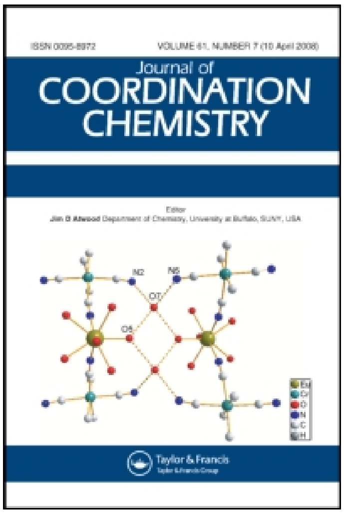

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, and reactivity studies in ethylene polymerization of cyclometalated palladium(II) complexes containing terdentate ligands with N,C,N-donors

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To cite this Article Hurtado, John , Portaluppi, Mariana , Quijada, Raúl , Rojas, René and Valderrama, Mauricio(2009) 'Synthesis, characterization, and reactivity studies in ethylene polymerization of cyclometalated palladium(II) complexes containing terdentate ligands with N,C,N-donors', Journal of Coordination Chemistry, 62: 17, 2772 — 2781

To link to this Article: DOI: 10.1080/00958970902929344

URL: http://dx.doi.org/10.1080/00958970902929344

Journal of Coordination Chemistry
Vol. 62, No. 17, 10 September 2009, 2772–2781

Synthesis, characterization, and reactivity studies in ethylene polymerization of cyclometalated palladium(II) complexes containing terdentate ligands with N,C,N-donors

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(*Received 9 October 2008; in final form 20 February 2009*)

The reaction of [Na_2PdCl_4] with 3,5-*bis*(2-pyridoxy)toluene ($L_{py}H$) in acetic acid yields the cyclometalated complex [$PdCl(L_{py}$-N, C, N)] (**1**). Complex **1** can be further converted into neutral species by metathesis reaction exchange of chloride by either iodide or thiocyanate to yield [$PdX(L_{py}$-N, C, N)] (X = I (**2**), SCN (**3**)). The chloride can be replaced by neutral ligands like pyridine or acetonitrile in the presence of silver tetrafluoroborate to give the corresponding cationic compounds [$PdL(L_{py}$-N, C, N)]BF_4 (L = Py (**4**), MeCN (**5**)). In contrast, the reaction of [Na_2PdCl_4] with 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene ($L_{pz}H$) under analogous conditions yields the neutral complex [$PdCl_2(L_{pz}H$-N, N)](**6**) with the ligand bidentate N,N-donor. The cyclometalated palladium complex [$PdCl(L_{pz}$-N, C, N)] (**7**) was prepared by the reaction of $Pd(OAc)_2$ with $L_{pz}H$ in acetic acid followed by a metathetic reaction with lithium chloride in acetone/water. Complexes **1**, **6**, and **7** in the presence of methylaluminoxane (MAO) lead to an active catalyst for the polymerization of ethylene.

Keywords: Palladium; Cyclometalated complexes; Ethylene polymerization

1. Introduction

Synthesis of transition metal complexes having terdentate ligands (pincer type) has received much attention due to their potential applications as catalysts, chemosensors, and in material science [1–3]. These complexes consist of a metal centre bonded to an anionic terdentate ligand of general formula $[2,6\text{-}(ECH_2)_2C_6H_3]^-$, where E is a neutral two-electron donor (N, P, O, S), as well as to a counterion or a neutral ligand, figure 1.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902929344

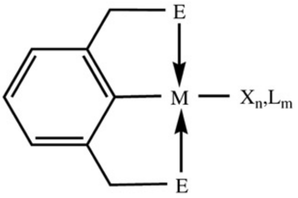


Figure 1.

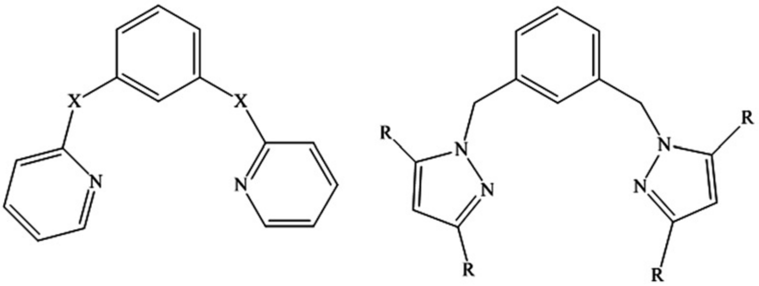


Figure 2. X = NH, CO, CHMe, O; R = H, Me, Ph.

These compounds are highly stable due to the formation of two five-membered metallocycles that provide additional stabilization to the carbon–metal bond. By varying the nature of the electron donors E, the electronic properties, and reactivity of the metal centre can be tuned [4, 5]. The most widely studied complexes are derivatives of platinum and palladium containing nitrogen or phosphorus donors [1].

Recently, some groups have explored more flexible six-membered rings, in particular those employing pyridine or pyrazole as donors connected to the central aryl ring by a spacer atom, which have potential to facilitate either regular meridional or facial geometry at the metal centre [6–12], figure 2.

Cyclopalladate complexes derived from these types of ligands have been used as catalyst precursors. For example, Yoon *et al.* [6] and Dijkstra *et al.* [10] reported that complexes derived from 1,3-*bis*(2-pyridoxy)benzene and 1,3-*bis*(3, 5-R_2pyrazol-1-ylmethyl)benzene ($R = H, Me$) are efficient catalysts for the Heck reaction between aryl halides and methyl acrylate and as Lewis acids in the double Michael reaction between methyl vinyl ketone and ethyl α-cyanoacetate.

We have been interested in synthesis of transition metal complexes that activate ethylene in homogeneous solution to form polyethylene [13]. This type of catalytic activity is not known for the above mentioned cyclopalladate complexes, and we expect the increased flexibility of the pincer complexes to facilitate dissociation of pyridine or pyrazole rings to generate an active coordinatively unsaturated catalyst system. In this article we report the synthesis and characterization of cyclometalated palladium(II) complexes [PdCl(κ^3-NCN)], containing 3,5-*bis*(2-pyridoxy)toluene (**1**) and 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene (**7**) as anionic terdentate ligands (NCN). The reactivity of the chloride ligand in **1** was studied with respect to its substitution with anionic or neutral ligands. In this work we also describe the activity of the neutral chloride complexes (**1**, **6**, and **7**) in ethylene polymerization.

2. Experimental

2.1. *General remarks*

The reactions were carried out in purified nitrogen. Solvents were dried, distilled, and stored under nitrogen. The starting compounds [$PdCl_2$(cod)] (cod = 1, 5-cyclooctadiene) [14] and 3,5-*bis*(2-pyridoxy)toluene [7] were synthesized as described in the literature. Other reagents were purchased from commercial sources and used without purification. Elemental analyses (C, H, N) were carried out on a Fisons EA 1108 CHNS-O microanalyzer. FTIR spectra were recorded in the region of 4000–250 cm^{-1}, with samples prepared as KBr discs, on a Bruker Vector-22 spectrophotometer. The NMR spectra were recorded on Bruker AC-200P and Avance-400 spectrometers and the chemical shifts are reported in ppm relative to $SiMe_4$ (^1H, ^{13}C). EI mass spectra were obtained at 70 eV on a Thermo-Finnigan MAT95 XP High Resolution Mass Spectrometer using perfluorokerosene (PFK) as reference. Melting points were determined using an Electrothermal melting point apparatus in open capillary tubes and are uncorrected.

2.2. *Synthesis of 3,5-bis(3,5-dimethylpyrazol-1-ylmethyl)toluene*

A mixture of 3,5-dimethylpyrazole (1.97 g; 20.5 mmol), potassium hydroxide (2.314 g; 41.2 mmol), tetrabutylammonium bromide (0.212 g; 0.63 mmol), and water (1 mL) was stirred at room temperature for 25 min. Then 3,5-*bis*(bromomethyl)toluene (2.668 g; 9.6 mmol) and toluene (25 mL) were added and the reaction mixture was refluxed for 72 h. The resultant mixture was treated with water and the organic layer separated and was dried with magnesium sulphate. The solution was evaporated to dryness to give a brown oil that solidifies with time. The product was dissolved in minimal diethyl ether and the solution was allowed to stand at –25°C. White-yellow crystals were formed, which were collected by filtration, washed with cold pentane, and dried under vacuum. Yield 1.716 g (58%), m.p.: 86–87°C. NMR ($CDCl_3$, 295 K): ^1H, δ 2.10 (s, 6H, pyrazolyl-CH_3), 2.23 (s, 9H, CH_3, pyrazolyl, tolyl-CH_3), 5.11 (s, 4H, CH_2), 5.82 (s, 2H, pyrazolyl-H), 6.53 (s, 1H, tolyl-H), and 6.74 (s, 2H, tolyl-H). $^{13}C\{^1H\}$, δ 11.1 (CH_3), 13.5 (CH_3), 21.3 (CH_3), 52.3 (CH_2), 105.5, 121.9, 126.3, 137.6, 138.9, 139.1, and 147.5 ppm (C, tolyl, and pyrazolyl rings). EI-MS (70 eV, *m*/*z*, %): 308.2 (M^+, 100). Anal. Calcd for $C_{19}H_{24}N_4$ (%): C, 74.0; H, 7.8; N, 18.2. Found: C, 73.5; H, 8.0; N, 18.0.

2.3. *Synthesis of complexes*

2.3.1. [PdCl{$MeC_6H_2(Opy)_2$-N, C, N}] (1). A solution of [Na_2PdCl_4] (1.41 g; 4.8 mmol) and 3,5-*bis*(2-pyridoxy)toluene (1.33 g; 4.8 mmol) in glacial acetic acid (70 mL) was refluxed for 24 h. The resulting mixture was cooled to room temperature, treated with 150 mL of distilled water, and extracted with 3 × 40 mL of chloroform. The organic extracts were combined and dried with $MgSO_4$. The filtered chloroform solution was evaporated to dryness to give a white solid. The complex was purified by silica gel column chromatography (type 60) using ethyl acetate as eluent. Yield 583 mg (29%). NMR ($CDCl_3$, 295 K): ^1H, δ 2.35 (s, 3 H, tolyl-CH_3), 6.84 (s, 2 H, tolyl-H), 7.09 (m, 2 H, pyridoxyl-H), 7.23 (m, 2 H, pyridoxyl-H), 7.84 (m, 2H, pyridoxyl-H), and

9.39 ppm (m, 2H, pyridoxyl-H). $^{13}C\{^1H\}$, δ 20.74 (CH_3), 114.45, 115.0, 119.01, 137.09, 141.32, 151.24, 152.87, and 158.5 ppm (C, tolyl, and pyridine rings). Anal. Calcd for $C_{17}H_{13}ClN_2O_2Pd$ (%): C, 48.7; H, 3.1; N, 6.7. Found: C, 48.5; H, 3.1; N, 6.7.

2.3.2. [PdX{MeC$_6$H$_2$(Opy)$_2$-N, C, N}] {X = I (2); SCN (3)}. To a solution of complex **1** (100 mg; 0.24 mmol) in acetone (6 mL), a solution of NaI or KSCN (0.24 mmol) in acetone (3 mL) was added dropwise. After stirring at room temperature for 48 h the reaction mixture was filtered through Kieselguhr and evaporated to dryness. The solid residue was dissolved in CH_2Cl_2 and chromatographed on Kieselgel (type 60) using ethyl acetate as eluent.

Complex **2**: Yellow solid, yield: 62 mg (68%). NMR ($CDCl_3$, 295 K): ^1H, δ 2.34 (s, 3 H, tolyl-CH_3), 6.98 (s, 2 H, tolyl-H), 7.02 (m, 2 H, pyridoxyl-H), 7.30 (m, 2 H, pyridoxyl-H), 7.86 (m, 2H, pyridoxyl-H), and 9.61 ppm (m, 2H, pyridoxyl-H). Anal. Calcd for $C_{17}H_{13}IN_2O_2Pd$ (%): C, 40.0; H, 2.6; N, 5.5. Found: C, 39.3; H, 2.2; N, 5.4.

Complex **3**: White solid, yield: 58 mg (64%). IR (KBr, cm^{-1}): ν(SCN), 2137 (w), 2084 (w). NMR ($CDCl_3$, 295 K): ^1H, δ 2.28 (s, 3 H, tolyl-CH_3), 6.54 (s, 2 H, tolyl-H), 7.16 (m, 2 H, pyridoxyl-H), 7.23 (m, 2 H, pyridoxyl-H), 7.78 (m, 2H, pyridoxyl-H), and 8.32 ppm(m, 2H, pyridoxyl-H). Anal. Calcd for $C_{18}H_{13}N_3O_2SPd$ (%): C, 48.9; H, 3.0; N, 9.5; S, 7.3. Found: C, 48.5; H, 2.9; N, 9.5; S, 7.2.

2.3.3. [PdL{MeC$_6$H$_2$(Opy)$_2$-N, C, N}]BF$_4$ {L = Py (4); MeCN (5)}. To a solution of **1** (100 mg; 0.24 mmol) in acetone (10 mL) a solution of $AgBF_4$ (48 mg; 0.24 mmol) in acetone (5 mL) was added. After stirring the mixture for 2 h at room temperature in the absence of light, the precipitated silver chloride was removed by filtration through Kieselguhr. A slight excess of ligand (py, 0.02 mL; MeCN, 9 mL) was added and the mixture was stirred again for 3 h. The resulting solution was evaporated to a small volume and the complex precipitated by adding diethyl ether.

Complex **4**: White solid, yield 68 mg (52%). IR (KBr, cm^{-1}): $\nu(BF_4^-)$, 1084 (s, br), 520 (m). NMR ($CDCl_3$, 295 K): ^1H, δ 2.47 (s, 3 H, tolyl-CH_3), 7.05 (s, 2 H, tolyl-H), 7.27 (m, 2 H, pyridoxyl-H), 7.68 (m, 2 H, pyridoxyl-H), 7.85(m, 4 H, pyridoxyl-H, pyridine-H), 8.26 (m, 3 H, pyridoxyl-H, pyridine-H), and 9.04 ppm (m, 2 H, pyridine-H). Anal. Calcd for $C_{22}H_{18}BF_4N_3O_2Pd$ (%): C, 48.1; H, 3.3; N, 7.6. Found: C, 47.5; H, 3.1; N, 7.9.

Complex **5**: White solid, yield 98 mg (82%). IR (KBr, cm^{-1}): $\nu(BF_4^-)$, 1056 (s, br), 520 (m); ν(CN), 2362 (w), 2288 (w). NMR ($CDCl_3$, 295 K): ^1H, δ 2.11 (s, 3 H, acetonitrile-CH_3), 2.46 (s, 3 H, tolyl-CH_3), 7.04 (s, 2 H, tolyl-H), 7.47 (m, 2 H, pyridoxyl-H), 7.69 (m, 2 H, pyridoxyl-H), 8.34 (m, 2 H, pyridoxyl-H) and 8.47 ppm (m, 2 H, pyridoxyl-H). Anal. Calcd for $C_{19}H_{16}BF_4N_3O_2Pd$ (%): C, 44.6; H, 3.2; N, 8.2. Found: C, 45.2; H, 3.9; N, 8.6.

2.3.4. [PdCl$_2$\{MeC$_6$H$_3$(CH$_2$Me$_2$pz)$_2$-N, N\}] (6). The complex can be prepared by two methods: (a) A solution of $[Na_2PdCl_4]$ (353 mg; 1.2 mmol) and 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene (363 g; 1.2 mmol) in glacial acetic acid (15 mL) was heated under reflux for 24 h. The resulting mixture was cooled to room temperature, treated with 150 mL of distilled water and extracted with chloroform (3 × 40 mL). The organic extracts were combined and dried with $MgSO_4$. The filtered chloroform solution was evaporated to dryness to give a yellow solid. The complex was purified by silica gel column chromatography (type 60) using ethyl acetate as eluent, and then crystallized from chloroform-pentane. Yield 119 mg (20%).

(b) A solution of [$PdCl_2$(cod)] (142.7 mg; 0.5 mmol) and 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene (154.2 mg; 0.5 mmol) in acetonitrile (20 mL) was stirred at room temperature for 21 h. Complete reaction of the starting palladium complex was followed by thin layer chromatography. The solution was evaporated under vacuum to give a yellow solid, which was crystallized from chloroform–diethyl ether. Yield 182 mg (82%). NMR ($CDCl_3$, 295 K): ^{1}H, δ 2.06 (s, 6 H, pyrazolyl-CH_3), 2.29 (s, 3 H, tolyl-CH_3), 2.92 (s, 6 H, pyrazolyl-CH_3), 5.72 (s, 4 H, CH_2), 5.91 (s, 2 H, pyrazolyl-H_4'), 6.91 (s, 2 H, tolyl-$H_{2,6}$), and 7.52 (s, 1 H, tolyl-H_4). $^{13}C\{^1H\}$, δ 12.1 (CH_3), 15.3 (CH_3), 21.3 (CH_3), 52.7 (CH_2), 107.9, 123.3, 127.6, 135.6, 138.9, 143.6, and 150.3 ppm (C, tolyl, and pyrazolyl rings). EI-MS (70 eV, m/z, %): 486.1 (M^+, > 1), 450.1 ($M^+ - HCl$, 2), 412.1 ($M^+ - HCl_2$, 10), 308.2 ($M^+ - PdCl_2$, 100). Anal. Calcd for $C_{19}H_{24}Cl_2N_4Pd$ (%): C, 47.0; H, 5.0; N, 11.5. Found: C, 46.8; H, 4.8; N, 11.0.

2.3.5. [PdCl{$MeC_6H_2(CH_2Me_2pz)_2$-N, C, N}] (7). A solution of palladium(II) acetate (126 mg; 0.57 mmol) and 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene (172 mg; 0.57 mmol) in glacial acetic acid (15 mL) was refluxed for 6 h. The solvent was removed under reduced pressure, and the resulting residue was stirred with lithium chloride (127 mg; 3 mmol) in an acetone: water mixture (9 : 6, 15 mL) for 3 days. The yellowish white residue obtained was filtered off, washed with acetone, and dried under vacuum. White crystals were obtained from dichloromethane-pentane. Yield 194 mg (65%). NMR ($CDCl_3$, 295 K): ^{1}H, δ 2.25 (s, 3 H, tolyl-CH_3), 2.32 (s, 6 H, pyrazolyl-CH_3), 2.62 (s, 6 H, pyrazolyl-CH_3), 4.84 (d, 2 H, $^2J(HH) = 14$ Hz, CH_2), 5.61 (d, 2 H, $^2J(HH) = 14$ Hz, CH_2), 5.79 (s, 2 H, pyrazolyl-H_4'), and 6.77 (s, 2 H, tolyl-$H_{2,6}$). $^{13}C\{^1H\}$, δ 11.6 (CH_3), 15.6 (CH_3), 20.5 (CH_3), 54.3 (CH_2), 107.0, 125.9, 134.0 (C-Pd), 135.9, 140.1, 140.9, and 152.4 ppm (C, tolyl, and pyrazolyl rings). EI-MS (70 eV, m/z, %): 450.1 (M^+, 15), 412.1 ($M^+ - Cl$, 100). Anal. Calcd for $C_{19}H_{23}ClN_4Pd$ (%): C, 50.8; H, 5.2; N, 12.5. Found: C, 50.3; H, 5.3; N, 12.4.

2.4. *Catalytic reactions*

Polymerizations were carried out by charging a 500 mL Parr autoclave with toluene (240 mL), the desired amount of cocatalyst (methylaluminoxane, MAO) and catalysts **1**, **6**, and **7** under nitrogen. The reactor was attached to an ethylene line, and the gas was fed continuously into the reactor at a specific pressure. The pressurized reaction mixture was stirred at 60°C controlled by the reactor heater. Ethylene consumption was monitored by mass flow controlled inline with the ethylene feed. At the end of the reaction the ethylene feed was removed, the vessel vented, and the reaction quenched with HCl–methanol (20% v/v). The polymers produced were separated by filtration and washed several times with acetone. They were then dried overnight under vacuum, and the polymerization activity was calculated from the mass of product obtained. The polymers were characterized by GPC (in a High Temperature Chromatograph, Pl-GPC 200). The polymer melting points were measured on a model DSC 2920 Differential Scanning Calorimeter at a rate of 10°C min^{-1} for three cycles in a temperature range of 50–200°C.

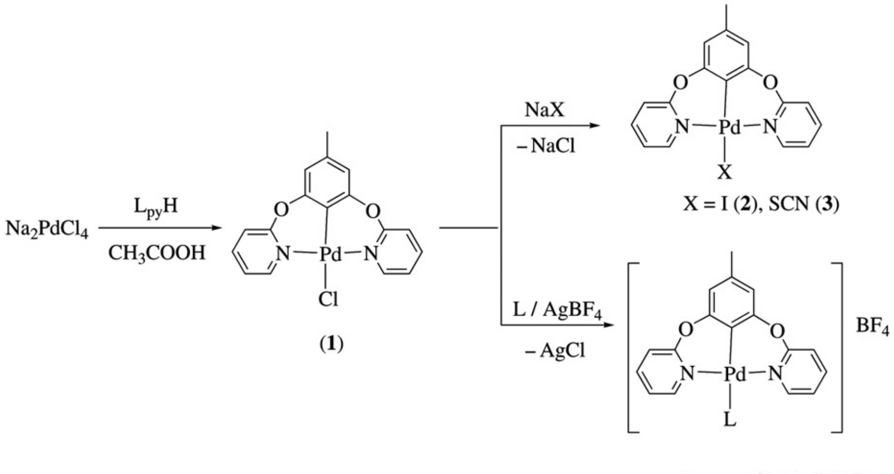
3. Results and discussion

3.1. *Synthesis and characterization of the complexes*

3,5-*bis*(2-pyridoxy)toluene ($L_{py}H$) was prepared according to a reported synthetic method [7]. 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene ($L_{pz}H$) was synthesized by reaction of 3,5-*bis*(bromomethyl)toluene with two equivalents of 3,5-dimethylpyrazolate, generated *in situ* using potassium hydroxide and tetrabutylammonium bromide (TBAB) in refluxing toluene.

[Na_2PdCl_4] reacts with stoichiometric amount of 3,5-*bis*(2-pyridoxy)toluene in refluxing acetic acid to give the neutral cyclometalated complex [PdCl(L_{py}-N, C, N)] (**1**) which was isolated as white solid, stable in air at room temperature. The chloride bonded *trans* to the Pd–C σ-bond shows remarkable lability due to the strong trans effect of the cyclometalated aryl ring [15]. Thus, chloride can easily be displaced by a metathetic reaction with NaX in acetone to give the neutral complexes [PX(L_{py}-N, C, N)] [$X = I^-$ (**2**), SCN^- (**3**)], and substituted by neutral ligands in the presence of silver salt to afford the corresponding cationic complexes [PdL(L_{py}-N, C, N)]BF_4 (L = Py, MeCN). The synthetic routes to the complexes are summarized in scheme 1.

All complexes were isolated as stable microcrystalline solids and characterized by elemental analysis, IR, and NMR spectrometry. The ^{1}H NMR spectra of the cyclometalated complexes **1**–**5** show slight variations in the positions of the proton resonances of the coordinated pincer ligand. These resonances were assigned by comparison with known values for the similar platinum(II) compounds [7]. The spectra show two singlets in the δ 2.2–2.5 and 6.8–7.0 ppm range, assigned to the methyl and H-tolyl protons, together with four multiplets in the δ 7.0–9.6 ppm range, corresponding to the pyridoxyl ring protons. Moreover, complex **4** exhibits three multiplets of the pyridine ring protons masked with the pyridoxyl resonances, and **5** has a singlet at δ 2.11 ppm, corresponding to the methyl group of the coordinated acetonitrile. The solid state IR spectra of the cationic complexes in KBr pellets show characteristic

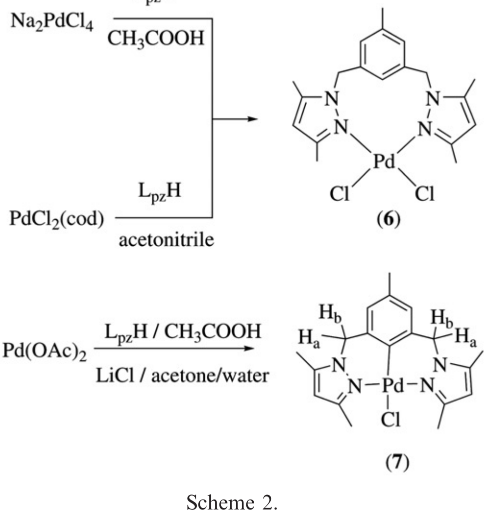


Scheme 1.

absorptions of uncoordinated BF_4^- (~1100 and 520 cm^{-1}), and **5** shows the absorptions of the coordinated acetonitrile, ν(CN), at 2362 and 2288 cm^{-1}.

Reaction of [Na_2PdCl_4] with $L_{pz}H$ in refluxing acetic acid only produced a yellow solid, characterized as the neutral complex [$PdCl_2(L_{pz}H$-N, N)] (**6**) with the ligand bidentate N,N-donor. This compound was synthesized in high yield by reaction of [$PdCl_2$(cod)] (cod = 1, 5-cyclooctadiene) with $L_{pz}H$ in acetonitrile. The cyclometalated palladium complex [PdCl(L_{pz}-N, C, N)] (**7**) was prepared by the reaction of $Pd(OAc)_2$ with $L_{pz}H$ in refluxing acetic acid, followed by a metathetic reaction with lithium chloride in acetone/water. All reactions are included in scheme 2.

Complexes **6** and **7** were fully characterized by microanalysis, NMR, and mass spectroscopy. The ^1H spectra of these complexes are consistent with the proposed formulations with resonances assigned to tolyl and pyrazolyl rings in the required intensity ratios. Thus, for **6** the ^1H NMR spectrum shows three singlets in the δ 2.0–3.0 ppm range assigned to methyl, two singlets at δ 5.52 and 5.91 ppm assigned to methylene and to the H_4' proton of the pyrazolyl ring, respectively, together with two singlets at low field, δ 6.91 and 7.52 ppm, corresponding to the tolyl protons $H_{2,6}$ and H_4, respectively. For **7**, the ^1H NMR shows a similar pattern of signals for the methyl, the H_4'-pyrazolyl and $H_{2,6}$-tolyl protons. However, the methylene protons are two doublets at δ 4.48 and 5.16 ppm ($^2J(HH) = 14$ Hz), corresponding to non-equivalent H_a and H_b. These results indicate that the square-planar palladium polyhedron (N, C, N, Cl) is twisted out of the plane of the toluene ring, placing the two pyrazolyl rings on opposite sites of the plane of the toluene ring, generating two different environments for the methylene protons [9]. The number of signals in the ^{13}C NMR spectra of **6** and **7** confirm the proposed structures. The spectrum of complex **7** shows five signals at low field, corresponding to quaternary carbons (DEPT). By comparison with the ^{13}C NMR spectrum of the ligand, the signal that appears at δ 134.0 ppm is assigned to the carbon bonded to palladium.



Scheme 2.

3.2. *Ethylene polymerization activities*

Reactivity of **1**, **6**, and **7** activated using MAO toward ethylene, was carried out under mild reaction conditions. The catalytic behavior and properties of the polymers are summarized in table 1.

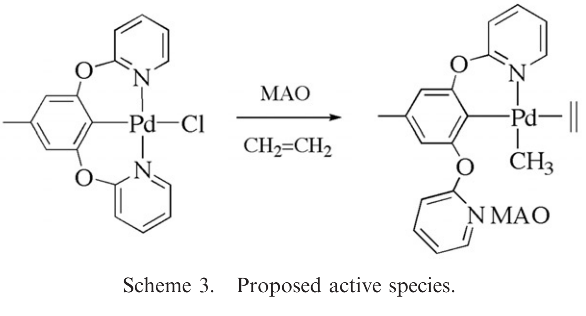
Complex **1** shows high activity, in accord with values normally obtained for non-metallocene complexes [16]. This activity is similar to that obtained by Perez *et al.* [17] for related cyclopalladate complexes derived from phenylhydrazones (C, N, N-donor). For these compounds, which have a single chloride, UV-visible spectroscopy supports the formation of successive steps in the polymerization reaction with formation of cationic species. On the basis of these results we believe that the polymerization reaction using the pincer complexes occurs by a similar mechanism, where the first step is replacement of the chloride by a methyl group that increase the electron density of the palladium centre (all the attempts to prepare the methyl derivatives [PdMe(L-N, C, N)] were unsuccessful. Thus, the treatment of complexes **1** and **7** with LiBu in THF at low temperature give rise to a mixture of uncharacterized solids. Traces of reduced palladium(0) is observed), followed by cleavage of a Pd–N bond which generates a vacancy at the metal centre. Moreover, it is probable that in the active species the lone nitrogen pair of free pyridine causes an interaction with the methylaluminoxane (scheme 3), which behaves as a Lewis acid [18]. This acid–base complexation has been recently reported in complexes bearing ligands with basic functionalities [13e, 19].

The similar cyclopalladated complex **7** shows lower activity, probably due to the fact that the stability of the Pd–N (pyrazole) bond decreases the rate of cleavage of the Pd–N bond, and additionally the higher electron density on the metal increases the insertion barrier of the coordinated ethylene. The dichloride complex **6** has moderate

Table 1. Ethylene polymerization data.[a]

Precatalysts	[Precat.] (mol × 10^6)	Yield (g)	Activity[b]	T_m (°C)	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
1	8.11	4.80	148	135	128,000	65,600	1.9
6	8.23	3.30	100	134	64,000	33,700	1.9
7	8.01	2.15	67	136	69,000	43,100	1.6

[a] Reaction conditions: solvent, toluene (240 mL); MAO/toluene 10% (15 mL); ratio Al/Pd = 3,000; polymerization time, 1 h; stirrer rate, 1000 rpm; reaction temperature, 60°C; pressure, 4 bar.
[b] kg polymer/(mol precat.)(h)(bar).



Scheme 3. Proposed active species.

activity, lower than that shown for related palladium compounds obtained with 1,3-*bis*(3, 5-R_2pyrazol-1-ylcarbonyl)benzene as N,N-bidentate ligand ($R = Me, {}^tBu, Ph$), in which the presence of a functional carbonyl group reduces the σ-donor ability of the nitrogens of the pyrazole ligands [20]. In this case the polymerization occurs through the general mechanism proposed for dichloride compounds, Cp_2ZrCl_2 [21]. Thus, the addition of MAO promotes the replacement of the chlorides by a methyl group and a vacant place for olefin coordination, and the metal acquires a positive charge stabilized by an $[MAO–Cl]^-$ counteranion.

FTIR, DSC, and GPC measurements were carried out to characterize the polymers. The FTIR spectra show signals corresponding to a typical polyethylene at 2918 and 2849 cm^{-1}, assigned to ν(CH), and at 1473 and 719 cm^{-1}, corresponding to δ (CH) and δ $(CH_2)_x$ ($x > 4$), respectively [22]. DSC analysis showed melting points in the range of 134–136°C, typical of linear polyethylene. The GPC analysis of the resulting polymers obtained with the three compounds showed that **1** produces high molecular weight polyethylene (M_w). Compounds **6** and **7** produce similar molecular weight products, but smaller than those of **1**. The PDI of the polyethylene obtained using **7** is narrow. However, the GPC traces of the PE obtained with both **6** and **7** are monomodal, suggesting that the catalytic species is probably the same. Further studies of analogous systems bearing new pincer ligands are currently underway.

4. Conclusions

We have synthesized and fully characterized new Pd(II) pincer complexes of 3,5-*bis* (2-pyridoxy)toluene and 3,5-*bis*(3, 5-dimethylpyrazol-1-ylmethyl)toluene with Na_2PdCl_4 and $Pd(OAc)_2$. The complexes show the terdentate ligands forming two six-membered fused palladacycles and a labile chloride. When activated with MAO, the cyclopalladate complexes show activity in ethylene polymerization under mild conditions. The molecular weight distribution corresponds to single-site catalysts, producing polymers with high molecular weight and narrow polydispersities.

Acknowledgements

We thank "Fondo de Desarrollo Científico y Tecnológico" (FONDECYT) and FONDAP, Chile, for financial support under projects 1060597 and 11980002, respectively. J.H. acknowledges VRAI, Pontificia Universidad Católica de Chile, for a doctoral fellowship.

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