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Allyl functionalized phosphinite and phosphonite ligands: Synthesis, transition metal chemistry and orthopalladation reactions

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Abstract. Allyl functionalized phosphinite $PPh_2(OAr)$ [Ar = C_6H_4(*o*-C_3H_5)] (**1**) and phosphonite $PPh(OAr)_2$ (**2**) ligands were prepared by the reactions of 2-allylphenol with PPh_2Cl and $PPhCl_2$, respectively. The ruthenium(II) complexes, [Ru(η^6-*p*-cymene)($PPh_2(OAr)$)Cl_2] (**3**) and [Ru(η^6-*p*-cymene)($PPh(OAr)_2Cl_2$)] (**4**) were obtained by reacting **1** or **2** with [Ru(η^6-*p*-cymene)Cl_2]$_2$ in 2:1 molar ratios, respectively. Reactions of **1** or **2** with $AuCl(SMe_2)$ gave [Au{$PPh_2(OAr)$}Cl] (**5**) or [Au{$PPh(OAr)_2$}Cl] (**6**) in good yield. The palladium complex, [Pd{$PPh(OAr)_2$}$_2Cl_2$] (**7**) was prepared by reacting $Pd(COD)Cl_2$ with **2** in 1:2 molar ratio. The reaction between $Pd(COD)Cl_2$ and **1** yielded a mixture of orthopalladated *cis*- and *trans*-[$Pd(Ph_2P(OAr))Cl]_2$ (**8a** and **8b**). The treatment of **8** with PPh_3 and $Ph_2PCH_2PPh_2$ resulted in the cleavage of chloro bridge to give respectively, [Ph_2(OAr)PPd(PPh_3)Cl] (**9**) and [Ph_2(ArO)PPd(η^2-dppm)]OTf (**10**). Single crystal X-ray structure of the ruthenium complex **3** is described.

Keywords. Phosphonites; palladium(II); orthopalladation; orthometallation; metal complexes; gold(I) and ruthenium(II) complexes.

1. Introduction

Phosphinite-metal complexes have become the most popular catalysts for several organic transformations because of their catalytic potential, easier synthetic methods and versatile coordination behaviour.[1] Orthopalladated phosphinite complexes attracted much attention because of their excellent activity in C–C and C–N couplings reactions.[2,3] Several methods have been employed for the preparation of palladacycles, the preeminent ones being, the C–H bond activation, oxidative addition of C–X or C–C bonds, transmetallation and addition of unsaturated bonds. The formation of palladacycles from phosphinite ligands is facile. The palladacycles contain carbon–palladium bond formed by an aromatic C–H activation (*ortho*-activation).[4] The majority of palladacycles contain one σ (Pd–C_{sp2}) bond and a coordinate bond via donor atom to form five- or six-membered metallacycles. Stable palladacycles usually contain five-membered rings. Larger rings are less stable as they often facilitate reductive elimination.[5] In this paper, we describe the synthesis, transition metal chemistry and orthopalladation reactions of olefin functionalized phosphinite and phosphonite ligands.

2. Experimental

All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.[6] [$Pd(COD)Cl_2$],[7] [Ru(η^6-cymene)Cl_2]$_2$,[8] and [$AuCl(SMe_2)$][9] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. The ^{1}H NMR and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded in Bruker AV 400 spectrometer operating at 400 and 162 MHz, respectively. TMS and 85% H_3PO_4 were used as internal and external standard for ^{1}H and ^{31}P{^{1}H} NMR, respectively. All the spectra were recorded in $CDCl_3$ solutions with $CDCl_3$ as internal lock; positive shifts lie downfield of the standard in all of the cases. The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. Mass spectra were recorded using Waters Q-Tof micro (YA-105).

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The melting points were observed in capillary tubes and are uncorrected.

2.1 *Synthesis of $PPh_2(OAr)$ [$Ar = C_6H_4(o\text{-}C_3H_5)$]* (**1**)

A solution of chlorodiphenylphosphine (1.4 mL 1.72 g, 7.68 mmol) in diethyl ether (20 mL) was added drop-wise to a mixture of 2-allylphenol (1 mL, 1.03 g, 7.68 mmol) and triethylamine (1.1 mL, 0.8 g, 7.8 mmol) also in diethyl ether (20 mL) under constant stirring at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The amine hydrochloride salt thus formed was filtered through a frit containing celite. All volatiles were removed under vacuum to give **1** as a colourless liquid. Yield: 90% (2.2 g). ^{1}H NMR (400 MHz, $CDCl_3$): 7.62–6.94 (m, ArH, 14H), 5.96 (m, CH, 1H), 4.90 (m, CH_2, 2H), δ 3.41 (d, $^3J_{HH}$ = 6.1 Hz, CH_2, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 107.9 (s). MS (EI): m/z = 319.2 (M+1).

2.2 *Synthesis of $PPh(OAr)_2$* (**2**)

To a stirred solution of dichlorophenylphosphine (1.03 mL, 1.34 g, 7.6 mmol) in diethyl ether, (20 mL) was added drop-wise to a mixture of 2-allylphenol (2 mL, 2.06 g, 15.3 mmol) and triethylamine (2.2 mL, 1.61 g, 16 mmol) in the same solvent (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirring was continued for another 12 h. The amine hydrochloride formed was filtered through a frit containing celite, all volatiles were removed under reduced pressure to give **2** as a colourless liquid. Yield: 95% (5.4 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–6.99 (m, ArH, 13H), 5.88 (m, CH, 2H), 4.96 (m, CH_2, 4H), 3.34 (m, CH_2, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 158.4 (s).

2.3 *Synthesis of Ru(η^6-p-cymene){$PPh_2(OAr)$}Cl_2* (**3**)

A solution of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.036 g, 0.058 mmol) in dichloromethane (10 mL) was added drop-wise to a solution of $PPh_2(OAr)$ (0.037 g, 0.116 mmol) in the same solvent (5 mL) at room temperature. The clear red coloured solution thus obtained was stirred for 4 h. The solvent was removed under reduced pressure and the product was washed with pet ether to give **3** as a red crystalline solid. Yield: 87% (0.065 g). Mp: 145 °C (dec). Anal. Calcd for $C_{31}H_{33}Cl_2OPRu$: C, 59.62; H, 5.33. Found: C, 59.64; H, 5.11. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.02 (m, ArH, 14H), 6.27 (m, CH, 1H), 5.22 (m, CH_2, 2H), 3.80 (d, $^3J_{HH}$ = 6.2 Hz, CH_2, 2H), 2.51 (m, CH, 1H), 1.58 (s, CH_3, 3H), 0.70 (d, $^3J_{HH}$ = 7 Hz, CH_3, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 113.6 (s). MS (EI): m/z = 589.2 (M-Cl).

2.4 *Synthesis of [Ru(η^6-p-cymene)Cl_2{$PPh(OAr)_2$}]$_2$* (**4**)

This was synthesized by a procedure similar to that of **3**, using **2** (0.04 g, 0.108 mmol) and [Ru(η^6-*p*-cymene)Cl_2] (0.033 g, 0.054 mmol). Yield: 83% (0.064 g). Mp: 180–184 °C. Anal. Calcd for $C_{34}H_{37}Cl_2O_2PRu$: C, 60.00; H, 5.48. Found: C, 59.20; H, 5.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.03 (m, ArH, 13H), 6.03 (m, CH, 2H), 5.41 (d, $^3J_{HH}$ = 6.4 Hz, CH_2, 2H), 5.25 (d, $^3J_{HH}$ = 6.4 Hz, CH_2, 2H), 5.16–5.10 (m, CH_2, 4H), 3.65 (m, CH_2, 4H), 2.73 (m, $^3J_{HH}$ = 7 Hz, CH, 1H), 1.74 (s, CH_3, 3H), 1.02 (d, $^3J_{HH}$ = 7 Hz, CH_3, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 141.6 (s). MS (EI): m/z = 644.8 (M-Cl).

2.5 *Synthesis of Au{$PPh_2(OAr)$}Cl* (**5**)

A solution of AuCl(SMe_2) (0.028 g, 0.093 mmol) in dichloromethane (10 mL) was added drop-wise to a solution of **1** (0.03 g, 0.093 mmol) also in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 4 h, with minimum exposure to light. Then the solvent was removed under reduced pressure and product was isolated as a white solid. Yield: 85% (0.056 g). Mp: 172–174 °C. Anal. Calcd for $C_{21}H_{19}AuClOP$: C, 45.80; H, 3.48. Found: C, 45.36; H, 3.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02–7.71 (m, ArH, 14H), 5.96 (m, CH, 1H), 4.97 (m, CH_2, 2H), 3.42 (d, $^3J_{HH}$ = 6.1 Hz, CH_2, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 111.2 (s).

2.6 *Synthesis of Au{$PPh(OAr)_2$}Cl* (**6**)

This was synthesized by a procedure similar to that of **5**, using **2** (0.04 g, 0.1068 mmol) and AuCl(SMe_2) (0.0315 g, 0.1068 mmol). Yield: 79% (0.051 g). Mp: 168 °C (dec). Anal. Calcd for $C_{24}H_{23}AuClO_2P$: C, 47.50; H, 3.82. Found: C, 48.09; H, 2.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.18 (m, ArH, 13H), 5.79 (m, CH, 2H), 4.96 (m, CH_2, 4H), 3.31 (m, CH_2, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 135.1 (s).

2.7 *Synthesis of [Pd{$PPh(OAr)_2$}$_2Cl_2$]* (**7**)

A solution of [Pd(COD)Cl_2] (0.013 g, 0.046 mmol) in dichloromethane (10 mL) was added drop-wise to

solution of **2** (0.035 g, 0.92 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for 4 h. The solvent was removed under vacuum, to get the product as a pale yellow solid. Yield: 91% (0.039 g). Mp: 156–160 °C, Anal. Calcd for $C_{48}H_{46}Cl_2O_4P_2Pd$: C, 62.25; H, 5.01. Found: C, 61.21; H, 4.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.09 (m, ArH, 26H), 5.63 (m, CH, 2H), 4.86 (m, CH_2, 4H), 3.19 (d, $^3J_{HH} = 6.1$ Hz, CH_2, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 118.9 (s).

2.8 *Synthesis of [Pd{PPh$_2$(OAr)}Cl]$_2$* (**8a** *and* **8b**)

A solution of [Pd(COD)Cl_2] (0.152 g, 0.534 mmol) in toluene (20 mL) was added to solution of PPh_2(OAr) (**1**) (0.17 g, 0.536 mmol) also in toluene (20 mL), and the solution was refluxed for 12 h. The reaction mixture was allowed to cool to room temperature and filtered through celite. The solvent was removed under *vacuo* to give **8** as a yellow coloured solid. Yield: 80% (0.2 g). Mp: 157–162 °C. Anal. Calcd for $C_{42}H_{36}Cl_2O_2P_2Pd$: C, 54.93; H, 3.95. Found: C, 55.77; H, 2.95. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–6.93 (m, ArH, 26H), 5.96 (m, CH, 2H), 5.44 (m, CH_2, 4H), 3.30 (m, CH_2, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 151.9 (s) and 151.1 (s). MS (EI): $m/z = 882.6$ (M-Cl).

2.9 *Synthesis of [Ph$_2$(OAr)PPd(PPh$_3$)Cl]* (**9a** *and* **9b**)

A solution of PPh_3 (0.025 g, 0.096 mmol) in toluene (5 mL) was added to a solution of **8a** and **8b** (0.041 g, 0.048 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure to give **9** as a yellow solid. Yield: 82% (0.057 g). Mp: 159 °C (dec). Anal. Calcd for $C_{39}H_{33}ClOP_2Pd$: C, 64.92; H, 4.61. Found: C, 65.59; H, 5.18. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–6.93 (m, ArH, 28H), 5.89 (m, CH, 1H), 5.38 (m, CH_2, 2H), 3.37 (m, CH_2, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 156.2 (d, $^2J_{PP} = 29$ Hz), 17.4 (d, $^2J_{PP} = 29$ Hz) and 146.6 (d, $^2J_{PP} = 439$ Hz), 30.8 (d, $^2J_{PP} = 439$ Hz). MS (EI): $m/z = 685.1$ (M-Cl).

2.10 *Synthesis of [Ph$_2$P{OC$_6$H$_3$(C$_3$H$_5$)-o}Pd(η^2-dppm)] OTf* (**10**)

A solution of [{PPh_2(OAr)}PdCl]$_2$(**8**)(0.042 g, 0.045 mmol) in tetrahydrofuran (10 mL) was added drop-wise to a solution of *bis*(diphenylphosphino) methane (dppm) (0.035 g, 0.091 mmol) and AgOTf (0.026 g, 0.1 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for 4 h, then filtered through celite and the solvent was removed under reduced pressure to give **10** as yellow solid. Yield: 80% (0.074 g). Mp: 127–130 °C. Anal. Calcd for $C_{47}H_{40}F_3O_4P_3PdS$: C, 58.97; H, 4.21. Found: C, 59.13; H, 4.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–6.66 (m, ArH, 33H), 5.98 (m, CH, 1H), 4.65 (m, CH_2, 2H), 3.19 (m, CH_2, 2H), 1.36 (d, $^2J_{PH} = 7$ Hz, CH_2, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ149.7 (dd, $^2J_{PP} = 385$ Hz, 18 Hz), -20.8 (dd, $^2J_{PP} = 385$ Hz, 63 Hz) and -25.7 (dd, $^2J_{PP} = 63$ Hz, 18 Hz). MS (EI): $m/z = 806.7$ (M-OTf).

2.11 *X-ray crystallography*

Single crystal X-ray structural study was performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instrument with low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo–K_α radiation ($\gamma_\alpha = 0.71073$ Å). The strategy for the data collection was evaluated by using the CRYSALISPRO CCD software. The data were collected by the standard 'phi-omega scan' techniques and were scaled and reduced

Table 1. Crystallographic data for complex **3.**

Empirical formula	$C_{31}H_{33}Cl_2OPRu.CHCl_3$
Fw	743.88
crystal system	Triclinic
space group	P1
a, Å	10.3415(3)
b, Å	10.4132(4)
c, Å	15.9431(5)
α, deg	87.380(3)
β, deg	80.473(2)
γ, deg	76.999(3)
V, Å^3	1649.74(9)
Z	2
$\rho_{calc.}$ gm^{-3}	1.498
μ (MoKα), mm^{-1}	0.953
F(000)	756
crystal size, mm	0.23 × 0.17 × 0.14
T (K)	150(2)
2θ range, (°)	3.30–25.00
total no. reflns	12084
no.of indep reflns	5799 [R_{int} 0.0220]
GOF (F^2)	1.128
R_1^a	0.0367
wR_2^b	0.1091

[a]$R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, [b]$R_w = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

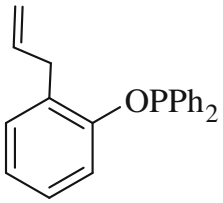
using CRYSALISPRO RED software. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97,[10] refining on F^2. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2*U eq of their parent atoms. Crystallographic data and other experimental details are summarized in table 1 and bond parameters are listed in table 2.

Table 2. Selected bond distances (Å) and bond angles (°) for **3.**

Bond distances (Å)		Bond angles (°)	
Ru1–Cl1	2.4126(8)	Cl1–Ru1–Cl2	87.58(3)
Ru1–Cl2	2.4112(8)	Cl1–Ru1–P1	88.16(3)
Ru1–P1	2.3120(8)	Cl2–Ru1–P1	91.14(3)
P1–C26	1.818(3)	O1–P1–C26	103.68(14)
P1–O1	1.627(2)		

3. Results and discussion

The reaction of chlorodiphenylphosphine with 2-allylphenol in 1:1 molar ratio at 0 °C, in the presence of triethylamine leads to the formation of $Ph_2P(OAr)$ [Ar = $C_6H_4(o\text{-}C_3H_5)$] (**1**). A similar reaction of dichlorophenylphosphine with 2-allylphenol in 1:2 molar ratio gave $PhP(OAr)_2$ (**2**), in good yield. The compounds **1** and **2** are air and moisture sensitive viscous liquids. The ^{31}P NMR spectra of **1** and **2** consist of single resonances at 107.8 ppm and 158.4 ppm, respectively. ^1H NMR spectra of **1** and **2** show multiplets around 3.4 and 6.9 ppm for allylic CH_2 and CH protons, respectively. Mass spectrum of **1** shows a molecular ion peak at 319.2 corresponding to M+1 ion.



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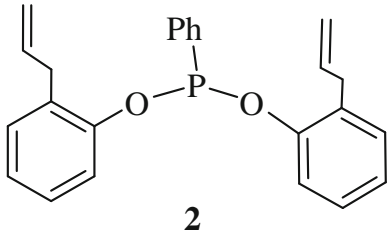
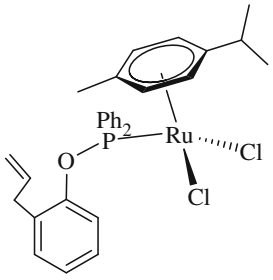


2

The slow addition of dichloromethane solution of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ to **1** or **2** in 1:2 molar ratio at room temperature afforded $[Ru\{PPh_2(OAr)\}(\eta^6\text{-}p\text{-cymene})Cl_2]$ (**3**) and $[Ru\{PPh(OAr)_2\}(\eta^6\text{-}p\text{-cymene})Cl_2]$ (**4**), respectively. The ^{31}P NMR spectrum of **3** shows a singlet at 113.6 ppm, whereas that of **4** appeared at 141.5 ppm. The ^1H NMR spectra of both the complexes are almost identical with the ligands, except peaks due to the *p*-cymene moiety. Mass spectra of **3** and **4** show peaks correspond to M-Cl ions at m/z 589.2 and 644.8, respectively. The structure of **3** was confirmed by a single crystal X-ray diffraction study.



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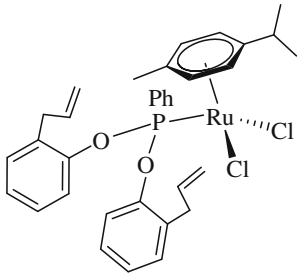
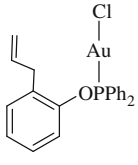


4

The treatment of $AuCl(SMe_2)$ with **1** or **2** in dichloromethane at room temperature resulted in the formation of $[Au\{PPh_2(OAr)\}Cl]$ (**5**) and $[Au\{PPh(OAr)_2\}Cl]$ (**6**). The ^{31}P NMR spectra of complexes **5** and **6** consist of single resonances, respectively, at 111.2 ppm and 135.1 ppm. The reaction between $Pd(COD)Cl_2$ and **2** affords $Pd\{PPh(OAr)_2\}_2Cl_2$ (**7**). The ^{31}P NMR spectrum of compound **7** shows a sharp singlet at 118.8 ppm. The ^1H NMR and elemental analyses data are in accordance with the proposed structures.



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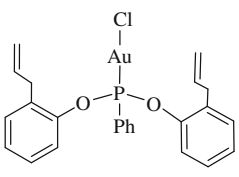

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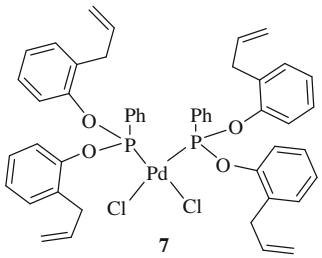

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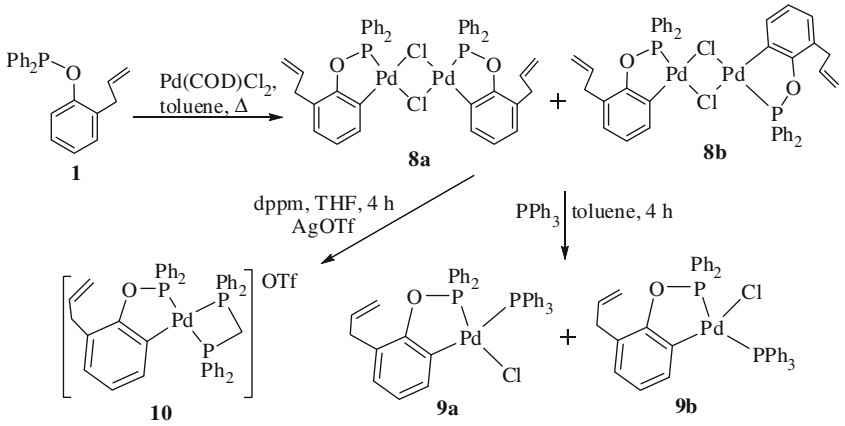

Scheme 1. Orthopalladation reaction of ligand **1**.

The reaction of $Pd(COD)Cl_2$ with $Ph_2P(OAr)$ (**1**) in toluene under reflux conditions yielded a mixture of *cis* and *trans* isomers $[Pd(PPh_2(OAr))Cl]_2$ (**8a** and **8b**), in 1:1 ratio as confirmed by ^{31}P NMR spectrum, which show two singlets at 151.9 and 151.1 ppm, probably for *cis* and *trans* isomers, respectively (scheme 1).[5] Evidence for orthometallation came from the elemental analysis, mass spectrometry and from further reactions. The *cis* and *trans* mixture (**8a** and **8b**) on treatment with one equivalent of triphenylphosphine in toluene at room temperature also afforded a mixture *cis*- and *trans*-$[Ph_2(OAr)PPd(PPh_3)Cl]$ (**9a** and **9b**), in 1:1 ratio, as indicated by its ^{31}P NMR spectrum. The presence of *cis* and *trans* isomers was unambiguously confirmed from its ^{31}P NMR spectrum due to the large difference in $^2J_{PP}$ values. The ^{31}P NMR spectrum of *cis* compound, **9a** shows two doublets centered at 156.2 and 17.4 ppm with a $^2J_{PP}$ of 29.2 Hz, whereas *trans* complex, **9b** consists of two doublets centered at 146.6 and 30.8 ppm with a $^2J_{PP}$ of 438.9 Hz. In mass spectrum, the mixture of **9a** and **9b** show a peak at m/z 685.1 for M-Cl ion.

To further confirm the orthometallation reaction, the mixture of **8a** and **8b** was treated with *bis*(diphenylphosphino)methane (dppm) in the presence of silver triflate in tetrahydrofuran at room temperature to yield a cationic complex, $[Ph_2P\{OC_6H_3(C_3H_5)\text{-}o\}Pd(\eta^2\text{-dppm})]OTf$ (**10**). The ^{31}P NMR spectrum (see figure 1) of **10** consists of three doublet of doublets centered at 149.7 ppm, −20.8 ppm and −25.7 ppm, thus confirming the presence of three different phosphorus centers. A doublet of doublets at 149.7 with $^2J_{PP}$ of 385.3 and 17.8 Hz was assigned to coordinated phosphorus of phosphinite ligand. The upfield resonances at −25.7 and −20.8 were assigned to phosphorus centers

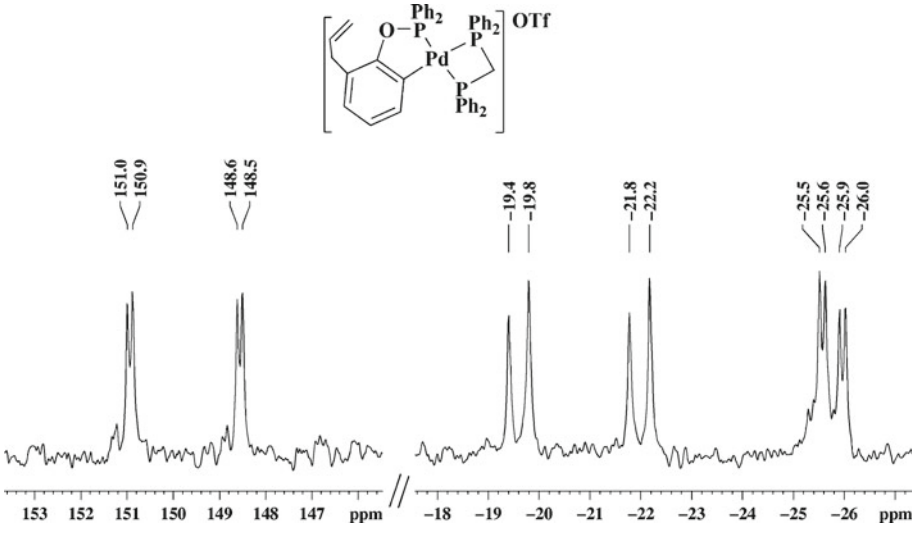

Figure 1. ^{31}P NMR spectrum of $[Ph_2P\{OC_6H_3(C_3H_5)\text{-}o\}Pd(\eta^2\text{-dppm})]OTf$ (**10**).

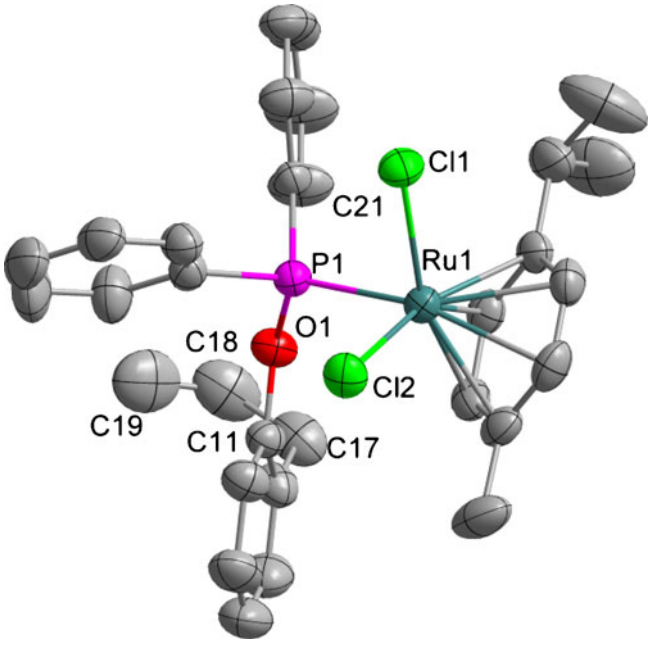

Figure 2. Crystal structure of complex **3** with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms are omitted for clarity.

of dppm, *cis* and *trans* to phosphinite ligand, respectively. Mass spectrum of **10** shows a peak at m/z 806.7 for M-OTf ion.

3.1 *X-ray structure analysis of* $[Ru\{Ph_2P(OAr)\}(\eta^6\text{-}p\text{-}cym)Cl_2]$ (**3**)

The crystals for single crystal X-ray diffraction study were obtained by the slow evaporation of chloroform–petroleum ether solution of **3** at room temperature. The crystallographic data are reported in table 1, and the molecular structure of the complex **3** is shown in figure 2 while selected bond lengths and angles are listed in table 1. The asymmetric unit contains one molecule of **3** and a $CHCl_3$ molecule as solvent of crystallization. The ruthenium center consists of a *p*-cymene group, coordinated in η^6-fashion to form a three-legged 'piano-stool' structure, along with one phosphorus and two chloride ions. The Cl1–Ru–P1 and Cl2–Ru–P1 bond angles are 88.16° and 91.14°, respectively. The Cl1–Ru–Cl2 bond angle is (87.58°) comparable with the same observed in analogues ruthenium complexes containing tertiary phosphines.[11]

4. Conclusion

In summary, allyl functionalized phosphinite and phosphonite ligands and their palladium(II), gold(I) and ruthenium(II) complexes were synthesized in good yield. The structure of ruthenium(II) complex (**3**) was determined by single crystal X-ray diffraction study which depicts ruthenium centre adopting typical piano-stool geometry. Ligand **1** undergoes orthometallation on treatment with $Pd(COD)Cl_2$ under reflux conditions.

Supplementary information

CCDC-870096 (**3**) contains the supplementary crystallographic data for this paper. This can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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