Polyhedron 30 (2011) 778–784

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Orthopalladation of phosphorus ylides in endo position with bidentate ligands

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ARTICLE INFO

Article history:
Received 21 October 2010
Accepted 10 December 2010
Available online 25 December 2010

Keywords:
Phosphorus ylides
Orthopalladation
Bidentate ligands

ABSTRACT

The ortho-metallated complexes $[Pd_2\{\kappa^2(C,C)\text{-}C_6H_4(PPh_2CHC(O)C_6H_5R\}_2(\mu\text{-}Cl)_2]$ (R = Ph (**1a**), NO_2 (**1b**), Br (**1c**)) were prepared by refluxing equimolar mixtures of $Ph_3P{=}CHC(O)C_6H_5R$, (R = Ph, NO_2, Br) and $Pd(OAc)_2$ in MeOH, followed by an excess of NaCl. The dinuclear complexes (**1a–1c**) react with silver trifluoromethylsulfonate and bidentate ligands [L = bipy (2,2′-bipyridine), phen (phenanthroline), dppe (bis(diphenylphosphino)ethane), dppp (bis(diphenylphosphino)propane)] giving the mononuclear stabilized orthopalladated complexes in *endo* position $[Pd\{\kappa^2(C,C)\text{-}C_6H_4(PPh_2CHC(O)R\}L](OTf)$ [R = Ph, L = phen (**2a**), bipy (**3a**), dppe (**4a**), dppp (**5a**); R = NO_2, L = phen (**2b**), bipy (**3b**), dppe (**4b**), dppp (**5b**); R = Br, L = phen (**2c**), bipy (**3c**), dppe (**4c**), dppp (**5c**); OTf = trifluoromethylsulfonate anion]. Orthometalation and ylidic C-coordination are demonstrated by an X-ray diffraction study of **2c** and **3c**. In the structures, the palladium atom shows a slightly distorted square-planar coordination geometry.

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1. Introduction

Phosphorus ylides have found use in a wide variety of reactions of interest, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity [1]. Metal mediated C–H bond activation is a conspicuous challenge in organic synthesis. The activation may occur either by forming the M–C bond (intermolecular or intramolecular) or *via* the functionalisation of the C–H group nearest to the metal center of the complex [2–30]. The orthometalation of phosphorus ylides [31–39] is produced, in the vast majority of cases, regioselectively at the Ph rings of the phosphine unit. Some recent contributions have shown, however, that it is possible to obtain orthopalladated complexes derived from CH activation at Ph rings belonging to R or R′ substituents of the ylidic carbon and, more precisely, belonging to benzamide moieties [40]. With the above in mind, and as a continuation of our current research study on phosphorus ylides [41,42], herein we report the synthesis, spectroscopic and structural characterization of orthopalladated complexes with bidentate ligands such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)propane (dppp).

2. Experimental

2.1. Physical measurements and materials

Melting points were measured on a Gallenhamp 9B 3707 F apparatus. Infrared spectra (4000–400 cm^{-1}) were recorded on a Jasco 680 FT-IR. ^1H NMR and $^{31}P\text{–}\{^1H\}$ NMR spectra were recorded on $CDCl_3$ at room temperature on a 500 MHz Bruker spectrometer. Chemical shifts (δ) are reported relative to internal TMS and external 85% phosphoric acid. Elemental analyses were carried out on a PE 2400 series II analyzer. $Pd(OAc)_2$, 1-([1,1′-biphenyl]-4-yl)-2-bromoethanone, 2-bromo-1-(4′-bromo-[1,1′-biphenyl]-4-yl)ethanone, 2-bromo-1-(4′-nitro-[1,1′-biphenyl]-4-yl)ethanone, 2,2′-bipyridine, 1,10-phenanthroline, bis(diphenylphosphino)ethane, bis(diphenylphosphino)propane, PPh_3 and AgOTf were purchased from Merck. THF was dried using magnesium sulfate powder just before use. All other solvents were used without further purification.

2.2. Synthesis

2.2.1. Preparation of PhBPPY (*a*)

To a solution of 1-([1,1′-biphenyl]-4-yl)-2-bromoethanone (825 mg, 3 mmol) in $CHCl_3$ (20 ml), a solution of PPh_3 (786 mg, 3 mmol) in $CHCl_3$ (5 ml) was added dropwise. After stirring at room temperature for 4 h, the solution was evaporated to dryness. The residue was reacted with NaOH (2 g, 0.5 mmol) in $EtOH/H_2O$

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0277-5387/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.poly.2010.12.014

(1:1 v/v, 20 ml), giving **a** as a yellow solid. Yield: 887 mg (65%). M.p. 230–231 °C. IR (KBr disk, cm^{-1}): ν 1507, ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 4.52 (d, 1H, CHP, $^2J_{HH}$ = 24 Hz), 7.38 (t, 1H, H_p, C_6H_5, $^3J_{HH}$ = 7 Hz), 7.48 (t, 2H, H_m, C_6H_5, $^3J_{HH}$ = 11 Hz), 7.47 (t, 2H, H_m, C_6H_4), 7.53 (m, 6H, H_m, PPh_3), 7.60 (m, 2H, H_o, C_6H_5, $^3J_{HH}$ = 6 Hz), 7.65 (t, 3H, H_p, PPh_3, $^3J_{HH}$ = 6 Hz), 7.84 (m, 6H, H_o, PPh_3), 8.08 (d, 2H, H_o, C_6H_4). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 17.2 (s, 1P, CHP).

*2.2.2. Preparation of [Pd(μ-Cl)(PhBPPY)]$_2$ (**1a**)*

A mixture of $Pd(OAc)_2$ (116 mg, 0.52 mmol) in CH_2Cl_2 (15 ml) and phosphorus ylide **a** (237 mg, 0.52 mmol) was refluxed for 24 h at 60 °C. Some decomposition (presence of black Pd) was evident. The mixture then was evaporated to dryness and the solid dissolved in MeOH and treated with an excess of NaCl (111 mg, 1.90 mmol). A yellow solid immediately precipitated. The stirring was maintained for 12 h at room temperature, then the solution was filtered, and the precipitate washed with Et_2O (5 ml) and water (10 ml) and dried in vacuum. Yield: 324 mg (52%). M.p. 298 °C. Anal. Calc. for $C_{64}H_{48}O_2Cl_2P_2Pd_2$. C, 64.34; H, 4.05; Found. C, 63.13; H, 3.81. IR (KBr, cm^{-1}): ν 1623, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.90 (s, CHP, minor), 4.97 (s, CHP, major), 7.12–8.12 (m, $4C_6H_5 + C_6H_4CO$, both isomers). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 18.41 (sbr both isomers).

*2.2.3. Preparation of [Pd(L)(PhBPPy)](OTf) with L = phen (**2a**), bipy (**3a**), dppe (**4a**) or (dppp) (**5a**)*

Compound **1a** (75 mg, 0.063 mmol for **2a**, **4a** and **5a**; 49 mg, 0.0407 mmol for **3a**) was dissolved in THF (20 mL) and treated with AgOTf (32 mg, 0.126 mol for **2a**, **4a** and **5a**; 21 mg, 0.082 mmol for **3a**). The resulting mixture was stirred for 30 min at room temperature and then filtered over $MgSO_4$. Afterwards an equimolar amount of the corresponding ligand L was added and the solution was stirred for four additional hours, and then the solvent was evaporated to dryness and the residue treated with Et_2O (5 ml) to give **2a** as a pale yellow solid or **3a**, **4a** and **5a** as white solids. Yields: 75 mg (73%) for **2a**, 39 mg (68%) for **3a**, 79 mg (66%) for **4a** or 71 mg (58%) for **5a**.

Complex **2a**. M.p. 190–194 °C (dec). IR (KBr, cm^{-1}): ν 1632, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 5.56 (s, 1H, CHP), 7.29–7.43 (m, 4H, C_6H_4), 7.41–7.89 (m, 15H, $PPh_2 + C_6H_5$), 7.77–7.79 (m, 2H, phen), 8.10–8.17 (m, 2H, C_6H_4CO), 8.17–8.18 (d, 2H, C_6H_4CO, $^3J_{HH}$ = 8 Hz), 8.23–8.24 (d, 1H, phen, $^3J_{HH}$ = 8 Hz), 8.53–8.54 (d, 1H, phen, $^3J_{HH}$ = 8 Hz), 8.89–8.90 (m, 2H, phen), 8.99–9.00 (d, 1H, phen, $^3J_{HH}$ = 5 Hz), 9.20 (sbr, 1H, phen).^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 22.28 (s, 1P, CHP).

Complex **3a**. M.p. 152–160 °C (dec). IR (KBr, cm^{-1}): ν 1633, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 5.20 (s, 1H, CHP), 7.25–7.40 (m, 4H, C_6H_4), 7.45 (t, 2H, H_o, bipy), 7.51–7.56 (m, 6H, H_m, $PPh_2 + H_m$, C_6H_5), 7.58–7.65 (m, 7H, H_p, bipy + H_p, $PPh_2 + H_p$, H_o, C_6H_5), 7.91–8.02 (m, 5H, H_o, $PPh_2 + C_6H_4CO$), 8.09 (d, 2H, C_6H_4CO, $^3J_{HH}$ = 8 Hz), 8.18 (d, 1H, H_o, PPh_2, $^3J_{HH}$ = 8 Hz), 8.31–8.32 (d, 1H, H_o, bipy, $^3J_{HH}$ = 8 Hz), 8.41–8.43 (d, 1H, H_o, bipy, $^3J_{HH}$ = 8 Hz), 8.57 (m, 1H, H_m, bipy). 8.60–8.61 (d, 1H, H_m, bipy, $^3J_{HH}$ = 6 Hz).^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 21.70 (s, 1P, CHP).

Complex **4a**. M.p. 218–222 °C (dec). IR (KBr, cm^{-1}): ν 1630, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 2.70 (m, 4H, CH_2, dppe), 4.99 (s, 1H, CHP), 7.01 (m, 4H, C_6H_4), 7.16 (m, 4H, Hm, PPh_2), 7.28 (m, 10H, H_m, dppe + H_p, PPh_2), 7.38 (m, 16H, H_o, $PPh_2 + H_o$, H_p, dppe), 7.55 (m, 5H, C_6H_5), 7.68 (m, 4H, C_6H_4CO). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 24.93 (s, 1P, CHP), 43.74 (s, 1P, PPh_2 trans CH), 53.32 (s, 1P, PPh_2 cis CH).

Complex **5a**. M.p. 214–217 °C (dec). IR (KBr, cm^{-1}): ν 1613, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 2.25 (m, 2H, CH_2, dppp), 2.45 (m, 4H, CH_2, dppp), 4.54 (t, 1H, CHP, $^2J_{PH}$ = 7 Hz), 6.67 (t, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 6.79 (t, 1H, C_6H_4, $^3J_{HH}$ = 7 Hz), 6.96 (m, 1H, C_6H_4), 7.05–7.31 (m, 14H, H_m, C_6H_5), 7.30–7.42 (m, 7H, H_p, C_6H_5), 7.43–7.52 (m, 10H, H_o, PPh_2, dppp + H_o, $PPh_2 + H_o$, C_6H_5), 7.60–8.13 (m, 4H, C_6H_4CO), 7.69 (dd, 2H, H_o, PPh_2, dppp, $^3J_{HH}$ = 8 Hz), 7.81 (t, 2H, H_o, PPh_2, dppp, $^3J_{HH}$ = 7 Hz). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = −2.14 (s, 1P, PPh_2 trans CH), 14.47 (s, 1P, PPh_2cis CH), 25.68 (s, 1P, CHP).

*2.2.4. Preparation of NO_2BPPY (**b**)*

To a solution of 2-bromo-1-(4′-nitro-[1,1′-biphenyl]-4-yl)ethanone (732 mg, 3 mmol) in $CHCl_3$ (20 ml), a solution of PPh_3 (786 mg, 3 mmol) in $CHCl_3$ (5 ml) was added dropwise. The mixture was stirred at room temperature for 4 h, then it was evaporated to dryness. The residue was reacted with NaOH (2 g, 0.5 mmol) in MeOH/H_2O (1:1 v/v, 20 ml), giving **b** as a yellow solid. Yield: 921 mg (72%). M.p. 153 °C. IR (KBr disk, cm^{-1}): ν 1521, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.53 (d, 1H, CHP, $^2J_{PH}$ = 23 Hz), 7.02 (m, 2H, C_6H_4CO), 7.52–7.59 (m, 6H, H_m, $3C_6H_5$), 7.61–7.69 (m, 3H, H_p, $3C_6H_5$), 7.72–7.76 (m, 6H, H_o, $3C_6H_5$), 8.10–8.23 (dd, 2H, C_6H_4CO, $^3J_{PH}$ = 9 Hz), ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 17.20 (s, 1P, CHP).

*2.2.5. Preparation of [Pd(μ-Cl)(NO_2BPPY)]$_2$ (**1b**)*

A mixture of $Pd(OAc)_2$ (104 mg, 0.46 mmol) in CH_2Cl_2 (15 ml) and phosphorus ylide **b** (195.5 mg, 0.46 mmol) was refluxed for 24 h at 60 °C. Some decomposition was evident. The mixture was then evaporated to dryness and the brown solid obtained was dissolved in MeOH (15 ml), treated with an excess of NaCl (108 mg, 1.84 mmol) and the solution further stirred for 12 h. A green solid precipitated which was filtered, washed with water (10 ml) and Et_2O (5 ml) and dried in vacuum. Yield: 400 mg (77%). M.p 199–205 °C (dec). IR (KBr, cm^{-1}): ν 1635, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.83 (s, CHP, minor), 4.95 (s, CHP, major), 7.24–8.15 (m, $C_6H_5 + C_6H_4CO + C_6H_4$, both isomers). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 19.86 (sbr both isomers).

*2.2.6. Preparation of [Pd(L)(NO_2BPPY)](OTf) with L = phen (**2b**), bipy (**3b**), dppe (**4b**) or (dppp) (**5b**)*

A solution of compound **1b** (100 mg, 0.088 mmol for **2b**; 20 mg, 0.017 mmol for **3b**; 60 mg, 0.053 mmol for **4b**; 80 mg, 0.071 mmol for **5b**) in THF (20 ml) was treated with AgOTf (45 mg, 0.176 mmol for **2b**; 9 mg, 0.035 mmol for **3b**; 27 mg, 0.105 mmol for **4b**; 36 mg, 0.140 mmol for **5b**). The resulting mixture was stirred for 30 min at room temperature and then filtered over $MgSO_4$. An equimolar amount of the corresponding ligand L was then added, the solution was stirred for four additional hours, the solvent was evaporated to dryness and the residue treated with Et_2O (5 ml for **2b**, **4b** and **5b**) or CH_2Cl_2/*n*-hexane mixture (1:5 v/v, 15 ml for **3b**) to give a pale yellow, pale orange, white or brown solid for **2b**, **3b**, **4b** or **5b** respectively. Yields: 107 mg (78%) for **2b**, 16 mg (68%) for **3b**, 340 mg (80%) for **4b** or 280 mg (84%) for **5b**.

Complex **2b**. M.p. 154–162 °C (dec). IR (KBr, cm^{-1}): ν 1632, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 5.79 (s, 1H, CHP), 7.42–7.56 (m, 4H, C_6H_4), 7.59–7.88 (m, 10H, PPh_2), 7.84–7.97 (m, 2H, phen), 8.12 (d, 2H, C_6H_4CO, $^3J_{HH}$ = 9 Hz), 8.23 (d, 2H, C_6H_4CO, $^3J_{HH}$ = 9 Hz), 8.29 (d, 2H, phen, $^3J_{HH}$ = 8 Hz), 8.57 (d, 2H, phen, $^3J_{HH}$ = 8 Hz), 9.01 (d, 1H, phen, $^3J_{HH}$ = 5 Hz), 9.45 (sbr, 1H, phen). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 22.47 (s, 1P, CHP).

Complex **3b**. M.p. 196–202 °C (dec). IR (KBr, cm^{-1}): ν 1628, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 5.51 (s, 1H, CHP), 7.42–7.47 (m, 3H, H_m, bipy + C_6H_4), 7.52–8.17 (m, 10H, PPh_2), 7.58–7.65 (m, 5H, H_p, bipy + C_6H_4), 8.10 (m, 2H, H_m, bipy), 8.29–8.31 (d, 2H, H_m, C_6H_4CO, $^3J_{HH}$ = 8 Hz), 8.61–8.62 (d, 1H, H_o, bipy, $^3J_{HH}$ = 5 Hz), 8.69–8.70 (d, 2H, H_o, C_6H_4CO, $^3J_{HH}$ = 4 Hz), 9.01 (sbr, 1H, H_o, bipy).

Complex **4b**. Mp. 152–158 °C (dec). IR (KBr, cm^{-1}): ν 1633, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 1.88 (m, 2H, CH_2, dppe), 2.31 (m, 2H, CH_2, dppe), 4.97 (s, 1H, CHP), 6.93 (m, 2H, C_6H_4), 6.98

(m, 2H, C_6H_4), 7.05–7.26 (m, 2H, H_m, dppe), 7.12–7.43 (m, 22H, PPh_2 + H_m, H_p, H_o, dppe), 7.52 (m, 4H, H_o, dppe), 7.76–7.84 (dd, 4H, C_6H_4CO, $^3J_{HH}$ = 9 Hz), 7.64 (m, 2H, H_p, dppe). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 24.67 (s, 1P, CHP), 43.21 (s, 1P, PPh_2 trans CH), 54.87 (s, 1P, PPh_2 cis CH).

Complex **5b**. M.p. 112–119 °C (dec). IR (KBr, cm^{-1}): ν 1627, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 1.88 (sbr, 1H, CH_2, dppp), 2.27 (t, 1H, CH_2, dppp, $^3J_{PH}$ = 13 Hz), 2.38 (dt, 1H, CH_2, dppp, $^3J_{PH}$ = 5 Hz), 2.56 (sbr, 2H, CH_2, dppp), 3.77 (t, 1H, CH_2, dppp, $^3J_{PH}$ = 6 Hz), 4.52 (t, 1H, CHP, $^3J_{PH}$ = 6 Hz), 6.67 (t, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 6.81 (t, 1H, C_6H_4, $^3J_{HH}$ = 7 Hz), 6.97 (m, 1H, C_6H_4), 7.05 (m, 1H, H_p, dppp), 7.12 (m, 2H, H_m, dppp), 7.15 (m, 4H, H_m, PPh_2), 7.26 (m, 2H, H_p, PPh_2), 7.31 (m, 2H, H_m, dppp), 7.39 (m, 4H, H_m, dppp), 7.44 (m, 3H, H_p, dppp), 7.55-7.78 (m, 8H, H_o, dppp), 7.60–7.69 (m, 1H, C_6H_4CO), 7.78–8.05 (m, 4H, H_o, PPh_2), 7.89 (d, 2H, C_6H_4CO, $^3J_{HH}$ = 9 Hz), 8.12 (t, 1H, C_6H_4CO, $^3J_{HH}$ = 7 Hz).^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = −2.61 (s, 1P, PPh_2 trans CH), 14.81 (s, 1P, PPh_2 cis CH), 25.38 (s, 1P, CHP).

2.2.7. Preparation of BrBPPY (**c**)

To a solution of 2-bromo-1-(4′-bromo-[1,1′-biphenyl]-4-yl)ethanone (834 mg, 3 mmol) in $CHCl_3$ (20 ml), a solution of PPh_3 (786 mg, 3 mmol) in $CHCl_3$ (5 ml) was added dropwise. The mixture was stirred at room temperature for 4 h, then it was evaporated to dryness. The residue was reacted with NaOH (2 g, 0.5 mmol) in MeOH/H_2O (1:1 v/v, 20 ml), giving **c** as a white solid. Yield: 556 mg (67%). M.p. 183 °C, IR (KBr, cm^{-1}): ν 1519, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.37 (d, CHP, $^2J_{PH}$ = 24 Hz), 7.02 (m, 2H, C_6H_4CO), 7.50 (m, 6H, H_m, $3C_6H_5$), 7.59 (m, 3H, H_p, $3C_6H_5$), 7.73 (m, 6H, H_o, $3C_6H_5$), 7.96 (m, 2H, C_6H_4CO). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 16.02.

2.2.8. Preparation of [Pd(μ-Cl)(BrBPPY)]$_2$ (**1c**)

To a solution of $Pd(OAc)_2$ (85 mg, 0.38 mmol) in CH_2Cl_2 (15 ml) phosphorus ylide **c** (176 mg, 0.38 mmol) was added, and the mixture refluxed for 24 h at 60 °C. Some decomposition (presence of black Pd) was evident. After evaporating the mixture to dryness, the solid residue was dissolved in MeOH, treated with an excess of NaCl (44 mg, 0.76 mmol) and further stirred for 12 h. A pale green solid immediately precipitated which was filtered, washed with Et_2O (5 ml) and water (10 ml) and dried in vacuum. Yield: 300 mg (66%). M.p. 258–260 °C (dec), Anal. Calc. for $C_{64}H_{48}O_2Cl_2P_2Pd_2$, C, 64.34; H, 4.05; Found: C, 63.13; H, 3.81; IR (KBr, cm^{-1}): ν 1623, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.90 (s, CHP, minor): 4.97 (s, CHP, major), 7.12–8.12 (m, $4C_6H_5$ + C_6H_4CO, both isomers). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 18.41 (sbr both isomers).

2.2.9. Preparation of [Pd(L)(BrBPPY)](OTf) with L = phen (**2c**), bipy (**3c**), dppe (**4c**) or (dppp) (**5c**)

A solution of compound **1c** (54 mg, 0.045 mmol for **2c** and **3c**; 25 mg, 0.021 mmol for **4c**; 37 mg, 0.031 mmol for **5c**) in THF (20 ml) was treated with AgOTf (23 mg, 0.090 mmol for **2c** and **3c**; 11 mg, 0.042 mmol for **4c**; 16 mg, 0.062 mmol for **5c**). The resulting mixture was stirred for 30 min at room temperature and then filtered over $MgSO_4$. An equimolar amount of the corresponding ligand L was then added, the solution was stirred for four additional hours, the solvent was evaporated to dryness and the residue treated with Et_2O (20 ml) to give a white solid for **2c**, **4c** and **5c** or a yellow solid for **3c**. Yields: 58 mg (79%) for **2c**, 52 mg (81%) for **3c**, 18 mg (45%) for **4c** or 44 mg (79%) for **5c**.

Complex **2c**. M.p. 172–176 °C (dec). IR (KBr, cm^{-1}): ν 1636, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 5.62 (s, 1H, CHP), 7.44–7.52 (m, 6H, H_m, PPh_2 + C_6H_4), 7.53–7.61 (m, 8H, H_p, H_o, PPh_2), 7.58–8.31 (dd, 2H, C_6H_4CO, $^3J_{HH}$ = 2 Hz), 7.87–8.01 (m, 8H, phen), 9.23 (dd, 2H, C_6H_4CO, $^3J_{HH}$ = 2 Hz). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 21.19 (s, 1P, CHP).

Complex **3c**. M.p. 138–140 °C, IR (KBr, cm^{-1}): ν 1637, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.95 (s, 1H, CHP), 7.18–7.78 (m, 14H, PPh_2 + C_6H_4), 7.29–7.31 (m, 2H, H_m, bipy), 7.47–7.49 (d, 2H, H_m, C_6H_4CO, $^3J_{HH}$ = 7 Hz), 7.69–7.71 (d, 2H, H_o, C_6H_4CO, $^3J_{HH}$ = 8 Hz) 7.83–8.04 (m, 2H, H_p, bipy), 8.01–8.20 (m, 2H, H_m, bipy), 8.38–8.44 (m, 2H, H_o, bipy). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 21.19 (s, 1P, CHP).

Complex **4c**. M.p. 234–236 °C (dec), Anal. Calc. for $C_{59}H_{48}F_3O_4P_3PdS$, C, 63.87; H, 4.36; Found, IR (KBr, cm^{-1}): ν 1625, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 1.88 (m, 2H, CH_2, dppe), 3.76 (m, 2H, CH_2, dppe), 4.95 (s, 1P, CHP), 6.98–7.09 (m, 4H, C_6H_4), 7.04–7.09 (m, 2H, H_m, PPh_2), 7.15–7.17 (m, 2H, H_m, PPh_2), 7.17–7.25 (m, 5H, H_m, PPh_2, dppe), 7.35–7.37 (m, 3H, H_m, PPh_2, dppe), 7.37–7.51 (m, 6H, H_p, C_6H_5), 7.51–7.61 (m, 12H, H_o, C_6H_5), 7.65–7.74 (m, 4H, C_6H_4CO). ^{31}P–{1H} NMR ($CDCl_3$, ppm): δ = 24.55 (s, 1P, CHP), 43.94 (s, 1P, PPh_2 trans CH), 53.92 (s, 1P, PPh_2 cis CH).

Complex **5c**. M.p. 222–224 °C (dec), Anal. Calc. for $C_{60}H_{50}F_3O_4P_3PdS$, C, 64.15; H, 4.49; Found, C, 64.01; H, 4.32, IR (KBr, cm^{-1}): ν 1623, ^1H NMR (500 MHz, ppm, $CDCl_3$): δ = 2.20–2.70 (m, 6H, CH_2, dppp), 4.43 (t, 1H, CHP, $^2J_{PH}$ = 7 Hz), 6.64–6.98 (m, 4H, C_6H_4), 7.02–7.22 (m, 4H, H_p, dppp), 7.07–7.20 (m, 8H, H_m, dppp), 7.37–7.67 (m, 10H, PPh_2), 7.37–8.01 (m, 9H, H_o, dppp + C_6H_4CO), 7.67 (m, 2H, C_6H_4CO), 8.09 (m, 1H, C_6H_4CO). ^{31}P–{1H} NMR ($CDCl_3$): δ = −2.48 (s, 1P, PPh_2 trans CH), 14.47 (s, 1P, PPh_2 cis CH), 25.57 (s, 1P, CHP).

2.3. X-ray crystallography

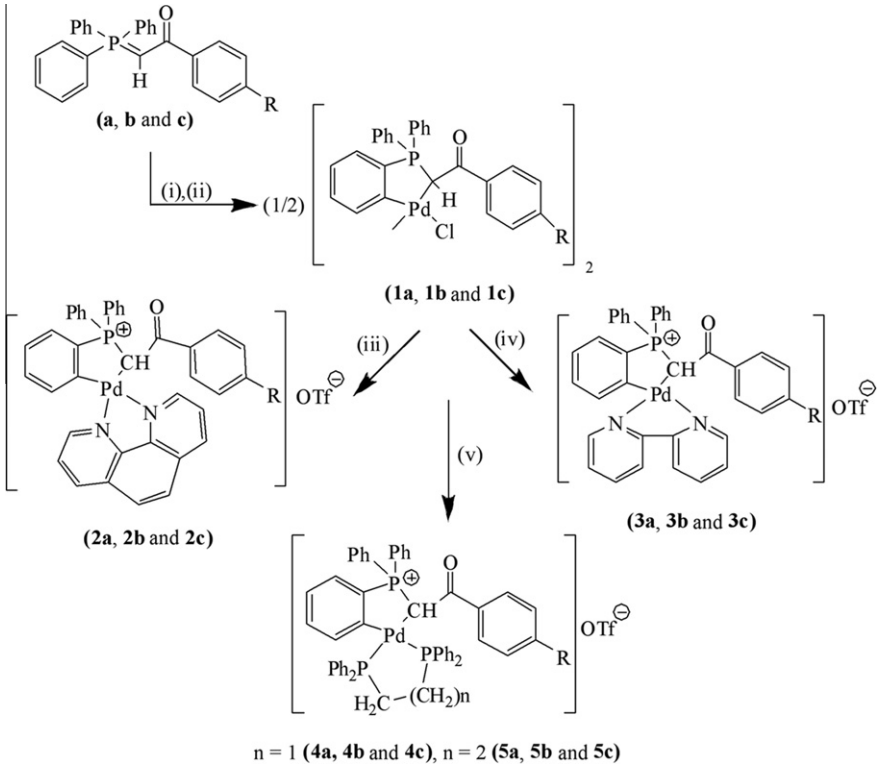
Single crystals of **2c** and **3c** suitable for X-ray crystallography were obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution of each complex. Intensity data were collected at ambient temperature (294(2) K) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker APEX-II CCD diffractometer for **2c** and on a Bruker SMART 1000 CCD diffractometer for **3c**. Data were corrected for absorption using the SABABS program [43].

In both complexes the triflate anion was found to be disordered over two positions (called A and B), with site occupancy factors of 0.6/0.4 in **2c** and 0.75/0.25 in **3c**. During the refinement, the S–O, O···O, C–F and F···F distances were constrained to 1.44(1), 2.42(2), 1.32(1) and 2.15(2) Å, respectively. The O, F and C atoms of the minor component of the disorder were refined isotropically. Moreover, in **3c** the S1A and F1A atoms were refined by restraining the anisotropic displacement parameters to be approximately isotropic. The dichloromethane solvent molecule in **3c** showed rather

Table 1
Relevant NMR data (δ, ppm) for phosphorus ylides **a**–**c** and complexes **2a**–**5c**.

Compound	δ(CH)	δ(P)	Δ[a]
a	4.52	17.20	
2a	5.56	22.28	
3a	5.20	21.70	
4a	4.99	24.93/43.74/53.32	56.16/65.74
5a	4.54	−2.14/14.47/25.68	15.03/31.64
b	4.50	17.27	
2b	5.79	22.47	
3b	5.51	22.11	
4b	4.97	24.67/43.21/54.87	55.6/67.3
5b	4.52	−2.61/14.81/25.38	14.6/32
c	4.37	16.02	
2c	5.62	22.43	
3c	4.96	21.19	
4c	4.95	24.55/43.94/53.92	56.4/66.3
5c	4.43	−2.48/14.48/25.57	14.7/31.6

[a] Δ = δ(coordinate) − δ(free). Values for ^{31}P chemical shifts of the free ligands dppe and dppp are δ = −12.42 and −17.17 ppm, respectively.



Scheme 1. R = Ph (**a**), NO_2 (**b**), Br (**c**); (i) $Pd(OAc)_2/CH_2Cl_2/\Delta$; (ii) NaCl/MeOH/reflux 24 h; (iii) AgOTf/THF/phen; (iv) AgOTf/THF/bipy; (v) AgOTf/THF/dppe and AgOTf/THF/dppp.

high thermal parameters, and its site occupancy factor was allowed to vary freely, converging to 0.705(5) [fixed at 0.70 in the last refinement cycles]. The C–Cl bond lengths were constrained to be 1.75(1) Å.

All H atoms were placed in calculated positions and treated as riding on their parent atoms, with C–H = 0.93–0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

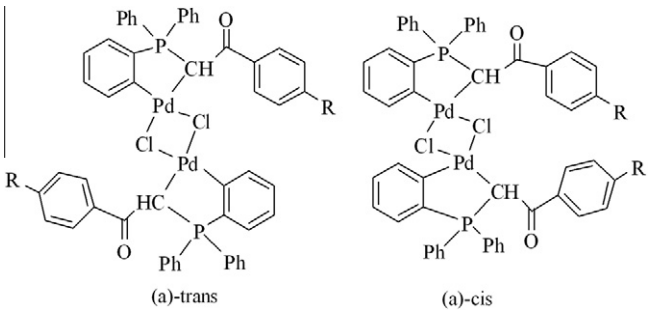
3. Results and discussion

3.1. Spectroscopy

The ν(CO) band which is sensitive to complexation occurs from 1505 to 1515 cm^{-1} in the parent ylides **a**–**c**. Coordination of ylide through the carbon atom causes an increase in the ν(CO) band, whereas for O-coordination a lowering of the ν(CO) band is expected [40]. The IR spectra of all complexes show a strong absorption in the range of 1620–1630 cm^{-1}, which has been shifted to higher frequency with respect to the parent ylides, meaning that the ylides are C-bonded to the palladium center and C-coordination has occurred. The ν(P–C) band frequencies which are also diagnostic of the coordination, occur at 881, 860 and 883 cm^{-1} in the parent ylides **a**, **b** and **c** respectively, and are shifted to lower frequencies for the complexes, suggesting some removal of the electron density of the P–C bands. The IR spectra of all complexes show significant absorptions at 1268 (vs), 1148 (s), 1032 (s), and 638 (s) cm^{-1} according to the presence of uncoordinated $CF_3SO_3^-$.

The ^{1}H NMR signals for the PCH group of complexes **2a**–**5c** are shifted downfield compared to that of the free ylide (Table 1), as a consequence of the inductive effect of the metal center. In the ^{1}H NMR spectra of **1a**, **1b** and **1c** signals due to the methinic proton are broad (minor) or broad doublet (major). The presence of two chiral carbon centers (forming diastereoisomers) in each of *cis* or *trans* complex **1**–**3** (Scheme 2) was confirmed using the ^{1}H NMR spectra as broad signals with unequal populations for the PdCH groups.

The ^{31}P–{1H} NMR spectra of **2a–2c** and **3a–3c** show one singlet at about 22 ppm (Table 1) which is attributed to the CHP of ylide. The ^{31}P–{1H} NMR spectra of **4a–4c** and **5a–5c** also show three different signals, corresponding to the three P atoms of the molecules, one due to the ylide, which shows the presence of the endo-metalated ligand and the other two to the bidentate diphosphine ligands dppe and dppp. The ^{31}P NMR spectra of the bidentate diphosphine have one signal, while the ^{31}P NMR spectra of Pd(II) complexes with a bidentate diphosphine show two signal due to different trans effect of arylic and ylidic carbons. It should be worth noting that in $CDCl_3$ solution the coupling constant between the phosphorus atoms of the chelate bidentate phosphine ligands is not observed in the ^{31}P NMR spectra of compounds **4a**–**4c** and **5a**–**5c**, possibly due to a fast equilibrium of the type $[Pd(\kappa^2\text{-C,C-ylide})(OTf)(\kappa^1\text{-P,P})] \leftrightarrow [Pd(\kappa^2\text{-C,C-ylide})(\kappa^2\text{-P,P}]^+OTf^-$. When the saturated 5-membered chelate ligand dppe coordinates to Pd(II) ion in orthopalladated complexes **4a**, **4b** and **4c**, the coordination



Scheme 2. R = Ph (**1a**), NO_2 (**1b**), Br (**1c**).

Table 2
Crystal data and structure refinement details for complexes **2c** and **3c**.

	2c	**3c**
Empirical formula	$C_{38}H_{27}BrN_2OPPd^+.CF_3O_3S^-.CH_2Cl_2$	$C_{36}H_{27}BrN_2OPPd^+.CF_3O_3S^-.0.7CH_2Cl_2$
Formula weight	978.89	929.39
Temperature (K)	294(2)	294(2)
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a(Å)	11.4606(4)	10.6026(17)
b(Å)	12.3861(4)	21.889(4)
c(Å)	15.6115(5)	17.254(3)
α(°)	91.6834(5)	90.00
β(°)	99.0562(6)	100.487(3)
γ(°)	111.8959(6)	90.00
V(Å^3)	2021.19(12)	3937.4(12)
Z	2	4
D_{cal} (Mg/m^3)	1.608	1.568
μ (mm^{-1})	1.728	1.730
Crystal size (mm^3)	0.22×0.14×0.12	0.12×0.08×0.07
No. of reflections collected	22649	38967
No. of independent reflections	7313	7135
No. of data/restraints/parameters	7313/39/533	7135/43/501
Goodness of fit on F2	1.031	0.999
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0432	R_1 = 0.0477
	wR_2 = 0.1209	wR_2 = 0.1097
R indices (all data)	R_1 = 0.0506	R_1 = 0.0983
	wR_2 = 0.1250	wR_2 = 0.1182

chemical shifts, $\Delta = \delta(\text{coordinate}) - \delta(\text{free})$, are about 56 and 66 ppm for ligand dppe, whereas the values for the saturated 6-membered chelate ligand dppp in complexes **5a**, **5b** and **5c** are about 14 and 31 ppm, much smaller than those for ligand dppe (Table 1). Thus, chemical shift ^{31}P–{1H} NMR study on all palladium complexes **2a**–**5c** for the CHP group illustrates clear shifts to downfield as compared to those in the parent ylides **a**, **b** and **c**.

The splitting of the chloride bridges in complexes **1a**, **1b** and **1c** with neutral bidentate ligands produced exclusively the corresponding mononuclear compounds **2a**–**2c**, **3a**–**3c**, **4a**–**4c**, and **5a**–**5c** (Scheme 1). The ^{1}H NMR spectra show the expected resonances for all of the groups present in these molecules and do not show any unusual features.

Table 3
Selected bond distances (Å) and angles (deg) and hydrogen bonding geometry (Å, °) for compounds **2c** and **3c**[a].

2c			**3c**	
Pd1–N1	2.137(3)		Pd1–N1	2.132(4)
Pd1–N2	2.094(3)		Pd1–N2	2.100(4)
Pd1–C1	2.115(3)		Pd1–C1	2.117(5)
Pd1–C9	1.991(3)		Pd1–C9	2.017(5)
P1–C1	1.794(3)		P1–C1	1.766(5)
P1–C14	1.774(3)		P1–C14	1.770(5)
P1–C15	1.811(3)		P1–C15	1.822(5)
P1–C21	1.809(3)		P1–C21	1.809(5)
N1–Pd1–N2	78.50(11)		N1–Pd1–N2	78.18(17)
N1–Pd1–C1	99.01(11)		N1–Pd1–C1	99.10(18)
N1–Pd1–C9	172.88(12)		N1–Pd1–C9	174.03(19)
N2–Pd1–C1	175.86(11)		N2–Pd1–C1	174.19(17)
N2–Pd1–C9	97.00(12)		N2–Pd1–C9	98.33(18)
C9–Pd1–C1	85.79(12)		C9–Pd1–C1	84.8(2)
2c				
D–H···A	D–H	H···A	D···A	D–H···A
C26–H26···O1	0.93	2.40	2.992(4)	122
C36–H36···O3A	0.93	2.44	3.136(10)	131
C4–H4···O1^{i}	0.93	2.51	3.331(13)	147
C20–H20···O2A^{ii}	0.93	2.46	3.186(6)	135
C27–H27···O2A^{ii}	0.93	2.52	3.321(10)	144
C29–H29···O4A^{iii}	0.93	2.48	3.254(9)	141
C40–H40A···O1^{iv}	0.97	2.50	3.435(7)	161
3c				
D–H···A	D–H	H···A	D···A	D–H···A
C8–H8···O4	0.93	2.52	3.447(8)	179
C22–H22···O4	0.93	2.51	3.410(9)	163
C38–H38B···O1	0.97	2.44	3.402(13)	170
C35–H35···F2A^{v}	0.93	2.52	3.395(16)	157

[a] Symmetry codes: (i) $-x$, $-y$, $2-z$; (ii) $-1+x$, y, z; (iii) $-x$, $-y$, $1-z$; (iv) $-x$, $1-y$, $2-z$; (v) $-1/2+x$, $1/2-y$, $1/2+z$.

3.2. X-ray crystallography study

Crystallographic data and parameters concerning data collection and structure solution and refinement are summarized in Table 2. Selected bond lengths (Å) and angles (°) and hydrogen bonding interactions for complexes **2c** and **3c** are listed in Table

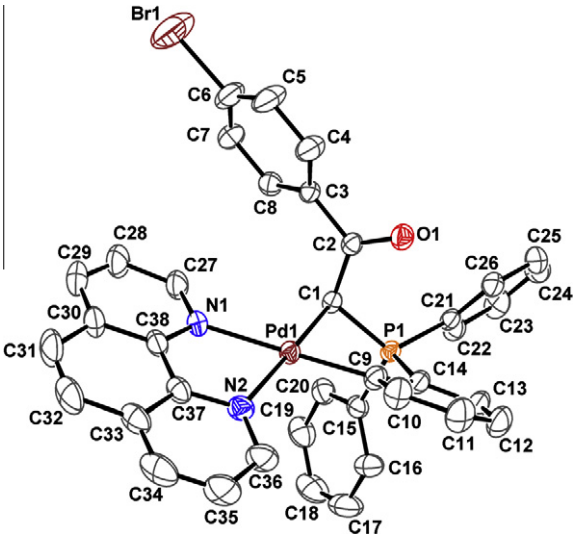


Fig. 1. The structure of the cation in **2c**, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

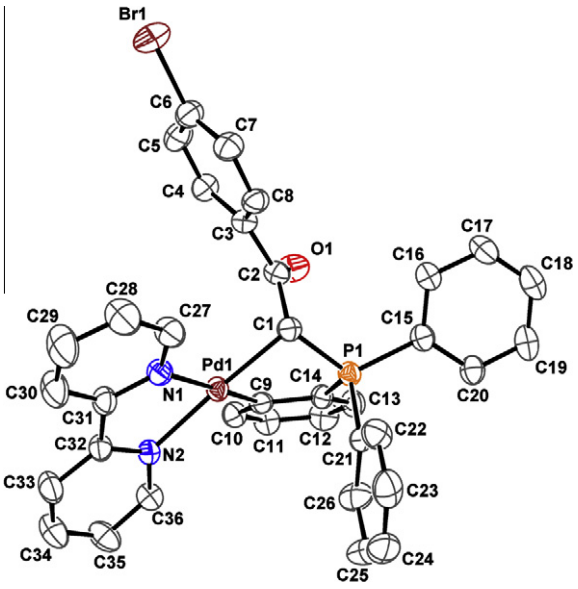


Fig. 2. The structure of the cation in **3c**, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

3. An ORTEP view of the cation of **2c** and **3c** is shown in Figs. 1 and 2, respectively.

The geometric parameters describing the coordination environment of the metal and the conformation of the five-membered metallacycles in the cations of both **2c** and **3c** are very similar. The square planar coordination geometry of the Pd atoms is slightly but not negligibly tetrahedrally distorted, with the metal atoms protruding from the plane of the N_2C_2 core by 0.0109(2) and 0.0098(4) Å in **2c** and **3c**, respectively. The distortion from the regular square planar geometry is indicated by the values of the bond angles subtended at the Pd centers (Table 3). The Pd1–C9 bond distances are not significantly different from those found in related complexes (1.999(8) Å in $[Pd\text{-}(C_6H_4\text{-}2\text{-}PPh_2C(H)\text{-}COCH_2PPh_3)(PPh_3)(NCMe)]^{2+}$ and 2.012(10) Å in $[Pd_2\text{-}Hg(\mu\text{-}Cl)_2(C_6H_4\text{-}2\text{-}PPh_2C(H)COC(H)(PPh_3))_2]^{2+}$ [44], respectively). The Pd—C1 bond lengths involving the ylidic carbon atoms are intermediate between the corresponding bonds reported in the mentioned related compounds (2.161(8) and 2.083(9) Å for [44], respectively). The Pd–N bond distances are almost equal and fall in the higher end of the normal range reported in the literature. The P1–C1 bond lengths are significantly longer than that observed in the related free ylide (1.711 Å) of formula $PPh_3C(H)COPh$ [45]. The Pd1···P1 separations are 3.0241(9) and 2.9638(13) Å in **2c** and **3c**, respectively. The PdN_2C_2 and PdC_3P five-membered metallacycles assume an envelope conformation, with atoms Pd1 and C1 displaced from the mean planes of the remaining four atoms by 0.3465(2) and 0.855(3) Å in **2c**, and 0.2622(4) and 0.962(5) Å in **3c**.

In the crystal structures, cations, anions and dichloromethane solvent molecules are linked into a three-dimensional network by intra- and intermolecular C–H···O and C–H···F hydrogen bonds (Table 3).

4. Conclusions

The present study describes the orthopalladation of stabilized α-keto phosphorus ylides $Ph_3P{=}CHC(O)C_6H_5R$ occurring regioselectively at the Ph rings of the phosphine unit in *endo* position giving the dinuclear complexes $[Pd(\mu\text{-}Cl)(PhBPPY)]_2$ (**1a**), $[Pd(\mu\text{-}Cl)(NO_2BPPY)]_2$ (**1b**) and $[Pd(\mu\text{-}Cl)(BrBPPY)]_2$ (**1c**). The reaction of the dinuclear complexes with AgOTf and neutral bidentate ligands phen, bipy, dppe and dppp promotes the synthesis of new mononuclear complexes, in which the five-membered Pd–C–P–C–C metallacycle remains stable.

Acknowledgements

The authors acknowledge the Department of Chemistry, Isfahan University of Technology, and Department of General and Inorganic Chemistry, University of Parma, University of Parma, for financial support. The author thanks the Isfahan University of Technology (IUT) Research Council and Center of Excellence in Sensor and Green Chemistry (IUT) for supporting this study.

Appendix A. Supplementary data

CCDC 783344 and 783353 contain the supplementary crystallographic data for compounds **2c** and **3c**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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