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Synthesis and Characterization of Palladium(II) and Platinum(II) Complexes with *N*,*N*',*N*-Tridentate Ligands Based on *N*,*N*-Di(2-picolyl)cycloalkylamine and Polymerization of Methyl Methacrylate

Dongil Kim^a, Sunghoon Kim^a, Eunhee Kim^a, Ha-Jin Lee^b, Hyosun Lee^{a,*}

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

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

Abstract

The reaction of Pd(CH₃CN)₂Cl₂ and NaClO₄ with the ancillary ligands *N*,*N*-di(2-picolyl)cyclopentylamine (**L**₁), *N*,*N*-di(2-picolyl)cyclohexylamine (**L**₂) and *N*,*N*-di(2-picolyl)cycloheptylamine (**L**₃) in ethanol yielded a new series of [(N,N',N)-PdCl]ClO₄ complexes, i.e. [PdL₁]ClO₄, [PdL₂]ClO₄ and [PdL₃]ClO₄, respectively. The reaction of Pt(CH₃CN)₂Cl₂ and NaClO₄ with the ancillary ligands **L**₁–**L**₃ gave only the stable [PtL₂]ClO₄ complex. The Pd and Pt atoms of all of the complexes had an almost square-planar geometry involving three nitrogen atoms and a chloro ligand. Moreover, the unit cell included a ClO₄⁻ anion as the counterion. The bond lengths between the metal and nitrogen atoms are a little affected by the substituted cycloalkyl group, however those between the metal and the chloro ligand are not affected. The catalytic activity of the Pd(II) and Pt(II) complexes toward the polymerisation of methyl methacrylate in the presence of modified methylaluminoxane resulted in a high molecular weight and a narrow polydispersity index; the highest activity was measured for [PdL₃]ClO₄ at 60 °C.

Keywords: palladium, platinum, N,N-di(2-picolyl)cycloalkylamine, MMA

1. Introduction

The chemistry of transition metal complexes with the *N*,*N*-bidentate ligand 2,2'dipyridylamine (dpa) and its derivatives has been extensively studied because of the potential applications as new luminescent materials for sensors [1-4], anticancer agents [5-10] and catalysts [11,12], including the polymerisation of α -olefins and polar olefins [13-15].

Specifically, various transition metal complexes with N-substituted picolyl derivatives such N, N, N', N'-tetrakis(2-pyridylmethylbenzene)-1,4-diamine (1,4-tpbd)[16], bis(2as pyridylmethyl)amine (bpma) [17-20], bis[2-(2-pyridylethyl)]-(2-pyridylmethyl)amine (pmap) [21], 1,2-bis(dipyridylaminomethyl)benzene [22], tris[2-(2-pyridyl)alkyl]amine [23] and bis(2,2'-dipicolyl)benzylamine [24] have been extensively studied for chemical and biological applications. Ni(II), Zn(II), Cu(II) and Pd(II) complexes with N-substituted di(2picolyl)amine derivatives [25-29] were prepared to investigate their enzymatic activities in biological systems, i.e. with respect to hydrolysis, catalytic CO_2 conversion to oxalate, photoluminescence, cytotoxic activity and kinetics [30-39]. The coordination compounds of Pd(II) and Pt(II) with tridentate ligands form very stable mononuclear square-planar complexes. However, the structures of Pd(II) and Pt(II) complexes with N,N',N-tridentate picolyl-based ligands containing N,N-dipicolylcycloalkyl and their utility in the polymerisation of methyl methacrylate (MMA) have not been established.

Accordingly, we describe here the synthesis and characterisation of complexes of Pd(II) and Pt(II) with the *N*,*N'*,*N*-tridentate ligands *N*,*N*-di(2-picolyl)cyclopentylamine (L_1), *N*,*N*-di(2-picolyl)cyclohexylamine (L_2) and *N*,*N*-di(2-picolyl)cycloheptylamine (L_3). The Pd(II) complexes were characterised by ¹H and ¹³C NMR spectroscopy, Fourier transform infrared (FTIR) spectroscopy and elemental analysis; the Pd(II) complexes [PdL₁]ClO₄, [PdL₂]ClO₄ and [PdL₃]ClO₄ and the Pt(II) complex [PtL₂]ClO₄ were also structurally characterised. The catalytic activities of the synthesized Pd(II) and Pt(II) complexes toward MMA polymerisation in toluene at 0, 25 and 60 °C were also investigated.

2. Experimental

2.1. Materials and physical measurements

 $PdCl_2$, $PtCl_2$, 2-picolylchloride hydrochloride, cyclopentylamine, cyclohexylamine, cycloheptylamine, $NaClO_4 \cdot H_2O$, NaOH and MMA were purchased from Sigma-Aldrich. Anhydrous solvents, such as ethanol, dimethylformamide (DMF), diethyl ether, acetonitrile and dichloromethane, were purchased from Merck KGaA and were used without further

purification. Deionised water was prepared using a Millipore Milli-Q system. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as a toluene solution (6.9 wt% aluminium) and was used without further purification. Elemental analyses (C, H, N) of the prepared complexes were carried out using an elemental analyser (EA 1108; Carlo-Erba). ¹H NMR (400 MHz) and ¹³C NMR (400 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer; chemical shifts were recorded in ppm units (relative to SiMe₄ as the internal standard. Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters. The molecular weights and molecular weight distributions of the obtained poly(methyl methacrylate) (PMMA) were determined using gel permeation chromatography (GPC) (CHCl₃, Alliance e2695; Waters Corp.). The glass transition temperature (T_g) was determined using a thermal analyser (Q2000; TA Instruments).

2.2. Preparation of the ligands

2.2.1. N,N-di(2-picolyl)cyclopentylamine (L1)

L₁ was prepared by a similar procedure as described in the literature [24,40-42]. A water solution (15.0 mL) of cyclopentylamine (1.70 g, 0.020 mol) was added to a water solution (15.0 mL) of 2-picolylchloride hydrochloride (6.58 g, 0.040 mol) and an added NaOH pellet (3.20 g, 0.080 mol). After 5 days of stirring at rt, the product was extracted with dichloromethane. The reaction solution was dried over MgSO₄, then the filtrate solvent was removed under reduced pressure to give a brown oil (4.01 g, 75.0%). Analysis calculated for C₁₇H₂₁N₃: C, 76.37; H, 7.92; N, 15.72. Found: C, 73.50; H, 7.72; N, 15.17%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.44 (d, 2H, *J* = 2.4 Hz, pyridine), 7.70 (t, 2H, *J* = 7.6 Hz, pyridine), 7.18 (t, 2H, *J* = 4.8 Hz, pyridine), 3.77 (s, 4H, *CH*₂-pyridine), 3.12 (m, 1H, -NC*H*-), 1.72 (m, 2H, cyclopentyl), 1.55 (m, 2H, cyclopentyl), 1.42 (m, 4H, cyclopentyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ : 162.34 (pyridine), 148.76 (pyridine), 136.78 (pyridine), 122.79 (pyridine), 120.44 (pyridine), 70.91 (N-*C*, cyclopentyl), 57.92 (-*C*H₂-pyridine), 28.96 (cyclopentyl), 23.90 (cyclopentyl). IR (liquid neat; cm⁻¹): 2950(w), 2866(w), 1588(w), 1471(w), 1433(w), 1355(s), 1124(w), 987(s), 755(w), 617(w).

2.2.2. N,N-di(2-picolyl)cyclohexylamine (L₂)

 L_2 [43] was prepared by an analogous method as described for L_1 , except utilizing cyclohexylamine. The product was obtained as a brown powder (4.61 g, 82.0%). Analysis

calculated for $C_{18}H_{23}N_3$: C, 40.14; H, 4.16; N, 8.26. Found: C, 40.10; H, 4.16; N, 8.33%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.42 (d, 2H, J = 4.8 Hz, pyridine), 7.70 (t, 2H, J = 7.6 Hz, pyridine), 7.52 (d, 2H, J = 7.6 Hz, pyridine), 7.19 (t, 2H, J = 7.2 Hz, pyridine), 3.78 (s, 4H, CH_2 -pyridine), 2.41 (m, 1H, -NC*H*-), 1.83 (m, 2H, cyclohexyl), 1.71 (m, 2H, cyclohexyl), 1.53 (m, 1H, cyclohexyl), 1.30 (m, 1H, cyclohexyl), 1.10 (m, 4H, cyclohexyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ : 162.28 (pyridine), 148.89 (pyridine), 136.81 (pyridine), 122.37 (pyridine), 122.22 (pyridine), 59.72 (N-*C*, cyclohexyl), 56.39 (-*C*H₂-pyridine), 32.70 (cyclohexyl), 26.08 (cyclohexyl), 24.42 (cyclohexyl). IR (solid neat; cm⁻¹): 2923(w), 2851(w), 1587(w), 1440(w), 1359(s), 1127(w), 754(s), 620(s).

2.2.3. N,N-di(2-picolyl)cycloheptylamine (L₃)

L₃ was prepared by an analogous method as described for **L**₁, except utilizing cycloheptylamine. The product was obtained as a yellow oil (4.02 g, 68.0%). Analysis calculated for C₁₈H₂₃N₃: C, 76.83; H, 8.24; N, 14.93. Found: C, 70.53; H, 8.64; N, 13.64%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.46 (d, 2H, *J* = 4.8 Hz, pyridine), 7.58 (t, 2H, *J* = 7.2 Hz, pyridine), 7.55 (d, 2H, *J* = 10.4 Hz, pyridine), 7.18 (t, 2H, *J* = 6.4 Hz, pyridine), 3.84 (s, 4H, CH₂-pyridine), 2.66 (m, 1H, -NCH-), 1.99 (m, 2H, cycloheptyl), 1.67 (m, 2H, cycloheptyl), 1.57 (m, 2H, cycloheptyl), 1.47 (m, 4H, cycloheptyl), 1.34 (m, 2H, cycloheptyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ : 161.87 (pyridine), 148.93 (pyridine), 136.89 (pyridine), 122.64 (pyridine), 121.42 (pyridine), 61.46 (N-*C*, cyclohexyl), 57.19 (-CH₂-pyridine), 30.98 (cycloheptyl), 28.74 (cycloheptyl), 26.30 (cycloheptyl). IR (liquid neat; cm⁻¹): 2921(w), 2853(w), 1587(w), 1436(w), 1361(s), 1124(w), 1048(s), 750(w), 618(s).

2.3. Preparation of the Pd(II) and Pt(II) complexes

2.3.1. N,N-di(2-picolyl)cyclopentylamino(chloro)palladium(II) perchlorate ([PdL1]ClO4)

A solution of L_1 (0.14 g, 0.50 mmol) and NaClO₄·H₂O (0.071 g, 0.50 mmol) in dried ethanol (10.0 mL) was added to a solution of anhydrous Pd(CH₃CN)₂Cl₂ [44-46] (0.13 g, 0.50 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of a white material occurred while stirring at room temperature for 12 hours. A yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.21 g, 83%). Crystals of [PdL₁]ClO₄, suitable for X-ray analysis, were obtained within three days from a diethyl ether (10.0mL) diffusion into a DMF solution (10.0 mL) of [PdL₁]ClO₄ (0.050 g). Analysis calculated for [C₁₇H₂₁ClN₃Pd]ClO₄: C, 40.14; H, 4.16; N, 8.26. Found: C, 40.10; H,

4.16; N, 8.33%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.57 (d, 2H, J = 4.8 Hz, pyridine), 8.19 (t, 2H, J = 7.8 Hz, pyridine), 7.74 (d, 2H, J = 10.0 Hz, pyridine), 7.62 (t, 2H, J = 6.4 Hz, pyridine), 5.52(d, 2H, J = 16.2 Hz, CH_2 -pyridine), 4.65 (d, 2H, J = 16.2 Hz, CH_2 -pyridine), 3.39 (m, 1H, -NC*H*-), 1.77 (m, 2H, cyclopentyl), 1.60 (m, 2H, cyclopentyl), 1.34 (m, 4H, cyclopentyl). ¹³C NMR (DMSO-d₆, 400 MHz): δ : 166.11 (pyridine), 150.32 (pyridine), 142.03 (pyridine), 125.30 (pyridine), 123.26 (pyridine), 73.62 (N-*C*, cyclopentyl), 66.39 (- CH_2 -pyridine), 29.83 (cyclopentyl), 22.22 (cyclopentyl). IR (solid neat; cm⁻¹): 3745(w), 3618(w), 1747(w), 1701(w), 1649(s), 1612(s), 1541(w), 1075(w), 760(s), 620(s).

2.3.2. N,N-di(2-picolyl)cyclohexylamino(chloro)palladium(II) perchlorate ([PdL2]ClO4)

[PdL₂]ClO₄ was prepared according to a similar procedure as described for [PdL₁]ClO₄. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.24 g, 90%). X-ray quality crystals of [PdL₂]ClO₄ were obtained within five days from a diethyl ether (10.0mL) diffusion into a DMF solution (10.0 mL) of [PdL₂]ClO₄ (0.05 g). Analysis calculated for [C₁₈H₂₃ClN₃Pd]ClO₄: C, 41.36; H, 4.44; N, 8.04. Found: C, 41.20; H, 4.43; N, 8.00%. ¹H NMR (DMSO-d₆, 400 MHz) δ: 8.56 (d, 2H, *J* = 6.0 Hz, pyridine), 8.19 (t, 2H, *J* = 8.0 Hz, pyridine), 7.73 (d, 2H, *J* = 7.8 Hz, pyridine), 7.61 (t, 2H, *J* = 6.4 Hz, pyridine), 5.47 (d, 2H, *J* = 16.4 Hz, CH₂-pyridine), 4.76 (d, 2H, *J* = 16.4 Hz, CH₂-pyridine), 1.49 (m, 1H, cyclohexyl), 1.23 (m, 5H, cyclohexyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ: 166.09 (pyridine), 150.38 (pyridine), 142.01 (pyridine), 125.31 (pyridine), 123.15 (pyridine), 70.14 (N-C, cyclohexyl), 64.18 (-CH₂-pyridine), 30.33 (cyclohexyl), 25.34 (cyclohexyl), 24.91 (cyclohexyl). IR (solid neat; cm⁻¹); 3199(w), 2939(w), 2862(s), 1616(w), 1491(s), 1443(w), 1076(w), 917(s), 765(s), 620(s).

2.3.3. N,N-di(2-picolyl)cycloheptylamino(chloro)palladium(II) perchlorate ([PdL₃]ClO₄)

[PdL₃]ClO₄ was prepared according to a similar procedure as described for **[PdL₁]ClO₄**. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.24 g, 88%). X-ray quality crystals of **[PdL₃]ClO₄** were obtained within five days from a diethyl ether (10.0mL) diffusion into a DMF solution (10.0 mL) of **[PdL₃]ClO₄** (0.05 g). Analysis calculated for $[C_{19}H_{25}ClN_3Pd]ClO_4$: C, 42.52; H, 4.69; N, 7.83. Found: C, 42.30; H, 4.71; N, 7.88%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.57 (d, 2H, *J* = 4.8 Hz, pyridine), 8.20 (t, 2H, *J* = 7.2 Hz, pyridine), 7.74 (d, 2H, *J* = 7.5 Hz, pyridine), 7.62

(t, 2H, J = 6.8 Hz, pyridine), 5.36 (d, 2H, J = 16.6 Hz, CH_2 -pyridine), 4.63 (d, 2H, J = 16.6 Hz, CH_2 -pyridine), 2.95 (m, 1H, -NC*H*-), 1.63 (m, 2H, cycloheptyl), 1.46 (m, 3H, cycloheptyl), 1.37 (m, 7H, cycloheptyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ : 165.75 (pyridine), 150.52 (pyridine), 141.99 (pyridine), 125.42 (pyridine), 123.53 (pyridine), 70.79 (N-*C*, cyclohexyl), 63.63 (-*C*H₂-pyridine), 31.46 (cycloheptyl), 27.03 (cycloheptyl), 24.71 (cycloheptyl). IR (solid neat; cm⁻¹); 3054(w), 2927(w), 2861(s), 1612(s), 1478(s), 1427(w), 1288(s), 1256(s), 1051(w), 846(s), 737(w), 707(w), 613(s).

2.3.4. N,N-di(2-picolyl)cyclohexylamino(chloro)platinum(II) perchlorate ([PtL2]ClO4).

A solution of L_2 (0.14 g, 0.50 mmol) and NaClO₄·H₂O (0.071 g, 0.50 mmol) in dried ethanol (10.0 mL) was added to a solution of anhydrous Pt(CH₃CN)₂Cl₂ (0.17 g, 0.50 mmol) in dried ethanol (10.0mL) at room temperature. Precipitation of a yellow material occurred while stirring at room temperature for 12 hours. The yellow powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.27 g, 88%). X-ray quality crystals of $[PtL_2]ClO_4$ [43] were obtained within three days from a diethyl ether diffusion into a DMF solution of [PtL₂]ClO₄. Analysis calculated for $[C_{18}H_{23}ClN_3Pt]ClO_4$: C, 35.36; H, 3.79; N, 6.87. Found: C, 35.31; H, 3.90; N, 6.99%. ¹H NMR (DMSO-d₆, 400 MHz) δ : 8.61 (d, 2H, J = 4.8 Hz, pyridine), 8.11 (t, 2H, J = 7.8 Hz, pyridine), 7.61 (d, 2H, J = 7.6 Hz, pyridine), 7.48 (t, 2H, J = 6.4 Hz, pyridine), 5.10 (d, 2H, 16.4 Hz, CH₂-pyridine), 4.86 (d, 2H, 16.4 Hz, CH₂-pyridine), 2.65 (m, 1H, -NCH-), 1.97 (m, 1H, cyclohexyl), 1.50 (m, 2H, cyclohexyl), 1.30 (m, 1H, cyclohexyl), 1.04 (m, 5H, cyclohexyl), 0.86 (m, 1H, cyclohexyl). ¹³C NMR (DMSO-d₆, 400 MHz) δ: 165.43 (pyridine), 147.63 (pyridine), 140.27 (pyridine), 124.07 (pyridine), 121.60 (pyridine), 70.74 (-NCH-, cyclohexyl), 64.24 (-NCH₂pyridine), 28.57 (cyclohexyl), 23.64 (cyclohexyl), 23.37 (cyclohexyl). IR (solid neat; cm⁻¹); 3744(w), 3297(w), 2941(w), 1699(s), 1649(w), 1587(w), 1524(s), 1453(w), 1308(s), 1101(w), 1067(w), 923(s), 779(s), 623(s), 580(s).

2.4. X-ray crystallographic studies

A yellow cubic-shaped crystal was picked up with paraffin oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo K α ($\lambda = 0.71073$ 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) software [47]. Semi-empirical absorption corrections based on equivalent reflections were applied by

SADABS [48]. The structure was solved by direct methods and refined by full-matrix leastsquares on F^2 using SHELXTL [49]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added in their geometrically ideal positions. The crystal and structure refinement data for all of the structures are summarised in Table 1. The final cycle of the refinement converged with R_1 [$I > 2\sigma(I)$] = 0.0506, wR_2 [$I > 2\sigma(I)$] = 0.1087 for [PdL₁]ClO₄, R_1 [$I > 2\sigma(I)$] = 0.0398, wR_2 [$I > 2\sigma(I)$] = 0.0803 for [PdL₂]ClO₄, R_1 [$I > 2\sigma(I)$] = 0.0448, wR_2 [$I > 2\sigma(I)$] = 0.1000 for [PdL₃]ClO₄ and R_1 [$I > 2\sigma(I)$] = 0.0365, wR_2 [$I > 2\sigma(I)$] = 0.0766 for [PtL₁]ClO₄.

Table 1

2.5 Catalytic activity of MMA polymerization

In a Schlenk line, the complex (7.6 mg for $[PdL_1]ClO_4$, 7.8 mg for $[PdL_2]ClO_4$, 8.0 mg for $[PdL_3]ClO_4$ and 9.1 mg for $[PtL_2]ClO_4$) was dissolved in dry toluene (2.3 mL), and then MMAO (3.25 mL, 7.50 mmol) was added as a co-catalyst. The solution was stirred for 20 min at 0, 25 or 60 °C. MMA (5.0 mL, 47.1 mmol) was added to the reaction mixture and stirred for 10 min to 2 h, as required, to obtain a viscous solution. Methanol (50.0 mL) was added to terminate the polymerisation. The reaction mixture was poured into a large quantity of MeOH (500 mL), and then 35% HCl (5.0 mL) was injected to remove the remaining MMAO co-catalyst. The PMMA was obtained by filtration and dried under vacuum at a mild temperature for 24 h.

3. Results and discussion

3.1. Synthesis and chemical properties

Scheme 1 shows the synthesis of the ligands and their Pd(II) and Pt(II) complexes. The ligands were obtained in yields of 75 (L_1), 82 (L_2) and 68% (L_3) from the cyclo(X)amine (X = pentyl, hexyl, heptyl) and 2-picolylchloride hydrochloride in water. The [PdL₁]ClO₄ (83%), [PdL₂]ClO₄ (90%), [PdL₃]ClO₄ (88%) and [PtL₂]ClO₄ (88%) complexes were obtained from the corresponding ligands and Pd(CH₃CN)₂Cl₂ and Pt(CH₃CN)₂Cl₂, respectively, in anhydrous ethanol. Attempts to synthesise [PtL₁]ClO₄ and [PtL₃]ClO₄ were not successful, despite changing the solvent, temperature and counter anion. The synthesis and DFT calculations of [PtL₂]ClO₄ were reported previously [43], however its molecular structure was not determined.

Scheme 1

The ¹H and ¹³C NMR and elemental analysis results were consistent with the formulation of the Pd(II) and Pt(II) complexes. The ¹H NMR peaks of the Pd(II) complexes were shifted to lower field by about 0.1-0.5 relative to the signals for the free ligands. Specifically, the ¹H NMR peaks for CH_2 -pyridine appeared as a singlet at 3.77 (L₁), 3.78 (L₂) and 3.84 (L₃), whilst the $CH_{2-pyridine}$ signal for the Pd(II) complexes appeared as two doublets centred at 5.52 (${}^{2}J_{H-H} = 16.2 \text{ Hz}$) and 4.65 (${}^{2}J_{H-H} = 16.2 \text{ Hz}$) for [PdL₁]ClO₄, 5.47 (${}^{2}J_{H-H} = 16.4 \text{ Hz}$) and 4.76 $(^{2}J_{H-H} = 16.4 \text{ Hz})$ for [PdL₂]ClO₄ and 5.36 $(^{2}J_{H-H} = 16.6 \text{ Hz})$ and 4.63 $(^{2}J_{H-H} = 16.6 \text{ Hz})$ Hz) for [PdL₃]ClO₄. The ¹H NMR peaks of the Pt(II) complex were shifted by about 0.1-1.5 to lower field relative to the signals for the free ligands. In particular, the ¹H NMR peak for CH₂-pyridine in the Pt(II) complex appeared as two doublets centred at $5.10 (^{2}J_{H-H} =$ 16.4 Hz) and 4.86 (${}^{2}J_{H-H} = 16.4$ Hz). This indicates that the ${}^{1}H$ NMR peaks for CH₂-pyridine in the Pd(II) and Pt(II) complexes are affected by the cyclo(X) (X = pentyl, hexyl, heptyl) Nsubstituent. This is because the cyclo(X) group is not coplanar with the planar pyridine group. The ¹³C NMR peaks of both the Pd(II) and Pt(II) complexes were found at lower field (by about 2-10) relative to the signals for the free ligands. The ${}^{13}C$ NMR peaks for CH_{2-} pyridine in the Pd(II) complexes appeared as a singlet because the two pyridine groups are coplanar; the signal moved downfield on increasing the ring size of the cycloalkyl moiety [cyclopentyl (66.39) > cyclohexyl (64.18) > cycloheptyl (63.63)].

3.2. Discussion of the X-ray crystal structures

The ORTEP drawings of the complexes are shown in Figs. 1-4 for $[PdL_1]ClO_4$, $[PdL_2]ClO_4$, $[PdL_2]ClO_4$, $[PdL_2]ClO_4$, and $[PtL_2]ClO_4$, respectively. Fundamental crystal data and experimental structure refinement for the Pd(II) and Pt(II) complexes are given Table 1. Selected bond lengths and angles are listed in Table 2. A single crystal suitable for X-ray crystallography was obtained by diffusing diethyl ether (10.0 mL) into a DMF solution (10.0 mL). The coordination geometry around the Pd(II) and Pt(II) centres is almost square planar, consisting of the three N atoms of the L_n ligands and one Cl atom ligand. Additionally, the unit cell of the Pd(II) and Pt(II) complexes includes a ClO_4^- anion as the counterion.

Fig. 3 Fig. 4 Table 2

The N atom of the cycloalkyl that is connected by three carbon atoms and a Pd or Pt atom nearly has the angle of an sp³ hybrid orbital. The y-z plane of the cycloalkyl group is perpendicular to the x-y plane of the Pd(II) and Pt(II) centre. This explains why the ¹H NMR CH_2 -pyridine signals for the Pd(II) and Pt(II) complexes appeared as two doublets. The Pd-N(cycloalkyl) bond lengths of the synthesised complexes are 2.028(6) Å for [PdL₁]ClO₄, 2.043(5) Å for [PdL₂]ClO₄ and 2.056(4) Å for [PdL₃]ClO₄, and these are slightly affected by steric hindrance from the cycloalkyl group. The bond lengths are longer for the Pd(II) complexes, which has larger rings. However, the other bond lengths are little affected by the presence of the cycloalkyl substituent compared to those of chloro{methyldi-[(6-methyl-2pyridyl)methyl]amine}palladium chloride, having a Pd-N(1) bond length of 2.018(8) Å [50]. Four of the cyclopentyl carbon atoms (C14, C15, C16, C17) of [PdL₁]ClO₄ are approximately coplanar, with the fifth carbon atom (C13) out of plane. The cyclohexyl group of $[PdL_2]ClO_4$ is in a stable chair formation. The cycloheptyl group of $[PdL_3]ClO_4$ appears in the stable twist-chair formation. The N(3)-Pd(1)-Cl(1) angles for the complexes are nearly linear and are 178.30(19)° for [PdL₁]ClO₄, 178.03(14)° for [PdL₂]ClO₄ and 178.94(14)° for $[PdL_3]ClO_4$. The average [N(3)-Pd(1)-N(2) and N(3)-Pd(1)-N(1)] bond angles of the two five-membered rings are 83.55° for [PdL₁]ClO₄, 83.85° for [PdL₂]ClO₄ and 84.01° for [PdL₃]ClO₄. These rings are bent because of ring strain, and are somewhat affected by the cycloalkyl ring size. In contrast, the Pt(1)-N(3) bond length in the complex [PtL₂]ClO₄ is 2.021(8) Å and the average of the Pt(1)–N(1) and Pt(1)–N(2) bond lengths is 2.008 Å.

The cyclohexyl groups in $[PtL_2]ClO_4$ and $[PdL_2]ClO_4$ are also in the stable chair formation. The N(3)–Pt(1)–Cl(1) angle for $[PtL_2]ClO_4$ is nearly linear (177.5°). The average of the N(3)–Pt(1)–N(1) and N(3)–Pt(1)–N(2) bond angles for the two five-membered rings is 83.4°; the rings are distorted because of ring strain. All of the bond distances and bond angles in $[PtL_2]ClO_4$ are very similar to those recently reported for $[Pt{bis}(2$ pyridylmethyl)amine)}Cl]Cl·H₂O [51].

Intramolecular Pd(II) or Pt(II)····C-H(and) weak interactions between a side chain of an N-cycloalkyl group and Pd(II) or Pt(II) are attributable to the location of the cycloalkyl group in the ligand structure. Compared to Pd complexes containing an *N*-alkyl substituted *N*,*N*-

di(2-picolyl)alkyl amine [26], these Pd(II) and Pt(II) complexes with N-cycloalkyl substituted *N*,*N*-di(2-picolyl)cycloalkylamine have similar C–H(and)···M and C()···M interactions (Table 3).

Table 3

[PdL₁]ClO₄, [PdL₂]ClO₄ and [PtL₂]ClO₄, with *N*-cyclopentyl and *N*-cyclohexyl substituents (Figs. 1, 2 and 4) exhibit weak C-H(and)…M contacts (Pd(II)…C = 2.926 and 2.964 Å, Pt(II) …C = 2.967 Å) that involve the second methylene group (C13 position) from the tertiary nitrogen atom (Table 3). The results indicate that the metal ion and the methylene group are weakly bonding [52-56].

2.4. Discussion of MMA polymerization

All of the Pd(II) complexes and [PtL₂]ClO₄ could be activated with MMAO to polymerise MMA. Since Pd(II) and Pt(II) complexes are cationic, their polymerizations of MMA were also carried out without MMAO. However, a tracee amount of PMMA was obtained. The obtained PMMA had a T_g value ranging from 120 to 145 °C [57-59]. The polymers were isolated as white solids and characterised by GPC in THF using standard polystyrene as the reference. The triad microstructure of the PMMA was analysed by ¹H NMR spectroscopy. The results of the polymerisations are summarised in Table 4 and include tacticity (isotactic (mm), heterotactic (mr), syndiotactic (rr)) and the polydispersity index (PDI) as the average degree of polymerisation in terms of the numbers of structural units and of molecules [60].

Table 4

To confirm the catalytic activity toward MMA polymerisation, a blank polymerisation of MMA was performed with $Pd(CH_3CN)_2Cl_2$, $Pt(CH_3CN)_2Cl_2$ and MMAO at a specified temperature. The tacticity of the PMMA was identified by the ¹H NMR peaks present at 0.85 (syndiotactic), 1.02 (heterotactic) and 1.21 (isotactic) [61]. The catalytic activities and PDIs for the Pd(II) complexes increased with the increasing ring size of the cycloalkyl group (cyclopentyl < cyclohexyl < cycloheptyl) and with increasing temperature (0 < 25 < 60 °C). Presumably, the electron-rich cloud around the Pd metal in [PdL₃]ClO₄ provided increased activity compared to the electronic effects with [PdL₁]ClO₄ and [PdL₂]ClO₄. The PDIs of the Pd(II) complexes were observed similarly in the range 1.92–2.41. The PDI range

decreased slightly with increasing PMMA molecular weight. These results are explained by the narrower PDI range of the higher-molecular-weight polymer [62,63]. [PdL₃]ClO₄ had the highest activity and provided PMMA with the narrowest PDI and highest molecular weight at 60 °C. This results is comparable to previous cobalt complexes with *N*,*N*-bis(1H-pyrazolyl-1methyl)aniline [64]. The activity of [PtL₂]ClO₄ towards the polymerisation of MMA at 60 °C was very low compared with the corresponding Pd(II) complex [PdL₂]ClO₄. However, the opposite was observed at 0 and 25 °C, i.e. higher activity was found for [PtL₂]ClO₄ than for [PdL₂]ClO₄. The syndiotacticity was not sufficiently high to infer a coordination polymerisation mechanism, but it was similar in all of the synthesised Pd(II) complexes. However, if it was considered that there was some contribution of a coordination polymerisation mechanism, the syndiotacticity was only slightly affected by the cycloalkyl ring size and the polymerisation temperature. Thus, the activity of these Pd(II) complexes toward MMA polymerisation should be considered in reference to the steric effect of the metal and the polymerisation temperature.

4. Conclusion

We have investigated the synthesis and X-ray crystallographic structures of $[PdL_1]ClO_4$, $[PdL_2]ClO_4$, $[PdL_3]ClO_4$ and $[PtL_2]ClO_4$, which were prepared by the substitution reaction of Pd(CH₃CN)₂Cl₂ and Pt(CH₃CN)₂Cl₂ with *N*,*N*-di(2-picolyl)cycloalkylamino ligands containing cycloalkyl bridging units. The coordination geometry around the Pd(II) and Pt(II) centres were almost square-planar. The catalytic activities of the Pd(II) complexes toward MMA polymerisation were determined: the PDI and molecular weight increased with increasing ring size of the substituent cycloalkyl bridge (cyclopentyl < cyclohexyl < cycloheptyl).

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Appendix A. Supplementary materials

CCDC 929887~929890 contain the supplementary crystallographic data for [PdL₁]ClO₄, [PdL₂]ClO₄ [PdL₃]ClO₄ and [PtL₂]ClO₄, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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

	[PdL ₁]ClO ₄	[PdL ₂]ClO ₄	[PdL ₃]ClO ₄	[PtL ₂]ClO ₄
Empirical formula	C ₁₇ H ₂₁ ClN ₃ Pd, ClO ₄	C ₁₈ H ₂₃ ClN ₃ Pd, ClO ₄	C ₁₉ H ₂₅ ClN ₃ Pd, ClO ₄	C ₁₈ H ₂₃ ClN ₃ Pt, ClO ₄
Formula weight	508.67	522.69	536.72	611.38
Temperature (K)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	$P2_1/c$	P2 ₁ /c	$P2_1/c$
Unit cell dimensions				
a (Å)	7.6306(3)	7.9172(3)	7.9255(3)	7.9631(4)
b (Å)	12.0847(4)	12.3689(5)	12.7413(5)	12.2958(6)
<i>c</i> (Å)	20.5565(8)	20.4344(7)	20.4875(8)	20.4364(9)
α (°)	90	90	90	90
β (°)	97.1580(10)	97.8260(10)	95.5860(10)	97.8630(10)
γ (°)	90	90	90	90
Volume (Å ³), Z	1880.81(12), 4	1982.44(13), 4	2059.03(14), 4	1982.17(16), 4
Density (calculated) (Mg/m ³)	1.796	1.751	1.731	2.049
Absorption coefficient (mm ⁻¹)	1.300	1.236	1.193	7.379
F(000)	1024	1056	1088	1184
Crystal size (mm ³)	0.23 x 0.23 x 0.18	0.27 x 0.25 x 0.24	0.32 x 0.24 x 0.21	0.28 x 0.21 x 0.19
Theta range for data collection (°)	1.96 to 28.28	1.93 to 28.28	1.88 to 28.28	1.94 to 28.30
Index ranges	-10 h 8	-10 h 10	-10 h 10	-10 h 8
	-16 k 14	-15 k 16	-14 k 16	-15 k 16
	-25 1 27	-27 1 20	-21 / 27	-27 1 27
	13531	14511	14402	13907
Reflections collected	4650 [R(int) = 0.0370]	4926 [R(int) = 0.0495]	5021 [R(int) = 0.0279]	4808 [R(int) = 0.028
Independent reflections	99.8 %	99.8 %	98.5 %	97.4%
Completeness to theta = 28.30°	None	None	None	None
Absorption correction	Full-matrix least-	Full-matrix least-	Full-matrix least-	Full-matrix least-
Refinement method	squares on F ²			
	4650 / 0 / 244	4926 / 0 / 253	5021 / 0 / 262	4808 / 0 / 253
Data / restraints / parameters	1.196	1.165	1.182	1.189
Goodness-of-fit on F ²	$R_1 = 0.0506$	$R_1 = 0.0398$	$R_1 = 0.0448$	$R_1 = 0.0365$
Final R indices [I>2sigma(I)]	$wR_2 = 0.1087$	$wR_2 = 0.0803$	$wR_2 = 0.1000$	$wR_2 = 0.0766$
	$R_1 = 0.0928$	$R_1 = 0.0849$	$R_1 = 0.0720$	$R_1 = 0.0677$
R indices (all data)	$wR_2 = 0.1880$	$wR_2 = 0.1449$	$wR_2 = 0.1620$	$wR_2 = 0.1427$
Largest diff. peak and hole (e Å ⁻³)	2.823 and -4.138	1.517 and -2.321	1.510 and -2.062	2.837 and -3.908

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

[PdL ₁]ClO ₄		[PdL ₂]ClO ₄		[PdL ₃]ClO ₄		[PtL ₂]ClO ₄				
Bond lengths										
Pd(1)-N(1)	2.009(8)	Pd(1)-N(1)	2.008(5)	Pd(1)-N(1)	2.009(5)	Pt(1)-N(1)	2.012(9)			
Pd(1)-N(2)	2.024(6)	Pd(1)-N(2)	2.022(5)	Pd(1)-N(2)	2.009(5)	Pt(1)-N(2)	2.004(9)			
Pd(1)-N(3)	2.028(6)	Pd(1)-N(3)	2.043(5)	Pd(1)-N(3)	2.056(4)	Pt(1)-N(3)	2.021(8)			
Pd(1)-Cl(1)	2.293(2)	Pd(1)-Cl(1)	2.2977(15)	Pd(1)-Cl(1)	2.2926(15)	Pt(1)-Cl(1)	2.297(3)			
N(3)-C(6)	1.507(9)	N(3)-C(6)	1.506(7)	N(3)-C(6)	1.496(7)	N(3)-C(6)	1.562(12)			
N(3)-C(7)	1.485(10)	N(3)-C(7)	1.509(7)	N(3)-C(7)	1.499(7)	N(3)-C(7)	1.496(13)			
N(3)-C(13)	1.521(9)	N(3)-C(13)	1.530(7)	N(3)-C(13)	1.514(7)	N(3)-C(13)	1.509(12)			
			Bond angle	es						
N(1)-Pd(1)-N(3)	84.2(3)	N(1)-Pd(1)-N(3)	83.02(19)	N(1)-Pd(1)-N(3)	83.23(18)	N(1)-Pt(1)-N(3)	84.7(3)			
N(3)- Pd(1)-N(2)	82.9(3)	N(3)- Pd(1)-N(2)	84.59(19)	N(3)- Pd(1)-N(2)	84.8(2)	N(3)-Pt(1)-N(2)	82.1(4)			
N(1)-Pd(1)-Cl(1)	97.2(2)	N(1)-Pd(1)-Cl(1)	95.49(14)	N(1)-Pd(1)-Cl(1)	95.75(14)	N(1)-Pt(1)-Cl(1)	97.3(3)			
N(2)-Pd(1)-Cl(1)	95.8(2)	N(2)-Pd(1)-Cl(1)	97.04(2)	N(2)-Pd(1)-Cl(1)	96.20(2)	N(2)-Pt(1)-Cl(1)	96.1(3)			
N(1)-Pd(1)-N(2)	165.7(3)	N(1)-Pd(1)-N(2)	165.7(2)	N(1)-Pd(1)-N(2)	166.1(2)	N(1)-Pt(1)-N(2)	165.3(4)			
N(3)-Pd(1)-Cl(1)	178.30(19)	N(3)-Pd(1)-Cl(1)	178.03(14)	N(3)-Pd(1)-Cl(1)	178.94(14)	N(3)-Pt(1)-Cl(1)	177.5(2)			
C(7)-N(3)-C(6)	112.3(6)	C(7)-N(3)-C(6)	111.9(4)	C(7)-N(3)-C(6)	113.0(4)	C(7)-N(3)-C(6)	110.6(7)			
C(7)-N(3)-C(13)	110.4(6)	C(6)-N(3)-C(13)	112.0(4)	C(6)-N(3)-C(13)	110.3(4)	C(6)-N(3)-C(13)	111.0(7)			
C(6)-N(3)-C(13)	112.6(6)	C(7)-N(3)-C(13)	113.5(4)	C(7)-N(3)-C(13)	113.0(4)	C(7)-N(3)-C(13)	110.9(8)			
C(7)-N(3)-Pd(1)	102.0(5)	C(7)-N(3)-Pd(1)	107.2(3)	C(7)-N(3)-Pd(1)	107.7(3)	C(7)-N(3)-Pt(1)	102.5(6)			
C(6)-N(3)-Pd(1)	108.7(5)	C(6)-N(3)-Pd(1)	101.3(3)	C(6)-N(3)-Pd(1)	100.1(3)	C(6)-N(3)-Pt(1)	107.9(6)			
C(13)-N(3)-Pd(1)	110.2(4)	C(13)-N(3)-Pd(1)	110.2(3)	C(13)-N(3)-Pd(1)	112.0(3)	C(13)-N(3)-Pt(1)	113.6(6)			

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

				0104	լլ գրշյ	0104		
	$Pd(1)\cdots C(13)$	2.924	Pd(1)…C(13)	2.945	Pd(1)…C(13)	2.975	Pt(1)…C(13)	2.967
	Pd(1)…H(13)	2.926	Pd(1)…H(13)	2.964	Pd(1)…H(13)	3.075	Pt(1)…H(13)	2.988
	Pd(1)…H(14a)	3.126	Pd(1)…H(18a)	2.806	Pd(1)…H(19a)	2.767	Pt(1)…H(14a)	2.823
	Pd(1)… H(14b)	3.722	Pd(1)… H(18b)	3.713	Pd(1)… H(19b)	3.475	Pt(1)… H(14b)	3.735
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Table 3. Selected C–H(and)···M and C()··· M bond distances (Å).

Entry	Catalyst ^a	Temp.(time)	Yield	Activity ^c	Tg		Tacticity		$M_{\rm w}{}^d$	M _w /M _n
		(°C)	(g)	(g/mol- Cat·h)×10 ⁴	(°C)	%mm	%mr	%rr	(g/mol)×10 ⁵	
1	$Pd(AN)_2Cl_2^e$	60(2hr)	0.88	2.93	131.47	7.66	22.81	69.53	0.66	2.90
2	$Pt(AN)_2Cl_2^e$	60(2hr)	0.36	1.20	128.31	9.69	23.87	66.44	9.66	1.88
3	$\mathbf{MMAO}^{\mathrm{f}}$	60(2hr)	0.42	1.40	119.61	37.20	10.92	51.88	6.78	2.09
4	[PdL ₁]ClO ₄	60(2hr)	1.09	3.63	128.46	8.20	29.71	62.09	2.76	2.06
5	[PdL ₂]ClO ₄	60(30min)	0.96	12.8	129.83	6.75	20.11	73.14	8.15	1.97
6	[PdL ₃]ClO ₄	60(10min)	1.44	19.2	128.58	7.36	22.06	69.58	8.42	1.92
7	[PtL ₂]ClO ₄	60(2hr)	0.40	1.3	127.25	9.53	24.83	65.64	4.58	6.02
8	$Pd(AN)_2Cl_2^e$	25(2hr)	0.55	1.83	129.93	8.84	19.73	71.43	0.72	2.97
9	$Pt(AN)_2Cl_2^e$	25(2hr)	0.15	0.5	124.23	15.15	27.37	57.48	0.97	3.15
10	$\mathrm{MMAO}^{\mathrm{f}}$	25(2hr)	0.14	0.47	125.29	15.46	28.36	56.18	1.12	3.95
11	[PdL ₁]ClO ₄	25(2hr)	0.21	0.70	121.40	13.53	29.51	56.96	0.41	2.25
12	[PdL ₂]ClO ₄	25(2hr)	0.24	0.80	120.31	13.30	29.43	57.27	0.35	2.14
13	[PdL ₃]ClO ₄	25(2hr)	0.47	1.57	122.27	7.77	18.94	73.29	0.39	1.93
14	[PtL ₂]ClO ₄	25(2hr)	0.64	2.1	126.29	7.85	19.04	73.11	2.46	7.54
15	$Pd(AN)_2Cl_2^e$	0(2hr)	0.38	1.27	129.05	9.22	18.91	71.87	9.93	1.70
16	$Pt(AN)_2Cl_2^e$	0(2hr)	0.17	0.57	127.25	12.15	23.70	64.15	2.73	4.13
17	MMAO ^f	0(2hr)	0.12	0.40	129.50	11.59	28.78	59.63	3.25	2.56
18	[PdL ₁]ClO ₄	0(2hr)	0.01	0.03	123.60	11.29	30.37	58.34	0.91	2.41
19	[PdL ₂]ClO ₄	0(2hr)	0.14	0.47	125.63	10.26	28.96	69.78	0.51	2.04
20	[PdL ₃]ClO ₄	0(2hr)	0.07	0.23	123.74	10.22	29.34	60.44	0.70	2.41
21	[PtL ₂]ClO ₄	0(2hr)	0.26	0.86	128.81	9.12	22.81	68.07	1.58	2.93

Table 4. Polymerisation of MMA by the Pd(II) and Pt(II) complexes in the presence of MMAO.

^a [Mt (II) catalyst]₀ = 15 μ mol, and [MMA]₀/[MMAO]₀/[Mt (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 Determined by GPC eluted with THF at room temperature by filtration with polystyrene calibration. ^e A blank polymerization in which Pd(AN)₂Cl₂ and Pt(AN)₂Cl₂ were also activated by MMAO. ^f A blank polymerization which was done solely by MMAO.



Fig. 1. ORTEP drawing of [PdL₁]ClO₄ with thermal ellipsoids at 50% probability. Some hydrogen atoms have been omitted for clarity.



Fig. 2. ORTEP drawing of $[PdL_2]ClO_4$ with thermal ellipsoids at 50% probability, showing two different views. Some hydrogen atoms have been omitted for clarity.



Fig. 3. ORTEP drawing of [PdL₃]ClO₄ with thermal ellipsoids at 50% probability. Some hydrogen atoms have been omitted for clarity.



Fig. 4. ORTEP drawing of [PtL₂]ClO₄ with thermal ellipsoids at 50% probability. All hydrogen atoms have been omitted for clarity.

Palladium(II) and Platinum(II) Complexes with *N*,*N*',*N*-Tridentate Ligands Based on *N*,*N*-Di(2-Picolyl)Cycloalkylamine: Synthesis, Characterisation and Polymerisation of Methyl Methacrylate

Dongil Kim^a, Sunghoon Kim^a, Eunhee Kim^a, Ha-Jin Lee^b, Hyosun Lee^{a,*}

The complexes $[PdL_1]ClO_4$, $[PdL_2]ClO_4$, $[PdL_3]ClO_4$ and $[PtL_2]ClO_4$, where, for example, L_1 is *N*,*N*-di(2-picolyl)cyclopentylamine, were synthesized and characterized by X-ray crystallography. The coordination geometry around the Pd(II) and Pt(II) centres were almost square-planar and the catalytic activities of the Pd(II) complexes toward MMA polymerisation were moderate.

MAS

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Graphical Abstract



Research Highlights

- > The synthesis and molecular structures of $[PdL_n]ClO_4$ with N,N-di(2picolyl)cycloalkylamino ligands are reported.
- The second secon > A square-planar geometry around Pd(II) and Pt(II) included a ClO_4^- anion in the unit cell.