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New orthopalladated complexes of phosphorus ylides: Crystal structure of $[Pd{CH{P(C_7H_6)(p-tolyl)_2}COCH_3}Cl{P(p-tolyl)_3}]$

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ABSTRACT

This work reports on the preparation of the complexes $[PdCl_2(Y^1)_2]$, $[PdCl_2(Y^2)_2]$ ($Y^1 = (p-tolyl)_3PCHCOCH_3$ (**1a**); $Y^2 = Ph_3PCHCO_2CH_2Ph$ (**1b**)), $[Pd\{CHP(C_7H_6)(p-tolyl)_2COCH_3\}(\mu-Cl)]_2$ (**2a**), $[Pd\{CHP(C_6H_4)Ph_2CO_2-CH_2Ph\}(\mu-Cl)]_2$ (**2b**), $[Pd\{CH\{P(C_7H_6)(p-tolyl)_2\}COCH_3\}Cl(L)]$ ($L = PPh_3$ (**3a**), $P(p-tolyl)_3$ (**4a**)) and $[Pd\{CH\{P(C_6H_4)Ph_2CO_2CH_2Ph\}Cl(L)]$ ($L = PPh_3$ (**3b**), $P(p-tolyl)_3$ (**4b**)). Orthometallation and ylide C-coordination in complexes **2a-4b** are demonstrated by an X-ray diffraction study of **4a**.

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1. Introduction

The activation of C-H bonds induced by transition metals is, at present, one of the most active fields of research in organometallic chemistry due to its implications, among others, in the fundamental steps in catalytic cycles, in the functionalization of simple substrates through orthometallation, and in other relevant chemical processes [1–14]. The orthometallation of the phosphorus ylides $R_3PC = (R')R''$ (R, R' and R'' = alkyl or aryl groups) [15–19] is produced, in the vast majority of cases, regioselectively at the Ph rings of the phosphine unit. In 1989, Vicente et al. [20] presented a method for the synthesis of orthopalladated adducts of the phosphorus ylide Ph₃P=CHCO₂Me. Some recent contributions have shown, however, that it is possible to obtain orthopalladated complexes derived from CH activation at Ph rings belonging to the R' or R" substituents of the ylidic carbon atom and, more precisely, belonging to benzamide moieties [21]. Although orthometallation of ylides is well-known [17,20,22-26], in this work we describe the synthesis and characterization of Pd(II) complexes of the titled phosphorus ylides. The X-ray crystal structure of complex 4a adequately shows the orthopalladation and ylide C-coordination in complexes 2a-4b.

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2. Experimental

2.1. Physical measurements and materials

Melting points were measured on a SMPI apparatus. Elemental analyses for C and H were performed using a PE 2400 series II analyzer. IR spectra were recorded on a Shimadzu FT IR 435-U-04 spectrophotometer (KBr pellets). NMR spectra were obtained on a 300 MHz Bruker FT-NMR spectrometer in DMSO-d₆ or CDCl₃ as the solvent. Chemical shifts (δ) are reported relative to internal TMS and external 85% phosphoric acid. The single crystal X-ray diffraction analysis for complex 4a was performed on a STOE IPDS-II two circle diffractometer at 120(2) K, using graphite monochromated Mo K α X-ray radiation (λ = 0.71073 Å). The data collection was performed at 120(2) K using the ω -scan technique and using the STOE X-AREA software package [27]. The crystal structure was solved by direct methods [28] and refined using the x-STEP32 crystallographic software package [29]. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in ideal positions. Methanol was dried using magnesium powder just before use. All other solvents were reagent grade and were used without further purification.

2.2. Sample preparation

The ligands $[(p-tolyl)_3PCHCOCH_3]$ (Y¹) and $[Ph_3PCHCO_2CH_2Ph]$ (Y²) were prepared based on the published methods [30,31].



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2.2.1. Synthesis of $[PdCl_2(Y^1)_2]$ (**1a**) general procedure

To a saturated solution of PdCl₂ (0.049 g, 0.28 mmol) in acetonitrile (10 ml) was added solid Y¹ (0.198 g, 0.55 mmol), and the suspension was stirred for 15 min. The resulting brown solution was concentrated (2 ml) and diethyl ether (10 ml) was added to precipitate the brown solid **1a**. *Anal*. Calc. for C₄₈H₅₀Cl₂O₂P₂Pd: C, 64.19; H, 5.61. Found: C, 64.0; H, 5.79%. Yield 0.185 g (75%), m.p. 170-172 °C. IR (KBr disk) ν (cm⁻¹): 1643 (C=O), 1599, 1498, 1399, 1347, 1293, 1191, 1147, 1104, 1020, 966, 873, 806 (P-C), 763, 658. ¹H NMR (CDCl₃) $\delta_{\rm H}$ (ppm): 2.25 (3H, s, COCH₃), 2.39 (9H, s, 3CH₃), 5.09 (br, CH), 7.26-7.66 (12H, m, arom.). ³¹P NMR (CDCl₃) $\delta_{\rm P}$ (ppm): 23.52 and 23.38 (2s, at 25 °C), 23.50 (1s, at 55 °C). ¹³C NMR (CDCl₃) $\delta_{\rm C}$ (ppm): 22.13 (s, 3CH₃), 32.63 (d, ³J_{PC} = 16.38 Hz, COCH₃), 119.28 (d, ¹J_{PC} = 149.8 Hz, *p*-tolyl, (*ipso*)), 135.04 (d, ²J_{PC} = 7.35 Hz, *p*-tolyl, (*ortho*)), 130.15 (d, ³J_{PC} = 21.64 Hz, *p*-tolyl, (*meta*)), 135.12 (d, ⁴J_{PC} = 7.35 Hz, *p*-tolyl, (*para*)), 205.16 (CO).

2.2.2. Data for $[PdCl_2(Y^2)_2]$ (**1b**)

Orange solid. *Anal.* Calc. for $C_{54}H_{46}Cl_2O_4P_2Pd$: C, 64.11; H, 4.89. Found: C, 64.97; H, 4.64%. Yield 0.217 g (78%), m.p. 184–186 °C. IR (KBr disk) v (cm⁻¹): 1683 (C=O), 1435, 1285, 1128, 1106, 836 (P– C), 801, 741, 688. ¹H NMR (DMSO-*d*₆) $\delta_{\rm H}$ (ppm): 4.95 (s, *CH*₂, minor diastereoisomer) 5.10 (s, *CH*₂, major diastereoisomer) 5.36 (bd, ²*J*_{PH} = 14.33 HZ, *CH*, two diastereoisomers), 7.22–7.81 (20H, m, arom.). ³¹P NMR (DMSO-*d*₆) $\delta_{\rm P}$ (ppm): 19.83 (trans, minor diastereoisomer), 20.80 (trans, major diastereoisomer), 27.84 (cis, minor diastereoisomer), 28.09 (cis, major diastereoisomer). ¹³C NMR (DMSO-*d*₆) $\delta_{\rm C}$ (ppm): 28.61 (d, ¹*J*_{PC} = 52.24 Hz, *CH*, minor diastereoisomer), 29.38 (d, ¹*J*_{PC} = 56.75 Hz, CH, major diastereoisomer), 64.94 (s, *CH*₂, minor diastereoisomer), 67.62 (s, *CH*₂, major diastereoisomer), 115.79–136.05 (arom.), 164.19 (CO, minor diastereoisomer), 170.45 (CO, major diastereoisomer).

2.2.3. Synthesis of $[Pd{CH{P(C_7H_6)(p-tolyl)_2}COCH_3}(\mu-Cl)]_2$ (**2a**) general procedure

To a suspension of PdCl₂ (0.090 g, 0.51 mmol) in acetonitrile (20 ml) was added solid Y¹ (0.376 g, 1.02 mmol). The mixture was refluxed for 8 h and then allowed to cool to room temperature. The suspension was filtered and the solid was washed with diethyl ether (10 ml) to give a greenish-yellow solid as product **2a**. The phosphonium salt [(*p*-tolyl)₃PCH₂COCH₃]Cl separated, as a by-product, via the mother liquor by washing solid **2a**. Anal. Calc. for C₄₈H₄₈Cl₂O₂P₂Pd₂: C, 57.50; H, 4.83. Found: C, 57.0; H, 5.06%. Yield 0.356 g (78%), m.p. 316–319 °C. IR (KBr disk) ν (cm⁻¹): 1645, 1599, 1441, 1292, 1193, 1152, 1108, 1030, 805 (P–C), 656.

2.2.4. Data for $[Pd{CHP(C_6H_4)Ph_2CO_2CH_2Ph}(\mu-Cl)]_2$ (2b)

Greenish-yellow solid. *Anal.* Calc. for $C_{54}H_{44}Cl_2O_4P_2Pd_2$: C, 58.82; H, 4.02. Found: C, 58.76; H, 4.40%. Yield 0.210 g (75%), m.p. 283–285 °C. IR (KBr disk) ν (cm⁻¹): 1695 (C=O), 1435, 1284, 1126, 1106, 836 (P–C), 734, 689.

2.2.5. Synthesis of $[Pd{CH{P(C_7H_6)(p-tolyl)_2}COCH_3}Cl(PPh_3)]$ (**3a**) general procedure

To a suspension of complex **2a** (0.046 g, 0.06 mmol) in CH₂Cl₂ (20 ml) was added solid PPh₃ (0.033 g, 0.13 mmol). The mixture was stirred for 30 min. The resulting colorless solution was concentrated (2 ml) and diethyl ether (30 ml) was added to precipitate the white solid **3a**. *Anal*. Calc. for C₄₂H₃₉ClOP₂Pd: C, 66.06; H, 5.15. Found: C, 65.89; H, 5.35%. Yield 0.064 g (82%), m.p. 246–248 °C. IR (KBr disk) ν (cm⁻¹): 1639, 1594, 1572, 1475, 1433, 1351, 1302, 1180, 1154, 1103, 803 (P–C), 747, 692, 556. ¹H NMR (CDCl₃) $\delta_{\rm H}$ (ppm): 1.66 (3H, s, COCH₃), 2.37 and 2.42 (9H, 2s, 3CH₃), 4.90 (dd, ${}^2J_{\rm PH}$ = 8.96 Hz, ${}^3J_{\rm PH}$ = 8.87 Hz, 1H, *CH*), 6.66–7.78 (26H, m, arom.). ³¹P NMR (CDCl₃) $\delta_{\rm P}$ (ppm): 12.00 (PPh₃) and 28.49 (P(*p*-to-lyl)₂) (2d, ${}^3J_{\rm PP}$ = 19.0 Hz). ¹³C NMR (CDCl₃) $\delta_{\rm C}$ (ppm): 21.65 (s,

3CH₃), 31.45 (d, ${}^{3}J_{PC}$ = 11.30 Hz, COCH₃), 50.09 (d, ${}^{1}J_{PC}$ = 63.64 Hz, CH), 124.02–142.96 (m, arom.), 201.68 (CO).

2.2.6. Data for $[Pd{CH{P(C_7H_6)(p-tolyl)_2}COCH_3}Cl(PPh_3)]$ (3b)

White solid. *Anal.* Calc. for $C_{45}H_{37}ClO_2P_2Pd$: C, 66.43; H, 4.58. Found: C, 66.09; H, 4.93%. Yield 0.079 g (81%), m.p. 222–224 °C. IR (KBr disk) ν (cm⁻¹): 1677 (C=O), 1434, 1303, 1132, 1109, 855 (P–C), 751, 690. ¹H NMR (CDCl₃) $\delta_{\rm H}$ (ppm): 4.19 (dd, ² $J_{\rm PH}$ = 9.02 Hz, ³ $J_{\rm PH}$ = 5.82 Hz, 1H, CH), 5.15 (s, CH₂), 6.9–7.8 (m, arom.). ³¹P NMR (CDCl₃) $\delta_{\rm P}$ (ppm): 13.70 (PPh₃) and 27.86 (P(*p*-tolyl)₂) (2d, ³ $J_{\rm PP}$ = 19.21 Hz). ¹³C NMR (CDCl₃) $\delta_{\rm C}$ (ppm): 35.55 (dd, ¹ $J_{\rm PC}$ = 70.69 Hz, ² $J_{\rm PC}$ = 61.25 Hz, CH), 65.31 (s, CH₂), 122.82–139.81 (m, arom.), 172.16 (s, CO).

2.2.7. Synthesis of [Pd{CH{P(C₇H₆)(p-tolyl)₂}COCH₃}Cl{P(p-tolyl)₃}] (**4a**) general procedure

To a suspension of complex **2a** (0.046 g, 0.06 mmol) in CH₂Cl₂ (20 ml) was added solid P(*p*-tolyl)₃ (0.039 g, 0.13 mmol). The mixture was stirred for 30 min. The resulting colorless solution was concentrated (2 ml) and diethyl ether (30 ml) was added to precipitate the white solid **4a**. *Anal.* Calc. for C₄₅H₄₅ClOP₂Pd: C, 67.09; H, 5.63. Found: C, 67.22; H, 5.89%. Yield 0.071 g (84%), m.p. 252–254 °C. IR (KBr disk) ν (cm⁻¹): 1641 (C=O), 1598, 1497, 1444, 1396, 1295, 1189, 1152, 1104, 1027, 802 (P–C), 649, 511 ¹H NMR (CDCl₃) $\delta_{\rm H}$ (ppm): 1.67 (3H, s, COCH₃), 2.31 and 2.43 (9H, 2s, 3CH₃), 4.88 (dd, ²*J*_{PH} = 9.85 Hz, ³*J*_{PH} = 9.22 Hz, 1H, *CH*), 7.03–7.62 (23H, m, arom.). ³¹P NMR (CDCl₃) $\delta_{\rm P}$ (ppm): 11.56 (P(*p*-tolyl)₃) and 26.97 (P(*p*-tolyl)₂) (2d, ³*J*_{PP} = 18.5 Hz). ¹³C NMR (CDCl₃) $\delta_{\rm C}$ (ppm): 21.43 (s, 3CH₃), 31.24 (d, ³*J*_{PC} = 11.06 Hz, COCH₃), 49.90 (d, ¹*J*_{PC} = 60.71 Hz, *CH*), 122.02–165.18 (m, arom.), 201.31 (*C*O).

2.2.8. Data for $[Pd{CH{P(C_6H_4)Ph_2}CO_2CH_2Ph}Cl{P(p-tolyl)_3}]$ (4b)

White solid. *Anal.* Calc. for $C_{48}H_{46}ClO_2P_2Pd$: C, 67.14; H, 5.40. Found: C, 66.27; H, 5.31%. Yield 0.087 g (85%); m.p. 234–236 °C. IR (KBr disk): v (cm⁻¹): 1688 (C=O), 1436, 1294, 1128, 844 (P– C), 806, 734, 692. ¹H NMR (CDCl₃) $\delta_{\rm H}$ (ppm): 4.18 (dd, ²J_{PH} = 9.05 Hz, ³J_{PH} = 5.31 Hz, 1H, CH), 5.156 (s, 2H, CH₂), 2.30 (s, 9H, 3CH₃), 6.9–8 (m, 31H, arom). ³¹P NMR (CDCl₃) $\delta_{\rm P}$ (ppm): 13.51 (P(*p*-tolyl)₃), 26.47 (PPh₂), (2d, ³J_{PP} = 18.5 Hz). ¹³C NMR (CDCl₃) $\delta_{\rm C}$ (ppm): 35.27 (dd, ¹J_{PC} = 69.3 Hz, ²J_{PC} = 61.02 Hz, CH), 65.12 (s, CH₂), 122.62–139.44 (m, arom.), 172.06 (s, CO).

3. Results and discussion

3.1. Spectroscopy

The v(CO) band, which is sensitive to complexation, occurs at 1600 and 1610 cm⁻¹ in the parent ylides Y¹ and Y², respectively [30,31]. Coordination of ylide through the carbon atom causes an increase in the v(CO) band, whereas for O-coordination a lowering of the v(CO) band is expected [32]. Thus the IR absorption bands for the complexes at higher frequencies indicate that C-coordination has occurred. The v(P-C) band frequencies, which are also diagnostic of the coordination mode, occur at 848 and 887 cm⁻¹ in the parent ylides Y¹ and Y², respectively, and are shifted to lower frequencies for the complexes, suggesting some removal of the electron density of the P–C bonds [33].

The presence of two chiral C centres (forming diastereoisomers) in **1b** (Scheme 1) is shown in the ¹H, ³¹P and ¹³C NMR spectra by two sets of signals with unequal populations for CH₂, CH, CO and PCH groups. The geometry of cis and trans may leads to the further peaks in the ³¹P NMR spectra: 19.83, 20.80, 27.84 and 28.09 ppm for **1b** and 23.38 and 23.52 ppm at 25 °C for **1a** [34,35].

The two geometries for **1a** equilibrate rapidly at higher temperatures, leading to one signal for phosphorus centre (δ_P = 23.50 ppm at 55 °C) (Fig. 1).



(2a and 2b)

(3a, 3b, 4a and 4b)

No	1a	2a	3a	4a	1b	2b	3b	4b
Ar	P(p-tolyl) ₃	P(p-tolyl) ₃	$P(p-tolyl)_3$	$P(p-tolyl)_3$	Ph	Ph	Ph	Ph
R^1	Me	Me	Me	Me	OCH ₂ Ph	OCH_2Ph	OCH ₂ Ph	OCH ₂ Ph
\mathbf{R}^2	-	Me	Me	Me	-	Н	Н	Н
L	-	-	PPh ₃	$P(p-tolyl)_3$	-	-	PPh ₃	$P(p-tolyl)_3$

Scheme 1.



Fig. 1. Variable temperature ³¹P NMR study on 1a.

In the ¹H NMR spectra for **1a** and **1b**, the signals due to the methinic proton are broad (**1a**) or are a broad doublet (**1b**). This broadening is probably due to the presence of different geometries and the above mentioned diastereoisomers. A related insoluble complex, [PdCl₂{CH(PPh₃)CO₂Me}₂], has been reported to be of a trans geometry on the basis of IR data [20]. An NMR study could not be performed on complexes **2a** and **2b** because they are very insoluble in the most common solvents. However their elemental analysis, IR spectra and the synthesis of **3a** and **4b** from complexes **2a** and **2b** be and **2b** because the performed and the synthesis of **3a** and **4b** from complexes **2a** and **2b** be and **2b** be and **2b** be and **2b** be and **2b** be and **2b** and **2b** be and **2b** be and **2b** and **2b** and **2b** and **2b** be and **2b** be and **2b** and **2b** be and **2b** and **2b** and **2b** be and **2b** and **2**

 Table 1

 Crystal data and structure refinement for 4a

Compound	4a			
Empirical formula	C45H45ClOP2Pd			
Formula weight	805.62			
Temperature (K)	120(2)			
Wavelength (Å)	0.71073			
Crystal system	triclinic			
Space group	ΡĪ			
a (Å)	9.973(2)			
b (Å)	13.211(3)			
<i>c</i> (Å)	16.830(4)			
α (°)	73.082(19)			
β(°)	89.549(19)			
γ (°)	68.566(18)			
Volume (Å ³)	1962.6(8)			
Ζ	2			
D_{Calc} (Mg/m ³)	1.363			
Absorption coefficient (mm ⁻¹)	0.656			
F(000)	832			
Crystal size (mm)	$0.50 \times 0.20 \times 0.10$			
θ Range for data collection (°)	1.74-29.51			
Reflections collected/unique (R _{int})	20212/10443 (0.0902)			
Limiting indices	$-12\leqslant h\leqslant 13$,			
	$-18\leqslant k\leqslant 18$,			
	$-23 \leqslant l \leqslant 21$			
Completeness to θ = 29.51° (%)	96.7			
Absorption correction	numerical			
Maximum and minimum transmission	0.930 and 0.850			
Refinement method	full-matrix least-squares on F^2			
Data/restraints/parameters	10443/0/450			
Goodness-of-fit on F ²	1.088			
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0905, wR_2 = 0.1877$			
R indices (all data)	$R_1 = 0.0999, wR_2 = 0.1959$			
Extinction coefficient	0.019(3)			
Largest difference in peak and hole ($e Å^{-3}$)	1.723 and -1.918			

and **2b** with PPh₃ and P(p-tolyl)₃ is highly selective, affording exclusively the corresponding mononuclear compounds **3a**, **4a**, **3b** and **4b**, respectively (Scheme 1). The ¹H and ³¹P signals for the PCH group of complexes **3a–4b** are shifted downfield compared to that of the free ylide, as a consequence of the inductive effect of the metal centre. The ¹H NMR spectra of complexes **3a–4b** show one doublet of doublets signal for the CH group that must



Fig. 2. ORTEP view of the X-ray crystal structure of [Pd{CH{P(C₇H₆)(*p*-tolyl)₂]COCH₃}Cl{P(*p*-tolyl)₃] (**4a**). Selected bond lengths (Å) and bond angles (°): Pd(1)–C(12), 2.021(5); Pd(1)–C(3), 2.166(5); Pd(1)–P(2), 2.2945(15); Pd(1)–Cl(1), 2.4241(14); C(2)–C(3), 1.478(8); C(2)–O(1), 1.219(8); C(11)–C(12), 1.415(7); C(11)–P(1), 1.782(6); C(3)–P(1), 1.780(5); C(12)–Pd(1)–C(3), 86.8(2); C(12)–Pd(1)–P(2), 93.06(14); C(3)–Pd(1)–P(2), 168.19(16); C(12)–Pd(1)–Cl(1), 170.58(14); C(3)–Pd(1)–Cl(1), 88.35(15); P(2)–Pd(1)–Cl(1), 93.33(5) (hydrogen atoms have been omitted for clarity).

arise from the simultaneously coupling with two phosphorus centres.

In ¹³C NMR spectra, a higher shielding of the ylidic carbon atoms compared to those of the parent ylides is expected and we observed this for 3a, 4a and 1b. Such a higher shielding was observed in $[PdCl(\eta^3-2-XC_3H_4)(C_6H_5)_3PCHCOR]$ (X = H, CH₃; R = CH₃, C₆H₅), and is due to the change in hybridization of the ylidic carbon atom on coordination [36]. Similar upfield shifts of 2–3 ppm with reference to the parent vlide were also observed in the case of $[(C_6H_5)_3PC_5H_4 \cdot HgI_2]_2$ [37] and in our synthesized complexes [30,38]. The downfield shift of the carbonyl C atom in 1a, 3a, 3b, 4a and **4b** compared to the same carbon atom in the parent ylides $(190.38 \text{ ppm } (\text{Y}^1) \text{ and } 170.46 \text{ ppm } (\text{Y}^2))$, indicate a much lower shielding of the CO group in these complexes [30,38–40]. In this work, it is interesting that the expected upfield shift of the ylidic C atoms in **3b** and **4b** and downfield shift of the carbonyl C atom in **1b** are not in accordance with the expected process. This is probably due to the steric nature of Y^2 , which is different from ketonic ylides.

3.2. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complex **4a**. The molecular structure and pertinent bond distances and angles are presented in Fig. 2.

Suitable crystals of **4a** were grown by the slow diffusion of diethyl ether into a chloroform solution. The Pd atom is located in a distorted square-planar environment, surrounded by one ylidic carbon (C3) and one metallated carbon (C12) that form a five-membered cycle, one chlorine (Cl1) and one phosphorus (P2) atom. The angles subtended by the ligands at the Pd(II) centre in **4a** vary from 86.8(2)° to 93.33(5)° and 168.19(16)° to 170.58(14)° indicating the distorted square-planar environment. The C(3)-Pd(1)-P(2) (168.19(16)°) and C(12)-Pd(1)-Cl(1) (170.58-(14)°) bond angles deviate a little from linearity. The Pd(1)-C(12) bond distance (2.021(5) Å) is statistically identical to those found in the orthopalladated complexes [Pd{ κ^2 -C, N-C₆H₄-1-[(3, 5-Me₂-C₃N₂)-CH₂-(η^5 -C₅H₄Fe(η^5 -C₅H₅)]}Cl(PPh₃)] (2.035(5) Å)

[41] and $[Pd{\kappa^2-C, O-C_6H_4{C(0)Me}-2}Br{P(o-To)_3}]$ (2.021(2) Å) [42]. The distances Pd(1)–C(12) [2.021(5) Å] and Pd(1)–C(3) [2.166(5) Å] are different, probably reflecting the different trans effect of the phosphorus and chlorine atoms. The stabilized resonance structure for the parent ylide is destroyed by the complex formation, thus the C(2)–C(3) bond length (1.478(8) Å) is significantly longer than the corresponding distance found in the similar uncomplexed phosphoranes (1.407(8) Å [43] and 1.401(2) Å [44]). Likewise the C(3)–P(1) bond length in a similar ylide is 1.7194(17) Å [44], which shows that the corresponding bond in **4a** is considerably elongated to 1.780(5) Å.

4. Conclusion

The present study describes the synthesis and characterization of orthometallated Pd(II) complexes of phosphorus ylides. On the basis of the physico-chemical and spectroscopic data we propose that these ligands herein exhibit C-coordination to the metal centre, which is further confirmed by the X-ray crystal structure of complex **4a**. The structural study involved in this work demonstrates that phosphorus ylides can show transition metal induced activation of C–H bonds.

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Appendix A. Supplementary data

CCDC 684309 contains the supplementary crystallographic data for **4a**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.07.017.

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