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Palladium(II) complexes containing *N,N′*-bidentate *N*-(pyridin-2-ylmethyl)aniline and its derivatives: Synthesis, structural characterisation, and methyl methacrylate polymerisation

Sunghoon Kim [a], Dongil Kim [a], Ha-Jin Lee [b,c], Hyosun Lee [a,*]

[a] Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, 1370 Sankyuk-dong, Buk-gu, Daegu-city 702-701, Republic of Korea
[b] Jeonju Center, Korea Basic Science Institute (KBSI), 634-18 Keumam-dong, Dukjin-gu, Jeonju-city 561-180, Republic of Korea
[c] Department of Chemistry, Chonbuk National University, Dukjin-gu, Jeonju-city 561-756, Republic of Korea

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ABSTRACT

The reaction of $[Pd(CH_3CN)_2Cl_2]$ with *N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_1}$) and its derivatives ($\mathbf{L_2}$–$\mathbf{L_6}$) in ethanol yields [(*NN′*)$PdCl_2$] complexes, namely [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_1}$–$\mathbf{L_6}$). The X-ray crystal structure of Pd(II) complexes revealed that the palladium atom in [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_1}$–$\mathbf{L_6}$) showed a square plane geometry involving two nitrogen atoms of *NN′*-bidentate and two chlorido ligands. Complex [$\mathbf{L_4}PdCl_2$] containing 2,4,6-trimethyl-*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_4}$) showed the highest catalytic activity for the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) with an activity of 1.41×10^5 g PMMA/mol Pd·h at 60 °C and poly(methyl methacrylate) (PMMA) syndiotacticity (characterised using ^{1}H NMR spectroscopy) of *ca.* 0.70.

1. Introduction

Transition metal complexes containing *N,N′*-bidentate ligands with pyridylmethylamines are common and diverse due to the easy synthesis of ligands and their versatile modification through the introduction of substituents on the amine residue and a pyridyl unit [1–16]. Several structural variations in pyridylmethylamines and their complexes have been reported, and their steric and electronic properties vary because the polydentate characteristics play a role during catalysis [17–29]. These variations result in abundant pyridylmethylamines and analogues of transition metal complexes with specific chemical applications. Specifically, structural variations are observed in group 10 (Ni, Pd, and Pt) with pyridylmethylamines and their derivatives. For example, Ni complexes exist as tetrahedral to octahedral monomers or dimers with two ligand units coordinated to Ni, achieving a five-coordinated or six-coordinated structure [30–38]. In contrast, palladium and platinum complexes mainly exist in a monomeric square-planar geometry [39–60]. The majority of transition metal complexes containing these ligands have been applied for synthesis, structural analysis, and spectroscopy [1–11,17–22,30–37,43–53,60], used for electronic materials [12,13], catalysts for organic transformation [14,16,23–25,41,42,54–58], biological applications [26–28,40,59], and olefin polymerisation [15,29,38,39].

Despite abundant previous reports on transition metal complexes with pyridylmethylamines and their derivatives, little is known regarding Pd(II) complexes with *N,N′*-bidentate pyridylmethylamines as catalysts for methyl methacrylate (MMA) polymerisation [15]. On the other hand, poly(methylmethacrylate) (PMMA) is a universal polymer with optical applications. A higher glass transition temperature (T_g) typically represents higher optical quality and syndiotacticity content of PMMA. The T_g of isotactic PMMA, which is produced by radical commercial processes, is around 65 °C. Thus, studies on non-radical-mediated polymerisation of MMA have been performed, and some transition metal complexes have been successfully applied [61–69]. Regarding co-ordination polymerisation of MMA mediated by transition metal complexes, previous studies explored Pd(II) and Pt(II) complexes with ligands bispyridylamine and iminopyridine as catalysts for MMA polymerisation [70,71]. Thus, we report the preparation, X-ray crystal structures, and MMA polymerisation of *N,N′*-bidentate pyridylmethylaniline ligands, *N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_1}$) [39], 4-methyl-*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_2}$) [16,43,46], ,5-dimethyl-*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_3}$), 2,4,6-trimethyl -*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_4}$), 2,6-diethyl-*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_5}$), 4-fluoro-*N*-(pyridin-2-ylmethyl)aniline ($\mathbf{L_6}$), and their Pd(II) complexes.

* Corresponding author. Tel.: +82 53 950 5337; fax: +82 53 950 6330.
E-mail address: hyosunlee@knu.ac.kr (H. Lee).

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2. Experimental

2.1. Physical measurement

$PdCl_2$, 2-pyridinecarboxaldehyde, 3,5-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diethylaniline, 4-fluoroaniline, magnesium sulfate, methyl methacrylate (MMA) were purchased from Aldrich and anhydrous solvents such as CH_3CN, C_2H_5OH, DMF, diethyl ether, dichloromethane were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem corporation as 6.9% weight aluminum of a toluene solution. Elemental analyses (C, H, N) of complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^{1}H NMR (operating at 400 MHz) and ^{13}C NMR (operating at 100 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer; chemical shifts were recorded in ppm units (δ) relative to $SiMe_4$ as the internal standard. Melting point was measured by electrothermal IA 9100 apparatus. Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha and the data are reported in reciprocal centimeters. The molecular weight and molecular weight distribution of the poly(methylmethacrylate) (PMMA) were carried out using gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). Glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q2000; TA Instruments, New Castle, DE).

2.2. Preparation of ligands and Pd(II) complexes

N-(pyridin-2-ylmethyl)aniline (**L_1**), *4-methyl-N-(pyridin-2-ylmethyl)aniline* (**L_2**) and their (dichloro)palladium(II) complexes ([**L_2**$PdCl_2$]) are previously reported [16,39,43,46].

2.2.1. 3,5-Dimethyl-N-(pyridin-2-ylmethyl)aniline (**L_3**)

3,5-Dimethylaniline (2.49 mL, 0.0200 mol) in dichloromethane (20.0 mL) was added 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol) in dichloromethane (20.0 mL). After 24 h stirring at room temperature, the dichloromethane solution was dried over the $MgSO_4$. $MgSO_4$ was filtered and the solvent was removed under reduced pressure. Crude 3,5-dimethyl-*N*-(pyridin-2-ylmethylene)aniline product was reduced by sodium borohydride (2.0 eq. 0.650 g, 0.500 mol) in anhydrous methanol (20.0 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed and crude was vacuum distilled to obtain light red oil (3.55 g, 83.6%). *Anal.* Calc. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.596; N, 13.20. Found: C, 79.01; H, 7.611; N, 12.98%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 8.17 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 7.82 (s, 1H, –$NC_5\mathbf{H}_4$–), 7.74 (t, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 6.58 (s, 1H, *p*-$(CH_3)_2C_6\mathbf{H}_3$–), 6.32 (s, 2H, *o*-$(CH_3)_2C_6\mathbf{H}_3$–), 4.49 (s, 1H, –N**H**$(CH_3)_2C_6H_3$–), 4.20 (s, 2H, –$\mathbf{CH}_2NC_5H_4$–), 2.39 (s, 6H, –$(\mathbf{CH}_3)_2C_6H_3$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.12 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$–), 156.33 (s, 1C, –$N\mathbf{C}_5H_4$–), 150.55 (s, 1C, *ipso*-$(CH_3)_2\mathbf{C}_6H_3$–), 133.89 (s, 1C, –$N\mathbf{C}_5H_4$–), 140.86 (s, 2C, *m*-$(CH_3)_2\mathbf{C}_6H_3$–), 135.86 (s, 1C, –$N\mathbf{C}_5H_4$–), 133.84 (s, 1C, –$N\mathbf{C}_5H_4$–), 128.44 (s, 1C, *p*-$(CH_3)_2\mathbf{C}_6H_3$–), 119.46 (s, 2C, *o*-$(CH_3)_2\mathbf{C}_6H_3$–), 42.86 (s, 1C, –$\mathbf{C}H_2NC_5H_4$–), 25.81 (s, 2C, –$(\mathbf{C}H_3)_2C_6H_3$–). IR (liquid neat; cm^{-1}): 3395 (w), 3016 (s), 2916 (s), 2858 (w), 1683 (s), 1597 (s), 1510 (s), 1469 (s), 1428 (s), 1335 (s), 1187 (s), 1147 (s), 1119 (s), 1041 (s), 991 (s), 919 (s), 820 (s), 753 (s), 688 (s), 613 (s).

2.2.2. 2,4,6-Trimethyl-N-(pyridin-2-ylmethyl)aniline (**L_4**)

L_4 was prepared by analogous method as described for **L_3** except utilizing 2,4,6-trimethylaniline (2.81 mL, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as light red oil (3.55 g, 78.4%). *Anal.* Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.016; N, 12.38. Found: C, 79.21; H, 8.019; N, 12.22%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.78 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.69 (d, 1H, J = 7.7 Hz, –$NC_5\mathbf{H}_4$–), 7.54 (d, 1H, J = 7.7 Hz, –$NC_5\mathbf{H}_4$–), 7.03 (s, 2H, –$(CH_3)_3C_6\ \mathbf{H}_2$–), 4.51 (s, 1H, –N**H**$(CH_3)_3C_6H_3$–), 3.94 (s, 2H, –$\mathbf{CH}_2NC_5H_4$–), 1.94 (s, 6H, *o*-$(\mathbf{CH}_3)_3C_6H_2$–), 1.72 (s, 3H, *p*-$(\mathbf{CH}_3)_3C_6H_2$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.87 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$–), 156.23 (s, 1C, –NC_5H_4–), 150.55 (s, 1C, *ipso*-$(CH_3)_3\mathbf{C}_6H_2$–), 133.89 (s, 1C, –$N\mathbf{C}_5H_4$–), 132.86 (s, 1C, *p*-$(CH_3)_3\mathbf{C}_6H_2$–), 130.86 (s, 2C, *m*-$(CH_3)_3\mathbf{C}_6H_2$–), 129.70 (s, 2C, *o*-$(CH_3)_3\mathbf{C}_6H_2$–), 130.57 (s, 1C, –$N\mathbf{C}_5H_4$–), 128.44 (s, 1C, –$N\mathbf{C}_5H_4$–), 42.86 (s, 1C, –$\mathbf{C}H_2NC_5H_4$–), 23.00 (s, 1C, *p*-$(CH_3)_3\mathbf{C}_6\ H_2$–), 21.81 (s, 3C, –$(\mathbf{C}H_3)_3C_5H_2$–). IR (liquid neat; cm^{-1}): 3362 (w), 3309 (s), 3007 (s), 2917 (w), 2858 (s), 2732 (s), 1632 (s), 1589 (s), 1481 (s), 1436 (s), 1381 (s), 1304 (s), 1226 (s), 1150 (s), 1093 (s), 1003 (s), 851 (s), 746 (s), 607 (s), 566 (s).

2.2.3. 2,6-Diethyl-N-(pyridin-2-ylmethyl)aniline (**L_5**)

L_5 [72]was prepared by analogous method as described for **L_1** except utilizing 2,6-diethylaniline (3.29 mL, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as light red oil (3.55 g, 73.9%). *Anal.* Calc. for $C_{16}H_{20}N_2$: C, 79.96; H, 8.387; N, 11.66. Found: C, 79.39; H, 8.194; N, 11.72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 8.17 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 8.13 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 7.82 (s, 1H, d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 6.58 (m, 3H, –$(CH_2CH_3)_2C_6$–$\mathbf{H}_3$–), 4.94 (s, 2H, –$\mathbf{CH}_2NC_5H_4$–), 4.64 (s, 1H, –N**H**$(CH_2CH_3)_2C_6H_3$–), 1.94 (m, 4H, –$(\mathbf{CH}_2CH_3)_2C_6H_3$–), 1.72 (t, 6H, J = 11 Hz, –$(CH_2\mathbf{CH}_3)_2\ C_6H_3$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.12 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$–), 155.33 (s, 1C, –$N\mathbf{C}_5H_4$–), 152.55 (s, 1C, *ipso*-$(CH_2CH_3)_2\mathbf{C}_6H_3$–), 138.89 (s, 1C, –$N\mathbf{C}_5H_4$–), 137.86 (s, 2C, *o*-$(CH_2CH_3)_2\mathbf{C}_6H_3$–), 136.86 (s, 2C, *m*-$(CH_2CH_3)_2\mathbf{C}_6H_3$–), 132.84 (s, 1C, –$N\mathbf{C}_5H_4$–), 131.74 (s, 1C, –$N\mathbf{C}_5H_4$–), 128.44 (s, 1C, *p*-$(CH_2CH_3)_2\mathbf{C}_6H_3$–), 52.86 (s, 1C, –$\mathbf{C}H_2NC_5H_4$–), 23.00 (s, 2C, –$(\mathbf{C}H_2CH_3)_2C_6H_3$–), 21.81 (s, 2C, –$(CH_2\mathbf{C}H_3)_2C_6H_3$–). IR (liquid neat; cm^{-1}): 3356 (w), 2964 (s), 2873 (s), 1641 (w), 1589 (s), 1447 (s), 1375 (s), 1339 (s), 1275 (s), 1201 (s), 1149 (s), 1108 (s), 1053 (s), 994 (s), 886 (s), 808 (s), 750 (s), 621 (s).

2.2.4. 4-Fluoro-N-(pyridin-2-ylmethyl)aniline (**L_6**)

L_6 was prepared by analogous method as described for **L_1** except utilizing 4-fluoroaniline (3.62 mL, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as light orange oil (3.55 g, 87.8%). *Anal.* Calc. for $C_{12}H_{11}N_2F$: C, 71.27; H, 5.482; N, 13.85, F, 9.394. Found: C, 71.09; H, 5.471; N, 13.53, F, 9.373%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.66 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.35 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.19 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 6.78 (m, 2H, –$FC_6\mathbf{H}_4$–), 6.63 (m, 2H, –$FC_6\mathbf{H}_4$–), 4.50 (s, 1H, –N**H**FC_6H_4–), 4.42 (s, 2H, –$\mathbf{CH}_2NC_5H_4$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.85 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$–), 158.99 (s, 1C, –$N\mathbf{C}_5H_4$–), 146.13 (s, 1C, *ipso*-$F\mathbf{C}_6H_4$–), 143.89 (s, 1C, *p*-$F\mathbf{C}_6H_4$–), 121.71 (s, 1C, –$N\mathbf{C}_5H_4$–), 118.72 (s, 1C, –$N\mathbf{C}_5H_4$–), 115.65 (s, 2C, *m*-$F\mathbf{C}_6H_4$–), 113.05 (s, 2C, *o*-$F\mathbf{C}_6H_4$–), 44.00 (s, 1C, –$\mathbf{C}H_2NC_5H_{10}$–). IR (liquid neat; cm^{-1}): 3356 (w), 2964 (s), 2873 (s), 1641 (w), 1589 (s), 1447 (s), 1375 (s), 1339 (s), 1275 (s), 1201 (s), 1149 (s), 1108 (s), 1053 (s), 994 (s), 886 (s), 808 (s), 750 (s), 621 (s).

2.2.5. N-(Pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([**L_1**$PdCl_2$])

A solution of **L_1** (0.0870 g, 0.473 mol) in anhydrous ethanol (10.0 mL) was added to a solution of $[Pd(CH_3CN)_2Cl_2]$ (0.122 g, 0.473 mol) [73,74], which is synthesized from the reaction between anhydrous [$PdCl_2$] and CH_3CN by refluxing, in dried ethanol (10.0 mL). The reaction mixture was stirred 12 h at room temperature. The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether

(10.0 mL × 2) to give a yellow solid (0.150 g, 88.3%). The X-ray crystals of [$\mathbf{L_1}$PdCl$_2$] were obtained within three days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of [$\mathbf{L_1}$PdCl$_2$] (0.0500 g). *Anal.* calculated for $C_{12}H_{12}N_2Cl_2Pd$: C, 39.86; H, 3.345; N, 7.747. Found: C, 39.86; H, 3.379; N, 8.281%. mp (°C): 278. ^{1}H NMR (DMSO-d$_6$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, 1H, ^3J = 6.0 Hz, –N**H**C$_6$H$_5$–), δ 8.59 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 7.65 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.63 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.61 (t, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.34 (m, 3H, *o,p*-C$_6$**H**$_5$–), 6.97 (t, 2H, J = 7.4 Hz, *m*-NC$_6$**H**$_5$–), 4.46 (d, 2H, ^3J = 14.8 Hz, ^3J = 5.8 Hz, –C**H**$_2$NC$_5$H$_4$–), 3.93 (d, 2H, ^2J = 14.8 Hz, ^3J = 5.8 Hz, –C**H**$_2$NC$_5$H$_4$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.73 (s, 1C, *ipso*-N**C**$_5$H$_4$–), 154.89 (s, 1C, *ipso*-**C**$_6$H$_5$–), 149.55 (s, 1C, –N**C**$_5$H$_4$–), 136.59 (s, 1C, –N**C**$_5$H$_4$–), 125.08 (s, 2C, *m*-**C**$_6$H$_5$–), 120.98 (s, 1C, –N**C**$_5$H$_4$–), 120.69 (s, 1C, –N**C**$_5$H$_4$–), 119.89 (s, 1C, *p*-**C**$_6$H$_5$–), 111.89 (s, 2C, *o*-C$_6$H$_5$–), 53.24 (s, 2C, –**C**H$_2$NC$_5$H$_4$–). IR (solid neat; cm^{-1}): 3234 (w), 3038 (w), 2951 (s), 2872 (s), 1915 (w), 1835 (s), 1747 (s), 1693 (s), 1649 (s), 1596 (s), 1517 (s), 1472 (s), 1319 (s), 1107 (s), 1045 (s), 994 (s), 936 (s), 850 (s), 772 (s), 657 (s).

2.2.6. 4-Methyl-N-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([$\mathbf{L_2}$PdCl$_2$])

Although [$\mathbf{L_2}$PdCl$_2$] was synthesized, there is no X-ray structure reported [46]. Thus, the [$\mathbf{L_2}$PdCl$_2$] was prepared according to a similar procedure described for [$\mathbf{L_1}$PdCl$_2$] except utilizing $\mathbf{L_2}$ (0.093 g, 0.473 mol) and [Pd(CH$_3$CN)$_2$Cl$_2$] (0.122 g, 0.473 mol). The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether (10.0 mL × 2) to give a yellow solid (0.160 g, 90.6%). The X-ray crystals of [$\mathbf{L_2}$PdCl$_2$] were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of [$\mathbf{L_2}$PdCl$_2$] (0.0500 g). *Anal.* Calc. for $C_{13}H_{14}N_2Cl_2Pd$: C, 41.57; H, 3.757; N, 7.458%. Found: C, 39.56; H, 3.670; N, 7.024%. mp (°C): 284. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.77 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), δ 8.70 (dd, 1H, ^3J = 5.2 Hz, –N**H**C$_5$H$_4$–), 8.21 (t, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 7.78 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.62 (m, 4H, –(CH$_3$)C$_6$**H**$_4$–), 7.13 (m, 2H, –(CH$_3$)C$_6$**H**$_4$–), 7.01 (m, 2H, –(CH$_3$)C$_6$**H**$_4$–), 4.98 (dd, 1H, ^2J = 17.4 Hz, ^3J = 6.0 Hz –C**H**$_2$NC$_5$H$_4$–), 4.36 (dd, 2H, ^2J = 16.8 Hz, ^3J = 5.2 Hz, –C**H**$_2$NC$_5$H$_4$–), 2.81 (s, 3H, –(C**H**$_3$)C$_6$H$_4$–). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 159.72 (s, 1C, *ipso*-N**C**$_5$H$_4$–), 154.78 (s, 1C, –N**C**$_5$H$_4$–), 149.59 (s, 1C, *ipso*-(CH$_3$)**C**$_6$H$_4$–), 126.98 (s, 2C, *m*-(CH$_3$)**C**$_6$H$_4$–), 126.21 (s, 1C, *p*-(CH$_3$)**C**$_6$H$_4$–), 120.69 (s, 1C, –N**C**$_5$H$_4$–), 118.69 (s, 1C, –N**C**$_5$H$_4$–), 115.48 (s, 2C, *o*-(CH$_3$)**C**$_6$H$_4$–), 110.38 (s, 1C, –N**C**$_5$H$_4$–), 58.78 (s, 1C, –**C**H$_2$NC$_5$H$_4$–), 34.23 (s, 1C, –(**C**H$_3$)C$_6$H$_4$–). IR (solid neat; cm^{-1}): 3275 (w), 3111 (s), 3009 (s), 2913 (w), 2775 (s), 2709 (s), 1920 (s), 1835 (s), 1745 (s), 1694 (s), 1649 (s), 1616 (s), 1525 (s), 1435 (s), 1323 (s), 1270 (s), 1214 (s), 1118 (s), 957 (s), 874 (s), 811 (s), 773 (s), 711 (s).

2.2.7. 3,5-Dimethyl-N-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([$\mathbf{L_3}$PdCl$_2$])

The [$\mathbf{L_3}$PdCl$_2$] was prepared according to the similar procedure described for [$\mathbf{L_1}$PdCl$_2$] except utilizing $\mathbf{L_3}$ (0.100 g, 0.473 mol) and [Pd(CH$_3$CN)$_2$Cl$_2$] (0.122 g, 0.473 mol). The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether (10.0 mL × 2) to give a yellow solid (0.170 g, 92.8%). The X-ray crystals of [$\mathbf{L_3}$PdCl$_2$] were obtained within five days from diethyl ether (10.0 mL) diffusion into an DMF solution (10.0 mL) of [$\mathbf{L_3}$PdCl$_2$] (0.0500 g). *Anal.* Calc. for $C_{14}H_{16}N_2Cl_2Pd$: C, 43.16; H, 4.139; N, 7.190. Found: C, 43.03; H, 4.082; N, 7.130%. mp (°C): 294. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.77(d, 1H, ^3J = 6.0 Hz, –N**H**(CH$_3$)$_2$C$_6$H$_3$–), δ 8.65 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 8.52 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 8.19 (s, 1H, –NC$_5$**H**$_4$–), 7.77 (t, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 7.61 (s, 1H, *p*-(CH$_3$)$_2$C$_6$**H**$_3$–), 7.34 (s, 2H, *o*-(CH$_3$)$_2$C$_6$**H**$_3$–), 4.96 (s, 1H, ^2J = 17.2 Hz, ^3J = 6.4 Hz, –C**H**$_2$(CH$_3$)$_2$C$_6$H$_3$–), 4.36 (s, 1H, ^2J = 17.2 Hz, ^3J = 6.4 Hz, –C**H**$_2$(CH$_3$)$_2$C$_6$H$_3$–), 2.20 (s, 3H, –(C**H**$_3$)$_2$C$_6$H$_3$–), 2.09 (s, 3H, –(C**H**$_3$)$_2$C$_6$H$_3$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.12 (s, 1C, *ipso*-N**C**$_5$H$_4$–), 156.33 (s, 1C, –N**C**$_5$H$_4$–), 150.55 (s, 1C, *ipso*-(CH$_3$)$_2$**C**$_6$H$_3$–), 133.89 (s, 1C, –N**C**$_5$H$_4$–), 140.86 (s, 2C, *m*-(CH$_3$)$_2$**C**$_6$H$_3$–), 135.86 (s, 1C, –N**C**$_5$H$_4$–), 133.84 (s, 1C, –N**C**$_5$H$_4$–), 128.44 (s, 1C, *p*-(CH$_3$)$_2$**C**$_6$H$_3$–), 119.46 (s, 2C, *o*-(CH$_3$)$_2$**C**$_6$H$_3$–), 42.86 (s, 2C, –**C**H$_2$NC$_5$H$_4$–), 25.81 (s, 2C, –(**C**H$_3$)$_2$C$_6$H$_3$–). IR (solid neat; cm^{-1}): 3236 (w), 3039 (s), 2913 (s), 2667 (w), 1919 (s), 1834 (s), 1744 (s), 1694 (s), 1649 (s), 1601 (s), 1526 (s), 1474 (s), 1320 (s), 1243 (s), 1196 (s), 1093 (s), 1054 (s), 988 (s), 940 (s), 890 (s), 843 (s), 762 (s), 700 (s), 632 (s).

2.2.8. 2,4,6-Trimethyl-N-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([$\mathbf{L_4}$PdCl$_2$])

The [$\mathbf{L_4}$PdCl$_2$] was prepared according to the similar procedure described for [$\mathbf{L_1}$PdCl$_2$] except utilizing $\mathbf{L_4}$ (0.106 g, 0.473 mol) and [Pd(CH$_3$CN)$_2$Cl$_2$] (0.122 g, 0.473 mol). The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether (10.0 mL × 2) to give a yellow solid (0.170 g, 89.6%). The X-ray crystals of [$\mathbf{L_4}$PdCl$_2$] were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of [$\mathbf{L_4}$PdCl$_2$] (0.0500 g). *Anal.* Calc. for $C_{15}H_{18}N_2Cl_2Pd$: C, 44.63; H, 4.494; N, 6.940. Found: C, 44.83; H, 3.840; N, 6.724%. mp (°C): 295. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.92 (d, 1H, ^3J = 5.6 Hz, –N**H**(CH$_3$)$_3$C$_6$H$_2$–), 8.12 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.78 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.56 (d, 2H, J = 7.7 Hz, –NC$_5$**H**$_4$–), 6.91 (s, 1H, –(CH$_3$)$_3$C$_6$**H**$_2$–), 6.80 (s, 1H, –(CH$_3$)$_3$C$_6$**H**$_2$–), 4.52 (s, 1H, ^2J = 11.2 Hz, ^3J = 3.2 Hz, –C**H**$_2$NC$_5$H$_4$–), 4.48 (s, 1H, ^2J = 11.2 Hz, ^3J = 3.2 Hz, –C**H**$_2$NC$_5$H$_4$–), 3.08 (s, 3H, *p*-(C**H**$_3$)$_3$C$_6$H$_2$–), 2.29 (s, 3H, *m*-(CH$_3$)$_3$NC$_6$H$_2$–), 2.18 (s, 3H, *m*-(CH$_3$)$_3$NC$_6$H$_2$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.35 (s, 1C, *ipso*-N**C**$_5$H$_4$–), 148.59 (s, 1C, –N**C**$_5$H$_4$–), 141.31 (s, 1C, *ipso*-(CH$_3$)$_3$**C**$_6$H$_2$–), 140.21 (s, 1C, –N**C**$_5$H$_4$–), 135.60 (s, 1C, *p*-(CH$_3$)$_3$**C**$_6$H$_2$–), 131.16 (s, 1C, *m*-(CH$_3$)$_3$**C**$_6$H$_2$–), 130.44 (s, 1C, *o*-(CH$_3$)$_3$**C**$_6$H$_2$–), 124.04 (s, 1C, –N**C**$_5$H$_4$–), 121.81 (s, 1C, –N**C**$_5$H$_4$–), 61.65 (s, 1C,–**C**H$_2$NC$_5$H$_4$–), 20.63 (s, 2C, *m*-(**C**H$_3$)$_3$C$_6$H$_2$–), 18.90 (s, 1C, *p*-(**C**H$_3$)$_3$C$_6$H$_2$–). IR (solid neat; cm^{-1}): 3214 (w), 3117 (s), 3037 (s), 2973 (w), 2912 (s), 2730 (s), 1744 (s), 1695 (s), 1649 (s), 1615 (s), 1517 (s), 1480 (s), 1290 (s), 1198 (s), 1163 (s), 1115 (s), 987 (s), 863 (s), 824 (s), 769 (s), 703 (s), 593 (s).

2.2.9. 2,6-Diethyl-N-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([$\mathbf{L_5}$PdCl$_2$])

The [$\mathbf{L_5}$PdCl$_2$] was prepared according to the similar procedure described for [$\mathbf{L_1}$PdCl$_2$] except utilizing $\mathbf{L_5}$ (0.113 g, 0.473 mol) and [Pd(CH$_3$CN)$_2$Cl$_2$] (0.122 g, 0.473 mol). The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether (10.0 mL × 2) to give a yellow solid (0.170 g, 86.6%). The X-ray crystals of [$\mathbf{L_5}$PdCl$_2$] were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of [$\mathbf{L_5}$PdCl$_2$] (0.0500 g). *Anal.* Calc. for $C_{16}H_{20}N_2Cl_2Pd$: C, 46.01; H, 4.826; N, 6.707. Found: C, 45.12; H, 4.054; N, 6.463%. mp (°C): 335. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.93 (d, 1H, ^3J = 6.4 Hz, –N**H**(CH$_2$CH$_3$)$_2$C$_6$H$_3$–), 8.12 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.87 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.78 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 7.58 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 7.21 (m, 2H, –(CH$_2$CH$_3$)$_2$C$_6$**H**$_3$–), 7.01 (m, 1H, –(CH$_2$CH$_3$)$_2$C$_6$**H**$_3$–), 4.47 (s, 1H, ^2J = 15.2 Hz, ^3J = 7.6 Hz, –C**H**$_2$NC$_5$H$_4$–), 4.24 (s, 1H, ^2J = 15.2 Hz, ^3J = 7.6 Hz, –C**H**$_2$NC$_5$H$_4$–) 1.43 (s, 6H, –(CH$_2$C**H**$_3$)$_2$C$_6$H$_3$–), 1.21 (s, 4H, –(C**H**$_2$ CH$_3$)$_2$C$_6$H$_3$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.89 (s, 1C, *ipso*-N**C**$_5$H$_4$–), 148.58 (s, 1C, –N**C**$_5$H$_4$–), 142.16 (s, 1C, *ipso*-(CH$_2$CH$_3$)$_2$**C**$_6$ H$_3$–), 140.22 (s, 1C, –N**C**$_5$H$_4$–), 137.06 (s, 1C, –N**C**$_5$H$_4$–), 136.42 (s, 1C, –N**C**$_5$H$_4$–), 127.06 (s, 2C, *m*-(CH$_2$CH$_3$)$_2$**C**$_6$H$_3$–), 124.09 (*o*-(CH$_2$CH$_3$)$_2$**C**$_6$H$_3$–), 121.83 (s, 1C, *p*-(CH$_2$CH$_3$)$_2$**C**$_6$H$_3$–), 63.22 (s, 1C, –**C**H$_2$NC$_5$H$_4$–), 24.62 (s, 2C, –(**C**H$_2$ CH$_3$)$_2$C$_6$H$_3$–), 16.06 (s, 2C, –(**C**H$_2$CH$_3$)$_2$C$_6$H$_3$–). IR (solid neat; cm^{-1}): 3213 (w), 3111 (s), 3023 (s), 2971 (w), 2880 (s), 1919 (s), 1833 (s), 1744 (s), 1692 (s), 1649 (s), 1448 (s), 1388 (s), 1332 (s), 1222 (s),

1158 (s), 1116 (s), 1052 (s), 989 (s), 952 (s), 862 (s), 811 (s), 762 (s), 712 (s).

2.2.10. 4-Fluoro-N-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([L_6PdCl_2])

The [L_6PdCl_2] was prepared according to a similar procedure described for [L_1PdCl_2] except utilizing L_6 (0.0950 g, 0.473 mol) and [$Pd(CH_3CN)_2Cl_2$] (0.122 g, 0.473 mol). The solid residue was filtered and washed with ethanol (10.0 mL × 2), followed by washing with diethyl ether (10.0 mL × 2) to give a yellow solid (0.160 g, 89.7%). The X-ray crystals of [L_6PdCl_2] were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of [L_6PdCl_2] (0.0500 g). *Anal.* Calc. for $C_{12}H_{11}FN_2Cl_2Pd$: C, 37.97; H, 2.921; N, 7.381. Found: C, 38.03; H, 2.833; N, 7.890%. mp (°C): 285. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.55 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.79 (d broad, 1H, –N**H**FC_6H_4–), 7.39 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.30 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 7.27 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 6.92 (m, 2H, –$FC_6\mathbf{H}_4$–), 6.60 (m, 2H, –$FC_6\mathbf{H}_4$–), 4.34 (dd, 1H, ^2J = 14.8 Hz, ^3J = 6.4 Hz, –$C\mathbf{H}_2NC_5H_4$–), 4.32 (dd, 1H, ^2J = 14.8 Hz, ^3J = 6.4 Hz, –$C\mathbf{H}_2NC_5H_4$–). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 163.87 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$–), 160.00 (s, 1C, *p*-$F\mathbf{C}_6H_4$–), 155.83 (s, 1C, –$N\mathbf{C}_5H_4$–), 153.54 (s, 1C, –$N\mathbf{C}_5H_4$–), 149.26 (s, 2C, *m*-$F\mathbf{C}_6H_4$–), 137.08 (s, 1C, *ipso*-$F\mathbf{C}_6H_4$–), 124.75 (s, 1C, –$N\mathbf{C}_5H_4$–), 116.51 (s, 1C, –$N\mathbf{C}_5H_4$–), 115.52 (s, 2C, *o*-$F\mathbf{C}_6H_4$–), 61.37 (s, 1C, –$\mathbf{C}H_2NC_5H_4$). IR (solid neat; cm^{-1}): 3273 (w), 3118 (s), 3043 (s), 2895 (w), 2765 (s), 2703 (s), 1834 (s), 1745 (s), 1694 (s), 1650 (s), 1613 (s), 1508 (s), 1330 (s), 1220 (s), 1110 (s), 1053 (s), 1016 (s), 957 (s), 821 (s), 771 (s), 616 (s).

2.3. X-ray crystallographic studies

A colorless cubic-shaped crystal was picked up with paraton oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a nitrogen cold stream (200 K). Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-PLUS (Bruker, 2001) [75]. Semiempirical absorption corrections based on equivalent reflections were applied by SADABS [76]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL [77]. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. Crystal and structure refinement data for all structures are summarized in Table 1.

2.4. Catalytic activity for MMA polymerization

In a Schlenk line, the complex (15.0 μmol, 5.40 mg for [L_1PdCl_2]; 5.60 mg for [L_2PdCl_2]; 5.80 mg for [L_3PdCl_2]; 6.10 mg for [L_4PdCl_2]; 6.30 mg for [L_5PdCl_2]; 5.70 mg for [L_6PdCl_2]) was dissolved in dried toluene (10.0 mL) followed by the addition of modified methylaluminoxane (MMAO) (3.25 mL, 7.50 mmol) as a cocatalyst. The solution was stirred for 30 min at 0, 25 and 60 °C, respectively. The MMA (5.00 mL, 47.1 mmol) was added to the above reaction mixture and stirred for 2 h to obtain a viscous solution. Methanol (2.00 mL) was added to terminate polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35% HCl (5.00 mL) was injected to remove the remaining co-catalyst MMAO. PMMA was obtained by filtration and repeating washing with methanol (250 mL × 2), and dried under vacuum for 24 h.

3. Results and discussion

3.1. Synthesis and chemical properties

Synthesis of *N′*-substituted pyridylmethylaniline ligands (L_3–L_6) was achieved through the condensation reaction between the appropriate aniline and 2-pyridinecarboxaldehyde, followed by reduction of the imine residue in anhydrous methanol by sodium borohydride (Scheme 1). Final ligands were obtained at yields ranging from 74% to 88%. Ligands L_1 and L_2 were reported previously and have been applied to palladium, platinum, and ruthenium complexes [16,39,43,46]. Complexes [L_nPdCl_2] (L_n = L_1–L_6) were obtained from the corresponding ligands with [$Pd(CH_3CN)_2Cl_2$] in anhydrous ethanol, with yields around 90%. ^{1}H NMR, ^{13}C NMR, and elemental analyses were consistent with ligand and Pd(II) complex formation.

The ^{1}H NMR characterisation of complexes [L_nPdCl_2] (L_n = L_1–L_6) was performed in d_6-DMSO solution due to the low solubility in solvents less polar than DMSO. ^{1}H NMR spectra showed a well-resolved ABX spin system for the hydrogen atoms of the diastereotopic methylene group of the chelating ring (H_A and H_B) and the aniline hydrogen atom (H_X) in [L_nPdCl_2] (L_n = L_1–L_6) (Table 1). For example, signals corresponding to these diastereotopic AB nuclei were separated by maximum value of δ 0.64 for [L_2PdCl_2] and minimum value of δ 0.02 for [L_6PdCl_2]. The coupling constant between these two nuclei, $^2J_{AB}$ ranged from 14.8 to 17.9 Hz. On the other hand, chemical shifts of the diastereotopic methylene group in ligands showed only one broad peak, ranged from δ 3.91 to δ 4.93. For the hydrogen (H_X) of the aniline moiety, ^{1}H NMR peaks of [L_nPdCl_2] (L_n = L_1–L_6) complexes (δ 7.78–8.91) were shifted toward the low field compared with the corresponding ligands, ranged from δ 4.50 to δ 4.77 as a singlet. The coupling constant $^3J_{AX}$, which is resulted from X nucleus on aniline moiety and H_A or H_B nuclei of methylene carbon, ranged from 5.6 to 7.6 Hz.

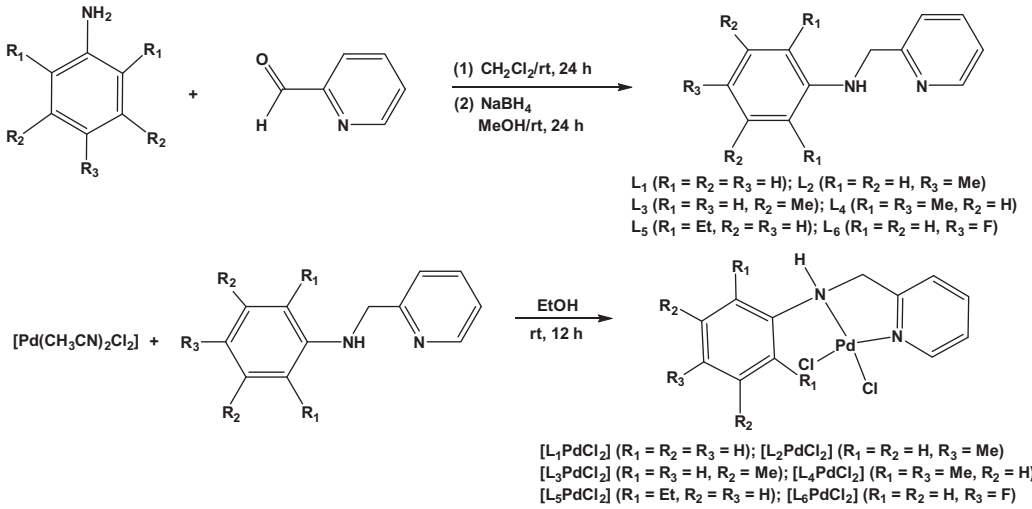
3.2. Crystal structures

ORTEP drawings of complexes are shown in Fig. 1 ([L_1PdCl_2]), Fig. 2 ([L_2PdCl_2]), Fig. 3 ([L_3PdCl_2]), Fig. 4 ([L_4PdCl_2]), Fig. 5 ([L_5PdCl_2]), and Fig. 6 ([L_6PdCl_2]). Crystal data and structural refinement for Pd(II) complexes are shown in Table 2. The selected bond lengths and angles are listed in Table 3. A single crystal suitable for

Table 1
Chemical shift and coupling constant for the diastereotopic methylenic hydrogens (H_a and H_b) and hydrogen (H_x) of aniline moiety.

Complexes	δ Ha(PyC***H***$_2$–NHR)	δ Hb(PyC***H***$_2$–NHR)	$^2J(H_aH_b)$ (Hz)	$^3J(H_aH_x)$ (Hz)	δ Hx(PyCH$_2$–N***H***R)
[L_1PdCl_2]	4.51 (4.46)[a]	3.98	14.8	5.6	8.70 (4.77)[b]
[L_2PdCl_2]	4.98 (4.42)	4.34	16.8	6.0	8.70 (4.59)
[L_3PdCl_2]	4.93 (3.91)	4.33	17.2	6.4	8.77 (4.49)
[L_4PdCl_2]	4.53 (4.20)	4.47	17.9	7.2	8.91 (4.51)
[L_5PdCl_2]	4.47 (4.93)	4.19	15.2	7.6	8.92 (4.63)
[L_6PdCl_2]	4.34 (4.42)	4.32	15.2	6.0	7.78 (4.50)

[a] Chemical shifts of diastereotopic methylenic hydrogens on pyridine amine moiety in ligands L_n (L_n = L_1–L_6) were presented in the prentice. The peak was not resolved and appeared as broad.
[b] Chemical shifts of the hydrogen on aniline moiety in ligands L_n (L_n = L_1–L_6) were presented in the prentice. The peak was not resolved and appeared as broad.



Scheme 1. Synthesis of ligands $\mathbf{L}_n$ ($\mathbf{L}_n = \mathbf{L_1}$–$\mathbf{L_6}$) and the corresponding Pd(II) complexes [$\mathbf{L}_n$PdCl$_2$].

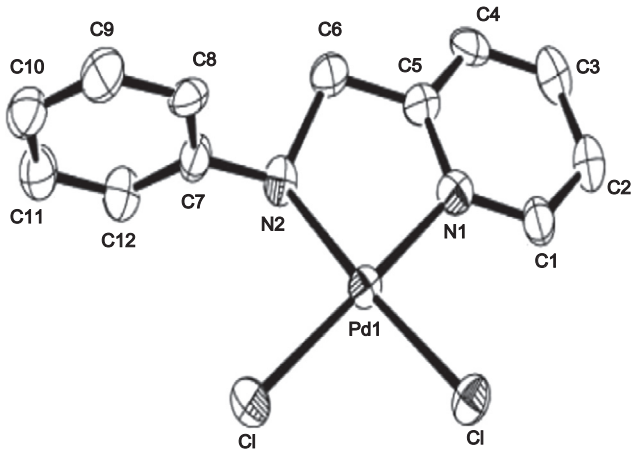


Fig. 1. ORTEP Drawing of [$\mathbf{L_1}$PdCl$_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

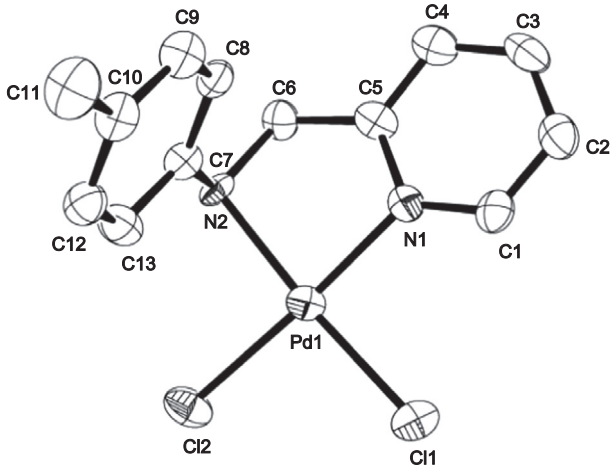


Fig. 2. ORTEP Drawing of [$\mathbf{L_2}$PdCl$_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

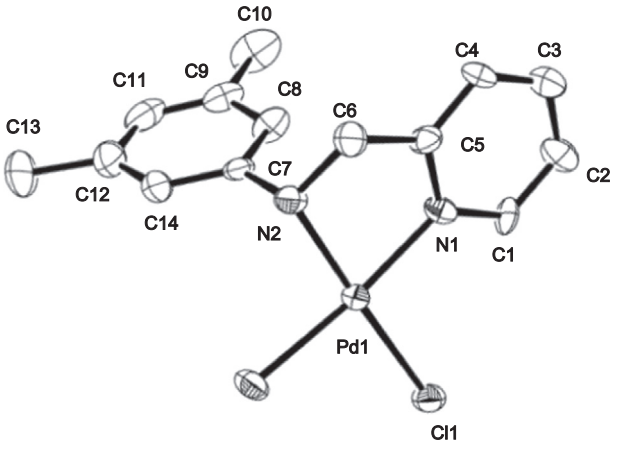


Fig. 3. ORTEP Drawing of [$\mathbf{L_3}$PdCl$_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

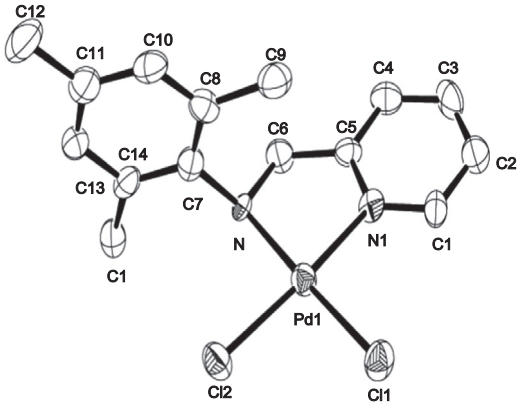


Fig. 4. ORTEP Drawing of [$\mathbf{L_4}$PdCl$_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

X-ray crystallography was obtained from diethyl ether (10.0 mL) diffusion into DMF solution (10.0 mL). The coordination geometry around the Pd(II) centre of the synthesised complexes can be described as a slightly distorted square plane, consisting of the two *N* atoms and two Cl atoms.

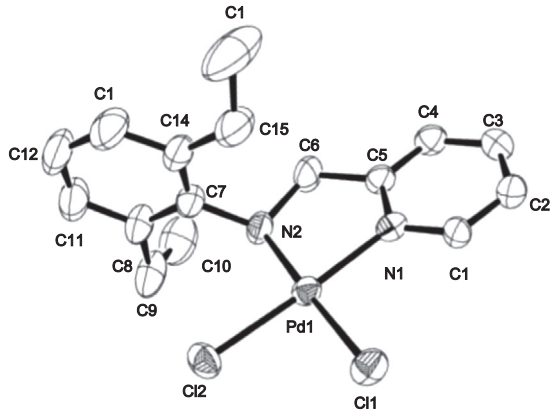


Fig. 5. ORTEP Drawing of [$\mathbf{L_5}PdCl_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

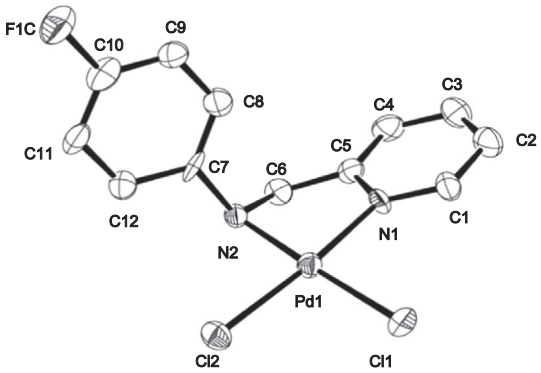


Fig. 6. ORTEP Drawing of [$\mathbf{L_6}PdCl_2$] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

The bond lengths of Pd–$N_{pyridine}$ [Pd(1)–N(1)] in [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_1}$–$\mathbf{L_6}$) ranged from 2.023(5)–2.040(5) Å, while that of Pd–$N_{aniline}$ [Pd(1)–N(2)] ranged from 2.040(6)–2.076(5) Å. The Pd–Cl bond lengths ranged from 2.2862(18)–2.315(3) Å. $N_{aniline}$–$C_{methylene}$ [N(2)–C(6)] bond distances of the complexes ranged from 1.474(11)–1.512(12) Å, which were in the range of accepted carbon–nitrogen single bonds. The C(5)–C(6) bond distances of the complexes ranged from 1.450(12)–1.513(8) Å, reflecting the lack of delocalised π-electrons in the pyridine ring [39,43,46]. Complexes [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_3}$, $\mathbf{L_4}$, $\mathbf{L_6}$) showed more distorted square planarity than [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_5}$). It judged from that for example, N(1)–Pd(1)–Cl(2) and N(2)–Pd(1)–Cl(1) angles in [$\mathbf{L_5}PdCl_2$] were 174.58(14)° and 176.37(14)°, respectively. However, those angles for complex [$\mathbf{L_5}PdCl_2$] were 169.66(19)° and 175.59(19)°, respectively. The average N(1)–Pd(1)–N(2) bond angle

Table 2
Crystal data and structure refinement for [$\mathbf{L_n}PdCl_2$] ($\mathbf{L_n}$ = $\mathbf{L_1}$–$\mathbf{L_6}$) complexes.

	[$\mathbf{L_1}PdCl_2$]	[$\mathbf{L_2}PdCl_2$]	[$\mathbf{L_3}PdCl_2$]	[$\mathbf{L_4}PdCl_2$]	[$\mathbf{L_5}PdCl_2$]	[$\mathbf{L_6}PdCl_2$]
Empirical formula	C_{12} H_{12} Cl_2 N_2 Pd	2($C_{13}H_{14}Cl_2N_2Pd$), C_3H_7NO	$C_{14}H_{16}Cl_2N_2Pd$	$C_{15}H_{18}Cl_2N_2Pd$	$C_{16}H_{20}Cl_2N_2Pd$	$C_{12}H_{11}Cl_2FN_2Pd$
Formula weight	361.54	824.22	386.59	403.61	417.64	379.53
T (K)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2(1)/_C$	$P2(1)/_C$	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions0						
a (Å)	17.9510(6)	8.5575(10)	11.8902(14)	11.4477(11)	8.9107(10)	10.0955(6)
b (Å)	18.4840(6)	11.8094(14)	9.4194(10)	14.8515(14)	8.9104(10)	8.4942(5)
c (Å)	17.8230(6)	16.4176(18)	13.2955(15)	18.5681(17)	21.308(2)	15.1538(10)
α (°)	90.	78.174(3)	90	90	90	90
β (°)	119.5390(10)	89.381(3)	97.377(2)	92.115(2)	101.075(2)	95.3940(10)
γ (°)	90	82.718(2)	90	90	90	90
V (Å^3)	5145.1(3)	1610.6(3)	1476.8(3)	3154.7(5)	1660.3(3)	1293.73(14)
Z	16	2	4	4	8	4
D_{calc} (Mg/m^3)	1.867	1.700	1.752	1.700	1.671	1.949
Absorption coefficient (mm^{-1})	1.835	1.480	1.605	1.506	1.434	1.840
F(000)	2848	824	776	1616	840	744
Crystal size (mm^3)	0.37 × 0.30 × 0.14	0.26 × 0.12 × 0.09	0.28 × 0.19 × 0.17	0.27 × 0.15 × 0.13	0.27 × 0.16 × 0.09	0.16 × 0.14 × 0.08
Theta range for data collection (°)	1.71–28.28	1.27–26.06	1.73–28.34	1.76–28.32	2.35–26.03	2.33–28.29
Index ranges	$-13 \leqslant h \leqslant 23$	$-10 \leqslant h \leqslant 10$	$-15 \leqslant h \leqslant 15$	$-15 \leqslant h \leqslant 15$	$-11 \leqslant h \leqslant 9$	$-12 \leqslant h \leqslant 13$
Reflections collected	$-24 \leqslant k \leqslant 23$	$-14 \leqslant k \leqslant 12$	$-12 \leqslant k \leqslant 8$	$-18 \leqslant k \leqslant 19$	$-11 \leqslant k \leqslant 9$	$-11 \leqslant k \leqslant 11$
	$-23 \leqslant l \leqslant 23$	$-20 \leqslant l \leqslant 13$	$-15 \leqslant l \leqslant 17$	$-21 \leqslant l \leqslant 24$	$-26 \leqslant l \leqslant 26$	$-20 \leqslant l \leqslant 18$
	17712	10267	10399	23284	9952	9210
Independent reflections (R_{int})	6272 (0.0264)	6312 (0.0425)	3623 (0.0302)	7818 (0.0749)	3246 (0.0264)	3197 (0.0410)
Completeness to theta = 28.30°	98.40%	98.80%	98.20%	99.40%	99.30%	99.30%
Absorption correction	none	none	none	none	none	none
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	6272/0/307	6312/36/375	3623/0/174	7818/12/367	3246/0/192	3197/0/0.7573
Goodness-of-fit (GOF) on F^2	1.163	1.121	1.219	1.033	1.158	1.174
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0357	R_1 = 0.0899	R_1 = 0.0556	R_1 = 0.0538	R_1 = 0.0357	R_1 = 0.0506
	wR_2 = 0.0800	wR_2 = 0.2368	wR_2 = 0.1637	wR_2 = 0.1197	wR_2 = 0.0794	wR_2 = 0.1059
R indices (all data)	R_1 = 0.0587	R_1 = 0.1385	R_1 = 0.0860	R_1 = 0.1205	R_1 = 0.0534	R_1 = 0.0980
	wR_2 = 0.1386	wR_2 = 0.3590	wR_2 = 0.2720	wR_2 = 0.1890	wR_2 = 0.1231	wR_2 = 0.1813
Largest difference in peak and hole (e Å^{-3})	1.350 and −2.072	3.226 and −2.830	2.388 and −2.981	1.367 and −2.721	0.746 and −0.985	2.156 and −3.880

Table 3
The selected bond lengths (Å) and angles (°) of [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) complexes.

[$\mathbf{L_1}$PdCl$_2$]		[$\mathbf{L_2}$PdCl$_2$]		[$\mathbf{L_3}$PdCl$_2$]		[$\mathbf{L_4}$PdCl$_2$]		[$\mathbf{L_5}$PdCl$_2$]		[$\mathbf{L_6}$PdCl$_2$]	
Bond lengths											
Pd(1)–N(1)–	2.025(5)	Pd(1)–N(1)	2.040(10)	Pd(1)–N(1)	2.026(6)	Pd(1)–N(2)	2.023(5)	Pd(1)–N(1)	2.040(5)	Pd(1)–N(1)	2.031(7)
Pd(1)–N(2)	2.076(5)	Pd(1)–N(2)	2.058(10)	Pd(1)–N(2)	2.040(6)	Pd(1)–N(1)	2.068(5)	Pd(1)–N(2)	2.068(5)	Pd(1)–N(2)	2.063(9)
Pd(1)–Cl(1)	2.2948(15)	Pd(1)–Cl(1)	2.315(3)	Pd(1)–Cl(1)	2.3108(19)	Pd(1)–Cl(2)	2.2862(18)	Pd(1)–Cl(1)	2.2924(16)	Pd(1)–Cl(1)	2.307(2)
Pd(1)–Cl(2)	2.3134(15)	Pd(1)–Cl(2)	2.293(3)	Pd(1)–Cl(2)	2.2909(19)	Pd(1)–Cl(1)	2.2992(18)	Pd(1)–Cl(2)	2.2973(15)	Pd(1)–Cl(2)	2.284(2)
N(1)–C(5)	1.358(8)	N(1)–C(5)	1.316(16)	N(1)–C(5)	1.369(10)	N(1)–C(5)	1.343(8)	N(1)–C(5)	1.352(7)	N(1)–C(5)	1.354(12)
N(2)–C(6)	1.502(8)	N(2)–C(6)	1.519(15)	N(2)–C(6)	1.474(11)	N(2)–C(6)	1.507(8)	N(2)–C(6)	1.482(8)	N(2)–C(6)	1.512(12)
N(2)–C(7)	1.438(8)	N(2)–C(7)	1.465(17)	N(2)–C(7)	1.475(9)	N(2)–C(7)	1.473(8)	N(2)–C(7)	1.476(7)	N(2)–C(7)	1.450(11)
C(5)–C(6)	1.503(9)	C(5)–C(6)	1.505(17)	C(5)–C(6)	1.450(12)	C(5)–C(6)	1.502(9)	C(5)–C(6)	1.513(8)	C(5)–C(6)	1.504(13)
Bond angles											
N(1)–Pd(1)–N(2)	82.1(2)	N(1)–Pd(1)–N(2)	82.4(4)	N(1)–Pd(1)–N(2)	81.4(3)	N(1)–Pd(1)–N(2)	83.6(2)	N(1)–Pd(1)–N(2)	82.96(19)	N(1)–Pd(1)–N(2)	82.7(3)
N(1)–Pd(1)–Cl(2)	174.24(14)	N(1)–Pd(1)–Cl(2)	171.3(3)	N(1)–Pd(1)–Cl(2)	169.66(19)	N(1)–Pd(1)–Cl(2)	174.42(16)	N(1)–Pd(1)–Cl(2)	174.58(14)	N(1)–Pd(1)–Cl(2)	173.4(2)
N(2)–Pd(1)–Cl(2)	94.09(15)	N(2)–Pd(1)–Cl(2)	90.1(3)	N(2)–Pd(1)–Cl(2)	90.18(19)	N(2)–Pd(1)–Cl(2)	90.98(15)	N(2)–Pd(1)–Cl(2)	91.80(14)	N(2)–Pd(1)–Cl(2)	90.8(2)
N(1)–Pd(1)–Cl(1)	93.76(15)	N(1)–Pd(1)–Cl(1)	94.4(3)	N(1)–Pd(1)–Cl(1)	95.90(19)	N(1)–Pd(1)–Cl(1)	94.71(16)	N(1)–Pd(1)–Cl(1)	94.26(13)	N(1)–Pd(1)–Cl(1)	94.7(2)
N(2)–Pd(1)–Cl(1)	175.672(15)	N(2)–Pd(1)–Cl(1)	173.3(3)	N(2)–Pd(1)–Cl(1)	175.59(19)	N(2)–Pd(1)–Cl(1)	177.65(15)	N(2)–Pd(1)–Cl(1)	176.37(14)	N(2)–Pd(1)–Cl(1)	177.3(2)
Cl(1)–Pd(1)–Cl(2)	90.10(6)	Cl(1)–Pd(1)–Cl(2)	93.51(12)	Cl(1)–Pd(1)–Cl(2)	92.84(7)	Cl(1)–Pd(1)–Cl(2)	90.72(7)	Cl(1)–Pd(1)–Cl(2)	90.91(6)	Cl(1)–Pd(1)–Cl(2)	91.78(9)
C(6)–N(2)–C(7)	113.0(5)	C(6)–N(2)–C(7)	113.3(10)	C(6)–N(2)–C(7)	115.1(6)	C(6)–N(2)–C(7)	114.3(5)	C(6)–N(2)–C(7)	114.0(5)	C(6)–N(2)–C(7)	115.3(8)
C(6)–N(2)–Pd(1)	107.3(4)	C(6)–N(2)–Pd(1)	106.1(7)	C(6)–N(2)–Pd(1)	106.9(5)	C(6)–N(2)–Pd(1)	109.4(4)	C(6)–N(2)–Pd(1)	110.7(4)	C(6)–N(2)–Pd(1)	105.5(5)

of five-membered rings ranged from 81.4(3)–83.6(2)° and were slightly affected by aniline rings. The Cl(1)–Pd(1)–Cl(2) angles in [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) ranged between 90.10(6)° and 93.51(12)°, which were traditional angles for square-planar coordination complexes. Compared to the inter-location on the plane of the aniline group and the plane of the palladium and pyridine in [$\mathbf{L_2}$PdCl$_2$], the plane of the aniline group and the plane of palladium and pyridine in [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$, $\mathbf{L_3}$, $\mathbf{L_6}$) were slightly twisted by *ca.* 10–15° rather than being exactly perpendicular (90°), as observed for specifically [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_4}$, $\mathbf{L_5}$).

3.3. MMA polymerisation

All Pd(II) complexes were activated by co-catalyst MMAO to polymerise MMA [61,62,65], yielding PMMA with T_g ranging from 124 to 132 °C. Polymers were isolated as white solids and characterised by gel permeation chromatography (GPC) in THF using standard polystyrene as a reference. The triad microstructure of PMMA was analysed using ^{1}H-NMR spectroscopy [78–80]. The tacticity of PMMA ranged around syndiotactic (*rr*, δ 0.85), atactic (*mr*, δ 1.02), and isotactic (*mm*, δ 1.21). The polymerisation results, including tacticity and polydispersity index (PDI), which represent the average degree of polymerisation in terms of the number of structural units and molecules, are summarised in Table 4.

To confirm the catalytic activity of MMA polymerisation, blank polymerisation of MMA was performed with [Pd(CH$_3$CN)$_2$Cl$_2$] and MMAO, respectively, at specific temperatures. The catalytic activities of the Pd(II) complexes were not significantly affected by steric effects of ligands around the metal centre. This is supported by the fact that the MMA polymerisation activity of complex [$\mathbf{L_4}$PdCl$_2$] (1.41×10^5 g PMMA/mol Pd·h), which has methyl group on two *ortho* position of aniline ring, was significantly higher than that of complex [$\mathbf{L_5}$PdCl$_2$] (2.73×10^4 g PMMA/mol Pd h), which has ethyl group on two *ortho* position of aniline ring. This may resulted from the increased solubility of [$\mathbf{L_4}$PdCl$_2$] in toluene due to the three methyl groups on the aniline ring moiety, compared to other Pd(II) complexes. Excluding complex [$\mathbf{L_2}$PdCl$_2$], which has moderate MMA polymerisation activity, the structure of [$\mathbf{L_4}$PdCl$_2$] was very similar to the other Pd(II) complexes, in which the two planes of the metallacyclic ring contain the pyridine and aniline ring. Thus, the aniline ring moiety would not interfere with the environment of the palladium metal centre.

The syndiotacticity of PMMA was around 0.70, which was similar to all [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) and to the starting material, [Pd(CH$_3$CN)$_2$Cl$_2$], regardless of the polymerisation temperature. For comparison, Cu(II) complexes with ligand *N*-(2-furanylmethyl)-*N*-(1–3,5-dimethyl-1H-pyrazolylmethyl)-*N*-(phenylmethyl)amines [68] were reported to be active catalysts for the MMA polymerisation to yield syndiotactic PMMA with an *rr* value up to 0.78. However, the conversion of MMA to PMMA was only 30%. In addition, Ni(II) complexes with ligands such as pentane-2,4-diol and phenoxy-imine showed syndiotacticity, ranging from 0.73 to 0.82 with activity of 4.20×10^4 g PMMA/mol Ni h [61,64,81–84]. Co(II) complexes with phenoxy-imine [62] and Fe(II) complexes with pyridylmethylamine [85] were also used as catalysts for MMA polymerisation with moderate activity and syndiotacticity. The moderate syndiotacticity of these Pd(II) complexes was not sufficient to confer a mechanism of coordination polymerisation, and

Table 4
MMA Polymerization by [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) complexes in the presence of MMAO.

Entry	Catalyst[a]	Temp. (time) °C (h)	Yield[b] (%)	Activity[c] (g/molCat h) × 10^4	T_g[d] (°C)	Tacticity			M_w[e] (g/mol) × 10^5	M_w/M_n[f]
						%mm	%mr	%rr		
1	Pd(AN)$_2$Cl$_2$[g]	60 (2 h)	18.8	2.93	131	7.60	22.8	69.6	0.66	2.90
2	MMAO[h]	60 (2 h)	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
3	[$\mathbf{L_1}$PdCl$_2$]	60 (2 h)	22.9	3.57	129	6.70	26.8	66.5	8.60	1.98
4	[$\mathbf{L_2}$PdCl$_2$]	60 (2 h)	15.6	2.43	130	8.30	23.6	68.1	0.47	2.15
5	[$\mathbf{L_3}$PdCl$_2$]	60 (2 h)	18.8	2.93	130	8.30	23.6	68.1	0.92	2.28
6	[$\mathbf{L_4}$PdCl$_2$]	60 (2 h)	71.2	14.1	128	8.10	22.7	69.2	9.76	1.61
7	[$\mathbf{L_5}$PdCl$_2$]	60 (2 h)	17.5	2.73	126	8.10	22.9	69.0	8.42	1.92
8	[$\mathbf{L_6}$PdCl$_2$]	60 (2 h)	16.0	2.50	130	7.20	21.5	71.3	1.80	2.50
11	Pd(AN)$_2$Cl$_2$[g]	25 (2 h)	39.1	1.83	130	8.80	19.7	71.5	0.72	2.97
12	MMAO[h]	25 (2 h)	2.99	0.47	125	15.4	28.4	56.2	0.66	1.32
13	[$\mathbf{L_1}$PdCl$_2$]	25 (2 h)	23.3	3.63	130	7.90	17.8	74.3	1.23	1.59
14	[$\mathbf{L_2}$PdCl$_2$]	25 (2 h)	25.2	3.93	128	8.00	19.0	73.0	0.78	1.56
15	[$\mathbf{L_3}$PdCl$_2$]	25 (2 h)	21.4	3.33	129	7.70	22.5	69.8	1.22	1.86
16	[$\mathbf{L_4}$PdCl$_2$]	25 (2 h)	22.6	3.53	128	8.10	22.7	69.2	2.16	1.73
17	[$\mathbf{L_5}$PdCl$_2$]	25 (2 h)	17.3	2.70	126	8.10	22.9	69.0	8.42	1.92
18	[$\mathbf{L_6}$PdCl$_2$]	25 (2 h)	5.56	0.87	128	14.1	25.4	60.5	0.56	2.37
21	Pd(AN)$_2$Cl$_2$[g]	0 (2 h)	8.11	1.27	129	9.20	18.9	71.9	9.93	1.70
22	MMAO[h]	0 (2 h)	2.56	0.40	130	11.6	28.8	59.6	3.25	2.56
23	[$\mathbf{L_1}$PdCl$_2$]	0 (2 h)	3.85	0.60	131	13.7	21.6	64.7	8.13	2.10
24	[$\mathbf{L_2}$PdCl$_2$]	0 (2 h)	5.77	0.90	129	11.4	22.3	66.3	10.11	1.71
25	[$\mathbf{L_3}$PdCl$_2$]	0 (2 h)	2.14	0.33	130	8.30	23.6	68.1	0.98	2.17
26	[$\mathbf{L_4}$PdCl$_2$]	0 (2 h)	5.56	0.87	128	10.1	26.8	63.1	0.67	1.17
27	[$\mathbf{L_5}$PdCl$_2$]	0 (2 h)	4.70	0.73	128	8.10	22.7	69.2	1.27	1.73
28	[$\mathbf{L_6}$PdCl$_2$]	0 (2 h)	4.27	0.67	129	10.8	20.4	68.8	0.93	1.99

[a] [Pd(II) catalyst]$_0$ = 15 μmol, and [MMA]$_0$/[MMAO]$_0$/[Pd(II) catalyst]$_0$ = 3100:500:1.
[b] Yield defined a mass of dried polymer recovered/mass of monomer used.
[c] Activity is g of PMMA/(mol 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.
[f] M_n refers the number average of molecular weights of PMMA.
[g] AN refers CH_3CN in Pd(AN)$_2$Cl$_2$. It is a blank polymerization in which Pd(AN)$_2$Cl$_2$ was also activated by MMAO.
[h] It is a blank polymerization which was done solely by MMAO.

the steric effect in [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) was not observed during MMA polymerisation. This result is comparable to previously reported Pd(II) complexes containing the bispyridylamine ligand, *N,N*-di(2-picolyl)cycloheptylamine, which clearly showed the steric and electronic effect of Pd(II) complexes during MMA polymerisation [70]. However, structural differences tuned by phenyl ring of imine moiety in [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$) did not sufficiently induce the steric hindrance on the palladium metal centre to show improved activity and syndiotacticity during MMA polymerisation.

4. Conclusions

We investigated the synthesis and X-ray crystallographic structures of [$\mathbf{L}_n$PdCl$_2$] ($\mathbf{L}_n$ = $\mathbf{L_1}$–$\mathbf{L_6}$), which were prepared through the substitution reaction of [Pd(CH$_3$CN)$_2$Cl$_2$] with the corresponding *N*′-substituted pyridylmethylamine ligands. The co-ordination geometry around the Pd(II) centres in complexes was square-planar. The catalytic activity of complex [$\mathbf{L_4}$PdCl$_2$] toward MMA polymerisation in the presence of MMAO resulted in very high activity of 1.41 × 10^5 g PMMA/mol Pd·h at 60 °C and moderate syndiotacticity of *ca.* 70%. The catalytic activity of these Pd(II) complexes was not affected by steric hindrance around the palladium metal centre in complexes.

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Appendix A. Supplementary data

CCDC 984067–984072 contain the supplementary crystallographic data for [$\mathbf{L_1}$PdCl$_2$], [$\mathbf{L_2}$PdCl$_2$], [$\mathbf{L_3}$PdCl$_2$], [$\mathbf{L_4}$PdCl$_2$], [$\mathbf{L_5}$PdCl$_2$] and [$\mathbf{L_6}$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.

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