



Palladium(II) complexes with diaminomaleonitrile-based Schiff-base ligands: Synthesis, characterization and application as Suzuki–Miyaura coupling catalysts



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ARTICLE INFO

Article history:

Received 5 April 2017

Accepted 8 June 2017

Available online 15 June 2017

Keywords:

Schiff base

Palladium complexes

X-ray crystallography

Suzuki–Miyaura

Homo-coupling

ABSTRACT

The characterization of synthesized Schiff base ligands (L^1 – L^5); (where L^1 = N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^2 = 3-methoxy-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^3 = 5-bromo-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^4 = 5-nitro-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, and L^5 = 5-methoxy-N-salicyliden-2,3-diamino-cis-2-butenedinitrile) and their palladium complexes $[PdL(PPh_3)]$ (L^1 – L^5) were carried out by FT-IR, UV-vis, 1H NMR, ^{13}C NMR and elemental analysis. The coordination geometry of $[PdL^3(PPh_3)]$ was determined by single crystal X-ray crystallography. In this structure the palladium center was in a partially distorted NNOP square planar coordination environment. The catalytic potential of the synthesized complexes was evaluated in Suzuki–Miyaura cross-coupling reaction by choosing different arylhalides and phenylboronic acid. The results showed that arylhalides with electron withdrawing substituents were more appropriate in this reaction. In all cases, the desired product of cross coupling Suzuki reaction was the major product. It is also worth to mention that the product of homo-coupling reaction was also observed as a minor product. In this regards, a blank reaction with just phenylboronic acid was performed and the results showed the occurrence of the homo-coupling product in a good yield.

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1. Introduction

Palladium as an important noble metal with common oxidation states of +II and +IV, has exclusive properties. It was applied in many electronics, ceramic capacitors and LCD displays [1–2]. Also, it has a key role in the technologies used in the fuel cells [3–4]. Its catalytic application in the organic synthesis was interested during the twentieth century [5–8]. In this regards, the coupling reactions in the presence of a palladium-containing catalyst, have arguably become one of the most utilized tools for the construction of C–C bonds [9–11]. Especially, the cross-coupling of the organic halides with aryl boronic acids, which is catalyzed by palladium, is one of the considerable procedure for the formation of C–C bonds. [12–14]. Suzuki reaction is taken into consideration due to its high importance in various fields including pharmaceutical, polymer and etc. [15–18]. Its superiority over the other coupling reactions is due to the mild reaction conditions, non-toxic nature of the process and stereoselectivity [19]. Soluble palladium(II) complexes

with a diversity of ligands, such as phosphines [20], oxime palladacycles [21], imidazole-phenolates [22], Schiff bases [23] and N-heterocyclic carbenes [24] have been utilized as efficient catalysts in Suzuki reaction. Schiff base compounds have the versatile catalytic application for a wide range of organic reactions [25–26]. The synthesis and catalytic activity of complexes bearing Schiff base ligands have been widely reported [27]. Also, there is a large interest to employ nitrogen containing Schiff base of palladium(II) for Suzuki–Miyaura coupling reactions [28]. They can be used as the active and selective catalyst for hydrogenation, hydrosilylation, and Suzuki/Heck C–C bond coupling reactions [29].

Herein, $[L^1$ – $L^5]$ ligands and $[PdL(PPh_3)]$ complexes (where L^1 = N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^2 = 3-methoxy-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^3 = 5-bromo-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^4 = 5-nitro-N-salicyliden-2,3-diamino-cis-2-butenedinitrile, L^5 = 5-methoxy-N-salicyliden-2,3-diamino-cis-2-butenedinitrile) were synthesized with the aim of highlighting the influence of substitutions on the catalytic properties. The complexes were systematically characterized by various analytical and spectroscopic techniques. The geometry of $[PdL^3(PPh_3)]$ was determined by X-ray

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crystallography. The catalytic activities of the tridentate Schiff base complexes for Suzuki reaction were also examined. This class of ligands exhibited a considerable stabilizing effect not only from the chelate formation, if compared to only phosphines as ligands, but also from stabilization of different oxidation states of metal ions. Also, facile and easy synthetic procedures were applied for their preparation compared to organometallic compounds. The effect of substitution patterns on the substrates, including electronic and steric effects, was investigated on the catalytic activities of the prepared complexes.

2. Experimental

2.1. General remarks

All materials were purchased from Merck and Aldrich used without further purification. The C, H and N contents were determined on a CHN-O-Heraeus elemental analyzer. Electronic spectra were measured on a Perkin Elmer, JASCO V-570 double beam spectrophotometer in the range of 200–700 nm. FT-IR spectra were obtained by using FT-IR JASCO-680 spectrophotometer 400–4000 cm^{-1} range using KBr discs at room temperature. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and 500 MHz spectrometers. Products of catalytic reactions were analyzed by an Agilent 6890N gas chromatograph equipped with a capillary HP-5⁺ column. The column properties were: 30 m long, 0.32 mm in inner diameter, and 0.25 μm film thickness.

2.2. General procedure for the synthesis of ligands

The Schiff base ligands were synthesized by the reaction between 1,2-diaminomaleonitrile (2,3-diamino-*cis*-2-butenedinitrile) and salicylaldehyde or its derivatives (1:1 M ratio) in methanol. The obtained solution was refluxed and stirred overnight. Finally, the products appeared as colored precipitates which were filtered and washed with methanol.

L¹: (Yield: 80%) $\text{C}_{11}\text{H}_8\text{N}_4\text{O}$: FT-IR (KBr cm^{-1}) $\bar{\nu}_{\text{max}}$, 3416 and 3308 (NH_2), 3193 (OH), 2234 and 2205 ($\text{C}\equiv\text{N}$), 1625 ($\text{C}=\text{N}$). UV-Vis, λ_{max} (nm), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Methanol): 213 ($\epsilon = 9.05 \times 10^3$), 264 ($\epsilon = 6.6 \times 10^3$), 328 ($\epsilon = 1.03 \times 10^4$) and 379 ($\epsilon = 1.08 \times 10^4$). ^1H NMR (DMSO-*d*₆, δ , ppm): 6.88–8.47 (m, 4H, aromatic), 8.60 (s, 2H, NH_2), 10.43 (s, 1H, $\text{HC}=\text{N}$), 11.18 (s, 1H, OH).

L²: (Yield: 82%) $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: FT-IR (KBr cm^{-1}) $\bar{\nu}_{\text{max}}$: 3408 (OH), 3323 and 3207 (NH_2), 3040, 2998 and 2888 (CH_3), 2244 and 2204 ($\text{C}\equiv\text{N}$), 1643 ($\text{C}=\text{N}$). UV-Vis, λ_{max} (nm), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Methanol): 226 ($\epsilon = 5.1 \times 10^3$), 271 ($\epsilon = 2.9 \times 10^3$) and 376 ($\epsilon = 6.8 \times 10^3$). ^1H NMR (DMSO-*d*₆, δ , ppm): 3.86 (s, 3H, OCH_3), 6.84–8.44 (m, 3H, aromatic), 8.62 (s, 2H, NH_2), 9.89 (s, 1H, $\text{HC}=\text{N}$), 10.93 (s, 1H, OH).

L³: (Yield: 80%) $\text{C}_{11}\text{H}_7\text{N}_4\text{OBr}$: FT-IR (KBr cm^{-1}) $\bar{\nu}_{\text{max}}$: 3403 (OH), 3301 and 3196 (NH_2), 2246 and 2210 ($\text{C}\equiv\text{N}$), 1631 ($\text{C}=\text{N}$). UV-Vis, λ_{max} (nm), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Methanol): 221 ($\epsilon = 4.3 \times 10^3$), 245 ($\epsilon = 3.3 \times 10^3$), 261 ($\epsilon = 2.9 \times 10^3$), 386 ($\epsilon = 5.9 \times 10^3$). ^1H NMR (DMSO-*d*₆, δ , ppm): 6.90–8.43 (m, 3H, aromatic), 8.51 (s, 2H, NH_2), 10.67 (s, 1H, $\text{HC}=\text{N}$), 11.15 (s, 1H, OH).

L⁴: (Yield: 80%) $\text{C}_{11}\text{H}_7\text{N}_5\text{O}_3$: FT-IR (KBr cm^{-1}) $\bar{\nu}_{\text{max}}$: 3407 (OH), 3308 and 3203 (NH_2), 2237 and 2217 ($\text{C}\equiv\text{N}$), 1629 ($\text{C}=\text{N}$), 1345 (NO_2). UV-Vis, λ_{max} (nm), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Methanol): 254 ($\epsilon = 2.34 \times 10^3$), 316 ($\epsilon = 2.36 \times 10^3$), 381 ($\epsilon = 3.95 \times 10^3$). ^1H NMR (DMSO-*d*₆, δ , ppm): 6.98–8.74 (m, 3H, aromatic), 8.93 (s, 2H, NH_2), 10.28 (s, 1H, $\text{HC}=\text{N}$), 11.88 (s, 1H, OH).

L⁵: (Yield: 77%) $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: FT-IR (KBr cm^{-1}) $\bar{\nu}_{\text{max}}$: 3461 (OH), 3338 and 3190 (NH_2), 3080, 2991 and 2845 (CH_3), 2243 and 2204 ($\text{C}\equiv\text{N}$), 1620 ($\text{C}=\text{N}$). UV-Vis, λ_{max} (nm), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Methanol): 209 ($\epsilon = 3.78 \times 10^3$), 245 ($\epsilon = 3.01 \times 10^3$), 265 ($\epsilon = 2.3 \times 10^3$), 350 ($\epsilon = 3.7 \times 10^3$), 400 ($\epsilon = 4.3 \times 10^3$). ^1H NMR (DMSO-*d*₆, δ ,

ppm): 3.76 (s, 3H, OCH_3), 6.84–8.44 (m, 3H, aromatic), 8.58 (s, 2H, NH_2), 9.97 (s, 1H, $\text{HC}=\text{N}$), 10.69 (s, 1H, OH).

2.3. Synthesis of complexes

Palladium(II) acetate (0.1 mmol, 0.0245 g) and Schiff base ligand (0.1 mmol) were dissolved in methanol (20 mL) and then, 0.1 mmol of triphenylphosphine (0.0263 g) was added to the solution. The obtained solution was stirred and heated for 3 h. The residue was isolated by gravity filtration, washed with methanol and air dried at room temperature. The resulting crystals were formed from chloroform/methanol by slow evaporation after 2–3 days (see Scheme 1).

[PdL¹(PPh₃)] (1a) (Yield: 88%). Elemental Anal. Calc. For $\text{C}_{29}\text{H}_{21}\text{N}_4\text{OPPd}$: C, 59.74%; H, 3.61%; N, 9.61%. Found: C, 59.50%; H, 3.61%; N, 9.42%. Characteristic IR absorptions: 3391 (NH), 3046 (C–H), 2228 and 2182 ($\text{C}\equiv\text{N}$), 1605 ($\text{C}=\text{N}$) cm^{-1} . UV-Vis (λ_{max}), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 248 ($\epsilon = 2.5 \times 10^2$), 318 ($\epsilon = 1.23 \times 10^3$), 426 ($\epsilon = 1.77 \times 10^3$), 452 ($\epsilon = 2.08 \times 10^3$) and ^1H NMR (500 MHz, DMSO-*d*₆, δ , ppm) 6.57–6.58 (d, 1H, Aromatic, $J = 5$ Hz), 6.69–6.72 (t, 1H, Aromatic, $J = 15$ Hz), 7.21–7.24 (m, 1H, Aromatic), 7.45–7.74 (d, 1H, Aromatic), 7.51–7.73 (m, 15H, Aromatic), 8.42–8.45 (d, 1H, $\text{HC}=\text{N}$, $J = 15$ Hz).

[PdL²(PPh₃)] (2a) (Yield: 88%). Elemental Anal. Calc. For $\text{C}_{30}\text{H}_{23}\text{N}_4\text{O}_2\text{PPd}$: C, 58.77%; H, 3.77%; N, 9.143%. Found: C, 58.72%; H, 3.85%; N, 9.09%. Characteristic IR absorptions: 3391(NH), 3046 (C–H), 2225 and 2184($\text{C}\equiv\text{N}$), 1606 ($\text{C}=\text{N}$) cm^{-1} , UV-Vis (λ_{max}), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 252 ($\epsilon = 2.9 \times 10^2$), 310 ($\epsilon = 1.45 \times 10^3$), 418 ($\epsilon = 1.54 \times 10^3$), 446 ($\epsilon = 1.47 \times 10^3$) and ^1H NMR (400 MHz, CDCl_3 , Me_4Si) 3.72 (s, 3H, OCH_3), 6.73–6.77 (t, 1H, Aromatic), 6.90–6.92 (d, 1H, Aromatic, $J = 8$ Hz), 7.19–7.21 (d, 1H, Aromatic, $J = 8$ Hz), 7.50–7.79 (m, 15H, Aromatic), 8.42–8.47 (d, 1H, $\text{HC}=\text{N}$, $J = 12$ Hz). ^{13}C NMR (CDCl_3 , δ , ppm): 56(C- OCH_3), 114–127 (C-Ar), 129–134 (C-PPh₃), 128 and 133 (C=C), 148 (CH=N), 152 and 154 ($\text{C}\equiv\text{N}$).

[PdL³(PPh₃)] (3a) (Yield: 79%). Elemental Anal. Calc. For $\text{C}_{29}\text{H}_{20}\text{N}_4\text{OBrPPd}$: C, 52.617%; H, 3.036%; N, 8.467%. Found: C, 52.510%; H, 3.135%; N, 8.364%. Characteristic IR absorptions: 3396 (NH), 3052 (C–H), 2225 and 2182($\text{C}\equiv\text{N}$), 1598 ($\text{C}=\text{N}$) cm^{-1} , UV-Vis (λ_{max}), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 248 ($\epsilon = 6.7 \times 10^2$), 320 ($\epsilon = 4.7 \times 10^2$), 432 ($\epsilon = 3.6 \times 10^2$), 454 ($\epsilon = 3.89 \times 10^2$), and ^1H NMR (400 MHz, CDCl_3 , Me_4Si) 6.86–6.87 (d, 1H, Aromatic, $J = 4$ Hz), 8.10–8.13 (dd, 1H, Aromatic, $J = 12$ Hz), 8.41–8.45 (d, 1H, Aromatic, $J = 16$ Hz), 7.54–7.72 (m, 15H, Aromatic), 8.61–8.62 (d, 1H, $\text{HC}=\text{N}$, $J = 4$ Hz). ^{13}C NMR (CDCl_3 , δ , ppm): 126–128 (C-Ar), 129–134 (C-PPh₃), 119 and 128 (C=C), 146 (CH=N), 131 and 131 ($\text{C}\equiv\text{N}$).

[PdL⁴(PPh₃)] (4a) (Yield: 82%). Elemental Anal. Calc. For $\text{C}_{29}\text{H}_{20}\text{N}_5\text{O}_3\text{PPd}$: C, 55.45%; H, 3.20%; N, 11.15%. Found: C, 55.40%; H, 3.18%; N, 10.94%. UV-Vis (λ_{max}), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 252 ($\epsilon = 2.7 \times 10^2$), 348 ($\epsilon = 2.09 \times 10^3$), 426 ($\epsilon = 1.61 \times 10^3$), 452 ($\epsilon = 1.7 \times 10^3$). Characteristic IR absorptions: 3384 (NH), 3054 (C–H), 2228 and 2189 ($\text{C}\equiv\text{N}$), 1606 ($\text{C}=\text{N}$) cm^{-1} .

[PdL⁵(PPh₃)] (5a) (Yield: 89%). Elemental Anal. Calc. For $\text{C}_{30}\text{H}_{23}\text{N}_4\text{O}_2\text{PPd}$: C, 58.77%; H, 3.77%; N, 9.143%. Found: C, 58.44%; H, 3.985%; N, 8.919%. Characteristic IR absorptions: 3395 (NH), 3053 (C–H), 2225 and 2183 ($\text{C}\equiv\text{N}$), 1605 ($\text{C}=\text{N}$) cm^{-1} , UV-Vis (λ_{max}), ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 248 ($\epsilon = 2.9 \times 10^2$), 324 ($\epsilon = 1.196 \times 10^3$), 414 ($\epsilon = 1.39 \times 10^3$), 466 ($\epsilon = 1.65 \times 10^3$) and ^1H NMR (500 MHz, DMSO-*d*₆, δ , ppm) 3.70 (s, 3H, OCH_3), 6.52–6.53 (d, 1H, Aromatic, $J = 5$ Hz), 6.92–6.94 (m, 1H, Aromatic), 7.30–7.31 (d, 1H, Aromatic, $J = 5$ Hz), 7.44–7.63 (m, 15H, Aromatic), 8.45–8.48 (d, 1H, $\text{HC}=\text{N}$, $J = 15$ Hz).

2.4. Crystal structure determination

The intensity data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo K radiation.

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