Polyhedron 69 (2014) 149–155

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Palladium(II) complexes containing N,N′-bidentate N-cycloalkyl 2-iminomethylpyridine and 2-iminomethylquinoline: Synthesis, characterisation and methyl methacrylate polymerisation

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

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

ARTICLE INFO

Article history:
Received 4 November 2013
Accepted 18 November 2013
Available online 5 December 2013

Keywords:
Schiff base
Pyridyl-imines
Palladium(II) complex
MMA polymerization

ABSTRACT

The reaction of $[Pd(CH_3CN)_2Cl_2]$ with N-cyclopentyl-1-(pyridin-2-yl)methanimine (**L_1**), N-cyclohexyl-1-(pyridin-2-yl)methanimine (**L_2**), N-(piperidin-1-yl)-1-(pyridin-2-yl)methanimine (**L_3**) or N-cyclopentyl-1-(quinolin-2-yl)methanimine (**L_4**) in ethanol yields the bidentate (*NN*′) $PdCl_2$ complexes **$[L_1PdCl_2]$**, **$[L_2PdCl_2]$**, **$[L_3PdCl_2]$** and **$[L_4PdCl_2]$**, respectively. The X-ray crystal structure of the Pd(II) complexes revealed that the Pd atom in **$[L_nPdCl_2]$** (L_n = L_1, L_2, L_3, L_4) shows a distorted square planar geometry involving two nitrogen atoms and two chloro ligands. The complexes **$[L_1PdCl_2]$** and **$[L_4PdCl_2]$** (of which the ligands are N-cyclopentyl substituted) showed the highest catalytic activity for the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) with an activity of 1.45×10^5 g PMMA/mol Pd h at 60 °C and a PMMA syndiotacticity (characterized using ^{13}C NMR spectroscopy) of *ca.* 0.70.

1. Introduction

Transition metal complexes containing ligands with an imine moiety are common, including Schiff bases such as α- and β-diimines [1–8], 2,6-bis(imino)pyridines [9–16], pyridyl-imines and N-substituted 2-iminoalkylpyridines [17–43]. In addition, these transition metal complexes have been used in the areas of synthesis and spectroscopy [17,18,20–23,27,28,30,35], photoluminescence and photochemistry [1], as catalysts for organic transformations [5,16,24,25,36,37,43], electrochemistry [29,32,41], bioinorganic chemistry [19,26], supramolecular chemistry [33,38], molecular magnetism [34,39], microbial activity [42] and olefin polymerisation [2–4,6–15,31,40]. Especially, transition metal complexes with α-diimine ligands have attracted considerable attention because of their catalytic activity, as demonstrated by Brookhart et al. who reported that diimine complexes of Ni(II) and Pd(II) act as catalysts for the polymerisation or oligomerisation of olefins [6–8]. Specifically, the highly active complexes with tridentate 2,6-bis(imino)pyridines, initially discovered independently by the groups of Brookhart [9–11] and Gibson [13–15], play important roles in cobalt and iron systems. Several structural variations in the diimines have been reported, and their steric and electronic properties vary because of the polydentate characteristics of these ligands. These variations include the presence of abundant pyridyl-imines and analogues, such as iminoquinoline [44–50], in the transition metal complexes. Structural variations are observed in group 10 (Ni, Pd, Pt) pyridyl-imines; for example, Ni complexes exist as dimers or two ligand units coordinated to Ni, achieving a 5-coordinated trigonal–bipyramidal structure [43,51–55]. In contrast, Pd and Pt complexes with pyridyl-imines appear as monomeric square-planar structures [52–54,56–75]. Despite previous reports on transition metal complexes with pyridyl-imine derivatives, little is known regarding palladium complexes with bidentate N-substituted 2-iminoalkylpyridines ligands as catalysts for methyl methacrylate (MMA) polymerisation [76]. Thus, we report the synthesis of bidentate N-cycloalkyl substituted 2-iminomethylpyridine and 2-iminomethylquinoline ligands, N-cyclopentyl-1-(pyridin-2-yl)methanimine (**L_1**), N-cyclohexyl-1-(pyridin-2-yl)methanimine (**L_2**), N-(piperidin-1-yl)-1-(pyridin-2-yl)methanimine (**L_3**) and N-cyclopentyl-1-(quinolin-2-yl)methanimine (**L_4**), and their Pd(II) complexes, as well as their X-ray crystal structures. Moreover, the catalytic activity of the Pd(II) complexes for MMA polymerisation in toluene was investigated at 0–60 °C.

2. Experimental

2.1. Physical measurements

$PdCl_2$, 2-picolylcarbaldehyde, quinoline-2-carbaldehyde, cyclopentylamine, cyclohexylamine, 1-aminopiperidine, magnesium

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

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.11.036

sulfate and methyl methacrylate (MMA) were purchased from Aldrich, and anhydrous solvents, such as C_2H_5OH, DMF, diethyl ether and dichloromethane, were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from the Tosoh Finechem Corporation as 6.9% weight aluminum, toluene solution and used without further purification. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^{1}H NMR (400 MHz) and ^{13}C NMR (400 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer; chemical shifts were recorded in ppm units (δ) relative to $SiMe_4$ as the internal standard. Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) spectrophotometer and the data are reported in reciprocal centimeters. The molecular weight and molecular weight distribution of the obtained polymethylmethacrylate (PMMA) were measured using gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). The glass transition temperature (T_g) was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

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

2.2.1. N-cyclopentyl-1-(pyridin-2-yl)methanimine (**L$_1$**)

Although **L$_1$** and **L$_2$** [21] have been synthesized previously, here we report a similar procedure as described in the literature with complementary spectroscopic data [40,77–79]. Cyclopentylamine (1.70 g, 0.020 mol) in dichloromethane (20.0 mL) was added to 2-picolylcarbaldehyde (2.14 g, 0.020 mol) in dichloromethane (20.0 mL). After 24 h of stirring at room temperature, water was removed from the reaction solution. The dichloromethane solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was vacuum distilled and dried to give a brown oil (3.41 g, 98.0%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.61 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 8.31 (s, 1H, –N=C**H**–NC$_5$H$_4$–), 7.92 (d, 1H, J = 8.6 Hz, –NC$_5$**H**$_4$–), 7.79 (t, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.38 (t, 1H, J = 7.4 Hz, –NC$_5$**H**$_4$–), 3.81 (m, 1H, ipso-C$_5$**H**$_9$–), 3.81 (m, 4H, –C$_5$**H**$_9$–), 1.59 (m, 4H, –C$_5$**H**$_9$–). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 159.73 (s, 1C, ipso-N**C**$_5$H$_4$-), 154.89 (s, 1C, –N=**C**H–NC$_5$H$_4$–), 149.55 (s, 1C, –N**C**$_5$H$_4$–), 136.59 (s, 1C, –N**C**$_5$H$_4$–), 125.08 (s, 1C, –N**C**$_5$H$_4$–), 120.98 (s, 1C, –N**C**$_5$H$_4$–), 71.69 (s, 1C, –ipso-C$_5$**H**$_9$–), 34.24 (s, 2C, –C$_5$**H**$_9$–), 24.75 (s, 2C, –C$_5$**H**$_9$–). IR (neat liquid, cm^{-1}): 3058(w), 2952(s), 2866(s), 1644(w), 1578(s), 1517(s), 1465(s), 1374(s), 1319(s), 1226(s), 1178(s), 1051(s), 989(s), 933(s), 893(s), 772(s), 614(s).

2.2.2. N-cyclohexyl-1-(pyridin-2-yl)methanimine (**L$_2$**)

L$_2$ [21]was prepared by an analogous method as described for **L$_1$**, except utilizing cyclohexylamine and 2-picolylcarbaldehyde. The product was obtained as a light orange oil (3.76 g, 98.0%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.63 (d, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 8.41 (s, 1H, –N=C**H**–NC$_5$**H**$_4$–), 7.97 (d, 2H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.71 (d, 1H, J = 8.4 Hz, –NC$_5$**H**$_4$–), 7.27 (t, 1H, J = 8.0 Hz, –NC$_5$**H**$_4$–), 3.29 (m, 1H, ipso-C$_6$**H**$_{11}$–), 1.81 (m, 4H, –C$_6$**H**$_{11}$–), 1.62 (m, 4H, –C$_6$**H**$_{11}$–), 1.27 (m, 2H, –C$_6$**H**$_{11}$–). ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 159.72 (s, 1C, ipso-N**C**$_5$H$_4$–), 154.78 (s, 1C, –N=**C**H–NC$_5$H$_4$–), 149.59 (s, 1C, –N**C**$_5$H$_4$–), 136.98 (s, 1C, –N**C**$_5$H$_4$–), 125.21 (s, 1C, –N**C**$_5$H$_4$–), 120.69 (s, 1C, –N**C**$_5$H$_4$–), 68.78 (s, 1C, ipso-**C**$_6$H$_{11}$–), 34.23 (s, 2C, –**C**$_6$H$_{11}$–), 25.54 (s, 1C, –**C**$_6$H$_{11}$–), 24.39 (s, 2C, –**C**$_6$H$_{11}$–). IR (neat liquid, cm^{-1}): 3058(w), 2926(s), 2854(s), 1646(w), 1579(s), 1519(s), 1447(s), 1377(s), 1341(s), 1298(s), 1145(s), 1069(s), 967(s), 890(s), 854(s), 772(s), 672(s), 617(s).

2.2.3. N-(piperidin-1-yl)-1-(pyridin-2-yl)methanimine (**L$_3$**)

L$_3$ was prepared by an analogous method as described for **L$_1$**, except utilizing 1-aminopiperidine and 2-picolylcarbaldehyde. The product was obtained as a light orange oil (3.55 g, 94.0%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.51 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.82 (d, 1H, J = 8.0 Hz, –NC$_5$**H**$_4$–), 7.61 (t, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 7.59 (s, 1H, –N=C**H**–NC$_5$H$_4$–), 7.08 (t, 1H, J = 7.8 Hz, –NC$_5$**H**$_4$–), 3.22 (t, 4H, J = 5.6 Hz, –NC$_5$**H**$_{10}$–), 1.72 (m, 4H, –NC$_5$**H**$_{10}$–), 1.53 (m, 2H, –NC$_5$**H**$_{10}$–). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 155.85 (s, 1C, ipso-N**C**$_5$H$_4$-), 148.99 (s, 1C, –N**C**$_5$H$_4$–), 136.13 (s, 1C, –N=**C**H–NC$_5$H$_4$–), 133.89 (s, 1C, –N**C**$_5$H$_4$–), 121.71 (s, 1C, –N**C**$_5$H$_4$–), 118.72 (s, 1C, –N**C**$_5$H$_4$–), 51.65 (s, 2C, –NC$_5$H$_{10}$–), 25.05 (s, 2C, –NC$_5$H$_{10}$–), 24.00 (s, 1C, –NC$_5$H$_{10}$–). IR (neat liquid, cm^{-1}): 3056(w), 2934(s), 2854(s), 2811(w), 1643(s), 1566(s), 1436(s), 1357(s), 1291(s), 1254(s), 1162(s), 1006(s), 989(s), 887(s), 771(s), 666(s), 620(s).

2.2.4. N-cyclopentyl-1-(quinolin-2-yl)methanimine (**L$_4$**)

L$_4$ was prepared by an analogous method as described for **L$_1$**, except utilizing cyclopentylamine and quinoline-2-carbaldehyde. The product was obtained as a light red oil (3.55 g, 96.0%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.54 (d, 1H, J = 8.0 Hz, –NC$_9$**H**$_6$–), 8.17 (s, 2H, –N=C**H**–NC$_9$**H**$_6$–, –NC$_9$**H**$_6$–), 8.13 (d, 1H, J = 8.2 Hz, –NC$_9$**H**$_6$–), 7.82 (s, 1H, –N=C**H**–NC$_9$**H**$_6$–), 7.74 (t, 1H, J = 7.8 Hz, –NC$_9$**H**$_6$–), 7.58(t, 1H, J = 7.8 Hz, –NC$_9$**H**$_6$–), 3.94 (t, 4H, J = 5.6 Hz, ipso-C$_5$**H**$_9$–), 1.94 (m, 4H, –C$_5$**H**$_9$–), 1.72 (m, 2H, –C$_5$**H**$_9$–). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 160.12 (s, 1C, ipso-N**C**$_9$H$_6$–), 156.33 (s, 1C, –N=**C**H–NC$_9$H$_6$–), 150.55 (s, 1C, –N**C**$_9$H$_6$–), 133.89 (s, 1C, –N**C**$_9$H$_6$–), 140.86 (s, 1C, –N**C**$_9$H$_6$–), 135.86 (s, 1C, –N**C**$_9$H$_6$–), 133.84 (s, 1C, –N**C**$_9$H$_6$–), 132.84 (s, 1C, –N**C**$_9$H$_6$–), 130.57 (s, 1C, –N**C**$_9$H$_6$–), 128.44 (s, 1C, –N**C**$_9$H$_6$–), 62.86 (s, 1C, ipso-**C**$_5$H$_9$–), 43.00 (s, 2C, –C$_5$**H**$_9$–), 25.81 (s, 2C, –C$_5$**H**$_9$–). IR (neat liquid, cm^{-1}): 3057(w), 2951(s), 2865(s), 1640(w), 1596(s), 1558(s), 1503(s), 1432(s), 1370(s), 1306(s), 1181(s), 1146(s), 1146(s), 1112(s), 1072(s), 960(s), 892(s), 831(s), 831(s), 751(s), 617(s).

2.2.5. N-cyclopentyl-1-(pyridin-2-yl)methanimine(dichloro)palladium(II) (**[L$_1$PdCl$_2$]**)

A solution of **L$_1$** (0.087 g, 0.50 mmol) in anhydrous ethanol (10.0 mL) was added to a solution of anhydrous $Pd(CH_3CN)_2Cl_2$ [80,81] (0.13 g, 0.50 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of a yellow material occurred while stirring at room temperature for 12 h. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.15 g, 88%). X-ray quality crystals of **[L$_1$PdCl$_2$]** were obtained within three days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_1$PdCl$_2$]** (0.050 g). *Anal.* Calc. for $C_{11}H_{14}N_2Cl_2Pd$: C, 37.58; H, 4.01; N, 7.97. Found: C, 37.41; H, 4.02; N, 8.12%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.97 (d, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 8.54 (s, 1H, –N=C**H**–NC$_5$H$_4$–), 8.33 (t, 1H, J = 7.6 Hz, –NC$_5$**H**$_4$–), 8.12 (d, 1H, J = 8.0 Hz, –NC$_5$**H**$_4$–), 7.83 (t, 1H, 8.0 Hz, –NC$_5$**H**$_4$–), 4.65 (m, 1H, –C$_5$H$_9$–), 2.05 (m, 2H, –C$_5$H$_9$–), 1.89 (m, 2H, –C$_5$H$_9$–), 1.74 (m, 2H, –C$_5$H$_9$–), 1.64 (m, 2H, –C$_5$H$_9$–). ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 168.10 (s, 1C, ipso-N**C**$_5$H$_4$–), 157.07 (s, 1C, –N=**C**H–NC$_5$H$_4$–), 150.19 (s, 1C, –N**C**$_5$H$_4$–), 141.58 (s, 1C, –N**C**$_5$H$_4$–), 128.77 (s, 1C, –N**C**$_5$H$_4$–), 128.63 (s, 1C, –N**C**$_5$H$_4$–), 68.62 (s, 1C, ipso-**C**$_5$H$_9$–), 32.73 (s, 2C, –**C**$_5$H$_9$–), 23.63 (s, 2C, –**C**$_5$H$_9$–). IR (solid, cm^{-1}): 3038(w), 2951(s), 2872(s), 1915(w), 1835(s), 1747(s), 1693(s), 1649(s), 1596(s), 1517(s), 1472(s), 1319(s), 1107(s), 1045(s), 994(s), 936(s), 850(s), 772(s), 657(s).

2.2.6. N-cyclohexyl-1-(pyridin-2-yl)methanimine(dichloro)palladium(II) (**[L$_2$PdCl$_2$]**)

[L$_2$PdCl$_2$] was prepared according to a similar procedure as described for **[L$_1$PdCl$_2$]**. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.16 g, 90%). X-ray quality crystals of **[L$_2$PdCl$_2$]** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_2$PdCl$_2$]** (0.05 g). *Anal.* Calc. for

$C_{12}H_{16}N_2Cl_2Pd$: C, 39.42; H, 4.41; N, 7.66. Found: C, 39.58; H, 4.45; N, 8.02%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.98 (d, 1H, J = 7.6 Hz, –$NC_5\mathbf{H}_4$–), 8.57 (s, 1H, –N=C**H**–NC_5H_4–), 8.33 (t, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 8.09 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 7.83 (t, 1H, 7.8 Hz, –$NC_5\mathbf{H}_4$–), 4.07 (m, 1H, –$C_6\mathbf{H}_{11}$–), 2.15 (m, 2H, –$C_6\mathbf{H}_{11}$–), 1.81 (m, 2H, –$C_6\mathbf{H}_{11}$–), 1.65 (m, 1H, –$C_6\mathbf{H}_{11}$–), 1.40 (m, 2H, –$C_6\mathbf{H}_{11}$–), 1.29 (m, 2H, –$C_6\mathbf{H}_{11}$–), 1.15 (m, 1H, –$C_6\mathbf{H}_{11}$–). ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 168.96 (s, 1C, ipso-N**C**$_5H_4$–), 157.14 (s, 1C, –N=**C**H–NC_5H_4–), 150.23 (s, 1C, –N**C**$_5H_4$–), 141.65 (s, 1C, –N**C**$_5H_4$–), 128.72 (s, 1C, –N**C**$_5H_4$–), 65.08 (s, 1C, ipso-**C**$_6H_{11}$–), 32.84 (s, 2C, –**C**$_6H_{11}$–), 25.37 (s, 2C, –**C**$_6H_{11}$–). IR (solid, cm^{-1}): 3035(w), 2931(s), 2852(s), 1753(w), 1691(s), 1597(s), 1539(s), 1446(s), 1388(s), 1315(s), 1237(s), 1193(s), 1108(s), 1050(s), 972(s), 890(s), 844(s), 779(s), 659(s).

2.2.7. N-(piperidin-1-yl)-1-(pyridin-2-yl)methanimine(dichloro)palladium(II) (**[L$_3$PdCl$_2$]**)

[L$_3$PdCl$_2$] was prepared according to a similar procedure as described for **[L$_1$PdCl$_2$]**. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.16 g, 88%). X-ray quality crystals of **[L$_3$PdCl$_2$]** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[L$_3$PdCl$_2$]** (0.05 g). *Anal.* Calc. for $C_{11}H_{15}N_3Cl_2Pd$: C, 36.04; H, 4.12; N, 11.46. Found: C, 35.58; H, 4.08; N, 11.53%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.87 (d, 1H, J = 7.2 Hz, –$NC_5\mathbf{H}_4$–), 8.14 (s, 1H, –N=C**H**–NC_5H_4–), 8.21 (t, 1H, J = 7.2 Hz, –$NC_5\mathbf{H}_4$–), 7.91 (d, 1H, J = 7.8 Hz, –$NC_5\mathbf{H}_4$–), 7.63 (t, 1H, J = 7.4 Hz, –$NC_5\mathbf{H}_4$–), 3.23 (t, 4H, J = 5.6 Hz, –$NC_5\mathbf{H}_{10}$–), 1.68 (m, 4H, –$NC_5\mathbf{H}_{10}$–), 1.49 (m, 2H, –$NC_5\mathbf{H}_{10}$–). ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 156.14 (s, 1C, ipso-N**C**$_5H_4$–), 150.37 (s, 1C, –N=**C**H–NC_5H_4–), 144.93 (s, 1C, –N**C**$_5H_4$–), 139.97 (s, 1C, –N**C**$_5H_4$–), 125.26 (s, 1C, –N**C**$_5H_4$–), 124.26 (s, 1C, –N**C**$_5H_4$–), 55.45 (s, 2C, –N**C**$_5H_{10}$–), 32.84 (s, 2C, –N**C**$_5H_{10}$–), 25.37 (s, 1C, –N**C**$_5H_{10}$–). IR (solid, cm^{-1}): 3060(w), 2939(s), 2835(s), 2529(w), 1691(s), 1651(s), 1604(s), 1463(s), 1341(s), 1279(s), 1172(s), 1103(s), 911(s), 843(s), 770(s), 730(s), 672(s).

2.2.8. N-cyclopentyl-1-(quinolin-2-yl)methanimine(dichloro)palladium(II) (**[L$_4$PdCl$_2$]**)

[L$_4$PdCl$_2$] was prepared according to a similar procedure as described for [**L$_1$PdCl$_2$**]. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.17 g, 89%). X-ray quality crystals 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$_2$]** (0.05 g). *Anal.* Calc. for $C_{15}H_{16}N_2Cl_2Pd$: C, 44.86; H, 4.02; N, 6.98. Found: C, 45.03; H, 4.08; N, 6.53%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.64 (d, 1H, J = 8.0 Hz, –$NC_9\mathbf{H}_6$–), 8.51 (s, 1H, –N=C**H**–NC_9H_6–), 8.51 (s, 1H, –$NC_9\mathbf{H}_6$–), 8.17 (d, 1H, J = 8.2 Hz, –$NC_9\mathbf{H}_6$–), 7.95 (d, 1H, –N=C**H**–$NC_9\mathbf{H}_6$–), 7.83 (t, 1H, J = 7.8 Hz, –$NC_9\mathbf{H}_6$–), 7.64(t, 1H, J = 7.8 Hz, –$NC_9\mathbf{H}_6$–), 2.17 (t, 4H, J = 5.6 Hz, ipso-$C_5\mathbf{H}_9$–), 1.71 (m, 4H, –$C_5\mathbf{H}_9$–), 1.67 (m, 2H, –$C_5\mathbf{H}_9$–). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 162.15 (s, 1C, ipso-N**C**$_9H_6$–), 158.34 (s, 1C, –N=**C**H–NC_9H_6–), 153.65 (s, 1C, –N**C**$_9H_6$–), 134.77 (s, 1C, –N**C**$_9H_6$–), 139.76 (s, 1C, –N**C**$_9H_6$–), 134.46 (s, 1C, –N**C**$_9H_6$–), 130.64 (s, 1C, –N**C**$_9H_6$–), 129.74 (s, 1C, –N**C**$_9H_6$–), 127.37 (s, 1C, –N**C**$_9H_6$–), 124.39 (s, 1C, –N**C**$_9H_6$–), 65.76 (s, 1C, ipso-**C**$_5H_9$–), 42.80 (s, 2C, –$C_5\mathbf{H}_9$–), 27.83 (s, 2C, –$C_5\mathbf{H}_9$–). 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).

2.3. X-ray crystallographic studies

In each case, a colorless cubic-shaped crystal was picked up with paraton oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a nitrogen cold stream (−100 °C). Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-Plus (Bruker, 2001) [82]. Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS [83]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL [84]. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added in their geometrically ideal positions. The crystal and structure refinement data for all the structures are summarized in Table 1. The final cycle of the refinement converged with R_1 [$I > 2\sigma(I)$] = 0.0480, wR_2 [$I > 2\sigma(I)$] = 0.1315 for **[L$_1$PdCl$_2$]**, R_1 [$I > 2\sigma(I)$] = 0.0511, wR_2 [$I > 2\sigma(I)$] = 0.1270 for **[L$_2$PdCl$_2$]**, R_1 [$I > 2\sigma(I)$] = 0.0566, wR_2 [$I > 2\sigma(I)$] = 0.1195 for **[L$_3$PdCl$_2$]** and R_1 [$I > 2\sigma(I)$] = 0.0394, wR_2 [$I > 2\sigma(I)$] = 0.0774 for **[L$_4$PdCl$_2$]**.

2.4. Catalytic activity for MMA polymerization

In a Schlenk line, the complex (15 μmol, 5.3 mg for **[L$_1$PdCl$_2$]**, 5.5 mg for **[L$_2$PdCl$_2$]**, 5.5 mg for **[L$_3$PdCl$_2$]** and 6.0 mg for **[L$_4$PdCl$_2$]**) was dissolved in dried toluene (2.3 mL) followed by the addition of modified methylaluminoxane (MMAO) (3.25 mL, 7.50 mmol) as a cocatalyst. The solution was stirred for 20 min at 0, 25 and 60 °C. The MMA (5.0 mL, 47.1 mmol) was added to the above reaction mixture and stirred for 10 min–2 h to obtain a viscous solution. Methanol (50.0 mL) was added to terminate the polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35% HCl (5.0 mL) was injected to remove the remaining co-catalyst (MMAO). PMMA was obtained by filtration and repeated washing with methanol, and then dried under vacuum for 24 h.

3. Results and discussion

3.1. Synthesis and chemical properties

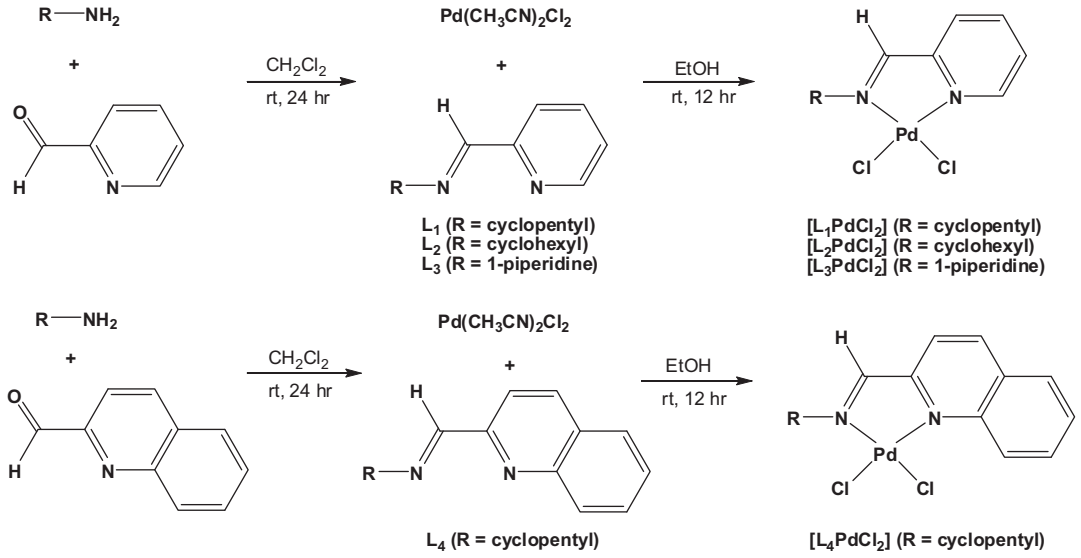
Scheme 1 shows the synthesis of the ligands and Pd(II) complexes. The ligands were obtained i yields of 98% (**L$_1$**), 98% (**L$_2$**), 94% (**L$_3$**) and 96% (**L$_4$**) from the condensation reaction between the appropriate X-amine (X = cyclopentyl, cyclohexyl, N-1-piperidine) and 2-picolylcarbaldehyde or quinoline-2-carbaldehyde in dichloromethane. The ligands **L$_1$** and **L$_2$** have been reported previously and have been applied to rhenium and copper complexes [21,77]. The **[L$_1$PdCl$_2$]** (88%), **[L$_2$PdCl$_2$]** (90%), **[L$_3$PdCl$_2$]** (88%) and **[L$_4$PdCl$_2$]** (89%) complexes 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 ligands and Pd(II) complex formulation. The ^{1}H NMR peaks of the Pd(II) complexes were shifted to low field by approximately δ 0.1–0.5 ppm as compared with the ligands, while the ^{13}C NMR peaks of the Pd(II) complexes were shifted to low field by approximately δ 2–10 ppm as compared with the ligands. In addition, an absorption band at around 1650 cm^{-1} for the imine moiety was identified.

3.2. Crystal structures

The ORTEP drawings of the complexes are shown in Fig. 1 (**[L$_1$PdCl$_2$]**), Fig. 2 (**[L$_2$PdCl$_2$]**), Fig. 3 (**[L$_3$PdCl$_2$]**) and Fig. 4 (**[L$_4$PdCl$_2$]**). Selected bond lengths and angles are listed in Table 2. Single crystals suitable for X-ray crystallography were obtained from diethyl ether (10.0 mL) diffusion into DMF solutions (10.0 mL) of the complexes. The coordination geometry around the Pd(II) centre of the synthesized complexes can be described as a slightly

Table 1
Crystal data and structure refinement for the Pd(II) complexes.

	[L_1PdCl_2]	**[L_2PdCl_2]**	**[L_3PdCl_2]**	**[L_4PdCl_2]**
Empirical formula	$C_{11}H_{14}Cl_2N_2Pd$	$C_{12}H_{16}Cl_2N_2Pd$	$C_{11}H_{15}Cl_2N_3Pd$	$C_{15}H_{16}Cl_2N_2Pd$
Formula weight	351.54	365.57	366.56	401.60
T (K)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2(1)/_c$
Unit cell dimensions				
a (Å)	35.1316(17)	38.799(11)	8.1462(9)	7.9134(8)
b (Å)	5.3706(3)	5.3558(15)	9.3693(10)	9.1944(10)
c (Å)	13.5589(7)	13.516(4)	9.6650(10)	20.525(2)
α (°)	90	90	112.804(2)	90
β (°)	104.0850(10)	101.295(6)	95.506(2)	94.036(2)
γ (°)	90	90	97.174(2)	90
V (Å^3)	2481.4(2)	2754.2(13)	666.23(12)	1489.7(3)
Z	8	8	2	4
D_{calc} (Mg/m^3)	1.882	1.763	1.827	1.791
Absorption coefficient (mm^{-1})	1.899	1.715	1.774	1.594
F(000)	1392	1456	364	800
Crystal size (mm^3)	0.25 × 0.16 × 0.11	0.31 × 0.19 × 0.16	0.25 × 0.19 × 0.17	0.20 × 0.14 × 0.12
θ (°)	1.20–28.27	1.07–28.31	2.31–28.32	1.99–28.33
Index ranges	$-46 \leqslant h \leqslant 46$, $-7 \leqslant k \leqslant 7$, $-12 \leqslant l \leqslant 17$	$-51 \leqslant h \leqslant 51$, $-6 \leqslant k \leqslant 7$, $-18 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 12$, $-12 \leqslant l \leqslant 11$	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 11$, $-27 \leqslant l \leqslant 26$
Reflections collected	8454	9460	4865	10785
Independent reflections (R_{int})	3025 (0.0299)	3387 (0.0380)	3227 (0.0122)	3714 (0.0503)
Completeness to θ = 28.30° (%)	98.7	99.2	97.5	99.8
Absorption correction	none	none	none	none
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3025/0/145	3387/6/154	3227/0/155	3714/0/181
Goodness-of-fit (GOF) on F^2	1.197	1.203	1.288	1.193
Final R indices [I > 2σ(I)]	R_1 = 0.0480, wR_2 = 0.1315	R_1 = 0.0511, wR_2 = 0.1270	R_1 = 0.0566, wR_2 = 0.1195	R_1 = 0.0394, wR_2 = 0.0774
R indices (all data)	R_1 = 0.0766, wR_2 = 0.2397	R_1 = 0.0877, wR_2 = 0.2201	R_1 = 0.1119, wR_2 = 0.2071	R_1 = 0.0904, wR_2 = 0.1396
Largest difference in peak and hole (e Å^{-3})	1.637 and −2.335	1.694 and −3.035	2.657 and −4.879	1.627 and −2.337



Scheme 1. Synthesis of the ligands and Pd(II) complexes.

distorted square plane, consisting of the two N atoms and two Cl atoms.

The Pd–$N_{pyridine}$ and Pd(1)–N(1) bond lengths in **[L_nPdCl_2]** (L_n = L_1, L_2, L_3, L_4) are in the range 2.020(7)–2.043(8) Å, while those of Pd–N_{imine} and Pd(1)–N(2) ranged from 2.023(8)–2.094(5) Å, similar to the Pd–N bond length of square planar imine Pd(II) complexes [52,85]. The Pd–N_{imine} bond length increased by approximately 0.02 Å, ranging in size from cyclopentyl (**[L_1-$PdCl_2$]**) < cyclohexyl (**[L_2PdCl_2]**) < 1-piperidinyl (**[L_3PdCl_2]**) < -cyclopentyl (**[L_4PdCl_2]**). The Pd–$N_{pyridine}$ bond lengths are shorter than those of Pd–N_{imine} due to the different basicity for the imine and pyridine groups. The Pd–Cl bond lengths ranged from 2.284(3)–2.303(2) Å. The double imine N(2)–C(6) distances of 1.304(10) (**[L_1PdCl_2]**), 1.293(11) (**[L_2PdCl_2]**) and 1.322(13) Å

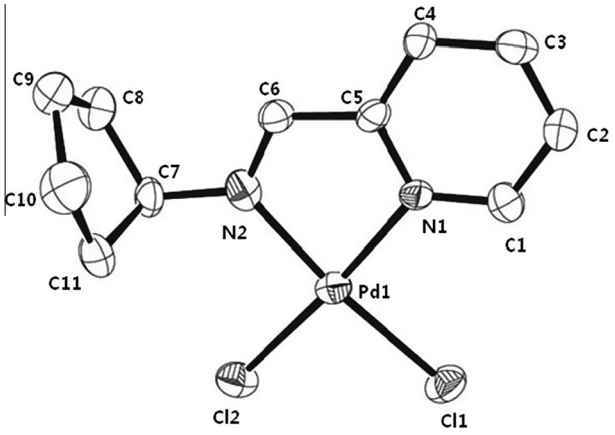


Fig. 1. ORTEP drawing of **[L_1PdCl_2]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

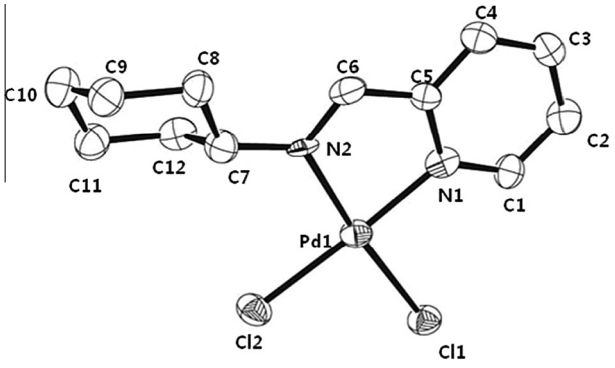


Fig. 2. ORTEP drawing of **[L_2PdCl_2]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

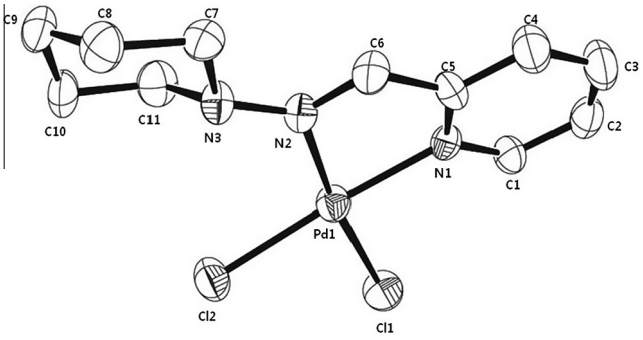


Fig. 3. ORTEP drawing of **[L_3PdCl_2]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

(**[L_3PdCl_2]**), and the corresponding imine N(2)–C(10) distance of 1.272(8) Å (**[L_4PdCl_2]**) are in the range of accepted carbon–nitrogen double bonds. The C(5)–C(6) bond distances of the complexes ranged from 1.446(14)–1.452(12) Å, reflecting delocalised π-electrons. The bond lengths of the synthesized palladium complexes are slightly affected by the N-cycloalkyl substituent group. The N(1)–Pd(1)–Cl(2) and N(2)–Pd(1)–Cl(1) angles for the complexes **[L_nPdCl_2]** (L_n = L_1, L_2, L_3) are nearly linear, being in the range 172.8(2)–175.98(17)°. However, the N(1)–Pd(1)–Cl(2) and N(2)–Pd(1)–Cl(1) angles for complex **[L_4PdCl_2]** are 173.44(14) and 167.45(16)°, respectively, showing a more distorted planarity than **[L_nPdCl_2]** (L_n = L_1, L_2, L_3). The average N(1)–Pd(1)–N(2) bond angle of the five membered rings range from 80.1(2)° to 80.7(3)° and are slightly affected by the substituted rings. The Cl(1)–Pd(1)–Cl(2)

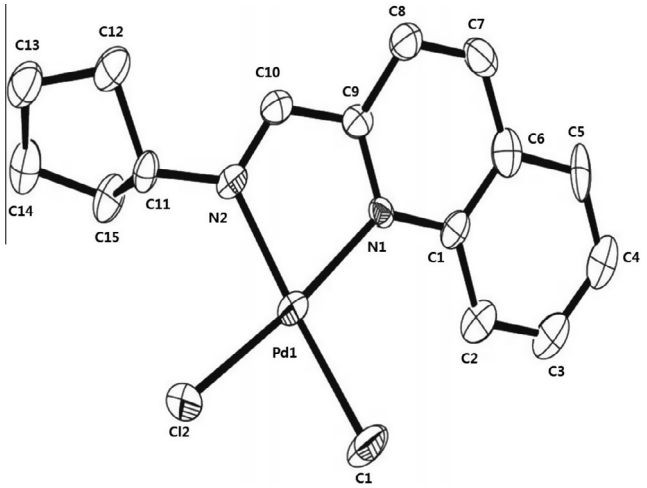


Fig. 4. ORTEP drawing of **[L_4PdCl_2]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

angles in **[L_nPdCl_2]** (L_n = L_1, L_2, L_3) are almost 90°, but this angle is 86.99(7)° for **[L_4PdCl_2]**. This trend was observed in related pyridyl-imine palladium [52,61,62,73,86] and platinum [67,68] systems. Interestingly, the plane of the N-cyclopentyl group and the plane of palladium and pyridine are perpendicular in **[L_1PdCl_2]**. Moreover, the plane of the N-cyclopentyl group and the plane of palladium and pyridine in **[L_4PdCl_2]** are slightly twisted by *ca.* 30° rather than being perpendicular (90°) for **[L_1PdCl_2]**. The N-cyclohexyl and N-piperidine groups in **[L_2PdCl_2]** and **[L_3PdCl_2]** are in the stable chair formation. Basically, both rings (N-cyclohexyl or N-piperidine group and palladium and pyridine) are located in the same plane.

3.3. MMA polymerisation

All the Pd(II) complexes were activated by MMAO to polymerise methyl methacrylate (MMA) [87–89], yielding PMMA with T_g ranging from 119 to 132 °C. The polymers were isolated as white solids and characterized by GPC in THF using standard polystyrene as the reference. The triad microstructure of PMMA was analyzed using ^{1}H NMR spectroscopy. The polymerisation results, including tacticity based on the isotactic (mm), heterotactic (mr) and syndiotactic (rr), and polydispersity index (PDI), which represents the average degree of polymerisation in terms of the number of structural units and molecules, are summarized in Table 3.

To confirm the catalytic activity of the MMA polymerisation, a blank polymerisation of MMA was performed with [$Pd(CH_3CN)_2Cl_2$] and MMAO at specific temperatures. The catalytic activities of the Pd(II) complexes increased with the decreasing ring size of the N-substituted cycloalkyl group (cyclohexyl, ~ 1-piperidinyl < cyclopentyl) at 60 °C and with increasing temperatures (0 < 25 < 60 °C). The complexes **[L_1PdCl_2]** and **[L_4PdCl_2]**, which have a perpendicular and twisted N-cyclopentyl group towards the plane of the iminopyridine-Pd residue, thus endow steric hindrance around the Pd metal center during the MMA Polymerization.

Moreover, the catalytic activity of **[L_4PdCl_2]**, containing an iminoquinoline ligand, was much higher than that of **[L_2PdCl_2]** and **[L_3PdCl_2]**, which contained an iminopyridine ligand. Presumably, the electron-rich cloud around the Pd metal in **[L_4PdCl_2]** provides increased activity compared to the electronic effect of **[L_2PdCl_2]** and **[L_3PdCl_2]**. Thus, the activity of these Pd(II) complexes toward MMA polymerisation is influenced by both steric effects and metal electronics. This result is comparable with previous reported

Table 2
Selected bond lengths (Å) and angles (°) of all the Pd(II) complexes.

[L_1PdCl_2]		**[L_2PdCl_2]**		**[L_3PdCl_2]**		**[L_4PdCl_2]**	
Bond lengths							
Pd(1)–N(1)	2.021(6)	Pd(1)–N(1)	2.020(7)	Pd(1)–N(1)	2.043(8)	Pd(1)–N(2)	2.030(5)
Pd(1)–N(2)	2.023(8)	Pd(1)–N(2)	2.044(6)	Pd(1)–N(2)	2.061(9)	Pd(1)–N(1)	2.094(5)
Pd(1)–Cl(1)	2.300(2)	Pd(1)–Cl(1)	2.286(2)	Pd(1)–Cl(1)	2.284(3)	Pd(1)–Cl(2)	2.2726(19)
Pd(1)–Cl(2)	2.292(2)	Pd(1)–Cl(2)	2.303(2)	Pd(1)–Cl(1)	2.284(3)	Pd(1)–Cl(1)	2.2984(17)
N(1)–C(5)	1.369(9)	N(1)–C(5)	1.360(10)	N(1)–C(5)	1.354(13)	N(1)–C(9)	1.331(8)
N(2)–C(6)	1.304(10)	N(2)–C(6)	1.293(11)	N(2)–C(6)	1.322(13)	N(2)–C(10)	1.272(8)
N(2)–C(7)	1.470(10)	N(2)–C(7)	1.463(11)	N(2)–N(3)	1.360(11)	N(1)–C(11)	1.478(8)
C(5)–C(6)	1.452(10)	C(5)–C(6)	1.452(12)	C(5)–C(6)	1.446(14)	C(9)–C(10)	1.437(9)
Bond angles							
N(1)–Pd(1)–N(2)	80.6(3)	N(1)–Pd(1)–N(2)	80.7(3)	N(1)–Pd(1)–N(2)	80.5(3)	N(1)–Pd(1)–N(2)	80.1(2)
N(1)–Pd(1)–Cl(2)	175.98(17)	N(1)–Pd(1)–Cl(2)	175.87(18)	N(1)–Pd(1)–Cl(2)	172.9(3)	N(1)–Pd(1)–Cl(2)	173.44(14)
N(2)–Pd(1)–Cl(2)	95.5(2)	N(2)–Pd(1)–Cl(2)	95.34(19)	N(2)–Pd(1)–Cl(2)	97.6(2)	N(2)–Pd(1)–Cl(2)	93.65(12)
N(1)–Pd(1)–Cl(1)	93.32(18)	N(1)–Pd(1)–Cl(1)	93.42(19)	N(1)–Pd(1)–Cl(1)	92.6(2)	N(1)–Pd(1)–Cl(1)	99.54(14)
N(2)–-Pd(1)–Cl(1)	173.7(2)	N(2)–Pd(1)–Cl(1)	173.75(19)	N(2)–Pd(1)–Cl(1)	172.8(2)	N(2)–Pd(1)–Cl(1)	167.45(16)
Cl(1)–Pd(1)–Cl(2)	90.59(8)	Cl(1)–Pd(1)–Cl(2)	90.46(8)	Cl(1)–Pd(1)–Cl(2)	89.10(11)	Cl(1)–Pd(1)–Cl(2)	86.99(7)
C(6)–N(2)–C(7)	121.7(7)	C(6)–N(2)–C(7)	121.8(7)	C(6)–N(2)–N(3)	122.2(9)	C(10)–N(2)–C(11)	121.9(5)
C(6)–N(2)–Pd(1)	114.2(5)	C(6)–N(2)–Pd(1)	113.1(5)	C(6)–N(2)–Pd(1)	112.8(7)	C(10)–N(2)–Pd(1)	112.1(4)
C(8)–C(7)–C(11)	102.5(7)	C(8)–C(7)–C(12)	111.9(8)	C(7)–N(3)–C(11)	112.7(9)	C(12)–C(11)–C(15)	102.1(5)
C(8)–C(7)–N(2)	115.5(7)	C(8)–C(7)–N(2)	114.6(7)	C(7)–N(3)–N(2)	116.7(8)	C(12)–C(11)–N(2)	117.7(6)
C(11)–C(7)–N(2)	109.0(7)	C(12)–C(7)–N(2)	109.6(7)	C(11)–N(3)–N(2)	111.7(8)	C(15)–C(11)–N(2)	110.6(5)

Table 3
Polymerization of MMA by the Pd(II) complexes in the presence of MMAO.

Entry	Catalyst[a]	Temp.(time)	Yield[b]	Activity[c]	T_g[d]	Tacticity			M_w[e]	M_w/M_n[f]
		(°C)	(g)	(g/mol-Cat h) × 10^4	(°C)	%mm	%mr	%rr	(g/mol) × 10^5	
1	$Pd(AN)_2Cl_2$[g]	60(2hr)	0.88	2.93	131.47	7.60	22.8	69.6	0.66	2.90
2	MMAO[h]	60(2hr)	0.42	1.40	119.61	37.2	10.9	51.9	0.61	2.20
3	**[L_1PdCl_2]**	60(30 min)	1.09	14.5	129.24	7.70	22.5	69.8	2.45	3.71
4	**[L_2PdCl_2]**	60(2hr)	0.73	2.43	129.51	8.30	23.6	68.1	1.72	4.31
5	**[L_3PdCl_2]**	60(2hr)	0.81	2.70	126.08	8.10	22.9	69.0	8.42	1.92
6	**[L_4PdCl_2]**	60(30 min)	1.06	14.1	128.30	8.10	22.7	69.2	6.47	5.18
7	$Pd(AN)_2Cl_2$[g]	25(2hr)	0.55	1.83	129.93	8.80	19.7	71.5	0.72	2.97
8	MMAO[h]	25(2hr)	0.14	0.47	125.29	15.4	28.4	56.2	1.12	3.95
9	**[L_1PdCl_2]**	25(2hr)	1.09	3.63	129.80	7.90	17.8	74.3	1.38	3.09
10	**[L_2PdCl_2]**	25(2hr)	1.18	3.93	128.32	8.00	19.0	73.0	0.43	2.99
11	**[L_3PdCl_2]**	25(2hr)	0.35	1.17	128.33	10.1	18.1	71.8	1.36	4.16
12	**[L_4PdCl_2]**	25(2hr)	0.86	2.87	130.11	8.50	22.8	68.7	0.63	1.17
13	$Pd(AN)_2Cl_2$[g]	0(2hr)	0.38	1.27	129.05	9.20	18.9	71.9	9.93	1.70
14	MMAO[h]	0(2hr)	0.12	0.40	129.50	11.6	28.8	59.6	3.25	2.56
15	**[L_1PdCl_2]**	0(2hr)	0.18	0.60	130.65	13.7	21.6	64.7	8.13	2.10
16	**[L_2PdCl_2]**	0(2hr)	0.27	0.90	128.88	11.4	22.3	66.3	10.11	1.71
17	**[L_3PdCl_2]**	0(2hr)	0.29	0.97	126.97	12.6	21.0	66.4	2.17	1.44
18	**[L_4PdCl_2]**	0(2hr)	0.26	0.87	128.27	10.1	26.8	63.1	0.67	1.17

[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 is g of PMMA/(mol-Pd h).
[d] T_g is the glass transition temperature, which is determined with a thermal analyzer.
[e] Determined by gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.
[f] M_n refers to the number average of molecular weights of PMMA.
[g] AN refers to CH_3CN in $Pd(AN)_2Cl_2$. It is a blank polymerization in which $Pd(AN)_2Cl_2$ was also activated by MMAO.
[h] It is a blank polymerization which was done solely by MMAO.

palladium complexes containing the bispyridylamine ligand N,N-di(2-picolyl)cycloheptylamine [90].

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 [91]. The syndiotacticity of PMMA was around 70%, which is similar for all **[L_nPdCl_2]** (L_n = L_1, L_2, L_3, L_4), regardless of the polymerisation temperature. Although the moderate syndiotacticity was not sufficient to confer a mechanism of coordination polymerisation, it clearly shows the steric and electronic effects in **[L_nPdCl_2]** (L_n = L_1, L_2, L_3, L_4) during the MMA polymerisation.

4. Conclusions

We investigated the synthesis and X-ray crystallographic structures of **[L_1PdCl_2]**, **[L_2PdCl_2]**, **[L_3PdCl_2]** and **[L_4PdCl_2]**, which were prepared by substitution reaction of $Pd(CH_3CN)_2Cl_2$ with the corresponding iminopyridine and iminoquinoline ligands. The coordination geometry around the Pd(II) centres in the iminopyridine-Pd(II) complexes were square-planar. The catalytic activity of complexes **[L_1PdCl_2]** and **[L_4PdCl_2]** towards the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane resulted in an activity of 1.45 × 10^5 g PMMA/mol Pd h at 60 °C, as well as moderate syndiotacticity, irrelevant of the polymerisation temperature.

Acknowledgments

This research was supported by the National Research Foundation of Korea (NRF) and funded by the Ministry of the Education,

Science and Technology (MEST) (Grant No. 2012-R1A2A2A01045730).

Appendix A. Supplementary data

CCDC 970000–970003 contains the supplementary crystallographic data for **[L_1PdCl_2]**, **[L_2PdCl_2]**, **[L_3PdCl_2]** and **[L_4PdCl_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.

References

[1] A. Vlcek Jr., Coord. Chem. Rev. 230 (2002) 225.
[2] R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 645 (2002) 158.
[3] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[4] M. Kettunen, C. Vedder, H.-H. Brintzinger, I. Mutikainen, M. Leskelä, T. Repo, Eur. J. Inorg. Chem. (2005) 1081.
[5] C.-M. Che, J.-S. Huang, Chem. Rev. 242 (2003) 97.
[6] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[7] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[8] S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65.
[9] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[10] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[11] B.L. Small, M. Brookhart, Macromolecules 32 (1999) 2120.
[12] C. Vedder, F. Schaper, H.-H. Brintzinger, M. Kettunen, S. Babik, G. Fink, Eur. J. Inorg. Chem. (2005) 1071.
[13] K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams, Organometallics 24 (2005) 280.
[14] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Stromberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.
[15] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.
[16] S. Schoumacker, O. Hamelin, J. Pécaut, M. Fontecave, Inorg. Chem. 42 (2003) 8110.
[17] Z.-F. Chen, Y.-Z. Tang, H. Liang, H.-K. Fun, K.-B. Yu, J. Coord. Chem. 59 (2006) 207.
[18] P. Govindaswamy, Y.A. Mozharivskyj, M. Rao, Polyhedron 24 (2005) 1710.
[19] J.J. Braymer, J.-S. Choi, A.S. DeToma, C. Wang, K. Nam, J.W. Kampf, A. Ramamoorthy, M.H. Lim, Inorg. Chem. 50 (2011) 10724.
[20] W. Wang, B. Spingler, R. Alberto, Inorg. Chim. Acta 355 (2003) 386.
[21] W. Massa, S. Dehghanpour, K. Jahani, Inorg. Chim. Acta 362 (2009) 2872.
[22] R.S. Herrick, K.L. Houde, J.S. McDowell, L.P. Kiczek, G. Bonavia, J. Organomet. Chem. 589 (1999) 29.
[23] M. Schulz, M. Klopfleisch, H. Gorls, M. Kahnes, M. Westerhausen, Inorg. Chim. Acta 362 (2009) 4706.
[24] S.S. Chavan, S.K. Sawant, V.A. Sawant, G.K. Lahiri, Inorg. Chim. Acta 363 (2010) 3359.
[25] D.A. Kanas, S.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chem. 47 (2008) 8727.
[26] C.M. Álvarez, R. García-Rodríguez, D. Miguel, Inorg. Chem. 51 (2012) 2984.
[27] S. Shakhatreh, J. Mohanraj, A. Czapik, D. Tzimopoulos, S. Kotoulas, M. Gdaniec, P.D. Akrivos, J. Mol. Struct. 1002 (2011) 51.
[28] C.M. Álvarez, R. García-Rodríguez, D. Miguel, J. Organomet. Chem. 692 (2007) 5717.
[29] P. Datta, S.K. Sarkar, T.K. Mondal, A.K. Patra, C. Sinha, J. Organomet. Chem. 694 (2009) 4124.
[30] L. Gonsalvi, J.A. Gaunt, H. Adams, A. Castro, G.J. Sunley, A. Haynes, Organometallics 22 (2003) 1047.
[31] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Laschi, Organometallics 22 (2003) 2545.
[32] S. Roy, T.K. Mondal, P. Mitra, E.L. Torres, C. Sinha, Polyhedron 30 (2011) 913.
[33] J. Zhang, W. Li, W. Bu, L. Wu, L. Ye, G. Yang, Inorg. Chim. Acta 358 (2005) 964.
[34] J. García-Tojala, T. Rojo, Polyhedron 18 (1999) 1123.
[35] B.P. Buffin, P.J. Squattrito, A.O. Ojewole, Inorg. Chem. Commun. 7 (2004) 14.
[36] D. Carmona, C. Vega, F.J. Lahoz, S. Elipe, L.A. Oro, M.P. Lamata, F. Viguri, R. García-Correas, C. Cativiela, M.P.L.-R. de Víu, Organometallics 18 (1999) 3364.
[37] C.-J. Qiu, Y.-C. Zhang, Y. Gao, J.-Q. Zhao, J. Organomet. Chem. 694 (2009) 3418.
[38] D. Bose, J. Banerjee, S.H. Rahaman, G. Mostafa, H.-K. Fun, R.D.B. Walsh, M.J. Zaworotko, B.K. Ghosh, Polyhedron 23 (2004) 2045.
[39] E.-Q. Gao, Y.-F. Yue, S.-Q. Bai, Z. He, C.-H. Yan, Cryst. Growth Des. 5 (2005) 1119.
[40] V.C. Gibson, R.K. O'Reilly, D.F. Wass, A.J.P. White, D.J. Williams, Dalton Trans. (2003) 2824.
[41] J. Schnödt, J. Manzur, A.-M. García, I. Hartenbach, C. Yong Su, J. Fiedler, W. Kaim, Eur. J. Inorg. Chem. (2011) 1436.
[42] Z.-L. You, X. Han, G.-N. Zhang, Z. Anorg. Allg. Chem. 634 (2008) 142.
[43] K. Nienkemper, V.V. Kotov, G. Kehr, G. Erker, R. Fröhlich, Eur. J. Inorg. Chem. (2006) 366.
[44] R. Kannappan, M. Matsumoto, J. Hallren, K.M. Nicholas, J. Mol. Catal. A-Chem. 339 (2011) 72.
[45] 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 (2003) 279.
[46] S. Song, Y. Li, C. Redshaw, F. Wang, W.-H. Sun, J. Organomet. Chem. 696 (2011) 3772.
[47] S. Song, W. Zhao, L. Wang, C. Redshaw, F. Wang, W.-H. Sun, J. Organomet. Chem. 696 (2011) 3029.
[48] G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, Inorg. Chim. Acta 362 (2009) 3507.
[49] A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans. (1979) 1899.
[50] S. Song, T. Xiao, L. Wang, C. Redshaw, F. Wang, W.-H. Sun, J. Organomet. Chem. 699 (2012) 18.
[51] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, Polyhedron 25 (2006) 1753.
[52] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela, J. Organomet. Chem. 606 (2000) 112.
[53] J. Kuwabara, D. Takeuchi, K. Osakada, Polyhedron 28 (2009) 2459.
[54] N. Andrade-Lopez, T.A. Hanna, J.G. Alvarado-Rodriguez, A. Luqueno-Reyes, B.A. Martinez-Ortega, D. Mendoza-Espinosa, Polyhedron 29 (2010) 2304.
[55] X. Tang, W. Sun, T. Gao, J. Hou, J. Chen, W. Chen, J. Organomet. Chem. 690 (2005) 1570.
[56] A. Bacchi, M. Carcelli, C. Pelizzi, G. Pelizzi, P. Pelagatti, S. Ugolotti, Eur. J. Inorg. Chem. (2002) 2179.
[57] V.G. Albano, D. Braga, V. De Felice, A. Panunzi, A. Vitagliano, Organometallics 6 (1987) 517.
[58] T. Birkle, A. Carbayo, J.V. Cuevas, G. García-Herbosa, A. Muñoz, Eur. J. Inorg. Chem. (2012) 2259.
[59] T. Irrgang, S. Keller, H. Maisel, W. Kretschmer, R. Kempe, Eur. J. Inorg. Chem. (2007) 4221.
[60] G.R. Owen, H.A. Burkill, R. Vilar, A.J.P. White, D.J. Williams, J. Organomet. Chem. 690 (2005) 5113.
[61] S.J. Scales, H. Zhang, P.A. Chapman, C.P. McRory, E.J. Derrah, C.M. Vogels, M.T. Saleh, A. Decken, S.A. Westcott, Polyhedron 23 (2004) 2169.
[62] W.M. Motswainyana, S.O. Ojwach, M.O. Onani, E.I. Iwuoha, J. Darkwa, Polyhedron 30 (2011) 2574.
[63] B.P. Buffin, E.B. Fonger, A. Kundu, Inorg. Chim. Acta 355 (2003) 340.
[64] L. Canovese, F. Visentin, G. Chessa, C. Santo, P. Uguagliati, L. Maini, M. Polito, J. Chem. Soc., Dalton Trans. (2002) 3696.
[65] J.G. Hinman, C.R. Baar, M.C. Jennings, R.J. Puddephatt, Organometallics 19 (2000) 563.
[66] S. Dehghanpour, A. Mahmoudi, S. Rostami, Polyhedron 29 (2010) 2190.
[67] S. Reinhardt, K. Heinze, Z. Anorg. Allg. Chem. 632 (2006) 1465.
[68] M.L. Conrad, J.E. Enman, S.J. Scales, H. Zhang, C.M. Vogels, M.T. Saleh, A. Decken, S.A. Westcott, Inorg. Chim. Acta 358 (2005) 63.
[69] J. Yorke, C. Dent, A. Decken, A. Xia, Inorg. Chem. Commun. 13 (2010) 54.
[70] Z. Zhu, M. Kojima, K. Nakajima, Inorg. Chim. Acta 358 (2005) 476.
[71] M. Crespo, Polyhedron 15 (1996) 1981.
[72] P. Pratihar, S. Jha, T.K. Mondal, G. Mostafa, C. Sinha, Polyhedron 26 (2007) 4328.
[73] A.S. Roy, P. Saha, P. Mitra, S.S. Maity, S. Ghosh, P. Ghosh, Dalton Trans. 40 (2011) 7375.
[74] S. Mori, M. Nambo, L.-C.h. Chi, J. Bouffard, K. Itami, Org. Lett. 10 (2008) 4609.
[75] M.L. Ferrara, F. Giordano, I. Orabona, A. Panunzi, F. Ruffo, Eur. J. Inorg. Chem. (1999) 1939.
[76] D.M. Haddleton, M.C. Crossman, B.H. Dana, D.J. Duncalf, A.M. Heming, D. Kukulj, A.J. Shooter, Macromolecules 32 (1999) 2110.
[77] R.N. Dominey, B. Hauser, J. Hubbard, J. Dunham, Inorg. Chem. 30 (1991) 4754.
[78] G.-E. Matsubayashi, M. Okunaka, T. Tanaka, J. Organomet. Chem. 56 (1973) 215.
[79] E.V. Dose, L.J. Wilson, Inorg. Chem. 17 (1978) 2660.
[80] B.B. Wayland, R.F. Schrammz, Inorg. Chem. 8 (1969) 971.
[81] R.A. Walton, Can. J. Chem. 46 (1968) 2347.
[82] SMART and SAINT-Plus v 6.22, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.
[83] G.M. Sheldrick, SADABS v 2.03, University of Göttingen, Germany, 2002.
[84] SHELXTL v 6.10; Bruker AXS Inc: Madison, Wisconsin, USA, 2000.
[85] Z.H. Zhang, X.H. Bu, Z.A. Zhu, Y.T. Chen, Polyhedron 15 (1996) 2787.
[86] W.M. Motswainyana, M.O. Onania, A.M. Madiehe, Acta Crystallogr., Sect. E 68 (2012) m380.
[87] X. He, Y. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang, Q. Wu, Organometallics 22 (2003) 4952.
[88] B.K. Bahuleyan, D. Chandran, C.H. Kwak, C.-S. Ha, I. Kim, Macromol. Res. 18 (2008) 745.
[89] W. Wang, P.A. Stenson, A. Marin-Becerra, J. McMaster, M. Schroder, D.J. Irvine, D. Freeman, S.M. Howdle, Macromolecules 37 (2004) 6667.
[90] D. Kim, S. Kim, E. Kim, H.-J. Lee, H. Lee, Polyhedron 63 (2013) 139.
[91] T. Kitaura, T. Kitayama, Macromol. Rapid Commun. 28 (2007) 1889.