 1C, J = 178.02 Hz, -N=C-CH=CH-CH=CH-), 143.55 (s, 1C,  $ipso-CH_3OC_6H_4$ -), 137.10 (d, 1C, *J* = 163.49 Hz, -N=C-CH=CH-CH=CH-), 122.25 (d, 1C, *J* = 165.30 Hz, -N=C-CH=CH-CH=CH-), 121.54 (d, 1C, *J* = 163.49 Hz, -N=C-CH=CH-CH=CH-), 114.50 (d, 2C, J = 158.95 Hz,  $o-CH_3OC_6H_4-$ ), 114.46 (d, 2C, J = 158.04 Hz, m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>-), 58.46 (t, 1C, J = 135.33 Hz,  $-NCH_3$ -CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-), 55.27 (q, 1C, J = 143.51 Hz,  $-CH_3$ OC<sub>6</sub>H<sub>4</sub>-), 40.36 (q, 1C, J = 135.33 Hz,  $-NCH_3$ -CH<sub>2</sub>-NC<sub>5</sub>H<sub>4</sub>-). IR (solid neat; cm<sup>-1</sup>): 3073 (w), 3032 (w), 3015 (w), 3003 (w), 2976 (w), 2950 (w), 2927 (w), 2898 (w), 2827 (w), 1605 (w), 1572 (w), 1512 (s), 1447 (m), 1250 (m), 794 (s), 779 (m), 765 (m), 746 (w), 716 (m), 647 (w).

# 2.3 | Catalytic activity for methyl methacrylate polymerization

In a Schlenk flask, the complex (15.0 µmol, 5.84 mg for [(L-a)PdCl<sub>2</sub>], 5.23 mg for [(L-a)ZnCl<sub>2</sub>], 14.5 mg for [(L-a)Cd(µ-Br)Br]<sub>2</sub>, 5.87 mg for [(L-b)PdCl<sub>2</sub>], 8.47 mg for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>], 10.5 mg for [(L-b)<sub>2</sub>CdBr<sub>2</sub>], 6.08 mg for [(L-c)PdCl<sub>2</sub>], 5.47 mg for [(L-c)ZnCl<sub>2</sub>] and 15.0 mg for  $[(L-c)Cd(\mu-Br)Br]_2$ ) 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]<sub>0</sub>/[M (II)  $catalyst]_0 = 500$ ) as a co-catalyst. The solution was stirred for 20 min at 60°C. MMA (5.00 mL, 47.1 mmol and  $[MMA]_0/[M (II) catalyst]_0 = 3100)$  was added to the above reaction mixture and stirred for 2 hr to obtain a viscous solution. MeOH (2.00 mL) was added to terminate polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35.0% HCl (5.00 mL) was injected to remove the remaining co-catalyst (MMAO). The product was obtained by filtration and washed with MeOH (250 mL  $\times$  2) to yield PMMA, and dried under vacuum at 60°C for 12 hr.

### 2.4 | X-ray crystallographic studies

The X-ray quality single crystals were coated with paratone-N oil and the diffraction data measured at 100(2) K with synchrotron radiation ( $\lambda = 0.700$  Å) for  $[(L-a)ZnCl_2],$  $[(L-b)_2ZnCl_2], [(L-c)PdCl_2], [(L-c)$ ZnCl<sub>2</sub>] and  $[(L-c)Cd(\mu-Br)Br]_2$  on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory, South Korea. The PAL BL2D-SMDC program<sup>[51]</sup> 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)<sup>[52]</sup> was used for cell refinement, reduction and absorption correction. An orange cubic-shaped crystal of [(L-b)PdCl<sub>2</sub>] and a colorless cubic-shaped crystal of [(L-b)<sub>2</sub>CdBr<sub>2</sub>] were picked up with paraton-N oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphitemonochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation source under nitrogen cold stream [200(2) K] at the Western

Seoul Center of Korea Basic Science Institute. Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001) software packages.<sup>[53]</sup> Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS.<sup>[54]</sup> All measured structures were solved by dual-space algorithms related with intrinsic phasing using SHELXT-2018/2,<sup>[55]</sup> and refined by full-matrix least-squares refinement using the SHELXL-2018/3<sup>[56]</sup> computer program. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2018/3 computer program. Crystallographic refinements and structural data are summarized in Table 1.

### **3** | **RESULTS AND DISCUSSION**

### 3.1 | Synthesis and chemical properties

Ligands ( $L_n = L-a-L-c$ ) in the current study were synthesized as reported previously.<sup>[25,45–47]</sup> Complexes, **[(L)**  $_{m}MX_{2}]_{m}$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2; 67–98% yields), were obtained by direct ligation of metal starting materials with ligands in 1:1 ratio in CH<sub>3</sub>CN or EtOH at ambient temperature (Scheme 1). The structures of these complexes were <sup>13</sup>C-NMR, by <sup>1</sup>H-NMR, Fourier characterized transform-infrared (FT-IR) and X-ray diffraction. <sup>1</sup>H-NMR spectra were consistent with ligands and Zn (II), Pd (II) and Cd (II) complexes formulation. <sup>1</sup>H-NMR peaks of the metal complexes were shifted to low field by approximately  $\delta$  0.01–4.68 compared with ligands due to the resonance effects of the N and C atoms of the donating moieties of ligand. Characteristic C-H peaks in the IR spectra were observed at 3108, 3077 and  $3073 \text{ cm}^{-1}$  for  $[(L-c)ZnCl_2]$ ,  $[(L-c)PdCl_2]$  and  $[(L-c)PdCl_2]$ c)Cd(µ-Br)Br]<sub>2</sub>, respectively. Moreover, the N-H stretching band appeared at 3240 and  $3235 \text{ cm}^{-1}$  for [(L-b)<sub>2</sub>ZnCl<sub>2</sub>] and [(L-b)<sub>2</sub>CdBr<sub>2</sub>], respectively. A considerable difference in IR stretching band for >C=Ngroup is observed due to complexation and appeared at (1600–1603 cm<sup>-1</sup>) range. Elemental analysis of the synthesized complexes was consistent with the proposed structures in Scheme 1 and confirmed the purity of the isolated complexes,  $[(L)_n M X_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2). All the synthesized complexes were stable in the air and could be stored for months at room temperature.

### 3.2 | Description of molecular structures

The ORTEP drawings of synthesized complexes are shown in Figure 1 ([(L-a)ZnCl<sub>2</sub>]), Figure 2 ([(L-b)<sub>2</sub>ZnCl<sub>2</sub>]), Figure 3 ([(L-b)PdCl<sub>2</sub>]), Figure 4 ([(L-b)<sub>2</sub>CdBr<sub>2</sub>]), Figure 5 ([(L-c)ZnCl<sub>2</sub>]), Figure 6 ([(L-c) PdCl<sub>2</sub>]) and Figure 7 ([(L-c)Cd( $\mu$ -Br)Br]<sub>2</sub>). The selected bond lengths and angles are listed in Table 2. [(L-a) ZnCl<sub>2</sub>] crystallized in the triclinic system with the *P*1 space group. The synthesized complexes, [(L-c)MCl<sub>2</sub>] (M = Zn and Pd) and [(L-b)<sub>2</sub>MX<sub>2</sub>] (M = Zn; X = Cl; M = Cd; X = Br), crystallized in the monoclinic system with the *P*2<sub>1</sub>/*c* space groups, while [(L-b)PdCl<sub>2</sub>] and [(L-c) Cd( $\mu$ -Br)Br]<sub>2</sub> crystallized in the orthorhombic system with *Pbca* space groups.

Pd (II) atom adopted slightly distorted square planar geometry in **[(L)PdCl<sub>2</sub>]** (L = L-b and L-c) by coordinating with two N atoms of bidentate ligand and two chloro ligands (Figures 3 and 6).<sup>[14,25,46,49]</sup> The bond lengths of Pd-N<sub>pyridine</sub> in **[(L)PdCl<sub>2</sub>]** (L = L-b and L-c) were in the range of 2.024(3)-2.026(4) Å, while that of Pd-N<sub>amine</sub> ranged from 2.053(4) to 2.094(3) Å, similar to the Pd-N bond length of square planar Pd (II) complexes.  $^{[12,25,46]}$  The Pd-N<sub>pyridine</sub> bond length in [(L-b) PdCl<sub>2</sub>] differs by approximately 0.002 Å compared with [(L-c)PdCl<sub>2</sub>]. On the other hand, the length of Pd-Namine length was longer by about 0.04 Å in [(L-c)PdCl<sub>2</sub>]. The Pd-Cl<sub>terminal</sub> bond lengths ranged from 2.2876(1) to 2.3166(1) Å. The N(2)-C(6) distances of 1.499(6) Å  $([(L-b)PdCl_2])$  and 1.498(3) Å  $([(L-c)PdCl_2])$  were in the range of accepted carbon-nitrogen single bonds. The C(5)-C(6) bond distances of the complexes ranged from 1.489(3) to 1.495(7) Å. The Me subsistent at the amine moiety slightly affected the bond lengths in [(Lc)PdCl<sub>2</sub>].

The N<sub>pyridine</sub>-Pd(1)-Cl<sub>terminal</sub> and N<sub>amine</sub>-Pd(1)-Cl<sub>terminal</sub> angles in **[LPdCl<sub>2</sub>]** (L = L-b and L-c) were nearly linear in the range of 170.52(1)–176.67(5)°. The average N<sub>pyridine</sub>-Pd(1)-N<sub>amine</sub> bond angles of fivemembered rings ranged from  $81.51(8)^\circ$  to  $82.55(2)^\circ$ , and were slightly affected by substituents of amine moieties. The Cl<sub>terminal</sub>-Pd(1)-Cl<sub>terminal</sub> angles in **[(L)PdCl<sub>2</sub>]** (L = L-b and L-c) agree well with the traditional angles for square-planar Pd (II)<sup>[14,25,46,49]</sup> and Pt (II)<sup>[46]</sup> complexes.

The geometry of  $[(L)ZnCl_2]$  (L = L-a and L-c) can be best described as distorted tetrahedral around the Zn center (Figures S1 and 5). The Zn-N<sub>pyridine</sub> lengths lie in the 2.0551(1)–2.1844(2) Å range. The Zn-N<sub>imine</sub> and Zn-Namine lengths in  $[(L)ZnCl_2]$  (L<sub>n</sub> = L-a and L-c) were found to be 2.088(2) and 2.1107(1) Å, respectively, similar to the Zn-N bond lengths of tetrahedral Zn (II) complexes.<sup>[10,49,57]</sup> The Zn-Cl<sub>terminal</sub> bond lengths ranged from 2.1940(5) to 2.2186(1) Å. The N(2)-C(6) distance of

CITATIN CITATING ALLA ALLA ALLA ALLA ALLA ALLA ALLA AL		$[(\pi - \pi)^m (2 \nabla \pi M)^m]$	a-n-v, m – 200, 1 u, v	– CI, IM – CU, A – L	11, 11, 111 – 1 UL 4)		
	[(L-a)ZnCl <sub>2</sub> ]	[(L-b)PdCl <sub>2</sub> ]	[(L-b) <sub>2</sub> ZnCl <sub>2</sub> ]	[(L-b) <sub>2</sub> CdBr <sub>2</sub> ]	[(L-c)PdCl <sub>2</sub> ]	$[(L-c)ZnCl_2]$	$[(L-c)Cd(\mu-Br)Br]_2$
Empirical formula	$C_{13}H_{12}Cl_2N_2OZn$	$\mathrm{C}_{13}\mathrm{H}_{14}\mathrm{Cl}_2\mathrm{N}_2\mathrm{OPd}$	$C_{26}H_{28}Cl_2N_4O_2Zn$	$C_{26}H_{28}Br_2N_4O_2Cd$	$\mathrm{C}_{14}\mathrm{H}_{16}\mathrm{Cl}_{2}\mathrm{N}_{2}\mathrm{OPd}$	$C_{14}H_{16}Cl_2N_2OZn$ CHCl <sub>3</sub>	$C_{28}H_{32}Br_4N_4O_2Cd_2$
Formula weight	348.52	391.56	564.79	700.74	405.59	483.92	1001.01
Temperature/K	100(2)	200(2)	100(2)	200(2)	100(2)	100(2)	100(2)
Wavelength/Å	0.700	0.71073	0.700	0.71073	0.700	0.700	0.700
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<u>PI</u>	Pbca	$P2_1/c$	$P2_1/_C$	$P2_1/_C$	$P2_1/_C$	Pbca
a/Å	7.9660(2)	10.2826(4)	6.6880(1)	6.9984(4)	14.860(3)	13.568(3)	15.926(3)
b/Å	9.3610(2)	14.3166(5)	14.597(3)	14.5904(8)	13.295(3)	9.895(2)	11.010(2)
c/Å	10.081(2)	19.4305(7)	12.236(2)	12.7323(8)	16.310(3)	15.623(3)	18.268(4)
α/ °	81.14(3)						
B/ °	81.90(3)		93.28(3)	91.8880(1)	109.17(3)	108.43(3)	
۰ / <i>۸</i>	70.82(3)						
Volume/Å <sup>3</sup> Z,	698.2(3), 2	2860.40(2), 8	1192.6(4), 2	1299.38(1), 2	3043.5(1), 8	1989.9(8), 4	3203.2(1), 4
Density (calculated) $/mg m^{-3}$	1.658	1.818	1.573	1.791	1.770	1.615	2.076
Absorption coefficient/mm <sup>-1</sup>	1.965	1.663	1.172	3.946	1.374	1.838	6.088
Absorption correction value	$T_{\rm min} = 0.481$ $T_{\rm max} = 1.268$	none	$T_{\rm min} = 0.218$ $T_{\rm max} = 1.039$	$T_{\rm min} = 0.218$ $T_{\rm max} = 1.039$	$T_{\rm min} = 0.240$ $T_{\rm max} = 1.234$	$T_{\rm min} = 0.905$ $T_{\rm max} = 1.000$	$T_{\rm min} = 0.874$ $T_{\rm max} = 1.000$
F(000)	352	1552	584	692	1616	976	1920
Crystal size/mm <sup>3</sup>	$0.10 \times 0.07 \times 0.03$	$0.18\times0.17\times0.13$	$0.08\times0.05\times0.03$	$0.28 \times 0.19 \times 0.18$	$0.10\times0.06\times0.03$	$0.08 \times 0.07 \times 0.03$	$0.10 \times 0.08 \times 0.04$
Reflections collected/unique	5618	20103	9307	9235	24 125	15 908	24 877
Independent reflections	3143	3555	2952	3205	7494	4883	4027
Data/restraints/parameters	3143/0/173	3555/0/173	2952/0/161	3205/0/161	7494/0/365	4883/0/219	4027/0/183
Goodness-of-fit on $F^2$	1.085	1.066	1.136	1.245	0.955	1.081	1.065
Final R indices $[I > 2$ sigma $(I)$ ]	$R_1 = 0.0418$ $wR_2 = 0.1136$	$R_1 = 0.0408$ $wR_2 = 0.0851$	$R_1 = 0.0351$ $wR_2 = 0.0897$	$R_1 = 0.0503$ $wR_2 = 0.1011$	$R_1 = 0.0277$ $wR_2 = 0.0599$	$R_1 = 0.0265$ $wR_2 = 0.0692$	$R_1 = 0.0307$ $wR_2 = 0.0795$
R indices (all data)	$R_1 = 0.0480$ $wR_2 = 0.1165$	$R_1 = 0.0907$ $wR_2 = 0.1217$	$R_1 = 0.0398$ $wR_2 = 0.0910$	$R_1 = 0.0945$ $wR_2 = 0.1897$	$R_1 = 0.0425$ $wR_2 = 0.0630$	$R_1 = 0.0293$ $wR_2 = 0.0701$	$R_1 = 0.0328$ $wR_2 = 0.0805$

= 1 or 2) Ш c: M = Zn. Pd: X = Cl: M = Cd: X = Br: n. = L-a-LŪ refinement for I(L), MX,1structure Crystal data and **TABLE 1** 



**SCHEME 1** Synthesis of ligands [L] (L = L-a-L-c) and complexes  $[(L)_n M X_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2)



FIGURE 1 ORTEP drawing of [(L-a)ZnCl<sub>2</sub>] with thermal ellipsoids at 70% probability. All hydrogen atoms are omitted for clarity

C13 CO C10 01 C12 C11 CI1#1 C1 CI1 C1#1 C12#1 C11#1 01#1 C10#1 C2#1 C7# C9#1 C5#1 C8#1 C13#1 C6#1 C3#1 C4#1

FIGURE 2 ORTEP drawing of [(L-b)2ZnCl2] with thermal ellipsoids at 70% probability. All hydrogen atoms are omitted for clarity

1.286(3) Å in [(L-a)ZnCl<sub>2</sub>] and 1.4827(2) Å in [(L-c) ZnCl<sub>2</sub>] were in the range of accepted carbon-nitrogen single or double bonds, respectively. The C(5)-C(6) bond distances of the complexes ranged from 1.470(3) to 1.510(2) Å, reflecting the lack of delocalized  $\pi$ -electrons in the pyridine ring. The average N<sub>pyridine</sub>-Zn(1)-N<sub>amine</sub> and  $Cl_{terminal}$ -Zn(1)-Cl<sub>terminal</sub> bond angles ranged from 80.92(8)° to 82.19(5)° and 114.06(3)° to 119.03(2)°,



**FIGURE 3** ORTEP drawing of **[(L-b)PdCl<sub>2</sub>]** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity



**FIGURE 4** ORTEP drawing of **[(L-b)<sub>2</sub>CdBr<sub>2</sub>]** with thermal ellipsoids at 60% probability. All hydrogen atoms are omitted for clarity



**FIGURE 5** ORTEP drawing of **[(L-c)ZnCl<sub>2</sub>'CHCl<sub>3</sub>]** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity



**FIGURE 6** ORTEP drawing of **[(L-c)PdCl<sub>2</sub>]** with thermal ellipsoids at 70% probability. All hydrogen atoms are omitted for clarity



**FIGURE 7** ORTEP drawing of  $[(L-c)Cd(\mu-Br)Br]_2$  with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity

respectively, which agreed well with the angles reported in related Zn  $(II)^{[49]}$  systems.

The molecular structures of six-coordinated **[(L-b)**<sub>2</sub>**MX**<sub>2</sub>**]** (M = Zn; X = Cl; M = Cd; X = Br) complexes revealed an octahedral geometry around Zn and Cd centers through 2-equivalents ligands ([L-b]), included two N atoms of pyridine moieties, two N atoms of 4methoxyaniline moieties and two halogen ligands, resulting in the formation of two five-membered rings (Figures 2 and 4).<sup>[11,15,58]</sup> The bond lengths of M-N<sub>pyridine</sub> and M-N<sub>amine</sub> in **[(L-b)**<sub>2</sub>**MX**<sub>2</sub>**]** (M = Zn; X = Cl; M = Cd; X = Br) were similar to the M-N bond length of octahedral M (II) complexes.

The M-N<sub>pyridine</sub> length differs by approximately 0.2 Å, ranging in size from  $[(L-b)_2ZnCl_2] < [(L-b)_2CdBr_2]$ . Moreover, the length of Cd-N<sub>amine</sub> was longer than Zn-

																		**1		Chemis	stry
	Br]2		2.281(2)	2.494(3)	2.6082(5)	2.5318(4)	2.8420(5)	1.477(3)	1.481(3)	1.503(4)	1.424(4)		72.89(8)	111.06(6)	96.87(5)	128.16(6)	93.24(6)	91.19(6)	160.96(5)	120.224(2)	109.3(2)
	[(L-c)Cd(μ-Br)]		2.0551(1) Cd(1)-N(1)	2.1107(1) Cd(1)-N(2)	2.1940(5) Cd(1)-Br(1)	2.2108(6) Cd(1)-Br(2)	1.3440(2) Cd(1)-Br(1) <sup>#1</sup>	1.4827(2) N(2)-C(6)	1.4926(2) N(2)-C(7)	1.510(2) C(5)-C(6)	1.419(2) O(1)-O(14)		82.19(5) N(1)-Cd(1)- N(2)	112.49(5) N(1)-Cd(1)- Br(2)	108.09(4) N(2)-Cd(1)- Br(2)	116.14(4) N(1)-Cd(1)- Br(1)	112.76(4) N(2)-Cd(1)- Br(1)	119.03(2) N(1)-Cd(1)- Br(1) <sup>#1</sup>	119.50(1) N(2)-Cd(1)- Br(1) <sup>#1</sup>	109.15(1) Br(1)-Cd(1)- Br(2)	102.31(9) C(6)-N(2)-C(7)
3r; $n, m = 1$ or 2)	$[(L-c)ZnCl_2]$		2.0243(3) Zn(1)-N(1)	2.0935(3) Zn(1)-N(2)	2.2949(1) Zn(1)-Cl(1)	2.2973(1) Zn(1)-Cl(2)	1.351(3) N(1)-C(5)	1.498(3) N(2)-C(6)	1.499(3) N(2)-C(7)	1.489(3) C(5)-C(6)	1.423(3) O(1)-C(14)		81.51(8) N(1)-Zn(1)- N(2)	93.24(6) N(1)-Zn(1)- Cl(1)	174.53(5) N(2)-Zn(1)- Cl(1)	176.67(5) N(1)-Zn(1)- Cl(2)	95.26(5) N(2)-Zn(1)- Cl(2)	90.01(3) Cl(1)-Zn(1)- Cl(2)	119.6(2) C(1)-N(1)- C(5)	107.59(2) C(6)-N(2)- C(7)	102.54(1) C(6)-N(2)- Zn(1)
d; $X = CI$ ; $M = Cd$ ; $X = I$	[(L-c)PdCl <sub>2</sub> ]		2.378(7) Pd(1)-N(1)	2.378(7) Pd(1)-N(2)	2.398(8) Pd(1)-Cl(1)	2.398(8) Pd(1)-Cl(2)	2.7109(1) N(1)-C(5)	2.7109(1) N(2)-C(6)	1.475(1) N(2)-C(7)	1.430(1) C(5)-C(6)	1.425(1) O(1)-C(14)		70.2(3) N(1)-Pd(1)- N(2)	109.8(3) N(1)-Pd(1)- Cl(1)	180.0 N(2)-Pd(1)- Cl(1)	180.0 N(1)-Pd(1)- Cl(2)	89.75(2) N(2)-Pd(1)- Cl(2)	86.33(2) Cl(1)-Pd(1)- Cl(2)	90.25(2) C(1)-N(1)- C(5)	93.61(2) C(6)-N(2)- C(7)	180.00(3) C(6)-N(2)- Pd(1)
$[2]_m$ (L = L-a-L-c; M = Zn, P	[(L-b) <sub>2</sub> CdBr <sub>2</sub> ]		2.1844(2) Cd(1)-N(1)	2.1844(2) Cd(1)-N(1) <sup>#1</sup>	2.2090(2) Cd(1)-N(2)	2.2090(2) Cd(1)-N(2) <sup>#1</sup>	2.4737(7) Cd(1)-Br(1)	2.4737(7) Cd(1)-Br(1) <sup>#1</sup>	1.4708(2) N(2)-C(6)	1.4340(2) N(2)-C(7)	1.4318(2) O(1)-C(11)		74.77(5) N(1)-Cd(1)- N(2)	105.23(5) N(1)-Cd(1)- N(2) <sup>#1</sup>	180.0 N(2)-Cd(1)- N(2) <sup>#1</sup>	180.0 N(1) <sup>#1</sup> -Cd(1)- N(1)	88.60(4) N(1)-Cd(1)- Br(1)	86.35(4) N(2)-Cd(1)- Br(1)	91.40(4) N(1)-Cd(1)- Br(1) <sup>#1</sup>	93.65(4) N(2)-Cd(1)- Br(1) <sup>#1</sup>	180.0 Br(1)-Cd(1)- Br(1) <sup>#1</sup>
) and angles (°) of <b>[(L)</b> <sub>n</sub> MX	$[(L-b)_2ZnCl_2]$		2.026(4) Zn(1)-N(1)	2.053(4) Zn(1)-N(1) <sup>#1</sup>	2.3166(1) Zn(1)-N(2)	2.2876(1) Zn(1)-N(2) <sup>#1</sup>	1.354(6) Zn(1)-Cl(1)	1.499(6) Zn(1)-Cl(1) <sup>#1</sup>	1.460(6) N(2)-C(6)	1.495(7) N(2)-C(7)	1.436(6) O(1)-C(13)		82.55(2) N(1)-Zn(1)- N(2)	95.00(1) N(1)-Zn(1)- $N(2)^{\#1}$	174.19(1) N(2)-Zn(1)- N(2) <sup>#1</sup>	170.52(1) N(1) <sup>#1</sup> -Zn(1)- N(1)	90.24(1) N(1)-Zn(1)- Cl(1)	92.74(5) N(2)-Zn(1)- Cl(1)	119.5(4) N(1)-Zn(1)- Cl(1) <sup>#1</sup>	114.1(4) N(2)-Zn(1)- Cl(1) <sup>#1</sup>	105.8(3) Cl(1)-Zn(1)- Cl(1) <sup>#1</sup>
$\mathfrak s$ selected bond lengths (Å)	[(L-b)PdCl <sub>2</sub> ]		2.068(2) Pd(1)-N(1)	2.088(2) Pd(1)-N(2)	2.2172(8) Pd(1)-Cl(1)	2.2186(1) Pd(1)-Cl(2)	1.349(3) N(1)-C(5)	1.286(3) N(2)-C(6)	1.425(3) N(2)-C(7)	1.470(3) C(5)-C(6)	1.437(3) O(1)-C(11)		80.92(8) N(1)-Pd(1)- N(2)	111.21(6) N(1)-Pd(1)- Cl(1)	121.06(7) N(2)-Pd(1)- Cl(1)	116.94(7) N(1)-Pd(1)- Cl(2)	108.88(7) N(2)-Pd(1)- Cl(2)	114.06(3) Cl(1)-Pd(1)- Cl(2)	118.7(2) C(1)-N(1)- C(5)	120.7(2) C(6)-N(2)- C(7)	111.13(2) C(6)-N(2)- Pd(1)
TABLE 2 The	[(L-a)ZnCl <sub>2</sub> ]	Bond lengths	Zn(1)-N(1)	Zn(1)-N(2)	Zn(1)-Cl(1)	Zn(1)-Cl(2)	N(1)-C(5)	N(2)-C(6)	N(2)-C(7)	C(5)-C(6)	O(1)-C(13)	Bond angles	N(1)-Zn(1)- N(2)	N(1)-Zn(1)- Cl(1)	N(2)-Zn(1)- Cl(1)	N(1)-Zn(1)- Cl(2)	N(2)-Zn(1)- Cl(2)	Cl(1)-Zn(1)- Cl(2)	C(1)-N(1)- C(5)	C(6)-N(2)- C(7)	C(6)-N(2)- Zn(1)

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(Continues)

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L-a)ZnCl <sub>2</sub> ]	[(L-b)PdCl <sub>2</sub> ]	$[(L-b)_2 ZnCl_2]$	$[(L-b)_2CdBr_2]$	[(L-c)PdCl <sub>2</sub> ]	[(L-c)ZnCl <sub>2</sub> ]	[(L-c)Cd(µ-Br)B	<b>r</b> ] <sub>2</sub>
C(8)-C(7)- N(2)	123.0(2) C(8)-C(7)- N(2)	120.0(4) C(6)-N(2)-C(7)	116.28(1) C(6)-N(2)-C(7)	118.4(7) C(9)-C(8)- N(2)	123.67(2) C(9)-C(8)- N(2)	123.60(1) C(6)-N(2)- Cd(1)	99.51(2)
C(12)-C(7)- N(2)	117.4(2) C(13)-C(7)- N(2)	120.0(4) C(6)-N(2)- Zn(1)	105.29(1) C(6)-N(2)- Cd(1)	104.6(5) C(8)-N(2)- C(7)	108.57(2) C(8)-N(2)- C(7)	109.95(1) C(8)-N(2)-C(7)	112.6(2)
C(10)-O(1)- C(13)	117.49(2) C(10)-O(1)- C(11)	117.4(4) C(10)-O(1)- C(13)	116.57(1) C(10)-O(1)- C(11)	117.8(8) C(11)-O(1)- C(14)	117.76(2) C(11)-O(1)- C(14)	117.00(1) C(11)-O(1)- C(14)	117.2(2)

**TABLE 2** (Continued)

 $N_{amine}$  by about 0.2 Å [Zn- $N_{amine}$  = 2.2090(2) Å, Cd- $N_{amine}$  = 2.398(8) Å]. The average equatorial bond lengths, Zn-(*L*-*b*)<sub>eq</sub> and Cd-(*L*-*b*)<sub>eq</sub>, are 2.197(1) and 2.388(1) Å, respectively. The axial bond lengths related with halogen ligands in **[(L-b)<sub>2</sub>ZnCl<sub>2</sub>]** and **[(L-b)<sub>2</sub>CdBr<sub>2</sub>]** are 2.4737(7) and 2.2.7109(1) Å, respectively. The **[(L-b)<sub>2</sub>CdBr<sub>2</sub>]** bond lengths are much longer than the **[(L-b)<sub>2</sub>ZnCl<sub>2</sub>]** bond lengths, which can be attributed to size effects of the coordinated metal ions. The average bond angles N(1)-M(1)-N(2) ranged from 70.2(3)° to 74.77(5)°, and the N(1)-M(1)-N(1)<sup>#1</sup>, N(2)-M(1)-N(2)<sup>#1</sup> and X(1)-M(1)-X(1)<sup>#1</sup> were linear, corresponding to similar angles in literature.

The dimeric Cd (II) complex, [(L-c)Cd(µ-Br)Br]<sub>2</sub>, exhibited a distorted trigonal bipyramidal geometry around Cd center, coordinating via two N atoms of 4methoxy-N-methyl-N-(pyridin-2-ylmethyl) aniline ligand, two bridged bromides and one terminal bromide. Cd-N-<sub>pyridine</sub> length in  $[(L-c)Cd(\mu-Br)Br]_2$  was 2.281(2)Å, while that of Cd–N<sub>amine</sub> was 2.494(3) Å, [50,59-61] and the Cd-Br<sub>bridged</sub>, Cd-Br<sub>terminal</sub> and Cd-Br<sub>bridged</sub><sup>#1</sup> bond lengths were 2.6082(5) Å, 2.5318(4) Å and 2.8420(5) Å, respectively. The base of the pyramid has been constructed from bidentate imine ligand and Brbridged<sup>#1</sup> ligand, whereas the axial positions are occupied by terminal and Br<sub>bridged</sub> ligands. It has been observed that axial bromo ligand length is longer compared with equatorial bromo ligand. The N<sub>pyridine</sub>-Cd(1)-Br<sub>bridged</sub>, N<sub>amine</sub>-Cd(1)-Br<sub>terminal</sub>, N<sub>pyridine</sub>-Cd(1)-Br<sub>terminal</sub> and Br<sub>terminal</sub>-Cd(1)-Br<sub>bridged</sub> angles for [(L-c)Cd( $\mu$ -Br)Br]<sub>2</sub> were 128.16(6)°, 96.87(5)°, 111.06(6)° and 120.224(2)°, respectively. N<sub>pyridine</sub>-Cd(1)-N<sub>amine</sub> angle was 72.89(8)°, whereas  $N_{amine}$ -Cd(1)-Br<sub>bridged</sub><sup>#1</sup> angle in [(L-c)Cd( $\mu$ -Br)Br]<sub>2</sub> was 160.96(5)°.

The new geometric parameters for the 4-coordinate compounds ( $\tau_4$ ) as improved simple metrics for quantitatively evaluating the geometry are presented in Table 3.<sup>[62]</sup> We have observed the degree of distortion based on the bond angles around the Pd and Zn centers using these structure indexes ( $\tau_4$ ). The  $\tau_4$  value of **[(L) PdCl<sub>2</sub>]** (L = L-a and L-c) and **[(L-a)PtCl<sub>2</sub>]** showed a square planar geometry distorted by 0.00695–0.108°, whereas **[(L)ZnCl<sub>2</sub>]** (L = L-a and L-c) showed a tetrahedral geometry distorted by 0.866–0.885°.

Similarly, from comparison of  $N_{imine}$ -Cd- $N_{pyridine}$ angles for  $[(L-a)Cd(\mu-Br)Br]_2$  (72.3°)<sup>[50]</sup> and [(L-c) $Cd(\mu-Br)Br]_2$  [72.89(8)°] along with 5-coordinate structure indices ( $\tau_5$ ) values it has been concluded that  $[(L-a)Cd(\mu-Br)Br]_2$  showed more distorted trigonal bipyramidal geometry compared with  $[(L-c)Cd(\mu-Br)Br]_2$ . The  $\tau_5$  value of  $[(L-a)Cd(\mu-Br)Br]_2$  (0.600) and  $[(L-c)Cd(\mu-Br)Br]_2$  (0.546) depending on the bond angles around the metal center showed trigonal **TABLE 3** Four-coordinate geometry indices ( $\tau_4$ ) for [(L)MCl<sub>2</sub>] (L = L-a-L-c; M = Zn, Pd) and representative examples from the literature

Complexes	Geometry	$ au_4$	<i>THC</i> <sub>DA</sub> /100	FCGP/100	Reference
Square planar (D <sub>4h</sub> )	Square planar	0.00	-1.43	-0.400	[62]
[(L-a)PdCl <sub>2</sub> ] <sup>a,b</sup>	Square planar	0.00695	-1.33	-0.249	[48]
[(L-a)ZnCl <sub>2</sub> ] <sup>c</sup>	Tetrahedral	0.866	0.395	0.349	[49]
[(L-b)PdCl <sub>2</sub> ] <sup>c</sup>	Square planar	0.108	-1.26	-0.200	[46]
[(L-c)PdCl <sub>2</sub> ]	Square planar	0.0626	-1.34	-0.265	This work
[(L-c)ZnCl <sub>2</sub> ]	Tetrahedral	0.885	0.432	0.452	This work
Tetrahedral $(T_d)$	Tetrahedral	1.00	1.00	0.00	[62]

<sup>a</sup>Assume that the geometry of [(L-a)PdCl<sub>2</sub>] is 4-coordinated.

<sup>b</sup>Four-coordinate geometry indices of [(L-a)PdCl<sub>2</sub>] are calculated using CIF file of [(L-a)PtCl<sub>2</sub>].<sup>[63]</sup>

<sup>c</sup>Although complex of **[(L-a)ZnCl<sub>2</sub>]** and **[(L-b)PdCl<sub>2</sub>]** is reported in the literature<sup>[46,49]</sup> with no X-ray crystallographic structure so CIF file of it is not available. In this work, we investigated the X-ray crystallographic structures.

**TABLE 4** Five-coordinate geometry indices ( $\tau_5$ ) for  $[(L)Cd(\mu-Br)Br]_2$  (L = L-a and L-c) and representative examples from the literature

Complexes	Geometry	$ au_5$	Reference
trigonal bipyramidal	trigonal bipyramidal	1.00	[64,65]
[(L-a)Cd(µ-Br)Br] <sub>2</sub>	trigonal bipyramidal	0.600	[50]
[(L-c)Cd(µ-Br)Br] <sub>2</sub>	trigonal bipyramidal	0.546	This work
square-pyramidal	square-pyramidal	0.00	[64,65]

bipyramidal geometry distorted by 0.546–0.600°, while an ideal trigonal bipyramidal arrangement has  $\tau_5$  value 14;= 1 (Table 4).<sup>[64,65]</sup>

Further, the plane angles between 4-methoxyaniline moiety and the plane of metal and pyridine were 6.010° for  $[(L-a)ZnCl_2]$ , 59.21° for  $[(L-b)_2ZnCl_2]$ , 77.51° for  $[(L-b)PdCl_2]$ , 59.81° for  $[(L-b)_2CdCl_2]$ , 34.60° for  $[(L-c)ZnCl_2]$ , 80.16° for  $[(L-c)PdCl_2]$  and 70.68° for  $[(L-c)Cd(\mu-Br)Br]_2$ , respectively.

### 3.3 | Methyl methacrylate polymerization

As a part of our ongoing investigations towards the stereoselective MMA catalyst based on pyridinylmethanimine moiety, the catalytic capabilities of 4-methoxy-N-(pyridin-2-ylmethylene) aniline-based Zn (II), Pd (II) and Cd (II) complexes were investigated for MMA polymerization in the presence of MMAO in toluene at 60°C. All the synthesized complexes polymerized MMA, yielding PMMA with  $T_{g}$  ranging from 121 to 128°C.<sup>[66]</sup> The polymers were isolated as white solids and characterized by GPC in THF using standard polystyrene as the reference. The polymerization results, including tacticity based on the isotactic (mm), heterotactic (mr) and syndiotactic (rr),<sup>[29,30,67,68]</sup> and PDI, which represent the average degree of polymerization in terms of the number of structural units and molecules, are summarized in Table 5.

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The catalytic activity of all the complexes showed a general tendency of L-a > L-c > L-b at 60°C, with the exception of  $[(L-b)PdCl_2]$ . The imine-bearing complexes  $[(L-a)MX_2]$  (M = Zn; X = Cl; M = Cd; X = Br) exhibited catalytic activities twice as high as the corresponding metal precursors/salts. However, the catalytic activity of  $[(L-b)PdCl_2]$  was much greater than  $[(L-a)PdCl_2]$ , presumably the electron-rich cloud around the Pd metal in  $[(L-b)PdCl_2]$  by amine ligand provided increased activity compared with the electronic effect of imine ligand.

It can be seen that  $[(L-b)_2MX_2]$  (M = Zn; X = Cl; M = Cd; X = Br) exhibited lower activities, which might be due to the fact that two equivalent amine and two halogen ligands around the metal center generate a coordination sphere that could not effectively accommodate any steric clashes between the incoming monomer, propagating polymer chain and ligand architecture during MMA polymerization. In addition, the catalyst's solubility in reaction media has significantly affected the catalytic activities.  $[(L-c)Cd(\mu-Br)Br]_2$  owing to its poor solubility exhibited lower activity (Table 5, entry 17).

To evaluate the total steric hindrance by ligands toward the metal center, it can be predicted and quantitatively calculated by comparison through a topographic steric map of  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X **TABLE 5** Polymerization of MMA by  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2) complexes in the presence of MMAO

		Yield <sup>b</sup>	Activity <sup>c</sup>	$T_{\rm g}^{\ \rm d}$		Tactici	ty	$M_{ m w}^{ m e}$	$M_{\rm w}/$
Entry	Catalysts <sup>a</sup>	(g)	$(\text{g mol}^{-1} \text{ Cat } \text{hr}^{-1}) \times 10^4$	(°C)	% <b>mm</b>	% <b>mr</b>	%rr	$(g \text{ mol}^{-1}) \times 10^5$	$M_{\rm n}^{\rm f}$
1	[PdCl <sub>2</sub> ] <sup>g</sup>	12.6	1.97	129	10.2	23.5	67.7	9.27	1.58
2	[ZnCl <sub>2</sub> ] <sup>g</sup>	11.1	1.73	129	9.20	24.2	66.6	1.33	1.58
3	$[CdBr_2 \cdot 4H_2O]^g$	10.2	1.58	131	7.60	22.8	69.6	0.66	2.90
4	MMAO <sup>h</sup>	6.83	1.07	120	37.2	10.9	51.9	6.78	2.09
5	[(L-a)PdCl <sub>2</sub> ] <sup>i</sup>	22.9	3.58	128	10.3	20.7	69.0	10.8	2.96
6	[(L-a)ZnCl <sub>2</sub> ] <sup>i</sup>	19.9	3.10	124	7.43	25.0	67.6	9.14	2.62
7	$[(L-a)Cd(\mu-Br)Br]_2^i$	21.6	3.37	121	7.04	22.5	70.4	9.78	2.49
8	[(L-b)PdCl <sub>2</sub> ] <sup>i</sup>	24.3	3.80	123	7.43	25.0	67.6	9.12	2.46
9	[(L-b) <sub>2</sub> ZnCl <sub>2</sub> ]	14.1	2.20	126	6.94	23.6	69.4	9.52	2.40
10	[(L-b) <sub>2</sub> CdBr <sub>2</sub> ]	12.9	2.02	126	6.99	23.1	69.9	9.55	2.54
11	[(L-c)PdCl <sub>2</sub> ]	19.8	3.08	126	7.53	24.0	68.5	9.62	2.54
12	[(L-c)ZnCl <sub>2</sub> ]	14.3	2.23	121	7.69	23.1	69.9	10.2	2.52
13	$[(L-c)Cd(\mu-Br)Br]_2$	17.5	2.73	125	7.59	24.1	69.0	9.37	2.59

 $^{a}$ [M (II) catalyst]<sub>0</sub> = 15 µmol, and [MMA]<sub>0</sub>/[MMAO]<sub>0</sub>/[M (II) catalyst]<sub>0</sub> = 3100:500:1, polymerization temp. = 60°C and time = 2 hr.

<sup>b</sup>Yield defined as a mass of dried polymer recovered/mass of monomer used.

<sup>c</sup>Activity is calculated (g of PMMA)/(mol<sup>-1</sup> M hr<sup>-1</sup>).

 ${}^{d}T_{g}$  is glass transition temperature, which is determined by a thermal analyzer.

<sup>e</sup>Determined by GPC eluted with THF at room temperature by filtration with polystyrene calibration.

 ${}^{\rm f}M_{\rm n}$  refers to the number average of molecular weights of PMMA.

<sup>g</sup>It is a blank polymerization in which PdCl<sub>2</sub>, ZnCl<sub>2</sub> and CdBr<sub>2</sub>·4H<sub>2</sub>O were also activated by MMAO.

<sup>h</sup>It is a blank polymerization that was done solely by MMAO.

<sup>i</sup>Complexes of [(L-a)PdCl<sub>2</sub>], [(L-a)ZnCl<sub>2</sub>], [(L-a)Cd(µ-Br)Br]<sub>2</sub> and [(L-b)PdCl<sub>2</sub>] are reported in the literature.<sup>[46,48-50]</sup>

= Cl; M = Cd; X = Br; n, m = 1 or 2) complexes by use of program 'SambVca' (see Supplementary materials).<sup>[69]</sup> Figure S1 in the Supplementary material shows the ball and stick model, space-filling model and topographic steric map of  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2) for presenting steric bulk of ligands around the metal center. Only considering total steric factor by topographic steric maps, it is evident that less sterically hindered complexes exhibited better catalytic performance. By comparing Pd complexes, **[(L)**  $PdCl_2$ ] (L = L-a-L-c), it is evident that [(L-b)PdCl\_2] (buried volume % is 37.7, activity  $3.80 \times 10^4$  g mol<sup>-1</sup> Pd hr<sup>-1</sup>) has higher activity compared with more sterically demanding [(L-c)PdCl<sub>2</sub>] (buried volume % is 42.4, activity  $3.08 \times 10^4$  g mol<sup>-1</sup> Pd hr<sup>-1</sup>) in 4-methoxy-N-(pyridin-2-ylmethylene) aniline derivatives bearing Pd (II) system. Similarly, the order of activity for [(L)  $_{n}MX_{2}]_{m}$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2) was found to be [(L-a)Cd( $\mu$ -Br) **Br**]<sub>2</sub> (buried volume % 31.4, activity  $3.37 \times 10^4$  g mol<sup>-1</sup> Cd hr<sup>-1</sup>) >  $[(L-c)Cd(\mu-Br)Br]_2$  (buried volume % 34.1,

activity  $2.73 \times 10^4$  g mol<sup>-1</sup> Cd hr<sup>-1</sup>); **[(L-a)ZnCl<sub>2</sub>]** (buried volume % 36.4, activity  $3.10 \times 10^4$  g mol<sup>-1</sup> Zn hr<sup>-1</sup>) > **[(L-c)ZnCl<sub>2</sub>]** (buried volume % 42.3, activity  $2.23 \times 10^4$  g mol<sup>-1</sup> Zn hr<sup>-1</sup>). However, the opposite trend has been observed in **[(L-b)MX<sub>2</sub>]** (M = Zn; X = Cl; M = Cd; X = Br) complexes. Despite apparently greater steric crowding, the buried volume was found to be lower compared with **[(L-c)MX<sub>2</sub>]** (M = Zn; X = Cl; M = Cd; X = Br) complexes. However, the polymerization activities were  $2.20 \times 10^4$  g mol<sup>-1</sup> Zn hr<sup>-1</sup> and  $2.02 \times 10^4$  g mol<sup>-1</sup> Cd hr<sup>-1</sup>, respectively. Thus, both steric and electronic effects of catalysts are needed to correlate the polymerization activity and structure of complexes. In addition, the solubility of complexes or active species in polymerization solvent also influenced the polymerization activity.

The influence of metal center variation is also studied. It is evident that using  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2) as a polymerization catalyst,  $[(L-b)PdCl_2]$  exhibited the highest catalytic activity (3.80 × 10<sup>4</sup> g PMMA mol<sup>-1</sup> Pd hr<sup>-1</sup>). The current results are consistent with our previously reported Zn (II), Pd (II) and Cd (II) initiators bearing *N*-substituted 2-iminoalkylpyridines for MMA polymerization, where the iminopyridine effectively creates electron-rich clouds around the palladium metal but does not affect Cd (II) and Zn (II) complexes.<sup>[32,33]</sup>

Previously studied Pd (II) complexes with N-(pyridin-2-ylmethyl) aniline derivatives<sup>[37]</sup> resulted in comparable activities and yielded PMMA with low molecular weights compared with [(L-b)PdCl<sub>2</sub>]. Our current system is superior in terms of activity and resulted in syndio-enriched high molecular weight PMMA compared with N-methyl--N-(pyridin-2-ylmethyl) aniline-based Pd (II)<sup>[25]</sup> complexes in our earlier report. Similarly, compared with previous Zn (II) complexes with N-(pyridin-2-ylmethylene) aniline and *N*-phenyl-(pyridin-2-yl)methanimine.<sup>[38,70]</sup> current Zn (II) systems effectively catalyzed MMA polymerization. The Cd (II) complexes, [(L-c)Cd(µ-Br)Br]<sub>2</sub> and [(L-c)Cd(µ-Br)Br]<sub>2</sub>, exhibited lower activities compared with our previously reported Cd (II) complexes bearing N,N-di(2-picolyl) amine ligand,<sup>[71]</sup> but resulted in high molecular weight PMMA with improved  $T_g$  (Table 5). Moreover, the PDIs of the resultant PMMA ranged from 2.40 to 2.96, which is in agreement with the fact that the PDI range narrowed with increasing molecular weights.<sup>[63,72,73]</sup> Judging from the low activity of **[(L-c)**  $MX_2$  (M = Zn; X = Cl; M = Cd; X = Br) similar to blank polymerization, the MMA polymerization activity of metal complexes in the current study should be considered as a function of the electron density about the metal center and steric factor of the substituents on the N atom of N-methylamine.

The syndiotacticity of PMMA was found to be 0.68-0.70, similar to all  $[(L)_n MX_2]_m$  (L = L-a-L-c; M = Zn, Pd; X = Cl; M = Cd; X = Br; n, m = 1 or 2) initiators regardless of the ligand architecture and metal center variation. However, the syndiotacticity was higher compared with co-catalyst, MMAO. Although the resultant syndiotactic enchainment was not satisfactorily high to predict a coordination polymerization mechanism, it was found to be similar for all of the synthesized complexes. The molecular weights were much influenced by the steric encumbrance provided by amine and Nmethylamine moieties, while having little dependence on the PDIs of resultant PMMA. The molecular weights of the resultant PMMA should be considered as a function of steric bulk around the metal center. In addition, experiments using 2,6,6,6-tetramethylpiperidinyloxy (TEMPO), a 5-equivalent radical inhibitor during the MMA polymerization, did not significantly reduce the yield of PMMA and showed a reduction in yield up to 2-5%, which supports the fact that the mechanism of polymerization is not a radical one. Further investigations to improve the catalytic performance in terms of ligand architecture and the resultant stereoselectivity of the MMA polymerization are ongoing.

### 4 | CONCLUSIONS

In summary, we have synthesized and structurally characterized a series of new Zn (II), Pd (II) and Cd (II) complexes supported by 4-methoxy-N-(pyridin-2ylmethylene) aniline derivatives. The molecular structures of 4-coordinate Pd (II) and Zn (II) complexes [(L) **MCl**<sub>2</sub>] (L = L-a and L-c; M = Zn and Pd) were distorted square planar and distorted tetrahedral, respectively, whereas the 6-coordinated Zn (II) and Cd (II) complexes  $[(L-b)_2MX_2]$  (M = Zn; X = Cl; M = Cd; X = Br) exhibited distorted octahedral geometries. However, the dimeric [(L-c)Cd(µ-Br)Br]<sub>2</sub> complex adopted distorted trigonal bipyramidal geometry. The catalytic activity of [(L-b)PdCl<sub>2</sub>] toward the polymerization of MMA in the presence of MMAO resulted in higher activity of  $3.80 \times$  $10^4$  g PMMA mol<sup>-1</sup> Pd hr<sup>-1</sup> compared with the rest of its analogs under identical conditions. Moderate syndiotacticity has resulted with all complexes with  $T_{g}$ in range of 121-128°C. The MMA polymerization activity in the current study should be considered as a function of the electron density about the metal center, and steric factor of imine, amine and N-amine moieties of ligand framework. The molecular weights of resultant PMMA were significantly affected by the steric bulk around the metal centers, whereas no clear trends could be found according to the steric bulk of the substituents for the PDIs and syndiotacticity.

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#### REFERENCES

- A. J. Hallett, T. M. O'Brien, E. Carter, B. M. Kariuki, D. M. Murphy, B. D. Ward, *Inorg. Chim. Acta* 2016, 441, 86.
- [2] S. Radi, Y. Toubi, M. Bacquet, S. Degoutin, F. Cazier, Sep. Sci. Technol. 2013, 48, 1349.
- [3] D. A. Tocher, M. G. B. Drew, S. Nag, P. K. Pal, D. Datta, *Chem. Eur. J.* 2230, 2007, 13.

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- [4] D. M. Haddleton, D. Kukulj, A. P. Radigue, Chem. Commun. 1999, 99.
- [5] S. S. Massoud, R. C. Fischer, F. A. Mautner, M. M. Parfait, R. Herchel, Z. Trávníček, *Inorg. Chim. Acta* 2018, 471, 630.
- [6] D. Zhou, C. Wang, M. Li, Z. Long, J. Lan, Chin. Chem. Lett. 2018, 29, 191.
- [7] L. Rostami, H. Golchoubian, J. Coord. Chem. 2017, 70, 3660.
- [8] A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, *Org. Lett.* **2017**, *19*, 3656.
- [9] S. Thangavel, H. B. Friedrich, B. Omondi, J. Mol. Catal. A Chem. 2017, 429, 27.
- [10] M. Schulz, M. Klopfleisch, H. Görls, M. Kahnes, *Inorg. Chim. Acta* 2009, 362, 4706.
- [11] Z. Huang, K. Song, F. Liu, J. Long, H. Hu, H. Gao, Q. Wu, J. Polym. Sci. Pol. Chem. 2008, 46, 1618.
- [12] A. Requet, O. Colin, F. Bourdreux, S. M. Salim, S. Marque, C. Thomassigny, C. Greck, J. Farjon, D. Prim, *Magn. Reson. Chem.* 2014, *52*, 273.
- [13] Y.-L. Wong, J.-F. Ma, F. Xue, T. C. W. Mak, D. K. P. Ng, Organometallics 1999, 18, 5075.
- [14] T. Yajima, Y. Shimazaki, N. Ishigami, A. Odani, O. Yamauchi, *Inorg. Chim. Acta* 2002, 337, 193.
- [15] A. Sood, M. T. Räisänen, E. Aitola, A. Sibaouih, E. Colacio, M. Ahlgren, M. Nieger, T. Repo, M. Leskelä, *Polyhedron* 2013, 56, 221.
- [16] M. Barboiu, F. Dumitru, E. Petit, Y.-M. Legrand, A. V. D. Lee, *Supramol. Chem.* 2014, 27, 393.
- [17] G. Paolucci, A. Zanella, M. Bortoluzzi, S. Sostero, P. Longo, M. Napoli, J. Mol. Catal. A Chem. 2007, 272, 258.
- [18] G. García-Friaza, A. Fernández-Botello, J. M. Pérez, M. J. Prieto, V. Moreno, J. Inorg. Biochem. 2006, 100, 1368.
- [19] J. M. Gichumbi, H. B. Friedrich, B. Omondi, J. Mol. Catal. A Chem. 2016, 416, 29.
- [20] J. M. Gichumbi, H. B. Friedrich, B. Omondi, *Inorg. Chim. Acta* 2017, 456, 55.
- [21] Y.-W. Dong, R.-Q. Fan, X.-M. Wang, P. Wang, H.-J. Zhang, L.-G. Wei, W. Chen, Y.-L. Yang, *Cryst. Growth Des.* **2016**, *16*, 3366.
- [22] L. Annunziata, G. Li, C. Pellecchia, J. Mol. Catal. A Chem. 2011, 337, 1.
- [23] E. M. Njogu, B. Omondi, V. O. Nyamori, *Inorg. Chim. Acta* 2017, 457, 160.
- [24] D. Kim, Y. Song, S. Kim, H.-J. Lee, H. Lee, J. Coord. Chem. 2014, 67, 2312.
- [25] S. Kim, Y. Song, H.-J. Lee, J. Jeon, S. H. Park, H. Lee, Bull. Korean Chem. 2015, 36, 609.
- [26] H. N. Najeeb, A. A. Balakit, G. A. Wahab, A. K. Kodeary, Part-I: Nat. Appl. Sci. 2014, 5, 48.
- [27] Y. Zhang, Y. Ning, L. Caporaso, L. Cavallo, E. Y.-X. Chen, J. Am. Chem. Soc. 2010, 132, 2695.
- [28] T. Uemura, N. Uchlda, M. Higuchi, S. Kitagawa, Macromolecules 2011, 44, 2693.
- [29] K. Endo, A. Inukai, T. Otsu, Macromol. Rapid Commun. 1994, 15, 893.

- [30] H. Sun, Q. Shen, X. Peng, M. Yang, Catal. Lett. 2002, 80, 11.
- [31] F. D. Lena, K. Matyjaszewshi, Prog. Polym. Sci. 2010, 35, 959.
- [32] S. Kim, E. Kim, H.-J. Lee, H. Lee, Polyhedron 2014, 69, 149.
- [33] Y. Song, D. Kim, H.-J. Lee, H. Lee, Bull. Korean Chem. Soc. 2014, 35, 2929.
- [34] D. Kim, S. Kim, E. Kim, H.-J. Lee, H. Lee, *Polyhedron* **2013**, *63*, 139.
- [35] S. Kim, D. Kim, Y. Song, H.-J. Lee, H. Lee, Aust. J. Chem. 2014, 67, 953.
- [36] Y. Song, D. Kim, H.-J. Lee, H. Lee, Inorg. Chem. Commun. 2014, 45, 66.
- [37] S. Kim, D. Kim, H.-J. Lee, H. Lee, Polyhedron 2014, 77, 66.
- [38] S. H. Ahn, J. Shin, S. Nayab, H. Lee, Bull. Korean Chem. Soc. 2016, 36, 763.
- [39] D. F. Grishin, L. L. Semenycheva, Russ. Chem. Rev. 2001, 70, 425.
- [40] V. C. Gibson, R. K. O'Reilly, D. F. Wass, A. J. P. White, D. J. Williams, *Dalton Trans.* 2003, 2824.
- [41] A. V. Yakimanskii, Polym. Sci. Ser. C 2005, 47, 1.
- [42] R. M. Islamova, G. R. Sadykova, I. A. Ionova, Y. Z. Voloshin, Y. N. Bubnov, I. S. Makarov, Y. Monakov, *Polym. Sci. Ser. B* 2009, 51, 219.
- [43] Y. Monakov, R. M. Islamova, I. A. Ionova, S. A. Syrbu, T. A. Ageeva, O. I. Koifman, *Mendeleev Commun.* 2010, 20, 33.
- [44] C. J. Mathews, P. J. Smith, T. Welton, J. Mol. Catal. A Chem. 2003, 206, 77.
- [45] J. Dai, S. Nanayakkara, T. C. Lamb, A. J. Clark, S.-X. Guo, J. Zhang, A. F. Patti, K. Saito, *New J. Chem.* **2016**, *40*, 3511.
- [46] V. Diez, J. Cuevas, G. García-Herbosa, G. Aullón, J. P. H. Charmant, A. Carbayo, A. Muñoz, *Inorg. Chem.* 2007, 46, 568.
- [47] K. Sreenath, Z. Yuan, M. Macias-Contreras, V. Ramachandran, R. J. Clark, L. Zhu, *Eur. J. Inorg. Chem.* **2016**, *2016*, 3728.
- [48] B. Crociani, F. D. Bianca, Inorg. Chim. Acta 1988, 141, 253.
- [49] A. S. Roy, P. Saha, P. Mitra, S. S. Maity, S. Ghosh, P. Ghosh, Dalton Trans. 2011, 40, 7375.
- [50] T. S. B. Baul, S. Kundu, S. W. Ng, N. Guchhait, E. R. T. Tiekink, J. Coord. Chem. 2013, 67, 96.
- [51] J. W. Shin, K. Eom, D. Moon, J. Synchrotron Rad. 2016, 23, 369.
- [52] Z. Otwinowski, W. Minor in *Methods in Enzymology* (Eds: C. W. Carter, Jr, R. M. Sweet), Part A, Academic Press, New York, 1997, pp. 276, 307.
- [53] SMART and SAINT-Plus v 6.22, Bruker AXS, Madison, Wisconsin, USA, 2000.
- [54] G. M. Sheldrick, SADABS v 2.03, University of Göttingen, Germany, 2002.
- [55] G. M. Sheldrick, Acta Cryst. 2015, A71, 3.
- [56] G. M. Sheldrick, Acta Cryst. 2015, C71, 3.
- [57] Z.-F. Huang, H.-Y. Gao, L. Zhang, Q. Wu, Chin. J. Polym. Sci. 2008, 26, 567.
- [58] S.-G. Teoh, S.-B. Teo, L.-K. Lee, Y.-L. Chong, Polyhedron 1995, 14, 2275.

- [59] T. S. B. Baul, S. Kundu, H. Höpfl, E. R. T. Tiekink, A. Linden, *Polyhedron* **2013**, *55*, 270.
- [60] T. S. B. Baul, S. Kundu, S. Mitra, H. Höpfl, E. R. T. Tiekink, A. Linden, *Dalton Trans.* 2013, 42, 1905.
- [61] L. Yang, D. R. Powell, R. P. Houser, Dalton Trans. 2007, 955.
- [62] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, J. Chem. Soc. Dalton Trans. 1984, 1349.
- [63] S. Reinhardt, K. Heinze, Z. Anorg. Allg. Chem. 2006, 632, 1465.
- [64] D. A. Safin, K. Robeyns, M. G. Babashkina, C. M. L. Vande Velde, Y. Filinchuk, *Cryst. Growth Des.* 2016, 16, 3763.
- [65] B. K. Bahuleyan, D. Chandran, C. H. Kwak, C.-S. Ha, I. Kim, *Macromol. Res.* 2008, 16, 745.
- [66] I. A. Opeida, M. A. Kompanets, O. V. Kushch, E. S. Papayanina, *Theor. Exp. Chem.* 2011, 47, 30.
- [67] A. S. Brar, G. Singh, R. Shankar, J. Mol. Struct. 2004, 703, 69.
- [68] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, Organometallics 2016, 35, 2286. For online program, see https://www.molnac.unisa.it/ OMtools/
- [69] J. Heo, S. Nayab, H. Lee, J. Coord. Chem. 2017, 70, 3837.
- [70] Y. Song, S. Nayab, J. Jeon, S. H. Park, H. Lee, J. Organomet. Chem. 2015, 783, 55.
- [71] G. T. Lewis, V. Nguyen, Y. Cohen, J. Polym. Sci. Polym. Chem. 2007, 45, 5748.
- [72] J. Llorens, E. Rudé, R. M. Marcos, Polymer 2003, 44, 1741.
- [73] F. Wiesbrock, R. Hoogenboom, C. H. Abeln, U. S. Schubert, Macromol. Rapid Commun. 2004, 25, 1895.

### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

CCDC 1871854–1871860 contains the supplementary crystallographic data for  $[(L-b)_2CdBr_2]$ ,  $[(L-b)PdCl_2]$ ,  $[(L-a)ZnCl_2]$ ,  $[(L-b)_2ZnCl_2]$ ,  $[(L-c)ZnCl_2]$ ,  $[(L-c)Cd(\mu-Br)Br]_2$  and  $[(L-c)PdCl_2]$ , respectively. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additionally, steric maps of all complexes that were calculated by the program 'SambVca' were also presented in the Supplementary materials.

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