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Synthesis, characterization and structural studies of new palladium(II) complexes including non-symmetric phosphorus ylides

Seyyed Javad Sabounchei [a,*], Sepideh Samiee [a], Davood Nematollahi [a], Ali Naghipour [b], David Morales-Morales [c,**]

[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran
[b] Department of Chemistry, Faculty of Science, University of Ilam, Ilam 69315, Iran
[c] Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, 04510, México D.F., Mexico

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ABSTRACT

The reaction of the non-symmetric phosphorus ylides, $Ph_2P(CH_2)_nPPh_2C(H)C(O)PhR$ [Y_1–Y_4: $n = 1$, R = Cl, Br, NO_2, OCH_3 and Y_5–Y_8: $n = 2$, R = Cl, Br, NO, OCH_3] with dichloro(1,5-cyclooctadiene)palladium(II) in dichloromethane under mild conditions afford the monomeric P–C chelated complexes, $[(Y)PdCl_2]$ ($Y = Y_1$–Y_8). These complexes were fully characterized by elemental analysis and spectroscopic techniques such as IR, ^1H, ^{31}P, and ^{13}C NMR. In addition, the identity of complexes $[(Y_5)PdCl_2]$ (**1b**) and $[(Y_8)PdCl_2]$ (**4b**) was unequivocally determined by single crystal X-diffraction techniques, both structures consisting of six-membered rings formed by coordination of the ligands through the phosphine group and the ylidic carbon atom to the metal center. The coordination geometry around the Pd atoms in both these complexes be defined as slightly distorted square planar. Furthermore, their electrochemical behavior was also investigated by cyclic voltammeters, thus the cyclic voltammetry of complex $[(Y_1)PdCl_2]$, in dichloromethane solution with Pt electrode, shows that the redox reaction of the pair Pd(II)/Pd(0) is irreversible with the cathodic peak potential at −1.08 V versus Ag wire.

1. Introduction

Phosphorus ylides are a group of very interesting ligands in organometallic chemistry, these compounds are also useful intermediates in organic synthesis [1–4]. Much of the interest in the coordination properties of resonance stabilized phosphorus ylides stems from their coordination versatility due to the presence of different functional groups in their molecular frame [5]. The α-keto stabilized ylides derived from bisphosphines, *viz.*, $Ph_2PCH_2PPh_2{=}C(H)C(O)R$ and $Ph_2PCH_2CH_2PPh_2{=}C(H)C(O)R$ (R = Me, Ph or OMe) [6] constitute an important class of hybrid ligands containing both phosphine and ylide functionalities, and can exist in ylidic and enolate forms. This versatility, has allowed the characterization of coordinated ylides in different bonding modes: C-coordinated (through the Cα atom), O-bonded (through the carbonyl O), P-bonded (through the P of the phosphine group), or even situations in which the same ylide shows a combination of bonding modes. Different types of bonding are shown as depicted in Chart 1 for $Ph_2P(CH_2)_nPPh_2C(H)C(O)PhR$ [see Chart 1].

The bonding mode (d) had been previously observed for Pd(II), Pt(II), Rh(I), Hg(II) [6–17] species. In addition, Rh(I) and Hg(II) were shown to exhibit the P-bonding mode (b) [10,15]. 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). The results of these studies including the full characterization of the obtained complexes (performed by elemental analysis, IR, multinuclear NMR techniques and electrochemical data) is presented and discussed in this paper.

2. Experimental

2.1. Materials

All synthetic procedures were performed using standard Schlenk tube techniques under dry nitrogen atmospheres. Starting materials were purchased from commercial sources and used without further purification. Solvents were dried according to the methods given in the literature and purified under inert conditions [18]. The starting material dichloro(1,5-cyclooctadiene)palladium(II) complex, $[PdCl_2(COD)]$ was prepared according to the published procedures [19].

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[*] Corresponding author.
[**] Corresponding author. Tel.: +98 8118272072; fax: +98 8118273231.
E-mail addresses: jsabounchei@yahoo.co.uk (S.J. Sabounchei), damor@unam.mx (D. Morales-Morales).

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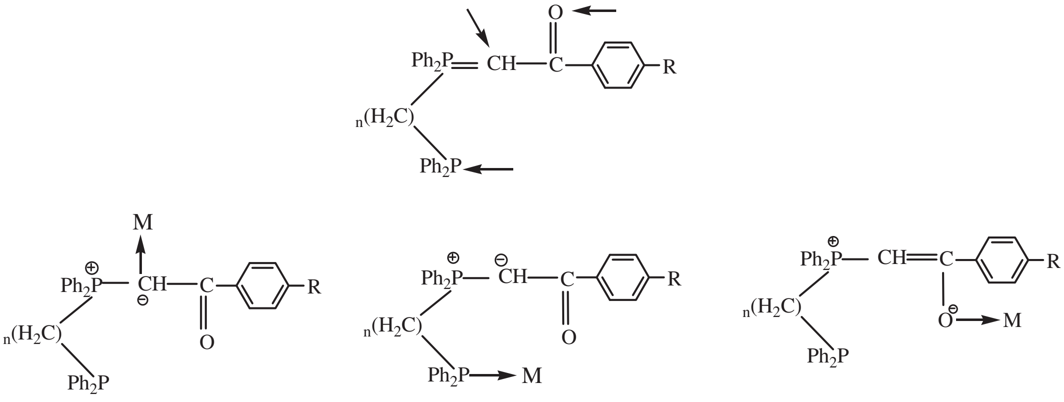


(a) C-bonding (b) P-bonding (c) O-bonding

(d) P, C-bonding, chelate (e) P, O-bonding, chelate

(f) P, C-bonding, bridging (g) P, O-bonding, bridging

Chart 1. The possible bonding modes of $Ph_2P(CH_2)_nPPh_2C(H)C(O)C_6H_4R$ (n = 1, 2 and R = Cl, Br, OCH_3, NO_2) to metal M.

2.2. Physical measurements

Melting points were measured on a SMPI apparatus and are reported without correction. Elemental analysis was performed using a Perkin–Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded either on a 300 MHz Bruker and a 90 MHz Jeol spectrometer in DMSO-d_6 or $CDCl_3$ as solvents at 25 °C. Cyclic voltammetry was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a Pt disc (2.2 mm diameter) and platinum wire was used as the counter electrode. The working electrode potentials were measured versus Ag wire (all electrodes from AZAR Electrodes).

Suitable crystals for complexes **1b** and **4b** were obtained from dimethylsulfoxide solution by slow evaporation of the solvent and mounted in random orientation on glass fibers. The X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD-based three-circle X-ray diffractometer system using graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation. The crystal structures were solved by direct methods and refined by using SHELXS-97 and SHELXL-97 crystallographic software packages [20–23]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms were located in ideal positions.

2.3. Sample preparation

The ligands $[Ph_2PCH_2PPh_2C(H)C(O)C_6H_4R]$ (R = Cl (Y_1), NO_2 (Y_3)) and $[Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4NO_2]$ (Y_7) were prepared based on the published methods [24,25].

2.3.1. Synthesis of ligands

*2.3.1.1. Synthesis of $[Ph_2PCH_2PPh_2C(H)C(O)C_6H_4Br]$ (**Y_2**).* Bis(diphenylphosphino)methane (dppm) (0.2 g, 0.52 mmol) was dissolved in 5 ml of chloroform and then a solution (5 ml, $CHCl_3$) of 4-bromophenacyl bromide (0.144 g, 0.52 mmol) was added dropwise. The resulting reaction mixture was stirred for 2 h at room temperature. Addition of 25 ml of diethyl ether, after the prescribed reaction time caused the precipitation of the phosphonium salts. The resulting phosphonium salts (0.3 g, 0.45 mmol) were treated with triethyl amine (0.5 ml) 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 the ligands as free-flowing white solids. The product was collected and dried under vacuum. *Anal.* Calc. for $C_{33}H_{27}BrOP_2$: C, 68.17; H, 4.68. Found: C, 67.91; H, 4.52%. Yield: 0.205 g (78%), m.p. 153–155 °C. Selected IR absorption in KBr (cm^{-1}): 1502 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$) δ_H (ppm): 3.63 (d, 2H, CH_2, $^2J_{PH}$ = 14.15 Hz), 4.22 (d, 1H, CH, $^2J_{PH}$ = 23.56 Hz), 7.24–7.73 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$) δ_P (ppm): −30.07 (d, PPh_2, $^2J_{PP}$ = 63.67 Hz), 11.39 (d, PCH, $^2J_{PP}$ = 62.98 Hz). ^{13}C NMR

(CDCl$_3$) δ_C (ppm): 24.61 (dd, CH$_2$, $^1J_{PC}$ = 56.22, 57.65 Hz), 50.51 (d, CH, $^1J_{PC}$ = 112.45 Hz), 123.62–140.12 (Ph), 183.58 (s, CO).

*2.3.1.2. Synthesis of [Ph$_2$PCH$_2$PPh$_2$C(H)C(O)C$_6$H$_4$OCH$_3$] (**Y$_4$**).* A solution consisting of dppm (0.2 g, 0.52 mmol) and 4-methoxyphenacyl bromide (0.119 g, 0.52 mmol) in acetone was stirred at room temperature for 4 h. The resulting white solid formed was filtered off, and dried under reduced pressure. Further treatment with triethyl amine (0.5 ml) led to elimination of triethyl amine hydrobromide, affording the free ligand **Y$_4$**. White solid. *Anal.* Calc. for C$_{34}$H$_{30}$O$_2$P$_2$: C, 76.68; H, 5.68. Found: C, 76.49; H, 5.56%. Yield: 0.202 g (76%), m.p. 148–150 °C. Selected IR absorption in KBr (cm^{-1}): 1507 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 3.64 (d, 2H, CH$_2$, $^2J_{PH}$ = 14.42 Hz), 3.79 (s, 3H, CH$_3$); 4.24 (br, 1H, CH), 6.78–7.84 (m, 24H, Ph). ^{31}P NMR (CDCl$_3$) δ_P (ppm): −29.67 (d, PPh$_2$, $^2J_{PP}$ = 62.36 Hz), 11.15 (d, PCH, $^2J_{PP}$ = 62.36 Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 24.87 (dd, CH$_2$, $^1J_{PC}$ = 56.67, 56.82 Hz), 49.02 (d, CH, $^1J_{PC}$ = 112.45 Hz), 55.30 (s, CH$_3$), 112.86–137.71 (Ph), 160.72 (s, COPh (*i*)), 184.61 (s, CO).

*2.3.1.3. Synthesis of [Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)C(O)C$_6$H$_4$Cl] (**Y$_5$**) general procedure.* A solution consisting of bis(diphenylphosphino)ethane (dppe) (0.398 g, 1 mmol) and 4-chlorophenacyl bromide (0.245 g, 1.05 mmol) in acetone was stirred at room temperature overnight. The resulting solution was filtered off, and the precipitate obtained washed with diethyl ether and dried. This product was further treated with triethyl amine (0.5 ml) leading to the elimination of triethyl amine hydrobromide, affording the free ligand Y$_5$ as sole product. White solid. *Anal.* Calc. for C$_{34}$H$_{29}$ClOP$_2$: C, 74.11; H, 5.31. Found: C, 74.52; H, 5.23%. Yield: 0.208 g (76%), m.p. 142–144 °C. Selected IR absorption in KBr (cm^{-1}): 1579 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 2.17 (m, 2H, CH$_2$), 2.77 (m, 2H, CH$_2$), 4.17 (br, 1H, CH), 7.32–7.84 (m, 24H, Ph). ^{31}P NMR (CDCl$_3$) δ_P (ppm): −15.13 (d, PPh$_2$, $^3J_{PP}$ = 46.13 Hz), 14.58 (d, PCH, $^3J_{PP}$ = 46.48 Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 20.53 (br, CH$_2$), 47.37 (d, CH, $^1J_{PC}$ = 110.56 Hz), 126.05–139.56 (Ph), 183.91 (s, CO).

*2.3.1.4. Data for [Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)C(O)C$_6$H$_4$Br] (**Y$_6$**).* The title compound was prepared by a similar procedure to that of ligand (Y$_5$). White solid. *Anal.* Calc. for C$_{34}$H$_{29}$BrOP$_2$: C, 68.58; H, 4.91. Found: C, 68.10; H, 4.75%. Yield: 0.224 g (75%), m.p. 137–139 °C. Selected IR absorption in KBr (cm^{-1}): 1579 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 2.25 (m, 2H, CH$_2$), 2.83 (m, 2H, CH$_2$), 4.18 (br, 1H, CH), 7.07–7.86 (m, 24H, Ph). ^{31}P NMR (CDCl$_3$) δ_P(ppm): −15.17 (d, PPh$_2$, $^3J_{PP}$ = 46.34 Hz), 14.55 (d, PCH, $^3J_{PP}$ = 48.26 Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 20.52 (br, CH$_2$), 47.14 (d, CH, $^1J_{PC}$ = 113.50 Hz), 123.77–139.80 (Ph), 183.95 (s, CO).

*2.3.1.5. Data for [Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)C(O)C$_6$H$_4$OCH$_3$] (**Y$_8$**).* The title compound was prepared by a similar procedure to that of ligand (Y$_5$). White solid. *Anal.* Calc. for C$_{35}$H$_{32}$O$_2$P$_2$: C, 76.91; H, 5.90. Found: C, 77.03; H, 5.85%. Yield: 0.224 g (82%), m.p. 129–131 °C. Selected IR absorption in KBr (cm^{-1}): 1603 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 2.27 (m, 2H, CH$_2$), 2.87 (m, 2H, CH$_2$), 3.84 (s, 3H, CH$_3$), 4.18 (d, 1H, CH, $^1J_{PH}$ = 18.09 Hz), 6.86–8.01 (m, 24H, Ph). ^{31}P NMR (CDCl$_3$) δ_P (ppm): −15.15 (d, PPh$_2$, $^3J_{PP}$ = 47.53 Hz), 14.33 (d, PCH, $^3J_{PP}$ = 47.42 Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 20.80 (br, CH$_2$), 46.28 (d, CH, $^1J_{PC}$ = 113.51 Hz), 113.10–137.37 (Ph), 160.84 (s, COPh (*i*)), 185.04 (s, CO).

2.3.2. Synthesis of Pd(II) halide complexes

*2.3.2.1. Synthesis of [(Y$_1$)PdCl$_2$] (**1a**) general procedure.* To a [PdCl$_2$(COD)] (0.142 g, 0.5 mmol) dichloromethane solution (5 ml), a solution of Y$_1$ (0.268 g, 0.5 mmol) (5 ml, CH$_2$Cl$_2$) was added dropwise. The resulting solution was stirred for 1 h at room temperature and then concentrated to a *ca.* 2 ml in volume and treated with *n*-hexane (*ca.* 15 ml) to afford a yellow solid. The product was collected and dried under vacuum. *Anal.* Calc. for C$_{33}$H$_{27}$Cl$_3$OP$_2$Pd: C, 55.49; H, 3.81. Found: C, 56.01; H, 3.45%. Yield: 0.288 g (81%), m.p. 201–203 °C. Selected IR absorption in KBr (cm^{-1}): 1620 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 4.86 (bt, CH$_2$, $^2J_{PH}$ = 14.61 Hz), 5.98 (br, CH), 7.27–8.30 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 26.96 (bd, PPh$_2$, $^2J_{PP}$ = 49.53 Hz), 38.02 (d, PCH, $^2J_{PP}$ = 46.01 Hz). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 31.90 (br, CH), 121.47–138.25 (Ph), 196.07 (s, CO), (CH$_2$, was not seen).

*2.3.2.2. Data for [(Y$_2$)PdCl$_2$] (**2a**).* This compound was prepared by a similar procedure to that of complex (**1a**). Yellow solid. *Anal.* Calc. for C$_{33}$H$_{27}$BrCl$_2$OP$_2$Pd: C, 52.24; H, 3.59. Found: C, 51.97; H, 3.38%. Yield: 0.321 g (85%), m.p. 197–199 °C. Selected IR absorption in KBr (cm^{-1}): 1621 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 4.76 (dd, CH$_2$, $^2J_{PH}$ = 12.27, 14.15 Hz), 5.99 (br, CH), 7.31–8.31 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 26.86 (bd, PPh$_2$, $^2J_{PP}$ = 47.79 Hz), 38.07 (d, PCH, $^2J_{PP}$ = 46.08 Hz). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 22.54 (b, CH$_2$), 32.73 (d, CH, $^2J_{PC}$ = 57.75), 121.47–137.03 (Ph), 196.19 (s, CO).

*2.3.2.3. Data for [(Y$_3$)PdCl$_2$] (**3a**).* This compound was prepared by a similar procedure to that of complex (**1a**). Orange solid. *Anal.* Calc. for C$_{33}$H$_{27}$Cl$_2$N$_2$O$_3$P$_2$Pd: C, 53.64; H, 3.68; N, 3.79. Found: C, 54.12; H, 3.26; N, 3.64%. Yield: 0.287 g (78%), m.p. 230–232 °C. Selected IR absorption in KBr (cm^{-1}): 1672 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 4.71 (dd, CH$_2$, $^2J_{PH}$ = 12.90, 13.35 Hz), 6.09 (br, CH), 7.30–8.29 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 26.87 (bd, PPh$_2$, $^2J_{PP}$ = 45.57 Hz), 37.89 (d, PCH, $^2J_{PP}$ = 45.21 Hz). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 33.72 (d, CH, $^2J_{PC}$ = 54.74), 121.21–150.07 (Ph), 195.71 (s, CO), (CH$_2$, was not seen).

*2.3.2.4. Data for [(Y$_4$)PdCl$_2$] (**4a**).* This compound was prepared by a similar procedure to that of complex (**1a**). Yellow solid. *Anal.* Calc. for C$_{34}$H$_{30}$Cl$_2$O$_2$P$_2$Pd: C, 57.53; H, 4.26. Found: C, 57.89; H, 4.17%. Yield: 0.284 g (80%), m.p. 270–272 °C. Selected IR absorption in KBr (cm^{-1}): 1595 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 3.79 (s, CH$_3$), 4.79 (b, CH$_2$), 5.85 (br, CH), 6.86–8.29 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 27.15 (bd, PPh$_2$, $^2J_{PP}$ = 49.42 Hz), 38.27 (d, PCH, $^2J_{PP}$ = 48.37 Hz). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 22.54 (b, CH$_2$), 32.83 (b, CH), 55.99 (s, CH$_3$), 113.51–134.21 (Ph), 163.60 (s, COPh (*i*)), 195.63 (s, CO), (CH$_2$, was not seen).

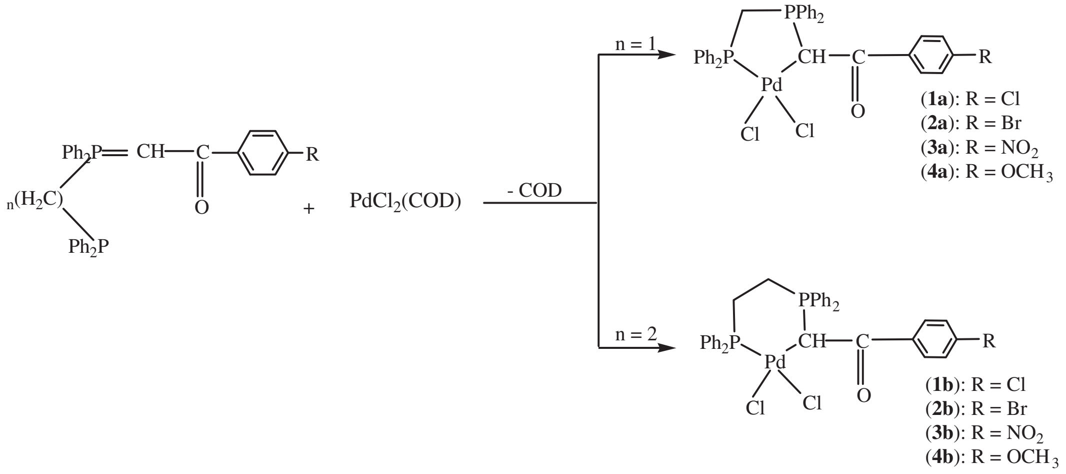
*2.3.2.5. Data for [(Y$_5$)PdCl$_2$] (**1b**).* This compound was prepared by a similar procedure to that of complex (**1a**). Yellow solid. *Anal.* Calc. for C$_{34}$H$_{29}$Cl$_3$OP$_2$Pd: C, 56.07; H, 4.01. Found: C, 55.65; H, 4.32%. Yield: 0.289 g (79%), m.p. 208–210 °C. Selected IR absorption in KBr (cm^{-1}): 1624 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 2.28 (b, CH$_2$, 2H merged with DMSO), 3.90 (m, CH$_2$, 2H merged with residual H$_2$O), 6.15 (b, CH), 7.37–8.46 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 22.82 (d, PCH, $^2J_{PP}$ = 23.46 Hz), 29.95 (b, PPh$_2$). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 19.93 (b, CH$_2$), 123.59–138.11 (Ph), 195.01 (s, CO), (CH$_2$, was not seen).

*2.3.2.6. Data for [(Y$_6$)PdCl$_2$] (**2b**).* This compound was prepared by a similar procedure to that of complex (**1a**). Yellow solid. *Anal.* Calc. for C$_{34}$H$_{29}$BrCl$_2$OP$_2$Pd: C, 52.84; H, 3.78. Found: C, 52.46; H, 3.66%. Yield: 0.321 g (83%), m.p. 214–216 °C. Selected IR absorption in KBr (cm^{-1}): 1625 ($\nu_{C=O}$). ^{1}H NMR (DMSO-d$_6$) δ_H (ppm): 2.29 (b, CH$_2$, 2H merged with DMSO), 3.90 (b, CH$_2$, 2H merged with residual H$_2$O), 6.16 (b, CH), 7.53–8.42 (m, 24H, Ph). ^{31}P NMR (DMSO-d$_6$) δ_P (ppm): 22.77 (d, PCH, $^2J_{PP}$ = 21.97 Hz), 30.15 (bd, PPh$_2$, $^2J_{PP}$ = 23.85 Hz). ^{13}C NMR (DMSO-d$_6$) δ_C (ppm): 19.46 (b, CH$_2$), 122.96–137.32 (Ph), 19.16 (s, CO), (CH$_2$, was not seen).

*2.3.2.7. Data for [(Y$_7$)PdCl$_2$] (**3b**).* This compound was prepared by a similar procedure to that of complex (**1a**). Orange solid. *Anal.* Calc.

for $C_{34}H_{29}Cl_2NO_3P_2Pd$: C, 55.27; H, 3.96; N, 1.90. Found: C, 55.83; H, 3.71; N, 1.73%. Yield: 0.326 g (77%), m.p. 190–192 °C. Selected IR absorption in KBr (cm^{-1}): 1631 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6) δ_H (ppm): 2.29 (b, CH_2, 2H merged with DMSO), 3.90 (b, CH_2, 2H merged with residual H_2O), 6.26 (b, CH), 7.58–8.51 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6) δ_P (ppm): 22.59 (d, PCH, $^2J_{PP} = 22.73$ Hz), 30.42 (bd, PPh_2, $^2J_{PP} = 23.17$ Hz). ^{13}C NMR (DMSO-d_6) δ_C (ppm): 19.73 (b, CH_2), 123.39–149.90 (Ph), 194.62 (s, CO), (CH_2, was not seen).

*2.3.2.8. Data for [(Y_8)$PdCl_2$] (**4b**).* This compound was prepared by a similar procedure to that of complex (**1a**). Yellow solid. *Anal.* Calc. for $C_{35}H_{32}Cl_2O_2P_2Pd$: C, 58.07; H, 4.46. Found: C, 57.74; H, 4.15%. Yield: 0.297 g (82%), m.p. 197–199 °C. Selected IR absorption in KBr (cm^{-1}): 1622 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6) δ_H (ppm): 2.29 (b, CH_2, 2H merged with DMSO), 3.90 (b, CH_2, 2H merged with residual H_2O), 3.80 (s, 3H, CH_3), 6.09 (b, CH), 6.83–8.49 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6) δ_P (ppm): 22.78 (d, PCH, $^2J_{PP} = 22.80$ Hz), 30.13 (bd, PPh_2, $^2J_{PP} = 24.36$ Hz). ^{13}C NMR (DMSO-d_6) δ_C (ppm): 19.68



Scheme 1. Synthetic route for preparation of Pd(II) complexes.

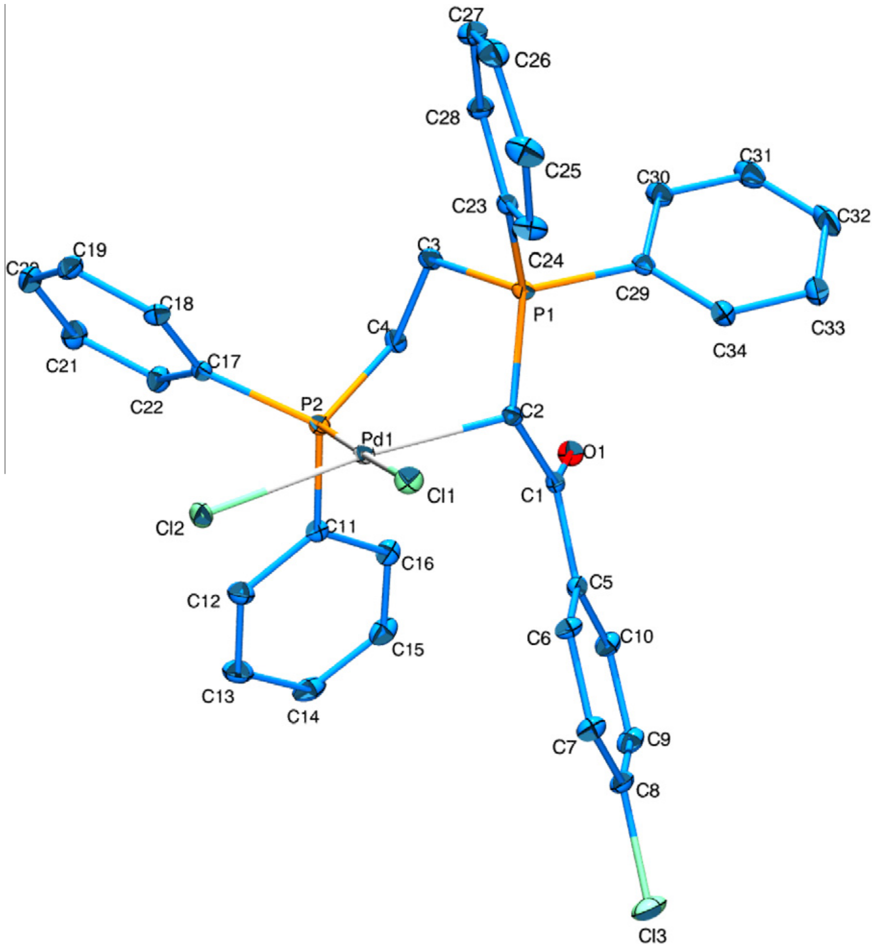


Fig. 1. ORTEP view of X-ray crystal structure of **1b**. Hydrogen atoms and DMSO molecule are omitted for clarity.

(b, CH_2), 55.95 (s, CH_3), 113.56–134.22 (Ph), 163.41 (s, COPh (*i*)), 194.87 (s, CO), (CH_2, was not seen).

3. Results and discussion

3.1. Synthesis

The reactions of [$PdCl_2$(COD)] with the non-symmetric phosphorus ylides Y_1–Y_8 in dichloromethane in a 1:1 molar ratio, at room temperature afforded, in all cases the P–C chelated complexes (see Scheme 1). These species being fairly soluble in halogenated solvents such as dichloromethane and chloroform but insoluble in non-polar solvents such as *n*-hexane.

3.2. Spectroscopy

The *ν*(CO), which is sensitive to complexation, occurs around 1500 cm^{-1} in the parent ylides [24,25]. Coordination of the ylide through carbon causes an increase in the *ν*(CO), while, when O-coordination occurs, a lowering in the value of the *ν*(CO) would be expected [26]. Thus the IR absorption bands for the complexes at higher frequencies indicate that C-coordination has occurred [13].

The ^{31}P chemical shift values for the complexes appear to be shifted downfield with respect to the parent ylide, also indicating that coordination of the ylide has occurred. In the ^{31}P NMR spectra (DMSO-d_6) the signal due to *P*CH appears as a broad doublet. The significant downfield shift of this signal from that of the free ylide is in agreement with the C-bonding of the ylides. The coordination *via* the phosphine moiety is also clearly evidenced from the strong downfield shifts of the signal due to PPh_2 group when compared to that of the same signal in the free ylides [13,14].

In the ^{1}H NMR spectra, the signals due to the methynic protons for complexes are broad. Similar behavior was observed earlier in the case of ylide complexes derived from $PtCl_2$ [27]. The expected lower shielding of both the ^{31}P and ^{1}H nuclei for the PC(H) group upon complexation in the case of C-coordination was observed in their corresponding spectra.

The most interesting features of the ^{13}C spectra of the series of complexes is the up-field shift of the signals due to the ylidic carbon. This up-field shift has been previously observed in the series of compounds [PdCl (η^3-2-XC_3H_4) $(C_6H_5)_3$PCHCOR] [X = H, CH_3; R = CH_3, C_6H_5] and attributed to the change in hybridization of the ylidic carbon [28]. Similar up-field shifts of about 2–3 ppm with reference to the parent ylide have also been observed in the case of the mercury derivative $[(C_6H_5)_3PC_5H_4HgI_2]_2$ [29]. In this case, the ^{13}C shifts of the CO group in the complexes were found around 190 ppm, compare to 180 ppm for the same carbon in the

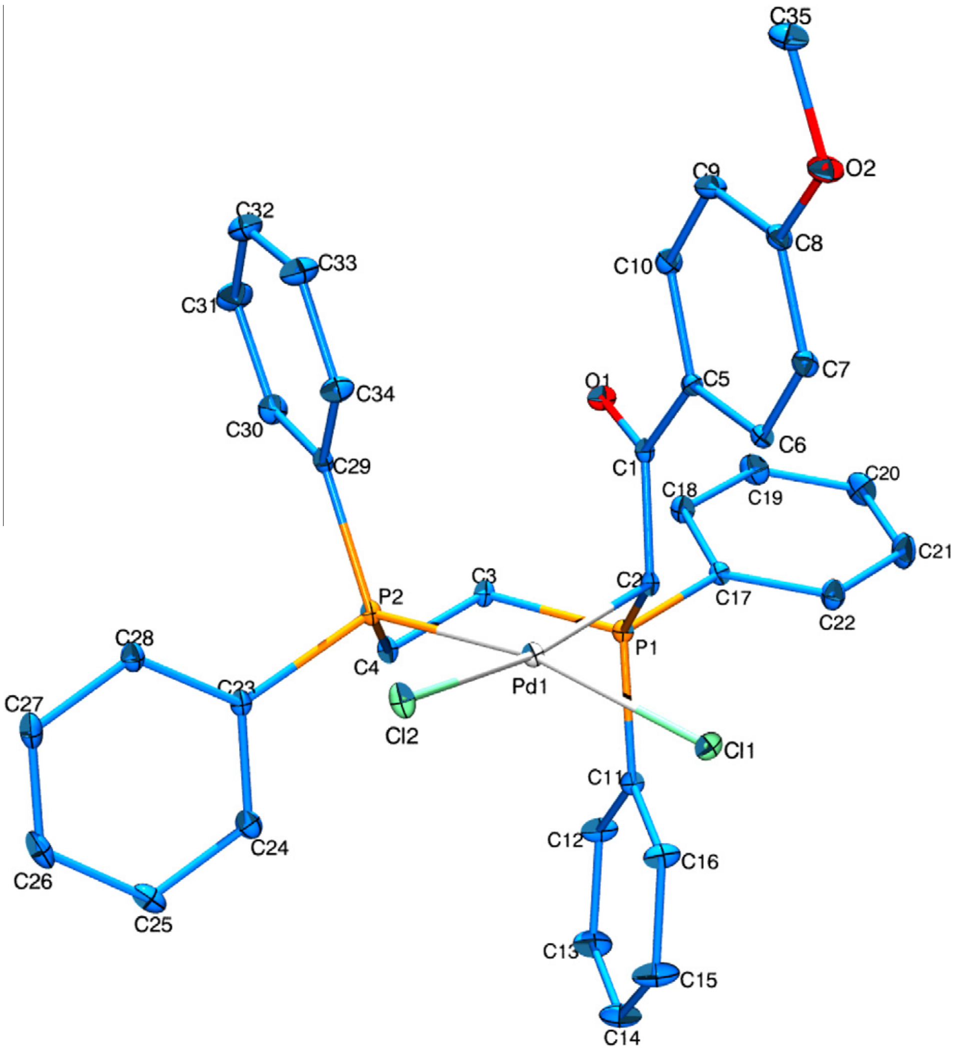


Fig. 2. ORTEP view of X-ray crystal structure of **4b**. Hydrogen atoms and DMSO molecule are omitted for clarity.

Table 1
Crystal data and structure refinement for **1b** and **4b**.

Compound	**1b**	**4b**
Empirical formula	$C_{36}H_{39}Cl_3O_4P_2PdS$	$C_{72}H_{70}Cl_4O_5P_2Pd_2S$
Formula weight	842.42	1525.82
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.7800(10)	12.1685(15)
b (Å)	20.7278(19)	16.705(2)
c (Å)	16.7468(15)	18.750(2)
α (°)	90	67.081(2)
β (°)	100.265(2)	89.597(2)
γ (°)	90	85.940(2)
Z	4	2
Absorption coefficient (mm^{-1})	0.903	0.836
θ Range for data collection (°)	1.58–25.36	1.68–25.33
Index ranges	$-12 \leqslant h \leqslant 12$ $-24 \leqslant k \leqslant 24$ $-20 \leqslant l \leqslant 20$	$-14 \leqslant h \leqslant 14$ $-20 \leqslant k \leqslant 20$ $-22 \leqslant l \leqslant 22$
Reflections collected	30105	29172
Independent reflections	6723 [R_{int} = 0.0534]	12760 [R_{int} = 0.0541]
Absorption correction	Integration	Analytical
Maximum and minimum transmission	0.8957 and 0.7850	0.9390 and 0.7619
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.928	0.886
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0343, wR_2 = 0.0736	R_1 = 0.0431, wR_2 = 0.0764
R indices (all data)	R_1 = 0.0472, wR_2 = 0.0772	R_1 = 0.0683, wR_2 = 0.0820
Largest difference in peak and hole (e Å^{-3})	0.614 and −0.346	0.685 and −0.387

Table 2
Selected bond distances (Å) and angles (°) for **1b** and **4b**.

	1b	**4b**
Bond distances		
Pd(1)–C(2)	2.400(3)	2.114(3)
Pd(1)–P(2)	2.2326(8)	2.2207(11)
Pd(1)–Cl(1)	2.3899(8)	2.4080(11)
Pd(1)–Cl(2)	2.3575(8)	2.3450(11)
O(1)–C(1)	1.219(3)	1.224(4)
P(1)–C(2)	1.790(3)	1.784(4)
P(2)–C(4)	1.828(3)	1.824(4)
C(2)–C(1)	1.505(4)	1.506(5)
Bond angles		
C(2)–Pd(1)–P(2)	93.25(8)	94.52(11)
C(2)–Pd(1)–Cl(2)	174.13(8)	168.06(11)
P(2)–Pd(1)–Cl(2)	89.12(3)	88.17(4)
C(2)–Pd(1)–Cl(1)	88.25(8)	88.71(11)
P(2)–Pd(1)–Cl(1)	176.74(3)	168.04(4)
Cl(1)–Pd(1)–Cl(2)	89.67(3)	91.03(4)

parent free ylides, indicating a much lower shielding of the carbon of the CO group in these complexes. Thus, the spectral data indicate the bidentate coordination of the ylides through both the phosphine group and the ylidic carbon atom.

3.3. X-ray crystallography

Complexes **1b** and **4b** were recrystallized by slow evaporation over several days from dimethylsulfoxide solutions. The molecular structures are shown in Figs. 1 and 2, respectively. Relevant parameters concerning data collection and refinement are given in Table 1 and selected bond distances and angles are collected in Table 2. Fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of the complexes are available as Supplementary material.

The X-ray analysis confirms unequivocally the P–C chelate mode of coordination of the ligands, $Ph_2P(CH_2)_nPPh_2C(H)$-$C(O)C_6H_4R$ to the Pd atom in complexes **1b** and **4b**. The Pd atom is surrounded by one P atom of the phosphine group, one ylidic carbon and two chlorine atoms leading to a slightly distorted square-planar geometry around the metal. The angles subtended by the ligand at the Pd(II) centre in **1b** vary from 88.25(8)° to 93.25(8)° (sum of the angles is 360.29) and 174.13(8)° to 176.74(3)° indicating the distortion from the square-planar environment, whereas in **4b** vary from 88.17(4)° to 94.52(11)° (sum of the angles is 362.43) and 168.04(4)° to 168.06(11)° indicating an even much distorted square-planar environment.

The two Pd–Cl distances in **1b** (2.389(8) and 2.357(8) Å) and in **4b** (2.4080(11) and 2.345(11) Å) are different, probably reflecting slightly different *trans* effect of the phosphorus and ylidic carbon atom. The Pd–C(ylide) bond lengths in these complexes (2.100(3) Å (**1b**) and 2.114(3) (**4b**) Å) are similar to that found in

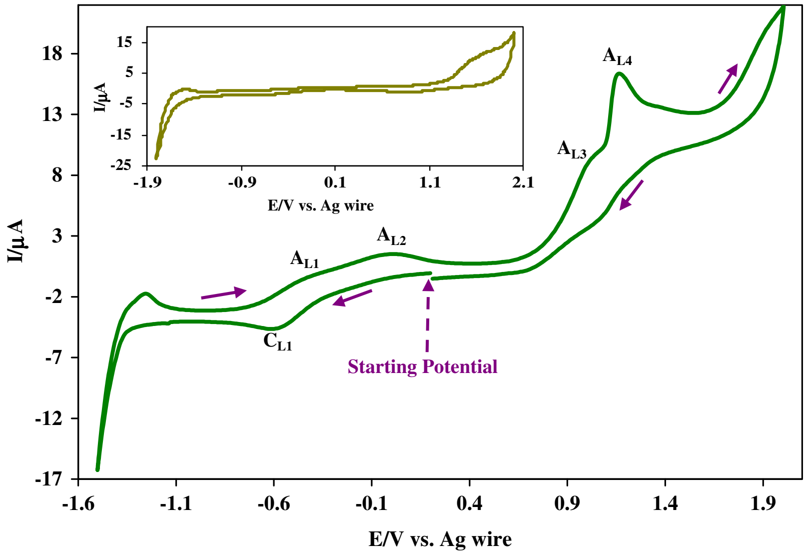


Fig. 3. Cyclic voltammogram of 1 mM of Y_1 in dichloromethane, containing 0.1 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte, at Pt electrode. Sweeping direction: reduction of Y_1 at the first stage and oxidation at the second stage. Scan rate: 100 mV s^{-1}; t = 25 °C. Vectors, show sweeping direction. Inset: cyclic voltammogram of background at the same conditions.

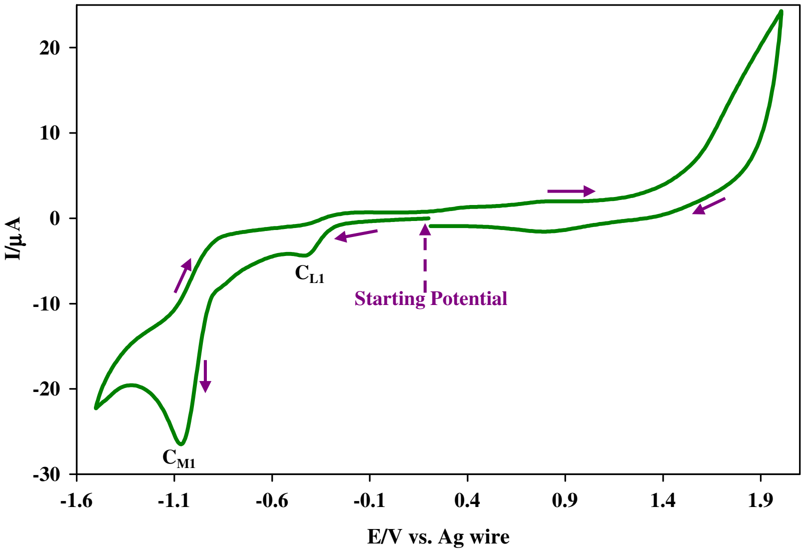


Fig. 4. Cyclic voltammogram of 1 mM of complex **2a** in dichloromethane, containing 0.1 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte, at Pt electrode. Sweeping direction: reduction of complex at the first stage and oxidation at the second stage. Scan rate: 100 mV s^{-1}; t = 25 °C.

[$PdCl_2\{PPh_2C(H)C(O)CH_2PPh_2C(H)\}$] (2.099(6) and 2.104(6) Å) [17]. The Pd(1)–P(2) bond lengths in **1b** [2.232(8) Å] and in **4b** [2.220(11) Å] are comparable to analogous distances in diphosphine palladium complexes such as [$PdCl_2$(dppe)] (dppe = 1,2-(diphenylphosphino)ethane)) [30], [$PdCl_2$ (dppb)] (dppb = 1,4-(diphenylphosphino)butane) [31].

The stabilized resonance structure for the parent ylide is destroyed by the complex formation, thus the C(1)–C(2) bond length in **1b** (1.478(8) Å) and **4b** (1.478(8) Å) are significantly longer than the corresponding distance found in the similar non-coordinated phosphoranes (1.404(3) Å [13] and 1.401(2) Å [32]). Likewise the C(2)–P(1) bond length in a similar ylide is 1.705(2) Å [13], which shows that the corresponding bond in **1b** and **4b** are considerably elongated to 1.790(3) Å and 1.784(4) Å, respectively.

3.4. Electrochemical studies

The electrochemical behavior of Y_1 and its Pd(II) complex, **2a**, was studied by cyclic voltammetry. Fig. 3 shows the cyclic voltammogram obtained for 1 mM Y_1 in dichloromethane, containing 0.2 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte recorded with a platinum electrode when reduction of Y_1 occurs at first stage. At this condition, voltammogram exhibit a reduction peak C_{L1} and four anodic peaks (A_{L1}, A_{L2}, A_{L3} and A_{L4}). In addition, another anodic peak observed at −1.24 V which also observed in cyclic voltammogram of background (dichloromethane/Bu_4NClO_4) (see Fig. 3).

The cyclic voltammogram of 1 mM solution of complex [$(Y_1)PdCl_2$], in the same condition, showed that the electron transfer was irreversible. At a scan rate of 100 mV/s, there was two cathodic peaks, C_{L1}, corresponding to the reduction of Y_1 and C_{M1} at −1.08 V versus Ag wire, corresponding to the redox pair Pd(II)/Pd(0). There is no anodic peak(s) observed on the reverse scan. This behavior is similar to that reported previously by Champness et al. [33], Batchelor et al. [34] and Downard et al. [35] in cyclic voltammetric study of various types of Pd(II)-complexes in aprotic solvents. This irreversibility may be due to the reaction of a Pd(0) complex with adventitious O_2 or other components of the solution [35].

Peak C_{M1} at −1.08 V versus Ag wire, can be assigned to the formation of a Pd(0) center with coordination number between 2 and 4 (or to an equilibrium mixture of several Pd(0) species) [35–37]. There are some examples of stable Pd(0) complexes; particularly relevant is $[Pd(L)_2]^0$ (L = 1,2-bis(dimethylarsino)benzene), which is adequately stable to be isolated as the solid [38]. These electrochemical data reconfirm complex formation between Pd(II) and Y_1 and showed the presence of Pd(II) in complex **2a**.

The overall two-electron reduction of the Pd(II) complexes is expected to take place in separate one-electron steps [33–35] and this might be achieved *via* manipulation of the thermodynamics or electrode kinetics of one or both steps by correct choice of the experimental conditions. In our experimental conditions, Pd(I)-complex is unstable with respect to disproportionate [35]. Thus peak C_{M1} in Fig. 4 corresponds to a two-electron reduction of Pd(II)-complex which is the consequence of the thermodynamic instability of the intermediate one electron product in our experimental conditions (Eq. (1)).

$$2Pd(I) \rightarrow Pd(II) + Pd(0) \tag{1}$$

4. Conclusion

The present study describes the very simple and efficient synthesis and characterization of a series of P–C chelate Pd(II) complexes. On the basis of the physicochemical and spectroscopic data we have proposed that ligands employed herein exhibit a chelate P–C coordination behavior to the metal center affording a five or six-membered chelate rings. This coordination fashion has been further confirmed by single crystal X-ray diffraction experiments of complexes **1b** and **4b**. Additionally, electrochemical results show the unstabilities of the Pd(I) and Pd(0) complexes which are largely affected by the nature of ligand, solvent-impurities, temperature and/or supporting electrolyte, whereas the divalent complex will be relatively stabilized under the experimental conditions employed.

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Appendix A. Supplementary material

CCDC 754889 and 753846 contains the supplementary crystallographic data for complexes **1b** and **4b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.072.

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