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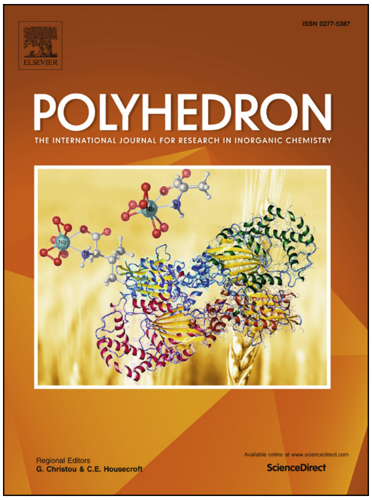

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New pallada- and platinacycle complexes of phosphorus ylide: synthesis, structural characterization, antioxidant capacity and catalytic behavior towards Mizoroki-Heck reactions

Seyyed Javad Sabounchei[a*], Ali Hashemi[a], Abed Yousefi[a], Parviz Gohari Derakhshandeh[b], Roya Karamian[c], Mostafa Asadbegy[c], Kristof Van Hecke[b*]

[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 65174, Iran

[b] XStruct, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium

[c] Department of Biology, Faculty of Science, Bu-Ali Sina University, P. O. Box 65175/4161, Hamedan - Iran

Abstract

The reactions of α-keto stabilized phosphorus ylide $Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br (**Y**) with $[MCl_2(cod)]$ (M = Pd or Pt; cod = 1,5-cyclooctadiene) in equimolar ratio using dichloromethane as a solvent are reported. These reactions led to the formation of new P, C-chelated pallada- and platinacycle complexes $[MCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br)] (M = Pd (**C1**) and Pt (**C2**)). Characterization of the obtained compounds was performed by elemental analysis and IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopic methods. Also, the

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[*] Corresponding author. E–mail address: jsabounchei@yahoo.co.uk; kristof.vanhecke@ugent.be.

unequivocal structures of these complexes were characterized crystallographically. Both structures consist of six-membered rings formed by coordination of the phosphorus ylide (**Y**) through the phosphine group and the ylidic carbon atom to the metal center. Furthermore, palladacycle **C1** was employed as an efficient catalyst in the Mizoroki-Heck coupling reaction of several aryl chlorides and olefins. The coupled products of these reactions were obtained under aerobic conditions in high yields using aqueous DMF as a solvent. Additionally, the antioxidant capacity of the reported compounds with butylated hydroxytoluene (BHT) as standard was evaluated by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging method. Apparently, all synthesized compounds possess strong antioxidant capacity (IC_{50}; 0.584 ± 0.009 to 0.751 ± 0.003 mg/ml).

Keywords: Pallada- and platinacycle; Phosphorus ylide; X-ray structure; Mizoroki-Heck reaction; Antioxidant capacity.

1. Introduction

Stabilized phosphorus ylides are an important class of compounds that have attracted considerable interest because of their value for a variety of industrial, biological and chemical synthetic uses [1-4]. Unsymmetrical α-keto stabilized ylides derived from diphosphines have shown more useful application in organometallic chemistry due to their ambidentate character as ligands [5-9].

Furthermore, they are valuable key intermediates in metal-mediated organic synthesis [10,11]. The coordination behavior of these compounds towards several metal ions has been studied and it was found that phosphorus ylides can coordinate to metal ions in three modes as depicted in Chart 1: monodentate (or unidentate), bidentate (or chelating) and bridging (or bridging bidentate) modes.

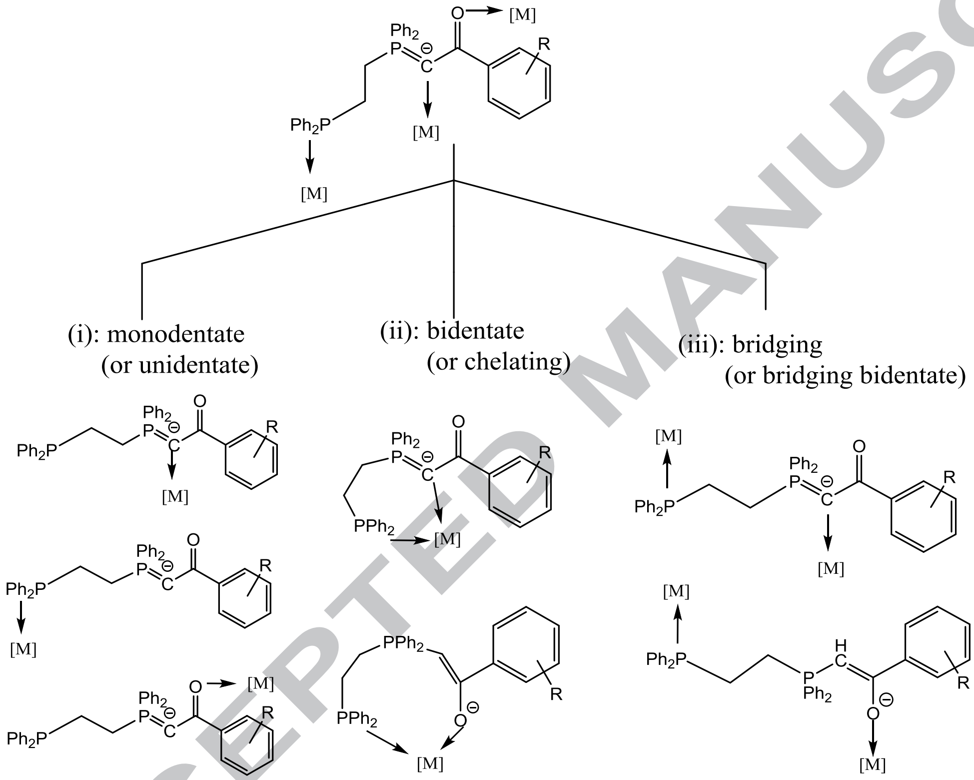


Chart 1. Possible binding modes of phosphorus ylides to the metal M.

When a metal ion such as Hg(II) or Ag(I) interacts only with the free P atom of the diphosphine group, the coordination structure is regarded as monodentate [12,13]. If the coordination of ylide occurs through the Cα atom of the ylidic group, it is categorized in the same above-mentioned coordination mode [14].

However, the ylides can also coordinate to the metal ions through the O atoms of the carbonyl group. A few examples of O-coordinated ylides are known, some of these complexes include a hard and very oxophilic metal center, such as Sn(IV) [15] or group 4 metal ions with a high oxidation number *e.g.* Ti(IV), Zr(IV) or Hf(IV) [16].

The bidentate (or chelating) coordination mode occurs when a metal ion (for example Pd(II) or Cu(I)) interacts with two P and C atoms of the ylidic group to give P, C-chelated complexes [17,18]. Although the P, O-chelated coordination mode is also possible, it has to the best of our knowledge only been observed in the Pd(II) complexes of mixed phosphine–β-ketophosphorus ylides [19]. Finally, the bridging coordination mode is observed when a metal ion binds to one phosphorus ylide through the P atom and another metal ion binds to the Cα or O atom [20]. The investigation of reactivity and coordination chemistry of carbonyl stabilized ylides is an important research field of our group [12-14,17,18]. Recently, we have reported the synthesis of palladium(II) complexes containing such phosphorus ylides [17,21-23]. Now, we aim to expand the scope of these complexes to new platinacycle complexes of bidentate phosphorus ylides.

As known from literature, palladium and platinum compounds might have promising potential antioxidant applications [24-26]. Reactive oxygen or nitrogen species (ROS or RNS), which are formed naturally in cells, have important roles in for example cell signaling. However, high amounts of free radicals are hazardous to the organisms and can damage major cell components, including DNA and RNA, polypeptides chains and phospholipids that play an important role in the development of diseases such as cancer and other disorders [27,28]. Antioxidants such as ascorbic acid may prevent free radical damages in biological systems [29,30]. In recent years, the syntheses of new compounds with antioxidant properties have become very interesting [31-33]. So we devoted this study to illuminate the potential of the reported compounds in free radical scavenging.

Additionally, Pd(II) complexes bearing phosphine groups have been extensively applied as efficient catalysts in cross-coupling reactions [21-23,34-37]. Specifically, the Mizoroki-Heck reaction, which has emerged as the most important and reliable method for construction of functionalized olefins, has been catalyzed with the P, C-chelated Pd(II) complexes of such phosphorus ylides [38-41]. Recently, a variety of catalytic systems for the Mizoroki-Heck coupling reaction has been reported using aqueous media [41-44]. Application of palladacycle complexes of phosphorus ylides as efficient catalysts in Mizoroki-Heck coupling reactions of aryl chlorides under relatively mild experimental conditions is one of the purposes of this work.

We have now focused our attention to the synthesis, spectroscopic (IR and NMR) and X-ray structural characterization of these new pallada- and platinacycle complexes of phosphorus ylide. Furthermore, the antioxidant capacity of these complexes and also the palladium(II) catalyzed Mizoroki-Heck coupling reaction of various aryl chlorides and olefins is reported.

2. Experimental

2.1. Materials and methods

Phosphorus ylide $Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br (**Y**) was prepared based on literature methods [12]. Synthesis of Pd/Pt(II) complexes was carried out under dry nitrogen using standard Schlenk techniques. $[MCl_2(cod)]$ (M = Pd or Pt) complexes were prepared according to previously published procedures [45]. Dichloromethane was used as reagent grade and dried over P_2O_5. Elemental analysis was performed on a Leco, CHNS-932 apparatus. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on BrukerAvance 500 MHz, 400 MHz and 250 MHz and Jeol 90 MHz spectrometers in $CDCl_3$ or DMSO-d_6 as solvents at 25 °C. IR spectra were recorded on KBr pellets using a Shimadzu 435-U04 spectrophotometer in the region of 4000-400 cm^{-1}.

2.2. Crystallography

For the structures of **C1** and **C2**, X-ray intensity data was collected at RT and 100 K, respectively, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and CuKα (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro [46]. Using Olex2 [47], the structures were solved by direct methods using the ShelXS [48] structure solution program and refined by full matrix least-squares on F^2 using the ShelXL [49] program package. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms.

2.3. Synthesis of complexes [$MCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br)] (M = Pd or Pt)

General procedure: to a [MCl_2(cod)] (M = Pd or Pt) (0.5 mmol) dichloromethane solution (5 ml), a solution of ylide **Y** (0.5 mmol) (5 ml, CH_2Cl_2) was added. The resulting solution was stirred for 2 h at room temperature and then concentrated to *ca.* 2 ml under reduced pressure and treated with n-hexane (15 ml) to afford the Pd(II) and Pt(II) complexes of phosphorus ylide.

2.3.1. Data for Pd(II) complex [$PdCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br)] (C1). Yield: 0.323 g (81%). M.p. 208-210 °C (dec.). Anal. Calcd. for $C_{34}H_{29}BrCl_2OP_2Pd$ (%): C, 52.85; H, 3.78. Found: C, 52.93; H, 3.84. IR (KBr

Disk) ν(cm^{-1}): 1625 (CO). ^{1}H NMR (250.13 MHz, DMSO-d$_6$) δ_H (ppm): 3.07–3.84 (br, CH$_2$, 4H merged with residual H_2O); 6.15 (br, CH); 7.03–8.39 (m, 24H, Ph). ^{31}P NMR (36.26 MHz, DMSO-d$_6$) δ_P (ppm): 22.74 (d, PPh$_2$, $^{2}J_{P\text{-}P}$ = 21.76 Hz); 30.93 (bd, PCH, $^{2}J_{P\text{-}P}$ = 23.85 Hz). ^{13}C NMR (62.90 MHz, DMSO-d$_6$) δ_C (ppm): 20.25 (b, CH$_2$); 121.84–140.18 (Ph); 194.58 (s, CO).

2.3.2. Data for Pt(II) complex [PtCl$_2$(Ph$_2$P(CH$_2$)$_2$PPh$_2$C(H)C(O)C$_6$H$_4$-*m*-Br)] (C2). Yield: 0.284 g (75%). M.p. 243-245 °C (dec.). Anal. Calcd. for $C_{34}H_{29}BrCl_2OP_2Pt$ (%): C, 45.76; H, 3.28. Found: C, 47.85; H, 3.38. IR (KBr Disk) ν(cm^{-1}): 1636 (CO). ^{1}H NMR (89.60 MHz, DMSO-d$_6$) δ_H (ppm): 3.01–3.78 (br, CH$_2$, 4H merged with residual H_2O); 6.26 (br, CH); 7.30–8.41 (m, 24H, Ph). ^{31}P NMR (36.26 MHz, DMSO-d$_6$) δ_P (ppm): 6.52 (dd, PPh$_2$, $^{1}J_{Pt\text{-}P}$ = 3952.% Hz, $^{2}J_{P\text{-}P}$ = 13.05 Hz); 20.75 (bdd, PCH, $^{2}J_{Pt\text{-}P}$ = 130.17 Hz, $^{2}J_{P\text{-}P}$ = 23.85 Hz). ^{13}C NMR (62.90 MHz, DMSO-d$_6$) δ_C (ppm): 19.97 (b, CH$_2$); 121.83–140.04 (Ph); 194.73 (s, CO).

2.4. Typical procedure for the Mizoroki-Heck coupling reaction

2.4.1. General procedure: palladacycle **C1** (0.005 mmol), olefin (0.75 mmol), aryl chloride (0.5 mmol), K_2CO_3 (1.0 mmol) and DMF/H_2O (2 ml, 1:1) were added to a small tube and the mixture was heated to 110 °C for 6 h in the presence of air. The reactions were monitored by thin-layer chromatography (TLC). At the end of the cross-coupling reactions, the mixture was cooled, extracted with *n*-hexane:EtOAc (8:2), filtered and purified by recrystallization from ethanol and water or purified by silica gel column chromatography (*n*-hexane:EtOAc, 8:2).

2.4.2. Data for Ph-CH=CH-Ph (3a). M.p. 122-124 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ_H (ppm): 7.10-7.51 (m, 12H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C (ppm): 137.81, 129.16, 128.10, 127.00 [50].

2.4.3. Data for *p*-CH_3O-Ph-CH=CH-Ph (3b). M.p. 132-134 °C. ^{1}H NMR (400.61 MHz, $CDCl_3$) δ_H (ppm): 3.75 (s, 3H, OCH_3), 6.82-7.43 (m, 11H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ_C (ppm): 159.32, 137.66, 130.16, 128.64, 128.22, 127.72, 127.21, 126.63, 126.25, 114.14, 55.34 (s, OCH_3) [51].

2.4.4. Data for *p*-CH_3OC-Ph-CH=CH-Ph (3c). M.p. 141-144 °C. ^{1}H NMR (89.60 MHz, $CDCl_3$) δ_H (ppm): 2.58 (s, 3H), 6.81–8.53 (m, 7H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C (ppm): 196.99 (s,CO), 139.59,135.41, 130.98, 129.77, 129.04, 128.91, 128.82, 128.35, 126.92, 126.61, 27.50 (s, CH_3) [51].

2.4.5. Data for Ph-CH=CHCOOEt (3d). ^{1}H NMR (89.60 MHz, $CDCl_3$) δ_H (ppm): 7.06-8.05 (m, 6H), 6.35 (d, 1H, *J* = 15.03 Hz), 4.09 (q, 2H, *J* = 5.07 Hz), 1.15 (t, 3H, *J* = 5.11 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ_C (ppm): 165.92 (s, CO), 148.40, 141.51, 140.51, 128.52, 124.08, 122.52, 60.92 (s, CH_2), 14.19 (s, CH_3) [52].

2.4.6. Data for *p*-CHO-Ph-CH=CHPh (3e). M.p. 112-114 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ_H (ppm): 7.13-8.03 (m, 11H), 10.06 (s, 1H). ^{13}C NMR (127.77 MHz, $CDCl_3$) δ_C (ppm): 192.71 (s, CO), 138.79, 137.26, 137.14, 132.73, 130.97, 129.79, 129.26, 129.21, 128.58, 127.61, 127.52, 127.12 [53].

The following compounds gave data consistent with those published: (E)-1-methyl-4-styrylbenzene [54], (E)-ethyl-3-(4-formylphenyl)acrylate [55], (E)-ethyl-3-(4-acetylphenyl)acrylate [52], (E)-ethyl-3-(4-methylphenyl)acrylate [56] and (E)-ethyl-3-(4-methoxyphenyl)acrylate [56].

2.5. Antioxidant capacity

Antiradical capacity of the compounds was measured according to Mensor et al. [57]. In order to obtain dilutions, different sample concentrations were prepared in DMSO (0.2 to 1 mg/ml) and 2.5 ml of each concentration was added to 1 ml of a DMSO solution of DPPH (0.3 mM). The samples were first kept in darkness at room temperature for 30 min and then bleaching of DPPH was read at 517 nm. The inhibition in percent for each concentration was calculated according to the following formula:

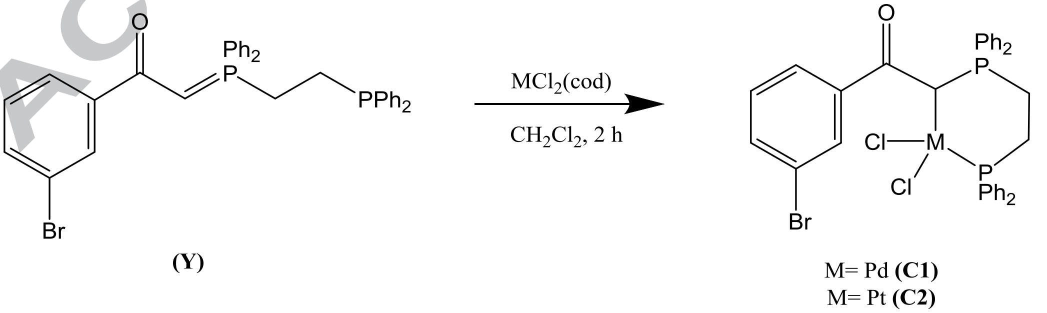
$$\text{Antioxidant capacity (\%)} = [1 - (A_s - A_b)/A_c] \times 100$$

Where, A_s contains 2.5 ml of samples + 1 ml of DPPH, A_b contains 2.5 ml of samples + 1 ml DMSO and A_c contains 1 ml of DPPH + 2.5 ml DMSO. Tests were carried out in triplicate and BHT was used as a positive control. The IC_{50} values, which represent the concentration of the sample that caused 50% inhibition, were calculated from the graph, plotting the inhibition percentage against sample concentration.

3. Results and discussion

3.1. Synthesis

Reaction of ligand **Y** with $[MCl_2(cod)]$ (M = Pd or Pt) in equimolar ratio yielded the new P, C-chelated pallada- and platinacycle complexes $[MCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br)] (M = Pd (**C1**) and Pt (**C2**)) (Scheme 1). All complexes are moderately soluble in dichloromethane and insoluble in non-polar solvents, such as n-hexane.



Scheme 1. Synthesis of pallada and platinacycle complexes **C1** and **C2**.

3.2. Spectroscopy

The structure of the complexes was successfully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopic methods and other conventional techniques such as IR and elemental analysis. Table 1 shows a brief summary of these data.

Table 1. Spectroscopic data for compounds **Y**, **C1** and **C2**

Compound	IR; ν(CO) cm^{-1}	^{1}H NMR; δ(PCH) ppm	^{13}C NMR; δ(CO) ppm	^{31}P NMR; δ(PCH) and (PPh_2) ppm
Y	1571	4.05	183.35	14.47, -15.63
1	1625	6.15	194.58	30.93, 22.74
2	1636	6.26	194.74	20.75, 6.52

Also, the exact structure of the complexes **C1** and **C2** at atomic resolution was unequivocally determined by single crystal X-ray diffraction. The CHN elemental analysis of the pallada- and platinacycle complexes indicated a 1:1 stoichiometry between the MCl_2 (M = Pd or Pt) and the phosphorus ylide.

Coordination of the ylide through the carbon atom (chelating mode) causes an increase in the ν(CO) frequency, while for O-coordination a lower shift for this frequency is expected [58]. The ν(CO), which is sensitive to complexation, occurs at around 1570 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides [59]. The IR absorption bands around 1630 cm^{-1} show a significantly higher frequency shift of ν(CO) than those of phosphorus ylide **Y** (see supplementary data). Thus, the IR data obtained indicates that the chelation of the ylide to Pd(II) and Pt(II) chlorides occurs through the ylidic carbon atom and PPh_2 group [17,20].

The ^{31}P chemical shift values for complexes **C1** and **C2** appear to be shifted downfield with respect to the parent ylide, indicating that coordination of the ylide occurred (Figure 1). The ^{31}P NMR spectrum of complex **C1** exhibits two doublets around 23 and 31 ppm, which can be assigned to the PPh_2 and PCH groups, respectively. Whereas, the ^{31}P NMR spectrum of **C2** shows these peaks around 6 and 21 ppm along with two satellite peaks due to ^{195}Pt-^{31}P coupling.

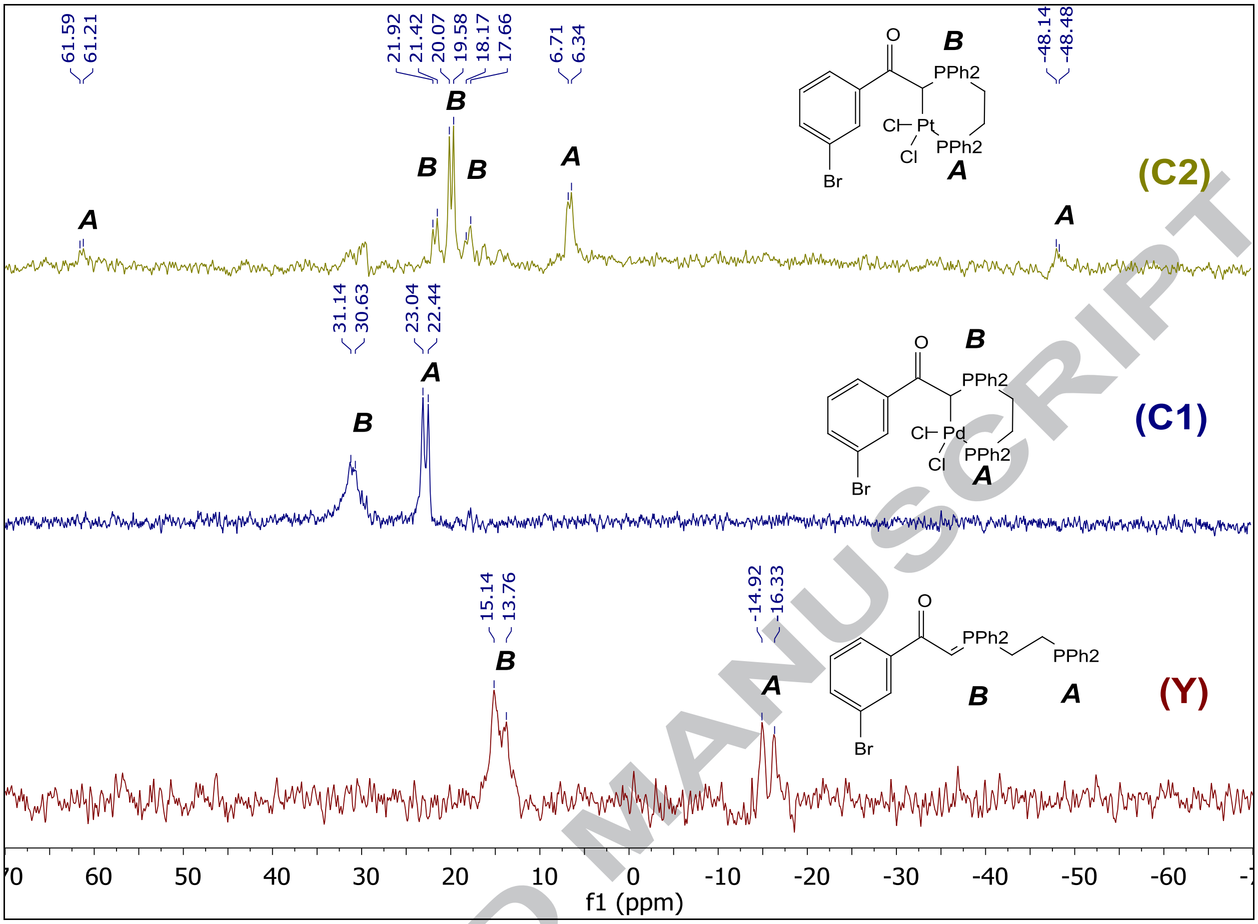


Figure 1. ^{31}P NMR spectra of **Y**, **C1** and **C2**.

Also, the ^{1}H NMR spectra show all the expected resonances of these complexes (see supplementary data). The ^{1}H chemical shift values for complexes **C1** and **C2** appear to be shifted downfield with respect to the parent ylide, as a consequence of the P, C-coordination character of the ylide. Similar behavior was observed earlier in the case of ylide complexes of copper(I) chlorides [18]. It must be noted that O-coordination of the ylides generally leads to the formation of *cis* and *trans* isomers, giving rise to two different signals in the ^{1}H and ^{31}P NMR spectra [60].

The most important aspect of ^{13}C NMR spectra of these complexes is the downfield shift of the signals due to the carbonyl group. The ^{13}C NMR spectra of complexes **1** and **2** show the characteristic peaks of the carbonyl group around 194 ppm, compared to 180 ppm for the same carbon in the parent free ylides, indicating a much lower shielding of the carbon of the CO group in these complexes (see supplementary data). This downfield shift has been previously observed in the series of compounds $[PdCl(\eta^3\text{-}2\text{-}XC_3H_4)(C_6H_5)_3PCHCOR]$ [X = H, CH_3; R = CH_3, C_6H_5] and was attributed to a change in hybridization of the ylidic carbon [61]. Thus, the spectral data clearly indicates the bidentate coordination of the ylides through both the phosphine group and the ylidic carbon atom.

3.3. Crystallography

Crystals, suitable for single-crystal X-ray analysis, of complexes **C1** and **C2** were grown by vapor diffusion of methanol into a DMSO solution. The molecular structures of these complexes are shown in Figure 2 and Figure 3. Relevant data collection and refinement statistics are given in Table 2.

Table 2. Data collection and refinement statistics for **C1** and **C2**

	C1	**C2**
Empirical formula	$(C_{34}H_{29}BrCl_2OP_2Pd)$, 0.75$(CH_2Cl_2)$	$(C_{34}H_{29}BrCl_2OP_2Pt)$, (CH_2Cl_2)
Formula weight (gmol^{-}	836.41	946.34

^{1})		
T (K)	293(2)	100(2)
λ (Å)	1.54184	1.54184
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	11.3709(3)	11.2414(3)
b (Å)	17.1681(5)	17.0630(4)
c (Å)	19.4374(4)	19.2633(4)
α (°)	99.055(2)	99.394(2)
β (°)	97.188(2)	97.003(2)
γ (°)	105.918(2)	106.476(2)
V (Å^3)	3546.50(16)	3440.00(15)
Z	4	4
ρ_{calc} (gcm^{-3})	1.567	1.827
μ (mm^{-1})	9.028	12.952
F(000)	1670	1840
Crystal dimensions (mm^3)	0.12 x 0.09 x 0.08	0.17 x 0.12 x 0.09
2θ_{max} (°)	150.80	151.27
Reflections collected	67184	65323
Independent reflections	14406	13983
Observed reflections [$I_o > 2\sigma (I_o)$]	9836	11768
Parameters refined	739	766
Final R indices [$I_o > 2\sigma (I_o)$]	$R_1 = 0.0590$	$R_1 = 0.0509$
	$\omega R_2 = 0.1473$	$\omega R_2 = 0.1271$
R indices (all data)	$R_1 = 0.0886$	$R_1 = 0.0621$
	$\omega R_2 = 0.1700$	$\omega R_2 = 0.1376$
Goodness-of-fit on F^2	1.041	1.028

The asymmetric unit of the structure of **C1** contains two palladacycle [$PdCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br)] complexes (Figure 2). The two complexes mainly differ in the conformation of the $Ph_2P(CH_2)_2PPh_2$ part and the orientation of the C_6H_4-*m*-Br ring. In fact, the C_6H_4-*m*-Br ring is ~180˚ flipped when comparing these two complexes (see Supplementary Information for a fit of the two complexes). The X-ray analysis unequivocally confirms the P-C chelating mode of coordination of the ligand $Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br to the Pd metal center. The Pd atom is four-coordinated by one P-atom of the phosphine group, one ylidic C-atom and two chlorine atoms, showing a slightly distorted square planar coordination environment. The P-Pd-C, P/C-Pd-Cl and Cl-Pd-Cl angles are in the ranges of 87.75(15)-93.29(15)˚ and 87.29(16)-93.77(16)˚, for the first and second complex, respectively, emphasizing the slightly distorted coordination geometry.

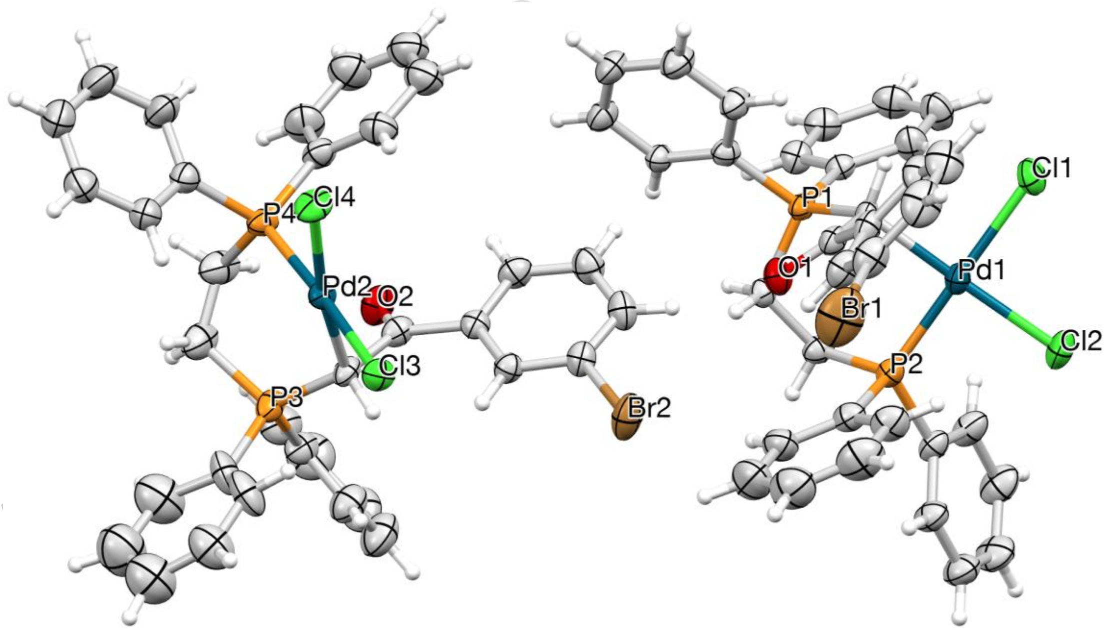


Figure 2. Asymmetric unit of the structure of **C1**, showing thermal displacement ellipsoids at the 30% probability level and labeling scheme of the hetero-atoms.

The Pd-Cl distances in the first complex (2.3824(18) *vs* 2.317(2) Å) and second complex (2.3779(17) *vs* 2.334(2) Å) are significantly different, reflecting a different *trans* effect of the phosphorus and ylidic carbon atoms [62]. The Pd-C(ylide) bond lengths are 2.125(6) and 2.114(6) Å, which are similar to the ones found in other Pd non-symmetric phosphorus ylides and Pd cyclic bis-ylides [62,63]. The Pd-P bond lengths (2.2318(16) and 2.2391(17) Å) are also comparable to analogous distances in dichloro-(1,2-bis(diphenylphosphino)ethane)-Pd(II) complexes [64-66]. The C(1)-C(2) and C(35)-C(36) bond lengths (1.479(10) and 1.480(10) Å) are significantly longer than the corresponding distances in non-coordinating phosphanes, showing that the stabilized resonance structure of the parent ylide is destroyed by the complex formation [67].

The structure of **C2** is isomorphous to that of **C1** and hence the asymmetric unit of the structure of **C2** contains two platinacycle $[PtCl_2(Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4\text{-}m\text{-}Br)]$ complexes (Figure 3). The structure also shows the ~180˚ flipped C_6H_4-*m*-Br ring, when comparing the two complexes (see Supplementary Information for a fit of the two complexes).

The Pt atom is four-coordinated in a similar fashion as for **C1**, showing a slightly distorted square planar coordination environment. Here, the P-Pt-C, P/C-Pt-Cl and Cl-Pt-Cl angles are in the ranges of 86.99(18)-94.35(18)˚ and 86.59(17)-94.29(17)˚, for the first and second complex, respectively.

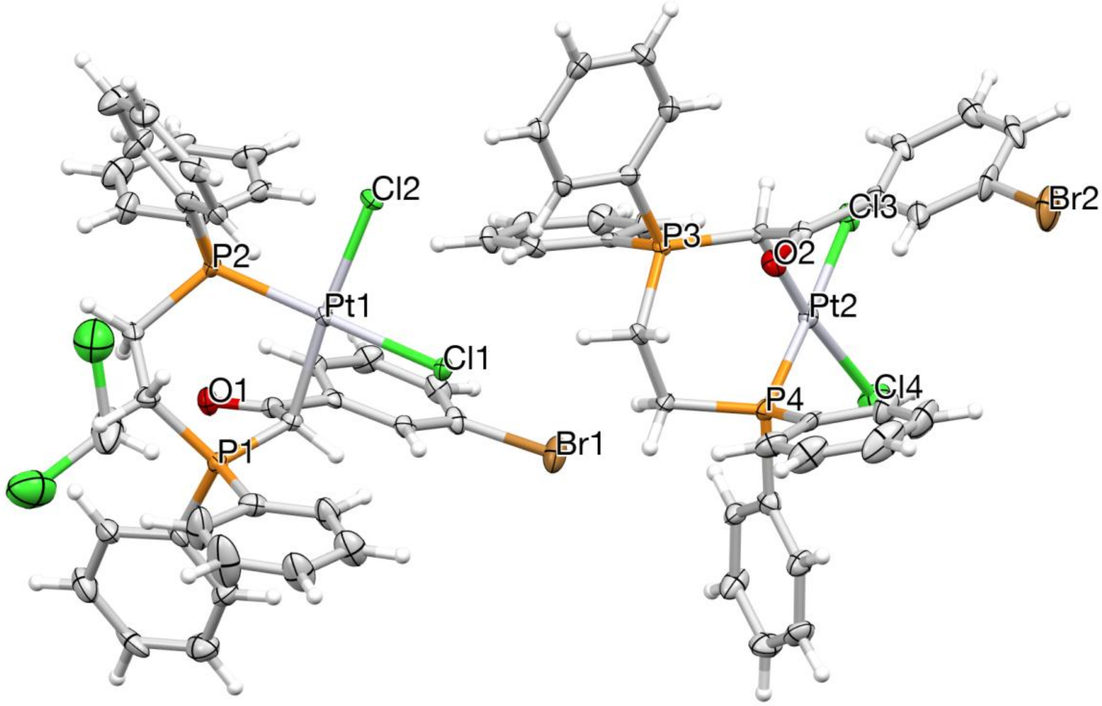


Figure 3. Asymmetric unit of the structure of **C2**, showing thermal displacement ellipsoids at the 50% probability level and labeling scheme of the hetero-atoms.

A similar *trans* effect of the phosphorus and ylidic carbon atoms is observed as in **C1**, with the Pt-Cl distances of 2.3696(16) *vs* 2.3373(17) Å and 2.3779(16) *vs* 2.3262(18) Å, for the first and second complex, respectively. The Pt-C(ylide) bond lengths (2.088(6) and 2.119(6) Å) and Pd-P bond lengths (2.2165(16) and 2.2048(15) Å) are somewhat shorter than the analogous distances with Pd in **C1**.

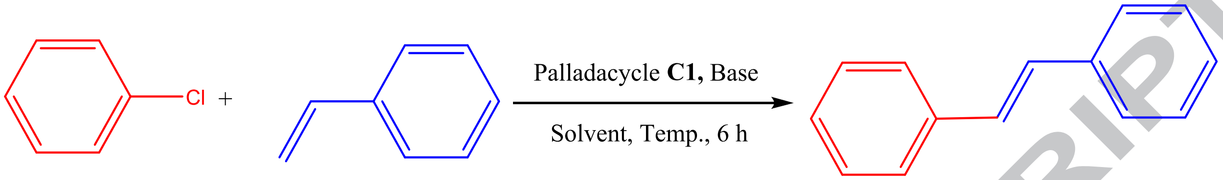
However, when searching the Cambridge Structural Database (CSD, version 5.38, update Feb 2017), no P-C chelates of phosphorus ylides with Pt are found [68].

Analogous to **C1**, the stabilized resonance structure of the parent ylide is destroyed by the complex formation, shown by C(1)-C(2) and C(35)-C(36) bond lengths of 1.500(10) and 1.497(10) Å [67].

3.4. Mizoroki-Heck coupling reaction of aryl chlorides

The catalytic activity of palladacycle **C1** in the Mizoroki-Heck coupling reaction was then examined. Initially, we carried out a model reaction to optimize the reaction conditions including base, solvent, temperature and catalyst loading (Table 3). The reaction of styrene with chlorobenzene in DMF/H_2O (1:1) at 110 °C in the presence of K_3PO_4 (1 mmol) and 0.05 mmol of **C1** as catalyst was chosen as a model reaction, which led to formation of the coupled product in 69% yield (Table 3, entry 1). Subsequently, a series of experiments was performed to find the optimum conditions.

Table 3. Optimizations for the Mizoroki-Heck coupling reaction[a]



Entry	Base	Solvent	Catalyst loading (mmol)	Temp. (°C)	Yield (%)[b]
1	K_3PO_4	DMF/H_2O	0.05	Reflux	69
2	K_2CO_3	DMF/H_2O	0.05	Reflux	79
3	NEt_3	DMF/H_2O	0.05	Reflux	58
4	K_3PO_4	Methanol/H_2O	0.05	Reflux	47
5	K_2CO_3	Methanol/H_2O	0.05	Reflux	50
6	NEt_3	Methanol/H_2O	0.05	Reflux	44
7	K_3PO_4	Toluene/H_2O	0.05	Reflux	51
8	K_2CO_3	Toluene/H_2O	0.05	Reflux	27
9	NEt_3	Toluene/H_2O	0.05	Reflux	38
10	K_2CO_3	H_2O	0.05	Reflux	41
11	K_2CO_3	DMF	0.05	Reflux	58
12	K_2CO_3	DMF/H_2O	0.005	Reflux	76
13	K_2CO_3	DMF/H_2O	0.0005	Reflux	32
14	K_2CO_3	DMF/H_2O	0.1	Reflux	88
15	K_2CO_3	DMF/H_2O	0.005	65	53
16	K_2CO_3	DMF/H_2O	0.005	25	36

[a] Reaction conditions for Mizoroki-Heck coupling reaction: chlorobenzene (0.5 mmol), styrene (0.75 mmol), base (1 mmol), solvent (2 ml), catalyst **C1**, in air.
[b] Isolated yield.

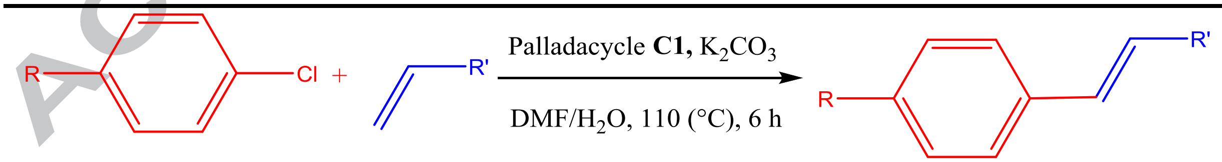
At the first stage of optimization, we studied the effect of base and solvent on the reaction. Since the solubility and basicity of the base strongly depend on the solvent used, these two parameters are closely connected. This optimization was done with commonly used bases and solvents, including organic and inorganic bases and aqueous protic and aprotic solvents. Coupling reactions carried out in the presence of K_2CO_3 and K_3PO_4 give the desired coupling product in moderate to high yields (Table 3, entries 2, 5 and 1, 4). However, the reactions in the presence of NEt_3 did not proceed efficiently even after prolonged stirring at reflux temperature of the solvents, probably due to the low solubility of this organic base in aqueous solvents (Table 3, entries 6 and 9). Among the tested aqueous solvents, DMF/H_2O gave higher yields of coupled product. Also, the reactions in water and non-aqueous DMF led to lower yields, indicating the important role of the solubility of the base in such catalytic systems (Table 3, entries 10 and 11).

Next, we investigated the effect of catalyst loading on the reaction. As expected, varying the catalyst loading has a significant effect on the performance of the catalyst. When the loading of palladacycle **C1** decreased to 0.005 mmol, the coupling reaction gave slightly lower product yield and the reaction resulted in negligible yield of coupled product when the catalyst loading decreased to 0.0005 mmol (Table 3, entries 12 and 13). Also, an excessive amount of catalyst did not increase the yield significantly (Table 3, entry 14). Therefore, with respect to the economic aspect, 0.005 mmol of catalyst was chosen as the best catalyst loading.

Finally, the reactions were carried out at different temperatures. Decreasing the temperature of the reactions led to a decrease of the yields and inherent increase of the reaction time for completion of the reactions (Table 3, entries 15 and 16). Thus, the optimum condition obtained for the Mizoroki-Heck coupling reaction consisted of DMF/H_2O as solvent, K_2CO_3 as base, 0.005 mmol of palladacycle **C1** as catalyst and reaction at reflux temperature (110 °C) for 6 h.

Using the optimized reaction conditions, palladacycle **C1** was applied in the reaction of various functionalized aryl chlorides bearing both electron-donating to electron-withdrawing groups with styrene. Aryl chlorides were converted into the corresponding coupled products in high yields (Table 4). Conversely, increasing electron density on the aryl chlorides lowered the catalyst activity. That is, high yields are achieved when styrene reacted with aryl chlorides bearing electron-withdrawing substituent -CHO and -$COCH_3$ (Table 4, entries 1 and 2). Deactivated aryl chlorides 4-chlorotoluene and 4-chloroanisol gave lower yields indicating that the reaction was sensitive to the electron density on the aryl chlorides (Table 4, entries 4 and 5). The reaction of electronically neutral chlorobenzene with styrene also produced good amounts of the product (Table 4, entry 3).

Table 4. Mizoroki-Heck coupling reaction of aryl chlorides catalyzed by palladacycle **C1**[a.]



Entry	R	R'	Product	Yield (%)[b]
1	CHO	Ph	*p*-OHC-Ph-CH=CHPh **(3e)**	85
2	$COCH_3$	Ph	*p*-CH_3OC-Ph-CH=CHPh **(3c)**	80
3	H	Ph	Ph-CH=CHPh **(3a)**	73

4	Me	Ph	*p*-Me-Ph-CH=CHPh	67
5	OCH_3	Ph	*p*-CH_3O-Ph-CH=CHPh **(3b)**	63
6	CHO	EtOOC	*p*-OHC-Ph-CH=CHCOOEt	88
7	$COCH_3$	EtOOC	*p*-CH_3OC-Ph-CH=CHCOOEt	82
8	H	EtOOC	Ph-CH=CHCOOEt **(3d)**	79
9	Me	EtOOC	*p*-Me-Ph-CH=CHCOOEt	74
10	OCH_3	EtOOC	*p*-CH_3O-Ph-CH=CHCOOEt	66

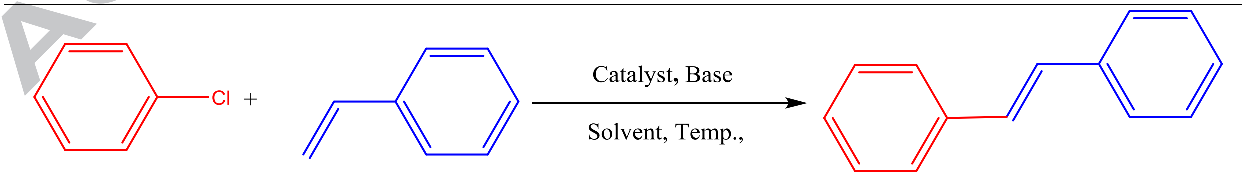
[a] Reaction conditions for Mizoroki-Heck coupling reaction: aryl chloride (0.5 mmol), olefin (0.75 mmol), K_2CO_3 (1 mmol), DMF/H_2O (2 ml), catalyst **C1** (0.005 mmol), in air.
[b] Isolated yield.

To extend the scope of our work, we next investigated the coupling reaction of aryl chloride substrates with the more reactive olefin, ethyl acrylate. As expected, an electron-withdrawing substituent on the olefin has an increasing effect on the yield of the reaction (Table 4, entries 6-10). However, the coupling reaction of deactivated aryl chlorides such as 4-chloroanisole gave the coupled acrylate derivatives in lower yields (Table 4, entry 10).

To evaluate the homogeneous or heterogeneous nature of the active species, we carried out the mercury drop test [69]. Since mercury leads to amalgamation of the surface of a heterogeneous catalyst, and in contrast, Hg(0) is not expected to have a poisoning effect on homogeneous palladium complexes, the results of this test can aid in determining the nature of the active species [70]. Addition of a drop of mercury to the reaction mixture at t = 0 did not affect the conversion of the reaction, which suggests that amalgamation had not occurred and the catalysis was homogeneous in nature.

As can be noticed in Table 4, by using aryl chlorides, good amounts of stilbene and acrylate derivatives are yielded. The higher C–Cl bond dissociation energy compared with C–Br and C–I bonds disfavors the oxidative addition step in catalytic coupling reactions [71]. However, the ideal substrates for coupling reactions are aryl chlorides, since they are cheaper and more widely available than their bromide or iodide analogues. Table 5 shows a comparison between the efficiency of this catalytic system in the Mizoroki-Heck coupling reaction of aryl chlorides and the other catalytic systems. The results of this comparison showed that the reported catalysts in literature need to be used in high loadings and showed lower activity with aryl chloride substrates [72-75]. From an industrial point of view, the low catalyst loading and short reaction time make this palladacycle an ideal catalyst for the Mizoroki-Heck coupling reaction.

Table 5. Comparison of Mizoroki-Heck coupling reactions of chlorobenzene and styrene using palladacycle **C1** and other catalytic systems



Entry	Pd source	Catalyst loading (mmol)	Condition	Yield (%)	Ref.

1	imidazole-based secondary phosphine oxide ligated Pd(II)	0.02	K_2CO_3, DMF, 60 °C, 12 h	62	[57]
2	poly(N,N-dipyrid-2-yl-endo-norborn-2-ene-5-carbamide) based Pd(II)	0.007	K_2CO_3, DMAc/TBAB, 140 °C, 90 h	89	[58]
3	2,6-bis (diphenylphosphino) pyridine/Pd(II)	0.001	K_2CO_3, DMAc/TBAB, 135 °C, 5 h	57	[59]
4	Polymer-Anchored Schiff Base Pd(II)	0.005	K_2CO_3, DMF, 100 °C, 24 h	12	[60]
5	P, C-chelated phosphorus ylide Pd(II)	0.005	K_2CO_3, DMF/H_2O, 110 °C, 6 h	73	This work

3.5. Antioxidant capacity

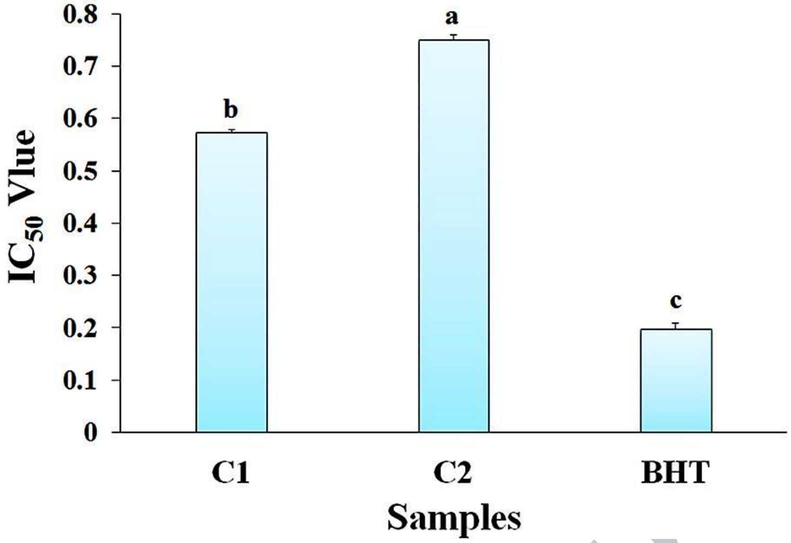
In the present study, the antioxidant capacity of the new compounds was determined (Table 6 and Figure 4). Antioxidant enzymes and compounds act as a health-protection factor in the human body and scientific evidence suggests that these factors are very important due to their role in reducing the risk of diseases such as cancer [27]. Our results showed that most of the synthesized compounds showed good dose-dependent (0.2-1 mg/ml) antiradical properties (33.25 to 69.11%), (Table 6). Antioxidant capacity is reflected in a lower IC_{50} value. BHT as a synthetic antioxidant represented a lower IC_{50} value (IC_{50}; 0.199 ± 0.006 mg/ml) than those of the two compounds studied here (IC_{50}; 0.584 ± 0.009 to 0.751 ± 0.003 mg/ml), (Figure 4).

Table 6. DPPH radical scavenging capacity (%) of new compounds and BHT as standard.

Conc.(mg/ml)	**C1**	**C2**	**BHT**
0.2	33.25 ± 0.9^a	42.42 ± 2.1^a	50.21 ± 1.3^a
0.4	37.11 ± 2.0^a	51.14 ± 0.6^b	68.16 ± 1.2^b
0.6	52.23 ± 1.3^b	48.29 ± 1.4^b	71.23 ± 2.2^b
0.8	55.27 ± 0.6^b	53.21 ± 0.6^b	70.65 ± 0.7^b
1	69.11 ± 2.3^c	58.43 ± 2.5^c	74.39 ± 2.3^b
Average	49.39	50.70	66.93

Experiment was performed in triplicate and expressed as mean ± SD. Values within column with different superscripts are significantly different ($P < 0.05$).

Figure 4. Comparison of DPPH radical scavenging ability (IC_{50} value) of the studied cumarins and BHT as a positive control.



4. Conclusions

In summary, we report the synthesis and full characterization of new pallada- and platinacycles **C1** and **C2**. On the basis of the spectroscopic data, we propose that ligand **Y** employed herein exhibits P, C-coordination behavior to the metal centers. Furthermore, this coordination fashion has been confirmed by single crystal X-ray diffraction experiments. The results show that chelation of ylide through the ylidic carbon atom and phosphine group affords a six-membered ring. Furthermore, the catalytic activity of palladacycle **C1** towards the Mizoroki-Heck coupling reaction was investigated. The results show that the coupling reactions of various aryl chlorides with olefins proceed in high yields. Additionally, our study clearly demonstrates that the new compounds exhibit biological properties (as antioxidant agents) and could be useful in the development of novel therapeutic agents.

Supplementary material

Physical measurements and selected ^{31}P, ^{13}C and ^{1}H NMR spectra of some compounds can be found in the online version.

CCDC 1514248-1514249 contain the supplementary crystallographic data for complexes **C1** and **C2**. 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).

Acknowledgements

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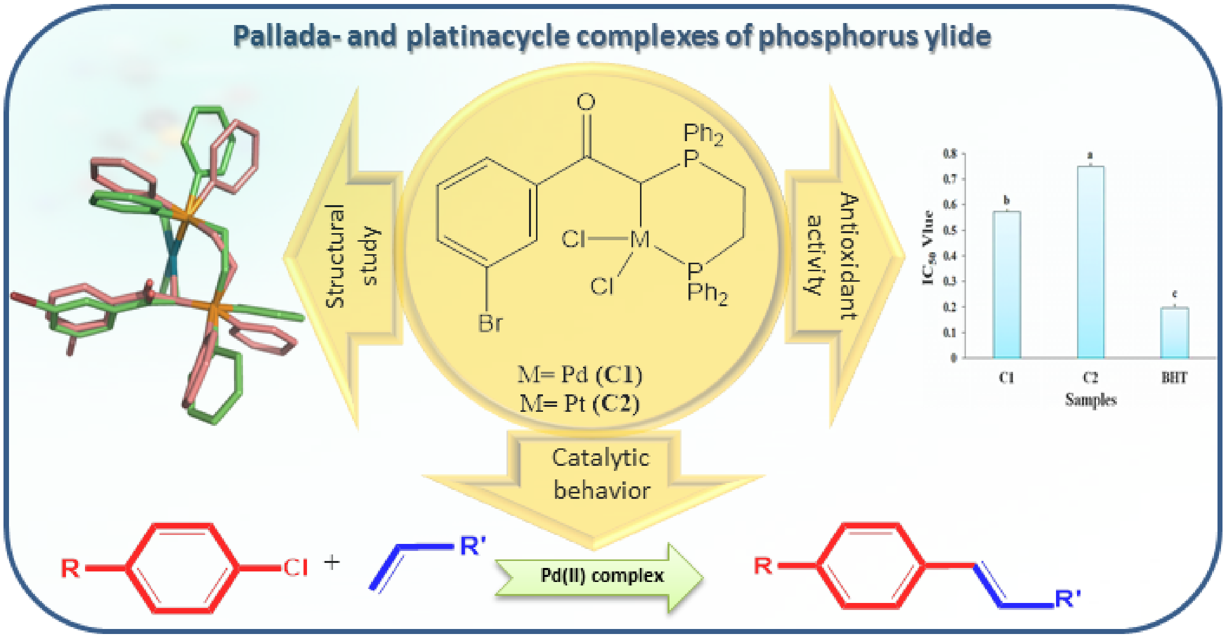
Graphical abstract-pictogram

New pallada- and platinacycle complexes of phosphorus ylide: synthesis, structural characterization, antioxidant capacity and catalytic behavior towards Mizoroki-Heck reactions

Seyyed Javad Sabounchei[a*], Ali Hashemi[a], Abed Yousefi[a], Parviz Gohari Derakhshandeh[b], Roya Karamian[c], Mostafa Asadbegy[c], Kristof Van Hecke[b*]



lGraphical abstract-synopsis

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[*] Corresponding author. E–mail address: jsabounchei@yahoo.co.uk; kristof.vanhecke@ugent.be.

New pallada- and platinacycle complexes of phosphorus ylide: synthesis, structural characterization, antioxidant capacity and catalytic behavior towards Mizoroki-Heck reactions

Seyyed Javad Sabounchei[a*], Ali Hashemi[a], Abed Yousefi[a], Parviz Gohari Derakhshandeh[b], Roya Karamian[c], Mostafa Asadbegy[c], Kristof Van Hecke[b*]

Novel pallada- and platinacycle complexes are reported, based on the reaction of phosphorus ylide $Ph_2P(CH_2)_2PPh_2C(H)C(O)C_6H_4$-*m*-Br with $[MCl_2(cod)]$ (M = Pd or Pt; cod = 1,5-cyclooctadiene). The structures were characterized spectroscopically and crystallographically. The palladacycle was employed as an efficient catalyst in Mizoroki-Heck coupling reactions of aryl chlorides and olefins, while both complexes possess strong antioxidant capacity.

Graphical abstract

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[*] Corresponding author. E–mail address: jsabounchei@yahoo.co.uk; kristof.vanhecke@ugent.be.