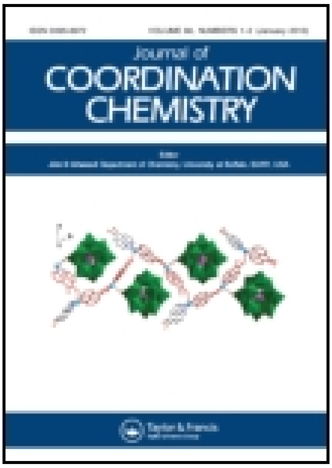
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:16
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

N,N′,X-bidentate versus N,N′,X-tridentate N-substituted 2-iminomethylpyridine- and 2-iminomethylquinoline-coordinated palladium(II) complexes

Dongil Kim[a], Yujin Song[a], Sunghoon Kim[a], Ha-Jin Lee[bc] & Hyosun Lee[a]
[a] Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu, Republic of Korea
[b] Jeonju Center, Korea Basic Science Institute (KBSI), Jeonju, Republic of Korea
[c] Department of Chemistry, Chonbuk National University, Jeonju, Republic of Korea

Accepted author version posted online: 24 Jul 2014.Published online: 18 Aug 2014.

To cite this article: Dongil Kim, Yujin Song, Sunghoon Kim, Ha-Jin Lee & Hyosun Lee (2014) N,N′,X-bidentate versus N,N′,X-tridentate N-substituted 2-iminomethylpyridine- and 2-iminomethylquinoline-coordinated palladium(II) complexes, Journal of Coordination Chemistry, 67:13, 2312-2329, DOI: 10.1080/00958972.2014.947971

To link to this article: http://dx.doi.org/10.1080/00958972.2014.947971

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

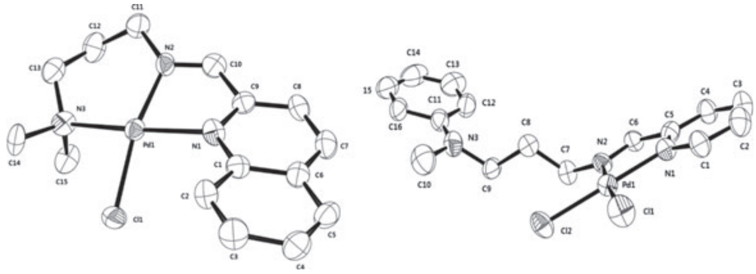
Journal of Coordination Chemistry, 2014
Vol. 67, No. 13, 2312–2329, http://dx.doi.org/10.1080/00958972.2014.947971

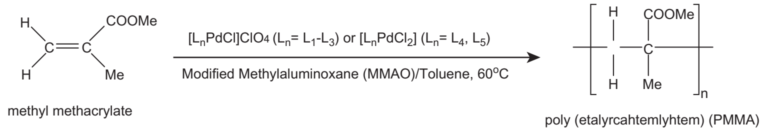
N,N′,X-bidentate *versus N,N′,X*-tridentate *N*-substituted 2-iminomethylpyridine- and 2-iminomethylquinoline-coordinated palladium(II) complexes

DONGIL KIM†, YUJIN SONG†, SUNGHOON KIM†, HA-JIN LEE‡§ and HYOSUN LEE*†

†Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu, Republic of Korea
‡Jeonju Center, Korea Basic Science Institute (KBSI), Jeonju, Republic of Korea
§Department of Chemistry, Chonbuk National University, Jeonju, Republic of Korea

(*Received 11 June 2014; accepted 7 July 2014*)





A new series of *N,N′,X*-tridentate complexes, **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and *N,N′,X*-bidentate complexes, **[L$_n$PdCl$_2$]** (L$_n$ = L$_4$, L$_5$) containing *N*-functional group-substituted 2-iminomethylpyridine and 2-iminomethylquinoline ligands (**L$_n$**) were synthesized and characterized by X-ray crystallography. It showed that the coordination geometry around the palladium center of all Pd(II) complexes was slightly distorted square planar. The catalytic activity of Pd(II) complexes for methyl methacrylate polymerization was investigated.

The reaction of **[Pd(CH$_3$CN)$_2$Cl$_2$]** with *N*-functional group-substituted 2-iminomethylpyridine and 2-iminomethylquinoline can produce *N,N′,X*-bidentate Pd(II) complexes and *N,N′,X*-tridentate Pd(II) complexes depending on the functional group substitution on the nitrogen of the imine moiety. For example, *N,N*-dimethyl-3-((pyridin-2-ylmethylene)amino)propan-1-amine (**L$_1$**), *N,N*-dimethyl-3-((quinolin-2-ylmethylene)amino)propan-1-amine (**L$_2$**), and *N*-(3-(methylthio)propyl)-1-(pyridin-2-yl) methanimine (**L$_3$**) were coordinated to palladium as *N,N′,X*-tridentate mode in the presence of

---

*Corresponding author. Email: hyosunlee@knu.ac.kr

$NaClO_4$ to yield two fused ring metallacyclic **[(*NN′X*)PdCl]ClO$_4$** complexes with high yield, i.e. **[L$_n$PdCl]ClO$_4$** (L_n = L_1, L_2, L_3), respectively. However, *N*-methyl-*N*-(3-((pyridin-2-ylmethylene) amino)propyl)aniline (**L$_4$**) and *N*-(3-methoxypropyl)-1-(pyridin-2-yl)methanimine (**L$_5$**) yield (in the absence of $NaClO_4$) *N,N′,X*-bidentate metallacyclic **[(*NN′*)PdCl$_2$]** complexes with high yield, i.e. **[L$_4$PdCl$_2$]** and **[L$_5$PdCl$_2$]**, respectively. The X-ray crystal structure of Pd(II) complexes revealed that the palladium in **[L$_n$PdCl]ClO$_4$** (L_n = L_1, L_2, L_3) and **[L$_n$PdCl$_2$]** (L_n = L_4, L_5) formed a slightly distorted square planar geometry involving two nitrogens of iminomethylpyridine ligand, one X, and one or two chlorides. The *N,N′,X*-tridentate complex **[L$_2$PdCl]ClO$_4$** and the *N,N′,X*-bidentate complex **[L$_5$PdCl$_2$]** showed high catalytic activity for polymerization of methyl methacrylate in the presence of co-catalyst, modified methylaluminoxane at 60 °C compared to the reference complex anhydrous **[PdCl$_2$]**. Specifically, the activities of **[L$_2$PdCl]ClO$_4$** and **[L$_4$PdCl$_2$]** were 1.43×10^5 and 1.08×10^5 g PMMA M^{-1} Pd h, respectively. The syndiotacticity of poly(methylmethacrylate) (PMMA), which was characterized using ^1H NMR spectroscopy, was about 0.70 for the **[L$_2$PdCl]ClO$_4$** and **[L$_4$PdCl$_2$]** complexes.

Keywords: Pyridylimines; Palladium(II) complex; Methyl methacrylate polymerization; Syndiotacticity

1. Introduction

Transition metal complexes containing pyridylimines and *N*-substituted 2-iminoalkylpyridines have attracted attention in the areas of synthetic, spectroscopic, and kinetic studies [1–12], as catalysts for organic transformation [13–18], electrochemistry [19–22], bioinorganic chemistry [23, 24], and olefin polymerization [25–37]. This is likely due to their structural variations in coordination modes from *N,N′*-bidentate to *N,N′,X*-tridentate, and even to *N,N′,X,X′*-tetradentate, in which coordination of X is determined by substitution on the pyridine ring and imine moiety. For example, by introducing various functional groups on the nitrogen of the imine moiety, *N,N′,X*-tridentate complexes can be efficiently generated. These variations include the presence of *N*-substituted 2-iminoalkylpyridines and corresponding analogs, such as *N*-substituted iminoquinoline, in transition metal complexes. Thus, according to their steric and electronic properties, structural variations in pyridylimines vary due to the polydentate characteristics of *N,N′,X*-tridentate pyridylimine ligands. In this study, we explore structural variations in Pd(II) complexes of pyridylimines to manipulate the coordination mode of pyridylimines to palladium [38–52]. The coordination modes for Pd(II) complexes are discussed in regards to a third appended donor *X* (*X* = N, S, O) group on the ligand. The appended 2-iminoalkylpyridine donor in ligands governs hapticity of Pd(II) complexes. The Pd(II) complexes mainly exist in monomeric square planar geometry.

Recently, we explored transition metal complexes as catalysts for homogeneous polymerization of methyl methacrylate (MMA) to produce highly syndiotactic poly(methylmethacrylate) (PMMA) with high conversion of MMA to PMMA. Studies on non-radical-mediated MMA polymerization, which can increase glass transition temperature (T_g) up to 140 °C, have been performed, and some transition metal complexes have been applied to this process [53–65]. Previously, we reported that *N,N′*-bidentate Pd(II) complex with *N*-substituted 2-iminoalkylpyridines [66] and *N,N′,N*-tridentate Pd(II) complex with *N,N*-di(2-picolyl)cycloalkylamine [67] have a very high activity for MMA polymerization. Thus, we report the synthesis and structural characterization of *N,N′,X*-tridentate *N*-functional group-substituted 2-iminomethylpyridine and 2-iminomethylquinoline ligands, i.e. *N,N*-dimethyl-3-((pyridin-2-ylmethylene)amino)propan-1-amine (**L$_1$**), *N,N*-dimethyl-3-((quinolin-2-ylmethylene)amino) propan-1-amine (**L$_2$**), *N*-(3-(methylthio)propyl)-1-(pyridin-2-yl)methanimine (**L$_3$**), and their Pd (II) complexes. In addition, although they are *N,N′,X*-tridentate *N*-functional group-substituted 2-iminomethylpyridine ligands, *N*-methyl-*N*-(3-((pyridin-2-ylmethylene)amino)propyl)aniline

(**L_4**) and *N*-(3-methoxypropyl)-1-(pyridin-2-yl)methanimine (**L_5**), as well as their *N,N′*,*X*-bidentate Pd(II) complexes, were prepared. Moreover, the catalytic activity of *N,N′,X*-tridentate **[L_nPdCl]ClO_4** ($L_n = L_1, L_2, L_3$) and *N,N′,X*-bidentate **[L_nPdCl_2]** ($L_n = L_4, L_5$) for MMA polymerization in toluene was compared to the reference complex **[$PdCl_2$]** at 60 °C.

2. Experimental

2.1. *Physical measurement*

Anhydrous **[$PdCl_2$]**, 2-pyridine aldehyde, 3-methoxypropan-1-amine, *N*-methyl-*N*-phenylpropane-1,3-diamine, 4-methoxyaniline, 2,6-diethylaniline, magnesium sulfate, and MMA were purchased from Sigma-Aldrich (St. Louis, MO) and anhydrous solvents such as C_2H_5OH, DMF, diethyl ether, and dichloromethane were purchased from Merck (Darmstadt, Germany) and used without purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation (Tokyo, Japan) as 6.9% aluminum (by weight) in a toluene solution and used without purification. Elemental analyses (C, H, N) of the prepared complexes were performed on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^1H NMR (operating at 400 MHz) and ^{13}C NMR (operating at 100 MHz) spectra were recorded on an Advance Digital 400 NMR spectrometer (Bruker, Billerica, MA); chemical shifts were recorded in ppm units (δ) relative to $SiMe_4$ as the internal standard. Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) and the data were reported in reciprocal centimeters. The molecular weight and molecular weight distribution of the obtained polymethylmethacrylate (PMMA) were determined using gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). T_g was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

2.2. *Preparation of ligands and Pd(II) complexes*

2.2.1. N,N-dimethyl-3-((pyridin-2-ylmethylene)amino)propan-1-amine (L$_1$). Although **L_1** has been reported previously, in this report we provide full spectroscopic data [22, 68]. *N,N*-Dimethylpropane-1,3-diamine (2.52 mL, 0.0200 M) in dichloromethane (20.0 mL) was added to 2-pyridine aldehyde (1.90 mL, 0.0200 M) in dichloromethane (20.0 mL). After 24 h of stirring at room temperature, the reaction solution was dried over $MgSO_4$ and filtered. The filtrate was removed under reduced pressure and vacuum distilled to give an orange oil (3.26 g, 85%). Analysis calculated for $C_{11}H_{17}N_3$: C, 69.1%; H, 8.96%; N, 22.0%. Found: C, 69.1%; H, 9.01%; N, 22.1%. ^1H NMR (DMSO-d$_6$, 400 MHz): δ 8.63 (d, 1H, $J = 5.6$ Hz), 8.34 (s, 1H), 7.94 (d, 1H, $J = 6.8$ Hz), 7.84 (t, 1H, $J = 4.4$ Hz), 7.43 (t, 1H, $J = 4.8$ Hz), 3.71 (t, 2H, $J = 6.8$ Hz), 2.52 (t, 2H, $J = 6.8$ Hz), 2.16 (s, 6H), 1.90 (m, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 162.7, 154.5, 149.6, 137.1, 125.4, 120.7, 59.7, 58.7, 45.7, 45.4. IR (liquid neat; cm^{-1}): 3054 (w), 2939 (m), 2856 (m), 2871 (m), 2771 (m), 1649 (s), 1582 (m), 1517 (w), 1459 (s), 1276 (m), 1038 (s), 992 (s), 855 (s).

2.2.2. N,N-dimethyl-3-((quinolin-2-ylmethylene)amino)propan-1-amine (L$_2$). **L_2** was prepared using an analogous method as described for **L_1**, except utilizing *N,N*-dimethylpropane-1,3-diamine (2.52 mL, 0.0200 M) and quinoline-2-carbaldehyde (3.14 g, 0.0200 M).

The product was obtained by vacuum distillation as light red oil (4.46 g, 92%). Analysis calculated for $C_{15}H_{19}N_3$: C, 74.7%; H, 7.94%; N, 17.4%. Found: C, 74.6%; H, 7.94%; N, 17.4%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.49 (s, 1H), 8.39 (d, 1H, *J* = 8.4 Hz), 8.08 (d, 2H, *J* = 8.4 Hz), 8.00 (d, 1H, *J* = 8.0 Hz), 7.79 (t, 1H, *J* = 7.2 Hz), 7.64 (t, 1H, *J* = 6.8 Hz), 3.69 (t, 2H, *J* = 6.8 Hz), 2.28 (t, 2H, *J* = 7.4 Hz), 2.12 (s, 6H), 1.79 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 162.4, 154.8, 147.6, 137.1, 130.4, 129.5, 128.7, 128.4, 127.9, 118.2, 58.8, 57.1, 45.4, 28.6. IR (liquid neat; cm^{-1}): 3057 (w), 2939 (m), 2859 (m), 2816 (m), 2769 (m), 1645 (s), 1598 (s), 1503 (m), 1455 (s), 1371 (s), 1308 (s), 1216 (s), 1040 (s), 959 (s), 886 (s).

2.2.3. 3-(Methylthio)-N-((pyridin-2-yl)methylene)propan-1-amine (L_3). **L_3** was prepared by analogous method as described for **L_1**, except utilizing 3-(methylthio)propan-1-amine (2.24 mL, 0.0200 M) and 2-pyridine aldehyde (1.90 mL, 0.0200 M). The product was obtained by vacuum distillation as light red oil (3.23 g, 83%). Analysis calculated for $C_{10}H_{14}N_2S$: C, 61.8%; H, 7.26%; N, 14.4%. Found: C, 61.8%; H, 7.26%; N, 14.4%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.62 (d, 1H, *J* = 7.6 Hz), 8.35 (s, 1H), 7.96 (d, 1H, *J* = 8.0 Hz), 7.81 (t, 1H, *J* = 7.6 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 3.67 (t, 2H, *J* = 6.4 Hz), 2.51 (t, 2H, *J* = 7.2 Hz), 2.02 (s, 3H), 1.88 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 162.4, 154.5, 149.6, 136.9, 125.2, 120.7, 59.4, 31.4, 30.0, 15.0. IR (liquid neat; cm^{-1}): 3285 (w), 3047 (w), 2911 (w), 1677 (w), 1593 (s), 1501 (s), 1427 (m), 1384 (m), 1325 (m), 1228 (m), 1173 (m), 1089 (s), 988 (s), 869 (s).

2.2.4. N-methyl-N-(3-((pyridin-2-ylmethylene)amino)propyl)aniline (L_4). **L_4** was prepared by analogous method as described for **L_1**, except utilizing N-methyl-N-phenylpropane-1,3-diamine (3.29 mL, 0.0200 M) and 2-pyridine aldehyde (1.90 mL, 0.0200 M). The product was obtained by vacuum distillation as light red oil (3.86 g, 76%). Analysis calculated for $C_{16}H_{19}N_3$: C, 75.9%; H, 7.56%; N, 16.6%. Found: C, 76.4%; H, 7.61%; N, 16.4%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.65 (d, 1H, *J* = 7.6 Hz), 8.39 (s, 1H), 8.02 (d, 1H, *J* = 6.8 Hz), 7.84 (t, 1H, *J* = 8.0 Hz), 7.41 (t, 1H, *J* = 6.0 Hz), 7.15 (t, 2H, *J* = 7.2 Hz), 6.70 (d, 2H, *J* = 8.8 Hz), 6.60 (t, 1H, *J* = 6.8 Hz), 3.63 (t, 2H, *J* = 6.8 Hz), 3.40 (t, 2H, *J* = 6.8 Hz), 2.85 (s, 3H), 1.85 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 162.3, 154.6, 149.7, 149.3, 137.1, 129.3, 125.3, 120.7, 115.9, 112.3, 58.3, 50.0, 38.2, 27.8. IR (liquid neat; cm^{-1}): 3060 (w), 2920 (s), 2854 (m), 1660 (m), 1584 (m), 1437 (m), 1362 (s), 1239 (s), 1122 (w), 1047 (w), 984 (s), 830 (s).

2.2.5. 3-Methoxy-N-((pyridin-2-yl)methylene)propan-1-amine (L_5). **L_5** was prepared by analogous method as described for **L_1**, except utilizing 3-methoxypropan-1-amine (2.05 mL, 0.0200 M) and 2-pyridine aldehyde (1.90 mL, 0.0200 M). The product was obtained by vacuum distillation as light red oil (2.78 g, 78%). Analysis calculated for $C_{10}H_{14}N_2O$: C, 67.4%; H, 7.92%; N, 15.7%. Found: C, 67.7%; H, 7.47%; N, 15.6%. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.64 (d, 1H, *J* = 7.6 Hz), 8.34 (s, 1H), 7.96 (d, 1H, *J* = 10.1 Hz), 7.85 (t, 1H, *J* = 8.2 Hz), 7.43 (t, 1H, *J* = 7.3 Hz), 3.65 (t, 2H, *J* = 7.7 Hz), 3.38 (t, 2H, *J* = 6.3 Hz), 3.22 (s, 3H), 1.85 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.9, 154.2, 149.3, 136.7, 124.9, 120.3, 69.6, 57.8, 57.1, 30.3. IR (liquid neat; cm^{-1}): 3057 (w), 2939 (m), 2859 (m), 2769 (m), 1645 (m), 1598 (m), 1503 (s), 1371 (w), 1308 (s), 1216 (s), 1154 (s), 1100 (s), 1040 (m), 959 (s), 886 (s).

2.2.6. N,N-dimethyl-3-((pyridin-2-ylmethylene)amino)propan-1-amine(chloro)palladium (II) perchlorate ([L$_1$PdCl]ClO$_4$).

A solution of **L$_1$** (956 mg, 0.500 mM) in anhydrous ethanol (10.0 mL) was added to a solution of **[Pd(CH$_3$CN)$_2$Cl$_2$]** [69] (130 mg, 0.500 mM) and NaClO$_4$ (600 mg, 0.500 mM) (caution: it is very flammable solid and oxidizing. It should be carefully handled.) CAS registry number: 7601-89-0) in anhydrous ethanol (10.0 mL) at room temperature. Precipitation of yellow material occurred while stirring at room temperature for 12 h. The yellow solid was filtered and washed with ethanol (25.0 mL × 2), followed by washing with diethyl ether (25.0 mL × 2) (0.190 g, 88%). Crystals suitable for X-ray study of **[L$_1$PdCl]ClO$_4$** were obtained within three days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_1$PdCl]ClO$_4$** (0.0500 g). Analysis calculated for $C_{11}H_{17}N_3Cl_2O_4Pd$: C, 30.5%; H, 3.96%; N, 9.71%. Found: C, 30.6%; H, 3.99%; N, 9.63%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.83 (d, 1H), 8.65 (s, 1H), 8.54 (d, 1H, J = 8.0 Hz), 8.03 (t, 1H, J = 7.8 Hz), 7.88 (t, 1H, J = 7.6 Hz), 2.64 (t, 2H, J = 16.2 Hz), 2.22 (s, 6H), 1.98 (t, 2H, J = 15.2 Hz), 1.43 (m, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 161.3, 158.3, 145.0, 136.7, 129.2, 124.2, 58.9, 48.1, 46.5, 33.9. IR (solid neat; cm^{-1}): 3054 (w), 2937 (m), 2874 (m), 1592 (m), 1146 (m), 1116 (w), 1085 (s), 1075 (m), 1025 (w), 988 (s), 961 (m), 871 (s).

2.2.7. N,N-dimethyl-3-((quinolin-2-ylmethylene)amino)propan-1-amine(chloro)palladium (II) perchlorate ([L$_2$PdCl]ClO$_4$).

[L$_2$PdCl]ClO$_4$ was prepared according to the procedure described for **[L$_1$PdCl]ClO$_4$**, except utilizing **L$_2$** (120 mg, 0.500 mM) and **[Pd(CH$_3$CN)$_2$Cl$_2$]** (130 mg, 0.500 mM). The yellow solid was filtered and washed with ethanol (25.0 mL × 2), followed by washing with diethyl ether (25.0 mL × 2) (0.180 g, 75%). Crystals suitable for X-ray study of **[L$_2$PdCl]ClO$_4$** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_2$PdCl]ClO$_4$** (0.0500 g). Analysis calculated for $C_{15}H_{19}Cl_2N_3O_4Pd$: C, 37.3%; H, 3.97%; N, 8.71%. Found: C, 37.3%; H, 3.95%; N, 8.71%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 9.04 (s, 1H), 9.01 (d, 1H, J = 8.0 Hz), 8.93 (d, 1H, J = 8.4 Hz), 8.21 (t, 2H, J = 8.4 Hz), 7.97 (t, 1H, J = 8.4 Hz), 7.87 (t, 1H, J = 6.8 Hz), 3.78 (t, 2H, J = 4.4 Hz), 2.84 (s, 6H), 2.68 (t, 2H, J = 5.2 Hz), 2.12 (m, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 162.9, 155.1, 148.1, 136.9, 130.1, 129.9, 129.1, 128.1, 127.7, 118.7, 59.9, 57.9, 45.8, 29.2. IR (solid neat; cm^{-1}): 3096 (w), 2985 (w), 2888 (w), 2806 (m), 2751 (m), 2372 (m), 1833 (m), 1699 (m), 1650 (m), 1541 (s), 1518 (s), 1456 (m), 1367 (s), 1216 (s), 1077 (s), 997 (s), 933 (s), 860 (s).

2.2.8. 3-(Methylthio)-N-((pyridin-2-yl)methylene)propan-1-amine(chloro)palladium(II) perchlorate ([L$_3$PdCl]ClO$_4$).

[L$_3$PdCl]ClO$_4$ was prepared according to the procedure described for **[L$_1$PdCl]ClO$_4$**, except utilizing **L$_3$** (97.2 mg, 0.500 mM) and **[Pd(CH$_3$CN)$_2$Cl$_2$]** (130 mg, 0.500 mM). The yellow solid was filtered and washed with ethanol (25.0 mL × 2), followed by washing with diethyl ether (25.0 mL × 2) (0.190 g, 98%). Crystals suitable for X-ray study of **[L$_3$PdCl]ClO$_4$** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_2$PdCl]ClO$_4$** (0.0500 g). Analysis calculated for $C_{10}H_{14}Cl_2N_2O_4SPd$: C, 27.6%; H, 3.24%; N, 6.43%. Found: C, 27.6%; H, 3.22%; N, 6.46%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.95 (s, 1H), 8.94 (d, 1H, J = 4.8 Hz), 8.45 (t, 1H, J = 7.6 Hz), 8.24 (d, 1H, J = 6.8 Hz), 7.98 (t, 1H, J = 5.6 Hz), 3.76 (broad, 2H), 2.77 (broad, 2H), 2.61 (s, 3H), 2.26 (broad, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 172.9, 154.4, 150.3, 142.8, 129.6, 129.1, 56.4, 30.1, 27.4, 18.9.

IR (solid neat; cm^{-1}): 3116(w), 2926 (w), 2850 (w), 2366 (m), 1451 (m), 1399 (m), 1278 (m), 1164 (m), 1059 (s), 973 (s), 895 (s).

2.2.9. N-methyl-N-(3-((pyridin-2-ylmethylene)amino)propyl)aniline(dichloro)palladium (II) ([L$_4$PdCl$_2$]). A solution of **L$_4$** (127 mg, 0.500 mM) in anhydrous ethanol (10.0 mL) was added to a solution of **[Pd(CH$_3$CN)$_2$Cl$_2$]** (130 mg, 0.500 mM) in anhydrous ethanol (10.0 mL) at room temperature. Precipitation of yellow solid occurred while stirring at room temperature for 12 h. The yellow solid was filtered and washed with ethanol (25.0 mL × 2), followed by washing with diethyl ether (25.0 mL × 2) (0.170 g, 79%). Crystals suitable for X-ray analysis of **[L$_4$PdCl$_2$]** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_4$PdCl$_2$]** (0.0500 g). Analysis calculated for $C_{16}H_{19}Cl_2N_3Pd$: C, 44.6%; H, 4.45%; N, 9.76%. Found: C, 44.6%; H, 4.18%; N, 9.66%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.95 (d, 1H, J = 5.6 Hz), 8.56 (s, 1H), 8.32 (t, 1H, J = 7.6 Hz), 8.00 (d, 1H, J = 8.0 Hz), 7.84 (t, 1H, J = 5.6 Hz), 7.13 (t, 2H, J = 7.2 Hz), 6.71 (d, 2H, J = 8.0 Hz), 6.59 (t, 1H, J = 7.2 Hz), 3.75 (t, 2H, J = 6.8 Hz), 3.39 (t, 2H, J = 7.2 Hz), 2.91 (s, 3H), 2.04 (m, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 171.5, 156.2, 150.3, 149.2, 141.6, 129.4, 128.7, 128.5, 116.1, 112.5, 57.5, 49.2, 38.1, 27.7. IR (solid neat; cm^{-1}): 3212 (w), 2919 (m), 2844 (m), 2371 (m), 2311 (m), 1694 (m), 1549 (s), 1462 (s), 1385 (s), 1289 (m), 1225 (w), 1126 (m), 1039 (s), 981 (s), 855 (s).

2.2.10. 3-(Methylthio)-N-((pyridin-2-yl)methylene)propan-1-amine(dichloro)palladium (II) ([L$_5$PdCl$_2$]). **[L$_5$PdCl$_2$]** was prepared according to the procedure described for **[L$_4$PdCl$_2$]**, except utilizing **L$_5$** (89.1 mg, 0.500 mM) and **[Pd(CH$_3$CN)$_2$Cl$_2$]** (130 mg, 0.500 mM). The yellow solid was filtered and washed with ethanol (25.0 mL × 2), followed by washing with diethyl ether (25.0 mL × 2) (0.150 g, 84%). Crystals suitable for X-ray study of **[L$_5$PdCl$_2$]** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_5$PdCl$_2$]** (0.0500 g). Analysis calculated for $C_{10}H_{14}Cl_2N_2OPd$: C, 33.8%; H, 3.97%; N, 7.88%. Found: C, 33.6%; H, 4.06%; N, 7.55%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.97 (d, 1H, J = 5.2 Hz), 8.59 (s, 1H), 8.35 (t, 1H, J = 7.6 Hz), 8.12 (t, 1H, J = 8.0 Hz), 7.87 (t, 1H, J = 7.6 Hz), 3.77 (t, 2H, J = 6.8 Hz), 3.39 (t, 2H, J = 6.4 Hz), 2.24 (s, 3H), 2.02 (m, 2H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 172.0, 156.2, 150.4, 141.7, 128.9, 128.6, 69.1, 58.2, 57.0, 30.1. IR (solid neat; cm^{-1}): 3024 (w), 2985 (w), 2886 (m), 2764 (m), 2315 (m), 1649 (m), 1516 (m), 1463 (m), 1163 (s), 1077 (s), 929 (s), 859 (s).

2.3. *X-ray crystallographic studies*

A crystal was isolated with paratone oil and mounted on a Bruker SMART CCD diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation source under a nitrogen cold stream (200 K). Data collection and integration were performed with SMART and SAINT-Plus software packages [70]. Semi-empirical absorption corrections based on equivalent reflections were applied using SADABS [71]. Structures were solved using direct methods and refined using a full-matrix least-squares method on F^2 using SHELXTL [72]. All non-hydrogen atoms were refined anisotropically. Hydrogens were added to their geometrically ideal positions. Crystallographic and structural data are summarized in table 1.

Table 1. Crystal data and structure refinement for **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$, L$_2$).

	[L$_1$PdCl]ClO$_4$	**[L$_2$PdCl]ClO$_4$**	**[L$_3$PdCl]ClO$_4$**	**[L$_4$PdCl$_2$]**	**[L$_5$PdCl$_2$]**
Empirical formula	$C_{11}H_{17}Cl_2N_3O_4Pd$	$C_{15}H_{19}Cl_2N_3O_4Pd$	$C_{10}H_{14}Cl_2N_2O_4SPd$	$C_{16}H_{19}Cl_2N_3Pd$	$C_{10}H_{14}Cl_2N_2OPd$
Formula weight	432.58	482.63	435.62	430.64	355.53
Temperature	200(2) K	200(2) K	200(2) K	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)/c*	*C2(1)/c*	*P2(1)/c*	*P2(1)/n*
Unit cell dimensions	a = 8.3077(9) Å b = 12.7866(15) Å c = 14.5928(17) Å α = 90° β = 94.108(2)° γ = 90°	a = 15.0734(15) Å b = 8.7048(9) Å c = 14.2063(14) Å α = 90° β = 106.118(2)° γ = 90°	a = 12.2187(12) Å b = 11.3705(11) Å c = 24.439(2) Å α = 90° β = 93.688(2)° γ = 90°	a = 15.890(2) Å b = 15.656(2) Å c = 14.9510(19) Å α = 90° β = 112.034(3)° γ = 90°	a = 10.1052(13) Å b = 9.2328(12) Å c = 13.6954(17) Å α = 90° β = 90.086(2)° γ = 90°
Volume *Z*	1546.2(3) Å^3, 4	1790.8(3) Å^3, 4	3388.4(6) Å^3, 4	3447.6(8) Å^3, 8	1277.8(3) Å^3, 4
Density (calculated)	1.858 g cm^{-3}	1.790 g cm^{-3}	1.837 g cm^{-3}	1.659 g cm^{-3}	1.848 g cm^{-3}
Absorption coefficient	1.563 mm^{-1}	1.360 mm^{-1}	1.555 mm^{-1}	1.385 mm^{-1}	1.851 mm^{-1}
F (0 0 0)	864	968	1860	1728	704
Crystal size	0.18 × 0.17 × 0.14 mm^3	0.37 × 0.23 × 0.21 mm^3	0.34 × 0.29 × 0.26 mm^3	0.24 × 0.21 × 0.17 mm^3	0.31 × 0.23 × 0.21 mm^3
Theta range for data collection	2.12°–28.34°	1.41°`–28.31°	2.45°–28.34°	1.38°–28.32°	2.50°–26.04°
Index ranges	$-11 \le h \le 11$ $-17 \le k \le 10$ $-19 \le l \le 19$	$-20 \le h \le 15$ $-11 \le k \le 11$ $-18 \le l \le 18$	$-16 \le h \le 15$ $-10 \le k \le 15$ $-32 \le l \le 32$	$-21 \le h \le 9$ $-20 \le k \le 20$ $-19 \le l \le 19$	$-12 \le h \le 12$ $-10 \le k \le 11$ $-13 \le l \le 16$
Reflections collected	11207	12374	11816	25107	7698
Independent reflections	3834 [*R*(int) = 0.0501]	4341 [*R*(int) = 0.0251]	4112 [*R*(int) = 0.0209]	8535 [*R*(int) = 0.0317]	2514 [*R*(int) = 0.0481]
Completeness to theta = 28.30°	99.6%	97.5%	97.3%	99.5%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
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
Data/restraints/parameters	3834/0/192	4341/0/229	4112/0/220	8535/0/399	2514/0/146
Goodness-of-fit on F^2	1.179	1.258	1.405	1.220	1.192
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$ $wR_2 = 0.0766$	$R_1 = 0.0566$ $wR_2 = 0.1645$	$R_1 = 0.0642$ $wR_2 = 0.2000$	$R_1 = 0.0552$ $wR_2 = 0.1273$	$R_1 = 0.0571$ $wR_2 = 0.1418$
R indices (all data)	$R_1 = 0.0978$ $wR_2 = 0.1412$	$R_1 = 0.0870$ $wR_2 = 0.2912$	$R_1 = 0.0907$ $wR_2 = 0.3252$	$R_1 = 0.1040$ $wR_2 = 0.2261$	$R_1 = 0.0839$ $wR_2 = 0.2440$
Largest diff. peak and hole	1.459 and −2.902 e Å^{-3}	2.213 and −2.367 e Å^{-3}	2.494 and −2.860 e Å^{-3}	2.497 and −4.120 e Å^{-3}	1.236 and −2.977 e Å^{-3}

2.4. *Catalytic activity for MMA polymerization*

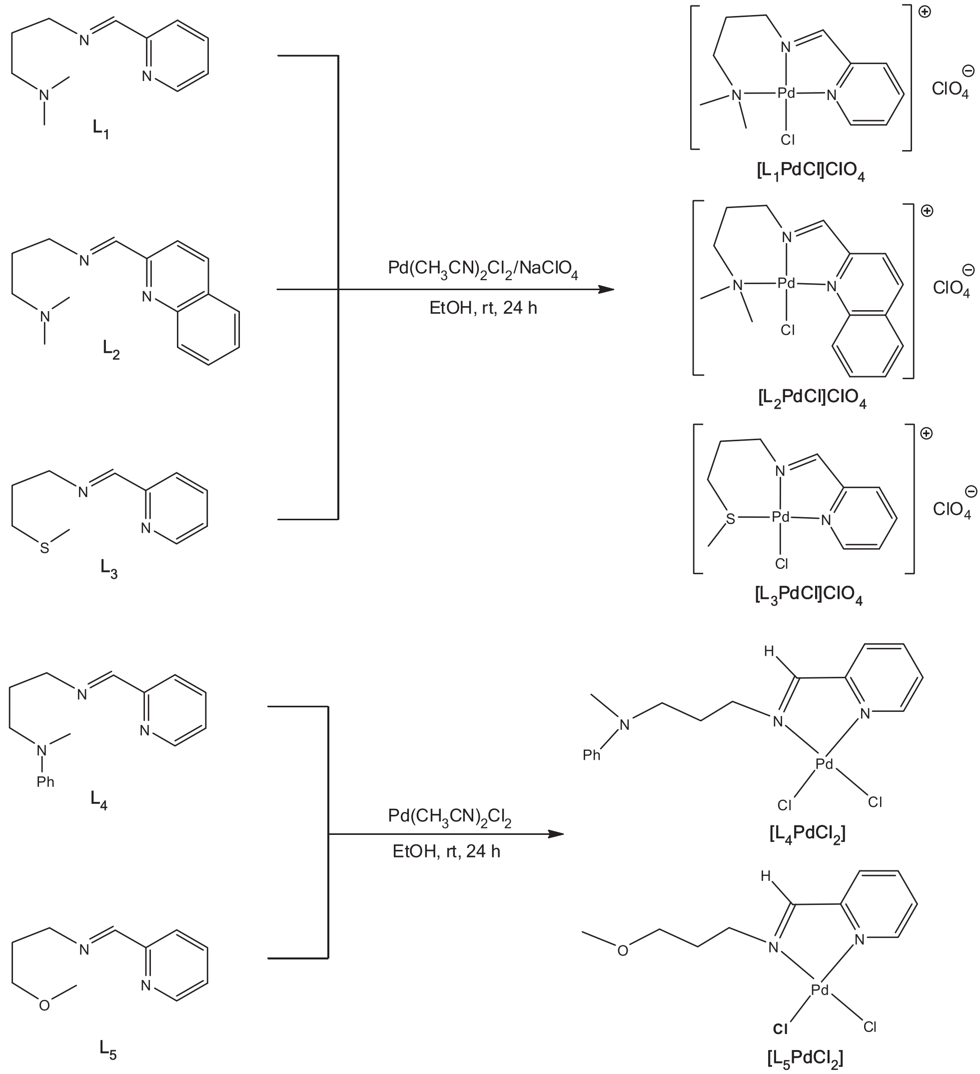
In a Schlenk line, the complex (15.0 µM: 6.50 mg for **[L_1PdCl]ClO$_4$**, 7.20 mg for **[L_2PdCl]ClO$_4$**, 6.50 mg for **[L_3PdCl]ClO$_4$**, 6.50 mg for **[L_4PdCl$_2$]**, and 5.30 mg for **[L_5PdCl$_2$]**) was dissolved in dried toluene (10.0 mL) followed by the addition of modified MMAO (6.90 wt% in toluene, 3.25 mL, and 7.50 mM, $[MMAO]_0/[Pd(II)\ catalyst]_0 = 500$) as a co-catalyst [63–65]. The solution was stirred at 60 °C for 20 min. The MMA (5.00 mL, 47.1 mM, $[MMA]_0/[Pd(II)\ catalyst]_0 = 3100$) was added to the above reaction mixture and stirred at 60 °C for 2 h to obtain a viscous solution. Methanol (2.00 mL) was added to terminate the polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL) and 35% HCl (5.00 mL) was injected to remove the remaining co-catalyst (MMAO). The resulting polymer was filtered and washed with methanol (250 mL × 2) to yield poly(methylmethacrylate) (PMMA), which was vacuum-dried at 60 °C.

3. Results and discussion

3.1. *Synthesis and chemical properties*

The syntheses of **L_1–L_5** were performed in different reaction solvents as described previously with minor modifications [12, 36, 73–75]. High purity of ligands by vacuum distillation were obtained at yields of **L_1** (85%), **L_2** (92%), **L_3** (92%), **L_4** (76%), and **L_5** (78%) from the condensation reaction between the appropriate *X*-amine (X = *N,N*-dimethylpropane-1,3-diamine, 3-(methylthio)propan-1-amine, *N*-methyl-*N*-phenylpropane-1,3-diamine, 3-methoxylamine) and 2-pyridine aldehyde or quinoline-2-carbaldehyde in dichloromethane, respectively. **L_1** has been reported previously and applied to yield *N,N′,N*-tridentate copper [22, 76], zinc [77], and platinum complexes [68]. Pd(II) complexes, **[L_1PdCl]ClO$_4$** (88%), **[L_2PdCl]ClO$_4$** (75%), and **[L_3PdCl]ClO$_4$** (98%), were obtained from **[Pd(CH$_3$CN)$_2$Cl$_2$]** with the corresponding ligands in the presence of NaClO$_4$ in anhydrous ethanol. However, **[L_4PdCl$_2$]** (79%) and **[L_5PdCl$_2$]** (84%) complexes were obtained from the corresponding ligands with **[Pd(CH$_3$CN)$_2$Cl$_2$]** in the absence of NaClO$_4$ in anhydrous ethanol (scheme 1). The *N,N′,X*-tridentate complexes **[L_nPdCl]ClO$_4$** (L_n = L_1, L_2, L_3) did not form the *N,N′,X*-bidentate complexes **[L_nPdCl$_2$]** (L_n = L_1, L_2, L_3) in the absence of NaClO$_4$. Alternatively, *N,N′,X*-bidentate complexes **[L_nPdCl$_2$]** (L_n = L_4, L_5) were decomposed in the presence of NaClO$_4$ to synthesize *N,N′,X*-tridentate complexes **[L_nPdCl]ClO$_4$** (L_n = L_4, L_5).

^{1}H NMR, ^{13}C NMR, and elemental analyses were consistent with ligand and Pd(II) complex formulation. ^{1}H NMR peaks of the *N,N′,X*-tridentate complexes **[L_nPdCl]ClO$_4$** (L_n = L_1, L_2, L_3) shifted to lower field by approximately δ 0.2–0.7 compared with corresponding ligands, while ^{13}C NMR peaks of the **[L_nPdCl]ClO$_4$** (L_n = L_1, L_2, L_3) shifted to lower field by approximately δ 3–11 compared with ligands. Similarly, ^{1}H NMR peaks of the *N,N′,X*-bidentate complexes **[L_nPdCl$_2$]** (L_n = L_4, L_5) shifted to lower field by approximately δ 0.1–0.5 compared with ligands, while ^{13}C NMR peaks of the **[L_nPdCl$_2$]** (L_n = L_4, L_5) complexes shifted to lower field by approximately δ 2–10 compared with corresponding ligands. In addition, the absorption band at 1639–1652 cm^{-1} for the imine moiety in ligands was identified as 1638–1650 cm^{-1} for both **[L_nPdCl]ClO$_4$** (L_n = L_1, L_2, L_3) and **[L_nPdCl$_2$]** (L_n = L_4, L_5).



Scheme 1. Representation of $\mathbf{[L_nPdCl]ClO_4}$ ($L_n = L_1, L_2, L_3$) and $\mathbf{[L_nPdCl_2]}$ ($L_n = L_1, L_2$).

3.2. *Description of X-ray crystal structures*

The ORTEP drawings of complexes are shown in figure 1 ($\mathbf{[L_1PdCl]ClO_4}$), figure 2 ($\mathbf{[L_2PdCl]ClO_4}$), figure 3 ($\mathbf{[L_3PdCl_2]ClO_4}$), figure 4 ($\mathbf{[L_4PdCl_2]}$) and figure 5 ($\mathbf{[L_5PdCl_2]}$). Selected bond lengths and angles are listed in table 2. A single crystal suitable for X-ray crystallography was obtained from diethyl ether solution diffusion into DMF solution for all Pd(II) complexes.

If the X is nitrogen such as $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_4}$, a bulky phenyl group on *X* (case of $\mathbf{L_4}$) may hamper *X* atom coordination to palladium; thus, $\mathbf{[L_1PdCl]ClO_4}$ and $\mathbf{[L_2PdCl]ClO_4}$ are stabilized as *N*,*N′*,*X*-tridentate complexes rather than *N*,*N′*,*X*-bidentate complexes. In contrast, $\mathbf{[L_4PdCl_2]}$ formed as *N*,*N′*,*X*-bidentate complex. Moreover, based on the crystal packing of

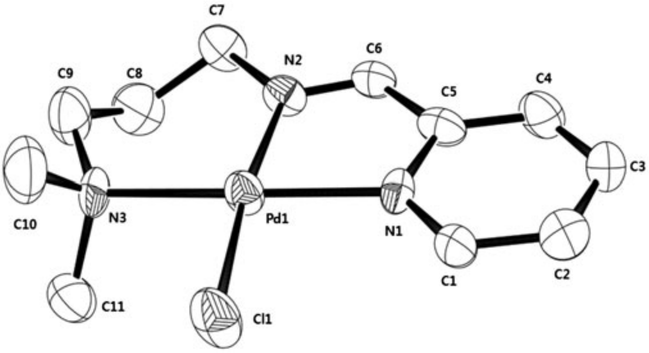


Figure 1. ORTEP drawing of **[L$_1$PdCl]ClO$_4$** with thermal ellipsoids at 50% probability. All hydrogens are omitted for clarity.

Pd(II) complexes of **L$_1$** and **L$_4$**, the phenyl group on the nitrogen in **L$_4$** induces π–π stacking interaction compared to the methyl group on nitrogen in **L$_1$** (figure 6). The benzene ring involving C13 is π–π stacked with an offset π–π interaction with the pyridine group involving N1 (axis: $2-x$, $1/2+y$, $1/2-z$). Benzene ring including C13 has a face-to-face π–π interaction with pyridine. The length of centroid–centroid was calculated as 3.695 Å and dihedral angle between benzene ring and pyridine ring was 9.039°. The pK$_a$ of dimethylamine and methylphenylamine were 10.73 and 4.85, respectively, in **L$_1$** and **L$_2$**, which contain a dimethylamine moiety as the *X* donor and act as a stronger base and better nucleophile than **L$_4$**, which has methylphenylamine as the *X* donor [78]. The soft sulfur as *X* donor in **L$_3$** is coordinated to palladium to generate *N*,*N′*,*X*-tridentate **[L$_3$PdCl]ClO$_4$**, and the oxygen as *X* donor in **L$_5$** is a hard base, which is not coordinated to soft palladium

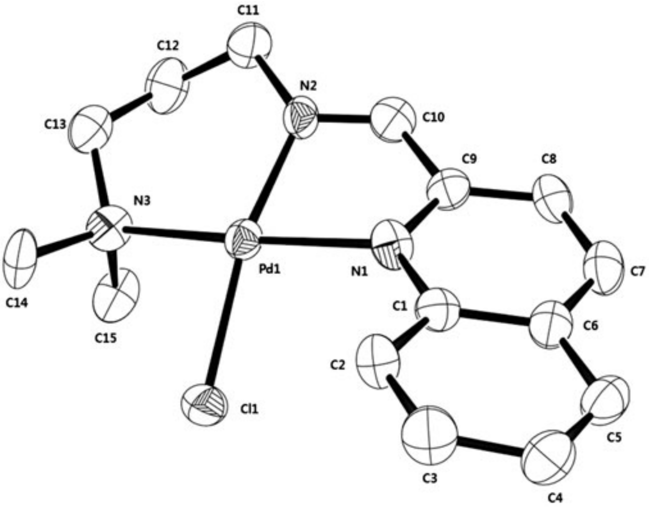


Figure 2. ORTEP drawing of **[L$_2$PdCl]ClO$_4$** with thermal ellipsoids at 50% probability. All hydrogens are omitted for clarity.

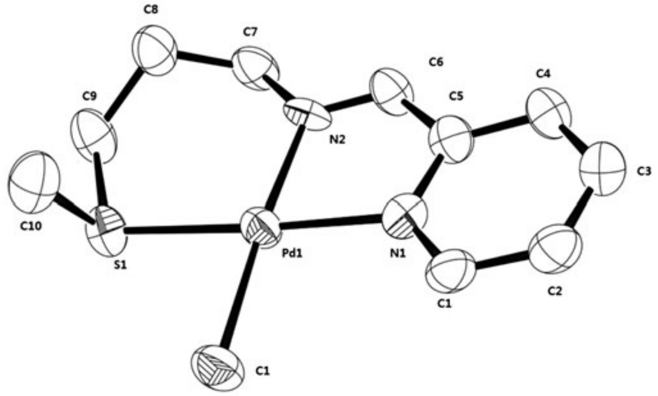


Figure 3. ORTEP drawing of **[L$_3$PdCl]ClO$_4$** with thermal ellipsoids at 50% probability. All hydrogens are omitted for clarity.

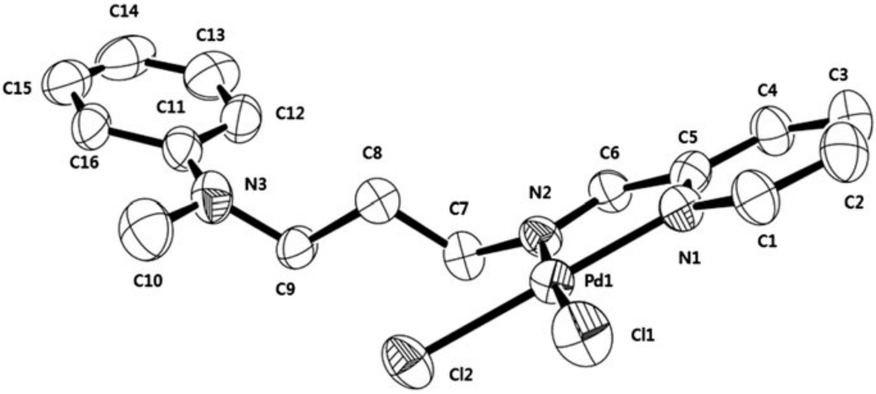


Figure 4. ORTEP drawing of **[L$_4$PdCl$_2$]** with thermal ellipsoids at 50% probability. All hydrogens are omitted for clarity.

producing stable N,*N′*,*X*-bidentate **[L$_5$PdCl$_2$]**. In addition, according to the crystal packing of **[L$_5$PdCl$_2$]**, **[L$_5$PdCl$_2$]** crystallizes in the lattice to hamper coordination of oxygen in **L$_5$** to palladium. The distance between two molecules was calculated as 2.896 Å with no room for coordination.

The bond lengths of Pd–N$_{\text{pyridine}}$ [Pd(1)–N(1)] in *N*,*N′*,*X*-tridentate **[L$_n$PdCl]ClO$_4$** (L_n = L_1, L_2, L_3) and *N*,*N′*,*X*-bidentate **[L$_n$PdCl$_2$]** (L_n = L_4, L_5) were 2.047(5)–2.092(6) Å and 2.027(5)–2.039(7) Å, respectively. Those of Pd–N$_{\text{imine}}$ [Pd(1)–N(2)] ranged from 2.019 (5) to 2.030(5) Å and 1.996(7) to 2.020(5) Å, respectively, which was similar to the Pd–N bond length of square planar imine-Pd(II) complexes. The bond length of Pd–N$_{\text{pyridine}}$ increased by approximately 0.03–0.07 Å compared to the bond length of Pd–N$_{\text{imine}}$ for *N*,*N′*,*X*-tridentate complexes **[L$_n$PdCl]ClO$_4$** (L_n = L_1, L_2, L_3), while the bond length of Pd–N$_{\text{imine}}$ and Pd–N$_{\text{imine}}$ were virtually the same for *N*,*N′*,*X*-bidentate complexes **[L$_n$PdCl$_2$]** (L_n = L_4, L_5). In general, the bond lengths of Pd–N$_{\text{pyridine}}$ were shorter than those of Pd–N$_{\text{imine}}$ due to different basicities between imine and pyridine. The Pd–Cl bond lengths

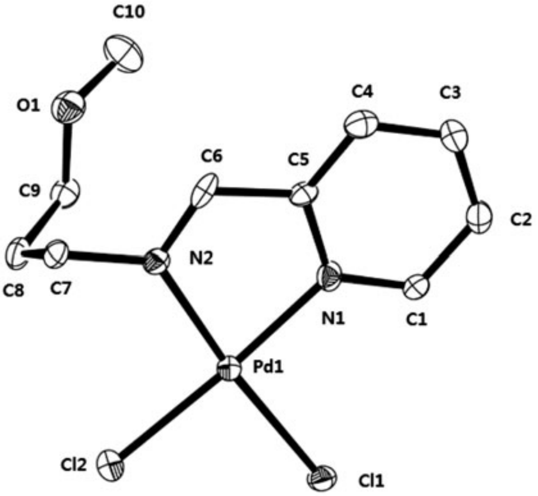


Figure 5. ORTEP drawing of $\mathbf{[L_5PdCl_2]}$ with thermal ellipsoids at 50% probability. All hydrogens are omitted for clarity.

in $\mathbf{[L_nPdCl]ClO_4}$ ($L_n = L_1, L_2, L_3$) and $\mathbf{[L_nPdCl_2]}$ ($L_n = L_4, L_5$) ranged from 2.2878(19) to 2.2948(14) Å. The bond distances of imine [N(2)–C(6) and N(2)–C(10)] were 1.271(9) Å ($\mathbf{[L_1PdCl]ClO_4}$), 1.262(10) Å ($\mathbf{[L_2PdCl]ClO_4}$), 1.247(10) Å ($\mathbf{[L_3PdCl]ClO_4}$), 1.278(10) Å ($\mathbf{[L_4PdCl_2]}$), and 1.269(9) Å ($\mathbf{[L_5PdCl_2]}$). These values were in the range of accepted carbon–nitrogen double bonds. The C(5)–C(6) bond distances of the complexes ranged from 1.440(11) to 1.467(8) Å, reflecting delocalized π-electrons in the imino-pyridine moiety. Thus, the bond lengths of synthesized Pd(II) complexes were not affected by coordination mode of *N,N′,X*-bidentate or *N,N′,X*-tridentate. The bond angles of five-membered rings N(1)–Pd(1)–N(2) in *N,N′,X*-tridentate $\mathbf{[L_nPdCl]ClO_4}$ ($L_n = L_1, L_2, L_3$) and *N,N′,X*-bidentate $\mathbf{[L_nPdCl_2]}$ ($L_n = L_4, L_5$) ranged from 79.7(3)° to 80.9(3)°, bent due to ring strain, and were not affected by the coordination mode of ligands. This trend was observed in related pyridylimine Pd(II) [40, 42, 47, 51, 79] and Pt(II) [80, 81] systems. The bond angles of six-membered rings N(2)–Pd(1)–X(1) in *N,N′,X*-tridentate $\mathbf{[L_nPdCl]ClO_4}$ ($L_n = L_1, L_2, L_3$) and *N,N′,X*-bidentate $\mathbf{[L_nPdCl_2]}$ ($L_n = L_4, L_5$) ranged from 95.6(3)° to 99.02(19)° and 94.6(2)° to 95.30(15)°, respectively, indicating that coordination mode of ligands did not relieve ring strain. *N*(2)–Pd(1)–Cl(1) angles in *N,N′,X*-tridentate $\mathbf{[L_nPdCl]ClO_4}$ ($L_n = L_1, L_2, L_3$) and *N,*

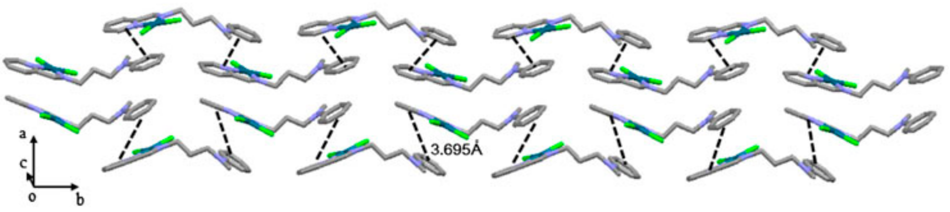


Figure 6. The view of crystal packing of $\mathbf{[L_4PdCl_2]}$. The benzene ring involving C13 is π–π stacked with an offset π–π interaction (dashed line) with the pyridine group involving N1 ($2-x$, $1/2+y$, $1/2-z$).

Table 2. Selected bond lengths (Å) and angles (°) of **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and **[L$_n$PdCl$_2$]** (L$_n$ = L$_1$, L$_2$).

[L$_1$PdCl]ClO$_4$		**[L$_2$PdCl]ClO$_4$**		**[L$_3$PdCl]ClO$_4$**		**[L$_4$PdCl$_2$]**		**[L$_5$PdCl$_2$]**	
Bond lengths									
Pd(1)-N(2)	2.019 (5)	Pd(1)-N(2)	2.020 (7)	Pd(1)-N(2)	2.030 (5)	Pd(1)-N(2)	1.996 (7)	Pd(1)-N(2)	2.020 (5)
Pd(1)-N(1)	2.047 (5)	Pd(1)-N(1)	2.092 (6)	Pd(1)-N(1)	2.076 (8)	Pd(1)-N(1)	2.039 (7)	Pd(1)-N(1)	2.027 (6)
Pd(1)-N(3)	2.080 (6)	Pd(1)-N(3)	2.093 (7)	Pd(1)-S(1)	2.282 (2)	Pd(1)-Cl(2)	2.269 (2)	Pd(1)-Cl(2)	2.282 (2)
Pd(1)-Cl(1)	2.2927 (19)	Pd(1)-Cl(1)	2.292 (2)	Pd(1)-Cl(1)	2.2878 (19)	Pd(1)-Cl(1)	2.292 (2)	Pd(1)-Cl(1)	2.2948 (14)
N(1)-C(1)	1.333 (9)	N(1)-C(9)	1.333 (10)	N(1)-C(1)	1.290 (10)	N(1)-C(1)	1.319 (11)	N(1)-C(1)	1.346 (9)
N(1)-C(5)	1.362 (8)	N(1)-C(1)	1.357 (10)	N(1)-C(5)	1.370 (10)	N(1)-C(5)	1.351 (11)	N(1)-C(5)	1.364 (8)
N(2)-C(6)	1.271 (9)	N(2)-C(10)	1.262 (10)	N(2)-C(6)	1.247 (10)	N(2)-C(6)	1.278 (10)	N(2)-C(6)	1.269 (9)
N(2)-C(7)	1.455 (9)	N(2)-C(11)	1.460 (10)	N(2)-C(7)	1.467 (9)	N(2)-C(7)	1.468 (11)	N(2)-C(7)	1.472 (7)
C(5)-C(6)	1.446 (10)	C(9)-C(10)	1.457 (11)	C(5)-C(6)	1.440 (11)	C(5)-C(6)	1.456 (11)	C(5)-C(6)	1.467 (7)
Bond angles									
N(1)-Pd(1)-N(2)	80.2 (2)	N(1)-Pd(1)-N(2)	79.7 (3)	N(1)-Pd(1)-N(2)	80.9 (3)	N(1)-Pd(1)-N(2)	80.5 (3)	N(1)-Pd(1)-N(2)	80.3 (2)
N(2)- Pd(1)-N(3)	96.5 (2)	N(2)- Pd(1)-N(3)	95.6 (3)	N(2)-Pd(1)-S(1)	99.02 (19)	N(2)-Pd(1)-Cl(2)	94.6 (2)	N(2)-Pd(1)-Cl(2)	95.30 (15)
N(1)-Pd(1)-N(3)	176.3 (3)	N(1)-Pd(1)-N(3)	174.5 (3)	N(1)-Pd(1)-S(1)	175.09 (19)	N(1)-Pd(1)-Cl(2)	174.87 (19)	N(1)-Pd(1)-Cl(2)	175.10 (17)
N(2)-Pd(1)-Cl(1)	172.54 (18)	N(2)-Pd(1)-Cl(1)	166.0 (2)	N(2)-Pd(1)-Cl(1)	175.25 (19)	N(2)-Pd(1)-Cl(1)	174.8 (2)	N(2)-Pd(1)-Cl(1)	174.45 (14)
N(1)-Pd(1)-Cl(1)	92.35 (17)	N(1)-Pd(1)-Cl(1)	94.36 (19)	N(1)-Pd(1)-Cl(1)	94.46 (19)	N(1)-Pd(1)-Cl(1)	94.4 (2)	N(1)-Pd(1)-Cl(1)	94.18 (17)
N(3)-Pd(1)-Cl(1)	90.91 (19)	N(3)-Pd(1)-Cl(1)	89.6 (2)	S(1)-Pd(1)-Cl(1)	85.71 (8)	Cl(1)-Pd(1)-Cl(2)	90.42 (9)	Cl(1)-Pd(1)-Cl(2)	90.17 (6)
C(1)-N(1)-C(5)	119.3 (6)	C(9)-N(1)-C(1)	120.2 (7)	C(1)-N(1)-C(5)	121.4 (7)	C(1)-N(1)-C(5)	119.3 (8)	C(1)-N(1)-C(5)	118.3 (6)
C(1)-N(1)-Pd(1)	127.6 (5)	C(9)-N(1)-Pd(1)	108.7 (5)	C(1)-N(1)-Pd(1)	128.1 (6)	C(1)-N(1)-Pd(1)	128.0 (6)	C(1)-N(1)-Pd(1)	127.5 (5)
C(6)-N(2)-C(7)	119.9 (6)	C(10)-N(2)-C(11)	120.7 (7)	C(6)-N(2)-C(7)	120.8 (6)	C(6)-N(2)-C(7)	119.0 (7)	C(6)-N(2)-C(7)	118.7 (5)
C(6)-N(2)-Pd(1)	113.7 (5)	C(10)-N(2)-Pd(1)	111.3 (6)	C(6)-N(2)-Pd(1)	112.8 (5)	C(6)-N(2)-Pd(1)	115.0 (6)	C(6)-N(2)-Pd(1)	113.7 (4)

N′,X-bidentate **[L$_n$PdCl$_2$]** (L$_n$ = L$_4$, L$_5$) ranged from 166.0(2)° to 174.85(2)°, showing that the coordination geometry around the Pd(II) center of all complexes could be described as a slightly distorted square plane.

3.3. *MMA polymerization*

N,N′,X-tridentate **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and *N,N′,X*-bidentate **[L$_n$PdCl$_2$]** (L$_n$ = L$_4$, L$_5$) were activated by co-catalyst MMAO to polymerize MMA [53, 54, 57], yielding PMMA with T_gs ranging from 123° to 130 °C [56]. Since *N,N′,X*-tridentate **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) complexes are cationic complexes, they were also used for MMA polymerization without activation by the MMAO and traceable amounts of PMMA were obtained. To confirm catalytic activity of the Pd(II) complexes in MMA polymerization, blank polymerization of MMA was performed with anhydrous **[$PdCl_2$]** and MMAO, respectively, at 60 °C. The polymerization yield by MMAO alone is very low (1.40×10^4 g PMMA M^{-1} MMAO h). MMAO acts as co-catalyst probably to produce complex cation as an active species and scavenger. We used 500 times of MMAO with respect to the amount of catalyst. Due to poor solubility of Pd(II) complexes, we used an excess of MMAO. We have conducted the MMA polymerization on reducing MMAO to 250 times during MMA polymerization; however, the yield of PMMA was much lower than in case of using 500 times of MMAO. On the other hand, the reference complex **[$PdCl_2$]** (1.97×10^4 g PMMA M^{-1} MMAO h) was activated by MMAO and applied to the MMA polymerization to give PMMA as low as co-catalyst MMAO. Poly(methylmethacrylate) (PMMA) was isolated as white solids and their molecular weight (M_w) and molecular weight distribution (M_n) were characterized by GPC in THF using standard polystyrene as the reference. The microstructure of PMMA was syndiotactic (rr, δ 0.85), heterotactic (mr, δ 1.02), and isotactic (mm, δ 1.21) as determined using ^{1}H NMR spectroscopy [82, 83]. The resulting polymer data are summarized in table 3.

Since increased optical quality of PMMA represents a higher T_g up to 140 °C, which resulted from the increased syndiotacticity of PMMA, non-radical-mediated polymerization of MMA using complex catalysts achieves a high T_g for processing or high content of syndiotactic PMMA [53, 56, 62–65]. On the other hand, isotactic PMMA, which is commercially produced using conventional radical processes, has a T_g around 65 °C.

We previously reported that *N,N′*-bidentate Pd(II) complex with *N*-cyclopentyl substituted 2-iminomethylpyridines (1.45×10^5 g PMMA M^{-1} Pd h), *N*-cyclopentyl substituted 2-iminomethylquinoline (1.41×10^5 g PMMA M^{-1} Pd h) [66], *N,N′,N*-tridentate Pd(II) complex

Table 3. Polymerization of MMA by **[$L_nPdCl]ClO_4$** ($L_n = L_1, L_2, L_3$) and **[L_nPdCl_2]** ($L_n = L_1, L_2$).

Entry	Catalyst[a]	Temp. (time) °C (h)	Yield[b] (%)	Activity[c] (g M^{-1}cat h) × 10^4	T_g[d] (°C)	Tacticity % mm	% mr	%rr	M_w[e] (g M^{-1}) × 10^5	M_w/M_n[f]
1	**[$PdCl_2$]**[g]	60(2 h)	13	1.97	129	10.2	23.5	66.3	7.52	1.63
2	MMAO[h]	60(2 h)	9	1.40	120	37.2	10.9	51.9	0.61	2.20
3	**[$L_1PdCl]ClO_4$**	60(2 h)	23	3.63	123	7.30	24.8	67.9	8.71	2.13
3	**[$L_2PdCl]ClO_4$**	60(2 h)	92	14.3	130	6.90	26.1	67.0	6.38	2.31
4	**[$L_2PdCl]ClO_4$**	25(2 h)	21	3.30	126	7.50	22.3	70.2	9.71	1.84
4	**[$L_3PdCl]ClO_4$**	60(2 h)	21	3.33	130	7.40	23.7	68.9	9.71	1.84
6	**[L_4PdCl_2]**	60(2 h)	21	3.40	126	7.80	21.3	70.9	9.43	1.83
7	**[L_5PdCl_2]**	60(2 h)	69	10.8	128	7.60	23.3	69.1	9.63	2.12
7	**[L_5PdCl_2]**	25(2 h)	8	1.27	128	10.1	26.8	63.1	9.48	1.88

[a] [Pd(II) catalyst]$_0$ = 15 µM, [MMA]$_0$/[MMAO]$_0$/[Pd(II) catalyst]$_0$ = 3100 : 500 : 1.
[b] Yield defined a mass of dried polymer recovered/a mass of monomer used.
[c] Activity is (g PMMA)/(M Pd·h).
[d] T_g is glass transition temperature determined using a thermal analyzer.
[e] Determined using gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.
[f] M_n refers to the number average of molecular weights of PMMA.
[g] It is a blank polymerization in which anhydrous **[$PdCl_2$]** was also activated by MMAO.
[h] It is a blank polymerization which was done solely by MMAO.

with *N,N*-di(2-picolyl)cyclohexylmethylamine (0.480×10^5 g PMMA M^{-1} Pd h) [67]. *N,N′,X*-tridentate **[L_2PdCl]ClO_4** (1.43×10^5 g PMMA M^{-1} Pd h), and *N,N′,X*-bidentate **[L_5PdCl_2]** (1.08×10^5 g M^{-1} Pd h) showed higher or comparable catalytic activities for other Pd(II) complexes and produced syndiotactic PMMA of a narrower polydispersity (PDI) at 60 °C. The PDIs of the Pd(II) complexes ranged from 1.83 to 2.31. In general, the PDI range narrowed with increasing molecular weights of PMMA [84, 85]. For comparison, bis(β-ketoamino)nickel(II) complexes were reported to have the highest activity of 4.20×10^4 g PMMA M^{-1} Ni h with no detection of syndiotacticity and low conversion rates [53]. The Co(II) complex with phenoxy-imine was also used as a catalyst for MMA polymerization with moderate activity and syndiotacticity of 78% [54]. In contrast, *N,N′,X*-tridentate **[L_2PdCl]ClO_4** and *N,N′,X*-bidentate **[L_5PdCl_2]** showed 92 and 69% conversion of MMA to PMMA for polymerization, respectively.

Obviously, catalytic activity was affected by substituents on the imine moiety, the coordination mode of ligands (hapticity), and polymerization temperature as determined by the relative amounts of PMMA yielded. The activity of MMA polymerization by Pd(II) complexes should be considered a function of the electron density and steric hindrance around palladium [86–88]. *N,N′,X*-tridentate **[L_2PdCl]ClO_4**, which has a quinoline on the imine moiety showed four times higher activity compared to the *N,N′,X*-tridentate **[L_1PdCl]ClO_4**, which has a pyridine on the imine moiety. Presumably, the electron-rich cloud around palladium in *N,N′,X*-tridentate **[L_1PdCl]ClO_4** and *N,N′,X*-tridentate **[L_2PdCl]ClO_4** would not be much different, the only difference is a little more steric inducement by quinoline moiety around the palladium center in *N,N′,X*-tridentate **[L_2PdCl]ClO_4**. On the other hand, the electronic effect around palladium during MMA polymerization may explain low activity of *N,N′,X*-tridentate **[L_1PdCl]ClO_4** and *N,N′,X*-tridentate **[L_3PdCl]ClO_4**, which has sulfur as the third donor, compared to having same binding mode in *N,N′,X*-tridentate **[L_2PdCl]ClO_4**. Alternatively, *N,N′,X*-bidentate **[L_5PdCl_2]** has a pyridine and the third donor oxygen on the imine moiety; but, however, different coordination modes from *N,N′,X*-tridentate **[L_1PdCl]ClO_4** showed comparable high activity to **[L_2PdCl]ClO_4**. Presumably, the electron-rich cloud around the palladium metal in *N,N′,X*-bidentate **[L_5PdCl_2]** increased the activity compared to the electronic effect of the remaining Pd(II) complexes. Comparing the activities by *N,N′,X*-bidentate **[L_4PdCl_2]** (0.127×10^5 g M^{-1} Pd h) and *N,N′,X*-bidentate **[L_5PdCl_2]** (1.08×10^5 g M^{-1} Pd h), both of which have the same hapticity, there is more steric bulkiness induced around palladium metal in *N,N′,X*-bidentate **[L_4PdCl_2]** than *N,N′,X*-bidentate **[L_5PdCl_2]**, judging from the crystal packing diagram. Moreover, *N,N′,X*-tridentate **[L_2PdCl]ClO_4** (0.330×10^5 g PMMA M^{-1} Pd h), more crowded around palladium metal and *N,N′,X*-bidentate **[L_5PdCl_2]** (0.127×10^5 g PMMA M^{-1} Pd h) and less crowded than *N,N′,X*-tridentate **[L_2PdCl]ClO_4**, has shown poor activity in MMA polymerization at 25 °C, indicating that the steric effect, resulting from the coordination mode of ligands (hapticity), along with electronic effect is important during MMA polymerization. Note that low activity of MMA polymerization at 25 °C also resulted from poor solubility of Pd(II) complexes. Thus, the activity of these Pd(II) complexes toward MMA polymerization is influenced by electronic effect, steric effect, and coordination mode of ligands, which may induce steric hindrance and electronic differences on the palladium. 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. To increase the syndiotacticity with sacrificing activity, MMA polymerization was performed at 25 and 0 °C using two highly active complexes: **[L_2PdCl]ClO_4** and **[L_5PdCl_2]**. However, the obtained moderate syndiotacticity was not affected by the polymerization temperature and was similar to that of **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and **[L$_n$PdCl$_2$]** (L$_n$ = L$_4$, L$_5$) at 60 °C. Although the moderate syndiotacticity of Pd(II) complexes around *ca.* Seventy percent was not sufficient to confer a mechanism of coordination polymerization, the experiment using five equivalents of radical inhibitor TEMPO (2,2,6,6-tetramethylpiperidinyloxy) during MMA polymerization does not much reduce the yield of PMMA (*ca.* 5% yield), supporting the mechanism of coordination polymerization is not a radical mechanism [54].

4. Conclusion

We investigated the synthesis and X-ray crystallographic structures of *N,N′,X*-tridentate **[L$_n$PdCl]ClO$_4$** (L$_n$ = L$_1$, L$_2$, L$_3$) and *N,N′,X*-bidentate **[L$_n$PdCl$_2$]** (L$_n$ = L$_4$, L$_5$), which were prepared through substitution of **[Pd(CH$_3$CN)$_2$Cl$_2$]** with the corresponding potential *N,N′*,*X*-tridentate or *N,N′,X*-bidentate (*X* = *N*, *O*, *S*) iminopyridine ligands **L$_n$** (L$_n$ = L$_1$ – L$_5$) with or without NaClO$_4$. The coordination geometry around palladium in all Pd(II) complexes were slightly distorted square planar. The catalytic activity of *N,N′,X*-tridentate **[L$_2$PdCl] ClO$_4$** and *N,N′,X*-bidentate **[L$_5$PdCl$_2$]** toward MMA polymerization in the presence of the co-catalyst MMAO was highest at 1.43×10^5 g PMMA M^{-1} Pd h and 1.08×10^5 g PMMA M^{-1} Pd h at 60 °C, respectively, showing moderate syndiotacticity of about 70%. The catalytic activity in MMA polymerization depends on steric and electronic effects of *X* substituents on the imine moiety, the coordination mode of ligands, and polymerization temperatures.

Supplementary material

CCDC 992007–992011 contain the supplementary crystallographic data for **[L$_1$PdCl]ClO$_4$**, **[L$_2$PdCl]ClO$_4$**, **[L$_3$PdCl]ClO$_4$**, **[L$_4$PdCl$_2$]**, and **[L$_5$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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

Funding

This research was supported by the National Research Foundation of Korea (NRF), funded by the Ministry of the Education, Science, and Technology (MEST) [grant number 2012-R1A2A2A01045730].

References

[1] Z.-F. Chen, Y.-Z. Tang, H. Liang, H.-K. Fun, K.-B. Yu. *J. Coord. Chem.*, **59**, 207 (2006).

[2] P. Govindaswamy, Y.A. Mozharivskyj, M. Rao Kollipara. *Polyhedron*, **24**, 1710 (2005).

[3] W. Wang, B. Spingler, R. Alberto. *Inorg. Chim. Acta*, **355**, 386 (2003).

[4] W. Massa, S. Dehghanpour, K. Jahani. *Inorg. Chim. Acta*, **362**, 2872 (2009).

[5] M. Schulz, M. Klopfleisch, H. Gorls, M. Kahnes, M. Westerhausen. *Inorg. Chim. Acta*, **362**, 4706 (2009).

[6] S. Shakhatreh, J. Mohanraj, A. Czapik, D. Tzimopoulos, S. Kotoulas, M. Gdaniec, P.D. Akrivos. *J. Mol. Struct.*, **1002**, 51 (2011).

[7] C.M. Alvarez, R. García-Rodríguez, D. Miguel. *J. Organomet. Chem.*, **692**, 5717 (2007).

[8] L. Gonsalvi, J.A. Gaunt, H. Adams, A. Castro, G.J. Sunley, A. Haynes. *Organometallics*, **22**, 1047 (2003).

[9] B.P. Buffin, P.J. Squattrito, A.O. Ojewole. *Inorg. Chem. Commun.*, **7**, 14 (2004).

[10] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).

[11] S.K. Kang, S.J. Yong, Y.-K. Song, Y.-I. Kim. *Bull. Korean Chem. Soc.*, **34**, 3615 (2013).

[12] S. Dalai, P.S. Mukherjee, M.G.B. Drew, T.-H. Lu, N.R. Chaudhuri. *Inorg. Chim. Acta*, **335**, 85 (2002).

[13] S.S. Chavan, S.K. Sawant, V.A. Sawant, G.K. Lahiri. *Inorg. Chim. Acta*, **363**, 3359 (2010).

[14] D.A. Kanas, S.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott. *Inorg. Chem.*, **47**, 8727 (2008).

[15] C.-J. Qiu, Y.-C. Zhang, Y. Gao, J.-Q. Zhao. *J. Organomet. Chem.*, **694**, 3418 (2009).

[16] K. Nienkemper, V.V. Kotov, G. Kehr, G. Erker, R. Fröhlich. *Eur. J. Inorg. Chem.*, 366 (2006).

[17] R. Kannappan, M. Matsumoto, J. Hallren, K.M. Nicholas. *J. Mol. Catal. A-Chem.*, **339**, 72 (2011).

[18] G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli. *Inorg. Chim. Acta*, **362**, 3507 (2009).

[19] P. Datta, S.K. Sarkar, T.K. Mondal, A.K. Patra, C. Sinha. *J. Organomet. Chem.*, **694**, 4124 (2009).

[20] S. Roy, T.K. Mondal, P. Mitra, E.L. Torres, C. Sinha. *Polyhedron*, **30**, 913 (2011).

[21] J. Schnödt, J. Manzur, A.-M. García, I. Hartenbach, C.-Yong Su, J. Fiedler, W. Kaim, *Eur. J. Inorg. Chem.*, 1436 (2011).

[22] P.S. Mukherjee, S. Dalai, G. Mostafa, T.-H. Lu, E. Rentschler, N.R. Chaudhuri. *New J. Chem.*, **25**, 1203 (2001).

[23] J.J. Braymer, J.-S. Choi, A.S. DeToma, C. Wang, K. Nam, J.W. Kampf, A. Ramamoorthy, M.H. Lim. *Inorg. Chem.*, **50**, 10724 (2011).

[24] C.M. Álvarez, R. García-Rodríguez, D. Miguel. *Inorg. Chem.*, **51**, 2984 (2012).

[25] M. Kettunen, C. Vedder, H.-H. Brintzinger, I. Mutikainen, M. Leskelä, T. Repo. *Eur. J. Inorg. Chem.*, 1081 (2005).

[26] S.D. Ittel, L.K. Johnson, M. Brookhart. *Chem. Rev.*, **100**, 1169 (2000).

[27] C. Vedder, F. Schaper, H.-H. Brintzinger, M. Kettunen, S. Babik, G. Fink. *Eur. J. Inorg. Chem.*, 1071 (2005).

[28] K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams. *Organometallics*, **24**, 280 (2005).

[29] V.C. Gibson, R.K. O'Reilly, D.F. Wass, A.J.P. White, D.J. Williams. *Dalton Trans.*, 2824 (2003).

[30] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Laschi. *Organometallics*, **22**, 2545 (2003).

[31] G.J.P. Britovsek, S.P.D. Baugh, O. Hoarau, V.C. Gibson, S.K. Spitzmesser, D.F. Wass, A.J.P. White, D.J. Williams. *Inorg. Chim. Acta*, **345**, 279 (2003).

[32] S. Song, W. Zhao, L. Wang, C. Redshaw, F. Wang, W.-H. Sun. *J. Organomet. Chem.*, **696**, 3029 (2011).

[33] S. Song, Y. Li, C. Redshaw, F. Wang, W.-H. Sun. *J. Organomet. Chem.*, **696**, 3772 (2011).

[34] S. Song, T. Xiao, L. Wang, C. Redshaw, F. Wang, W.-H. Sun. *J. Organomet. Chem.*, **699**, 18 (2012).

[35] T. Xiao, J. Lai, S. Zhang, X. Hao, W.-H. Sun. *Catal. Sci. Technol.*, **1**, 462 (2011).

[36] S.A. Turner, Z.D. Remillard, D.T. Gijima, E. Gao, R.D. Pike, C. Goh. *Inorg. Chem.*, **51**, 10762 (2012).

[37] S. Perrier, D. Berthier, I. Willoughby, D. Batt-Coutrot, D.M. Haddleton. *Macromolecules*, **35**, 2941 (2002).

[38] J. Kuwabara, D. Takeuchi, K. Osakada. *Polyhedron*, **28**, 2459 (2009).

[39] A. Bacchi, M. Carcelli, C. Pelizzi, G. Pelizzi, P. Pelagatti, S. Ugolotti. *Eur. J. Inorg. Chem.*, 2179 (2002).

[40] W.M. Motswainyana, S.O. Ojwach, M.O. Onani, E.I. Iwuoha, J. Darkwa. *Polyhedron*, **30**, 2574 (2011).

[41] Z. Zhu, M. Kojima, K. Nakajima. *Inorg. Chim. Acta*, **358**, 476 (2005).

[42] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela. *J. Organomet. Chem.*, **606**, 112 (2000).

[43] N. Andrade-Lopez, T.A. Hanna, J.G. Alvarado-Rodriguez, A. Luqueno-Reyes, B.A. Martinez-Ortega, D. Mendoza-Espinosa. *Polyhedron*, **29**, 2304 (2010).

[44] T. Birkle, A. Carbayo, J.V. Cuevas, G. García-Herbosa, A. Muñoz. *Eur. J. Inorg. Chem.*, 2259 (2012).

[45] T. Irrgang, S. Keller, H. Maisel, W. Kretschmer, R. Kempe. *Eur. J. Inorg. Chem.*, 4221 (2007).

[46] G.R. Owen, H.A. Burkill, R. Vilar, A.J.P. White, D.J. Williams. *J. Organomet. Chem.*, **690**, 5113 (2005).

[47] 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**, 2169 (2004).

[48] B.P. Buffin, E.B. Fonger, A. Kundu. *Inorg. Chim. Acta*, **355**, 340 (2003).

[49] J. Yorke, C. Dent, A. Decken, A. Xia. *Inorg. Chem. Commun.*, **13**, 54 (2010).

[50] P. Pratihar, S. Jha, T.K. Mondal, G. Mostafa, C. Sinha. *Polyhedron*, **26**, 4328 (2007).

[51] A.S. Roy, P. Saha, P. Mitra, S.S. Maity, S. Ghosh, P. Ghosh. *Dalton Trans.*, 7375 (2011).

[52] S. Mori, M. Nambo, L.-Ch. Chi, J. Bouffard, K. Itami. *Org. Lett.*, **10**, 4609 (2008).

[53] X. He, Y. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang, Q. Wu. *Organometallics*, **22**, 4952 (2003).

[54] B.K. Bahuleyan, D. Chandran, C.H. Kwak, C.-S. Ha, I. Kim. *Macromol. Res.*, **18**, 745 (2008).

[55] B. Lian, C.M. Thomas, O.L. Casagrande Jr., C.W. Lehmann, T. Roisnel, J.-F. Carpentier. *Inorg. Chem.*, **46**, 328 (2007).

[56] J. Li, H. Song, C. Cui. *Appl. Organomet. Chem.*, **24**, 82 (2010).

[57] W. Wang, P.A. Stenson, A. Marin-Becerra, J. McMaster, M. Schroder, D.J. Irvine, D. Freeman, S.M. Howdle. *Macromolecules*, **37**, 6667 (2004).

[58] Z. Zhang, D. Cui, A.A. Trifonov. *Eur. J. Inorg. Chem.*, 2861 (2010).

[59] C. Lansalot-Matras, F. Bonnette, E. Mignard, O. Lavastre. *J. Organomet. Chem.*, **693**, 393 (2008).

[60] E. Kim, H.Y. Woo, S. Kim, H. Lee, D. Kim, H. Lee. *Polyhedron*, **42**, 135 (2012).
[61] M. Yang, W.J. Park, K.B. Yoon, J.H. Jeong, H. Lee. *Inorg. Chem. Commun.*, **14**, 189 (2011).
[62] Y.-J. Hu, H.H. Zou, M.-H. Zeng, N.S. Weng. *J. Organomet. Chem.*, **694**, 366 (2009).
[63] C. Carlini, M. Martinelli, E. Passaglia, A.M.R. Galletti, G. Sbrana. *Macromol. Rapid Commun.*, **22**, 664 (2001).
[64] G. Tang, G.-X. Jin. *Dalton Trans.*, 3840 (2007).
[65] Y.-B. Huang, G.-R. Tang, G.-Y. Jin, G.-X. Jin. *Organometallics*, **27**, 259 (2008).
[66] S. Kim, E. Kim, H.-J. Lee, H. Lee. *Polyhedron*, **69**, 149 (2014).
[67] D. Kim, S. Kim, E. Kim, H.-J. Lee, H. Lee. *Polyhedron*, **63**, 139 (2013).
[68] J.G. Hinman, C.R. Baar, M.C. Jennings, R.J. Puddephatt. *Organometallics*, **19**, 563 (2000).
[69] R.A. Walton. *Can. J. Chem.*, **46**, 2347 (1968).
[70] *SMART and SAINT-Plus (v 6.22)*, Bruker AXS Inc., Madison, WI (2000).
[71] G.M. Sheldrick. *SADABS (v 2.03)*, University of Göttingen, Germany (2002).
[72] *SHELXTL (v 6.10)*, Bruker AXS Inc., Madison, WI (2000).
[73] B. de Klerk-Engels, H.-W. Friibauf, K. Vrieze, H. Kooijman, A.L. Spek. *Inorg. Chem.*, **32**, 5528 (1993).
[74] P. Bamfield, R. Price, R.G.J. Miller. *J. Chem. Soc. A*, 1447 (1969).
[75] G. Zakrzewski, L. Sacconi. *Inorg. Chem.*, **7**, 1034 (1968).
[76] Y.-X. Sun. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **36**, 621 (2006).
[77] S. Kasselouri, A. Garoufis, S.P. Perlepes, F. Lutz, R. Bau, S. Gourbatsis, N. Hadjiliadis. *Polyhedron*, **17**, 1281 (1998).
[78] D.R. Lide. *Handbook of Chemistry and Physics*, 89th Edn, CRC Press, Cleveland, OH, Sections 8-42, 8-47 (2014).
[79] W.M. Motswainyana, M.O. Onania, A.M. Madiehe. *Acta Cryst.*, **E68**, m380 (2012).
[80] S. Reinhardt, K. Heinze. *Z. Anorg. Allg. Chem.*, **632**, 1465 (2006).
[81] 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**, 63 (2005).
[82] T. Kitaura, T. Kitayama. *Macromol. Rapid Commun.*, **28**, 1889 (2007).
[83] I.A. Opeida, M.A. Kompanets, O.V. Kushch, E.S. Papayanina. *Theor. Exp. Chem.*, **47**, 30 (2011).
[84] J. Llorens, E. Rudé, R.M. Marcos. *Polymer*, **44**, 1741 (2003).
[85] G.T. Lewis, V. Nguyen, Y. Cohen. *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 5748 (2007).
[86] M. Schmid, R. Eberhardt, M. Klinga, M. Leskelä, B. Rieger. *Organometallics*, **20**, 2321 (2001).
[87] C. Popeney, Z. Guan. *Organometallics*, **24**, 1145 (2005).
[88] C.S. Popeney, C.M. Levins, Z. Guan. *Organometallics*, **30**, 2432 (2011).