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Synthesis, X-ray structural and DFT studies of *n*-membered ring P, C-chelated complexes of Pd(II) and Pt(II) derived fromunsymmetrical phosphorus ylides and application of Pd(II) complexes as catalyst in Suzuki reaction

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The phosphonium salts $[Ph_2P(CH_2)_nPPh_2CH_2C(O)C_6H_4-m-OMe]Br (n=1 (S_1) and n=2 (S_2))$ were synthesized in the reaction of bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe) with 2-bromo-3'-methoxy acetophenone, respectively. Further treatment with NEt₃ gave the phosphorus vlides $Ph_2P(CH_2)_nPPh_2C(H)C(O)C_6H_4$ -m-OMe $(n=1 (Y_1) \text{ and } n=2 (Y_2))$. These ligands $(Y_1 \text{ and } Y_2)$ were treated with $[MCl_2(cod)]$ (M= Pd or Pt; cod = 1,5-cyclooctadiene)to give the P, C-chelated complexes, $[MCl_2(Ph_2P(CH_2)_nPPh_2C(H)C(O)C_6H_4-m-OMe)]$ (n=1, M= Pd (3), Pt (4) and n=2, M= Pd (5), Pt (6)). These compounds were characterized by elemental analysis, spectroscopic methods, UV-visible and fluorescence emissionspectra. Further, the structures of complexes 3 and 6 were characterized crystallographically. These structures consist of five- and six-membered rings formed by coordination of the ligand through the phosphine group and the ylidic carbon atom to the metal center. The palladium complexes 3 and 5 proved to be excellent catalysts for the Suzukireactions of various aryl chlorides and arylboronic acids in mixed DMF/H₂O media. Also, a theoretical study on the structure of complexes 3-6 has been investigated at the BP86/def2-SVP level of theory. The strength and nature of donor-acceptor bonds between the phosphorus ylides (L) and MCl₂ fragment in the [LMCl₂] (M= Pd, Pt, L= Y_1 , Y_2) were studied by NBO and energydecomposition analysis (EDA), as well as their natural orbitals for chemical valence variation

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(EDA-NOCV). The results confirmed that the contributions of the electrostatic interaction in the $L \rightarrow M$ bonds in the complexes are about 56-58%.

Keywords: Palladium and platinum; Ylide; X-ray structure; Suzuki reaction; DFT, EDA Analysis; EDA-NOCV, Nature of bond

1. Introduction

The coordination and organometallic chemistry of unsymmetrical α -keto stabilized phosphorus ylides have been investigated extensively and their ambidenticity explained in terms of a delicate balance between electronic and steric factors [1-3]. Much of the interest in the coordination properties of α -keto stabilized phosphorus ylides stems from their coordination versatility due to the presence of different functional groups in their molecular structure [4]. Thus, these ligands can engage in different kinds of bonding with different metal ions: P-bonded (through the phosphine group), C-bonded (through the C α atom), O-bonded (through the carbonyl O), or even situations in which the same ylide shows a combination of bonding modes. Different types of bonding are depicted in Chart 1 for Ph₂P(CH₂)_nPPh₂C(H)C(O)C₆H₄R.

In Chart 1, when a metal ion such as Rh(I), Hg(II) or Ag(I) interacts only with the free P atom of the diphosphine group (**a**), the coordination structure is regarded as monodentate [5, 6]. If the coordination of ylide occurs through the C α atom of the ylidic group (**b**), it is categorized in the same above mentioned coordination mode [7], although the ylides can also coordinate to the metal ions through the O atoms of the carbonyl group (**c**). A few examples of O-coordinated ylidesare known; some of these complexes include a hard and very oxophilic metal center, such as Sn(IV) [8], Ti(IV), Zr(IV) or Hf(IV) [9].

The P, C-coordination mode (**d**) of stabilized phosphorus ylides had been previously observed for Pd(II), Pt(II), Rh(I), Hg(II) and Cu(I) species [10-18]. Although the P, O-coordination mode (**e**) is also possible, to the best of our knowledge, it has only been observed in the Pd(II) complexes of a mixed phosphine– β -ketophosphorus ylide [19]. Finally, the bridging coordination mode (**f** and **g**) is observed when a metal ion binds to one phosphorus ylide through the P atom and another metal ion binds 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 [5-7, 21]. Recently, our group reported the synthesis and application of Pd(II) and Cu(I)

complexescontaining phosphine-ylide ligands [13, 17]. It was shown that the reaction of phosphine-ylide ligands with Pd(II) and Cu(I) give the P, C-chelated complexes. In this context, we have now focused our attention in the study of the coordination modes adopted by the resonance stabilized ylides when ligated to Pd(II) and Pt(II).



Chart 1. Possible bonding modes of phosphorus ylides to the metal M.

Bidentate diphosphines are valuable ligands for metal-catalyzed reactions. Metalcatalyzed cross-coupling reactions have gained popularity over the past 30 years, in particular as convenient techniques for the formation of C-C bonds [22-24].Palladium-catalyzed reactions, such as C-C bond formation, have attracted considerable interest [25, 26]. Specifically, the Suzuki reaction which emerged as the most important and reliable method for construction of functionalized biaryl compounds, has been catalyzed recently with the P, C-chelated Pd(II) complexes of such phosphorus ylides [27-31].Current technologies demand new catalysts, which are inexpensive, readily accessible, moisture- and air-stable, and most importantly, highly effective under low catalyst loading [32]. Recently, our group reported the synthesis and application of palladium complexes of phosphorus ylides as efficient catalysts for some classical Suzuki reactions[24, 33-35]. These compounds, due to their readily preparation, high activity and relative stability, can be used as efficient catalyst precursors in Suzuki reactions of various aryl bromides under relatively mild experimental conditions. The results of these studies including the full characterization of the obtained complexes (performed by elemental analysis,X-ray structural,IR, multinuclear NMR techniques, theoretical studyand also application of the new palladium(II) complexes of phosphorus ylide Suzuki reaction) is presented and discussed in this paper.

2. Experimental

2.1. Materials and methods

Manipulations were performed in typical Schlenk systems under an atmosphere of dry nitrogen, and the progress of reactions was monitored by IR and NMR spectroscopies. The starting complexes [PdCl₂(cod)] and [PtCl₂(cod)] were prepared according to previously published procedures [36]. Reactants and reagentswere obtained from Merck chemical company and used without purification. The solvents were dried and distilled using standard methods [37]. Elemental analyses for C, H and N were performed using a PerkinElmer 2400 series analyzer. Melting points were measured on a SMPI apparatus and are reported without correction. The¹H, ¹³C and ³¹P NMR spectra were run on a BrukerAvance 500 MHz, 250 MHz and Jeol 90 MHz spectrometers in CDCl₃ or DMSO-d₆ as solvents at 25 °C. The chemical shifts (d) are referred to Me₄Si (using the residual proton peaks of deuterated solvents) and to external 85% H₃PO₄.IR spectra were taken by a FT-IR Shimadzu 435-U-04 of the Nicolet Instrument Corporation (4000–400 cm⁻¹) spectrophotometer. UV-vis spectra were recorded on a Perkin voyager DE-PRO spectrometer in the region of 300–800 nm and the fluorescence emissionspectra wereperformed on a Varian Cary spectrofluorometer.

2.2. X-ray crystallography

Suitable crystalsof**3** and**6** were selected and mounted on a Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas diffractometer. Data collection and reduction was carried out using CrysalisPro [38], with the data for both structures being corrected for absorption using Gaussian integration. The crystal was kept at 130.00(10) K during data collection. Using Olex2 [39], the structure was solved with the ShelXS [40] structure solution program using direct methods and refined with the ShelXL [41] refinement package using Least Squares minimization. All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were constrained to geometrical estimates, with an isotropic displacement parameter of 1.5 times (Me) or 1.2 times (other) the parent carbon atom.

2.3.Computational details

The geometries of the bidentate phosphorus ylide (Y_1 and Y_2) complexes of metal halides palladium and platinum with general formula [LMCl₂] (M=Pd, Pt, L= Y_1 , Y_2) have been optimized at the BP86 [42, 43]/def2-SVP [44] level of theory. It has been shown that in former studies the BP86 is a suitable level for calculation of bonding situation between the M←L in these complexes [45-52]. All calculations were performed using the Gaussian 09 set of programs [53]. NBO analyses [54] were also carried out with the internal model GAUSSIAN 09. For bonding analyses, the terms of EDA analysis were carried out at BP86/TZ2P(ZORA)//BP86/def2-SVP with C1 symmetry. The basis sets for all elements have triple-f quality augmented by one set of polarization functions (ADF basis set TZ2P (ZORA)) with the program package ADF2009.01.

2.4. Preparation of compounds

2.4.1.Synthesis of phosphonium salts S_1 and S_2 . *General procedure*: To a solution of bis(diphenylphosphino)methane (dppm)orbis(diphenylphosphino)ethane (dppe)(0.52 mmol) in 5 ml of chloroform, a solution (5 ml, CHCl₃) of 2-bromo-3'-methoxy acetophenone (0.118 g, 0.52 mmol) was added dropwise. The resulting reaction mixture was stirred for 15 h at room temperature. The solution was concentrated under reduced pressure to 2 ml, and diethyl ether (20 ml) was added. The yellow solid formed was filtered off, washed with diethyl ether and dried under reduced pressure.

2.4.1.1. Data for (3-methoxybenzoylmethyldiphenyldiphenylphosphinomethylphosphonium)bromide(S_1). Yield: 0.28 g (88%). Anal. Calc. for C₃₄H₃₁O₂P₂Br (%): C, 66.57; H, 5.09. Found: C, 66.49; H, 5.04. M.p. 187–189°C. Selected IR absorption in KBr (cm⁻¹): 1671 (v C=O). ¹H NMR (89.60 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 3.90 (s, 3H, OCH₃); 4.28 (d, 2H, PCH₂P, ²*J*_{P-H} = 14.69 Hz); 5.92 (d, 2H, PCH₂CO, ²*J*_{P-H}= 11.82 Hz); 7.26–8.02 (m, 24H, Ph).³¹P NMR (36.26 MHz, CDCl₃) $\delta_{\rm P}$ (ppm): -29.00 (d, PPh₂, ²*J*_{P-P} = 62.16 Hz); 21.07 (d, PCH₂, ²*J*_{P-P}= Downloaded by [University of Florida] at 06:58 27 October 2017

62.45 Hz). ¹³C NMR (62.90 MHz, CDCl₃) δ_{C} (ppm): 192.20 (s, CO); 112.51-159.84 (m, Ph); 56.07 (s, OCH₃); 36.86 (d, PCH₂CO, ¹*J*_{P-C}= 60.38 Hz); 22.12 (dd, PCH₂, ¹*J*_{P-C} = 53.46 Hz).

2.4.1.2. Data for (3-methoxybenzoylmethyldiphenyl-2-diphenylphosphinoethylphosphonium)bromide (S_2). Yield: 0.30 g (98%). Anal. Calcd for C₃₅H₃₃O₂BrP₂(%): C, 66.99; H, 5.30. Found: C, 67.05; H, 5.34. M.p 170–172°C. Selected IR absorption in KBr (cm⁻¹): 1660(v C=O).¹H NMR (89.60 MHz, CDCl₃) $\delta_{\rm H}$ (ppm):2.32 (m, 2H, PCH₂), 3.29 (m, 2H, PCH₂), 3.95 (s, 3H, OCH₃), 6.02 (dd, ${}^{2}J_{\rm P-H}$ = 12.00, 2H, PCH₂CO), 7.27–8.12 (m, 24H, Ph). ³¹P NMR (36.23 MHz, CDCl₃) $\delta_{\rm P}$ (ppm): -12.07 (br, PPh₂), 24.02 (d, PCH₂,³J_{P-P} = 48.41 Hz).¹³C NMR (62.90 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 192.01 (s, CO), 112.74-159.83 (m, Ph), 55.97 (s, OCH₃), 35.90 (d, PCH₂CO, ¹J_{P-C} = 59.12), 22.46 (d, PCH₂, ¹J_{P-C} = 66.67), 16.79 (d, PCH₂, ¹J_{P-C} = 52.83).

2.4.2. Synthesis of phosphorus ylides Y_1 and Y_2. *General procedure*: The phosphonium salts S_1 and S_2 (0.45 mmol) were treated with triethyl amine (0.5 ml, 3.57 mmol) in toluene (15 ml). The triethyl amine hydrobromide produced was filtered off and the toluene layer concentrated to 5 ml which upon further addition of petroleum ether (25 ml) results in the precipitation of Y_1 and Y_2 as free-flowing white solids. The productswere collected and dried under vacuum.

2.4.2.1.Data for 3-methoxybenzoylmethylenediphenyldiphenylphosphinomethylphosphorane (Y_I). Yield: 0.21 g (78%). Anal. Calc. for C₃₄H₃₀O₂P₂ (%): C, 76.68; H, 5.68. Found: C, 76.61; H, 5.59. M.p. 168–170°C. Selected IR absorption in KBr (cm⁻¹): 1586(vC=O).¹H NMR (89.60 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 3.67 (d, 2H, PCH₂P, ² $J_{\rm P-H}$ = 13.44 Hz); 3.83 (s, 3H, OCH₃); 4.02 (m, 1H, CH); 6.86–7.76 (m, 24H, Ph). ³¹P NMR (36.26 MHz, CDCl₃) $\delta_{\rm P}$ (ppm): -29.55 (d,PPh₂, ² $J_{\rm P-P}$ = 63.50 Hz); 11.34 (d, PCH, ² $J_{\rm P-P}$ = 62.99 Hz). ¹³C NMR (62.90 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 184.68 (s, CO);111.06-159.35 (m, Ph); 55.32 (s, OCH₃); 50.39 (d, PCH, ¹ $J_{\rm P-C}$ = 113.22 Hz);24.73 (dd, CH₂, ⁴ $J_{\rm P-C}$ = 90.57 Hz).

2.4.2.2.Data for 3-methoxybenzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (*Y*₂). Yield: 0.194 g (73%).*Anal*. Calc. for $C_{35}H_{32}O_2P_2(\%)$: C, 76.91; H, 5.90. Found: C, 77.14; H, 6.02. M.p 136-140 °C. Selected IR absorption in KBr (cm⁻¹): 1524(v C=O).¹H NMR (89.60 MHz, CDCl₃) $\delta_{\rm H}(\rm ppm)$: 2.28 (m, 2H, PCH₂), 2.77 (m, 2H, PCH₂), 3.85 (s, 3H, OCH₃),

4.15 (br, 1H, PCH), 6.91–7.49 (m, 24H, Ph). ³¹P NMR (36.27 MHz, CDCl₃) $\delta_P(\text{ppm})$: -13.63 (d, PPh₂,³ $J_{P-P} = 47.87$ Hz), 17.59 (d, PCH,³ $J_{P-P} = 47.87$ Hz). ¹³C NMR (75.47 MHz, CDCl₃) δ_C (ppm): 185.02 (s, CO), 111.19-159.52 (m, Ph), 55.36 (s, OCH₃), 47.03 (d, PCH,¹ $J_{P-C} = 113.51$), 20.80 (m, CH₂).

2.4.3. Synthesis of Pd(II) and Pt(II)complexes. *General procedure*: To a $[MCl_2(cod)]$ (M= Pd or Pt) (0.5 mmol) dichloromethane solution (5 ml), a solution of Y_1 or $Y_2(0.5 \text{ mmol})$ (5 ml, CH_2Cl_2) was added dropwise. The resulting solution was stirred for 2 h at room temperature and then concentrated to *ca*.2 ml under reduced pressure and treated with n-hexane (15 ml) to afford Pd(II) and Pt(II) complexes.

2.4.3.1. Data for dichloro(3-methoxybenzoylmethylenediphenyldiphenylphosphino-

methylphosphorane)palladium(II)(3). Yield: 0.28 g (80%). *Anal.* Calc. for $C_{34}H_{30}Cl_2O_2P_2Pd(\%)$: C, 57.53; H, 4.26. Found: C, 57.64; H, 4.17. M.p. 192-194 °C (dec). Selected IR absorption in KBr (cm⁻¹) v(CO): 1619. ¹H NMR (500.13 MHz, DMSO-d₆) δ_H (ppm): 3.82 (s, 3H, OCH₃); 4.78 (d,CH₂, 2H, ²*J*_{P-H} = 185.04 Hz); 5.94 (s, 1H, PCH); 7.15–8.28 (m, 24H, Ph). ³¹P NMR (202.45 MHz, DMSO-d₆) δ_P (ppm): 28.34 (d, PPh₂, ²*J*_{P-P} = 55.33 Hz); 38.77 (d, PCH, ²*J*_{P-P} = 58.63 Hz). ¹³C NMR (62.90 MHz, DMSO-d₆) δ_C (ppm): 196.81 (s, CO), 113.93-139.17(m, Ph), 55.83 (s, OCH₃),27.94 (d, PCH), 21.93 (d, CH₂, ¹*J*_{P-C} = 58.49 Hz).

2.4.3.2. Data for dichloro(3-methoxybenzoylmethylenediphenyldiphenylphosphinomethylphosphorane)platinum(II)(4). Yield: 0.30 g (78%). Anal. Calc. for C₃₄H₃₀Cl₂O₂P₂Pt(%): C, 51.14; H, 3.79. Found: C, 51.29; H, 3.92. M.p. 210-212 °C (dec). Selected IR absorption in KBr (cm⁻¹) v(CO): 1627. ¹H NMR (250.13 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 3.79 (s, 3H, OCH₃);4.64 (br, PCH₂P, 2H); 5.68 (t, 1H, PCH); 7.17–8.25 (m, 24H, Ph). ³¹P NMR (101.25 MHz, DMSO-d₆) $\delta_{\rm P}$ (ppm): 4.43 (d, PPh₂, ¹J_{Pt-P}= 3970.98 Hz, ²J_{P-P}= 39.48 Hz);42.22 (d, PCH, ²J_{P-P} = 39.48 Hz). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 196.71 (s, CO); 121.92-135.08(m, Ph); 55.94 (s, OCH₃);28.00 (d, PCH, ¹J_{P-C} = 66.04 Hz).

2.4.3.3.Data for dichloro(3-methoxybenzoylmethylenediphenyl-2diphenylphosphinoethylphosphorane)palladium(II) (5).Yield: 0.29 g (82%). Anal. Calc. for C₃₅H₃₂Cl₂O₂P₂Pd(%): C, 58.07; H, 4.46. Found: C, 57.98; H, 4.41. M.p. 191-193 °C (dec). Selected IR absorption in KBr (cm⁻¹) v(CO): 1626. ¹H NMR (89.60 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 3.55-4.00 (br, CH₂, 4H merged with residual H₂O); 3.78 (s, 3H, OCH₃); 6.18 (b, 1H, PCH), 7.11–8.44 (m, 24H, Ph). ³¹P NMR (101.25 MHz, DMSO-d₆) $\delta_{\rm P}$ (ppm): 22.77 (d, PPh₂, ²*J*_{*P*-*P*} = 29.36 Hz), 30.90 (d, PCH, ²*J*_{*P*-*P*} = 23.28 Hz). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 195.97 (s, CO), 114.09-159.30(m, Ph), 55.78 (s, OCH₃), 28.82 (d, PCH), 19.45(m, CH₂).

2.4.3.4. Data fordichloro(3-methoxybenzoylmethylenediphenyl-2-

diphenylphosphinoethylphosphorane)platinum(II) (6). Yield: 0.303 g (80%). *Anal*. Calc. for $C_{35}H_{32}Cl_2O_2P_2Pt(\%)$: C, 51.74; H, 3.97. Found: C, 51.87; H, 4.10. M.p. 237-239 °C (dec). Selected IR absorption in KBr (cm⁻¹) v(CO): 1634. ¹H NMR (89.60 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 2.2 (br,CH₂, 2Hmerged with DMSO); 3.78 (b, 3H, OCH₃); 4.24 (br,CH₂, 4Hmerged with residual H₂O); 5.49 (b, 1H, PCH), 7.01–8.44 (m, 24H, Ph). ³¹P NMR (36.26 MHz, DMSO-d₆) $\delta_{\rm P}$ (ppm): 6.60 (d, PPh₂, ¹*J*_{Pt-P}= 3979.03 Hz, ²*J*_{P-P}= 17.77 Hz), 20.14 (d, PCH, ²*J*_{Pt-P}= 132.73 Hz, ²*J*_{P-P}= 17.77 Hz). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 196.11 (s, CO), 114.07-159.28(m, Ph), 55.76 (s, OCH₃), 35.30 (d, PCH), 19.90 (m, CH₂).

2.5. General procedure for the Suzuki reaction

A mixture ofaryl halide (0.75 mmol), K_2CO_3 (1.5 mmol), phenylboronic acid (1 mmol), 0.005 mmol of Pd(II) complex **3**ascatalystand 2 mL DMF/H₂O (1:1) as solvent was heated at 130 °C using an oil bath and the progress of the reactionwas monitored byTLC. The reaction mixture was then cooled to room temperature. After completion of the reaction, the mixture was diluted with n-hexane (15 mL) and water (15 mL). The combined organic layerwas washed with brine (15 mL) and dried over CaCl₂. Then solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

2.5.1. Data for4-nitrobiphenyl (7a). Yield: 0.183 g (92%).M.p. 112-113 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 7.26-8.34 (m, 9H, phenyl). ¹³C NMR (62.89 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 147.68, 146.97, 128.92, 127.84, 124.10.

2.5.2. Data for 4-phenylbenzaldehyde (**7b**). Yield: 0.151 g (83%). M.p. 89-91 °C. ¹H NMR (89.6 MHz, CDCl₃) δ_H (ppm): 9.91 (s, 1H, CHO), 7.30- 7.86 (m, 9H, phenyl). ¹³C NMR (100.62 MHz, CDCl₃) δ_C (ppm): 191.91 (s, CO), 147.09, 139.60, 135.07, 130.21, 128.95, 128.41, 127.60, 127.29.

2.5.3. Data for biphenyl (**7c**). Yield: 0.107 g (70%). M.p. 67-69 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 7.01-7.51 (m, 10H, phenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 141.29, 128.8, 127.30, 127.22.

2.5.4. Data for 4-methylbiphenyl (7d). Yield: 0.112 g (67%). M.p. 48–50 °C. ¹H NMR (89.6 MHz, CDCl₃, ppm): δ = 7.25–7.60 (m, phenyl, 9H), 2.45 (s, CH₃, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 141.1, 138.3, 136.9, 129.4, 130.1, 128.6, 126.9, 21.0.

2.5.5. Data for 4-methoxybiphenyl (**7e**). Yield: 0.112 g (61%). M.p. 90-92 °C. ¹H NMR (89.6 MHz, CDCl₃) δ_H (ppm): 3.86 (s, 3H, OCH₃), 6.93-7.50 (m, 9H, phenyl). ¹³C NMR (100.62 MHz, CDCl₃) δC (ppm): 159.19, 140.77, 133.69, 128.72, 128.20, 126.78, 114.18, 55.41.

2.5.6. Data for 4-acetyl-4'-ethyl-biphenyl (7f). Yield: 0.168 g (75%). M.p. 105-108 °C.¹H NMR (250.13 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 7.96- 7.18 (m, 8H, phenyl), 2.63 (q, CH₂, 2H), 2.51 (s, CH₃, 3H), 1.21 (t, CH₃ (ethyl), 3H). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 197.77, 145.75, 144.59, 137.20, 135.60, 128.91, 128.51, 127.20, 127.00, 28.58, 26.67, 15.56.

2.5.7. Data for 4-methyl-4'-ethyl-biphenyl (**7g**). Yield: 0.119 g (61%). M.p. 59-61°C. ¹H NMR (89.6 MHz, CDCl₃) δ_H (ppm): 7.29- 7.62 (m, 8H, phenyl), 2.69 (q, CH₂, 2H), 2.47 (s, CH₃, 3H), 1.36 (t, CH₃ (ethyl), 3H). ¹³C NMR (100.62 MHz, CDCl₃) δ_C (ppm): 143.02, 138.49, 138.26, 136.64, 129.40, 128.20, 126.85, 126.80, 28.47, 21.06, 15.60.

3. Results and discussion

3.1. Synthesis

The preparation of the phosphonium salts of dppm (S_1) and dppe (S_2) was carried out by reaction of the corresponding diphosphine with 2-bromo-3'-methoxy acetophenone. Further treatment

of these phosphonium salts with NEt₃ led to elimination of HBr and formation of new unsymmetrical phosphorus ylides Y_1 and Y_2 .Reaction of these ligands with [MCl₂(COD)] (M= Pd or Pt) in a 1:1 M ratio at room temperature afforded inall cases the P–C chelated Pd(II) and Pt(II) complexes (see scheme 1).



Scheme 1. Synthesis of S₁, S₂, Y₁, Y₂and 3-6.

3.2. Spectroscopy

The structure of the products was characterized by ¹H, ¹³C and ³¹P NMR spectroscopic methods and other conventional techniques such as IR, UV–visible, fluorescence emission and elemental analysis. Table 1 shows a brief summary of these data.

Also, the exact structure of **3** and **6** with atomic resolution was determined by single crystal X-ray diffraction. The CHN elemental analysis of the Pd(II) and Pt(II) complexes indicated a 1:1 stoichiometry between the MCl₂ (M= Pd or Pt) and phosphorus ylide.

The v(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 P=Cdouble bond and decrease of C=O bond order. As noted previously [55], coordination of the ylide through the carbon atom (chelating mode) or oxygen atom causes a significant increase or decrease, respectively, in the v(CO) frequency. Thus, the infrared absorption band for all complexes at higher frequencies indicates that coordination of the ylideoccurs through ylidic carbon atomand PPh₂ group (see Supplementary Data) [21,56].

The ³¹P NMR spectra of S_1 and S_2 exhibit two doublets around 21, -29 and 24,-12 ppm, which are assigned to the PCH and PPh₂groups, respectively. In ³¹P NMR spectra of Y_1 and Y_2 , the phosphonium groups of these compounds show upfield shifts compared to that of parent phosphonium salts. These peaks were shifted to around 11, -29 and 17, -13 ppm, respectively (see Supplementary Data). Furthermore, the ³¹Pchemical shift values for **3-6** appear to be shifted downfield with respect to the parentphosphorus ylides, indicating that coordination of the ylidehas occurred. The ³¹P NMR spectra of Pd(II) complexes**3** and **5** exhibit two doublets around 38, 28 and 30, 22 ppm, which can be assigned to the PPh₂ and PCH groups, respectively. The ³¹P NMR spectra of Pt(II) complexes**4** and **6** show these peaks around 42,4 and 20,6 ppm along with two satellite peaks due to ¹⁹⁵Pt-³¹P coupling (figure 1).

Also, the ¹H NMRspectra of phosphorus ylides Y_1 and Y_2 show an upfield shift for the CH signals compared to those of phosphonium salts S_1 and S_2 , indicating that synthesis of the ylides hasoccurred. Downfield shifts and broadening of the doublet signal were observed for the ylidic proton in the ¹H NMR spectra of **3-6** [42]. Similar behavior was observed earlier in the case of ylide complexes of copper(I) chloride [12]. This signal for Pt(II) complexes is flanked by their corresponding satellites due to coupling with the ¹⁹⁵Pt isotope.

In the ¹³C NMR spectra of Y_1 and Y_2 , the signals due to the carbonyl group shifted to higher field compared to the parent phosphonium salts. The most important aspect of the¹³C NMR spectra of **3**-**6** is the downfield shift of the signals due to the carbonyl group. The ¹³C NMR spectra of the carbonyl group in these complexes are around 194 ppm, compared to 180 ppm for the same carbon in the parent free phosphorus ylides, indicating a much lower shielding of the carbon of the CO group in these complexes (see Supplementary Data). Thus, the spectral data clearly indicates the bidentate coordination of the ylides through both the phosphine group and the ylidic carbon atom.

The palladium and platinum complexes have +2 oxidation states, indicating diamagnetism. The electronic spectra at room temperature in DMSO solution of these complexes show two bands at 300-500 nm. The electronic absorption spectra of these phosphorus ylides

showed spectral bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. On complexation, these bands shift toward higher wavelength (figure S1a and S1b in Supplementary Data).

The fluorescence emissions of all compounds were investigated at room temperature in DMSO solution with a concentration 1×10^{-5} M. Complexes **3**and**5**exhibited two weaker bands at 460 and 487 nm upon excitation at $\lambda_{ex} = 350$ nm as well as one strong emission at 517 nm, as illustrated in figure S2c in the Supplementary Data. The emission at 460 nm is due to the ligand based intramolecular emission $\pi \rightarrow \pi^*$ (IL). Such a similar band was observed around 397 and 423 nm for a DMSO solution of the phosphorus ylides ($\lambda_{ex} = 350$ nm (see figureS2b in Supplementary Data). The broad emission band centered at 487 nm is assigned to the metal to ligand charge transfer (MLCT). Also, emission spectra of a DMSO solution of **4**and **6** upon excitation at $\lambda_{ex} = 350$ nm have been shown in Supplementary Data. The first emission around 486 nm in these complexes is assigned to the d(Pt) $\rightarrow \pi^*$ ligand (MLCT) upon excitation at $\lambda_{ex} = 350$ nm (figure 2d in Supplementary Data).

3.3. Crystallography

Crystals, suitable for single-crystal X-ray analysis, of **3** and **6** were grown by slow evaporation over several days from DMSO/methanolsolution. The molecular structures of these complexes are shown in figures2and 3. Relevant parameters concerning data collection and refinement are given in table 2 and selected bond distances and angles for the unit cells are displayed in table 3. Crystallographic data for the structure in this paper can be found in the Supplementary Data.

The asymmetric unit of **3** contains two crystallographically independent palladacyclic $[PdCl_2(Ph_2P(CH_2)PPh_2C(H)C(O)C_6H_4-m-OMe)]$ molecules (figure 2). The only major difference is in the orientation of the methoxy substituent on the aromatic ring; formolecule 1 the methoxy substituent is oriented *trans* to the C=O group (O1-C2...C7-O2 179.0°), while for molecule 2 the orientation is *cis* (O3-C36...C39-O4 -21.5°). The X-ray analysis in **3** reveals the P, C-chelated mode of coordination of the ligand $[Ph_2P(CH_2)PPh_2C(H)C(O)C_6H_4-m-OMe]$ to the Pd(II) ion in this complex. The Pd atom is surrounded by one P atom of the phosphine group, one ylidic carbon and two chloride ions, leading to a slightly distorted square-planar geometry around the metal. The angles subtended by the ligand at the Pd(II) center in **3** vary from 87.54(4)° to

92.14(4)° (sum of the angles is 360.14°) and $170.78(4)^{\circ}$ to $173.57(14)^{\circ}$, indicating the distortion from the square planar environment.Weak C-H...Cl and C-H...O interactions link the molecules along the *c*-axis (table S1 in Supplementary Data).

The asymmetric unit of 6 contains two crystallographically independent platinacyclic $[PtCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4-m-OMe)]$ molecules (figure 3). In each the Pt is in an approximately square planar environment, coordinated by twochloride ions and by one phosphorus and one carbon atom from the ligand; for molecule 2 the maximum deviation from the least squares plane is 0.0437(8) Å, while for molecule 1 the maximum deviation from the least squares plane is 0.1568(8) Å, indicating a tetrahedral distortion. The major difference between the molecules is in the conformation of the six-membered ring involving the Pt atom. For the first molecule, the six-membered ring is in a chair conformation, while for the second molecule, the six-membered ring is in a distorted half-boatconformation (four adjacent atoms planar, with the other two adjacent atoms out of plane). Other geometric parameters for the two molecules are similar, with only slight differences between the conformation of the two molecules as evidenced by the torsion angles O1-C1-C2-Pt1 98.4(3)° and O3-C36-C37-Pt2 108.8(3)°. The angles subtended by the ligand at the Pt(II) center in 6 vary from 88.07(2)°.36 to 91.02(3)° (sum of the angles is 360.14°) and 170.62(8)° to 172.15(3)°, indicating the distortion from the square planar environment. Both molecules have weak C-H...O and C-H...Cl interactions; the intermolecular C-H. Clinteractions link the molecules along the baxis(table S2 in Supplementary Data). Although structures of six-membered palladacyclic ylide complexes are known, a search of the Cambridge Structural Database (version 5.38, update Feb. 2017 [57]) indicated 6 to be the first example of a structure of a six-membered platinacycle ylide complex.

3.4. Theoretical studies

A theoretical study on the structures and nature of $L \rightarrow M$ bonds in $[LMCl_2](M=Pd, Pt L=Y_1, Y_2)$ complexes **3**-**6** is reported at the BP86 level of theory using the def2-SVP basis set. The X-ray crystal structures obtained in this work(see figures 2 and 3) show that **3** formed monomeric P,C chelate complexes with five-membered rings which lie in a square planar geometry around the metal center. Also, this work and previous experimental data [58,59] confirm that upon

complexation of the Y_1 and Y_2 ligands, the monomeric P,C chelate complexes are formed as five- and six-membered rings with a square planar geometry around the metal center.

The optimized structures of the [LMCl₂](M=Pd, Pt, L=Y₁, Y₂) complexes are shown in figure4 and the trends for variation of the corresponding structural data and their comparison with experimental data are given intable 4. The results showed that changing the ligand from Y₁to Y₂ and M atom from Pd to Pt have an insignificant effect on values of bond lengths of C \rightarrow M and P \rightarrow M and the calculated and experimental C \rightarrow M and P \rightarrow M bond lengths in the complexes are in ranges of 2.10–2.12Å and 2.21–2.25Å, respectively, On the other hand, the Cl-M-Cl bond angle in five-membered ring complexes are greater than six-membered rings complexes (see figure 4 and table 4). The nature of L \rightarrow M bonds in [LMCl₂](M=Pd, Pt, L=Y₁, Y₂) complexes(3-6)have been investigated by NBO and energy decomposition analysis (EDA).

The partial charge amounts of the P, $C_{(ylide)}$ and M atoms of $C \rightarrow M$ and $P \rightarrow M$ bonds in the complexes and also the total charge amounts of the MCl₂fragment (M=Pd, Pt) were also investigated (see table 5). Concerning [LMCl₂] complexes, the P atom of the P \rightarrow M bond carry positive charges, but the $C_{(ylide)}$ and MCl₂ fragment carry negative charges[60]. Also the amount of negative charge of $C_{(ylide)}$ in [Y₁MCl₂] (**3-4**)complexes are slightly larger than that in [Y₂MCl₂](**5-6**).

The Wiberg bond indices (WBIs) for $C \rightarrow M$ and $C \rightarrow P$ bonds of $[LMCl_2]$ (M=Pd, Pt,L =**Y**₁, **Y**₂) complexes(**3-6**)are also compared in table 5. As can be seen, the value of WBI of $C \rightarrow P$ bond in the complexes is larger than $C \rightarrow M$ bond. Also with the same L ligand and changing the M atoms from Pd to Pt, the values of WBIs of $C \rightarrow M$ and $C \rightarrow P$ bonds in the complexes are increased.

In recent years, Morokuma [60] and Ziegler *et al.*[61] presented the "energy decomposition analysis" (EDA) method. With the help of this technique, a quantitative computational pattern for the explanation of the strength of M \leftarrow L σ donation and M \rightarrow L back bonding in the main group and transition metal complexes with different types of ligands is in hand [62-71].

In continuation, through the energy decomposition analyses (EDA), the strength and nature of donor–acceptor bonds between the phosphorus ylides (L) and MCl₂ fragment have been investigated at BP86/TZ2P(ZORA)//BP86/def2-SVP with C1 symmetry using the program package ADF2009.01.

The results of EDA analyses for all aforementioned complexes are given in table 6. In the EDA, the bonding formation of interacting fragments would result from four main components as follows:

where is electrostatic interaction, is Pauli repulsion, is orbital interaction and is dispersion energy between two fragments. The result of EDA analysis confirms that the main portions of , about 56-58% in the complexes are allocated to (see table 6).

Also, the visualizations of the NOCV pairs ($\Delta \rho$) between the donor orbitals of phosphorus ylides (L) and the acceptor orbitals of MCl₂ fragment are shown in figures5 and 6. As can be seen, the dominant term of for all aforementioned complexes arises from σ -orbital interactions ($\Delta \rho 1$, $\Delta \rho 2$ and $\Delta \rho 3$). The calculated data show that the σ -orbital interactions account for 70.69- 75.29% of the term for studied complexes. Also, the shapes of the orbital pairs of $\Delta \rho 3$ and $\Delta \rho 4$ refer to π back-donations which are in-plane and out-of-plane, respectively, and account for about 9.63-10.87% of the term (see table 6 and figures 5 and 6).

3.5. Suzuki reaction of aryl bromide

In order to examine the catalytic activity of Pd(II) complexes in the Suzukireaction, the reaction between bromobenzene with phenylboronic acid in the presence of catalyst **3** was chosen as model reaction.Influences of different parameters such as base, temperature, solvent and catalyst concentration were examined to obtain the best possible combination.

At the first stage of optimization, we studied 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 the presence of K₃PO₄and K₂CO₃give the desired coupling product in moderate to high yields (table 7, entries 1, 4 and 2, 5). However, the reactions in the presence of NEt₃did not proceed efficiently even after prolonged stirring at reflux temperature of the solvents, probably due to the low solubility of this organic base in aqueous solvents(table 7, entries 3, 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 the solubility of the base in such catalytic systems (table 7, entries 10 and 11).

During the optimization process, we investigated 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 **3** decreased to 0.005 mmol, the coupling reaction gave slightly lower product yield and the reaction resulted in negligible yield of coupled product when the catalyst loading decreased to 0.0005 mmol (table 7, entries 12 and 13). Also, an excessive amount of catalyst did not increase the yield significantly (table 7, entry 14). Therefore, 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 the reactions led to a decrease of the yields and inherent increase of the reaction time for completion of the reactions (table 7, entries 15 and 16).

The optimized conditions are:DMF/H₂O as solvent, K_2CO_3 as base, 0.005 mmol of **3** as catalyst and reaction at reflux temperature (110 °C) for 6 h.

After optimizing the reaction conditions, the scope of the reaction was explored with aryl bromides with electron-withdrawing and electron-donating groups and phenylboronic acid. The results are summarized in table 8. As illustrated in table 8, aryl bromides were converted into the corresponding coupled products in high yields. Conversely, increasing electron density on the aryl bromides lowered the catalyst activity. That is, excellent yields are achieved when phenylboronic acidis treated with aryl bromides bearing electron-withdrawing substituentsNO₂, – CHO and -COCH₃(table 8, entries 1-3). Deactivated aryl bromides 4-bromotoluene and 4-bromoanisol gave lower yields, indicating that the reaction was sensitive to the electron density on the aryl bromides (table 8, entries 5 and 6). The reaction of electronically neutral bromobenzene with phenylboronic acid was also produced good amounts of the product (table 8, entry 4). As seenin table 8, we observed that in all cross-coupling reactions, **3** and **5** had approximatelythe same catalytic activities and similar yields.

To extend the scope of our work, we investigated the coupling reaction of aryl bromidesubstrates with ethyl substituted phenylboronic acid. As expected, an electron-donating substituenton the arylboronic acid has adecreasing effect on the yield of the reaction (table 8, entries 7-10).However, the coupling reaction of activated aryl bromides such as 4-phenylbenzaldehydegave thecoupled boronic acid derivatives in higher yields (table 8, entry 11).

Table 9 shows a comparison between the efficiency of this catalytic system in the Suzuki reaction of aryl bromides and other catalytic systems. The results of this comparison showed that the reported catalysts inliterature need to be used in high loadings and showed lower activity with aryl bromidesubstrates [72-75]. From an industrial point of view, the low catalyst loading and short reactiontime make this Pd complex an ideal catalyst for the Suzuki reaction.

4. Conclusion

The present study describes the very simple and efficient synthesis and characterization of new phosphonium salts, phosphorus ylides and a series of P-C chelated Pd(II) and Pt(II)complexes. On the basis of the spectroscopic data, we have proposed that ligands herein exhibit a chelate P-C coordination behavior to the metal center affording a five- or six-membered chelate rings. This coordination fashion has beenfurther confirmed by single crystal X-ray diffraction experiments of 3 and 6. Also, we used 3 and 5 as highly active and efficient catalysts for promoting the Suzuki reaction of various aryl bromides to produce the corresponding products in high yields. Results showed that the coupling reaction of various aryl bromides with arylboronic acid was performed in high yields. The theoretical studies on the structures and nature of $L \rightarrow M$ bonds in $[LMCl_2]$ (M= Pd, Pt, $L = Y_1, Y_2$) complexes are reported by using NBO, EDA and EDA-NOCV analysis. The results of NBO analysis confirmed that the value of WBI of $C \rightarrow P$ bond in the latter complexes is larger than $C \rightarrow M$ bond. Also with the same L ligand and changing the M atoms from Pd to Pt, the values of WBIs of $C \rightarrow M$ and $C \rightarrow P$ bonds in the complexes increased. The result of EDA analysis confirms that the main portions of , about 56-58% in the complexes are allocated to Δr . Also the NOCV pairs ($\Delta \rho$) between the donor orbitals of phosphorus ylides (L) and the acceptor orbitals of MCl₂ fragment showed that the dominant term of for all aforementioned complexes arises from σ -orbital interactions (about 70.69-75.29%).

Supplementary material

Supplementary data (CCDC 1475346 - 1547211 contain the supplementary crystallographic data for **3**and**6**).These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44 0 1223 762911; or E-mail: deposit@ccdc.cam.ac.uk.

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Graphical abstract









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Compound	IR; v(CO)	¹ HNMR;	¹³ CNMR;	³¹ PNMR; δ (PCH)
	cm ⁻¹	δ(PCH) ppm	δ(CO) ppm	and (PPh ₂) ppm
S ₁	1671	5.92	192.20	21.07, -29.00
S ₂	1671	6.07	192.01	24.01, -12.06
Y ₁	1586	4.02	184.68	11.34, -29.55
Y ₂	1585	4.08	185.10	17.58, -13.64
3	1619	5.94	196.81	38.67, 28.30
4	1627	5.68	196.71	42.22, 4.43
5	1626	6.18	195.97	30.90, 22.77
6	1634	5.49	196.11	20.14, 6.60

Table 1. Spectroscopic data for S_1 , S_2 , Y_1 , Y_2 and 3-6.



	Compound 3	Compound 6
Empirical formula	$C_{34}H_{30}Cl_2O_2P_2Pd$	C ₃₅ H ₃₂ Cl ₂ OP ₂ Pt
Formula weight	709.82	812.53
<i>T</i> [K]	130.00(10)	130.00(10)
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
<i>a</i> [Å]	11.3894(5)	30.21378(18)
<i>b</i> [Å]	16.4861(5)	12.80070(8)
<i>c</i> [Å]	16.9176(6)	16.64819(11)
α [°]	81.880(3)	90
<i>B</i> [°]	81.766(3)	98.9218(6)
γ [°]	81.447(3)	90
<i>V</i> [Å ³]	3085.4(2)	6360.91(7)
Ζ	4	8
$\rho_{calc} g/cm^3$	1.528	1.697
μ [mm ⁻¹]	7.665	10.994
F(000)	1440.0	3200.0
Crystal size [mm ³]	$0.22 \times 0.194 \times 0.05$	$0.245 \times 0.082 \times 0.038$
2θ range [°]	7.912 to 154.14	7.514 to 154.286
Index ranges	$-14 \le h \le 14$, $-20 \le k \le 18$, $-21 \le 1 \le 20$	$-38 \le h \le 33$, $-15 \le k \le 16$, $-19 \le l \le 20$
Reflections collected	33843	70624
Independent reflections	$12892 [R_{int} = 0.0433]$	$13409 [R_{int} = 0.0387]$
Data/restraints /parameters	12892/0/741	13409/0/759
Goodness-of-fit on F ²	1.062	1.034
$R_1/wR_2[I > 2\sigma(I)]$	0.0502/0.1304	0.0260/0.0612

Table 2. Crystal data and structure refinement for **3** and **6**.

			8						\square
Bond dista	Bond distances							\langle	
Compoun	d 3				Compound 6			$\langle \rangle \rangle$	
First mole	First molecule Second molecule			First mole	cule		Second mo	olecule	
Pd1-Cl1	2.374	6(10)	Pd2-Cl3	2.3600(11)	Pt1-Cl1	2.38	06(7)	Pt2-Cl3	2.3758(6)
Pd1-Cl2	2.332	9(11)	Pd2-Cl4	2.3530(11)	Pt1-Cl2	2.339	3(7)	Pt2-Cl4	2.3533(6)
Pd1-P2	2.215	7(11)	Pd2-P4	2.2136(11)	Pt1-P2	2.214	1(7)	Pt2-P4	2.2189(7)
Pd1-C1	2.115	(4)	Pd2-C35	2.105(4)	Pt1-C2	2.09	2(3)	Pt2-C37	2.091(3)
O1-C2	1.219	(6)	O3-C36	1.226(6)	01-C1	1.23	0(4)	O3-C36	1.226(4)
C1-C2	1.513	(7)	C35-C36	1.496(6)	C1-C2	1.50	3(4)	C36-C37	1.493(4)
P1-C1	1.782	(4)	P3-C35	1.779(4)	P1-C2	1.792	2(3)	P3-C37	1.791(3)
P2-C22	1.852	(4)	P4-C56	1.848(5)	P2-C4	1.83	3(3)	P4-C39	1.829(3)
Bond ang	les								
Compoun	d 3			$\langle \mathcal{L} \rangle$	Compound	d 6			
		Cl2-P	d1-Cl1	92.14(4)	~		Cl2-P	t1-Cl1	88.07(2)
		C1-Pc	11-P2	89.88(12)	C2-Pt		:1-P2	95.01(8)	
Molecule	1	C1-Pc	11-Cl2	173.57(14)	Molecule	1	C2-Pt	:1-Cl2	170.62(8)
		P2-Pd	11-Cl1	170.78(4)			P2-Pt	1-Cl1	172.15(3)
		P2-Pd	11-Cl2	87.54(4)	P2-Pt		1-Cl2	91.02(3)	
		Cl4-P	d2-Cl3	93.85(4)			Cl4-P	t2-Cl3	88.72(2)
		C35-F	Pd2-P4	90.54(12)			C37-I	Pt2-P4	94.31(7)
Molecule	2	C35-F	2d2-Cl4	173.67(13)	Molecule	2	C37-I	Pt2-Cl4	175.53(7)
		P4-Pd	2-Cl3	176.13(4)			P4-Pt	2-Cl3	177.39(2)
	P4-Pd2-Cl4		85.82(4)			P4-Pt	2-Cl4	89.07(2)	
\mathcal{C}	$\mathbb{C}^{\mathbb{N}}$								
	ノ								
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Table 3.Selected bond lengths [Å] and angles [°] for 3and6.

Table 4. Selected bond lengths (Å) and angles (°) of $[LMCl_2]$ (M= Pd, Pt, L=Y₁, Y₂) complexes(**3-6**) at the BP86/def2-SVP level of theory. Values given in parentheses correspond to the experimental data.

	[Y ₁ PdCl ₂]	[Y ₂ PdCl ₂]	[Y ₁ PtCl ₂]	[Y ₂ PtCl ₂]
	Bond lengths (Å)	Bond lengths (Å)	Bond lengths (Å)	Bond lengths (Å)
M-C(ylide)	2.12(2.10)	2.13	2.11	2.12(2.10)
М-Р	2.25(2.21)	2.26	2.24	2.25(2.22)
M–Cl	2.38(2.36)	2.39	2.40	2.41(2.35)
	Bond angle (°)	Bond angle (°)	Bond angle (°)	Bond angle (°)
Cl-M-Cl	90.84	97.61	90.64	97.49

N				CONSIS	D	MOL
and M atoms and M	Cl_2 fragment in	3-6 complexes.				
T-1.1. 5 W.1 1	. 1 : 1: (W/T	L. M. D. C.	D 1/1.			fC
				\cdot		2 ~

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		l'o deompiexes.				
Name of complex	WBI C-Pd	WIB P-Pd	M	C(Ylide)	Р	MCl ₂
$[Y_1PdCl_2](3)$	0.41	0.57	0.13	-0.89	1.09	-0.79
$[Y_1PtCl_2](4)$	0.49	0.70	-0.01	-0.88	1.14	-0.93
$[Y_2PdCl_2](5)$	0.39	0.57	-0.009	-0.84	1.05	-0.76
$[Y_2PtCl_2](6)$	0.49	0.72	-0.17	-0.81	1.11	-0.86
		\sim				

X	Parameter	Value	Χ	Parameter	Value	
	ΔE int	-124.24		ΔE int	-124.01	
[Y ₂ PdCl ₂]	ΔEpauli	268.28	[Y ₁ PdCl ₂]	ΔEpauli	275.43	
[- <u>2</u>	ΔEelast	-223.36(56.90)	(3)	ΔEelast	-230.54(57.71)	
(0)	ΔEorb	-149.61(38.11)		ΔEorb	-150.22(37.60)	
	ΔEdis	-19.56(4.98)		ΔEdis	-18.67(4.67)	
	ΔEorb, σd	-78.32(52.34)] <	AEorb, σd	-80.06(53.29)	
	ΔEorb, σd	-20.67(13.81)	\land	ΔEorb, σd	-18.05(12.01)	
	ΔEorb,σd	-10.29(6.87)		AEorb, σd	-13.23(8.80)	
	ΔEorb, π ∥	-10.25(6.85)		ΔEorb, πl	-9.61(6.39)	
	Δ Eorb, π^{\perp}	-6.02(4.02)		ΔEorb, π [⊥]	-5.86(3.90)	
	ΔEorb, rest	-11.14		ΔEorb, rest	-9.48	
[Y ₂ PtCl ₂]	ΔE int	-165.83	W ₁ PtCl ₂]	ΔE int	-159.02	
(6)	ΔEpauli	343.95	(4)	ΔEpauli	352.29	
(0)	ΔEelast	-291.56(57.19)		ΔEelast	-297.06(58.09)	
	ΔEorb	-191.97(37.65)		ΔEorb	-189.96(37.15)	
	ΔEdis	-26.25(5.14)		ΔEdis	-24.29(4.75)	
	ΔEorb, σd	-91.42(47.62)		ΔEorb, σd	-90.65(47.72)	
	ΔEorb, σd	-31.61(16.46)		ΔEorb, σd	-37.14(19.55)	
	Δ Eorb, σ d	-12.69(6.61)		ΔEorb, σd	-15.25(8.02)	
	ΔEorb, π	-12.79(6.66)		∆Eorb, π∥	-13.25(6.97)	
	$\Delta Eorb, \pi^{\perp}$	-5.71(2.97)		ΔEorb, π [⊥]	-5.62(2.95)	
	ΔEorb , rest	-11.56		ΔEorb, rest	-12.98	
ΔEorb, rest -11.56 ΔEorb, rest -12.98						

Table 6. EDA analysis (BP86/SVP(ZORA)//BP86/def2-SVP) of [LMCl₂] (M=Pd or Pt, L= Y_1 , Y_2) complexes (3-6)with the C1 symmetry (ΔE values are at kcal.mol⁻¹).

R	Br + (HO) ₂ B	complex Solvent,	ex 3, Base R		
Entry	Base	Solvent	Catalyst loading	Temp.	Yield (%) ^b
			(mmol)	(°C)	
1	K ₃ PO ₄	DMF/H ₂ O	0.05	1)10	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	110	47
5	K ₂ CO ₃	Methanol/H ₂ O	0.05	110	51
6	NEt ₃	Methanol/H ₂ O	0.05	110	45
7	K ₃ PO ₄	Toluene/H ₂ O	0.05	110	54
8	K ₂ CO ₃	Toluene/H ₂ O	0.05	110	35
9	NEt ₃	Toluene/H ₂ O	0.05	110	40
10	K ₂ CO ₃	H_2O	0.05	110	44
11	K ₂ CO ₃	DMF	0.05	110	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	0.1	110	83
15	K_2CO_3	DMF/H ₂ O	0.005	65	58
16	K ₂ CO ₃	DMF/H ₂ O	0.005	25	40

Table 7. Optimizations for th	ne Suzukireaction ^a .
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^aReaction conditions for Suzuki reaction: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), solvent (2 mL), catalyst **3**, in the air.

^bIsolated yield.

	Br + (HO) ₂ B	R ['] Complex	$re 3 \text{ or } 5, K_2CO_3 \rightarrow R$	R'
Entry	R	R'	Product	Yield (%) ^b
1	NO ₂	Н	p-NO ₂ -Ph-Ph (7a)	92, 95
2	СНО	Н	p-OHC-Ph-Ph(7b)	83, 85
3	COCH ₃	Н	<i>p</i> -CH ₃ OC-Ph-Ph	78, 82
4	Н	Н	Ph-Ph(7c)	70, 68
5	Me	Н	<i>p</i> -Me-Ph-Ph (7d)	67, 69
6	OCH ₃	Н	p-CH ₃ O-Ph-Ph(7e)	61, 62
7	СНО	Et	p-OHC-Ph-Ph-Et	78, 83
8	COCH ₃	Et	p-CH3OC-Ph-Ph-Et (7f)	75, 73
9	Н	Et	Ph-Ph-Et	66, 65
10	Me	Et	<i>p</i> -Me-Ph-Ph-Et (7g)	61, 64
11	OCH ₃	Et	<i>p</i> -CH ₃ O-Ph-Ph-Et	57, 62

Table 8.Suzuki reaction of aryl bromides catalyzed by 3and5^a.

^a Reaction conditions for Suzuki reaction: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (1 mmol), DMF/H₂O (2 ml), catalyst **3** or **5** (0.005 mmol), in the air.

^bIsolated yields for coupling reactions in presence of 3and 5, respectively.

Table 9. Comparison of Suzuki reaction of bromobenzene and phenylboronic acidusing palladium complex 3 and other catalytic system.

panadium complex 5 and other catalytic system.					
$\begin{array}{ c c c c c }\hline & & \hline & & \hline & & \hline & & \hline & & & \hline & & & \hline & & & & \hline & & & & & \hline & & & & & & \hline & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & & & & \hline & & & & & & & & & & & & & & & & & & & \\ \hline & & & &$					
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	[53]
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	[54]
3	2,6-bis (diphenylphosphino) pyridine/Pd(II)	0.001	K ₂ CO ₃ , DMAc/TBAB, 135 °C, 5 h	57	[55]
4	Polymer-Anchored Schiff Base Pd(II)	0.005	K ₂ CO ₃ , DMF, 100 °C, 24 h	12	[56]
5	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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