Palladium(II) Complexes with *N*,*N*′-Bidentate *N*-Methyl-*N*-(pyridin-2-ylmethyl)aniline and its Derivatives: Synthesis, Characterization, and Methyl Methacrylate Polymerization

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The *N*,*N*′-bidentate **[(*N*,*N*′)PdCl$_2$]** complexes [*i.e.*, **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_5$)] were synthesized by the reaction of **[Pd(CH$_3$CN)$_2$Cl$_2$]** with *N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_1$**) and its derivatives (**L$_2$–L$_5$**) in ethanol. The molecular structures of **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_3$) were characterized using X-ray crystallography, which showed that the Pd atom in the Pd(II) complexes had a square planar geometry involving two nitrogen atoms of *N*,*N*′-bidentate and two chlorido ligands. The complexes **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_5$) were investigated for methyl methacrylate (MMA) polymerization in the presence of modified methylaluminoxane (MMAO) at 60 °C. Specifically, complex **[L$_1$PdCl$_2$]** showed moderate catalytic activity toward MMA polymerization with an activity of 3.03×10^4 g poly(methylmethacrylate) (PMMA)/mol Pd·h and PMMA syndiotacticity (characterized by ^{1}H NMR spectroscopy) of ~0.68.

Keywords: *N*-Methyl-*N*-(pyridin-2-ylmethyl)aniline, Palladium(II) complex, Induced chirality, MMA polymerization, Syndiotacticity

Introduction

Transition-metal complexes with pyridylmethylamines have been extensively studied in the areas of synthesis, structure, and spectroscopy[1–16] as catalysts for organic transformation,[17–24] biological applications,[25–28] and olefin polymerization.[29–32] These ligands are popular because of their easy synthesis and versatile modification through the introduction of substituents on the amine residue on either pyridyl unit. Specifically, structural variations have been observed in group 10 [nickel (Ni), palladium (Pd), platinum (Pt)] with pyridylmethylamines and their derivatives. For example, Ni complexes exist as tetrahedral to octahedral monomers or dimers, each of which has two ligand units coordinated to Ni metal, achieving a five- or six-coordinated geometry.[31,33–40] In contrast, Pd and Pt complexes mainly appear with a monomeric square-planar geometry.[32,41–47] These variations result in abundant pyridylmethylamines and analogs in the transition-metal complexes having chemical applications. For *N*-methyl-*N*-(pyridin-2-ylmethyl)aniline, its derivative ligands, and their Pd(II) complexes, the diastereotopic methylene unit in the Pd(II) complexes is more distinguished from the ligands. Moreover, Pd(II) complexation with these ligands induced chirality (*i.e.*, *R* or *S* configuration) on the amine nitrogen atom bonded to four different substituents, such as methyl, phenyl, Pd, and pyridylmethyl units. At the same time, another chirality originates from the nonplanar chelating ring of pyridine and five-membered metallocycle, adopting two conformations of δ and λ.

To the best of our knowledge, despite abundant previous reports on group 10 metals with pyridylmethylamines and their derivatives, little is known regarding Pd(II) complexes with specific *N*,*N*′-bidentate *N*-methyl-substituted pyridylmethylamines[29,43,48] as catalysts for methyl methacrylate (MMA) polymerization. Regarding coordination polymerization of MMA mediated by transition-metal complexes, few reports have explored Pd(II) and Pt(II) complexes as catalysts for MMA polymerization.[49,50] In addition, we explored the effect of a chiral environment of Pd(II) complexes with *N*-methyl-*N*-(pyridin-2-ylmethyl)aniline derivatives on controlling the tacticity of poly(methylmethacrylate) (PMMA).

Thus, we report the preparation of *N*,*N*′-bidentate *N*′-methyl-substituted pyridylmethylaniline ligands, *i.e.*, *N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_1$**), *N*,4-dimethyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_2$**), 4-fluoro-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_3$**), 2,6-diethyl-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_4$**), 2,4,6-tetramethyl-*N*-(pyridin-2-ylmethyl)aniline (**L$_5$**), and their Pd(II) complexes, as well as their molecular structures. Moreover, the catalytic activity of Pd(II) complexes for MMA polymerization in toluene are investigated at 60 °C.

Experimental

Materials and Instrumentation. [$PdCl_2$], 2-pyridinecarboxaldehyde, aniline, 2,4,6-trimethylaniline, 2,6-diethylaniline, 4-fluoroaniline, *p*-toluidine, magnesium sulfate, and methyl methacrylate (MMA) were purchased from Aldrich (St. Louis, MO, U.S.A.), and anhydrous solvents such as C_2H_5OH, DMF, diethyl ether, dichloromethane were purchased from Merck (Frankfurter Straße 250, 64293 Darmstadt, Deutschland), and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation (Shiba, Minato-Ku, Tokyo, JAPAN) 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 (Billerica, MA 01821-3991, USA); chemical shifts were recorded in ppm units (δ) relative to $SiMe_4$ as the internal standard. Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha as neat, 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, USA). Glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q2000; TA Instruments, New Castle, DE, USA).

***N*-Methyl-*N*-(pyridin-2-ylmethyl)aniline (L_1):** To aniline (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 of stirring at room temperature, the dichloromethane solution was dried over the $MgSO_4$. Then, $MgSO_4$ was filtered and the solvent was removed under reduced pressure. Crude *N*-phenyl-1-(pyridin-2-yl)methanimine was reduced by sodium borohydride (2.0 equiv, 1.51 g, 0.0400 mol) in anhydrous methanol (30.0 mL). The reaction mixture was stirred at room temperature for 24 h and the solvent was removed under reduced pressure. Iodomethane (1.1 equiv, 1.36 mL, 0.0220 mol) was added to crude *N*-(pyridin-2-ylmethyl)aniline in dichloromethane (30.0 mL) by a syringe. The reaction mixture was stirred at room temperature for 24 h, and lithium hydroxide (1.1 equiv, 0.530 g, 0.0220 mol) was added to the reaction solution. The reaction mixture was stirred at room temperature for 4 h and the solid residue was filtered off. The solvent was removed under reduced pressure and vacuum distilled to obtain a light red oil (3.14 g, 79.2%). Analysis calculated for $C_{13}H_{14}N_2$: C, 78.8%; H, 7.12%; N, 14.1%. Found: C, 78.5%; H, 7.09%; N, 14.3%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.77 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.63 (t, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.12 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.74 (t, 4H, J = 7.8 Hz, *o*-, *m*-$C_6\mathbf{H}_5$—), 6.58 (s, 1H, *p*-$C_6\mathbf{H}_5$—), 4.31 (s, 3H, —$C\mathbf{H}_3NC_6H_5$—), 3.94 (s, 2H, –$C\mathbf{H}_2NC_5H_4$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.11, 158.31, 153.55, 153.89, 140.86, 135.86, 133.84, 132.84, 128.44, 49.86, 45.81. IR (liquid neat; cm^{-1}): 3033 (w), 2988 (s), 2863 (s), 1657 (w), 1569 (s), 1561 (s), 1522 (s), 1436 (s), 1384 (s), 1344 (s), 1258 (s), 1264 (s), 1189 (s), 1033 (s), 1024 (s), 991 (s), 899 (s), 831 (s), 822 (s), 756 (s), 667 (s).

***N*,4-Dimethyl-*N*-(pyridin-2-ylmethyl)aniline (L_2): L_2** was prepared by a method analogous to that described for L_1 except for utilizing *p*-toluidine (2.14 g, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as a light red oil (2.98 g, 70.2%). Analysis calculated for $C_{14}H_{16}N_2$: C, 79.2%; H, 7.60%; N, 13.2%. Found: C, 79.4%; H, 7.29%; N, 12.8%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.77 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$—), 7.59 (d, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.54 (t, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.03 (d, 2H, J = 7.5 Hz *o*—$CH_3C_6\mathbf{H}_4$—), 6.83 (d, 2H, J = 7.7 Hz, *m*-$CH_3C_6\mathbf{H}_4$—), 4.41 (s, 3H, —$C\mathbf{H}_3NC_6H_4CH_3$—), 3.94 (s, 2H, —$C\mathbf{H}_2NC_5H_4$—), 2.94 (s, 3H, —$C\mathbf{H}_3C_6H_4$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.88, 157.23, 151.59, 133.86, 132.88, 130.65, 129.70, 128.44, 118.84, 50.88, 49.90, 23.81. IR (liquid neat; cm^{-1}): 3035 (w), 2999 (s), 2853 (s), 1657 (w), 1534 (s), 1513 (s), 1491 (s), 1461 (s), 1355 (s), 1376 (s), 1191 (s), 1147 (s), 1139 (s), 1021 (s), 1011 (s), 996 (s), 889 (s), 843 (s), 821 (s), 757 (s), 669 (s).

4-Fluoro-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (L_3): L_3 was prepared by a method analogous to that described for L_1 except for utilizing 4-fluoroaniline (1.89 mL, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as a light red oil (2.66 g, 61.5%). Analysis calculated for $C_{13}H_{13}FN_2$: C, 72.2%; H, 6.06%; N, 13.0%. Found: C, 71.7%; H, 6.04%; N, 12.7%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.97 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.69 (d, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.49 (t, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.13 (d, 2H, J = 7.6 Hz, *o*-$C_6\mathbf{H}_4F$—), 6.94 (d, 2H, J = 7.5 Hz, *m*-$C_6\mathbf{H}_4F$—), 4.41 (s, 3H, —$C\mathbf{H}_3NC_6H_4F$—), 3.94 (s, 2H, —$C\mathbf{H}_2NC_5H_4$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.74, 159.33, 156.59, 133.99, 132.88, 130.65, 129.70, 127.44, 118.84, 51.38, 48.96. IR (liquid neat; cm^{-1}): 3057 (w), 3011 (s), 2969 (s), 1718 (w), 1695 (s), 1654 (s), 1500 (s), 1464 (s), 1416 (s), 1291 (s), 1236 (s), 1146 (s), 1012 (s), 976 (s), 897 (s), 833 (s), 761 (s), 619 (s).

2,6-Diethyl-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (L_4): L_4 was prepared by a method analogous to that described for L_1 except for utilizing 2,6-diethylaniline (2.81 mL, 0.0200 mol) and 2-pyridinecarboxaldehyde (1.90 mL, 0.0200 mol). The product was obtained as light red oil (2.88 g, 56.6%). Analysis calculated for $C_{17}H_{22}N_2$: C, 80.3%; H, 8.72%; N, 11.0%. Found: C, 79.8%; H, 8.37%; N, 11.4%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 8.16 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 8.11 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.82 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.58 (m, 3H, —$(CH_3CH_2)_2C_6\mathbf{H}_3$—), 4.94 (s, 3H, —$C\mathbf{H}_3N(CH_3CH_2)_2C_6H_3$—), 4.64 (s, 2H, —$C\mathbf{H}_2NC_5H_4$—), 1.94 (q, 4H, J = 11.0 Hz —$(CH_3C\mathbf{H}_2)_2C_6H_3$—), 1.72 (t, 6H, J = 11.5 Hz, —$(C\mathbf{H}_3CH_2)_2C_6H_3$—). ^{13}C NMR ($CDCl_3$, 100 MHz):

δ 159.12, 155.33, 152.55, 138.89, 137.86, 136.86, 132.84, 131.74, 128.44, 52.86, 49.86, 23.00, 21.81. IR (liquid neat; cm^{-1}): 3057 (w), 3031 (s), 2966 (s), 1659 (s), 1533 (s), 1521 (s), 1470 (s), 1406 (s), 1281 (s), 1246 (s), 1046 (s), 1012 (s), 972 (s), 960 (s), 897 (s), 838 (s), 833 (s), 761 (s), 619 (s).

2,4,6-Tetramethyl-*N*-(pyridin-2-ylmethyl)aniline (L_5): L_5 was prepared by a method analogous to that described for L_1 except for 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 a light red oil (3.12 g, 64.9%). Analysis calculated for $C_{16}H_{20}N_2$: C, 80.0%; H, 8.39%; N, 11.7%. Found: C, 79.1%; H, 8.27%; N, 11.5%. ^{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 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.82 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.58 (s, 2H, —$(CH_3)_3C_6\mathbf{H}_2$—), 4.89 (s, 2H, —$C\mathbf{H}_2NC_5H_4$—), 4.64 (s, 3H, —$C\mathbf{H}_3N(CH_3)_3C_6H_2$—), 1.94 (s, 3H, $(C\mathbf{H}_3)_3C_6H_2$—), 1.72 (s, 6H, —$(C\mathbf{H}_3)_3C_6H_2$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.12, 155.33, 152.55, 138.89, 137.86, 136.86, 132.84, 131.74, 128.44, 52.86, 50.66, 23.00, 21.81. IR (liquid neat; cm^{-1}): 3066 (w), 3031 (w), 1708 (w), 1696 (s), 1658 (s), 1533 (s), 1521 (s), 1470 (s), 1406 (s), 1281 (s), 1246 (s), 1046 (s), 1012 (s), 972 (s), 960 (s), 897 (s), 838 (s), 833 (s), 761 (s), 619 (s).

***N*-Methyl-*N*-(pyridin-2-ylmethyl)aniline(dichloro)palladium(II) ($[L_1PdCl_2]$):** A solution of L_1 (99.0 mg, 0.500 mmol) in anhydrous ethanol (10.0 mL) was added to a solution of anhydrous $[Pd(CH_3CN)_2Cl_2]$[51,52] (130 mg, 0.500 mmol) in anhydrous ethanol (10.0 mL). The reaction mixture was stirred for 12 h at room temperature, and the solid residue was filtered. The solid was washed with ethanol (10.0 mL × 2) followed by diethyl ether (10.0 mL × 2) to give a yellow solid (140 mg, 74.5%). Crystals for X-ray analysis of $[L_1PdCl_2]$ were obtained within 3 days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of $[L_1PdCl_2]$ (50.0 mg). Analysis calculated for $C_{13}H_{14}Cl_2N_2Pd$: C, 41.6%; H, 3.76%; N, 7.46%. Found: C, 41.4%; H, 3.75%; N, 7.44%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.59 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.96 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.73 (t, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.10 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.94 (t, 3H, J = 7.8 Hz, *o*-,*m*-$C_6\mathbf{H}_5$—), 6.66 (s, 2H, *p*-$C_6\mathbf{H}_5$—), 4.11 (s, 3H, —$C\mathbf{H}_3NC_6H_5$—), 4.04 (d, 1H, ^2J = 16.0 Hz, —$C\mathbf{H}_2NC_5H_4$—), 3.74 (d, 1H, ^2J = 16.4 Hz, —$C\mathbf{H}_2$-NC_5H_4—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 162.33, 157.37, 152.95, 153.89, 141.16, 134.56, 131.64, 130.84, 127.44, 50.16, 47.71. IR (solid neat; cm^{-1}): 3032 (w), 2983 (s), 2859 (s), 1666 (w), 1577 (s), 1554 (s), 1523 (s), 1441 (s), 1394 (s), 1339 (s), 1264 (s), 1243 (s), 1179 (s), 1039 (s), 1026 (s), 992 (s), 899 (s), 834 (s), 831 (s), 759 (s), 670 (s).

***N*,4-Dimethyl-*N*-(pyridin-2-ylmethyl)aniline(dichloro)palladium(II) ($[L_2PdCl_2]$): $[L_2PdCl_2]$** was prepared according to a procedure similar to that described for $[L_1PdCl_2]$ except for utilizing L_2 (106 mg, 0.500 mmol) and $[Pd(CH_3CN)_2Cl_2]$ (130 mg, 0.500 mmol). The solid residue was filtered and washed with ethanol (10.0 mL × 2) followed by diethyl ether (10.0 mL × 2) to give a yellow solid (150 mg, 77.0%). Crystals for X-ray analysis of $[L_2PdCl_2]$ were obtained within 5 days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of $[L_2PdCl_2]$ (50.0 mg). Analysis calculated for $C_{14}H_{16}Cl_2N_2Pd$: C, 43.2%; H, 4.14%; N, 7.19%. Found: C, 43.1%; H, 4.11%; N, 7.00%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.55 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.87 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.60 (d, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.44 (t, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.13 (d, 2H, J = 7.6 Hz *o*-$CH_3C_6\mathbf{H}_4$—), 6.93 (d, 2H, J = 7.4 Hz, *m*-$CH_3C_6\mathbf{H}_4$—), 4.31 (s, 3H, —$C\mathbf{H}_3NC_6H_4$ CH_3—), 4.14 (d, 1H, ^2J = 15.2 Hz, —$C\mathbf{H}_2$-NC_5H_4—), 4.01 (d, 1H, ^2J = 15.6 Hz, —$C\mathbf{H}_2$—NC_5H_4—), 2.93 (s, 3H, —$C\mathbf{H}_3C_6H_4$—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.34, 158.11, 153.59, 134.89, 133.48, 131.65, 128.67, 126.44, 117.84, 51.01, 48.91, 22.99. IR (solid neat; cm^{-1}): 3034 (w), 2993 (s), 2854 (s), 1655 (w), 1541 (s), 1512 (s), 1489 (s), 1462 (s), 1354 (s), 1374 (s), 1193 (s), 1148 (s), 1134 (s), 1022 (s), 1019 (s), 995 (s), 890 (s), 844 (s), 823 (s), 756 (s), 668 (s).

4-Fluoro-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ($[L_3PdCl_2]$): $[L_3PdCl_2]$ was prepared according to a procedure similar to that described for $[L_1PdCl_2]$ except for utilizing L_3 (108 mg, 0.500 mmol) and $[Pd(CH_3CN)_2Cl_2]$ (130 mg, 0.500 mmol). The solid residue was filtered and washed with ethanol (10.0 mL × 2) followed by diethyl ether (10.0 mL × 2) to give a yellow solid (139 mg, 70.6%). Crystals for X-ray analysis of $[L_3PdCl_2]$ were obtained within 5 days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of $[L_3PdCl_2]$ (50 mg). Analysis calculated for $C_{13}H_{13}Cl_2FN_2Pd$: C, 39.7%; H, 3.33%; N, 7.12%. Found: C, 39.5%; H, 3.30%; N, 7.01%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.61 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 8.01 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 7.79 (d, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.54 (t, 1H, J = 7.7 Hz, —$NC_5\mathbf{H}_4$—), 7.22 (d, 2H, J = 7.6 Hz, *o*-$C_6\mathbf{H}_4$F—), 6.92 (d, 2H, J = 7.6 Hz, *m*-$C_6\mathbf{H}_4$F—), 4.43 (s, 3H, —$C\mathbf{H}_3NC_6H_4$F—), 4.01 (d, 1H, ^2J = 16.4 Hz, —$C\mathbf{H}_2$-NC_5H_4—), 3.91 (d, 1H, ^2J = 16.4 Hz, —$C\mathbf{H}_2$—NC_5H_4—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.09, 158.11, 154.44, 135.11, 133.81, 131.66, 129.69, 126.44, 118.86, 50.38, 47.96. IR (solid neat; cm^{-1}): 3053 (w), 3010 (s), 2963 (s), 1708 (w), 1696 (s), 1655 (s), 1501 (s), 1463 (s), 1412 (s), 1290 (s), 1234 (s), 1147 (s), 1013 (s), 975 (s), 899 (s), 832 (s), 763 (s), 610 (s).

2,6-Diethyl-*N*-methyl-*N*-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ($[L_4PdCl_2]$): $[L_4PdCl_2]$ was prepared according to a procedure similar to that described for $[L_1PdCl_2]$ except for utilizing L_4 (123 mg, 0.500 mmol) and $[Pd(CH_3CN)_2Cl_2]$ (130 mg, 0.500 mmol). The solid residue was filtered and washed with ethanol (10.0 mL × 2) followed by diethyl ether (10.0 mL × 2) to give a yellow solid (161 mg, 77.1%). Crystals for X-ray analysis of $[L_4PdCl_2]$ were obtained within 5 days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of $[L_4PdCl_2]$ (50.0 mg). Analysis calculated for $C_{17}H_{22}Cl_2N_2Pd$: C, 47.3%; H, 5.14%; N, 6.49%. Found: C, 47.1%; H, 5.05%; N, 6.46%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.51

(d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 8.11 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$-), 8.01 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.83 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.68 (m, 3H, —$(CH_2CH_3)_2C_6\mathbf{H}_3$—), 4.64 (s, 3H, —$CH_3$—N—$(CH_2CH_3)_2C_6H_3$—), 4.14 (d, 1H, ^2J = 16.0 Hz, —CH_2—NC_5H_4—), 4.00 (d, 1H, ^2J = 16.0 Hz, —CH_2—NC_5H_4—), 2.01 (m, 4H, —$(CH_2CH_3)_2C_6H_3$—), 1.92 (t, 6H, J = 11 Hz, —$(CH_2CH_3)_2C_6H_3$—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 160.12 (s, 1C, *ipso*-$N\mathbf{C}_5H_4$—), 154.55 (s, 1C, —NC_5H_4—), 153.33 (s, 1C, *ipso*-$(CH_2CH_3)_2\mathbf{C}_6H_3$—), 139.11 (s, 1C, —$N\mathbf{C}_5H_4$—), 136.83 (s, 2C, *o*-$(CH_2CH_3)_2\mathbf{C}_6H_3$-), 134.88 (s, 2C, *m*-$(CH_2CH_3)_2\mathbf{C}_6H_3$-), 131.96 (s, 1C, —$N\mathbf{C}_5H_4$—), 131.61 (s, 1C, –$N\mathbf{C}_5H_4$—), 128.36 (s, 1C, *p*-$(CH_2CH_3)_2\mathbf{C}_6H_3$—), 51.99 (s, 1C, —$CH_2$—$NC_5H_4$—), 50.11 (s, 1C, —$CH_3$—N—$(CH_2CH_3)_2\mathbf{C}_6H_3$—), 22.96 (s, 2C, —$(CH_2CH_3)_2C_6H_3$—), 21.83 (s, 2C, —$(CH_2CH_3)_2C_6H_3$—). IR (solid neat; cm^{-1}): 3059 (w), 2951 (s), 2858 (s), 1836 (w), 1746 (s), 1695 (s), 1649 (s), 1517 (s), 1462 (s), 1365 (s), 1209 (s), 1148 (s), 1100 (s), 1049 (s), 976 (s), 925 (s), 868 (s), 819 (s), 757 (s), 707 (s), 656 (s).

2,4,6-Tetramethyl-*N*-(pyridin-2-ylmethyl)aniline (dichloro)palladium(II) ([L_5PdCl_2]): [L_5PdCl_2] was prepared according to a method similar to that described for **[L_1PdCl_2]** except for utilizing **L_5** (120 mg, 0.500 mmol) and **[$Pd(CH_3CN)_2Cl_2$]** (130 mg, 0.500 mmol). The solid residue was filtered and washed with ethanol (10.0 mL × 2) followed by diethyl ether (10.0 mL × 2) to give a yellow solid (151 mg, 70.0%). Crystals for X-ray analysis of **[L_5PdCl_2]** were obtained within 5 days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L_5PdCl_2]** (50.0 mg). Analysis calculated for $C_{16}H_{20}Cl_2N_2Pd$: C, 46.0%; H, 4.83%; N, 6.71%. Found: C, 45.9%; H, 4.84%; N, 6.72%.^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.53 (d, 1H, J = 7.6 Hz, —$NC_5\mathbf{H}_4$—), 8.18 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 8.10 (t, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 7.91 (d, 1H, J = 7.8 Hz, —$NC_5\mathbf{H}_4$—), 6.56 (s, 2H, —$(CH_3)_3C_6\mathbf{H}_2$—), 4.88 (d, 1H, ^2J = 17.2 Hz, —$C\mathbf{H}_2$-NC_5H_4—), 4.76 (d, 1H, ^2J = 16.8 Hz, —$C\mathbf{H}_2NC_5H_4$—), 4.63 (s, 3H, —$C\mathbf{H}_3N(CH_3)_3C_6H_2$—), 2.01 (s, 3H, —$(C\mathbf{H}_3)_3C_6H_2$—), 1.71 (s, 6H, —$(C\mathbf{H}_3)_3C_6H_2$—). ^{13}C NMR (DMSO-$d_6$, 100 MHz): δ 160.11, 156.41, 153.93, 138.11, 136.81, 136.11, 133.71, 130.76, 128.41, 51.86, 49.76, 23.11, 20.73. IR (solid neat; cm^{-1}): 3059 (w), 2951 (s), 2858 (s), 1836 (w), 1746 (s), 1695 (s), 1649 (s), 1517 (s), 1462 (s), 1365 (s), 1209 (s), 1148 (s), 1100 (s), 1049 (s), 976 (s), 925 (s), 868 (s), 819 (s), 757 (s), 707 (s), 656 (s).

Catalytic Activity for MMA Polymerization. In a Schlenk line, the complex (15.0 μmol, 5.60 mg for **[L_1PdCl_2]**, 5.80 mg for **[L_2PdCl_2]**, 5.90 mg for **[L_3PdCl_2]**, 6.20 mg for **[L_4PdCl_2],** and 6.50 mg for **[L_5PdCl_2]**) was dissolved in dried toluene (10.0 mL) followed by the addition of MMAO (3.25 mL, 7.50 mmol) as a cocatalyst. The solution was stirred for 20 min at 60 °C. Then, MMA (5.0 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 cocatalyst (MMAO). PMMA was obtained by filtration and repeated washing with methanol and dried under vacuum for 24 h.

X-Ray Crystallographic Studies. A colorless cubic-shaped crystal was picked up with paratone-N oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatized 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).[53] Semiempirical absorption corrections based on equivalent reflections were applied by SADABS.[54] The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL.[55] All the nonhydrogen 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.

Results and Discussion

Synthesis of *N*-methyl-substituted pyridylmethylaniline ligands, **L_n** (L_n = L_1–L_5), was achieved through the condensation reaction between 2-pyridinecarboxaldehyde and the appropriate aniline, followed by reduction of the imine residue in anhydrous methanol by sodium borohydride. Final ligands were obtained and subsequently methylated by MeI at yields ranging from 57 to 80% (Scheme 1). Ligand L_1 has been recently described.[56,57] Complexes **[L_nPdCl_2]** (L_n = L_1–L_5) were obtained from the corresponding ligands with **[$Pd(CH_3CN)_2Cl_2$]** in anhydrous ethanol. ^{1}H NMR, ^{13}C NMR, and elemental analyses were consistent with the ligand and Pd(II) complex formulation. The ^{1}H NMR characterization of complexes **[L_nPdCl_2]** (L_n = L_1–L_5) was performed in d_6-dimethyl sulfoxide (DMSO) solution because of the low solubility in solvents less polar than DMSO. ^{1}H NMR spectra showed a well-resolved AB spin system for the hydrogen atoms of the diastereotopic methylene group of the chelating ring (H_A and H_B) in **[L_nPdCl_2]** (L_n = L_1–L_5) (Table 1). For example, signals corresponding to these diastereotopic AB nuclei in the complexes were separated by a maximum value of δ 0.30 for **[L_1PdCl_2]** and a minimum value of δ 0.10 for **[L_3PdCl_2]**. The coupling constant between these two nuclei, $^2J_{AB}$, ranged from 15.6 to 16.8 Hz. In contrast, chemical shifts

Table 1. Chemical shift and coupling constant for the diastereotopic methylene hydrogens (H_a and H_b).

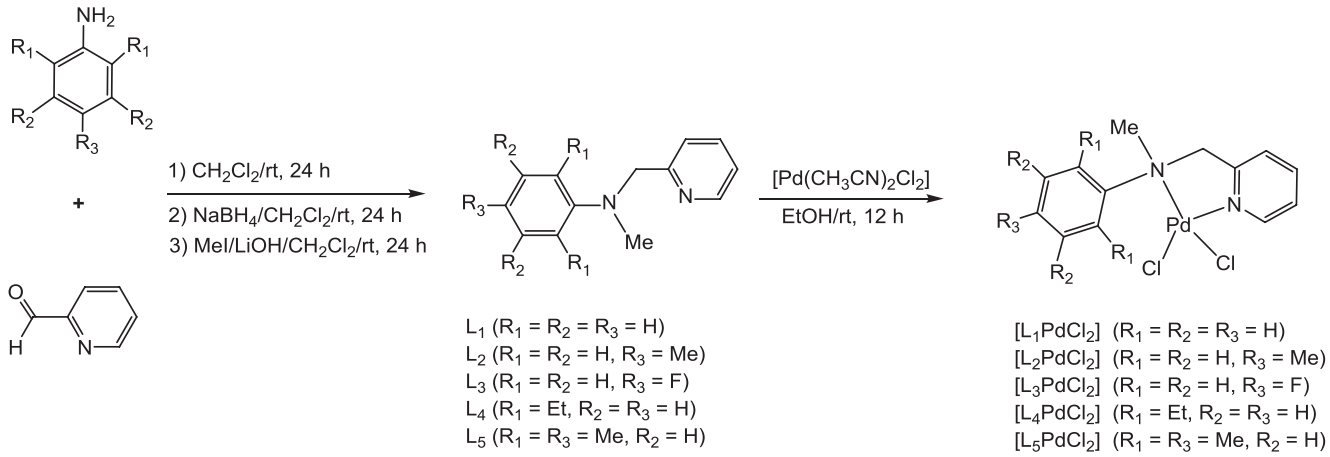
Complexes	δ H_a (PyC***H***$_2$—NHR)	δ H_b (PyC***H***$_2$—NHR)	^2J (H_aH_b)
[L_1PdCl_2]	4.04 (3.94)[a]	3.74	16.0
[L_2PdCl_2]	4.14 (3.94)	4.01	15.6
[L_3PdCl_2]	4.01 (3.94)	3.91	16.4
[L_4PdCl_2]	4.14 (4.64)	4.00	16.0
[L_5PdCl_2]	4.88 (4.89)	4.76	16.8

[a] Chemical shifts of diastereotopic methylene hydrogens on the pyridine amine moiety in ligands L_n (L_n = L_1–L_5) are shown in parentheses. The peak was not resolved and appeared broad.

of the diastereotopic methylene group in ligands showed only one broad peak ranging from δ 3.94 to δ 4.89.

ORTEP drawings of the complexes are shown in Figure 1 (**[L_1PdCl_2]**), Figure 2 (**[L_2PdCl_2]**), and Figure 3 (**[L_3PdCl_2]**). Crystal data and structural refinement for Pd(II) complexes are shown in Table 2. Selected bond lengths and angles are listed in Table 3. A single crystal suitable for 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) center of the synthesized complexes could be described as square-planar, consisting of two nitrogen atoms and two chloride atoms. The bond lengths of Pd—$N_{pyridine}$ [Pd(1)—N(1)] in **[L_nPdCl_2]** ($L_n = L_1$–L_3) ranged from 2.028(6) to 2.044(6) Å, while those of Pd—$N_{aniline}$ [Pd(1)—N(2)] ranged from 2.089(7) to 2.111(6) Å. The Pd—Cl bond lengths ranged from 2.288(2) to 2.297(2) Å. $N_{aniline}$—$C_{methylene}$ [N(2)—C(6)] bond distances of the complexes ranged from 1.509 (10) to 1.510(9) Å, which were in the range of accepted carbon–nitrogen single bonds. The C(5)—C(6) bond distances of the complexes ranged from 1.481 (11) to 1.512(11) Å, reflecting the lack of delocalized π-electrons in the pyridine ring.[32,43,46] All complexes **[L_nPdCl_2]** ($L_n = L_1$–L_3) showed similar square planarity, based on the N(1)—Pd(1)—Cl(2) and N(2)—Pd(1)—Cl(1) angles of 174.88(9)° and 174.67(18)° in **[L_1PdCl_2]**, respectively. The average N(1)—Pd(1)—N(2) bond angle of five-membered rings ranged from 81.7(3)° to 82.5(2)° and were slightly affected by the aniline rings. The Cl(1)—Pd(1)—Cl(2) angles in **[L_nPdCl_2]** ($L_n = L_1$–L_3) ranged between 90.27(9)° and 91.69(8)°, which were traditional angles for square-planar coordination complexes.

Compared to the interlocation on the plane of the aniline group and the plane of the Pd and pyridine in **[L_1PdCl_2]**,



Scheme 1. Synthesis of ligands and **[L_nPdCl_2]** ($L_n = L_1$–L_5) complexes.

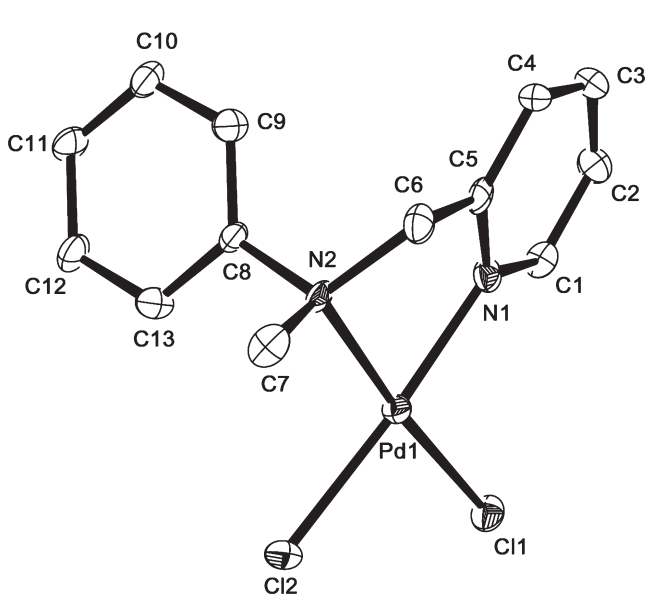


Figure 1. Molecular structure of **[L_1PdCl_2]** with thermal ellipsoids at 50% probability. The hydrogen atom is omitted for clarity.

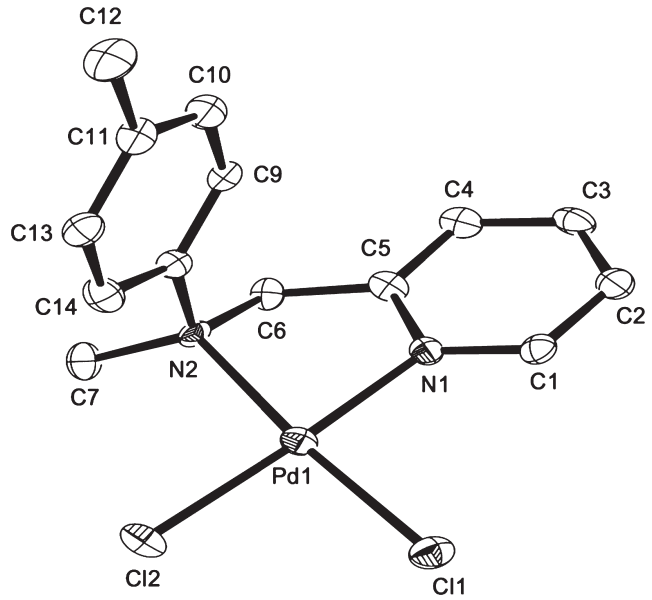


Figure 2. Molecular structure of **[L_2PdCl_2]** with thermal ellipsoids at 50% probability. The hydrogen atom is omitted for clarity.

the plane of the aniline group and the plane of Pd and pyridine in **[L$_2$PdCl$_2$]** were slightly twisted by ~20° rather than being exactly perpendicular (90°), as observed for **[L$_1$PdCl$_2$]**. Moreover, both the plane of the aniline group and the plane of Pd and pyridine were located in the same plane in **[L$_3$PdCl$_2$]**.

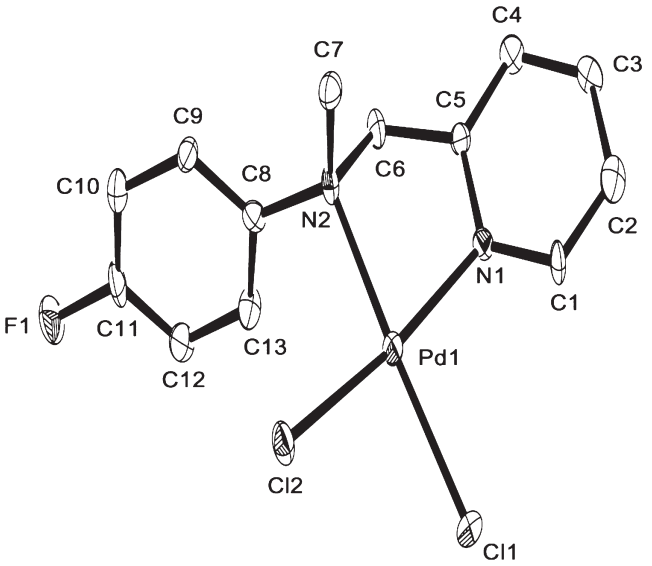


Figure 3. Molecular structure of **[L$_3$PdCl$_2$]** with thermal ellipsoids at 50% probability. The hydrogen atom is omitted for clarity.

Alternatively, the plane of the aniline group and the plane of Pd and pyridine in **[L$_2$PdCl$_2$]** were perfectly twisted by 90° rather than being perpendicular (90°) for **[L$_1$PdCl$_2$]**. **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_5$) had two sources of chirality, resulting in four different isomers.

The coordinated aniline nitrogen atom contained four different substituents, leading to a chiral center that could adopt *R* and *S* configurations. The second induced chirality originated from the deviation of coplanarity when the Pd chelated to the pyridine ring and the five-membered metallocycle ring, which caused two conformations δ and λ (Scheme 2). Although dynamic isomerization behavior may occur in solution, **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_3$) represents two chiralities showing an enantiomeric relationship of diastereomers *S*λ, *R*δ , and *S*δ, respectively, in the solid state.[43,58–61]

In general, a higher glass transition temperature (T_g) of PMMA represents higher optical quality and syndiotacticity content of PMMA. The T_g of isotactic PMMA that is produced by commercial radical processes, is ~65 °C. Thus, studies on nonradical-mediated MMA polymerization have been performed, and some transition-metal complexes have been generated.[62–74] All Pd(II) complexes were activated by MMAO to polymerize MMA, yielding PMMA with T_g values ranging from 127 to 130 °C. The polymers were isolated as white solids and characterized by GPC in tetrahydrofuran using standard polystyrene as a reference. The triad microstructure

Table 2. Crystal data and structural refinement of **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$–L$_3$) complexes.

	[L$_1$PdCl$_2$]	**[L$_2$PdCl$_2$]**	**[L$_3$PdCl$_2$]**
Empirical formula	$C_{13}H_{14}Cl_2N_2Pd$	$C_{14}H_{16}Cl_2N_2Pd$	$C_{13}H_{13}Cl_2N_2Pd$
Formula weight (amu)	375.56	389.59	393.55
Temperature (K)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, *P*43	Monoclinic, *P*21/*n*	Monoclinic, *P*21/*c*
Unit cell dimensions			
a (Å) and α (°)	8.5205(2)	10.1805(7)	10.0460(7)
b (Å) and β (°)	8.5205(2)	11.3095(7) and 91.989(1)	9.9490(7) and 102.248(1)
c (Å) and γ (°)	18.9050(9)	12.7540(9)	14.000(1)
Volume (Å^3)	137248(8)	1467.6(2)	1367.4(2)
Z, Calculated density (Mg/m^3)	4, 1.818	4, 1.763	4, 1.912
μ (mm^{-1})	1.723	1.615	1.745
F(000)	744	776	776
Crystal size (mm)	0.30 × 0.29 × 0.23	0.24 × 0.18 × 0.17	0.26 × 0.21 × 0.20
θ range (°)	2.39–28.27	2.41–28.31	2.07–26.04
Limiting indices	$-11 \le h \le 11$	$-12 \le h \le 13$	$-11 \le h \le 12$
	$-11 \le k \le 5$	$-15 \le k \le 14$	$-12 \le k \le 12$
	$-24 \le l \le 25$	$-11 \le l \le 17$	$-17 \le l \le 16$
Reflections collected/unique	9758/3261 [*R*(int) = 0.0277]	10350/3605 [*R*(int) = 0.0273]	8322/2697 [*R*(int) = 0.0354]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3261/1/164	3650/0/174	2697/0/173
Goodness of fit on F^2	1.271	1.198	1.260
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0286$, w$R_2 = 0.0584$	$R_1 = 0.0356$, w$R_2 = 0.0626$	$R_1 = 0.0361$, w$R_2 = 0.0710$
R indices (all data)	$R_1 = 0.0433$, w$R_2 = 0.1014$	$R_1 = 0.0700$, w$R_2 = 0.1043$	$R_1 = 0.0709$, w$R_2 = 0.1399$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	1.018 and −1.281	2.137 and −3.078	1.588 and −2.404

Table 3. Selected bond lengths (Å) and angles (°) of **[L_nPdCl$_2$]** (L_n = L_1–L_3) complexes.

[L_1PdCl$_2$]		**[L_2PdCl$_2$]**		**[L_3PdCl$_2$]**	
Bond lengths (Å)					
Pd(1)—N(1)	2.044(6)	Pd(1)—N(1)	2.028(6)	Pd(1)—N(1)	2.044(6)
Pd(1)—N(2)	2.111(6)	Pd(1)—N(2)	2.090(6)	Pd(1)—N(2)	2.089(7)
Pd(1)—Cl(1)	2.300(2)	Pd(1)—Cl(1)	2.289(2)	Pd(1)—Cl(1)	2.297(2)
Pd(1)—Cl(2)	2.297(2)	Pd(1)—Cl(2)	2.293(2)	Pd(1)—Cl(2)	2.288(2)
N(1)—N(5)	1.335(9)	N(1)—N(5)	1.36(1)	N(1)—N(5)	1.36(1)
N(2)—N(6)	1.520(9)	N(2)—N(6)	1.51(1)	N(2)—N(6)	1.51(1)
N(2)—N(7)	1.485(9)	N(2)—N(7)	1.49(1)	N(2)—N(7)	1.48(1)
C(5)—C(6)	1.48(1)	C(5)—C(6)	1.48(1)	C(5)—C(6)	1.51(1)
Bond angles (°)					
N(1)—Pd(1)—N(2)	81.2(2)	N(1)—Pd(1)—N(2)	81.7(3)	N(1)—Pd(1)—N(2)	82.5(2)
N(1)—Pd(1)—Cl(2)	175.9(2)	N(1)—Pd(1)—Cl(2)	176.2(2)	N(1)—Pd(1)—Cl(2)	172.0(2)
N(2)—Pd(1)—Cl(2)	94.9(2)	N(2)—Pd(1)—Cl(2)	94.8(2)	N(2)—Pd(1)—Cl(2)	92.1(2)
N(1)—Pd(1)—Cl(1)	93.5(2)	N(1)—Pd(1)—Cl(1)	93.3(1)	N(1)—Pd(1)—Cl(1)	93.9(2)
N(2)—Pd(1)—Cl(1)	174.7(2)	N(2)—Pd(1)—Cl(1)	174.7(2)	N(2)—Pd(1)—Cl(1)	176.1(2)
Cl(1)—Pd(1)—Cl(2)	90.45(8)	Cl(1)—Pd(1)—Cl(2)	90.27(9)	Cl(1)—Pd(1)—Cl(2)	91.69(8)
C(6)—N(2)—C(7)	107.2(6)	C(6)—N(2)—C(7)	107.3(6)	C(6)—N(2)—C(7)	108.8(7)
C(6)—N(2)—Pd(1)	101.2(4)	C(6)—N(2)—Pd(1)	103.4(4)	C(6)—N(2)—Pd(1)	106(5)

Scheme 2. Representation of the conformation δ and λ. C∗ refers to the asymmetric carbon.

of PMMA was analyzed using ^{1}H NMR spectroscopy.[75,76] The polymerization results, including tacticity based on the isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*), and the polydispersity index (PDI), which represents the average degree of polymerization in terms of the number of structural units and molecules, are summarized in Table 4. To confirm the catalytic activity of MMA polymerization, blank polymerization of MMA was performed with anhydrous **[PdCl$_2$]** and MMAO at specific temperatures. The tacticity of PMMA was determined in the range around syndiotactic (δ 0.85), heterotactic (δ 1.02), and isotactic (δ 1.21) based on ^{1}H NMR. The syndiotacticity of PMMA was ~70%, which was similar to all **[L_nPdCl$_2$]** (L_n = L_1–L_5) at a 60 °C polymerization temperature. The catalytic activities of the Pd(II) complexes were not significantly affected by the steric effects of ligands and local chirality around the metal center.

This is supported by the fact that the MMA polymerization activity of complex **[L_nPdCl$_2$]** (L_n = L_1–L_5) was similar to that of the reference complex **[PdCl$_2$]** (2.73×10^4 g PMMA/mol Pd·h), indicating that *N*-methyl-substituted pyridylmethylaniline ligands did not result in any steric and electronic effects to confer a mechanism of coordination polymerization. Moreover, the local chirality in Pd(II) complexes does not play a role in governing the tacticity of PMMA. The syndiotacticity of PMMA was ~0.70, which was similar to all **[L_nPdCl$_2$]** (L_n = L_1–L_5) and to the reference material **[PdCl$_2$]**, regardless of the polymerization temperature. For comparison, copper(II) [Cu(II)] complexes with ligand *N*-(2-furanylmethyl)-*N*-(1-3,5-dimethyl-1*H*-pyrazolylmethyl)-*N*-(phenylmethyl) amines[69] were reported to be active catalysts for MMA polymerization to yield syndiotactic PMMA with an *rr* value of up to 0.78. However, the conversion of MMA to PMMA was only 30%. In addition, Ni(II) complexes[62,65,71–73] with ligands such as pentane-2,4-diol and phenoxy-imine showed syndiotacticity ranging from 0.73 to 0.82 with an activity of 4.20×10^4 g PMMA/molNi·h. Cobalt(II) [Co(II)] complexes with phenoxy-imine[63] were also used as catalysts for MMA polymerization with moderate activity and syndiotacticity. Thus, the moderate syndiotacticity of **[L_nPdCl$_2$]** (L_n = L_1–L_5) complexes was not sufficient to confer a mechanism of coordination polymerization, and the chirality in **[L_nPdCl$_2$]** (L_n = L_1–L_5) did not play a role during MMA polymerization. In addition, the presence of 5 equiv of radical inhibitor 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) during MMA polymerization did not significantly reduce the yield of PMMA (~5% yield), supporting that the mechanism of coordination polymerization is not a radical mechanism.[63] These results were comparable to previously reported Pd(II) complexes containing the bispyridylamine ligand, namely *N*,*N*-di(2-picolyl) cycloheptylamine,[49] *N*-cycloalkyl 2-iminomethylpyridine ligand,[50] and *N*-(pyridin-2-ylmethyl)aniline and its derivatives,[50] which clearly showed steric and electronic effects of Pd(II) complexes during MMA polymerization. However, structural differences caused by the phenyl ring of the aniline moiety in **[L_nPdCl$_2$]** (L_n = L_1–L_5) with *N*-methyl-*N*-(pyridin-2-ylmethyl)aniline and its derivatives did not sufficiently induce steric hindrance or electronic effects

Table 4. Polymerization of MMA by **[L_nPdCl$_2$]** (L_n = L_1–L_5) complexes in the presence of MMAO.

Entry	Catalyst[a]	Temperature (°C)	Yield[b] (%)	Activity[c] (g/molCat h)	T_g[d] (°C)	Tacticity (% mm)	(% mr)	(% rr)	M_w[e] (g/mol) × 10^5	M_w/M_n[f]
1	**[PdCl$_2$]**	60	12.6	1.97	129	10.2	23.5	66.3	7.52	1.63
4	MMAO[g]	60	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
5	**[L_1PdCl$_2$]**	60	19.4	3.03	129	7.90	24.1	68.0	1.49	1.21
6	**[L_2PdCl$_2$]**	60	19.0	2.98	130	7.40	25.3	67.3	1.13	1.09
7	**[L_3PdCl$_2$]**	60	17.7	2.77	129	7.60	24.1	68.3	1.21	1.33
8	**[L_4PdCl$_2$]**	60	17.9	2.81	129	6.70	23.7	69.6	1.73	1.11
9	**[L_5PdCl$_2$]**	60	13.7	2.12	127	6.80	22.7	70.5	7.42	1.84

[a] [Pd(II) catalyst]$_0$ = 15 μmol and [MMA]$_0$/[MMAO]$_0$/[Pd(II) catalyst]$_0$ = 3100:500:1. [b] Yield defined as the mass of dried polymer recovered/mass of monomer used. [c] Activity represents (gPMMA)/(molPd h). [d] T_g is the glass transition temperature determined using a thermal analyzer. [e] Determined using GPC eluted with tetrahydrofuran at room temperature by filtration with polystyrene calibration. [f] M_n refers to the number average molecular weight of PMMA. [g] Blank polymerization performed with MMAO alone.

on the Pd metal center to improve the activity and syndiotacticity during MMA polymerization.

Conclusions

We investigated the synthesis and X-ray crystallographic structures of **[L_nPdCl$_2$]** (L_n = L_1–L_5), which were prepared by the substitution reaction of **[Pd(CH$_3$CN)$_2$Cl$_2$]** with the corresponding *N*′-methyl substituted pyridylmethylamine ligands. The coordination geometries around the Pd(II) centers in these complexes were square planar. The catalytic activity of **[L_nPdCl$_2$]** (L_n = L_1–L_5) toward the MMA polymerization resulted in moderate activity (3.03×10^4 g PMMA/mol Pd·h for **[L_1PdCl$_2$]**) with PMMA syndiotacticity of ~0.68 compared to the reference complex **[PdCl$_2$]** (1.97×10^4 g PMMA/mol Pd·h), indicating that *N*′-methyl substituted pyridylmethylamine ligands were not effectively coordinated to the Pd metal to exert high MMA polymerization activity. Moreover, the induced chirality in Pd(II) complexes did not control the tacticity of PMMA.

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Supporting Information. CCDC 1001593–1001595 contains the supplementary crystallographic data for **[L_1PdCl$_2$]**, **[L_2PdCl$_2$]**, and **[L_3PdCl$_2$]**, 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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