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Date:

2017-12-01

Citation:

Sabounchei, S. J., Sedghi, A., Hashemi, A., Hosseinzadeh, M., Bayat, M. & Gable, R. W. (2017). Pallada- and platinacycle complexes of phosphorus ylides; synthesis, X-ray characterization, theoretical and electrochemical studies and application of Pd(II) complexes as catalyst in Suzuki-Miyaura coupling reaction. *Applied Organometallic Chemistry*, 31 (12), <https://doi.org/10.1002/aoc.3850>.

Persistent Link:

<https://hdl.handle.net/11343/292894>

Pallada- and platinacycle complexes of phosphorus ylides; Synthesis, X-ray characterization, theoretical and electrochemical studies and application of Pd(II) complexes as catalyst in Suzuki-Miyaura coupling reaction

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Abstract: The new unsymmetrical phosphonium salts $[\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{R}]\text{Br}$ ($\text{R} = m\text{-Br}$ (S_1) and $p\text{-CN}$ (S_2)) were synthesized in the reaction of 1,1-bis(diphenylphosphino)methane (dppm) and $\text{BrCH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{R}$ ($\text{R} = m\text{-Br}$ and $p\text{-CN}$) ketones, respectively. Further treatment with NEt_3 gave the α -keto stabilized phosphorus ylides $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{R}$ ($\text{R} = m\text{-Br}$ (Y_1) and $p\text{-CN}$ (Y_2)). These ligands were reacted with $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}$ and Pt ; $\text{cod} = 1,5\text{-cyclooctadiene}$) to give the pallada- and platinacycle complexes $[\text{MCl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{R})]$ ($\text{M} = \text{Pd}$, $\text{R} = m\text{-Br}$ (**3**); $\text{R} = p\text{-CN}$ (**4**) and $\text{M} = \text{Pt}$, $\text{R} = m\text{-Br}$ (**5**); $\text{R} = p\text{-CN}$ (**6**)). Cyclic voltammetry, elemental analysis, IR and NMR (^1H , ^{13}C and ^{31}P) spectroscopic methods were used for characterization of the obtained compounds. Further, the structure of complexes **3** and **4** were characterized crystallographically. Palladacycles **3** and **4** were proved to be excellent catalysts for the Suzuki-Miyaura coupling reactions of various aryl chlorides and arylboronic acids in mixed DMF/ H_2O media. Also, the bonding situations between

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This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: [10.1002/aoc.3850](https://doi.org/10.1002/aoc.3850)

two interacted fragments $[\text{PtCl}_2]$ and Y_1 and Y_2 ligands in platinacycles **5** and **6** were investigated based on DFT method by using NBO, EDA and ETS-NOCV analysis.

Keywords: Pallada- and platinacycle; Phosphorus ylide; Theoretical studies; Suzuki-Miyaura reaction; DFT method.

1. Introduction

Stabilized phosphorus ylides are an important class of compounds that have attracted considerable interest because of their value for a variety of industrial, biological and chemical synthetic uses.^[1-4] Unsymmetrical α -keto stabilized ylides derived from diphosphines have shown more useful application in organometallic chemistry due to their ambidentate character as ligands.^[5-9] Furthermore, they are valuable key intermediates in metal-mediated organic synthesis.^[10, 11] The coordination behavior of these compounds towards several metal ions has been studied and it was found that phosphorus ylides can coordinate to metal ions in three modes as depicted in Chart 1: monodentate (or unidentate), bidentate (or chelating) and bridging (or bridging bidentate) modes.

Chart 1 here

When a metal ion such as Hg(II) or Ag(I) interacts only with the free P atom of phosphorus group, the coordination structure is regarded as monodentate mode.^[12, 13] If the coordination of ylide occurs through the $\text{C}\alpha$ atom of ylidic group, it was also categorized in above mentioned coordination mode.^[14] Though the ylides can coordinate to the metal ions through the O atoms of

carbonyl group, there are few examples of O-coordinated ylides which are known. Some of these complexes include a hard and very oxophilic metal center, such as Sn(IV)^[15] or group 4 metal ions with high oxidation number *e.g.* Ti(IV), Zr(IV) and Hf(IV).^[16]

Bidentate (or chelating) coordination mode occurs when a metal ion (for example Pd(II) or Cu(I)) interacts with two P and C atoms of ylidic group to give the P, C-chelated complexes.^[17, 18] Although the P, O-chelated coordination mode was also possible, but to the best of our knowledge, it was only observed in the Pd(II) complexes of a mixed phosphine- β -ketophosphorus ylide.^[19] Finally, the bridging coordination mode can be seen when a metal ion bound to one phosphorus ylide through P atom and another metal ion bound to the C α or O atom.^[20] The investigation of reactivity and coordination chemistry of carbonyl stabilized ylides is an important research field of our group.^[12-14, 17, 18] Recently, we reported the synthesis of palladium(II) complexes containing such phosphorus ylides.^[17, 21-23] We aim to expand the scope of these complexes to the new platinacycle complexes of bidentate phosphorus ylides.

Pd(II) complexes bearing phosphine groups have been extensively applied as efficient catalysts in some cross-coupling reactions.^[21-27] Specifically, the Suzuki-Miyaura reaction which emerged as the most important and reliable method for construction of functionalized biaryl, have been catalysed with the P, C-chelated Pd(II) complexes of such phosphorus ylides.^[28-31] Recently, it was reported a variety of catalytic systems for the Suzuki-Miyaura coupling reaction using mixed aqueous media.^[31-34] Application of palladacycle complexes of phosphorus ylides as efficient catalyst in Suzuki-Miyaura coupling reactions of aryl chlorides under relatively mild

experimental conditions is one of the purposes of this work. Although there is no X-ray structure available in this report to prove the molecular structures of platinacycles, however DFT theoretical studies by using NBO, EDA and ETS-NOCV analysis have been performed to elucidate the physical and chemical nature of interactions. We have now focused our attention to the synthesis, spectroscopic (IR and NMR) and electrochemical study of the new pallada- and platinacycles complexes of phosphorus ylide.

2. Experimental

2.1. Materials and methods

The synthesis reaction of phosphorus ylides and their Pd/Pt(II) complexes was carried out under dry nitrogen using standard Schlenk techniques. 2,3'-dibromoacetophenone, 2-bromo-4'-cyanoacetophenone and dppm were purchased from commercial sources and used without further purification. $[MCl_2(cod)]$ (M= Pd and Pt) complexes were prepared according to the published procedures.^[35] Toluene and chloroform were used as reagent grade and dried over Na/benzophenone and P_2O_5 , respectively. Elemental analysis was performed on a Leco, CHNS-932 apparatus. The NMR spectra (1H , ^{13}C and ^{31}P) were recorded on BrukerAvance 400 MHz, 250 MHz and Jeol 90 MHz spectrometers in $CDCl_3$ or $DMSO-d_6$ as solvents at 25 °C. IR spectra

were recorded on KBr pellets using a Shimadzu 435-U 04 spectrophotometer in the region of 4000-400 cm^{-1} . Cyclic voltammetry was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm^2 area), and a platinum wire was used as the counter electrode. The working electrode potentials were measured versus the Ag/AgCl electrode (all electrodes were purchased from AZAR Electrodes co.).

2.2. Synthesis of phosphonium salts

General procedure: A chloroform solution (5 mL) of dppm (0.5 mmol) and ketone (0.55 mmol) was stirred at room temperature for 15 h. The resulting solution was concentrated to *ca.* 3 mL under reduced pressure and then treated with diethyl ether to precipitate phosphonium salt.

2.2.1. Data for phosphonium salt $[\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C(O)C}_6\text{H}_4\text{-}m\text{-Br}]\text{Br}$ (S_1). Yield: 0.314 g (94%). Anal. Calcd for $\text{C}_{33}\text{H}_{28}\text{Br}_2\text{OP}_2$ (%): C, 59.84; H, 4.26. Found: C, 59.77; H, 4.22. M.p. 196–198 $^\circ\text{C}$. Selected IR absorption in KBr (cm^{-1}) $\nu(\text{CO})$: 1676. ^1H NMR (89.6 MHz, CDCl_3) δ_{H} (ppm): 4.31 (d, 2H, PCH_2P , $^2J_{\text{P-H}} = 12.23$), 5.96 (d, 2H, PCH_2CO , $^2J_{\text{P-H}} = 12.81$), 7.30–7.99 (m, 24H, Ph). ^{31}P NMR (36.26 MHz, CDCl_3) δ_{P} (ppm): -28.67 (d, PPh_2 , $^2J_{\text{P-P}} = 62.37$ Hz), 21.12 (d, PCH_2CO , $^2J_{\text{P-P}} = 63.85$ Hz). ^{13}C NMR (62.90 MHz, CDCl_3) δ_{C} (ppm): 191.40 (d, CO, $^2J_{\text{P-C}} = 5.85$), 117.15-151.83 (m, Ph), 37.38 (d, CH_2 , $^1J_{\text{P-C}} = 60.38$), 21.95 (dd, CH_2 , $^1J_{\text{P-C}} = 51.96$, 34.47).

2.2.2. Data for phosphonium salt $[\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-CN}]\text{Br}$ (S_2). Yield: 0.301 g (98%). Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{BrNOP}_2$ (%): C, 67.12; H, 4.64; N, 2.30. Found: C, 67.01; H, 4.51; N, 2.41. M.p. 191–194 °C. Selected IR absorption in KBr (cm^{-1}) $\nu(\text{CO})$: 1682. ^1H NMR (250.13 MHz, CDCl_3) δ_{H} (ppm): 4.25 (d, 2H, PCH_2P , $^2J_{\text{P-H}} = 14.75$), 6.08 (d, 2H, PCH_2CO , $^2J_{\text{P-H}} = 12.75$), 7.24–7.89 (m, 24H, Ph). ^{31}P NMR (202.45 MHz, CDCl_3) δ_{P} (ppm): -25.83 (d, PPh_2 , $^2J_{\text{P-P}} = 64.17$ Hz), 24.41 (d, PCH_2CO , $^2J_{\text{P-P}} = 63.57$ Hz). ^{13}C NMR (62.90 MHz, CDCl_3) δ_{C} (ppm): 191.66 (s, CO), 117.13–137.95 (m, Ph), 36.90 (d, CH, $^1J_{\text{P-C}} = 62.40$), 21.93 (dd, CH_2 , $^1J_{\text{P-C}} = 70.86$, 35.29).

2.3. Synthesis of phosphorus ylides

General procedure: The resulted phosphonium salt was further treated with triethyl amine (0.5 mL) in dry toluene. The triethyl amine hydrobromide was filtered off. Concentration of the toluene solution to *ca.* 3 mL and subsequent addition of petroleum ether (20 mL) resulted in the precipitation of phosphorus ylide.

2.3.1. Data for phosphorus ylide $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}m\text{-Br}$ (Y_1). Yield: 0.234 g (80%). Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{BrOP}_2$ (%): C, 68.17; H, 4.68 Found: C, 68.11; H, 4.59. M.p. 157–160 °C. Selected IR absorption in KBr (cm^{-1}) $\nu(\text{CO})$: 1572. ^1H NMR (89.60 MHz, CDCl_3) δ_{H} (ppm): 3.64 (d, 2H, PCH_2P , $^2J_{\text{P-H}} = 14.06$ Hz), 4.31 (br, 1H, PCH), 6.70–7.91 (m, 24H, Ph). ^{31}P NMR (36.26 MHz, CDCl_3) δ_{P} (ppm): -26.82 (d, PPh_2 , $^2J_{\text{P-P}} = 66.71$ Hz), 14.53 (d, PCH, $^2J_{\text{P-P}} = 65.99$ Hz). ^{13}C NMR (62.90 MHz, CDCl_3) δ_{C} (ppm): 183.07 (s, CO), 121.99–143.22 (m, Ph), 50.62 (d, CH, $^1J_{\text{P-C}} = 111.39$), 24.42 (dd, CH_2 , $^1J_{\text{P-C}} = 57.86$, 32.07).

2.3.2. Data for phosphorus ylide $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C(H)C(O)C}_6\text{H}_4\text{-p-CN}$ (Y_2). Yield: 0.194 g (73%). *Anal.* Calc. for $\text{C}_{34}\text{H}_{27}\text{NOP}_2$ (%): C, 77.41; H, 5.16; N, 2.66. Found: C, 77.38; H, 5.12; N, 2.72. M.p. 149-153 °C. Selected IR absorption in KBr (cm^{-1}) $\nu(\text{CO})$: 1572. ^1H NMR (500.13 MHz, CDCl_3) δ_{H} (ppm): 3.68 (d, 2H, PCH_2P , $^2J_{\text{P-H}} = 14.00$ Hz), 4.33 (t, 1H, PCH), 7.27–7.90 (m, 24H, Ph). ^{31}P NMR (202.45 MHz, CDCl_3) δ_{P} (ppm): -26.48 (d, PPh_2 , $^2J_{\text{P-P}} = 64.18$ Hz), 15.35 (d, PCH, $^2J_{\text{P-P}} = 63.98$ Hz). ^{13}C NMR (62.90 MHz, CDCl_3) δ_{C} (ppm): 183.18 (s, CO), 127.40-144.76 (m, Ph), 45.62 (s, CH), 25.35 (dd, CH_2 , $^1J_{\text{P-C}} = 59.03$, 32.20).

2.4. Synthesis of the Pd/Pt(II) complexes

General procedure: To a dichloromethane solution of $[\text{MCl}_2(\text{cod})]$ ($\text{M}=\text{Pd}$ or Pt) (0.5 mmol, 5 mL), a solution of ylide (0.5 mmol) (5 mL, CH_2Cl_2) was added. The resulting solution was stirred for 2 h at room temperature and then concentrated to a *ca.* 2 mL under reduced pressure and treated with n-hexane (15 mL) to afford the Pd(II) or Pt(II) complexes of phosphorus ylide.

2.4.1. Data for Pd(II) complex $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C(H)C(O)C}_6\text{H}_4\text{-m-Br})]$ (3**).** Yield: 0.303 g (80%). *Anal.* Calc. for $\text{C}_{33}\text{H}_{27}\text{BrCl}_2\text{OP}_2\text{Pd}$ (%): C, 52.24; H, 3.59. Found: C, 52.18; H, 3.62. M.p. 198-201 °C (dec). Selected IR absorption in KBr (cm^{-1}) $\nu(\text{CO})$: 1619. ^1H NMR (89.60 MHz, DMSO-d_6) δ_{H} (ppm): 4.65 (br, PCH_2P , 2H), 5.98 (s, 1H, PCH), 7.25–8.31 (m, 24H, Ph). ^{31}P NMR (36.26 MHz, DMSO-d_6) δ_{P} (ppm): 26.73 (d, PPh_2 , $^2J_{\text{P-P}} = 49.07$ Hz), 38.04 (d, PCH, $^2J_{\text{P-P}} = 47.29$ Hz). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ_{C} (ppm): 195.80 (s, CO), 121.32-140.04 (m, Ph), 32.62 (d, PCH, $^1J_{\text{P-C}} = 56.48$ Hz).

2.4.2. Data for Pd(II) complex [PdCl₂(Ph₂PCH₂PPh₂C(H)C(O)C₆H₄-*p*-CN)] (4). Yield: 0.248 g (90%). *Anal.* Calc. for C₃₄H₂₇NCl₂OP₂Pd (%): C, 57.94; H, 3.86; N, 1.99. Found: C, 57.83; H, 3.82; N, 2.08. M.p. 190-192 °C (dec). Selected IR absorption in KBr (cm⁻¹) ν(CO): 1620. ¹H NMR (250.13 MHz, DMSO-d₆) δ_H (ppm): 4.86 (t, PCH₂P, 2H), 6.03 (s, 1H, PCH), 7.20–8.12 (m, 24H, Ph). ³¹P NMR (101.24 MHz, DMSO-d₆) δ_P (ppm): 27.51 (b, PPh₂), 37.66 (d, PCH, ²J_{P-P} = 42.21 Hz). ¹³C NMR (62.90 MHz, DMSO-d₆) δ_C (ppm): 196.12 (s, CO), 115.03–141.73 (m, Ph), 33.43 (d, PCH, ¹J_{P-C} = 54.97 Hz).

2.4.3. Data for Pt(II) complex [PtCl₂(Ph₂PCH₂PPh₂C(H)C(O)C₆H₄-*m*-Br)] (5). Yield: 0.305 g (72%). *Anal.* Calc. for C₃₃H₂₇BrCl₂OP₂Pt (%): C, 46.77; H, 3.21. Found: C, 46.90; H, 3.34. M.p. 231-233 °C (dec). Selected IR absorption in KBr (cm⁻¹) ν(CO): 1634. ¹H NMR (250.13 MHz, CDCl₃) δ_H (ppm): 4.77 (br, PCH₂P, 2H), 5.56 (s, 1H, PCH, ³J_{Pt-H} = 65.07 Hz), 7.05–8.29 (m, 24H, Ph). ³¹P NMR (101.24 MHz, CDCl₃) δ_P (ppm): 3.91 (d, PPh₂, ¹J_{Pt-P} = 3947.73 Hz, ²J_{P-P} = 36.85 Hz), 41.14 (d, PCH, ²J_{P-P} = 36.97 Hz). ¹³C NMR (62.90 MHz, CDCl₃) δ_C (ppm): 194.47 (s, CO), 119.95–141.72 (m, Ph), 27.73 (d, PCH, ¹J_{P-C} = 56.37 Hz).

2.4.4. Data for Pt(II) complex [PtCl₂(Ph₂PCH₂PPh₂C(H)C(O)C₆H₄-*p*-CN)] (6). Yield: 0.311 g (79%). *Anal.* Calc. for C₃₄H₂₇NCl₂OP₂Pt (%): C, 51.46; H, 3.43; N, 1.77. Found: C, 51.59; H, 3.57; N, 1.90. M.p. 218-220 °C (dec). Selected IR absorption in KBr (cm⁻¹) ν(CO): 1601. ¹H NMR (250.13 MHz, CDCl₃) δ_H (ppm): 4.85 (dd, PCH₂P, 2H), 5.58 (s, 1H, PCH, ³J_{Pt-H} = 70.04 Hz), 6.98–8.04 (m, 24H, Ph). ³¹P NMR (101.24 MHz, CDCl₃) δ_P (ppm): 2.00 (d, PPh₂, ¹J_{Pt-P} = 3921.02 Hz, ²J_{P-P} = 38.47 Hz), 39.62 (d, PCH, ²J_{P-P} = 39.48 Hz). ¹³C NMR (62.90 MHz, CDCl₃)

δ_C (ppm): 197.17 (s, CO), 120.60-136.32 (m, Ph), 119.17 (s, CN), 31.92 (d, PCH, $^1J_{P-C} = 53.46$ Hz).

2.5. Crystallography

Data collection for complex **3** was performed on an Oxford Diffraction SuperNova diffractometer using mirror monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 130 K. Using Olex2^[36], the structure was solved with the ShelXT^[37] structure solution program using Direct Methods and refined with the ShelXL^[38] refinement package using Least Squares minimization on F^2 . Gaussian absorption corrections were applied to the data. All non-hydrogen atoms were refined with anisotropic displacement parameters, using all data.

Also, Crystallographic data for complex **4** were collected on an MAR345 dtb diffractometer equipped with image plate detector using Mo K α X-ray radiation. The structure was solved by direct methods using SHELXS-97, and refined using full-matrix least-squares method on F^2 , SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and refined using a riding model.

2.6. Computational studies

The geometries of the aforementioned Pt(II) complexes were fully optimized at BP86^[39, 40]/def2-SVP^[41] level of theory. It has been shown that BP86 is a suitable level for calculation of bonding situation between the M←L in such as these complexes.^[42-50] All calculations were performed using the Gaussian 09 set of programs.^[51] NBO analyses^[52] were also carried out with

the internal model GAUSSIAN 09. For bonding analyses between two fragment (Ylide and PtCl_2), the terms of energy decomposition analysis (EDA) were carried out at BP86/TZ2P (ZORA)//BP86/def2-TZVPP with C1 symmetry. The basis sets for all elements have triple- ζ quality augmented by one set of polarization functions (ADF basis set TZ2P (ZORA)) with the program package ADF2009.01.

2.7. Typical procedure for the Suzuki-Miyaura coupling reaction

General procedure: A mixture of aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), palladacycle complex (0.005 mmol) and K_2CO_3 (1 mmol) was heated at 110 °C in DMF/ H_2O (2 mL, 1:1) for 6 h in the presence of air. The reactions were monitored by thin-layer chromatography (TLC). The reaction mixture was then cooled to room temperature. After completion of reaction, the mixture was diluted with n-hexane (15 mL) and water (15 mL). The organic layer was washed with brine (15 mL) and dried over CaCl_2 . The solvent was evaporated under reduced pressure and a crude product was obtained, which was analyzed by ^1H and ^{13}C NMR.

2.7.1. Data for Ph-Ph (7a). M.p. 67-69 °C. ^1H NMR (400.61 MHz, CDCl_3) δ_{H} (ppm): 7.40-7.64 (m, 10H, phenyl). ^{13}C NMR (100.62 MHz, CDCl_3) δ_{C} (ppm): 141.29, 128.79, 127.29, 127.21.

2.7.2. Data for *p*-CHO-Ph-Ph (7b). M.p. 89-91 °C. ^1H NMR (400.61 MHz, CDCl_3) δ_{H} (ppm): 7.40-7.86 (m, 9H, phenyl), 9.98 (s, 1H, CHO). ^{13}C NMR (100.62 MHz, CDCl_3) δ_{C} (ppm): 191.94 (s, CO), 147.23, 139.74, 135.22, 130.29, 129.03, 128.49, 127.71, 127.39.

2.7.3. Data for *p*-CH₃O-Ph-Ph (7c). M.p. 90-92 °C. ^1H NMR (400.61 MHz, CDCl_3) δ_{H} (ppm): 3.78 (s, 3H, OCH₃), 6.89-7.49 (m, 9H, phenyl). ^{13}C NMR (100.62 MHz, CDCl_3) δ_{C} (ppm): 159.15, 140.84, 133.79, 128.73, 128.17, 127.75, 126.75, 126.67, 114.30, 114.20, 55.36 (s, OCH₃).

2.7.4. Data for *p*-CH₃OC-Ph-Ph-Et (7d). M.p. 105–108 °C. ^1H NMR (400.61 MHz, CDCl_3) δ_{H} (ppm): 1.24 (t, 3H, CH₃), 2.51 (s, 3H, CH₃), 2.59 (q, 2H, CH₂), 7.25-8.01 (m, 8H, phenyl). ^{13}C NMR (100.62 MHz, CDCl_3) δ_{C} (ppm): 197.76 (s, CO), 154.74, 144.57, 137.18, 135.58, 129.3, 128.89, 128.49, 127.18, 126.90, 28.55 (s, CH₂), 26.64 (s, CH₃), 15.52 (s, CH₃).

2.7.5. Data for *p*-CH₃-Ph-Ph (7e). M. p. 51-53 °C. ^1H NMR (89.61 MHz, CDCl_3) δ_{H} (ppm): 2.61 (s, 3H, CH₃), 7.46-8.09 (m, 9H, phenyl). ^{13}C NMR (100.62 MHz, CDCl_3) δ_{C} (ppm): 137.60, 137.46, 134.67, 129.73, 129.09, 128.76, 127.85, 126.85, 126.77, 21.27 (s, CH₃).

3. Results and discussion

3.1. Synthesis

Reaction of diphosphine $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ with 1 equiv. of 2,3'-dibromoacetophenone or 2-bromo-4'-cyanoacetophenone gave the new phosphonium salts S_1 and S_2 . Further treatment of these salts with triethyl amine led to elimination of HBr and formation of new unsymmetrical phosphorus ylides Y_1 and Y_2 . Reaction of these ligands with $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}$ and Pt) in equimolar ratio yielded the new P, C-chelated pallada- and platinacycle complexes **3-6** (Scheme 1).

Scheme 1 here

3.2. Spectroscopy

The structure of products was characterized successfully by ^1H , ^{13}C and ^{31}P NMR spectroscopic methods and other conventional techniques such as IR and elemental analysis. Table 1 shows the brief summary of these data.

Table 1 here

Also, the exact structure of complexes **3** and **4** with atomic resolution were being unequivocally determined by single crystal X-ray diffraction technique. The CHN elemental analysis of pallada- and platinacycle complexes indicates a 1:1 stoichiometry between the MCl_2 ($\text{M} = \text{Pd}$ and Pt) and phosphorus ylide.

The $\nu(\text{CO})$ band in the IR spectra of phosphorus ylides Y_1 and Y_2 were observed at lower frequencies compared to the related phosphonium salts S_1 and S_2 , indicating formation of $\text{P}=\text{C}$ double bond and decrease of $\text{C}=\text{O}$ bond order. Coordination of ylide through the carbon atom

(chelating mode) causes an increase in the $\nu(\text{CO})$ frequency, while for O-coordination a lowering shift for this frequency is expected.^[53] The $\nu(\text{CO})$ in IR spectra of complexes **3-6** occurs around 1600-1630 cm^{-1} and shows significantly shift to higher frequency than those of related phosphorus ylides. Thus, the obtained IR data indicates that the chelation of ylide to Pd(II) and Pt(II) occurs through the ylidic carbon atom and PPh_2 group (see supplementary data).^[17, 20]

The ^{31}P NMR spectra of phosphonium salts **S₁** and **S₂** show two doublets around 21, -28 and 24, -25 ppm, which are assigned to the PCH and PPh_2 groups, respectively. In ^{31}P NMR spectra of ylides **Y₁** and **Y₂**, the phosphonium group of these compounds shows upfield shifts compared to that of parent phosphonium salts. These peaks were shifted to around 14, -26 and 15, -26 ppm, respectively, consistent with some increase of electron density in the $\text{P}=\text{C}$ bonds. The ^{31}P chemical shift values for complexes **3-6** appear to be shifted to downfield with respect to phosphorus ylides **Y₁** and **Y₂**, indicating that coordination of the ylide has been occurred. The ^{31}P NMR spectra of palladacycles **3** and **4** exhibit two doublets around 26, 38 and 27, 37 ppm, which are assigned to the PPh_2 and PCH groups, respectively. Whereas, the ^{31}P NMR spectra of platinacycles **5** and **6** show these peaks around 41, 4 and 40, 2 ppm along with two satellite peaks due to ^{195}Pt - ^{31}P coupling (see supplementary data).

Also, the ^1H NMR spectra show all the expected resonances of compounds **S₁**, **S₂**, **Y₁**, **Y₂** and **3-6**. The ^1H NMR spectra of ylides **Y₁** and **Y₂** show an upfield shift for the CH signals compared to the those of phosphonium salts **S₁** and **S₂** indicating that synthesis of the ylides has occurred. The ^1H chemical shift values for complexes **3-6** appear to be shifted to downfield with respect to

the parent ylide, as a consequence of P, C-coordination character of the ylide. Similar behavior was observed earlier in the case of ylide complexes of copper(I) chlorides.^[18]

In the ^{13}C NMR spectra of ylides **Y**₁ and **Y**₂, a downfield shift of the signals due to the ylidic carbon is also observed and it was attributed to the change in hybridization of the ylidic carbon atom. Further, the signals due to the carbonyl group in ^{13}C NMR spectra of ylides **Y**₁ and **Y**₂ shifted to higher field compared to the parent phosphonium salts. The most important aspect of ^{13}C NMR spectra of these complexes is the downfield shift of signals due to the carbonyl group. The ^{13}C NMR spectra of complexes **3-6** show the characteristic peaks of carbonyl group around 196 ppm, compare to 183 ppm for the same carbon in the parent free ylides, indicating a much lower shielding of the carbon of the CO group in these complexes (see supplementary data). Thus, the spectral data indicate the bidentate coordination of the ylides through both the phosphine group and the ylidic carbon atom.

3.3. Crystallography

Suitable single crystals of complexes **3** and **4** were grown by vapor diffusion of methanol into DMSO solution. The molecular structures of **3** and **4** were shown in Fig. 1 and Fig. 2, respectively. Relevant parameters concerning data collection and refinement were given in Table 2. Selected bond distances and angles for the unit cells of **3** and **4** are displayed in Table 3.

Fig. 1 here

Fig. 2 here

Table 2 here

Table 3 here

Hydrogen atoms of complex **3** were located in ideal positions. There were two independent molecules in the asymmetric unit. For one of the molecules, the 3-bromophenylethanone group and one of the phenyl rings were found to be disordered and no evidence of disorder was seen in the rest of the molecule. The main difference between them is in the orientation of the 3-bromophenylethanone group, with the torsion angle O1 - C2...C5 - Br1 being $-177.51(19)^\circ$, for molecule 1 and the torsion angle O2 - C35...C38 - Br2 being $-22.6(18)^\circ$ for molecule 2. The dihedral angles of the keto group with the aromatic rings are $2.79(15)^\circ$ and $21.0(5)^\circ$, respectively.

For molecule 1 there are three weak intramolecular C-H...Cl interactions, between hydrogen atoms on the aromatic rings and the coordinated chloride. All other C-H...X interactions are intermolecular interactions that link the molecules into a 3D network. Refinement was carried out with the atoms of both groups distributed over 2 positions, the geometry of each component being restrained to be equal. The final occupancy factors were 0.8057(17) and 0.1943(17), for the 3-bromophenylethanone group, and 0.575(19) and 0.425(19).

The coordinates of the two molecules were chosen such that C1 and C34 had both the S configuration. Both Pd atoms are in a tetrahedrally distorted square planar environment, with the P-Pd-Cl and the C-Pd-Cl angles being significantly less than 180° . This distortion is more

pronounced for molecule 1 than molecule 2. The Pd-containing five-membered rings both adopts a half-chair conformation, with C1 lying above (0.507(3) Å) and P1 lying below (-0.368(3) Å) the plane of the other 3 atoms. For molecule 2, C34 lies below (-0.269(3) Å) and P1 lies above (0.487(3) Å) the plane.

3.4. Theoretical studies

In 2014, Samiee and his co-worker confirmed that the structure of $[R_2P(CH_2)_nPRC(H)C(O)R)MX_2]$ ($R=Me, Ph$; $M=Ni, Pt$ and Pd and $X= Cl, Br, I$; $n= 1, 2, 3$) complexes are square planar. In these structures, two halogen atoms are oriented in cis position.^[54] Thus according to this reports, we considered the square planar structures for $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ ($Y_1= Ph_2PCH_2PPh_2C(H)C(O)C_6H_4-m-Br$ and $Y_2= Ph_2PCH_2PPh_2C(H)C(O)C_6H_4-p-CN$) complexes. A theoretical study on structure and nature of bond in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes with square planar structures have been reported at the BP86 level using def2-SVP basis set. The optimized structures of $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes at the BP86/def2-SVP level of theory are given in Fig. 3, and important bond lengths and bond angles extracted from optimized geometry are given in Table 4.

Fig. 3 here

Table 4 here

The result show that the optimized' bond lengths and bond angles for $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ are same and these data are in good agreement with those which recently reported with Samiee and his co-worker for $[(Ph_2P(CH_2)_2PPh_2CHC(O)CH_3)PtCl_2]$ complexes (see Table 4).^[54]

For studying the nature of metal-ligand bond and/or possible interactions in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes, the NBO analysis was performed.^[51] The values of the Wiberg (WBI) and partial charges on Pt, C and Cl atoms involved in the bonding interactions between $PtCl_2$ and Y_1 and Y_2 fragments in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes as well as total charge of Y_1 and Y_2 fragments were also evaluated through natural population analysis and are given in Table 5.

Table 5 here

The result showed that the calculated partial charge (q) on both the Pt and C atoms in the Pt–C bonds is negative. Also, the negative value of q(C) is greater than that for q(Pt) (see Table 5). On the other hand, the negative values of the total charge of $[PtCl_2]$ fragments show the charge transfer about 0.85 occurred from Y_1 and Y_2 ligands to $[PtCl_2]$ fragments in the complexes. A second-order perturbation theory analysis of the Fock matrix was carried out to evaluate the donor–acceptor interactions on the base of NBO analysis. The values of donor–acceptor interactions in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes are given in Tables 6.

Table 6 here

The results showed that in the aforementioned complexes, the important donor–acceptor interactions in the case of Pt–C bond were carried out from the $\sigma(Pt-C)$ and $\sigma(Pt-P)$ as donors to $\sigma^*(Pt-P)$ and $\sigma^*(Pt-C)$ as acceptors (See Table 6).

for better analysis of the nature of the Pt–C bonding between the Y_1 and Y_2 and $[PtCl_2]$ fragments in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes, the quantum chemical calculations in the terms of energy-decomposition analysis at the BP86-D3/TZ2P(ZORA)//BP86/def2-SVP with C_1 symmetry by using the program package ADF2009.01 were carried out. The results of the EDA analyses for aforementioned complexes are given in Table 7.

Table 7 here

As can be seen, the ΔE_{int} between two interacted fragments in both $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes are 156.81 and 153.80 kcal mol⁻¹ respectively (See Table 7). The breakdown of the ΔE_{int} values into the Pauli repulsion (ΔE_{Pauli}) and the three attractive components (ΔE_{elstat} , ΔE_{orb} and ΔE_{dis}) show that roughly 58% of total interaction comes from the electrostatic attraction (ΔE_{elstat}) while ~37% comes from the orbital term (ΔE_{orb}) and the remaining (4.7%) concern to $\Delta E_{dispersion}$. Thus the values of ΔE_{elstat} showed that the nature of Pd–C bonding in both $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes are more electrostatic. These data are in good agreement with the results of NBO analysis which shows charge transfer of about 0.85 from Y_1 and Y_2 to $[PtCl_2]$ fragment (see Table 6) and the WBI value of 0.49 for Pt–C bonds in the complexes.

The covalent bonding between the $[PtCl_2]$ fragment and Y_1 and Y_2 Ligands in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes becomes visible by the calculated deformation densities $\Delta\rho$. Fig. 4 shows the important deformation densities $\Delta\rho$ and the associated energy values which provide about 90 % of the overall orbital interactions for the complex. As it is illustrated in Fig. 4a and 4b, the dominant terms of ΔE_{orb} for $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes arise from $\Delta\rho_1$ and $\Delta\rho_2$,

showing σ donation from C(ylide) and P atoms of Y_1 and Y_2 fragments to $[PtCl_2]$ in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes.

Also Fig. 4c, d, e, and f display the deformation density $\Delta\rho_3$, $\Delta\rho_4$, $\Delta\rho_5$ and $\Delta\rho_6$ which show the π -back donation from the $[PtCl_2]$ fragment to Y_1 and Y_2 ligand in latter complexes. In the above theoretical studies, the effect of R group (R= Br or CN) substituted on aromatic part of ylides (Y_1 and Y_2) in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes is negligible.

Fig. 4 here

Rest of Fig. 4 here

3.5. Cyclic voltammetry

The electrochemical behaviors of the free ylides, Y_1 and Y_2 , and their related Pd(II) and Pt(II) complexes, **3-6**, were studied by cyclic voltammetry. CV curves of the all compounds at a 50 mVs⁻¹ scan rate in acetonitrile solutions (1 mM) are given in Fig. 5. The reduction of Pd(II)/Pd(0) was observed for the Pd(II) complexes and the reduction of Pt(II)/Pt(0) for the Pt(II) complexes.

Fig. 5 here

Fig. 5 shows two cathodic peaks for the ylides Y_1 and Y_2 , C_1 and C_2 , at - 1.00 and - 0.98 V versus Ag/AgCl, respectively. Under the same conditions, the cyclic voltammogram of a 1 mM solution of the complexes, showed irreversible electron transfer. At a scan rate of 50 mVs⁻¹, there were two cathodic peaks for **3**, C_3 and C_{Y3} , at - 0.91 and - 0.58 V and one cathodic peak for **5**,

C₅, at – 0.89 V corresponding to the redox pair Pd(II)/Pd(0), the reduction of ylide **Y**₁ and the redox pair Pt(II)/Pt(0), respectively (Fig. 5, curves a and b). This behavior is similar to that reported previously by Champness et al.^[55], Batchelor et al.^[56] and Kvam et al.^[57] voltammetric studies of various types of Pd(II) and Pt(II) complexes in aprotic solvents.

The cyclic voltammogram of **6** shows one irreversible reduction peak, C₆, at – 0.72 V corresponding to the redox pair Pt(II)/Pt(0) (Fig. 5, curve c). Pt(I) and Pt(III) complexes are noted for instability and any reduction or oxidation processes centralized on metal orbitals of Pt(II) complexes typically exhibit irreversible behavior.^[57, 58] In **4**, such as **3**, peak C₄ (– 0.77 V) is assigned to the two electron reduction of Pd(II) center in the complex and the second reduction peak, C_{Y2} (– 0.49 V), is related to the reduction of ylide **Y**₂ (Fig. 5, curve d).^[17, 59] The overall two-electron reduction of the Pd(II) complexes is expected to take place in separate one-electron steps^[55, 56, 60] and this might be achieved via manipulation of the thermodynamics or electrode kinetics of either step by correct choice of the experimental conditions. Under our experimental conditions, the Pd(I) complexes are unstable. Thus peaks C₃ and C₄ in Fig. 5 corresponds to a two-electron reduction of the Pd(II) complex which is a consequence of the thermodynamic instability of the intermediate one-electron product under our experimental conditions. A comparison of curves a and b with curves c and d in Fig. 5 clearly confirms the presence of Pd(II) and Pt(II) centers in the complexes with different chemical environments.

3.6. Suzuki-Miyaura coupling reaction of aryl chlorides

The catalytic activity of palladacycles **3** and **4** in Suzuki-Miyaura coupling reaction was then examined. Initially, we carried out a model reaction to optimize the reaction conditions including base, solvent, temperature and catalyst loading (Table 8). Reaction of phenylboronic acid with chlorobenzene in DMF/H₂O (1:1) at 110°C in the presence of K₃PO₄ (1 mmol) and 0.05 mmol of catalyst **3** was chosen as model reaction. The reaction led to formation of coupled product in 70% yield (Table 8, entry 1). Then, a series of experiments was performed to find optimum conditions.

Table 8 here

At the first stage of optimization, we study the effect of base and solvent on the reaction. Since the solubility and basicity of base strongly depend on the solvent used, these two parameters are closely connected. This optimization was done with commonly used bases and solvents, including organic and inorganic bases and aqueous protic and aprotic solvents. Coupling reactions carried out in presence of K₂CO₃ and K₃PO₄ give the desired coupling product in moderate to high yields (Table 8, entries 2, 5 and 1, 4). However, the reactions in presence of NEt₃ did not proceed efficiently even after prolonged stirring at reflux temperature of solvents (Table 8, entries 6 and 9). Among the tested aqueous solvents, DMF/H₂O gave higher yields of coupled product. Also, the reactions in water and non-aqueous DMF led to lower yields, indicating the important role of solubility of base in such catalytic systems (Table 8, entries 10 and 11).

Next, we investigate the effect of catalyst loading on the reaction. As expected, varying the catalyst loading has a significant effect on the performance of the catalyst. When the loading of palladacycle **3** decreased to 0.005 mmol, the coupling reaction gave slightly lower yield of product and the reaction resulted in negligible yield of coupled product when the catalyst loading decreased to 0.0005 mmol (Table 8, entries 12 and 13). A control experiment showed that the reaction fails in blank run (in the absence of Pd-catalyst) and the coupling reaction did not occur during 6 h (Table 8, entry 14). Also, excessive amount of catalyst increased the yield significantly (Table 8, entry 15). However, with respect to the economic aspect, 0.005 mmol of catalyst was chosen as the best catalyst loading.

Finally, the reactions were carried out at different temperatures. Decreasing the temperature of reactions has led to the fall of the yields and increasing the reaction time to completion of reactions (Table 8, entries 16 and 17). Thus, the optimum condition obtained for Suzuki-Miyaura coupling reaction consisting the DMF/H₂O as solvent, K₂CO₃ as base, 0.005 mmol of palladacycle **3** as catalyst and reaction at 110 °C for 6 h.

Using the optimized reaction conditions, palladacycles **3** and **4** were applied in reaction of various functionalized aryl chlorides bearing both electron-donating to electron-withdrawing groups with phenylboronic acid. Aryl chlorides were converted into the corresponding coupled products in high yields (Table 9). Conversely, increasing electron density on the aryl chlorides lowered the catalyst activity. That is, excellent yields are achieved when phenylboronic acid reacted with aryl chlorides bearing electron-withdrawing substituent -CHO and -COCH₃ (Table

9, entries 1 and 2). Deactivated aryl chlorides 4-chlorotoluene and 4-chloroanisole gave lower yields indicating that the reaction was sensitive to the electron density on the aryl chlorides (Table 9, entries 4 and 5). The reaction of electronically neutral chlorobenzene with phenylboronic acid also produced good amounts of the product (Table 9, entry 3). As can be seen in Table 9, we observed that in all cross-coupling reactions catalyst **3** and **4** had approximately same catalytic activities. It seems that palladacycles **3** and **4** produce similar catalytically active species in reactions, since the *m*-Br or *p*-CN substituents on the end of the aryl group in phosphorus ylide moiety could not affect significantly the release of catalytically active species.

Table 9 here

To extend the scope of our work, we next investigated the coupling reaction of aryl chloride substrates with ethyl substituted phenylboronic acid. As expected, electron-donating substituent on arylboronic acid has decreasing effect on the yield of reaction (Table 9, entries 6-10). However, coupling reaction of activated aryl chlorides such as 4-chloroacetophenone gave the coupled boronic acid derivatives in higher yields (Table 9, entry 10).

To evaluate the homogeneous or heterogeneous nature of the active species, we carried out the mercury drop test.^[61] Since mercury leads to amalgamation of the surface of a heterogeneous catalyst, and in contrast, Hg(0) is not expected to have a poisoning effect on homogeneous palladium complexes, the results of desired test help us to determine the nature of the active species.^[62] Addition of a drop of mercury to the reaction mixture at *t*=0 did not affect

the conversion of the reaction, which suggests that amalgamation had not occurred and the catalysis was homogeneous in nature.

As can be seen in Table 9, by using aryl chlorides good amounts of functionalized biaryl derivatives are yielded. The higher C–Cl bond dissociation energy compared with C–Br and C–I bonds disfavors oxidative addition step in catalytic coupling reactions.^[63] However, the ideal substrates for coupling reactions are aryl chlorides, since they are cheaper and more widely available than their bromide or iodide analogous. Table 10 shows a comparison between the efficiency of this catalytic system in Suzuki-Miyaura coupling reaction of aryl chlorides and other catalytic systems. The results showed that the most active palladacycles, N-heterocyclic carbenes (NHCs) and pyridine-enhanced precatalyst preparation stabilization and initiation (PEPPSI)-type Pd complexes need to be used in high loadings and showed lower activity with aryl chloride substrates.^[64-72] From an industrial view point, the low catalyst loading and short reaction time make this palladacycle as an ideal catalyst for the Suzuki-Miyaura coupling reaction.

Table 10 here

4. Conclusions

In summary, we report the synthesis and characterization of new phosphinium salts **S**₁ and **S**₂, phosphorus ylides **Y**₁ and **Y**₂, and pallada- and platinacycle **3-6**. The palladacycles **3** and **4** were characterized fully by spectroscopic methods as well as X-ray crystallography method. Results

showed that chelation of ylide through the ylidic carbon atom and phosphine group afforded a five-membered ring. Also, the catalytic activity of palladacycles **3** and **4** towards Suzuki-Miyaura coupling reaction was investigated. Results showed that the coupling reaction of various aryl chlorides with arylboronic was performed in high yields. The bonding situations between two interacted fragments $[MCl_2]$ and Y_1 and Y_2 ligands in platinacycles **5** and **6** were investigated based on DFT method by using NBO, EDA, and ETS-NOCV analysis. The NBO shows the charge transfer about 0.85e from Y_1 and Y_2 ligands to $[PtCl_2]$ fragment in the complexes. The EDA analysis confirms that the nature of bonds between two interacted fragments in latter complexes is mostly electrostatic, and its contribution in total interaction energy is about 58%. The ETS-NOCV analyses confirm that the mainly contribution to ΔE_{orb} in $[Y_1PtCl_2]$ and $[Y_2PtCl_2]$ complexes arise from σ -donation and shortly from π back donation.

Acknowledgements

Funding of our research from the Bu-Ali Sina University is gratefully acknowledged.

Supplementary material

Physical measurements and selected ^{31}P , ^{13}C and 1H NMR spectra of some compounds can be found in the online version. CCDC 1431938 and 1418881 contains the supplementary crystallographic data for the complexes **3** and **4**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data

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Table 1. Spectroscopic data for compounds **S₁**, **S₂**, **Y₁**, **Y₂** and **3-6**

Compound	IR; $\nu(\text{CO}) \text{ cm}^{-1}$	^1H NMR; $\delta(\text{PCH}) \text{ ppm}$	^{13}C NMR; $\delta(\text{CO}) \text{ ppm}$	^{31}P NMR; $\delta(\text{PCH})$ and $(\text{PPh}_2) \text{ ppm}$
S₁	1676	5.96	191.40	21.12, -28.67
S₂	1682	6.08	191.66	24.41, -25.83
Y₁	1572	4.31	183.07	14.53, -26.82
Y₂	1572	4.33	183.18	15.35, -26.48
3	1619	6.02	195.80	38.04, 26.73
4	1620	6.03	196.12	37.66, 27.51
5	1634	5.56	194.47	41.14, 3.91
6	1601	5.58	197.17	39.62, 2.00

Table 2. Crystal data and structure refinement for **3** and **4**.

	Compound 3	Compound 4
Empirical formula	C ₃₃ H ₂₇ Cl ₂ BrOP ₂ Pd	C ₃₄ H ₂₇ Cl ₂ NOP ₂ Pd
Formula weight	758.69	704.81
<i>T</i> [K]	130.00(10)	293
Crystal system	triclinic	Monoclinic
Space group	P-1	C2/c
<i>a</i> [Å]	11.2716(3)	23.033 (5)
<i>b</i> [Å]	16.2651(4)	15.327 (3)
<i>c</i> [Å]	16.9243(3)	24.769 (9)
α [°]	84.1776(16)	
β [°]	83.9247(16)	134.500 (15)
γ [°]	84.684(2)	
<i>V</i> [Å ³]	3058.92(12)	6237 (3)
<i>Z</i>	4	8
<i>D_c</i> [Mg m ⁻³]	1.647	1.501
μ [mm ⁻¹]	2.218	0.90
<i>F</i> (000)	1512.0	2848
λ (Mo-K α)	0.71073	0.71073
<i>2</i> θ range [°]	5.6-64.5	3.2-52.0
Index ranges	-15 $\leq h \leq$ 16, -23 $\leq k \leq$ 24, -25 $\leq l \leq$ 23	-28 $\leq h \leq$ 26, -18 $\leq k \leq$ 18, -30 $\leq l \leq$ 30
Refl. collected	45890	19650
Independent reflections	19733 [<i>R</i> _{int} = 0.0226]	6108 [<i>R</i> _{int} = 0.035]
Data/restr./param.	19733/35/765	6108/0/379
Goodness-of-fit on <i>F</i> ²	1.022	1.03
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0290/0.0648	0.030/0.073

Table 3. Selected bond lengths [Å] and bond angles [°] for **3** and **4**.

	Compound 3		Compound 4
Bond distances			
Pd1-Cl1	2.3756(4)	Pd1-Cl1	2.3747 (7)
Pd1-Cl2	2.3383(4)	Pd1-Cl2	2.3477 (7)
Pd1-P2	2.2153(5)	Pd1-P1	2.2341 (6)
Pd1-C1	2.1075(17)	Pd1-C2	2.095 (2)
O1-C2	1.228(2)	O1-C3	1.231 (3)
C1-C2	1.496(3)	C2-C3	1.486 (3)
P1-C1	1.7817(17)	P2-C2	1.787 (2)
P2-C21	1.8442(17)	P1-C1	1.866 (2)
Bond angles			
Cl2-Pd1-Cl1	92.509(16)	Cl2-Pd1-Cl1	92.71 (3)
C1-Pd1-P2	89.90(5)	C2-Pd1-P1	88.70 (6)
C1-Pd1-Cl1	91.10(5)	C2-Pd1-Cl1	91.16 (7)
P2-Pd1-Cl1	170.607(18)	P1-Pd1-Cl1	170.97 (2)
P2-Pd1-Cl2	87.343(16)	P1-Pd1-Cl2	88.37 (3)

Table 4. Selected bond lengths (Å) and bond angles (°) of [Y₁PtCl₂] and [Y₂PtCl₂] complexes at the BP86/def2-SVP level of theory.

[Y ₁ PtCl ₂]		[Y ₂ PtCl ₂]		[(Ph ₂ P(CH ₂) ₂ PPh ₂ CHC(O)CH ₃)PtCl ₂] ^a
Bond Lengths	Value	Bond Lengths	Value	Value
Pt(63)-P(1)	2.241	Pt(63)-P(1)	2.242	2.352
Pt(63)-C(14)	2.117	Pt(63)-C(14)	2.117	2.121
Pt(63)-Cl(65)	2.399	Pt(63)-Cl(65)	2.399	2.461
Pt(63)-Cl(64)	2.385	Pt(63)-Cl(64)	2.385	2.454
Bond angles	Value	Bond angles	Value	Value
Cl(65)-Pt(63)-P(1)	172.23	Cl(65)-Pt(63)-P(1)	171.19	174.84
Cl(64)-Pt(63)-C(14)	175.95	Cl(64)-Pt(63)-C(14)	176.40	170.98

C (14)-Pt(63)-P(1)	90.922	C (14)-Pt(63)-P(1)	91.32	97.67
Cl(64)-Pt(63)-Cl(65)	91.614	Cl(64)-Pt(63)- Cl(65)	91.46	91.09

^a See reference [55].

Table 5. Wiberg bond indices(WBI) of Pt–C and Pt-Cl bonds and natural charges of Pt, C and Cl atoms as well as total charge of Y₁ and Y₂ fragments bonds in the complexes studied here at BP86/def2-SVP level of theory.

		[Y ₁ PtCl ₂]	[Y ₂ PtCl ₂]
WBIs	Pt-C	0.49	0.49
	Pt-Cl	0.71	0.71

NPA	Pt	-0.015	-0.013
	C	-0.88	-0.88
	P	1.58(1.14)	1.59(1.14)
	Y1	0.85	-
	Y ₂	-	0.85

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Table 6. The most important donor→ acceptor interactions energy concern to Pt—C bonds in the complexes studied here at BP86/def2-SVP level of theory.

Donor	Acceptor	Type	E ² (kcal/mol) [Y ₁ PtCl ₂]	E ² (kcal/mol) [Y ₂ PtCl ₂]
P(1)–Pt(63)	Pt(63)	$\sigma \rightarrow \text{Lp}^*$	4.18	4.29
P(1)–Pt(63)	P(1)–Pt(63)	$\sigma \rightarrow \sigma^*$	9.78	9.98
P(1)–Pt(63)	C(14)–Pt(63)	$\sigma \rightarrow \sigma^*$	30.27	30.40
C(14)–Pt(63)	Pt(63)	$\sigma \rightarrow \text{Lp}^*$	10.72	10.76
C(14)–Pt(63)	P(1)–Pt(63)	$\sigma \rightarrow \sigma^*$	34.53	34.42
C(14)–Pt(63)	P(2)–C(8)	$\sigma \rightarrow \sigma^*$	18.64	18.83
C(14)–Pt(63)	C(14)–C(16)	$\sigma \rightarrow \sigma^*$	10.33	10.67

Table 7. EDA analysis (BP86/TZ2P(ZORA)//BP86/def2-SVP) of [Y₁PtCl₂] and [Y₂PtCl₂] complexes with the C1 symmetry.

Compound name	$\Delta E(\text{int})^a$	$\Delta E(\text{pauli})$	$\Delta E(\text{elstate})$	$\Delta E(\text{orb})$	$\Delta E(\text{disp})$
[Y ₁ PtCl ₂]	-156.81	350.87	-295.40(58.18)	-188.43(37.14)	-23.85(4.7)
[Y ₂ PtCl ₂]	-153.80	351.59	-295.11(58.16)	-188.39(37.13)	-23.88(4.7)

^a The value in parenthesis gives the percentage contribution to the total orbital interactions $\Delta E(\text{orb})$.

Table 8. Optimizations for the Suzuki-Miyaura coupling reaction^a

Entry	Base	Solvent	Catalyst loading (mmol)	Temp. (°C)	Yield (%) ^b
1	K ₃ PO ₄	DMF/H ₂ O	0.05	110	70
2	K ₂ CO ₃	DMF/H ₂ O	0.05	110	77
3	NEt ₃	DMF/H ₂ O	0.05	110	58
4	K ₃ PO ₄	Methanol/H ₂ O	0.05	70	47
5	K ₂ CO ₃	Methanol/H ₂ O	0.05	70	51
6	NEt ₃	Methanol/H ₂ O	0.05	70	45
7	K ₃ PO ₄	Toluene/H ₂ O	0.05	90	54
8	K ₂ CO ₃	Toluene/H ₂ O	0.05	90	35
9	NEt ₃	Toluene/H ₂ O	0.05	90	40
10	K ₂ CO ₃	H ₂ O	0.05	100	44
11	K ₂ CO ₃	DMF	0.05	130	61
12	K ₂ CO ₃	DMF/H ₂ O	0.005	110	70
13	K ₂ CO ₃	DMF/H ₂ O	0.0005	110	32
14	K ₂ CO ₃	DMF/H ₂ O	None	110	-
15	K ₂ CO ₃	DMF/H ₂ O	0.1	110	92
16	K ₂ CO ₃	DMF/H ₂ O	0.005	65	58
17	K ₂ CO ₃	DMF/H ₂ O	0.005	25	40

^a Reaction conditions for Suzuki-Miyaura coupling reaction: chlorobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), solvent (2 mL), catalyst **3**, in the air.

^b Isolated yield.

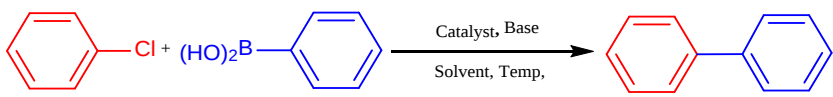
Table 9. Suzuki-Miyaura coupling reaction of aryl chlorides catalyzed by palladacycles **3** and **4**^a.

Entry	R	R'	Product	Yield (%) ^b
1	CHO	H	<i>p</i> -OHC-Ph-Ph	83, 85
2	COCH ₃	H	<i>p</i> -CH ₃ OC-Ph-Ph	79, 81
3	H	H	Ph-Ph	70, 68
4	Me	H	<i>p</i> -Me-Ph-Ph	67, 69
5	OCH ₃	H	<i>p</i> -CH ₃ O-Ph-Ph	61, 62
6	CHO	Et	<i>p</i> -OHC-Ph-Ph-Et	78, 80
7	COCH ₃	Et	<i>p</i> -CH ₃ OC-Ph-Ph-Et	75, 73
8	H	Et	Ph-Ph-Et	66, 65
9	Me	Et	<i>p</i> -Me-Ph-Ph-Et	61, 64
10	OCH ₃	Et	<i>p</i> -CH ₃ O-Ph-Ph-Et	57, 60

^a Reaction conditions for Suzuki-Miyaura coupling reaction: aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), K₂CO₃ (1 mmol), DMF/H₂O (2 mL), catalyst **3** or **4** (0.005 mmol), in the air.

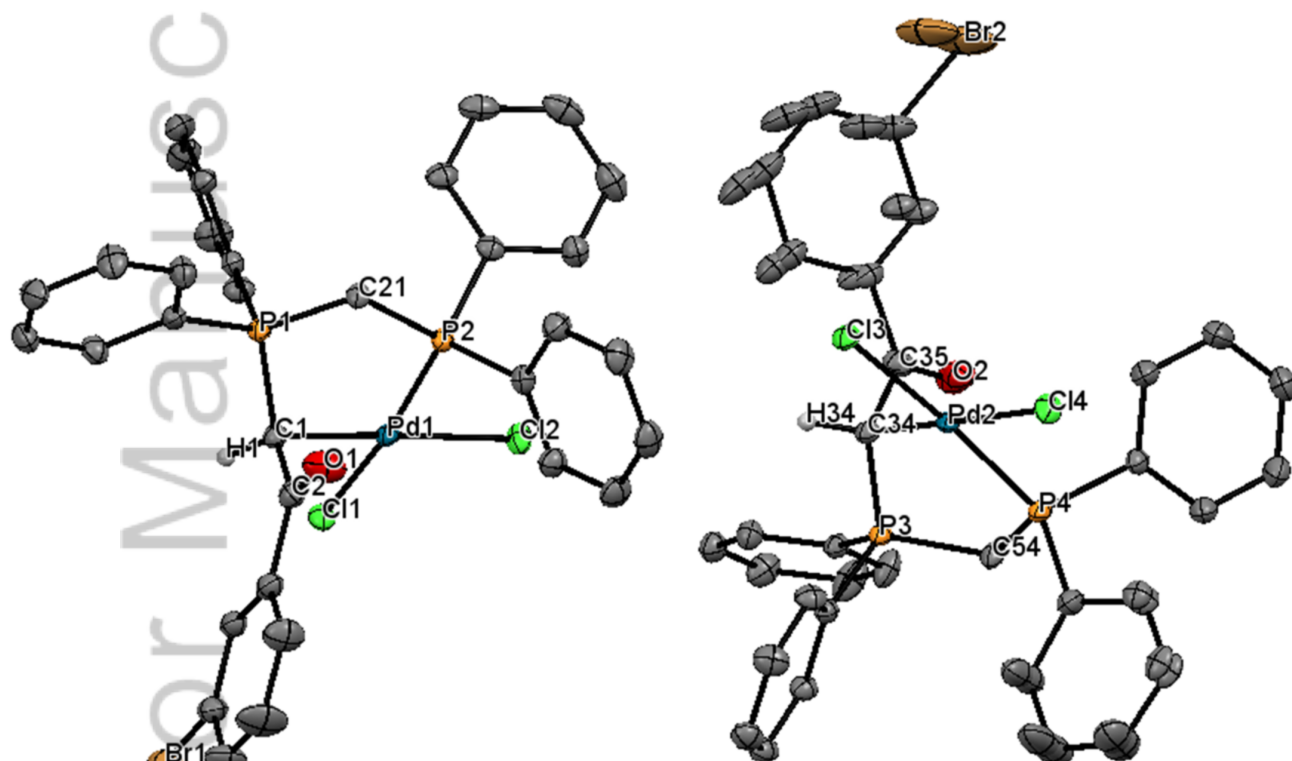
^b Isolated yields for coupling reactions in presence of palladacycles **3** and **4**, respectively.

Table 10. Comparison of Suzuki-Miyaura coupling reaction of chlorobenzene and phenylboronic acid using palladacycle **3** and other catalytic systems.

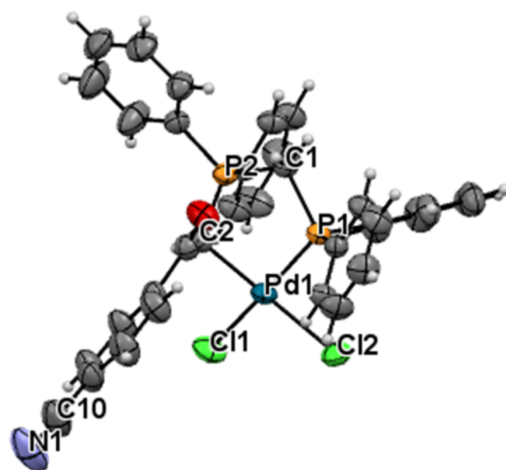


Entry	Pd source	Catalyst loading (mmol)	Condition	Yield (%)	Ref.
1	Imidazole-based secondary phosphine oxide ligated Pd(II)	0.02	K ₂ CO ₃ , DMF, 60 °C, 12 h	62	[64]

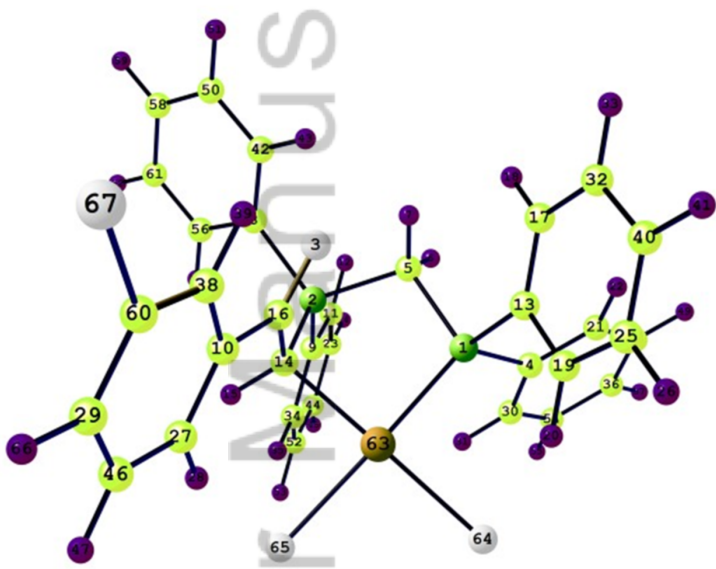
2	Poly(N,N-dipyrid-2-yl-endo-norborn-2-ene-5-carbamide) based Pd(II)	0.007	K ₂ CO ₃ , DMAc/TBAB, 140 °C, 90 h	89	[65]
3	2,6-Bis (diphenylphosphino) pyridine/Pd(II)	0.001	K ₂ CO ₃ , DMAc/TBAB, 135 °C, 5 h	57	[66]
4	Polymer-anchored Schiff base Pd(II)	0.005	K ₂ CO ₃ , DMF, 100 °C, 24 h	12	[67]
5	1,3-Dimesitylimidazol-2-ylidene PEPPSI-type Pd(II)	0.001	Na ₂ CO ₃ , EtOH/CHCl ₃ , TBAB, 80 °C, 16 h	2	[68]
6	Amino acid-derived PEPPSI-NHC Pd(II)	0.01	K ₂ CO ₃ , H ₂ O/TBAB, 60 °C, 24 h	11	[69]
7	N-heterocyclic carbene-Pd(II)-pyridine (PEPPSI)	0.01	K ₂ CO ₃ , DMF/H ₂ O, 80 °C, 3 h	85	[70]
8	Ferrocene tertiary amine palladacycle	0.02	K ₃ PO ₄ , Toluene, 60 °C, 8 h	60	[71]
9	2-Phenylpyridine/DMSO palladacycle	0.1	K ₂ CO ₃ , Toluene, 25 °C, 2 h	65	[72]
10	P, C-chelated phosphorus ylide Pd(II)	0.005	K ₂ CO ₃ , DMF/H ₂ O, 110 °C, 6 h	70	This work



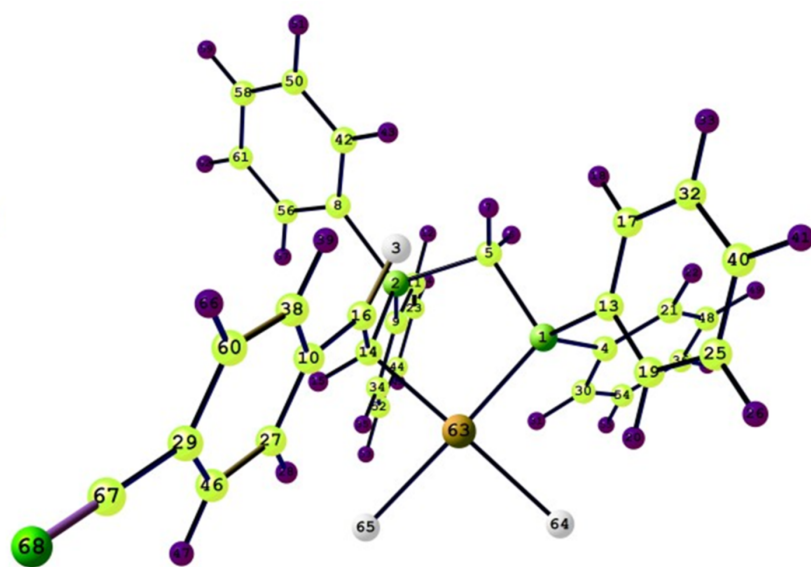
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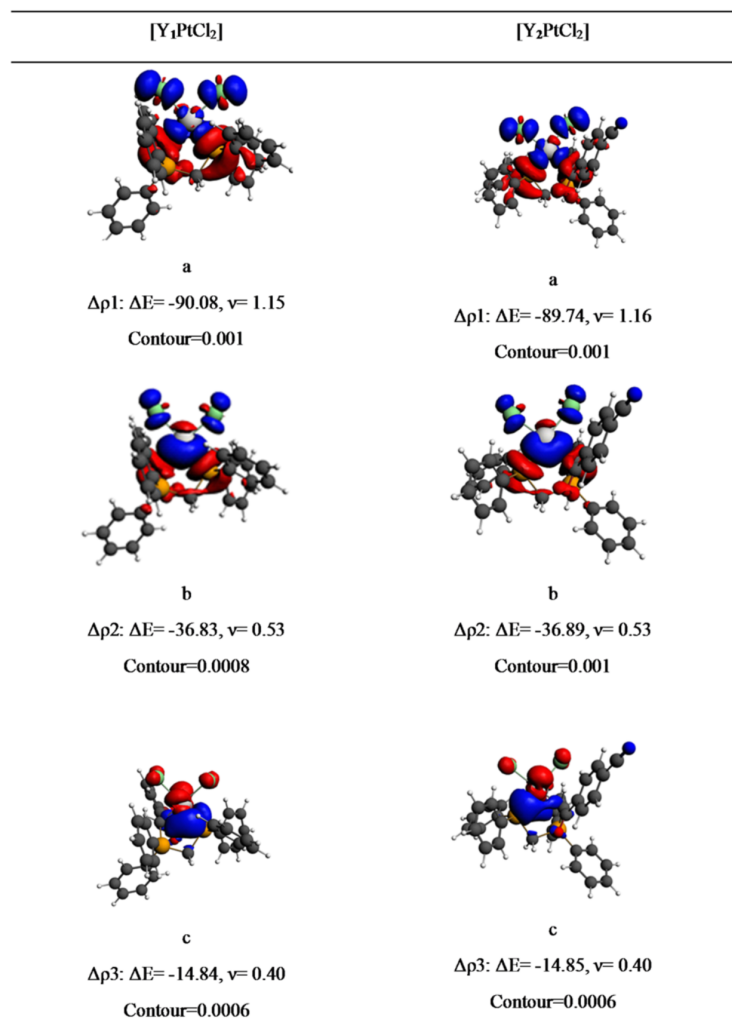


3a

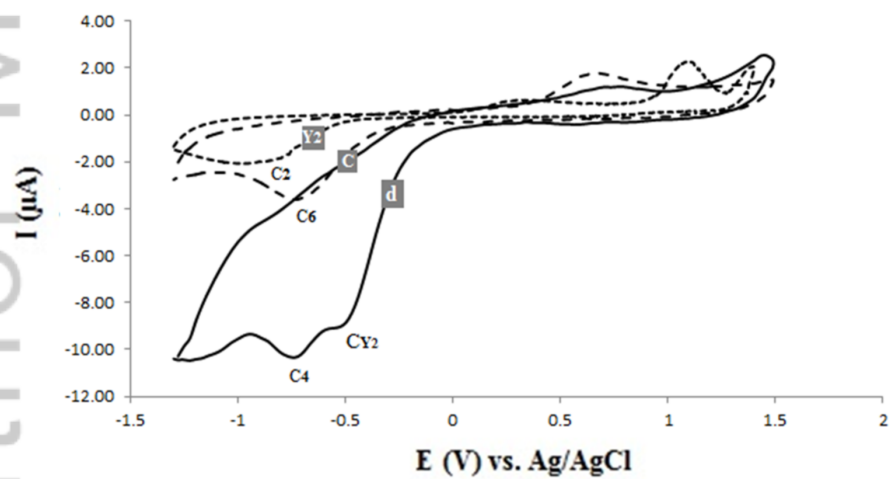
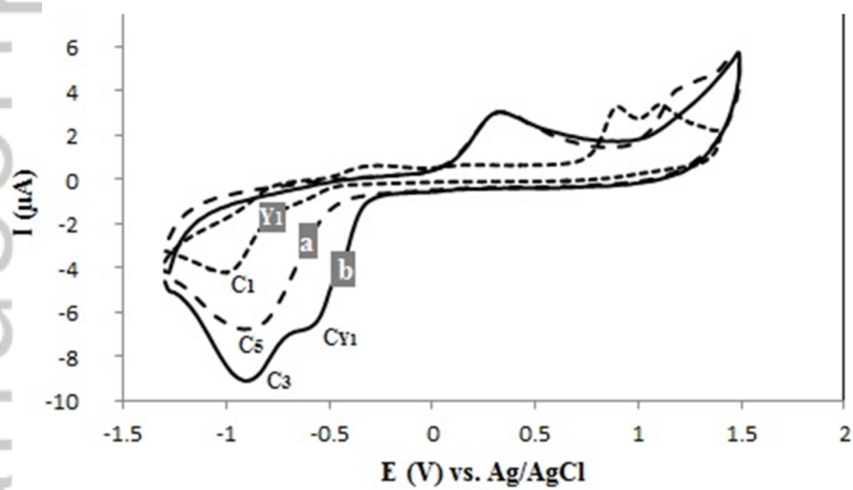


3b

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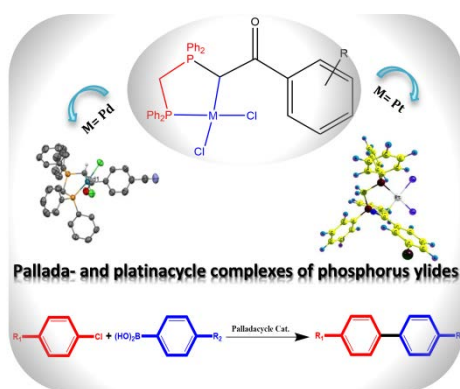
Table of Contents Entry

Pallada- and platinacycle complexes of phosphorus ylides; Synthesis, X-ray characterization, theoretical and electrochemical studies and application of Pd(II) complexes as catalyst in Suzuki-Miyaura coupling reaction

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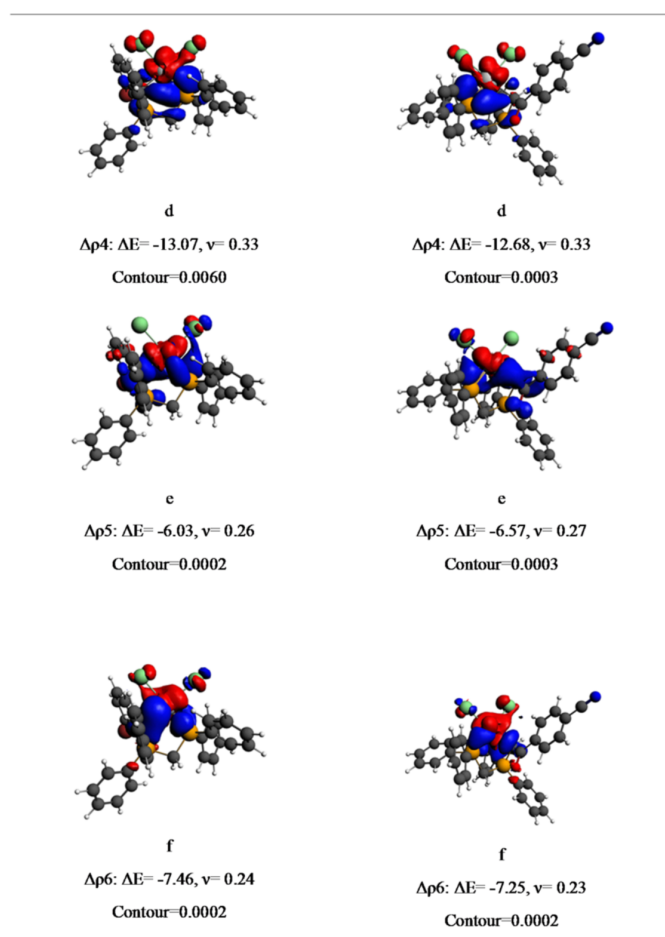
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We report the synthesis and characterization of new pallada- and platinacycle complexes $[MCl_2(Ph_2PCH_2PPh_2C(H)C(O)C_6H_4R)]$ ($M = Pd$ and Pt , $R = m$ -Br and p -CN) and application of Pd(II) complexes as catalyst in Suzuki-Miyaura coupling reaction.

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