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

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## ARTICLE INFO

## 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, $^1$H 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 carbines [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 $^1$H 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.

L$^1$: (Yield: 80%) C$_{11}$H$_8$N$_4$O: FT-IR (KBr cm$^{-1}$) $\bar{v}_{max}$, 3416 and 3308 (NH$_2$), 3193 (OH), 2234 and 2205 (C≡N), 1625 (C=N). UV–Vis, $\lambda_{max}$ (nm), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) (Methanol): 213 ($\varepsilon$ = 9.05 × 10$^3$), 264 ($\varepsilon$ = 6.6 × 10$^3$), 328 ($\varepsilon$ = 1.03 × 10$^4$) and 379 ($\varepsilon$ = 1.08 × 10$^4$). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 6.88–8.47 (m, 4H, aromatic), 8.60 (s, 2H, NH$_2$), 10.43 (s, 1H, HC=N), 11.18 (s, 1H, OH).

L$^2$: (Yield: 82%). C$_{12}$H$_{10}$N$_4$O$_2$: FT-IR (KBr cm$^{-1}$) $\bar{v}_{max}$: 3408 (OH), 3323 and 3207 (NH$_2$), 3040, 2998 and 2888 (CH$_3$), 2244 and 2204 (C≡N), 1643(C=N). UV–Vis, $\lambda_{max}$ (nm), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) (Methanol): 226 ($\varepsilon$ = 5.1 × 10$^3$), 271 ($\varepsilon$ = 2.9 × 10$^3$) and 376 ($\varepsilon$ = 6.8 × 10$^3$). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 3.86 (s, 3H, OCH$_3$), 6.84–8.44 (m, 3H, aromatic), 8.62 (s, 2H, NH$_2$), 9.89 (s, 1H, HC=N), 10.93 (s, 1H, OH).

L$^3$: (Yield: 80%). C$_{11}$H$_7$N$_4$OBr: FT-IR (KBr cm$^{-1}$) $\bar{v}_{max}$: 3403 (OH), 3301 and 3196 (NH$_2$), 2246 and 2210 (C≡N), 1631(C=N). UV–Vis, $\lambda_{max}$ (nm), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) (Methanol): 221($\varepsilon$ = 4.3 × 10$^3$), 245 ($\varepsilon$ = 3.3 × 10$^3$), 261 ($\varepsilon$ = 2.9 × 10$^3$), 386 ($\varepsilon$ = 5.9 × 10$^3$). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 6.90–8.43 (m, 3H, aromatic), 8.51 (s, 2H, NH$_2$), 10.67 (s, 1H, HC=N), 11.15 (s, 1H, OH).

L$^4$: (Yield: 80%). C$_{11}$H$_7$N$_5$O$_3$: FT-IR (KBr cm$^{-1}$) $\bar{v}_{max}$: 3407 (OH), 3308 and 3203 (NH$_2$), 2237 and 2217 (C≡N), 1629 (C=N), 1345 (NO$_2$). UV–Vis, $\lambda_{max}$ (nm), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) (Methanol): 254 ($\varepsilon$ = 2.34 × 10$^3$), 316 ($\varepsilon$ = 2.36 × 10$^3$), 381 ($\varepsilon$ = 3.95 × 10$^3$). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 6.98–8.74 (m, 3H, aromatic), 8.93 (s, 2H, NH$_2$), 10.28 (s, 1H, HC=N), 11.88 (s, 1H, OH).

L$^5$: (Yield: 77%). C$_{12}$H$_{10}$N$_4$O$_2$: FT-IR (KBr cm$^{-1}$) $\bar{v}_{max}$: 3461 (OH), 3338 and 3190 (NH$_2$), 3080, 2991 and 2845 (CH$_3$), 2243 and 2204 (C≡N), 1620 (C=N). UV–Vis, $\lambda_{max}$ (nm), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) (Methanol): 209 ($\varepsilon$ = 3.78 × 10$^3$), 245 ($\varepsilon$ = 3.01 × 10$^3$), 265 ($\varepsilon$ = 2.3 × 10$^3$), 350 ($\varepsilon$ = 3.7 × 10$^3$), 400 ($\varepsilon$ = 4.3 × 10$^3$). $^1$H NMR (DMSO-$d_6$, $\delta$,

ppm): 3.76 (s, 3H, OCH$_3$), 6.84–8.44 (m, 3H, aromatic), 8.58 (s, 2H, NH$_2$), 9.97 (s, 1H, HC=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).

**[PdL$^1$(PPh$_3$)] (1a)** (Yield: 88%). Elemental Anal. Calc. For C$_{29}$H$_{21}$N$_4$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 (C≡N), 1605 (C=N) cm$^{-1}$. UV–Vis ($\lambda_{max}$), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$): 248 ($\varepsilon$ = 2.5 × 10$^2$), 318 ($\varepsilon$ = 1.23 × 10$^3$), 426 ($\varepsilon$ = 1.77 × 10$^3$), 452 ($\varepsilon$ = 2.08 × 10$^3$) and $^1$H NMR (500 MHz, DMSO-$d_6$, $\delta$, 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, HC=N, $J$ = 15 Hz).

**[PdL$^2$(PPh$_3$)] (2a)** (Yield: 88%). Elemental Anal. Calc. For C$_{30}$H$_{23}$N$_4$O$_2$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(C≡N), 1606 (C=N) cm$^{-1}$, UV–Vis ($\lambda_{max}$), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$): 252 ($\varepsilon$ = 2.9 × 10$^2$), 310 ($\varepsilon$ = 1.45 × 10$^3$), 418 ($\varepsilon$ = 1.54 × 10$^3$), 446 ($\varepsilon$ = 1.47 × 10$^3$) and $^1$H NMR (400 MHz, CDCl$_3$, Me$_4$Si) 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, HC=N, $J$ = 12 Hz). $^{13}$C NMR (CDCl$_3$, $\delta$, ppm): 56(C-OCH$_3$), 114–127 (C-Ar), 129–134 (C-PPh$_3$), 128 and 133 (C=C), 148 (CH=N), 152 and 154 (C≡N).

**[PdL$^3$(PPh$_3$)] (3a)** (Yield: 79%). Elemental Anal. Calc. For C$_{29}$H$_{20}$N$_4$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(C≡N), 1598 (C=N) cm$^{-1}$, UV–Vis ($\lambda_{max}$), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$): 248 ($\varepsilon$ = 6.7 × 10$^2$), 320 ($\varepsilon$ = 4.7 × 10$^2$), 432 ($\varepsilon$ = 3.6 × 10$^2$), 454 ($\varepsilon$ = 3.89 × 10$^2$), and $^1$H NMR (400 MHz, CDCl$_3$, Me$_4$Si) 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, HC=N, $J$ = 4 Hz). $^{13}$C NMR (CDCl$_3$, $\delta$, ppm): 126–128 (C-Ar), 129–134 (C-PPh$_3$), 119 and 128 (C=C), 146 (CH=N), 131 and 131 (C≡N).

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

**[PdL$^5$(PPh$_3$)] (5a)** (Yield: 89%). Elemental Anal. Calc. For C$_{30}$H$_{23}$N$_4$O$_2$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 (≡N), 1605 (C=N) cm$^{-1}$, UV–Vis ($\lambda_{max}$), $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$): 248 ($\varepsilon$ = 2.9 × 10$^2$), 324 ($\varepsilon$ = 1.196 × 10$^3$), 414 ($\varepsilon$ = 1.39 × 10$^3$), 466 ($\varepsilon$ = 1.65 × 10$^3$) and $^1$H NMR (500 MHz, DMSO-$d_6$, $\delta$, 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, HC=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.

Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans [30–32]. The structure was solved by direct methods (SHELXS [33]) and refined by full-matrix least squares techniques against $F_o^2$ (SHELXL-97 [33]). The hydrogen atoms bonded to the amine-group N2 were located by difference Fourier synthesis and refined isotropically. All other hydrogen atom positions were included at calculated positions with fixed thermal parameters. XP [34] was used for structural representations.

*Crystal Data for* **3a**: $C_{29}H_{20}BrN_4OPPd$, $Mr = 657.77$ gmol$^{-1}$, orange prism, size $0.132 \times 0.128 \times 0.102$ mm$^3$, triclinic, space group $P\bar{1}$, $a = 8.9663(3)$, $b = 10.9700(3)$, $c = 15.0305(6)$ Å, $\alpha = 68.680(1)$, $\beta = 82.625(2)$, $\gamma = 69.914(2)°$, $V = 1293.45(8)$ Å$^3$, $T = -140$ °C, $Z = 2$, $\rho_{calcd.} = 1.689$ g cm$^{-3}$, μ (Mo Kα) = 23.54 cm$^{-1}$, multi-scan, transmin: 0.6102, transmax: 0.7456, $F(000) = 652$, 13,355 reflections in $h(-11/9)$, $k(-14/14)$, $l(-18/19)$, measured in the range $2.104° \leq \theta \leq 27.485°$, completeness $\theta_{max} = 99.3\%$, 5849 independent reflections, $R_{int} = 0.0345$, 4884 reflections with $F_o > 4\sigma(F_o)$, 338 parameters, 0 restraints, $R_{obs}^1 = 0.0491$, $wR_{obs}^2 = 0.0971$, $R_{all}^1 = 0.0645$, $wR_{all}^2 = 0.1057$, GOOF = 1.051, largest difference peak and hole: $1.029/-1.044$ e Å$^{-3}$. Crystals of **3a** were grown by slow evaporation from chloroform/MeOH solution. The ORTEP drawing of the inner coordination sphere at the Pd core with the atom numbering scheme is shown in Fig. 2.

### 2.5. General experimental procedure for Suzuki cross-coupling reaction

For the homogeneous Suzuki–Miyaura coupling reactions, a range of substituted aryl halides as substrates was employed. A mixture of aryl halides (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (6 mL) and catalyst (0.01 mmol) was stirred at 70 °C in the air. Optimization of the reaction conditions was summarized in Tables 3–7. Also, the reaction mixtures were collected at different time and measured by GC analysis in order to study the progress of the reaction.

## 3. Results and discussions

### 3.1. FT-IR spectra

The FT-IR characteristic bands are seen in Section 2.2 and 2.3 for the ligands and complexes. The FT-IR spectra of all ligands exhibit an intense band in the region of 1620–1643 cm$^{-1}$, which can be assigned to the stretching vibration of the C=N group. The NH$_2$

**Table 1**
Selected Crystallographic data for **3a**.

| Compound | (A) |
|---|---|
| Formula | $C_{29}H_{19}BrN_4OPPd$ |
| Formula weight | 656.76 |
| $T$ (K) | 133(2) |
| $\lambda$ (Å) | 0.710 |
| Crystal system | *Triclinic* |
| Space group | $P\,bar\,1$ |
| $Z$ | 2 |
| Crystal size (mm) | $0.132 \times 0.128 \times 0.102$ |
| $a$ (Å) | 8.9663 (3) |
| $b$ (Å) | 10.9700 (3) |
| $c$ (Å) | 15.0305 (6) |
| $\alpha$ (°) | 68.680 (1) |
| $\beta$ (°) | 82.625 (2) |
| $\gamma$ (°) | 69.914 (2) |
| $D_{calc}$ (g cm$^{-1}$) | 1.686 |
| $\theta$ ranges for data collection | 2.10–27.48 |
| $F(000)$ | 650 |
| $V$ (Å$^3$) | 1293.45(8) |

**Table 2**
Selected bond distances and angles for **3a**.

| Bond distances | | Bond angles | |
|---|---|---|---|
| Pd1–O1 | 1.966(3) | O(1)–Pd(1)–N(1) | 95.56(14) |
| Pd1–N1 | 2.034(4) | O(1)–Pd(1)–N(2) | 174.50(16) |
| Pd1–N2 | 1.975(4) | O(1)–Pd(1)–P(1) | 95.45(10) |
| Pd1–P1 | 2.275(12) | N(1)–Pd(1)–P(1) | 176.95(11) |
| Br1–C4 | 1.904(5) | N(2)–Pd(1)–P(1) | 94.88(13) |
| P1–C12 | 1.812(5) | N(2)–Pd(1)–N(1) | 82.12(16) |
| O1–C1 | 1.310(6) | C(7)–N(1)–Pd(1) | 124.7(3) |
| N1–C7 | 1.300(6) | C(7)–N(1)–C(8) | 124.5(4) |
| N1–C8 | 1.399(6) | C(3)–C(4)–Br(1) | 118.1(4) |
| N2–C9 | 1.324(6) | C(9)–C(8)–N(1) | 114.2(4) |
| N3–C10 | 1.149(6) | N(1)–C(8)–C(10) | 122.0(4) |
| N4–C11 | 1.140(6) | N(2)–C(9)–C(8) | 120.5(4) |
| C1–C6 | 1.417(7) | N(3)–C(10)–C(8) | 177.9(5) |
| C8–C9 | 1.385(6) | N(4)–C(11)–C(9) | 179.2(5) |
| | | O(1)–C(1)–C(2) | 116.1(4) |

**Table 3**
Suzuki cross-coupling of bromobenzene and phenylboronic acid catalyzed by different catalyst.



| Entry | Catalyst | Yield (%) |
|---|---|---|
| 1 | [PdL$^1$(PPh$_3$)] (**1a**) | 79 |
| 2 | [PdL$^2$(PPh$_3$)] (**2a**) | 83 |
| 3 | [PdL$^3$(PPh$_3$)] (**3a**) | 86 |
| 4 | [PdL$^4$(PPh$_3$)] (**4a**) | 56 |
| 5 | [PdL$^5$(PPh$_3$)] (**5a**) | 89 |

Reaction conditions: bromobenzene (0.5 mmol); phenyl boronic acid (0.75 mmol); K$_2$CO$_3$ (1.5 mmol); catalyst (0.01 mmol); toluene (5 ml); $T = 70$ °C; $t = 5$ h.

**Table 4**
Effect of solvent on Suzuki coupling catalyzed by [PdL$^5$(PPh$_3$)].

| Entry | Solvent | Yield (%) |
|---|---|---|
| 1 | DMF | 22 |
| 2 | MeOH | 31 |
| 3 | CH$_3$CN | 50 |
| 4 | Toluene | 89 |
| 5 | CH$_2$Cl$_2$ | 84 |

Reaction conditions: bromobenzene (0.5 mmol); phenyl boronic acid (0.75 mmol); K$_2$CO$_3$ (1.5 mmol); catalyst (**5a**) (0.01 mmol); solvent (5 ml); $T = 70$ °C; $t = 5$ h.

**Table 5**
Effect of base on Suzuki coupling catalyzed by [PdL$^5$(PPh$_3$)].

| Entry | Base | Yield (%) |
|---|---|---|
| 1 | Na$_2$CO$_3$ | 78 |
| 2 | K$_2$CO$_3$ | 88 |
| 3 | KOH | 49 |
| 4 | Et$_3$N | 52 |

Reaction conditions: bromobenzene (0.5 mmol); phenyl boronic acid (0.75 mmol); Base (1.5 mmol); catalyst (**5a**) (0.01 mmol); toluene (5 ml); $T = 70$ °C; $t = 5$ h.

stretching frequencies are seen in the range of 3190–3416 cm$^{-1}$. The hydroxyl vibration band is seen in the 3400 cm$^{-1}$. As seen in the FT-IR spectra, the CN stretching shows two bands in the region of 2204–2217 and 2234–2246 cm$^{-1}$ which these bands shift to lower frequencies after coordination of the ligand to the palla-

**Table 6**
Effect of time on Suzuki coupling catalyzed by [PdL⁵(PPh₃)].

| Entry | Time (h) | Yield (%) |
|---|---|---|
| 1 | 1 | – |
| 2 | 2 | 48 |
| 3 | 3 | 70 |
| 4 | 4 | 75 |
| 5 | 5 | 89 |
| 6 | 6 | 89 |
| 7 | 8 | 90 |
| 8 | 12 | 91 |

Reaction conditions: bromobenzene (0.5 mmol); phenyl boronic acid (0.75 mmol); Base (1.5 mmol); catalyst (**5a**) (0.01 mmol); toluene (5 ml); $T = 70\,°C$.

**Table 7**
Effect of temperature on Suzuki coupling catalyzed by [PdL⁵(PPh₃)].

| Entry | Temperature (°C) | Yield (%) |
|---|---|---|
| 1 | 25 | 15 |
| 2 | 50 | 52 |
| 3 | 60 | 88 |
| 4 | 70 | 89 |
| 5 | 90 | 91 |
| 6 | 110 | 93 |

Reaction conditions: bromobenzene (0.5 mmol); phenyl boronic acid (0.75 mmol); Base (1.5 mmol); catalyst (**5a**) (0.01 mmol); toluene (5 ml); $t = 5\,h$.

dium(II) ion. The stretching frequency of $NO_2$ in $L^4$ ligand is seen at 1345 cm⁻¹. In the [PdL(PPh₃)] complexes containing $L^1$–$L^5$, as shown in the Section 2, the C=N band shifts to the lower frequencies relative to the free ligand in the coordination compounds. A sharp band observed in the region of 3331–3396 cm⁻¹ assigned to $\bar{\nu}$(N–H) which shows that the $NH_2$ functional group has been changed to the NH after coordination of the Schiff base ligands. In coordination of ligands to the metal ion the characteristic band of the hydroxyl group was absence. Also, the bands at about 3053 cm⁻¹ are related to the aromatic C–H vibration of PPh₃ in complexes.

### 3.2. Electronic spectra

The UV–Vis spectra of $L^1$–$L^5$ ligands and [PdL(PPh₃)] (L = $L^1$–$L^5$) complexes were measured at room temperature in the region of 200–700 nm. The bands which located in the region of 300–400 nm were involved $\pi \rightarrow \pi^*$ transition related to azomethine group. The electronic intra-ligand $\pi \rightarrow \pi^*$ transitions related to aromatic rings were observed in the region lower than 300 nm. As it can be seen, upon complexation these bands were shifted to higher wavelengths.

### 3.2.1. ¹H NMR and ¹³C NMR spectra

The NMR spectroscopic data of palladium(II) complexes were presented in Section 2.3. For **2a**, the assignment of the signals

was carried out with the aid of 2D NMR spectra including {¹H–¹H} COSY (correlation spectroscopy), and {¹H–¹³C} HSQC (heteronuclear single quantum correlation) experiments (Figs. 1 and 2). The ¹H NMR data of the synthesized complexes has shown that the aromatic hydrogens (6.73–8.45 ppm) were in the similar range (6.84–8.47) to the ligands. Also, the assignment of the aromatic hydrogens (Scheme 2) was confirmed in (H–H) COSY (Fig. 1). The $NH_2$ and OH protons were seen at 8.64 and 11.16 ppm, respectively. In the palladium complexes, no signals were recorded for the phenolic hydrogen, which is an indication of Schiff bases *ortho* hydroxyl group deprotonation. The hydrogen of imine in the free ligands appeared as a singlet (8.60–10.67 ppm) while the related signals for palladium(II) complexes were appeared as a doublet (8.44–8.62 ppm) due to the coupling with phosphorus atom. In **2a** and **5a** the $OCH_3$ signal was observed at 3.72 and 3.70 ppm, respectively.

The molecular structures of **2a** and **3a** were also investigated by ¹³C NMR experiments. The signal of carbon atom of the methoxy group in the **2a** was assigned at 56.34 ppm. The six different signals of the aromatic carbons related to the Schiff base moiety were shown in the range of 112–127 ppm, while the chemical shifts of the triphenylphosphine carbons were seen in the range of 129–134 ppm. In these complexes, C=C, C≡N resonances were shown as two peaks in the region of 128–131 and 132–154 ppm, respectively. The most relevant features observed in the ¹³C {¹H} NMR spectra of the synthetic palladium(II) compounds were the upfield shifts of imine carbon signals, which it was appeared at 147 ppm. HSQC NMR in Fig. 2 confirms the signals in **2a**.

### 3.3. Structural description of [PdL³(PPh₃)]; (3a)

The structure of [PdL³(PPh₃)] complex was determined by X-ray crystallography. The molecule crystallized in the triclinic $P\bar{1}$ space group, with two molecular entities present in the asymmetric unit. As observed in [PdL³(PPh₃)], structure of **3a** is given in Fig. 3. Tables 1 and 2 shown X-ray crystallography data, the selected bond lengths and angles. This complex was contained tridentate ONN Schiff base and a monodentate triphenylphosphine ligand. Palladium atom was in a slightly distorted square planar coordination environment consisting of N1, N2, O1 and P1 atoms from ligands. The Pd–N1, Pd–N2, Pd–O1 and Pd–P1 distances appeared in the range of 2.035 (4), 1.986 (4), 1.970 (3) and 2.275 (12) Å, respectively. The O1–Pd1–N1, O1–Pd1–P1, N2-Pd1–P1 and N2-Pd1–N1 bond angles (92.60 (1), 90.37 (1), 94.64 (12) and 82.40 (16), respectively) deviate from 90°, the O1–Pd1–N2 and N2–Pd1–N1 angles (174.82 (16) and 176.98 (12), respectively) deviate from the 180° angle showed that the coordination geometry of the palladium ion distorted from the square planar. In [PdL³(PPh₃)] complex, the hydrogen bonding between the C≡N nitrogen and the hydrogens of triphenyl phosphine (2.56 Å) leads to an extended network of the complex.



X = H, 3-OMe, 5-Br, 5-NO2, 5-OMe
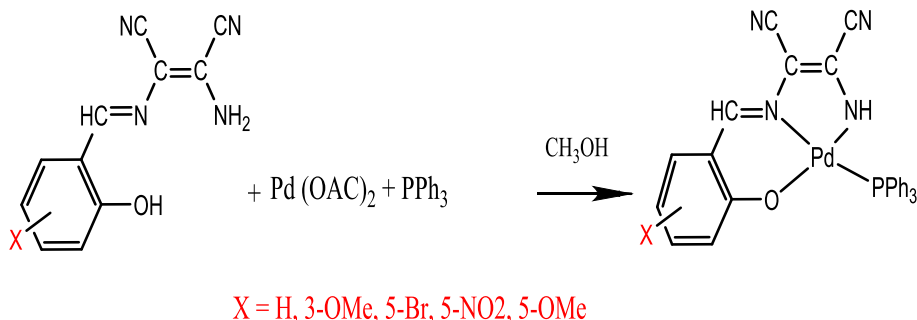
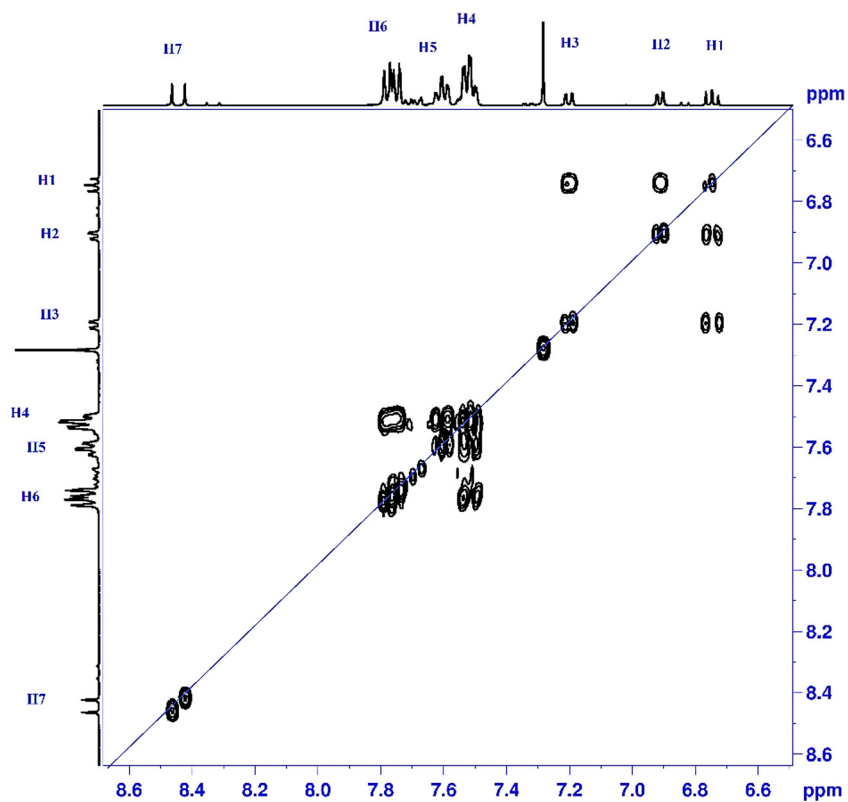**Scheme 1.** The structure of Schiff bases and their complexes.

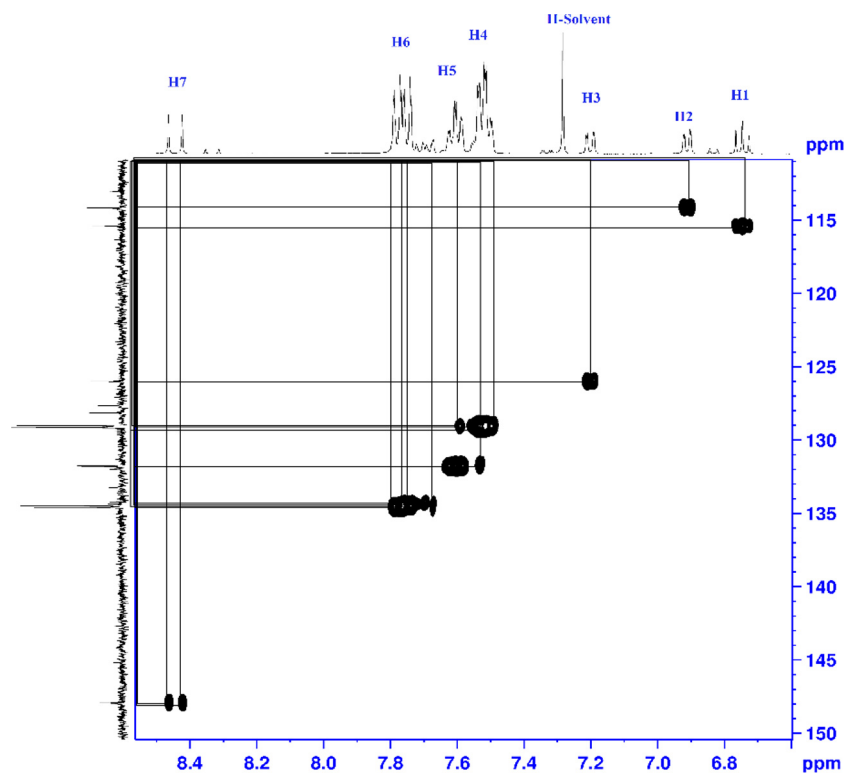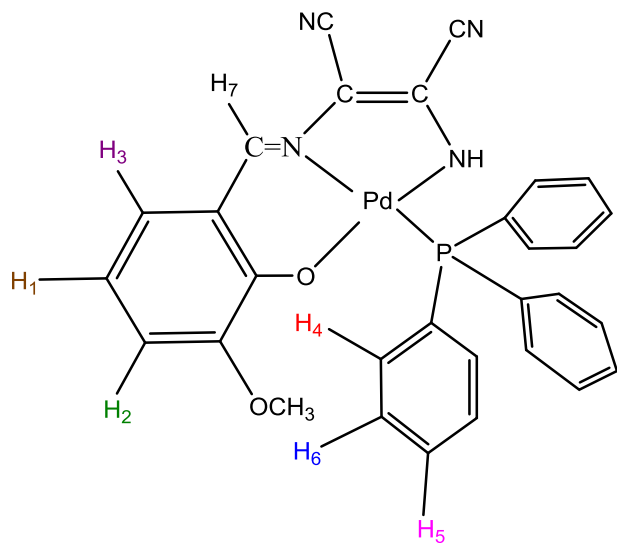**Fig. 1.** The assignment of the aromatic hydrogens in (H–H) COSY.



**Fig. 2.** The assignment of the aromatic hydrogens in ($^1$H–$^{13}$C) HSQC.

**Scheme 2.** The various type of hydrogen atoms in [PdL²(PPh₃)] (**2a**) complex.

### 3.4. Optimization of the reaction conditions for Suzuki reaction

To check the potency of the catalytic activity of Schiff base palladium catalysts, they were used in the coupling of bromobenzene and phenylboronic acid as a model reaction in the Suzuki cross-coupling reaction. The reaction was achieved at 70 °C by using $K_2CO_3$ as base and the molar ratio of bromobenzene: phenylboronic acid: $K_2CO_3$ was 2:3:6.

The catalytic activity of synthesized Palladium(II) complexes containing Schiff base and triphenylphosphine ligands were investigated under the same conditions and the results are summarized in Table 3. Compared with the homogeneous palladium-phosphine complexes, these complexes are easily synthesized and the use of Schiff base ligands improved their catalytic properties for Suzuki coupling reaction [9,35]. The Schiff-base complexes were stable under the different oxidation states [25], so they have a good effect in catalytic reactions.

In addition, compare to complexes containing phosphorus, the complexes prepared from tridentate Schiff bases and phosphines enhanced the catalytic efficiency through the modulating of the steric crowding around the palladium(II) ion [36]. The $\pi$-acceptor ability of the phosphine and $\sigma$-donor ability of imine-nitrogen make the metal center more susceptible to catalytic reactions. As illustrated in Table 3, the best yield was obtained from the [PdL⁵(-PPh₃)] (**5a**) complex containing *para*-methoxy group, while the worst one was related to the [PdL⁴(PPh₃)] (**4a**) including *para*-nitro group as a catalyst.

Firstly, the solvent effect such as DMF, MeOH, $CH_3CN$, toluene, and $CH_2Cl_2$ in the presence of 0.01 mmol of the catalyst at 70 °C for 5 h were studied. As could be seen (Table 4), the toluene solvent for the best solubility of the component with the highest yield and DMF with the lowest yield were obtained. Similar to reported work [5], N-donor atoms of DMF compete with the imine of Schiff base ligand in coordinating to the palladium centre and resultant catalyst could be less active than others. Base is considered to be important in the Suzuki coupling reaction. The bases, including $Na_2CO_3$, $K_2CO_3$, KOH, and $Et_3N$ were investigated (Table 5) and among them, $K_2CO_3$ was found to be the best one. The effect of temperature and the reaction time was also investigated and the results were listed in Tables 6 and 7. Increasing the temperature has a significant effect on catalyst performance through increasing the yield of reaction [5,7]. Also, as shown in Table 8, a wide range of aryl halides with different functional groups have been assessed. X. Liu et al. prepared iminopyridylphosphine palladium(II) complexes which for these complexes containing electron-withdrawing substituents was investigated in the good yield (75–98%) [37]. in this work the excellent yields of 80–93% were obtained for the reactants containing electron withdrawing substituents. It can be inferred that the electronic effects of the substituents on the aryl bromide show that the electron withdrawing substituents were more appropriate for the coupling reaction. From the reaction of aryl halides with different functional groups and boronic acid, the products of cross coupling (Suzuki reaction) and homo-coupling (HC) of boronic acid were observed at the same time. The main product with 68–93% yields was obtained from the Suzuki cross coupling reaction while the biphenyl with 5–24% yield was homo- coupling (HC) product. Additionally, the catalytic reaction
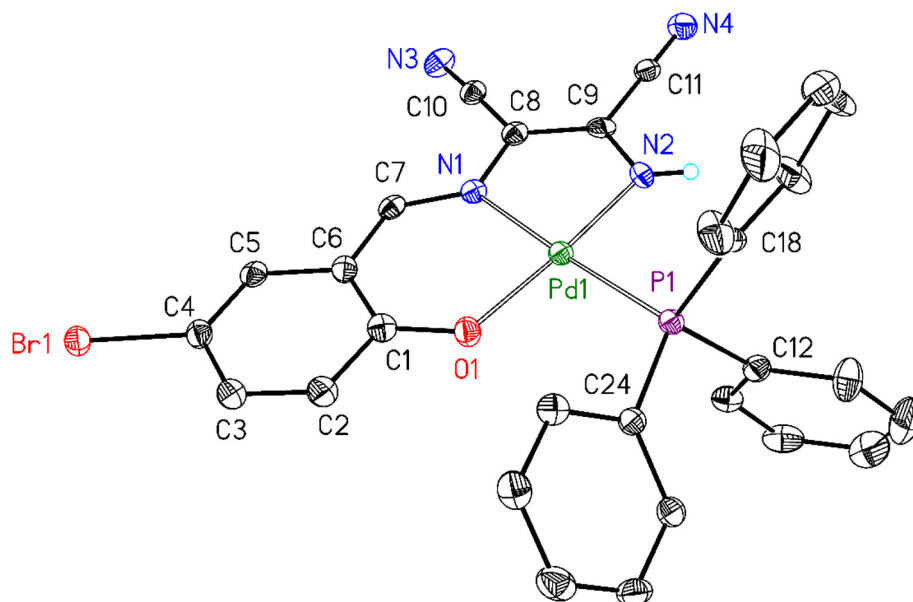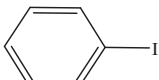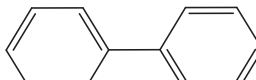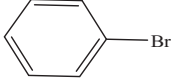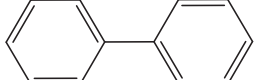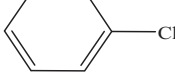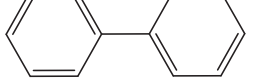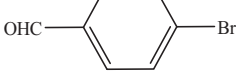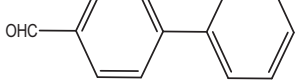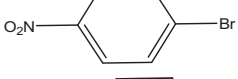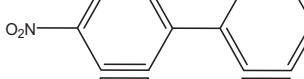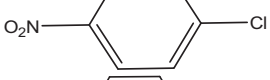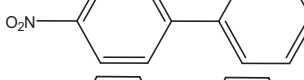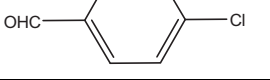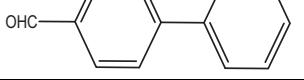


**Fig. 3.** The crystal structures of the [PdL³(PPh₃)].

**Table 8**
Suzuki cross-couplings of various aryl halides and phenylboronic acid.

| Entry | Aryl halide | product | Yield (%) (S/HC)* |
|---|---|---|---|
| 1 | | | 95/0 |
| 2 | | | 89/0 |
| 3 | | | 65/0 |
| 4 | | | 93/5 |
| 5 | | | 91/8 |
| 6 | | | 68/24 |
| 7 | | | 73/14 |

Reaction conditions: aryl halides (0.5 mmol); phenylboronic acid (0.75 mmol); $K_2CO_3$ (1.5 mmol); catalyst (0.01 mmol); toluene (5 ml); $T$ = 70 °C.
* S = Suzuki product, HC = Homo-coupling product.

was also performed in the absence of aryl halide and 70% yield was obtained for homo- coupling of boronic acids [38].

Regarde to Ch. Zhang et al. the $Pd_2(dba)_3$ complex had a good efficiency on coupling of aryl chloride and phenylboronic acid through the Suzuki reaction. In this complex the imidazol-2-ylidenes ligand with high nucleophilic character had a stabilizing effect over the complex [39]. Similarly to these observation, the [PdL$^5$(-PPh$_3$)] complex also, is a good catalyst for cross-coupling of aryl chloride and phenylboronic acid. Although, as shown in (Table 8) among the coupling reactions, aryl chlorides with high dissociation energy [25] have lower yields (65–73%), but these results are noticeable.

## 4. Conclusions

In summary, some new palladium(II) complexes containing the tridentate Schiff base ligands were synthesized and characterized. The distorted square planer structure was obtained for the [PdL$^3$(-PPh$_3$)] complex. In this work the Suzuki reaction was carried out in the presence of an aryl halide and phenyl boronic acid. The yield of the reactions was obtained via GC analyses. The palladium(II) complexes were used as catalyst for the Suzuki cross-coupling reaction of several aryl halides with phenylboronic acid. Comparing with complexes of phosphorus ligands, the advantage of using Schiff base is that they are air stable and moisture insensitive. Also, tridentate Schiff bases by modulating of the steric around the palladium center are appropriate ligands for catalytic reactions. The presence of substituents groups on the Schiff base ligands seems to play a special role in the catalytic activity of the complexes. Also, excellent yields were obtained in the reaction of aryl halides with electron withdrawing substituents. The results of the competition reactions between aryl halides and phenylboronic acid shows that the desired Suzuki reaction appear as a main product which followed by homo-coupling product as a byproduct of the reaction.

Also, this work involved the homo- coupling of phenylboronic acid without aryl halides as a good yield by common condition of reaction.

## Appendix A. supplementary data

CCDC 1531112 contains the supplementary crystallographic data for **3a**. These data can be obtained free of charge via http://dx.doi.org/10.1016/j.poly.2017.06.009, 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] S.F. Wang, J.P. Dougherty, J. Am. Ceram. Soc. (1994) 3051.
[2] Y. Sato, H. Kanai, Y. Yamashita, J. Am. Ceram. Soc. 79 (1996) 261.
[3] S.J. Hoseini, M. Bahrami, M. Zanganeh, M. Roushani, M. Rashidi, RSC Adv. (2016) 1.
[4] S.J. Hoseini, M. Bahrami, M. Roushani, RSC Advances. 4 (2014) 46992.
[5] T. Mahamo, M.M. Mogorosi, J.R. Moss, S.F. Mapolie, J.C. Slootweg, K. Lammertsma, G.S. Smith, J. Organomet. Chem. 703 (2012) 34.
[6] A.M. Tajuddin, H. Bahron1, K. Kassim1, W.N. Wan Ibrahim, B.M. Yamin, Malaysian J. Anal. Sci. 16 (2012) 79.
[7] J. Tonga, H. Wanga, X. Caia, Q. Zhanga, H. Maa, Z. Leia, Appl. Organometal. Chem. 28 (2014) 95.
[8] H. Khojasteh, V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, J. Nano Struct. 5 (2015) 271.
[9] K. Karami, Z. Karami, M. Moghadama, Hosseini Kharata, Univ. J. Chem. 2 (2014) 23.
[10] C. Cao, Y. Zhuang, J. Zhao, Y. Peng, X. Li, Z. Shi, G. Pang, Y. Shi, Inorg. Chim. Acta. 363 (2010) 3914.

[11] L. Botella, C. Nájera, Angew. Chem. Int. Ed. 41 (2002) 179.
[12] M.J. Jin, D.H. Lee, Angew. Chem. Int. Ed. 49 (2010) 1119.
[13] M. Keleş, H. Keleş, D. Melis Emir, Appl. Organometal. Chem. 29 (2015) 543.
[14] I. Maluenda, O. Navarro, Molecules 20 (2015) 7528.
[15] A. Desforges, R. Backov, H. Deleuze, O. Mondain-Monval, Adv. Funct. Mater. 15 (2005) 1689.
[16] M. Hocek, A. Holy, I. Votruba, H. Dvorakova, J. Med. Chem. 43 (2000) 1817.
[17] G.A. Edwards, M.A. Trafford, A.E. Hamilton, Audrey M. Buxton, M.C. Bardeaux, J.M. Chalker, J. Org. Chem. 79 (2014) 2094.
[18] C. Torborg, M. Beller, Adv. Synth. Catal. 351 (2009) 3027.
[19] C.F.R.A.C. Lima, J.E. Rodriguez-Borges, L.M.N.B.F. Santos, Tetrahedron 67 (2011) 689.
[20] R. Martin, S.L. Buchwald, Acc. Chem. Res. 41 (2008) 1461.
[21] J.F. Civicos, D.A. Alonso, C. Najera, Eur. J. Org. Chem. 19 (2012) 3670.
[22] (a) A.O. Eseola, H. Görls, J.A.O. Woods, W. Plass, J. Mol. Catal. A 406 (2015) 224;
     (b) A.O. Eseola, O. Akogun, H. Görls, O. Atolani, G.A. Kolawole, W. Plass, J. Mol. Catal. A 387 (2014) 112;
     (c) A.O. Eseola, D. Geibig, H. Görls, W.-H. Sun, X. Hao, J.A.O. Woods, W. Plass, J. Organomet. Chem. 754 (2014) 39.
[23] (a) P. Liu, X.-J. Feng, R. He, Tetrahedron 66 (2010) 631;
     (b) S. Nasifa, B. Biplab, D. Pankaj, Tetrahedron let. 54 (2013) 2886.
[24] V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, J. Organomet. Chem. 595 (2000) 186.
[25] X. Liu, X. Zhao, M. Lu, J. Organomet. Chem. 768 (2014) 23.
[26] S.M. Islam, P. Mondal, K. Tuhina, A.S. Roy, S. Mondal, D. Hossain, J. Inorg. Organomet. Polym. 20 (2010) 264.
[27] A.M. Abu-Dief, I.M.A. Mohamed, Beni-suef Univ. J. Basic Appl. Sci. 4 (2015) 119.
[28] K. Dhara, K. Sarkar, D. Srimani, S.K. Saha, P. Chattopadhyay, A. Bhaumik, Dalton Trans. 39 (2010) 6395.
[29] N. Debono, M. Iglesias, F. Sanchez, Adv. Synth. Catal. 349 (2007) 2470.
[30] Collect, Data Collection Software; Nonius B.V., Netherlands, 1998.
[31] Z. Otwinowski, W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, in: C.W. Carter & R.M. Sweet (eds.), Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, Academic Press, San Diego, USA, 1997, pp. 307–326.
[32] SADABS 2.10, Bruker-AXS inc., 2002, Madison, WI, U.S.A.
[33] G.M. Sheldrick, Acta Cryst. A46 (2008) 112.
[34] Siemens (1994). XP. Siemens Analytical X-ray Instruments Inc, Madison, Wisconsin, USA.
[35] D. Song, W.B. Yi, J. Mol. Catal. A Chem. 280 (2008) 20.
[36] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 4575.
[37] A. Kumar, M. Agarwal, A.K. Singh, R.J. Butcher, Inorg. Chim. Acta 362 (2009) 3208.
[38] Carlos F.R.A.C. Lima, Ana S.M.C. Rodrigues, Vera L.M. Silva, Artur M.S. Silva, Luis M.N.B.F. Santos, Chem. Cat. Chem. 6 (2014) 1291.
[39] Ch. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.