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Revised

Palladium(II) complexes containing *N*,*N*'-bidentate imine ligands derived from picolinaldehyde and substituted anilines: Synthesis, structure and polymerisation of methyl methacrylate

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Abstract

Palladium(II) complexes, L_nPdCl_2 ($L_n = L_A - L_I$), with *N*,*N*-bidentate imine ligands derived from picolinaldehyde and substituted anilines have been synthesized and structurally characterized. Molecular structures revealed a distorted square plane geometry around Pd(II) centre in L_nPdCl_2 ($L_n = L_A - L_C$) obtained via coordination with pyridine and imine nitrogens and two chloro ligands. Pd(II) complexes L_nPdCl_2 ($L_n = L_A - L_I$) initiate polymerisation of methylmethacrylate (MMA) in the presence of modified methylaluminoxane (MMAO). The complex L_IPdCl_2 (of which the ligand was N-furfuryl substituted) showed the highest catalytic activity for the polymerisation of MMA with an activity of 7.08×10^4 g PMMA/mol·Pd·h at 60 °C. All the complexes yielded syndio-rich poly(methyl methacrylate) (PMMA) ([rr] = 0.70). Notably, the substituents on the imine moiety of the iminopyridine fragments affects the activities towards MMA polymerization, whereas the stereoslectivities remained unchanged.

Keywords: N,*N*-bidentate imine ligands, Palladium(II) complexes, Square planar geometry, Methyl methacrylate polymerisation, Syndiotacticity

1. Introduction

Metal-mediated polymerisation of methyl methacrylate (MMA) has received much attention recently due to its ability to promptly produce high molecular weight (M_W) poly(methylmethacrylate) (PMMA) with improved stereoregularity and optical properties [1]. There has been growing interest in the development of late transition metal initiators for the polymerisation of polar vinyl monomers such as MMA [2-5]. Late transition metal catalysts are preferred for polymerisation of polar monomers due to their reduced oxophilicity and more functional group tolerance [6,7]. To date several reports have been documented on iminopyridines and N-substituted-2-iminoalkylpyridines based late transition metal complexes for MMA polymerisation. For instance, the Kim group demonstrated that late transition metal complexes such as $(\alpha$ -diimine)nickel(II), (pyridyl bis-imine) iron(II) and (pyridyl bis-imine)cobalt(II) proved to be effective catalysts in combination with MAO to yield syndiotactic poly(methyl methacrylate) (PMMA) [3a]. The Gibson group studied wellcontrolled polymerisation of both styrene and MMA with iminopyridine based iron complexes [8]. Similarly, recently we have reported imino-pyridyl based Pd(II), Zn(II), Cd(II) and Pt(II) initiators with a variety of pendant groups for MMA polymerisation. These catalysts were effective and afforded high molecular weight PMMAs with mediocre to high syndiotacticities [9]. In particular, palladium was the most active metal when MMA polymerisation by any other metal was performed [10].

The catalyst performance (activity and stereoregularity) in the polymerisation can be controlled through ligand modification as well as varying the identity of the central metal. Thus, appropriate choice of ligand framework and metal centre is crucial for controlled polymerisation. Schiff bases containing pyridine moiety such as pyridyl-imines [11], bispyridine-imines [12], 2,6-bis(imino)pyridines ligands [13] and *N*-substituted 2-

iminoalkylpyridines [14,15] contributed significantly for their applications as ligands for a variety of transition metal-based initiators [16-19] owing to their convenient synthesis and thermal stability. Additionally, the asymmetry in *N*-substituted 2-iminopyridines ligands allow easy optimization of the ligand scaffold by installing various pendant groups and to fine tune the steric and electronic properties.

As a continuation of our efforts towards the synthesis of an effective MMA catalyst, we herein report the synthesis and X-ray structures of Pd(II) complexes with *N*,*N*-bidentate imine ligands derived from picolinaldehyde and substituted anilines. These complexes were assessed for MMA polymerisation in the presence of modified methylaluminoxane (MMAO). Further, the effects of structural variation of the ligand on the activities of catalysts and polymer microstructure are described.

2. Experimental

2.1. Physical measurement

2-Pyridinecarboxaldehyde, 2,6-diethylaniline, 2,4,6-trimethylaniline, 4-nitroaniline, 4bromoaniline, aniline, 2,6-dimethylaniline, *p*-anisidine, 4-fluoroaniline, furfurylamine, magnesium sulfate (MgSO₄) and methyl methacrylate (MMA) were purchased from Aldrich. **PdCl₂** was purchased from Kojima Chemicals and **Pd(MeCN)₂Cl₂** was prepared according to the literature method [20]. Anhydrous solvents such as acetonitrile (MeCN), ethanol (EtOH), dimethylformamide (DMF), diethyl ether (Et₂O) and dichloromethane (CH₂Cl₂) were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 5.90 % weight aluminum of a toluene solution and used without further purification. Elemental analysis (C, H, N) of the

prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). Melting point was measured by electro-thermal apparatus, IA 9100. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were reported on a Bruker Avance Digital 500 NMR spectrometer; chemical shifts were recorded in ppm units (δ) relative to SiMe₄ 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 weight average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the obtained poly(methylmethacrylate) (PMMA) were carried out using gel permeation chromatography (GPC) in THF (Alliance e2695; Waters Corp., Milford, MA). Glass transition temperature (T_g) was determined using a thermal analyzer (DSC 4000; PerkinElmer).

2.2. Preparation of ligands and palladium(II) complexes

(*E*)-2,6-Diethyl-*N*-((pyridin-2-yl)methylene)aniline $(\mathbf{L}_{\mathbf{A}}),$ (E)-2,4,6-trimethyl-N-((pyridin-2-yl)methylene)aniline (L_B), (E)-4-nitro-N-((pyridin-2-yl)methylene)aniline (L_C), (*E*)-4-bromo-*N*-((pyridin-2-yl)methylene)aniline $(\mathbf{L}_{\mathbf{D}}),$ (E)-N-((pyridin-2yl)methylene)aniline (L_E), (E)-2,6-dimethyl-N-((pyridin-2-yl)methylene)aniline (L_F), (E)-4methoxy-N-((pyridin-2-yl)methylene)aniline $(L_{G}),$ (E)-4-fluoro-N-((pyridin-2yl)methylene)aniline (L_H) and (E)-1-(furan-2-yl)-N-(pyridin-2-ylmethylene)methanamine (L_I) prepared were reported previously [16c,21-23,35]. N-((pyridin-2as yl)methylene)anilinepalladium(II) chloride $(L_E PdCl_2)$ 2,6-dimethyl-N-((pyridin-2yl)methylene)anilinepalladium(II) chloride (L_FPdCl_2) 4-methoxy-N-((pyridin-2yl)methylene)anilinepalladium(II) chloride (L_GPdCl_2) 4-fluoro-N-((pyridin-2-yl)methylene) anilinepalladium(II)chloride $(L_{H}PdCl_{2})$ (furan-2-yl)-N-((pyridin-2-

yl)methylene)methanaminepalladium(II) chloride (L_1PdCl_2) were synthesized using reported synthetic protocol [24-28].

2.2.1. 2,6-Diethyl-N-((pyridin-2-yl)methylene)anilinepalladium(II) chloride (L_APdCl₂)

 L_A (1.00 g, 4.20 mmol) was added to a solution of $Pd(MeCN)_2Cl_2$ (1.09 g, 4.20 mmol) in CHCl₃ (50 mL), and the resulting mixture was stirred at room temperature for 14 h. The resultant orange precipitate was washed with cold CHCl₃ (30 mL \times 2), followed by washing with Et₂O (30 mL \times 3). The precipitate was dried in *vacuo* to get final product (1.15 g, 65.9 %). Analysis calculated for $C_{16}H_{18}Cl_2N_2Pd$ (%): C, 46.2; H, 4.36; N, 6.74. Found: C, 46.7; H, 4.35; N, 6.73. mp ($^{\circ}$ C): 318. ¹H NMR (DMSO-d₆, 500 MHz): δ 9.08 (dd, 1H, J = 5.6, 1.0 Hz, -PryH-), 8.77 (s, 1H, -N=CH-PyrH-), 8.43 (td, 1H, ${}^{3}J = 7.8$, 1.0 Hz, -PryH-), 8.20 (dd, 1H, J = 7.6, 0.8 Hz, -PyrH-), 8.00 (ddd, 1H, J = 7.8, 1.0 Hz, -PyrH-), 7.29 $(t, 1H, J = 7.63 \text{ Hz}, -(\text{MeCH}_2)_2\text{Ar}H), 7.15 (d, 2H, J = 7.6 \text{ Hz}, -(\text{MeCH}_2)_2\text{Ar}H), 2.77 - 2.61$ $(m, 4H, -(MeCH_2)_2ArH-), 1.21$ (t, 6H, J = 7.5 Hz, $-(MeCH_2)_2ArH-).$ ¹³C NMR (DMSO-d₆, 125 MHz): δ 174.52 (d, J = 185 Hz, -N=CH-PyrC-), 154.97 (s, *ipso-N=C-PyrC-*), 150.44 (d, J = 190 Hz, -PyrC-), 144.51 (s, 1C, *ipso-*(MeCH₂)₂ArC-), 141.48 (d, J = 171 Hz, -PyrC-), 135.58 (s, *ipso*-(MeCH₂)₂ArC-), 129.89 (d, J = 172 Hz, -PyrC-), 129.80 (d, J = 172 Hz, -PyrC-), 127.91 (d, J = 162 Hz, p-(MeCH₂)₂ArC-), 125.51 (d, J = 160.76 Hz, m- $(MeCH_2)_2ArC_-)$, 24.04 (t, J = 127 Hz, $-(MeCH_2)_2ArC_-)$, 13.90 (q, J = 127 Hz, -(*Me*CH₂)₂ArC-). IR (solid neat; cm⁻¹): 2997 w(C-H), 1591 m(C=N), 1464 w(C=C), 595 w(Pd-N).

2.2.2. 2,4,6-Trimethyl-N-((pyridin-2-yl)methylene)anilinepalladium(II) chloride (L_BPdCl_2)

 L_BPdCl_2 was prepared according to a similar procedure as described for L_APdCl_2 except utilizing L_B (0.70 g, 3.12 mmol) and $Pd(MeCN)_2Cl_2$ (0.809 g, 3.12 mmol) in MeCN

(50 mL) to yield an orange solid (1.18 g, 94.2 %). Analysis calculated for $C_{15}H_{16}Cl_2N_2Pd$ (%): C, 44.9; H, 4.02; N, 6.97. Found: C, 44.8; H, 3.96; N, 6.91. mp (°C): 293. ¹H NMR (DMSOd₆, 500 MHz): δ 9.06 (dd, 1H, J = 5.6, 0.9 Hz, -PyrH-), 8.63 (s, 1H, -N=CH-Pyr-), 8.42 (td, 1H, J = 7.8, 1.0 Hz, -PyrH-), 8.16 (dd, 1H, J = 7.7, 0.7 Hz, -PyrH-), 7.98 (ddd, 1H, J = 7.8, 1.1 Hz, -PyrH-), 6.92 (s, 2H, $-(Me)_3ArH-$), 2.24 (s, 3H, $-(Me)_3ArH-$), 2.23 (s, 6H, $-(Me)_3ArH-$). ¹³C NMR (DMSO-d₆, 125 MHz): δ 174.64 (d, J = 185 Hz, -N=CH-PyrC-), 155.13 (s, *ipso*-PyrC-) 150.18 (d, J = 189 Hz, -PyrC-), 143.40 (s, *ipso*-(Me)_3ArC-), 141.24 (d, J = 171 Hz, -PyrC-), 136.50 (s, *ipso*-(Me)_3ArC-), 129.80 (s, *ipso*-(Me)_3ArC-), 129.67 (d, J = 172 Hz, -PyrC-), 129.50 (d, J = 173 Hz, -PyrC-), 128.12 (d, J = 163 Hz, m-(Me)_3ArC-), 20.53 (q, J = 126 Hz, $-(Me)_3ArC-$), 18.12 (q, J = 127.16 Hz, $-(Me)_3ArC-$). IR (solid neat; cm⁻¹): 2991 w(C-H), 1585 m(C=N), 1468 w(C=C), 597 w(Pd-N).

2.2.3. 4-Nitro-N-((pyridin-2-yl)methylene)anilineepalladium(II) chloride (LcPdCl₂)

L_CPdCl₂ was prepared according to a similar procedure as described for L_APdCl₂ except utilizing L_C (0.80 g, 3.52 mmol) and Pd(MeCN)₂Cl₂ (0.913 g, 3.52 mmol) in MeCN to give orange solid (1.38 g, 96.9 %). Analysis calculated for C₁₂H₉Cl₂N₃O₂Pd (%): C, 35.6; H, 2.24; N, 10.39. Found: C, 35.9; H, 2.29; N, 10.37. mp (°C): 301. ¹H NMR (DMSO-d₆, 500 MHz): δ 9,07 (dd, 1H, *J* = 5.6, 1.2 Hz, -PyrH–), 8.87 (s, 1H, -N=CH–Pyr–), 8.43 (td, 1H, *J* = 7.8, 1.5 Hz, -PyrH–), 8.34 (m, 2H, -NO₂ArH–), 8.25 (dd, 1H, *J* = 7.8, 1.6 Hz, Hz, -PyrH–), 7.98 (dd, 1H, *J* = 7.7, 0.8 Hz, -PyrH–), 7.68 (m, 2H, -NO₂ArH–). ¹³C NMR (DMSO-d₆, 125 MHz): δ 174.10 (d, *J* = 187 Hz, -N=CH–PyrC–), 155.64 (s, *ipso*-NO₂ArC–), 151.64 (s, *ipso*-PyrC–), 150.18 (d, *J* = 189 Hz, PyrC–), 146.75 (s, *ipso*-NO₂ArC–), 141.39 (d, *J* = 172 Hz, PyrC), 130.00 (d, *J* = 175 Hz, -PyrC–), 129.56 (d, *J* = 174 Hz, -PyrC–), 125.53 (d, *J* = 171 Hz, -NO₂ArC–). IR (solid neat; cm⁻¹): 3101 w(C-H),

1581 m(C=N), 1481 w(C=C), 686 w(Pd-N).

2.2.4. 4-Bromo-N-((pyridin-2-yl)methylene)anilinepalladium(II) chloride (L_DPdCl₂)

L_D**PdCl**₂ was prepared according to a similar procedure as described for **L**_A**PdCl**₂ except utilizing **L**_D (1.00 g, 3.83 mmol) and **Pd(MeCN)**₂**Cl**₂ (0.99 g, 3.83 mmol) in MeCN to yield a yellowish orange solid (1.59 g, 94.7 %). Analysis calculated for C₁₂H₉BrCl₂N₂Pd (%): C, 32.9; H, 2.07; N, 6.39. Found: C, 33.3; H, 2.06; N, 6.57. mp (°C): 310. ¹H NMR (DMSO-d₆, 500 MHz): δ 9.05 (dd, 1H, J = 5.5 Hz, -Pyr*H*-), 8.76 (s, 1H, -N=C*H*-PyrH-), 8.40 (td, 1H, J = 7.8, 1.2 Hz, -Pyr*H*-), 8.21 (dd, 1H, J = 7.8, 1.6 Hz, -Pyr*H*-), 7.95 (m, 1H, - Pyr*H*-), 7.67 (m, 2H, -BrAr*H*-), 7.38 (m, 2H, -BrAr*H*-). ¹³C NMR (DMSO-d₆, 125 MHz): δ 172.98 (d, J = 185 Hz, -N=CH-PyrC-), 155.75 (s, -PyrC-), 150.09 (d, J = 190 Hz, PyrC-), 146.02 (s, -ArC-), 141.32 (d, J = 170 Hz, -PyrC-), 131.10 (d, J = 169 Hz, -BrAr*C*-), 129.62 (d, J = 172 Hz, -PyrC-), 129.21 (d, J = 172 Hz, -PyrC-), 126.16 (d, J = 167 Hz, -BrAr*C*-), 121.50 (s, *ipso*-BrArC-). IR (solid neat; cm⁻¹): 3074 w(C-H), 1585 m(C=N), 1480 w(C=C), 574 w(Pd-N).

2.3. X-Ray crystallographic studies

A yellowish cubic-shaped crystal of L_APdCl_2 was picked up with paraton-*N* oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation source under nitrogen cold stream (200(2) K). Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001) software packages [29]. Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS [30]. Structures were solved by direct

methods and refined using a full-matrix least-squares method on F^2 using SHELXTL or SHELXTL-2016 [31]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their geometrically ideal positions. Similarly, the X-ray-quality single crystal was coated with paratone-N oil and the diffraction data measured at 100(2) K with synchrotron radiation ($\lambda = 0.61000$ Å) for L_BPdCl₂ and 100(2) K with synchrotron radiation $(\lambda = 0.62073 \text{ Å})$ for L_CPdCl₂ on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, South Korea. The ADSC Q210 ADX program [32] was used for data collection (detector distance is 63 mm, omega scan; $\Delta \omega = 1^{\circ}$, exposure time is 1 sec per frame) and HKL3000sm (Ver. 703r) [33] was used for cell refinement, reduction and absorption correction. ($T_{min} = 0.868$, $T_{max} =$ 0.962). Structures were solved by direct methods, and refined by full-matrix least-squares refinement using the SHELXL-2014 [34] computer program. The positions of all nonhydrogen 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-2014, SHELXL-2016 computer program. Crystallographic data and structural refinements for the Pd(II) complexes L_nPdCl_2 $(L_n = L_A - L_C)$ are summarized in **Table S1**.

2.4. Catalytic activity for MMA polymerisation

Methyl methacrylate (MMA) was dried over molecular sieves and distilled under reduced pressure before use. In a Schlenk line, a complex (15.0 μmol, 6.20 mg for L_APdCl₂, 6.00 mg for L_BPdCl₂, 6.10 mg for L_CPdCl₂, 6.60 mg for L_DPdCl₂, 5.40 mg for L_EPdCl₂, 5.80 mg for L_FPdCl₂, 5.80 mg for L_GPdCl₂, 5.70 mg for L_HPdCl₂ and 5.50 mg for L_IPdCl₂)

was dissolved in dried toluene (10 mL) followed by the addition of modified methylaluminoxane (MMAO) (5.90 wt% in toluene, 3.80 mL, 7.50 mmol and $[MMAO]_0/[M(II) \text{ catalyst}]_0=500$) as a co-catalyst. The solution was stirred for 20 min at 60 °C. MMA (5.0 mL, 47.1 mmol and $[MMA]_0/[M(II) \text{ catalyst}]_0 = 3100$) was added to the above reaction mixture and stirred for 2 h to obtain a viscous solution. For termination MeOH (2 mL) was added to polymerisation solution. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35.0 % HCl (5 mL) was injected to remove the remaining co-catalyst (MMAO). The resultant PMMA was obtained by filtration following by washing with MeOH (250 mL × 2) and dried under vacuum at 60 °C for 12 h.

3. Results and Discussion

3.1. Synthesis and chemical properties

Ligands ($L_n = L_A - L_I$) were obtained in yields of 60 –87% from the condensation reaction of X-aniline and furfurylamine (X = 2,6-dimethyl, 2,6-diethyl, 4-nitro, 4-bromo, 2,4,6-trimethyl, 4-methoxy, 4-fluoro) with 2-pyridinecarboxaldehyde in an appropriate solvent as reported previously [16c,21-23,35]. These ligands with variety of substituents at imine moiety were used in the current study to investigate their steric and electronic properties of resultant Pd(II) complexes.

The new mononuclear Pd(II) complexes L_nPdCl_2 ($L_n = L_A - L_D$) (62 – 97 % yield) were obtained by treating ligands ($L_n = L_A - L_I$) with Pd(MeCN)₂Cl₂ in 1:1 ratio at ambient temperature (Scheme 1). The synthesized complexes were characterized by ¹H NMR, ¹³C NMR and IR spectroscopy along with X-ray diffraction. In ¹H NMR spectra of Pd(II) complexes, L_nPdCl_2 ($L_n = L_A - L_D$), singlet peaks between 8.63 and 8.87 ppm were

indicative of imine moiety [35]. Similarly in ¹³C NMR spectra the imine carbon appeared in range of 174.64 – 172.98 ppm consistent with the reported imino-pyridyl Pd(II) complexes [36]. The absorption band for imine functionality (> C=N-) in IR spectra is typically between 1581 and 1591cm⁻¹. Absorption bands at 686 – 574 cm⁻¹ are due to formation of Pd–N bonds in L_nPdCl_2 ($L_n = L_A - L_D$). Elemental analyses of newly synthesized complexes were consistent with the proposed structures shown in Scheme 1 and confirmed the purity of the isolated complexes L_nPdCl_2 ($L_n = L_A - L_D$). The reported synthetic protocol has been followed for the synthesis of L_nPdCl_2 ($L_n = L_E - L_I$) [24-28].

3.2. Description of X-ray crystal structures

Crystals suitable for the X-ray diffraction studies of $[L_nPdCl_2]$ ($L_n = L_A - L_C$) were obtained from Et₂O diffusion into DMF solution of complexes. L_APdCl_2 and L_BPdCl_2 crystallized in the monoclinic system with $P2_1/c$ space group, whereas L_CPdCl_2 crystallized in the triclinic system with *P*-1 space group. The ORTEP drawings of L_nPdCl_2 ($L_n = L_A - L_C$) are shown in Fig. 1-3 along with their selected bond lengths and angles. L_APdCl_2 and L_BPdCl_2 were found to be solvent-free and existed in a four coordinated monomeric form. We failed to get X-ray quality crystals of L_DPdCl_2 .

Pd–N_{pyridine} and Pd–N_{imine} bond lengths in L_nPdCl_2 ($L_n = L_A - L_C$) lie in the range of 2.0294(1) - 2.038(2) Å and 2.0219(1) - 2.039(2) Å, respectively, similar to the Pd–N bond lengths of square planar pyridyl-imine Pd(II) complexes [17a,19a,25,27,28]. The Pd–Cl bond lengths in 2.2724(9) - 2.2896(5) Å range compared well with the average bond length of 2.290(13) Å observed for similar Pd(II) complexes [37]. The Pd–N_{imine} length increased in order of $L_BPdCl_2 < L_APdCl_2 < L_CPdCl_2$, ranging in length from 0.003 – 0.016 Å. The Pd–

N_{pyridine} bond lengths of L_APdCl₂ and L_BPdCl₂ were found to be longer than Pd–N_{imine} lengths. In contrast, the Pd–N_{pyridine} length was shorter than Pd–N_{imine} in L_CPdCl₂ (Fig. 3). The double bond N(2)–C(6) distances of 1.298(8) Å (L_APdCl₂), 1.2899(2) Å (L_BPdCl₂) and 1.291(3) Å (L_CPdCl₂) were in the range of accepted >C=N- bond distances [25,38]. The C(5)–C(6) bond distances of the complexes L_nPdCl₂ (L_n= L_A – L_C) were in the ranged 1.441(8) – 1.432(3) Å, reflecting delocalized π -electrons and the bond lengths of the synthesized palladium complexes were slightly affected by the *N*-phenyl substituent group.

The central palladium atom in L_nPdCl_2 ($L_n = L_A - L_C$) was four coordinated and adopted distorted square planner geometry by coordinating to the nitrogen atoms of pyridyl and imine moieties of N,N-bidentate ligands and two chloro ligands. The N_{Pyridine}-Pd(1)-N_{imine} bond angles in L_nPdCl_2 ($L_n = L_A - L_C$) ranged from 80.31(5)° to 80.6(2)° as observed in reported pyridyl-imine palladium systems [18b,25,28,38]. The Cl(1)-Pd(1)-Cl(2) angles were 91.71(7)° L_APdCl_2 , 91.20(2)° L_BPdCl_2 and 90.05(3)° L_CPdCl_2 and were slightly affected by the substituents of the imine moiety. The N(1)-Pd(1)-Cl(2) and N(2)-Pd(1)-Cl(1) angles for the complexes $L_nPdCl_2(L_n = L_A - L_C)$ were nearly linear in the range of 173.90(6)° $-175.47(6)^{\circ}$ [28]. Interestingly, the planes of the N-phenyl group and the plane of palladium and pyridine were perpendicular in L_APdCl_2 and L_BPdCl_2 (each 84.3°, 79.6°). Moreover, the plane of the N-nitrophenyl group and the plane of palladium and pyridine in L_cPdCl_2 were only slightly twisted by ca. 57.2° rather than 84.3° for LAPdCl₂. In addition, we also observed the degree of distortion of N-((pyridin-2-yl)methylene)amine ligands and Pd(II) complexes by the new 4-coordinate structure index (τ_4). The new geometric parameters for the four coordinate compounds (τ_4) are presented in **Table S2** as improved simple metrics for quantitatively evaluating the geometry of the four coordinate complexes and compounds [39]. In Table S2, the τ_4 value of [L_nPdCl₂] (L_n = L_A - L_C, L_F and L_I) showed a square planar

distorted by 0.0753 – 0.0819.

3.3. MMA polymerisation

The catalytic capabilities of synthesized Pd(II) complexes were assessed towards the polymerisation of MMA in the presence of MMAO. The polymerisation was conducted at 60 °C and all the complexes L_nPdCl_2 ($L_n = L_A - L_1$) polymerized MMA yielding PMMA with T_g (glass transition temperature) ranging from 120 to 131 °C. The resultant polymers (PMMA) were isolated as a white solid and characterized by GPC in THF using standard polystyrene as the reference. The major polymer characteristics are summarized in Table 1.

Metal complexes with appropriate ligand architecture are vital for accomplishing a high degree control of polymerisation process due to the fact that metal complexes influence all steps of polymerisation such as initiation, propagation, and termination [8,40,41]. It is evident from polymerisation data that substituents on imine moiety influence the catalytic efficacy which was determined by the relative amounts of PMMA product. The presence of sterically demanding substituents around the metal centre is presumed to have a negative effect on MMA activation as the steric bulk might inhibit monomer access to the metal centre [42]. For instance, L_APdCl_2 with a 2,6-diethylphenyl substituent on the imine moiety exhibited lower catalytic activity compared with L_BPdCl_2 with a 2,6-dimethylphenyl substituent on the imine moiety (Table 1; entries 4 & 5). The iminopyridine-based Pd(II) complexes showed activity in the order of $L_CPdCl_2 > L_BPdCl_2 > L_APdCl_2$, depending on the steric bulk provided by the ortho substituents on phenyl group of imine moiety (Fig 1-3) around the metal centre. Further, the orientation of the imine substituents to the *xy*-plane of the pyridine ring and metal centre also influence the activity towards MMA polymerisation. L_APdCl_2 with the 2,6-

diethylphenyl group that is perpendicular and slightly twisted toward the xy plane of the *N*-((pyridin-2-yl)methylene)amine-Pd moiety by 84.3° has greater steric hindrance and exhibited lower activity than L_BPdCl_2 , in which the distortion angle of the 2,4,6trimethylphenyl group towards the xy plane of the *N*-((pyridin-2-yl)methylene)amine-Pd moiety was by 79.6°. Further L_BPdCl_2 exhibited lower activity than L_CPdCl_2 , in which the distortion angle of the 4-nitrophenyl group towards the xy plane of the *N*-((pyridin-2yl)methylene)amine-Pd moiety was by 57.2°. It can be seen that ortho ethyl substituent receives some degree of steric hindrance compared to other ligands. Thus, both of 2,6diethylphenyl substituted ring and metallacyclic ring are almost perpendicular. Further the distance of C(15)-Pd(1) and C(9)-Pd(1) in L_APdCl_2 was calculated as 3.755 and 4.025 Å to give obvious steric hindrance of 2,6-diethylphenyl substituent ring than phenyl substituent ring in the *N*-((pyridin-2-yl)methylene)amine-Pd(II) complexes.

To evaluate the total steric hindrance by bulky ligands to metal centre, the program "SambVca" [43] was used to compare and predict and quantitatively calculate the topographic steric map of the Pd(II) complexes. Fig. S1 shows ball and stick model, spacefilling model and topographic steric map of L_nPdCl_2 ($L_n = L_A-L_C$, L_F , L_I) to provide a three dimensional bulk ligand. Only considering total steric factor by topographic steric map of [L_nPdCl_2] ($L_n = L_A - L_C$), [L_CPdCl_2] (buried volume % is 35.4), which has a smaller steric hindrance than L_APdCl_2 (buried volume % is 39.9), has higher polymerisation activity (L_CPdCl_2 : 4.79 × 10⁴ g PMMA/mol·Pd·h > L_APdCl_2 : 4.00 × 10⁴ g PMMA/mol·Pd·h). Similarly L_APdCl_2 (buried volume % is 39.9, 4.00 × 10⁴ g PMMA/mol·Pd·h) < L_BPdCl_2 (buried volume % is 39.8, 4.30 × 10⁴ g PMMA/mol·Pd·h) < L_CPdCl_2 (buried volume % is 35.4, 4.79 × 10⁴ g PMMA/mol·Pd·h). When L_nPdCl_2 was used as a polymerisation catalyst, L_1PdCl_2 exhibited the highest catalytic activity (7.08 × 10⁴ g PMMA/mol·Pd·h). It is

evident from **Fig. S1** that L_CPdCl_2 (buried volume % is 35.4, 4.79 × 10⁴ g PMMA/mol·Pd·h) with lesser steric bulk exhibited lower activity than L_1PdCl_2 (buried volume % is 35.9, 7.08 × 10⁴ g PMMA/mol·Pd·h). These catalytic systems clearly showed steric and electronic effects of Pd(II) complexes during MMA polymerisation. For instance, L_FPdCl_2 showed better catalytic activity (buried volume % is 39.8, 5.44 × 10⁴ g PMMA/mol·Pd·h) than L_BPdCl_2 (buried volume % is 39.8, 4.30 × 10⁴ g PMMA/mol·Pd·h) with identical steric bulk (**Fig. S1**). Thus, both steric and electronic effects of initiators are needed to correlate the polymerisation activity and structure of L_nPdCl_2 ($L_n = L_A - L_1$) complexes. It is evident from polymerisation data (**Table 1**) that L_EPdCl_2 despite of having unsubstituted phenyl group at imine moiety showed a profound loss of catalytic activity under same experimental conditions. Moreover, the lowest catalytic activity of L_DPdCl_2 (Table 1; entry 7) compared to rest of its analogous, i.e. L_nPdCl_2 ($L_n = L_A - L_C$ and $L_E - L_1$), was due to its poor solubility in the reaction media. Hence the solubility of the catalytic species in the reaction solution also influences the catalytic activities.

In comparison to our previously reported Pd(II) complexes bearing *N*-substituted 2iminoalkylpyridines, *N*,*N*-di(2-picolyl)cycloalkylamine, and *N*-substituted 2iminomethylpyridine- and 2-iminomethylquinoline coordinated palladium(II) [9c-d], the current system exhibited better polymerisation control under same experimental control. Similarly, the Pd(II) complexes in the current study are faster (activity 7.08 × 10⁴ g PMMA/mol·Pd·h) and yielded higher molecular weight PMMA (11.0 ×10⁵ g/mol) with moderate stereoselectivities compared with Zn(II) initiators bearing *N*-cycloalkyl 2iminomethylpyridine- and 2-iminomethylquinoline-based ligands (activity 3.33 × 10⁴ g PMMA/mol·Zn·h) [9a].

The blank polymerisation of MMA was processed with PdCl₂ and Pd(MeCN)₂Cl₂

in presence of MMAO or MAO only under identical experimental conditions (**Table 1**; entries 1-3). It is evident that the synthesized Pd(II) complexes garnered higher activities with better polymerisation control and better selectivities compared to starting material. Thus, the activity of these Pd(II) complexes toward MMA polymerisation is influenced by electronic and steric effect of ligand framework which may induce steric hindrance and electronic differences on the palladium centre. This result is comparable with previous Pd(II) complexes containing the *N*,*N'*-bidentate *N*-substituted 2-iminomethylpyridines and *N*,*N'*,*N*-tridentate *N*,*N*-di(2-picolyl)cycloalkylamine, which showed *N*-substitution's steric effects and electronic effects of ligands. The PDIs of the Pd(II) complexes in the current system are in the range 2.16 - 3.10 at 60 °C (**Table 1**). In general, the PDI range narrowed as the molecular weight of PMMA increased [44,45]. L_EPdCl₂ yielded the narrowest PDI and the highest molecular weight of PMMA at 60 °C (**Table 1**; entry 8).

The tacticity of PMMA was determined in the range around syndiotactic (rr, δ 0.85), heterotactic (mr, δ 1.02), and isotactic (mm, δ 1.21), based on ¹H NMR data [46]. Unexpectedly, the stereoselectivity and PDIs were not strongly affected by the substituents attached to imine moiety in our current study. All the Pd(II) complexes **L**_nPdCl₂ (L_n = L_A – L₁) yielded syndiotactic PMMA. Syndiotacticity was not sufficiently high to offer a mechanism for the coordination polymerisation but was similar for all the synthesised Pd(II) complexes. In addition, experiments using 2,6,6,6-tetramethylpiperidinyloxy (TEMPO), a 5-equiv. radical inhibitor during the MMA polymerisation, did not significantly reduce the yield of PMMA and showed a yield reduction of at least 2 % up to 5 % supporting the mechanism of coordination polymerized MMA with moderate activity and syndiotacticity. S i m i l a r l y , Cu(II) complexes bearing *N*-(2-furanylmethyl)-*N*-(1-3,5-dimethyl-1*H*-

pyrazolylmethyl)-*N*-(phenylmethyl)amines yielded syndiotactic PMMA (rr = 0.78) with only 30% conversion [48]. Recently, lanthanide metal organosamarium(II) complex with bispy rrolylaldiminato ligand produces isotactic PMMA with an *mm* value of 98% [49]. Moreover, it is evident from polymerization data that steric hindrance of substituents at the imine moiety significantly affected the activity of these complexes towards MMA polymerisation. However, slight the molecular weights of resultant PMMAs have been increased slightly with decrease of the steric bulk at imine moiety. We are currently carrying out further investigations to improve the catalytic activity in terms of ligand framework variations and the resultant stereoregularities.

4. Conclusions

A series of Pd(II) complexes, $[L_nPdCl_2]$ ($L_n = L_A - L_I$) have been synthesized and structurally characterized. The coordination geometry around the Pd(II) centres in iminopryridine-Pd(II) complexes were distorted square-planar. L_1PdCl_2 exhibited high activity (7.08 ×10⁴ g PMMA/mol·Pd·h) in the presence of MMAO at 60 °C towards MMA polymerisation. Moreover, it has been observed that steric hindrance of substituents at the imine moiety plays a major role in determining the catalytic efficacy of these complexes for MMA polymerisation. The catalytic activity of complexes with less steric hindrance is higher than complexes with sterically demanding substituents at imine moiety. However, the syndiotacticity and molecular weights of resultant PMMs were not significantly affected by ligand architecture.

5. Supplementary materials

CCDC 1837589–1837591 contain the supplementary crystallographic data for complexes L_APdCl_2 , L_BPdCl_2 and L_CPdCl_2 , respectively. The data can be obtained free of charge <u>via</u> <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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References

- [1] E.Y.-X. Chen, Chem. Rev. 109 (2009) 5157.
- [2] (a) K. Endo, Macromol. Chem. Phys. 200 (1999) 1722;
 - (b) K. Endo, A. Inukai, Polymer Int. 49 (2000) 110;
 - (c) C. Carlini, M. Martinelli, A. M. Raspolli Galletti, G. Sbrana, J. Pol. Sci. Part A: Polym. Chem. 41 (2003) 1716.
- [3] (a) I. Kim, J.M. Hwang, J.K. Lee, C.S. Ha, S.I. Woo, Macromol. Rapid Commun. 24 (2003) 508;
 - (b) X. He, Y. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang, Q. Wu, Organometallics 22 (2003) 4952.
- [4] (a) K. Shibayama, Polym. J. 35 (2003) 711;
 - (b) R.T. Stibrany, D.N. Schulz, S. Kacker, A.O. Patil, L.S. Baugh, S.P. Rucker, S. Zushma, E. Berluche, J.A. Sissano, Macromolecules 36 (2003) 8584.

[5] (a) P.M. Castro, M.P. Lankinen, A.-M. Uusitalo, M. Leskelä, T. Repo, Macromol. Symp. 213 (2004) 199;

(b) J.-Y. Liu, Y. Zheng, Y.-S. Li, Polymer 45 (2004) 2297;

- (c) E. Ihara, Y. Maeno, H. Yasuda, Macromol. Chem. Phys. 202 (2001) 1518;
- (d) L. Wang, Y. Li, F. Zhu, Q. Wu, Polym. Bull. 57 (2006) 73.
- [6] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428;

(b) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;

(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.

[7] (a) L.S. Boffa, B.M. Novak, Chem. Rev. 100 (2000) 1479;

(b) F. Speiser, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784;

(c) J. Zhang, X. Wang, G.X. Jin, Coord. Chem. Rev. 250 (2006) 95.

- [8] V.C. Gibson, R.K. O'Reilly, D.F. Wass, A.J.P. White, D.J. Williams, Dalton Trans. (2003) 2824.
- [9] (a) J. Heo, H. Lee, S. Nayab, J. Coord. Chem. 70 (2017) 3837;
 - (b) Y. Song, D. Kim, H.-J. Lee, H. Lee, Bull. Korean Chem. Soc. 35 (2014) 2929;
 - (c) S. Kim, E. Kim, H.-J. Lee, H. Lee, Polyhedron 69 (2014) 149;
 - (d) D. Kim, Y. Song, S. Kim, H.-J. Lee, H. Lee, J. Coord. Chem. 67 (2014) 2312;
 - (e) D. Kim, S. Kim, E. Kim, H.-J. Lee, H. Lee. Polyhedron 63 (2013) 139.

[10] G. Cárdenas-Triviño, R.C. Camilo, K.J. Klabunde, Polym. Bull. 25 (1991) 315.

- [11] (a) K. Nienkemper, V.V. Kotov, G. Kehr, G. Erker, R. Fröhlich, Eur. J. Inorg. Chem.(2006) 366;
 - (b) R.N. Dominey, B. Hauser, J. Hubbard, J. Dunham, Inorg. Chem. 30 (1991) 4754;
 - (c) Q. Dai, X. Jia, F. Yang, C. Bai, Y. Hu, X. Zhang, Polymers 8 (2016) 1;
 - (d) S. Dehghanpour, N. Bouslimani, R. Welter, F. Mojahed, Polyhedron 26 (2007) 154;

(e) V.G. Bähr, H.-G. Döge, Z. Anorg. Allg. Chem. 292 (1957) 119.

[12] (a) R. Ziessel, Coord. Chem. Rev. 216 (2001) 195;

[13] (a) G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728;

(b) J. Manzur, A.M. García, A. Vega, A. Ibañez, Polyhedron 26 (2007) 115;

- (c) T.W. Myers, T.J. Sherbow, J.C. Fettinger, L.A. Berben, Dalton Trans. 45 (2016) 5989;
- (d) C. Pellecchia, M. Mazzeo, D. Pappalardo, Macromol. Rapid Commun. 19 (1998)651.
- [14] (a) J. Zhang, W. Li, W. Bu, L. Wu, L. Ye, G. Yang, Inorg. Chim. Acta 358 (2005) 964;
 (c) B.P. Buffin, P.J. Squattrito, A.O. Ojewole, Inorg. Chem. Commun. 7 (2004) 14;
 (d) D. Carmona, C. Vega, F.J. Lahoz, S. Elipe, L.A. Oro, M.P. Lamata, F. Viguri, R. García-Correas, C. Cativiela, M.P.L.-R. de Víu, Organometallics 18 (1999) 3364;
 (e) C.-J. Qiu, Y.-C. Zhang, Y. Gao, J.-Q. Zhao, J. Organomet. Chem. 694 (2009) 3418.
- [15] (a) E.-Q. Gao, Y.-F. Yue, S.-Q. Bai, Z. He, C.-H. Yan, Cryst. Growth Des. 5 (2005) 1119;
 (g) J. Schnödt, J. Manzur, A.-M. García, I. Hartenbach, C. Yong Su, J. Fiedler, W. Kaim, Eur. J. Inorg. Chem. (2011) 1436;

(h) Z.-L. You, X. Han, G.-N. Zhang, Z. Anorg. Allg. Chem. 634 (2008) 142.

- [16] (a) G.-E. Matsubayashi, M. Okunaka, T. Tanaka, J. Organomet. Chem. 56 (1973) 215;
 (b) 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. 16 (2016) 3366;
 - (c) Y.-W. Dong, R.-Q. Fan, X.-M. Wang, P. Wang, H.-J. Zhang, L.-G. Wei, Y. Song, X.

⁽b) J. Wang, S. Onions, M. Pilkington, H. Stoeckli-Evans, J.C. Halfpenny, J.D. Wallis, Chem. Commun. (2007) 3628.

Du, W. Chen, Y.-L. Yang, Eur. J. Inorg. Chem. (2016) 3598.

[17] (a) A.S. Roy, P. Saha, P. Mitra, S.S. Maity, S. Ghosh, P. Ghosh, Dalton Trans. 40 (2011)7375;

(b) D.H. Jara, L. Lemus, L. Farías, E. Freire, R. Baggio, J. Guerrero, Eur. J. Inorg. Chem. (2012) 1579.

- [18] (a) A.N. Jadhav, S.B. Pawal, S.S. Chavan, Inorg. Chim. Acta 440 (2016) 77;
 (b) M.L. Conrad, J.E. Enman, S.J. Scales, H. Zhang, C.M. Vogels, M.T. Saleh, A. Decken, S.A. Westcott, Inorg. Chim. Acta 358 (2005) 63.
- [19] (a) T. Birkle, A. Carbayo, J.V. Cuevas, G. García-Herbosa, A. Muñoz, Eur. J. Inorg. Chem. (2012) 2259;
 - (b) T.S.B. Baul, S. Kundu, H. Höpfl, E.R.T. Tiekink, A. Linden, J. Coord. Chem. 67 (2014) 1061;

(c) E.M. Njogu, B. Omondi, V.O. Nyamori, J. Mol. Struct. 1135 (2017) 118;

- (d) S. Dehghanpour, R. Aleesha, Synth. React. Inorg. Met.-Org. Nano-Metal Chem. 42 (2012) 1132.
- [20] (a) B.B. Wayland, R.F. Schramm, Inorg. Chem. 8 (1969) 971;
 (b) C.J. Mathews, P.J. Smith, T. Welton, J. Mol. Catal. A: Chem. 206 (2003) 77.
- [21] S. Dehghanpour, A. Mahmoudi, Main Group Chem. 6 (2007) 121
- [22] (a) C.-H. Chien, S. Fujita, S. Yamoto, T. Hara, T. Yamagata, M. Watanabe, K. Mashima, Dalton Trans. (2008) 916;
 - (b) J. Dai, S. Nanayakkara, T.C. Lamb, A.J. Clark, S.-X. Guo, J. Zhang, A.F. Patti, K. Saito, New J. Chem. 40 (2016) 3511.
- [23] H. Sun, L. Wang, Y. Pan, J. Am. Soc. Mass Spectrom. 25 (2014) 169.
- [24] J. Cloete, S.F. Mapolie, J. Mol. Catal. A: Chem. 243 (2006) 221.

- [25] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112.
- [26] B. Crociani, F.D. Bianca, Inorg. Chim. Acta 141 (1988) 253.
- [27] S.J. Scales, H. Zhang, P.A. Chapman, C.P. McRory, E.J. Derrah, C.M. Vogels, M.T. Saleh, A. Decken, S.A. Westcott, Polyhedron 23 (2004) 2169.
- [28] W.M. Motswainyana, S.O. Ojwach, M.O. Onani, E.I. Iwuoha, J. Darkwa, Polyhedron 30 (2011) 2574.
- [29] SMART and SAINT-Plus v 6.22, Bruker AXS Inc., Madison, Wisconsin, USA, (2000).
- [30] G.M. Sheldrick, SADABS v 2.03, University of Göttingen, Germany, (2002).
- [31] SHELXTL v 6.10; Bruker AXS, Inc: Madison, Wisconsin, USA, (2000).
- [32] A.J. Arvai, C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation, Poway, CA, USA (1983).
- [33] Z. Otwinowski, W. Minor, Methods in Enzymology, C.W. Carter, Jr., R.M. Sweet (Eds.), Vol. 276, Part A, p. 307, Academic Press, New York (1997).
- [34] G.M. Sheldrick. Acta Cryst. A64 (2008) 112.
- [35] Y. Song, Z. Xu, Q. Sun, B. Su, Q. Gao, H. Liu, J. Zhao, J. Coord. Chem. 60 (2007) 2351.
- [36] W. Zhang, W.-H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Chen, P. Hao, J. Organomet. Chem. 691 (2006) 4759.
- [37] F.H. Allen, Acta Cryst. B58 (2002) 380.
- [38] (a) S. Reinhardt, K. Heinze, Z. Anorg. Allg. Chem. 632 (2006) 1465;
 - (b) S. Dehghanpour, A. Mahmoudi, S. Rostami, Polyhedron 29 (2010) 2190.
- [39] L. Yang, D.R. Powell, R.P. Houser, Dalton Trans. (2007) 955.
- [40] (a) D.F. Grishin, L.L. Semyonycheva, Russ. Chem. Rev. 70 (2001) 425;
 - (b) A.V. Yakimanskii, Polym. Sci. Ser. C 47 (2005) 1.

- [41] (a) R.M. Islamova, G.R. Sadykova, Y.B. Monakov, Y.Z. Voloshin, I.S. Makarov, Y.N. Bubnov, Russ. J. Appl. Chem. 82 (2009) 1467;
 (b) Y.B. Monakov, R.M. Islamova, I.A. Ionova, S.A. Syrbu, T.A. Ageeva, O.I. Koifman, Mendeleev Commun. 20 (2010) 33.
- [42] S. Shin, S.H. Ahn, M.J. Jung, S. Nayab, H. Lee, J. Coord. Chem. 69 (2016) 2391.
- [43] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, Organometallics 35 (2016) 2286. For online program, see <u>https://www.molnac.unisa.it/OMtools/sambvca2.0/index.html.</u>
- [44] J. Llorens, E. Rudé, R.M. Marcos, Polymer 44 (2003) 1741.
- [45] G.T. Lewis, V. Nguyen, Y. Cohen, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 5748.
- [46] (a) T. Kitaura, T. Kitayama, Macromol. Rapid Commun. 28 (2007) 1889;(b) Y. Isobe, T. Nakano, Y. Okamoto, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 1463.
- [47] B.K. Bahuleyan, D. Chandran, C.H. Kwak, C.-S. Ha, I. Kim, Macromol. Res. 16 (2008)745.
- [48] C. Lansalot-Matras, F. Bonnette, E. Mignard, O. Lavastre, J. Organomet. Chem. 693 (2008) 393.
- [49] C. Cui, A. Shafir, C.L. Reeder, J. Arnold, Organometallics 22 (2003) 3357.
- [50] S. Kim, D. Kim, H.-J. Lee, H. Lee, Polyhedron 77 (2014) 66.
- [51] S. Kim, Y. Song, H.-J. Lee, J. Jeon, S.H. Park, H. Lee, Bull. Korean Chem. Soc. 36 (2015) 609.
- [52] S. Kim, D. Kim, Y. Song, H.-J. Lee, H. Lee, Aust. J. Chem. 67 (2014) 953.



Scheme 1. Synthetic route of Pd(II) complexes bearing picolinaldehyde based imine ligands,

 $\mathbf{L_nPdCl_2} \ (\mathbf{L_n} = \mathbf{L_A} - \mathbf{L_I}).$

Table 1. Polymerisation of MMA by L_nPdCl_2 ($L_n = L_A - L_I$) in the presence of MMAO.

	Entry	Catalyst ^a	Yield ^b	Activity ^c	$T_g^{\ d}$	Tacticity			${\mathbf M_{\mathrm{w}}}^{\mathrm{e}}$	PDI ^f
			(g)	$(g/mol-Cat\cdot h) \times 10^4$	(°C)	%mm	%mr	%rr	(g/mol)×10 ⁵	
	1	PdCl₂ ^g	12.6	1.97	129	10.2	23.5	67.7	9.27	1.58
	2	Pd(MeCN) ₂ Cl ₂ ^g	18.8	2.93	131	7.60	22.8	69.6	0.61	2.20
	3	MMAO ^h	8.97	1.40	120	37.2	10.9	51.9	6.78	2.09
	4	L _A PdCl ₂	25.5	4.00	121	9.82	21.5	68.7	11.0	3.10
	5	L _B PdCl ₂	27.5	4.30	120	8.33	22.2	69.4	11.2	2.33

6	L _C PdCl ₂	30.7	4.79	121	8.82	23.5	67.6	11.0	2.38
7	L _D PdCl ₂	14.8	2.30	122	8.33	25.0	66.7	8.39	2.31
8	L _E PdCl ₂ ^j	22.9	3.33	124	10.3	20.5	69.2	12.5	2.16
9	L _F PdCl ₂ ⁱ	34.9	5.44	121	9.68	22.6	67.7	8.76	2.24
10	$\mathbf{L}_{\mathbf{G}}\mathbf{PdCl}_{2}^{j}$	22.9	3.58	128	10.3	20.7	69.0	10.8	2.96
11	$\mathbf{L}_{\mathbf{H}}\mathbf{PdCl}_{2}^{j}$	26.2	4.09	123	9.09	21.2	69.7	12.1	2.40
12	$\mathbf{L_{I}PdCl_{2}^{i}}$	45.4	7.08	122	8.82	23.5	67.7	8.45	2.52

^a $[Pd(II) catalyst]_0 = 15 \mu mol, and [MMA]_0/[MMAO]_0/[Pd(II) catalyst]_0 = 3100:500:1, polymerisation temp. = 60 °C and time = 2 h.$

^b Yield defined a mass of dried polymer recovered/mass of monomer used.

^c Activity is calculated (g of PMMA)/(mol·Pd·h).

^d T_g is glass transition temperature which is determined by a thermal analyzer.

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

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

^g It is a blank polymerisation in which PdCl₂ and Pd(MeCN)₂Cl₂ were also activated by MMAO.

^h It is a blank polymerisation which was done solely by MMAO.

ⁱComplexes of L_FPdCl_2 and $[L_IPdCl_2$ are reported in our earlier work [25,28], however, data in Table 1 comes from this work.

^jComplexes of L_EPdCl₂, L_FPdCl₂, L_GPdCl₂, L_HPdCl₂ and L_IPdCl₂ are reported in the literature [24-28].



Fig. 1. ORTEP drawing of **L**_A**PdCl**₂ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°), Pd(1)–N(2) 2.023(5), Pd(1)–N(1) 2.035(5), Pd(1)–Cl(2) 2.273(2), Pd(1)–Cl(1) 2.283(2); N(2)–Pd(1)–N(1) 80.6(2), N(2)–Pd(1)–Cl(2) 93.67(2), N(1)–Pd(1)–Cl(2) 174.27(2), N(2)–Pd(1)–Cl(1) 174.23(2), N(1)–Pd(1)–Cl(1) 94.02(2), Cl(2)–Pd(1)–Cl(1) 91.71(7).

CCE



Fig. 2. ORTEP drawing of **L**_B**PdCl**₂ with thermal ellipsoids at 70% probability. All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°), Pd(1)–N(2) 2.0219(1), Pd(1)–N(1) 2.0294(1), Pd(1)–Cl(2) 2.2850(6), Pd(1)–Cl(1) 2.2896(5); N(2)–Pd(1)–N(1) 80.31(5), N(2)–Pd(1)–Cl(2) 94.25(4), N(1)–Pd(1)–Cl(2) 174.53(3), N(2)–Pd(1)–Cl(1) 174.55(4), N(1)–Pd(1)–Cl(1) 94.24(4), Cl(2)–Pd(1)–Cl(1) 91.20(2).

ACCE



Fig. 3. ORTEP drawing of **L**_C**PdCl**₂ with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°), Pd(1)–N(2) 2.039(2), Pd(1)–N(1) 2.038(2), Pd(1)–Cl(2) 2.2724(9), Pd(1)–Cl(1) 2.2871(9), N(2)–Pd(1)–N(1) 80.35(9); N(2)–Pd(1)–Cl(2) 95.53(6), N(1)–Pd(1)–Cl(2) 175.47(6), N(2)–Pd(1)–Cl(1) 173.90(6), N(1)–Pd(1)–Cl(1) 94.15(7), Cl(2)–Pd(1)–Cl(1) 90.05(3).

Graphical Abstract (Pictorial)



Graphical Abstract (Synopsis)

Palladium(II) complexes L_nPdCl_2 ($L_n = L_A - L_I$) with N,N-bidentate imine ligands derived from picolinaldehyde and substituted anilines have been synthesized and characterized. Pd(II) complexes effectively initiate MMA polymerisation in the presence of MMAO yielding syndio-enriched PMMA. The substituent at imine moiety of iminopyridine framework significantly affect the catalytic activity. Substituents at imine moiety in L_nPdCl_2 ($L_n = L_A - L_I$) weri. play a vital role in controlling their activities toward MMA polymerization.