Transition Met Chem (2011) 36:363–367
DOI 10.1007/s11243-011-9478-y

Oxygen- versus carbon-coordination of the alpha-stabilized phosphorus ylide $Ph_3P=C(H)R$ in palladacycles bearing secondary amines

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Received: 10 February 2011 / Accepted: 2 March 2011 / Published online: 18 March 2011
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Abstract The ortho-metalated complex [Pd(x){κ^2(*C*,*N*)-[$C_6H_4CH_2NRR'$ (Y)}] (**2a–4a** and **2b–3b**) was prepared by refluxing in benzene equimolecular amounts of $Pd(OAc)_2$ and secondary benzylamine [**a**, $EtNHCH_2Ph$; **b**, t-$BuNHCH_2Ph$ followed by addition of excess NaCl. The reaction of the complexes [Pd(x){κ^2(*C*,*N*)-[$C_6H_4CH_2NRR'$ (Y)}] (**2a–4a** and **2b–3b**) with a stoichiometric amount of $Ph_3P=C(H)COC_6H_4$-4-Z (Z = Br, Ph) (ZBPPY) (1:1 molar ratio), in THF at low temperature, gives the cationic derivatives [Pd(OC(Z-4-$C_6H_4C=CHPPh_3$){κ^2(*C*,*N*)-[$C_6H_4CH_2NRR'$(Y)}] (**5a–9a**, **4b–6b**, and **4b′–6b′**), in which the ylide ligand is O-coordinated to the Pd(II) center and trans to the ortho-metalated C(6)H(4) group, in an "end-on carbonyl". Ortho-metallation, ylide O-coordination, and C-coordination in complexes (**5a–9a**, **4b–6b**, and **4b′–6b′**) were characterized by elemental analysis as well as various spectroscopic techniques.

Introduction

Phosphorus ylides constitute an important class of compound in the field of organometallic chemistry, particularly due to their interesting applications in metal-promoted organic syntheses [1]. Carbonyl stabilized phosphorus ylides are interesting ligands because they can behave as C or O donors owing to the delocalization of the ylidic electron pair [2]. This class of ligand shows an ambidentate character (C- versus O-coordination) that can be rationalized in terms of the potential resonance forms **a–c** (Scheme 1), together with the isomeric form **d** (Scheme 1). Form **b** would account for the C-coordination, while isomers **c** and **d** would explain O-coordination. This ambidentate character facilitates the preparation of stable metal complexes (Scheme 2) in which the ylide can be O- (both cisoid and transoid forms) [3] or C-coordinated [4–9].

The activation of C–H bonds in organic compounds promoted by transition metals is an important research topic nowadays [10]. Synthesis of cyclo-palladated complexes has attracted considerable attention from a number of research groups, due to its implication, in the fundamental steps of several catalytic cycles, in the functionalization of simple substrates through ortho-metallation, and in other relevant chemical processes [11–16].

Experimental

All chemicals were purchased from Fluka and Merck companies. ^{1}H NMR (500 MHz) and ^{31}P NMR (202 MHz) spectra were recorded in $CDCl_3$ solutions at room temperature (TMS was used as an internal standard) on a Bruker Avance spectrometer.

Preparation of PhBPPY (**1**)

To a solution of 2-bromo-4-phenylacetophenon (0.825 g, 3 mmol) in $CHCl_3$ (20 mL), a solution of PPh_3 (0.786 g, 3 mmol) in $CHCl_3$ (5 mL) was added dropwise. The mixture was stirred at room temperature for 4 h, and then it was evaporated to dryness. The residue was reacted with NaOH (2 g, 0.5 mmol) in EtOH/H_2O (20 mL), giving $Ph_3PCHC(O)C_6H_5Ph$ as a yellow solid. Yield: 1.87 g, 81.9%. M.p. 230–231 °C. IR (KBr disk, cm^{-1}): υ 1507, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 4.5$ (d, 1H, CHP,

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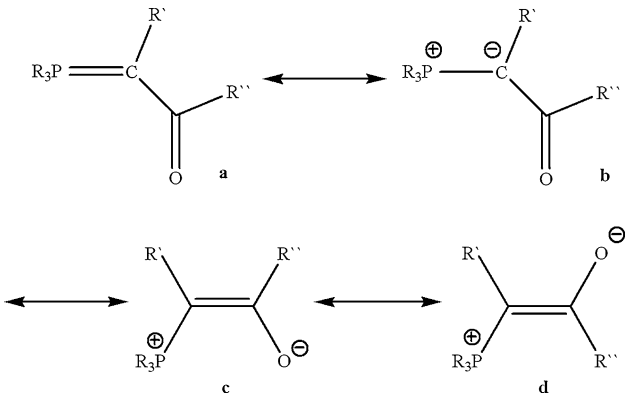
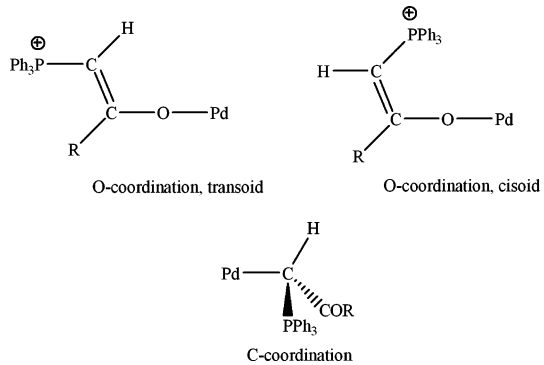


Scheme 1 Resonance forms of keto-phosphorus ylides (free)



Scheme 2 Resonance forms of keto-phosphorus ylides (complex)

$^{2}J_{HH}$ = 24 Hz), 7.4 (t, 1H, H_p, C_6H_5, $^{3}J_{HH}$ = 7 Hz), 7.5 (t, 2H, H_m, C_6H_5, $^{3}J_{HH}$ = 10.5 Hz), 7.5 (t, 2H, H_m, C_6H_4), 7.5 (m, 6H, H_m, PPh_3), 7.6 (m, 2H, H_o, C_6H_5, $^{3}J_{HH}$ = 6 Hz), 7.7 (t, 3H, H_p, PPh_3, $^{3}J_{HH}$ = 6 Hz), 7.8 (m, 6H, H_o, PPh_3), 8.1 (d, 2H, H_o, C_6H_4). ^{31}P {^{1}H} NMR ($CDCl_3$, ppm): δ = 17.2 (s, 1P, CHP) [2, 9, 17].

Preparation of BrBPPY (**2**)

To a solution of 2,4-dibromoacetophenone (0.834 g, 3 mmol) in $CHCl_3$ (20 mL), a solution of PPh_3 (0.786 g, 3 mmol) in $CHCl_3$ (5 mL) was added dropwise. The mixture was stirred at room temperature for 4 h, and then it was evaporated to dryness. The residue was reacted with NaOH (2 g, 0.5 mmol) in MeOH/H_2O (20 mL), giving $PPh_3CHC(O)C_6H_5Br$ as a white solid. Yield: 0.56 g, 67.9%. m.p. 183 °C, IR (KBr, cm^{-1}): ν 1519, ^{1}H NMR (500 MHz, ppm, $CDCl_3$): δ = 4.4 (d, CHP, $^{2}J_{PH}$ = 23.9), 7.0 (m, 2H, C_6H_4CO), 7.5 (m, 6H, H_m, $3C_6H_5$), 7.6 (m, 3H, H_p, $3C_6H_5$), 7.7 (m, 6H, H_o, $3C_6H_5$), 8 (m, 2H, C_6H_4CO). ^{31}P {^{1}H} NMR ($CDCl_3$, ppm): δ = 16.00 ppm [2, 9, 17].

General procedure for the synthesis of cyclo-palladated complexes {Pd($C_6H_4CH_2NRR'$)Y(ZBPPY)} (R = H, R′ = Et, t-Bu; Y = 4-Picoline, Me_3Py, PPh_3; Z = Ph, Br)

To a solution of $Pd(OAc)_2$ (0.116 g, 0.52 mmol) in benzene (15 mL), secondary benzylamine [**a**, $EtNHCH_2Ph$; **b**, $t\text{-}BuNHCH_2Ph$; 1 mmol] was added. The mixture was refluxed for 24 h at 50 °C. The mixture was then evaporated to dryness, MeOH was added to the solid, and the green suspension was treated with NaCl or NaBr (1.118 mmol) at room temperature.

A yellow suspension was immediately produced, and stirring was maintained for 12 h at room temperature, after which the precipitate was filtered off, then addition of 4-picoline, Me_3Py, or PPh_3 (1.0 mmol) in CH_2Cl_2 (15 cm^3) gave a clear solution immediately. After stirring for 8 h at room temperature, the solution was filtered through a plug of Celite or $MgSO_4$. Crude complexes resulted that precipitated as solids.

These solids were dissolved in CH_2Cl_2 at room temperature, and *n*-hexane were added to give a powder, which was filtered off and then air-dried to give complexes **2a, 3a, 4a, 2b**, and **3b** in Scheme 1. Then, to a suspension of **(2a, 3a, 4a, 2b,** and **3b)** (0.1194 g, 0.1 mmol) in THF (12 mL) was added AgTfO (0.032 g, 0.126 mmol).

The resulting mixture was stirred for 30 min at room temperature with exclusion of light and then filtered over magnesium sulfate. Phosphorus ylide (0.237 g, 0.52 mmol) (**1** or **2**) was added, and the resulting solution was stirred for 45 min after the reaction time. The solvent was evaporated to dryness, and the residue was treated with *n*-hexane (10 mL) to give (**5a, 6a, 7a, 8a, 9a, 4b**, **4b′**, **5b**, **5b′**, **6b**, and **6b′**) in Scheme 1.

5a) Yield: 0.10 g (80%), m.p: 173–175 °C. FT-IR (cm^{-1}, KBr); ν (N–H) 3200, ν (C=O) 1481. ^{1}H NMR (500 MHz, $CDCl_3$, ppm); δ = 0.9 (t, 3H, CH_3, $^{2}J_{HH}$ = 5 Hz), 1.3 (m, 1H, CH_2), 2.4 (m, 1H, CH_2), 3.0 (s, 3H, CH_3), 3.1 (s, 1H, NH), 3.8 (dbr, 1H, CH_2), 4.5 (m, 1H, CH_2), 4.5 (s, 1H, CHP), 6.7 (s, 1H, Ph), 7–8. (m, +3H, Ph, +9H, Ph, +4H, Py, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.4 (s, 1P, PPh_3). Elemental analysis Calc.: C, 61.4; H, 4.6; N, 3.0. Found: C, 61.4; H, 4.7; N, 3.1%. Λ: 112 Ω^{-1} mol^{-1} cm^2.

6a) Yield: 0.08 g (75%), m.p: 170–174 °C. FT-IR (cm^{-1}, KBr); ν (N–H) 3216, ν (C=O) 1493. ^{1}H NMR (500 MHz, $CDCl_3$, ppm); δ = 0.9 (t, 3H, CH_3, $^{2}J_{HH}$ = 5 Hz), 1.32 (m, 1H, CH_2), 2.4 (m, 1H, CH_2), 2.4 (s, 3H, CH_3), 2.9 (s, 1H, NH), 3.8 (d, 1H, CH_2, $^{2}J_{HH}$ = 15 Hz), 4.6 (d, 1H, CH_2, $^{2}J_{HH}$ = 15 Hz), 4.4 (dbr, 1H, CHP), 6.0 (sbr, 1H, Ph), 6.7–7.1 (m, 3H, Ph), 7.5–7.8 (m, 4H, Ph, $+2H_m$, Py, $+2H_o$, Py, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3). ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.6 (s, 1P, PPh_3).

Elemental analysis Calc.: C, 53.6; H, 4.1; N, 3.0. Found: C, 53.6; H, 4.1; N, 3%. Λ: 122 Ω^{-1} mol^{-1} cm^2.

7a) Yield: 0.11 g (81%), m.p: 189–192 °C. FT-IR (cm^{-1}, KBr); *v* (N–H) 3221, *v* (C=O) 1481. ^1H NMR (500 MHz, $CDCl_3$, ppm); $\delta = 1.63$ (t, 3H, CH_3), 2.4 (s, 3H, CH_3), 3.0 (s, 3H, CH_3), 3.2 (s, 3H, CH_3), 3.8 (d, 1H, CH_2, $^2J_{HH} = 20$ Hz), 4.5 (d, 1H, CH_2, $^2J_{HH} = 20$ Hz), 4.8 (s, 1H, NH), 4.1 (d, 1H, CHP, $^2J_{PH} = 8$ Hz), 5.7 (s, 1H, Ph), 6.7–7 (m, 3H, Ph), 7.1–8.0 (m, +9H, Ph, +2H, Py_m, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.2$ (s, 1P, PPh_3). Elemental analysis Calc.: C, 62.1; H, 4.90; N, 2.9. Found: C, 62.1; H, 5.0; N, 3.0%. Λ: 139 Ω^{-1} mol^{-1} cm^2.

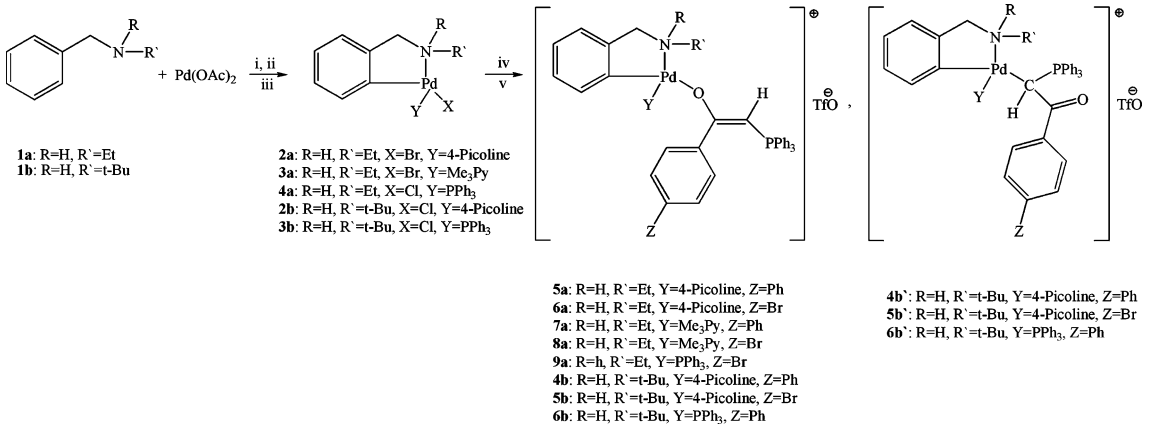
8a) Yield: 0.11 g (81%), m.p: 178–180 °C. FT-IR (cm^{-1}, KBr); *v* (N–H) 3226, *v* (C=O) 1492. ^1H NMR (500 MHz, $CDCl_3$, ppm); $\delta = 0.9$ (t, 3H, CH_3, $^2J_{HH} = 7$ Hz), 1.3–1.5 (m, 2H, CH_2), 2.4 (s, 3H, CH_3), 3.0 (s, 3H, CH_3), 3.2 (s, 3H, CH_3), 3.8 (d, 1H, CH_2, $^2J_{HH} = 10$ Hz), 4.5 (d, 1H, CH_2, $^2J_{HH} = 10$ Hz), 4.8 (s, 1H, NH), 4.4 (d, 1H, CHP, $^2J_{PH} = 21$ Hz), 5.7 (s, 1H, Ph), 6.7–7.0 (m, 3H, Ph), 7.1–7.8 (m, +4H, Ph, +2H, Py, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): $\delta = 17.2$ (s, 1P, PPh_3). Elemental analysis Calc.: C, 54.5; H, 4.4; N, 2.9. Found: C, 54.6; H, 4.6; N, 3.1%. Λ: 115 Ω^{-1} mol^{-1} cm^2.

9a) Yield: 0.11 g (72%), m.p: 174–177 °C. FT-IR (cm^{-1}, KBr); *v* (N–H) 3218, *v* (C=O) 1494. ^1H NMR (500 MHz, $CDCl_3$, ppm); $\delta = 0.9$ (t, 3H, CH_3), 3.0 (m, 1H, CH_2), 3.2 (m, 1H, CH_2), 3.9 (dbr, 1H, CH_2), 4.8 (dbr, 1H, CH_2), 4.4 (d, 1H, CHP, $^2J_{PH} = 10$ Hz), 2.2 (sbr, 1H, NH), 6.3 (m, 1H, Ph), 6.4 (tbr, 1H, Ph), 6.9 (tbr, 1H, Ph), 7.0 (dbr, 1H, Ph), 7.4–7.8 (m, 4H, Ph, $+12H_m$, PPh_3, $+6H_p$, PPh_3, $+12H_o$, PPh_3). ^{31}P $\{^1H\}$ NMR (202.44 MHz, $CDCl_3$, ppm): $\delta = 17.2$ (s, 1P, PPh_3), 40.8 (s, 1P, Pd-PPh_3). Elemental analysis Calc.: C, 58.4; H, 4.2; N, 1.3. Found: C, 58.5; H, 4.3; N, 1.4%. Λ: 109 Ω^{-1} mol^{-1} cm^2.

4b, **4b′**) Yield: 0.052 g (61%), m.p: 188–190 °C. FT-IR (cm^{-1}, KBr); *v*(N–H) 3217, *v* (C=O) 1478, 1619. ^1H NMR (300 MHz, $CDCl_3$, ppm); $\delta = 0.9$–1.3 (m, 9H, CH_3), 2.4 (s, 3H, CH_3), 3.9 (sbr, 1H, CHP), 4.0 (d, 1H, CH_2, $^2J_{HH} = 12$ Hz), 4.5 (d, 1H, CH_2, $^2J_{HH} = 12$ Hz), 3.8 (sbr, 1H, NH), 5.4 (sbr, 1H, CHP), 6.0–7.0 (m, 4H, Ph),7.2–9.2 (m, 9H, Ph, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3, $+2H_m$, Py, $+2H_o$, Py, both isomer). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.2$ (s, 1P, PPh_3), 17.2 (s, 1P, PPh_3), 22.5 (s.1P, PPh_3). Elemental analysis Calc.: C, 62.1; H, 4.90; N, 2.9. Found: C, 62.20; H, 5.0; N, 3.0%. Λ: 120 Ω^{-1} mol^{-1} cm^2.

5b, **5b′**) Yield: 0.08 g (92%), m.p: 183–185 °C. FT-IR (cm^{-1}, KBr); *v*(N–H) 3219, *v* (C=O) 1491, 1620. ^1H NMR (300 MHz, $CDCl_3$, ppm); $\delta = 0.9$–1.3 (m, 9H, CH_3), 2.4 (s, 3H, CH_3), 3.9 (dbr, 1H, CHP), 4.4–4.5 (d, 2H, CH_2), 3.8 (sbr, 1H, NH), 5.4 (sbr, 1H, CHP), 6.1 (sbr, 1H, Ph), 6.5–6.9 (m, 3H, Ph),7.2–9.2 (m, 9H, Ph, $+6H_m$, PPh_3, $+3H_p$, PPh_3, $+6H_o$, PPh_3, $+2H_m$, Py, $+2H_o$, Py, both isomer). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.0$ (s, 1P, PPh_3), 17.1 (s. 1P, PPh_3), 24.2(s, 1P, PPh_3). Elemental analysis Calc.: C, 54.5; H, 4.4; N, 2.9. Found: C, 54.6; H, 4.5; N, 3.0%. Λ: 125 Ω^{-1} mol^{-1} cm^2.

6b, **6b′**) Yield: 0.08 g (80%), m.p: 173–177 °C. FT-IR (cm^{-1}, KBr); *v* (N–H) 3233, *v* (C=O) 1480, 1601. ^1H NMR (300 MHz, $CDCl_3$, ppm); $\delta = 1.2$–1.3 (m, 9H, CH_3), 1.9 (sbr, 1H, NH), 3.9 (d, 1H, CHP, $^2J_{PH} = 15$ Hz), 4.5 (d, 1H, CH_2, $^2J_{HH} = 2.4$ Hz), 4.7 (d, 1H, CH_2, $^2J_{HH} = 1.4$ Hz), 5.6 (sbr, 1H, CHP), 6.2 (m, 1H, Ph), 6.3 (m, 1H, Ph), 6.80 (m, 1H, Ph), 6.90 (m, 1H, Ph), 7.2–8.2 (m, 9H, Ph, $+12H_m$, PPh_3, $+6H_p$, PPh_3, $+12H_o$, PPh_3, both isomer). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.4$ (s, 1P, PPh_3), 23.8 (s, 1P, PPh_3) 40.3 (s, 1P, Pd-PPh_3), 41.2 (s, 1P, Pd-PPh_3). Elemental analysis Calc.: C, 65.5; H, 4.9; N, 1.2. Found: C, 65.7 H, 3.00; N, 1.40%. Λ: 131 Ω^{-1} mol^{-1} cm^2 (Scheme 3).



Scheme 3 i) Benzene, Reflux 24 h, 60 °C. ii) MeOH, NaX (X = Cl, Br), 12 h. iii) CH_2Cl_2, Y, 8 h. iv) AgTfO, THF. V) ZBPPY (Z = Ph, Br)

Result and discussion

Spectroscopic study

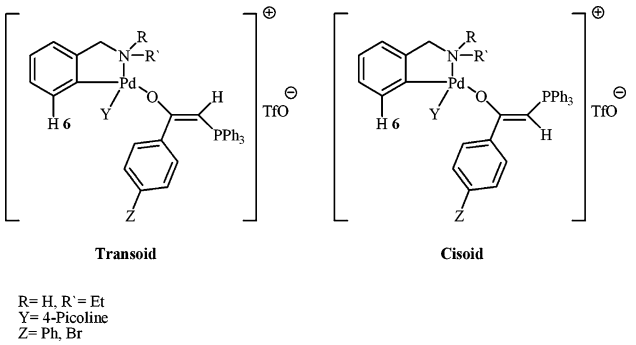
The ν(CO) bands, which are sensitive to complexation, occur at 1,507 and 1,519 cm^{-1} in the parent ylides, as in the case of other resonance-stabilized ylides [17, 18, 20]. In general, coordination of the ylide through C causes an increase in ν(CO), while for O-coordination, a lowering of ν(CO) is expected. Spectroscopic techniques such as IR and NMR spectroscopy enable one to distinguish between O(carbonyl)- and C(methine)-coordination.

The IR absorption bands observed for complexes **5a–9a** show a lowering of ν(CO) at 1,481, 1,493, 1,481, 1,492, and 1,494 cm^{-1}, indicating coordination of the ylide oxygen for these complexes. The IR spectra of the **4b–6b** complexes show an intense absorption at 1,478, 1,491, and 1,480 cm^{-1} respectively, corresponding to the stretching ν(CO). This absorption has been shifted to lower energies with respect to the free ylides.

Moreover, the IR spectra of complexes **4b′–6b′** show a sharp, very strong absorption at 1,619, 1,620, and 1,601 cm^{-1} respectively, corresponding to the carbonyl absorption. This absorption is shifted to higher energies with respect to that in the free ylides (1507 and 1519 cm^{-1}) [10]. The observation of this positive shift for ν(CO) in the complexes indicates that the ylides are C-coordinated to Pd(II).

The $\nu(P^+–C^-)$ band which is also diagnostic of the coordination occurs at 845, 829 cm^{-1} in $(C_6H_5)_3P^+–CH_2COC_6H_4$-Ph and $(C_6H_5)_3P^+–CH_2COC_6H_4$-Br (phosphonium salt), respectively, and at 861, 846 cm^{-1} in $(C_6H_5)_3PCHCOC_6H_4$-Ph and $(C_6H_5)_3PCHCOC_6H_4$-Br, respectively. In this study, the $\nu(P^+–C^-)$ values for **5a**, **6a**, **7a**, **8a**, **9a**, **4b**, **4b′**, **5b**, **5b′**, **6b**, and **6b′** complexes (811, 810, 805, 800, 803, 807, 808, and 802 cm^{-1}) were shifted to lower frequency, suggesting some removal of electron density from the P–C bond.

Analysis of the aromatic region of the ^{1}H NMR spectra of the complexes **5a–6b′** confirmed the metallation. In the ^{1}H NMR spectra of the complexes **5a–6b′** containing unsubstituted phenyl rings, a set of four different signals (sometimes described as a set of three different signals or a multiplet) in the aromatic region corresponding to the four protons in the ortho-palladated ring is found. Moreover, for PPh_3 and pyridine derivatives, the aromatic proton **H6** appears at a considerably lower frequency relative to the free amines due to the anisotropic shielding by the adjacent pyridine, that is, coordinated nearly perpendicular to the square-planar palladium(II) plane, or the P-phenyl rings. This effect supports the mutually *trans* position of the pyridine or phosphine ligand and the N(RR′) group in solution [19].



Scheme 4 Geometric isomers for O-coordinated complex

The ^{1}H NMR spectra of the complexes **5a–6b** show a doublet or broad signal attributed to the proton methine CH at 3.8–4.4 ppm in O-bound complexes [3, 17, 20–22] and the C-bound complexes **4b′–6b′** observed in 5.4–5.6 ppm. The ^{1}H NMR spectra of the complexes showed only one signal for the CH methine with a coupling constant $^2J_{(P–H)}$ near to that of the free ylides and close to those observed in other O-bonded complexes, this coupling is usually smaller in C-linked ylides [4–9, 20, 23, 24].

Moreover, the $^{31}P\{^1H\}$ NMR spectra of the **5a–6a** complexes show a broad signal attributed to the PCH group at 16.3–16.6 ppm, the presence of broad signal can be explained by the presence of two isomers, namely transoid and cisoid in these complexes (Scheme 4), and the **7a–9a** complexes show a sharp singlet at 17.2–17.8 ppm.

The $^{31}P\{^1H\}$ NMR spectrum of the **4b** complex shows two sharp signals attributed to the PCH group at 14.2, 17.2 ppm, and the **5b** complex shows these at 14.0, 17.1 ppm. The presence of two lines of different intensities can be explained by the presence of two isomers in these complexes. The $^{31}P\{^1H\}$ NMR spectrum of the **6b** complex shows a sharp signal attributed to the PCH group at 18.4 ppm, shifted slightly upfield relative to the free ylides and is again in agreement with O-coordination [3, 17, 20–22].

The $^{31}P\{^1H\}$ NMR spectra of the **4b′–6b′** complexes show a sharp signal attributed to the PCH group at 22.5, 24.1, and 23.8 ppm, respectively, which are shifted to downfield with respect to the parent ylides, in good agreement with the C-bonding of the ylides. The ^{31}P-$\{^1H\}$ NMR spectrum of the **9a** complex shows a sharp signal attributed to the PPh_3 group coordinated to the Pd metal at 40.8 ppm, and the **6b**, **6b′** complexes show two sharp signals attributed to the PPh_3 group coordinated to the Pd metal at 40.3 and 41.2 ppm, the presence of two lines of different intensities can be explained by the steric effects of tertiarybutylbenzylamine and PPh_3, causing the presence of two isomers in these complexes.

These complexes are stable in the solid state or in acetone solution. The molar conductivity of complexes corresponds to univalent electrolyte (100–135 Ω^{-1} mol^{-1} cm^2 [25]).

Conclusions

In this work, the synthesis and characterization of ortho-palladated complexes of phosphorus ylides have been investigated. The preference of stabilized ylides to bind to a given metal through one-specific donor atom is closely related to the hard or soft nature of the metal. The alternance in the O- and C-bonding modes in complexes **4b**–**6b** is reported to be due exclusively to steric factors.

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