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Synthesis, spectroscopic and structural characterization of orthopalladated complexes with 4-phenylbenzoylmethylene triphenyl phosphorane ylide

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Abstract The orthometalated complex $[Pd(\mu\text{-}Cl)(C_6H_5\text{-}C_6H_4C(O)CHPPh_2C_6H_4\text{-}\kappa^2\text{-}C,C)]_2$ (**1**) was prepared by refluxing in $MeOH/CH_2Cl_2$ equimolecular amounts of $Pd(OAc)_2$ and $(Ph)_3PCHCOC_6H_4$-Ph-4 (=PhBPPY) followed by addition of excess NaCl. Complex **1** reacts with 4-picoline to give the mononuclear derivative $[Pd(PhC_6H_4\text{-}COCHPPh_2C_6H_4)(4\text{-picoline})]$ (**2**) whose crystal structure has been determined by X-ray diffraction. The precursor complex (**1**) could not be isolated in a pure form, but it can be used as a starting material for the synthesis of derivatives of mononuclear cyclo-palladated complexes. Orthometallation and ylide C-coordination in complexes **3**–**5** were characterized by elemental analysis as well as various spectroscopic techniques.

Introduction

The activation of C–H bonds in organic compounds promoted by transition metals is an important research topic nowadays [1]. Synthesis of cyclopalladated complexes has attracted considerable attention by a number of research groups, due to its implication, in the fundamental steps of several catalytic cycles, in the functionalization of simple substrates through orthometallation and in other relevant chemical processes [2–12]. It is usual to find two or more C–H bonds in the same compound that can be activated to metallation. A method for the synthesis of orthopalladated adducts of the phosphorus ylide $Ph_3P{=}CHCO_2Me$ has been reported [13, 14]. It is possible to obtain orthopalladated complexes derived from CH activation at Ph rings belonging to PPh_3 moieties. In this work, we describe the synthesis and characterization of Pd(II) complexes (**1**–**5**) of new phosphorus ylides (Scheme 1). The X-ray crystal structure of complex **2** shows both the orthopalladation and ylide C-coordination in this complex and confirms the *endo* metalation of the phosphorus ylide.

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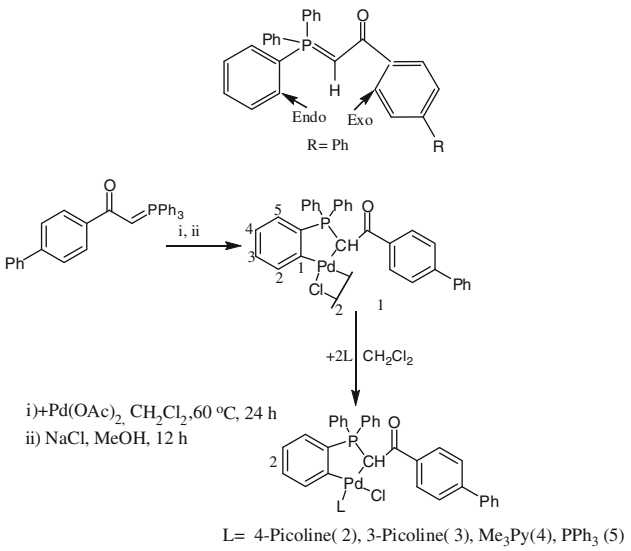
Experimental

Pd $(OAc)_2$, 2-Bromo-4′-Phenylacetophenone, and triphenyl phosphine were purchased from Merck. The ylides were synthesized by the reaction of triphenylphosphine with a chloroform solution of 2-bromo compounds and dehydrogenated with NaOH [15]. All solvents were reagent grade and used without further purification. Solution-state ^1H and ^{31}P NMR spectra at 300 K were obtained in $CDCl_3$ using a 500 MHz Bruker spectrometer operating at 500.13 MHz for 1H and 161.97 MHz for ^{31}P and referenced to H_3PO_4 (85%) for $^{31}P\{1H\}$NMR spectra. IR spectra were recorded on an FTIR JASCO 680 spectrophotometer, using KBr disks. Melting points were measured on a Gallenhamp 9B 3707 F apparatus. Elemental analysis for C, H and N was performed using a Perkin-Elmer 2400 series analyzer.

Synthesis of $PhC_6H_4COC{=}HPPh_3$ (PhBPPY)

To a dichloromethane solution (15 mL) of 2-bromo 4′-phenyl acetophenone (1.38 g, 5 mmol) was added PPh_3 (1.31 g, 5 mmol) and the resulting mixture was stirred for 5 h. The suspension was filtered and the precipitate washed



Scheme 1

with diethyl ether and air-dried. Further treatment with aqueous NaOH (0.5 M) led to elimination of HBr, giving free PhBPPY.

M.p. 230–231 °C; Yield: 1.87 g, 82%; IR (KBr, cm^{-1}): ν(CO) 1,507; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 4.52$ (d, 1H, CHP, $^2J_{PH} = 24$ Hz), 7.38 (t 1H, H_p, C_6H_5) 7.48 (t, 2H, H_m, C_6H_5), 7.47 (t 2H, H_m, C_6H_4) 7.53 (m, 6H, H_m, PPh_3), 7.6 (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 ($CDCl_3$): $\delta = 17.2$ (s, 1P, CHP).

^{13}C NMR ($CDCl_3$) δ C: 51.3 (d, $^1J_{PC} = 111.2$ Hz, CH); 125.4 (C_6H_5 (i)); 126.2 (d, $^1J_{PC} = 93.24$ Hz, PPh_3 (i)); 126.8 (C_6H_5 (m)); 127.81 (COPh (m)); 128.4 (C_6H_5 (p)); 128.88 (PPh_3 (p)); 129.34 (d, ^{3}JPC = 12.41 Hz, PPh_3 (m)); 128.4 (C_6H_5 (o)); 131.80 (d, $^4J_{PC} = 2.81$ Hz, COPh (o)); 133.40 (d, $_2J_{PC} = 10.25$ Hz, PPh_3 (o)); 135.86 (COPh (p)); 140.63 (d, ^{2}JPC = 14.69 Hz, COPh (i)); 185.3 (d, $^2J_{PC} =$ 3.3 Hz, CO).

Synthesis of [Pd(μ-Cl)($C_6H_5C_6H_4C(O)CHPPh_2C_6H_4$-$\kappa^2$-C,C)]$_2$ (**1**)

$Pd(OAc)_2$ (0.0673 g, 0.3 mmol) was added to a solution of PhBPPY (0.1365 g, 0.3 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was refluxed overnight. The solvent was then evaporated and the yellow solid residue was dissolved in MeOH (10 mL) and anhydrous NaCl (0.0342 g, 0.6 mmol) was added, where upon a pale yellow solid precipitated immediately. The mixture was stirred for 12 h at room temperature and the resulting suspension was filtered. The yellow solid was washed with H_2O (5 mL) and Et_2O (15 mL) and air-dried to produce complex **1**.

M.p. 298 °C (dec); yield (0.234 g, 40%); Anal Found. for $C_{64}H_{48}O_2Cl_2P_2Pd_2$ C, 63.1; H, 3.8; Calcd C, 64.3; H, 4.0; IR (KBr, cm^{-1}): ν (CO) 1,623; ^{1}H NMR (500 MHz, ppm, $CDCl_3$)): $\delta = 4.90$ (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): 18.41 (s br both isomers).

Synthesis of [Pd(Cl)($C_6H_5C_6H_4C(O)CHPPh_2C_6H_4$-$\kappa^2$-C,C)(4-Picoline)] (**2**)

To a suspension of complex **1** (0.1194 g, 01 mmol) in dichloromethane (15 cm^3) at room temperature, 4-picoline (0.02 mL, 02 mmol) was added. The suspension gave a clear solution immediately. After 12-h stirring, the resulting solution was filtered over a Celite pad. The solvent was completely removed by evaporation under vacuum and CH_2Cl_2 (2 mL) plus *n*-hexane (15 mL) or Et_2O (7 mL) was added to give mononuclear complex 2 as a pale green precipitate, which was filtered off and air-dried.

Yield: 0.1008 g, 73%; Anal. Found for $C_{32}H_{26}$NOBrClPPd.H_2O: C, 53.4; H, 3.4; N, 1.8; Calcd. C, 53.9; H, 3.4; N, 2.0. IR (KBr, cm^{-1}); ν(CO) 1,619; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 2.13$ (s, 3H, Me major isomers), 2.39 (s, 3H, Me minor isomer), 5.16 (br s, 1H, CHP, major isomer), 5.23 (d, 1H, CHP minor isomers, $^3J_{PH} = 4$ Hz), 6.6 (d, 1H, H_6, C_6H_4, $^3J_{HH} = 7.6$ Hz major isomer), 6.65 (d, 2H, H_5, H_4, C_6H_4, $^3J_{HH} = 5.8$ Hz minor isomers), 7.06 (d, 2H, H_5, H_4, C_6H_4, $^3J_{HH} = 6$ Hz major isomers), 7.10 (m, 1H, H_6, C_6H_4, major isomer), 7.20 (m, 2H, H_3, C_6H_4, both isomers), 7.50 (m, 12H, Hm, PPh_2 + Hm, C_6H_5 both isomers), 7.60 (m, 8H, H_m, C_6H_4CO + Hm, 4-MePy both isomers), 7.69 (m, 12H, H_o, $PPh_2 + H_o$, C_6H_5 both isomers), 7.74 (m, 2H, H_p, C_6H_5 both isomers), 7.90 (t, 4H, H_p, PPh_2, $^3J_{HH} = 6$ Hz, both isomer), 8.26 (m, 2H, H_o, 4-MePy minor isomers), 8.37 (m, 4H, H_o, C_6H_4CO both isomers), 8.41 (m, 2H, H_o, 4-MePy major isomers), 8.62 (d, 2H, H_o, C_6H_4CO major isomers), $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.96$ (s, 1P, CHP, minor isomer), 20.32 (s, 1P, CHP, major isomer). $^{13}C\{^1H\}$ NMR: $\delta = 21.16$, 21.51 (C, Me both isomer), $C_{aromatic}$ for both isomer {$\delta = 125.48$, 125.92, 126.84, 127.04, 127.5, 127.6, 127.7, 128.56, 128.65, 128.95, 129.05, 129.2, 129.4, 129.7, 129.8, 129.9, 130.25, 130.47, 133.11 (d, $j_{PC} = 9.56$ Hz), 133.32, 133.58 (d, $j_{PC} = 9.43$ Hz), 136.5, 136.6,136.72}199.2 (CO, both isomers), 201.8 (CO both isomers).

Synthesis [Pd(Cl)($C_6H_5C_6H_4C(O)CHPPh_2C_6H_4$-$\kappa^2$-C,C)(3-Picoline)] (**3**)

To a suspension of complex **1** (0.1194 g, 01 mmol) in dichloromethane (15 cm^3) at room temperature, 3-picoline (0.02 mL. 02 mmol) was added. The resulting suspension gave a clear solution immediately. After 12-h stirring, the

resulting solution was filtered over a Celite pad. The solvent was completely removed by evaporation under vacuum and CH_2Cl_2 (2 mL) plus *n*-hexane (15 mL) or Et_2O (7 mL) was added to give mononuclear complex 3 as a pale green precipitate, which was filtered off and air-dried.

M.p. 202–204 °C (dec), yield (0.0988 g, 72%), Anal. Found for $C_{38}H_{31}NOClPPd$: C, 65.08; H, 4.21; N, 1.91 Calcd C, 66.10; H, 4.52; N, 2.03, IR (cm^{-1}), *v* (C=O): 1624.73.

Complex 3 was characterized (NMR) as a mixture of two isomers in 1.5/1 M ratio; ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.9$ (s, Me major isomers), 2.29 (s, Me minor isomer), 5.19 (brs, 1H, CHP, major isomer), 5.24 (s, 1H, CHP minor isomers, $^3J_{PH} = 4$ Hz), 6.55 (d, H_6, C_6H_4, $^3J_{HH} = 7.6$ Hz minor isomer), 6.65 (dd, H_6, C_6H_4, $^3J_{HH} = 6$ Hz major isomers), 6.99–7.11 (m, 3H, H_5, H_4, H_3, C_6H_4, minor isomer), 7.11–7.13 (m, m, 3H, H_5, H_4, H_3, C_6H_4, major isomer), 7.14 (m, H_2, 3MePy, both isomers), 7.58-761 (m, 7H, Hm, PPh_2 + Hm + Hp, C_6H_5, both isomers), 7.65–7.72 (m, 10H, $H_{o,p}$, PPh_2, Hm, C_6H_4CO + H_o, C_6H_5 both isomers), 7.86 (m, H_o, C_6H_4CO + H_p, C_6H_5 major isomers), 8.39 (m, H_o, C_6H_4CO + H_p, C_6H_5 minor isomers), 8.42 (m, H_4, H_5, MePy both isomers + H_6, MePy minor isomer), 8.25 (d, H_6, 3-MePy, $^3J_{H-H} = 8.5$ Hz major isomers); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.95$ (s, 1P, CHP, minor isomer), 20.43 (s, 1P, CHP, major isomer).

$^{13}C\{^1H\}$ NMR: $\delta = 21.16$, 21.51 (C, Me both isomer), $C_{aromatic}$ for both isomer {$\delta = 125.48$, 125.92, 126.84, 127.04, 127.5, 127.6, 127.7, 128.56, 128.65, 128.95, 129.05, 129.2, 129.4, 129.7, 129.8, 129.9, 130.25, 130.47, 133.11 (d, $^3j_{PC} = 9.56$ Hz), 133.32, 133.58 (d, $^3j_{PC} = 9.43$ Hz), 136.5, 136.6, 136.72}, 198.3 (CO, both isomers), 200.3 (CO both isomers).

Synthesis of [Pd(Cl)($C_6H_5C_6H_4C(O)CHPPh_2C_6H_4$-$\kappa^2$-C,C)($Me_3py$)] (**4**)

Complex 4 was prepared in a similar manner to complex 3.

Yield (0.0965 g, 67 %); Anal Found for $C_{44}H_{34}ClFOP_2PdCl$: C, 65.4; H, 4.0 Calcd C, 65.9; H, 4.3; IR (KBr, cm^{-1}): *v* C=O): 1,621 ^1H NMR (500 MHz, $CDCl_3$, ppm); $\delta = 2.10$ (s, 3H, Me), 2.27 (s, 3H, Me), 2.96 (s, 3H, Me), 5.27 (d, 1H, CHP, $^3J_{PH} =$ Hz), 6.57 (d, 1H, H_6, $C_6H_{4,}$), 6.94 (s, 2H, H_5, H_4, C_6H_4), 7.18 (m, 1H, H_3, C_6H_4), 7.40 (t, 1H, Me3Py, $^3J_{HH} =$ Hz), 7.46 (m, 4H, Hm, PPh_2), 7.52 (t, 2H, H_p, PPh_2), 7.60 (m, 1H, Me3Py), 7.69 (m, 7H, H_o, PPh_2 + H_m, H_p, C_6H_5) 7.93 (dd, 2H, Hm, C_6H_4CO), 8.27 (m, 2H, H_o, C_6H_5), 8.59 (d, 2H, H_o, C_6H_4CO), $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.92 (s, 1P, CHP).

$^{13}C\{^1H\}$NMR: $\delta = 21.14$, 26.58, 27.185 (s, 3C, Me), 35 (d, CHP, $^1j_{PC} = 59.45$ Hz), 124.93 (s, Ci, C_6H_5), 124.39(d, C_1, $^1j_{PC} = 13.20$ Hz), 129.625 (d, C_6, $^2j_{PC} = 11.95$ Hz), 130.49 (d, C_i PPh_2, $^1j_{PC} = 15.22$ Hz), 133.78 (d, C_5, $^3j_{PC} = 9.o5$ Hz), 134.96 (d, Co, PPh_2, $^2j_{PC} = 10.06$ Hz), 137.93 (d,C_3, $^3j_{PC} = 9.18$ Hz), 137.93 (d, C_2, $^2j_{PC} = 12.83$ Hz), 158.47 (d, Co, PPh_2, $^2j_{PC} = 10.31$ Hz). Other $C_{aromatic}$ {$\delta = 123.63$, 124.1, 126.7, 126.9, 126, 127.23, 127.67, 128.1, 129.1, 130.23, 132.68, 134.48, 139.1, 140.01, 141.03}, 196.2 (CO).

Synthesis of [Pd(Cl)($C_6H_5C_6H_4C(O)CHPPh_2C_6H_4$-$\kappa^2$-C,C)($PPh_3$)] (**5**)

To a suspension of complex **1** (0.1194 g, 0.1 mmol) in CH_2Cl_2 (15 mL) was added PPh_3 (0.0524 g, 0.2 mmol). The initial yellow suspension gradually dissolved, and after 8-h stirring at room temperature, the resulting solution was filtered over a Celite pad. The clear solution was evaporated to dryness and treatment of the residue with Et_2O (30 mL) gave **5** as a yellow solid.

M.p.146 °C; yield (0.1014 g, 59%); Anal found for $C_{44}H_{34}ClFOP_2PdCl$. C, 65.4; H, 4.0, Calcd C, 65.9; H, 4.3; IR (KBr, cm^{-1}): *v* C=O): 1,619 ^1H NMR (500 MHz, $CDCl_3$, ppm); $\delta = 5.5$ (s, 1H, CHP), 6.5 (m, 2H, C_6H_4), 6.90 (m, 1H, C_6H_4), 7.19 (m, 6H, H*m*, PPh_3), 7.32 (m, 6H, H*m*, PPh_2 + Hm, C_6H_5), 7.44 (m, 6H, H*p*, C_6H_5 +PPh_2 + PPh_3), 7.6 (m, 6H, H_o, PPh_3), 7.66 (m, 2H, H*m*, C_6H_4CO), 7.88 (m, 2H, H_o, C_6H_5), 8.02 (m, 2H, H_o, PPh_2), 8.29 (m, 2H, H_o, PPh_2), 8.31 (d, 2H, H_o, C_6H_4CO, $^3J_{HH} = 7.1$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.09 (s, 1P, CHP), 31.86 (s, 1P, Pd-PPh_3).

$^{13}C\{^1H\}$NMR: $\delta = 40.47$ (dd, CHP, $^1j_{PC} = 63.13$ Hz, $^2j_{PC} = 21$ Hz), 123.72 (d, C_1, $^1j_{PC} = 13.20$ Hz), C aromatic{$\delta = 126.71$, 127.46, 128.12 (d, C_o PPh_2 or C_o PPh_3, $^2j_{PC} = 10.19$ Hz), 129.08 (d, C_m PPh_2, $^3j_{PC} = 6.03$ Hz), 129.68 (d, C_i, PPh_2, $^2j_{PC} = 11.82$ Hz), 130.02, 130.53, 130.66, 131.72, 132.84, 134.64, 138.06, 139.2, 140.8, 144.2}, $\delta = 133.31$ (d, C_3, $^3j_{PC} = 9.31$ Hz), $\delta = 135.16$ (d, C_i PPh_3, $^2j_{PC} = 11.82$ Hz), $\delta = 197.5$ (CO).

X-ray crystal structure determination

A suitable single crystal was chosen for the crystallographic study and mounted on the goniometer of a STOE IPDS II diffractometer. All diffraction measurements were taken at room temperature (296 K) using graphite monochromated MoKa radiation ($k = 0.71073$ Å). The data collection was performed using the X-scan technique and using the STOE X-AREA software package [16]. The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELXL97 [17] and using the ORTEP-3 crystallographic software package [18]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2r$ (I). Hydrogen atoms were inserted at calculated positions using a riding mode with fixed thermal parameters.

Results and discussion

The IR spectrum of PhBPPY shows a strong absorption at 1,507 cm^{-1}, due to the carbonyl stretch, while the ^{31}H NMR spectrum shows a doublet at 4.30 ppm assigned to methinic protons. The absorption due to the carbonyl stretch appears at lower energies than expected (about 1,720 cm^{-1}), due to the conjugation of the C=O bond with the P=C bond. The localization of the density charge in the P–C–C–O bond system is responsible for the stability of these compounds and can also be inferred from the $^{31}P\{^{1}H\}$ NMR spectra [13, 14, 19]. These spectra show a single peak at about 17.2 ppm, a position shifted to low field with respect to that observed in other non-stabilized systems (about 0-6 ppm) and showing the lower shielding of the P atom in the stabilized compounds due to delocalization. The IR spectra of complexes **1–5** show a sharp, very strong absorption in the 1,618–1,625 cm^{-1} range (see Table 1), corresponding to the carbonyl absorption. This absorption is shifted to higher energies with respect to that in the free ylide (1,507 cm^{-1}) [1]. The observation of this positive shift for ν_{CO} in the complexes indicates that the ylide is C-coordinated to Pd(II). In the ^{1}H NMR spectrum of **1**, the signals due to the methinic proton were broad (minor) or broad doublet (major). The presence of two chiral carbon centers (forming diastereoisomers) in **1** was confirmed using the ^{1}H NMR spectra as two sets of signals with unequal populations for the CH and PCH groups.

Table 1 Crystal data and structure refinement for complex **5**

Formula	2 (C38 H31Cl N O P Pd)Cl
Formula weight	1416.37
Crystal system	Triclinic
Space group	$P-1$
a	10.3826(14)
b	12.7884(18)
c (Å)	13.8852(17)
Alpha	110.363(10)
Beta	101.145(10)
Gamma (°)	95.724(11)
V ($Å^3$)	1667.6(4)
Z	1
D(calc) (g/cm^3)	1.41
Mu(MoKa) (mm)	0.755
F(000)	721
Crystal size (mm)	0.05 × 0.20 × 0.46
Temperature (K)	296
Radiation (Å)	MoKα 0.71073
Theta min–max (°)	1.6, 26.5
Dataset	−13: 13; −16: 16; −17: 17
Tot., Uniq. Data, *R*(int)	16,240, 6,909, 0.109
Observed data [$I > 2.0$ sigma(I)]	3480
Nref, Npar	6,909, 398
R, wR_2, S	0.0640, 0.1016, 0.90
Min. and Max. Resd. Dens. [$e/Å^3$]	−0.68, 0.55

In the ^{1}H NMR spectra of complexes **1–5**, the signals due to the methinic protons are doublets or broad. Similar behavior was observed earlier in the case of ylide complexes of palladium(II) [19]. The expected downfield shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. The $^{31}P\{^{1}H\}$ NMR spectrum of **1** showed two sets of single peaks at 18.82 (major) and 19.41 ppm (minor). The presence of two lines of different intensities can be explained by the presence of two diastereoisomers (*RR/SS* and *RS/SR*), as a result of the C-bonding of the ylide and the binuclear nature of **1**. The bridge-splitting reactions of **2** with neutral ligands produced exclusively the corresponding mononuclear compounds **2–5**. The ^{1}H and $^{31}P\{^{1}H\}$ NMR signals for the PCH group of all the complexes were shifted downfield in comparison with those in free ylides, as a consequence of the inductive effects of the metal center. The $^{2}J_{(PH)}$ values for complexes **2–5** were smaller than those in the free ylides and phosphonium salts; this behavior has already been observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes because the hybridization changes in the ylidic carbon (Sp^2 to Sp^3) in the C-coordination mode [20]. The ^{1}H NMR spectra of complexes **2** and **3** showed two signals for the CH group that are assigned to a fast equilibrium between the *cis* and *trans* isomers or a dynamic activity for exchange of Methyl Py and Cl groups in solution [21]. The ^{1}H NMR spectrum of complex **4** showed one signal for the CH group at 5.16 ppm, while the $^{31}P\{^{1}H\}$ NMR spectrum shows only one sharp singlet at 18.92 ppm. The appearance of single signals for the PCH group in each of the ^{31}P and ^{1}H NMR spectra indicates the presence of only one molecule for this complex, as expected for C-coordination [1, 22, 23]. The ^{1}H NMR spectrum of complex **5** showed one signal for the CH group at 5.5 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum of **5** showed two singlet resonances in this case (range 15.09 and 31.86 ppm), which are shifted to low field with respect to the parent ylide, in good agreement with the C-bonding of the ylides.

The ^{13}C NMR spectra of the complexes 2–5 show upfield shifts of the signals due to the ylidic carbon atoms. Such shifts were observed in other complexes, due to the change in hybridization of the ylidic carbon atom on coordination [20]. Similar upfield shifts of 2–3 ppm with reference to the parent ylide were also observed for other complexes [20, 23]. The ^{13}C shifts of the CO group in the complexes are between 196 and 202 ppm, which is higher field than the 185.3 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon atom of the CO group in the complexes. For complex 5, the

ylidic protons appear as doublets of doublets at $\delta = 40.47$ ppm, meaning that each carbon is coupled with two different P nuclei (PPh_3 and C=P). The coupling constants ($^1j_{PC} = 63.13$ Hz, $^2j_{PC} = 21$ Hz) suggest that the PPh_3 is located *trans* to the ylidic carbon [23], in good agreement with the expected *trans* effect between the PPh_3 and the arylic carbon [24].

X-ray crystallography study

The X-ray crystal structure of complex **2** is shown in Fig. 1. Crystallographic data and parameters concerning data collection and structure solution and refinement are summarized in Table 1 and some selected bond lengths (Å) and angles (°) for complex **2** are collected in Table 2.

These crystals were grown by the diffusion of *n*-hexane into a CH_2Cl_2 solution. In complex **2**, each palladium atom has a slightly distorted square-planar environment, surrounded by the orthometalated C(7) atom, the ylide C(19), that forms a five-member cycle, one chlorine (Cl1) and one phosphorus (P1) atom. Complex **2** crystallized in the triclinic system with space group $P-1$. The absolute configuration of the C(19) atom is depicted in the structure shown in Fig. 1. The summation of the bond angles around the palladium is almost 360 °C. Although the orthometallated ligand is remarkably warped, the environment around the Pd is planar. The Pd1-C7 bond distance (2.002(6) Å) is similar to those found in other ortho-palladated complexes [1, 13] and the Pd-N(1) distance falls also in the usual range found for this bond [25]. The bond length of P(1)–C(19) in the similar ylide is 1.706 Å [1, 26] which shows that the above bond has considerably elongated to 1.775 (6) Å in complex **2**. The Pd1–C19 bond distance (2.101(6) Å) in complex **2** with respect to published examples appears at the low end of the usual range [(2.090(3)–2.161(8)] [1, 13].

Table 2 Selected bond lengths (Å) and angles (°) for complexes **2**

Pd1–Cl1	2.359(2)	Cl1–Pd1–N1	88.19(18)
Pd1–N1	2.136(6)	Cl1–Pd1–C7	93.6(2)
Pd1–C7	2.002(6)	Cl1–Pd1–C19	176.76(16
Pd1–C19	2.101(6)	N1–Pd1–C7	175.8(2)
P1–C1	1.803(5)	N1–Pd1–C19	94.8(2)
P1–C12	1.777(6)	C7–Pd1–C19	83.5(3)
P1–C13	1.794(8)	C1–P1–C12	110.1(3)
P1–C19	1.775(6)	C1–P1–C13	105.4(3)
O1–C20	1.231(7)	C1–P1–C19	116.2(3)
N1–C33	1.321(8)	C12–P1–C13	111.1(3)
N1–C37	1.340(10)	C12–P1–C19	98.2(3)
C19–C20	1.494(8)	C13–P1–C19	115.8(3)
C20–C21	1.482(8)	Pd1–N1–C33	119.5(5)
P1–C19–C20	118.1(4)	Pd1–N1–C37	122.5(5)
O1–C20–C19	120.6(5)	Pd1–C19–P1	97.9(3)

The angles subtended by the ligands at the Pd(II) center in complex **2** varied from 83.5(3)) to 94.8(2) and 175.8(2) to 176.76(16), indicating a distorted square-planar environment. The Cl1–Pd1–C19 (176.76(16) Å) and N1–Pd1–C7 (175.8(2)) bond angles deviated only a little from

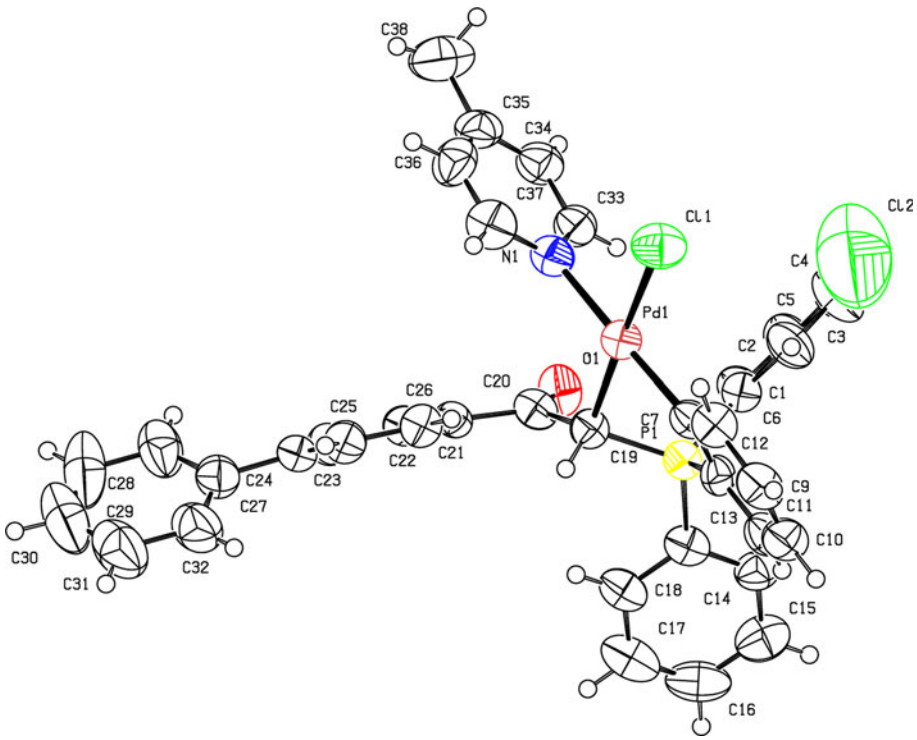


Fig. 1 ORTEP view of the X-ray crystal structure of complex **2**

Table 3 IR data for PhBPPY and complexes **1–5**

Compound	C=O	C=C	C=N	P–C
Ligand PhBPPY	1,507	1,566	–	881
[Pd(μ-Cl)(PhBPPY)]$_2$ (1)	1,623	1,564	–	839
[PdCl(PhBPPY)4-Picoline)] (2)	1,619	1,566	1,601	854
[PdCl(PhBPPY)3-Me Py] (3)	1,625	1,564	1,602	852
[PdCl(PhBPPY)(Me_3Py)] (4)	1,621		1601.6	
[PdCl(PhBPPY)PPh_3] (5)	1,619	1,562	–	850

linearity. The Pd(1)–C(7) bond distance (2.002(6) Å) was statistically identical to those found in the other orthopalladated complexes (2.035(5) Å) [27, 28]. The distances Pd(1)–C(1) [2.002(6) Å] and Pd(1)–C(19) [2.101(6) Å] for **2** were different, probably reflecting the different *Trans* effects of the nitrogen and chlorine atoms. The stabilized resonance structure for the parent ylide was destroyed due to the complex formation, thus the C(19)–C(20) bond lengths (1.494(8) Å) in complex **2** were significantly longer than the corresponding distances found in the similar uncomplexed phosphoranes (1.407(8) Å [1, 23, 29] and 1.401(2) Å [29, 30]). Likewise, the C(19)–P(1) bond lengths in similar ylides were 1.7194(17) Å [1, 29] which showed that the corresponding bonds in **2** have considerably elongated to 1.775(6) or (5) Å. In complex **2**, one phenyl ring of PPh_3 has undergone a CH bond activation process. The structure of **2** may be proposed as *endo* on the basis of its NMR data and the X-ray structure.

Conclusions

In this work, the synthesis and characterization of orthopalladated complexes of phosphorus ylides have been investigated. The X-ray crystal structure of complex **5** confirmed the C-coordination of the ylides. The results obtained in the investigation into the C–H bond activation process, induced by Pd(II) salts, in the ylide ligand, showed that the cyclopalladation has occurred at one phenyl ring of the PPh_3 (*endo*) with an additional chiral carbon center. Based on the physicochemical and spectroscopic data, we propose that ylide PhBPPY exhibits monodentate C-coordination to the metal center (Table 3).

Supplementary data

CCDC 749675 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/deposit or deposit@ccdc.cam.ac.uk.

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