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# Synthesis and transition metal chemistry of a bridging diphosphinite, 1,4 bis(diphenylphosphinoxy)benzene

Maravanji S. Balakrishna<sup>a,\*</sup>, D. Suresh<sup>a</sup>, Pawan Kumar<sup>a</sup>, Joel T. Mague<sup>b</sup>

<sup>a</sup> Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India <sup>b</sup> Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

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#### ABSTRACT

Diphosphinite ligand,  $[Ph_2POC_6H_4OPPh_2]$  (1), is obtained by reacting chloro diphenylphosphine, with 1,4-dihydroxy benzene in presence of triethylamine. Treatment of **1** with elemental sulfur or selenium resulted in the formation of bis(chalcogenide) derivatives,  $[Ph_2(E)POC_6H_4OP(E)Ph_2]$  (**2**, E = S; **3**, E = Se) in almost quantitative yield. The binuclear complex  $[\{(\eta^6-p-cymene)RuCl_2\}_2(Ph_2POC_6H_4OPPh_2)]$  (**4**) is produced in the reaction between  $[Ru(\eta^6-p-cymene)Cl_2]_2$  and diphosphinite **1**. Similarly the reaction of **1** with  $[Rh(COD)Cl]_2$  afforded a binuclear complex  $[\{(COD)RhCl\}_2(Ph_2POC_6H_4OPPh_2)]$  (**5**), whereas the macrocyclic complex  $[\{(CO)RhCl\}(Ph_2POC_6H_4OPPh_2)]_2$  (**6**) is isolated in the reaction of **1** with 0.5 equiv of  $[RhCl(CO)_2]_2$ . Compound **1** on treatment with  $[Pd(COD)Cl_2]$  or  $[PdCl_2(SMe_2)_2]$  in 1:1 molar ratio produced the chloro-bridged binuclear complex  $[\{(PPh_2O)Pd(\mu-Cl)(PPh_2OH)\}_2]$  (**7**) through P–O bond cleavage. Treatment of **1** with two equivalents of Cul in dichlormethane/acetonitrile (1:1) afforded a coordination polymer,  $[\{Cu_2(\mu-l)_2(Ph_2POC_6H_4OPPh_2)]_{\infty}]$  (**8**) in moderate yield. The binuclear complex,  $[\{AuCl\}_2(\mu-Ph_2POC_6H_4OPPh_2)]$  (**9**) is obtained in the reaction of compound **1** with two equiv of AuCl(SMe\_2), where the ligand exhibits bridged bidentate mode of coordination. The molecular structures of **1–4**, and **6** are determined by X-ray diffraction studies.

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#### 1. Introduction

The interest in making new bidentate ligands is two-fold: one is to make chelate complexes especially with platinum metals because of their usefulness in homogeneous catalysis [1-10]. Secondly, the bidentate ligands, capable of bridging two metal centers are equally interesting because of their ability to form di-, tri-, tetra or polynuclear complexes and, are most sought after ligand systems in supramolecular chemistry [11-23]. Rigid nitrogen-donor ligands such as 4,4'-bipyridine, 4,4'-dibenzonitrile, pyrazine or triazenes have been extensively used as linkers in coordination chemistry to generate multidimensional, multiorganic materials with diverse properties [24–28]. In this context, it would be interesting to make analogous phosphorus-based bridging ligands as they are easily tunable in terms of both electronic and steric properties. Such ligands would be even better in molecular assembly as they can stabilize even the low-valent transition metals because of their flexibility in  $\sigma$ -donor and  $\pi$ -acceptor abilities. Recently we have extended the scope of this

E-mail addresses: krishna@chem.iitb.ac.in, msb\_iitb@yahoo.com (M.S. Balakrishna).

chemistry by preparing tetra- and hexaphosphonite ligands [29–33]. As a part of our interest in phosphorus-based ligands and their coordination chemistry [34–36], we describe herein the synthesis of a bis(phosphinite) ligand and its transition metal complexes.

# 2. Results and discussion

#### 2.1. Synthesis of ligand and its chalcogen derivatives

The reaction of 1,4-dihydroxy benzene with two equivalents of chloro diphenylphosphine in diethyl ether in the presence of triethylamine afforded the bis(phosphinite) ligand [Ph<sub>2</sub>POC<sub>6</sub>H<sub>4</sub>OPPh<sub>2</sub>] (1) in good yield. Treatment of bis(phosphinite) 1 with two equivalents of elemental sulfur or gray selenium under refluxing condition resulted in the formation of bis(chalcogenide) derivatives [Ph<sub>2</sub>(E)POC<sub>6</sub>H<sub>4</sub>OP(E)Ph<sub>2</sub>] (2, E = S; 3, E = Se) as shown in Scheme 1. The bis(phosphinite) 1 is a white crystalline solid, moderately stable toward air and moisture, whereas the sulfide and selenide derivatives (2 and 3) are highly stable and soluble in most of the common organic solvents. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of compounds 1–3 consist of single resonances at 110.5, 80.3 and 85.1 ppm, respectively. The bis(selenide) 3 shows a <sup>1</sup>J<sub>PSe</sub> coupling of 824 Hz.

<sup>\*</sup> Corresponding author. Tel.: +91 22 2576 7181; fax: +91 22 2576 7152/2572 3480.

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Scheme 1. Synthesis and derivatization of diphosphinite 1.

The <sup>1</sup>H NMR spectra of compounds **1–3** show multiplets in the region of 7.58–7.15 ppm for  $-P(C_6H_5)_2$  protons and the  $(-OC_6H_4O-)$  protons appear around 6.99–6.78 ppm. The molecular structures of compounds **2** and **3** were confirmed by single crystal X-ray diffraction studies.

# 2.2. Transition metal chemistry of bis(phosphinite) ligand

Treatment of  $[Ru(\eta^6-p-cymene)Cl_2]_2$  with bis(phosphonite) **1** in 1:1 molar ratio in dichloromethane resulted in the formation of a binuclear complex [{( $\eta^6$ -p-cymene)Ru-Cl\_2}<sub>2</sub>(Ph<sub>2</sub>POC<sub>6</sub>H<sub>4</sub>OPPh<sub>2</sub>)] (4) as orange-red crystalline solid. The  ${}^{31}P{}^{1}H$  NMR spectrum of 4 shows a single resonance at 113.6 ppm with a coordination shift of 3.1 ppm. The signals at 2.75 (septet), 2.15 (singlet) and 1.59 (doublet) ppm in the <sup>1</sup>H NMR spectrum confirm the presence of *p*-cymene group. The EI mass spectrum of **4** shows molecular ion peak at 1055.6 corresponds to [M–Cl]. The reaction of equimolar ratio of **1** with [Rh(COD)Cl]<sub>2</sub> in dichloromethane yielded a binuclear complex [{(COD)RhCl}<sub>2</sub>(Ph<sub>2</sub>POC<sub>6</sub>H<sub>4</sub>OPPh<sub>2</sub>)] (5) in good yield. Slow addition of [RhCl(CO)<sub>2</sub>]<sub>2</sub> to 1 in 1:2 molar ratio produced a binuclear complex,  $[{(CO)RhCl}(Ph_2POC_6H_4OPPh_2)]_2$  (**6**) as shown in Scheme 2. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of rhodium(I) complexes **5** and **6** show doublets centered at 122.9 and 121.1 ppm with the  ${}^{1}J_{RhP}$ couplings of 180 and 140 Hz, respectively. The relatively low  ${}^{1}J_{RhP}$  is attributed to the trans disposition of the phosphorus centers which confirms the formation of a binuclear complex **6**. The rhodium(I) complex **6** shows  $v_{CO}$  at 1990 cm<sup>-1</sup>. The molecular structures of ruthenium (4) and rhodium (6) complexes were confirmed by X-ray diffraction studies.

The reaction of bis(phosphonite) **1** with  $[Pd(COD)Cl_2]$  or  $[PdCl_2(SMe_2)_2]$  in 1:1 molar ratio resulted in the formation of a chloro-bridged binuclear complex  $[{(PPh_2O)Pd(\mu-Cl)(PPh_2OH)}_2]$ (**7**) [37]. The reaction probably proceeds *via* the moisture assisted P–O bond cleavage to form the intermediate  $[Cl_2Pd(PPOH)_2]$  which on elimination of HCl gives the chloro-bridged binuclear complex **7** with interesting chemical reactivity [38]. Previously, the complex **7** was obtained in the reaction between K<sub>2</sub>PdCl<sub>4</sub> and Ph<sub>2</sub>POH/Ph<sub>2</sub>PCl in a mixture of water and acetone [39]. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **7** shows a single resonance at 76.7 ppm. Interaction of bis(phosphonite) **1** with two equivalents of Cul in dichlormethane/acetonitrile (1:1) afforded a coordination polymer, [ $Cu_2(\mu-I)_2(Ph_2POC_6H_4OPPh_2)$ ] $_{\infty}$ ] in moderate yield (Scheme 3). Treatment of **1** with [AuCl(SMe<sub>2</sub>)] in dichloromethane yields a binuclear gold(I) complex [ $AuCl_2(\mu-Ph_2POC_6H_4OPPh_2)$ ] (**9**) in excellent yield. The copper(I) coordination polymer is soluble only in hot dimethyl sulphoxide while the highly soluble binuclear gold(I) complex is found to be light sensitive. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **8** and **9** show singlets at 90.8 and 112.9 ppm, respectively. The <sup>1</sup>H NMR spectral data and the elemental analyses data of complex **7** are consistent with the proposed structure. The molecular structure of **7** was further confirmed by X-ray diffraction study.

#### 2.3. Molecular structures of compounds 1-4, and 6

Perspective views of the molecular structures of **1**–**4** and **6** along with atom labeling schemes are shown in Figs. 1–5, while the selected bond lengths (Å) and bond angles (°) are given as caption to figures. The details of the structure determination are given in Table 1.

Slow evaporation of dichloromethane/petroleum ether mixture kept at room temperature yielded the colorless crystals of **1** suitable for single crystal X-ray diffraction study. The ligand **1** possesses crystallographically imposed  $C_2$  symmetry in which the asymmetric unit contains half the molecule of **1**. Further it crystallizes in Triclinic crystal system with the space group *P1* (No. 02). One of the phenyl rings on phosphorus is almost perpendicular to the plane of hydroquinone moiety. The phosphorus atoms are in a distorted tetrahedral geometry with maximum deviation shown by the O1–P1–C1 bond where the bond angle is 97.20(12)°.

Very similar to the ligand **1**, the chalcogen derivatives also contain crystallographically imposed  $C_2$  symmetry. The bis(sulfide) **2** crystallizes in monoclinic crystal system with the space group P21/c (No. 14). The phosphorus atoms are in a distorted tetrahedral geometry being bound to one sulfide, one oxygen and two carbon



Scheme 2. Ruthinum(II) and rhodium(I) complexes of diphosphinite 1.



Scheme 3. Palladium(II), copper(I) and gold(I) complexes of diphosphinite 1.

atoms of phenyl groups. The largest deviation from the ideal geometry is reflected by the O1–P1–C4 and S1–P1–C4 bonds whose bond angles are 103.28(6)° and 114.76(5)°, respectively. The P1–S1 bond length is 1.9283(6) Å which is shorter than the same present in Ph<sub>3</sub>P=S (P–S, 1.9355(4) Å). This is due to the electron withdrawing nature of phosphorus atoms which enhance the back bonding and thus shortening the P–S bond distance.

The bis(selenide) **3** is isomorphous to bis(sulfide) derivative **2** which is crystallized in monoclinic crystal system with space group P21/c (No. 14). The P–Se (2.0792(4) Å) bond distance is shorter than the Ph<sub>3</sub>P=Se (P–Se, 2.106(1) Å) as expected. The other bond parameters of **3** follow the same pattern as that of **2**.

The orange–red crystals of **4** suitable for single crystal X-ray diffraction study were obtained by slow evaporation of dichloromethane/petroleum ether mixture at room temperature. The asymmetric unit contains one molecule of **4** and a distorted dichloromethane molecule as a solvent of crystallization. Each ruthenium center contain a *p*-cymene group coordinated in a  $\eta^6$ -fashion, a phosphorus center and two chloride atoms to form a typical three-legged "piano-stool" structure. The Cl1–Ru1–P1 and Cl2–Ru1–P1 bond angles are 87.59(3)° and 90.74(3)°, respectively. The Cl1–Ru1–Cl2 bond angle is 86.27(3)°. The Ru–C bond distances range from 2.187(3) Å (Ru2–C47) to 2.262(4) Å (Ru2–C44) in which the Ru–C bonds (Ru1–C18, 2.239(3) Å) *trans* to phosphine are longer than those *trans* to the chlorine atoms (Ru1–C15, 2.209(3) Å) and this is essentially due to the steric bulk of phosphorus substituents which lifts the carbon atoms close to phosphorus slightly upward. The Ru–P bond lengths (Ru1–P1, 2.3185(9) Å and Ru2–P2, 2.3055(9)Å) vary slightly as do the P–O bond lengths (P1–O3, 1.635(2) Å and P2–O4, 1.629(2) Å).

The molecular structure of **6** is shown in Fig. 5. The structure consists of two trans-{Rh(CO)Cl} units bridged by two bis(phosphinite) ligands to form a centro-symmetric 18-membered macrocycle with rhodium centers in slightly distorted square planar environments. The Rh–P1 and Rh–P2 distances are 2.2977(9) and 2.3032(9) Å, respectively. The Cl1–Rh1–C31 (175.76(11)°) and P1–Rh1–P2 (174.82(3)°) bond angles indicate the slight distortion in the square planar geometry around rhodium centers. The Cl1–Rh1–P1 and Cl1–Rh1–P2 bond angles are 89.97(3)° and 88.91(3)°, respectively.

The molecular structure of 7 (Fig. 6) is identical to that of the structure reported previously by Priya et al. [37] and others [40].

# 3. Conclusions

Bis(phosphonite) **1** is a typical bidentate ligand showing invariably the bridged bidentate mode of coordination. Reactions of **1** with chalcogens afford the corresponding bis(chalcogenide) derivatives. The coordination behavior of bis(phosphonite) ligand was explored with various transition metal precursors. The ligand



**Fig. 1.** Perspective view of molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å): P1–O1, 1.662(2); P1–C1, 1.826(3); P1–C7, 1.834(3); O1–C13, 1.394(3). Selected bond angles (°): O1–P1–C1, 97.19(12); O1–P1–C7, 101.95(12); C1–P1–C7, 99.36(14).



**Fig. 2.** Perspective view of molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å): S1–P1, 1.9283(6); P1–O1, 1.6173(11); P1–C4, 1.8005(16); P1–C10, 1.7961(15); O1–C1, 1.4068(17). Selected bond angles (°): S1–P1–O1, 115.89(4); S1–P1–C4, 114.76(5); S1–P1–C10, 114.82(5); O1–P1–C4, 103.28(6); O1–P1–C10, 99.26(6); C4–P1–C10, 107.08(7).



**Fig. 3.** Perspective view of molecular structure of **3.** Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Sel-P1, 2.0792(4); P1–O1, 1.6218(10); P1–C4, 1.8025(15); P1–C10, 1.7981(14); O1–C1, 1.4075(17). Selected bond angles (°): Se1–P1–O1, 115.54(4); Sel–P1–C4, 114.98(5); Se1–P1–C10, 114.67(5); O1–P1–C4, 103.66(6); O1–P1–C10, 99.51(6); C4–P1–C10, 106.77(6).

exhibits bridged bidentate mode of coordination with Ru(II), Rh(I) and Au(I) derivatives to give binuclear complexes. The cleavage of P–O bond had occurred during the reaction with Pd(II) derivative to form a chloro-bridged dimeric complex. Presently we are trying to use these ligands along with pyridyl ligands to form 2D and 3D coordination polymers and high nuclearity supramolecules for their possible utility as catalysts in appropriate organic transformations.

#### 4. Experimental section

# 4.1. General procedures

All experimental manipulations were carried out under dry nitrogen or argon atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. The precursors  $[(COD)_2PdCl_2]$  [41],  $[\{Rh(\mu-Cl)(CO)_2\}_2]$  [42],  $[\{Rh(\mu-Cl)(COD)\}_2]$  [43],  $[\{(\eta^6-p-cymene)\}_2\}$ 



**Fig. 4.** Perspective view of molecular structure of **4.** Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms and the solvated dichloromethane molecules were omitted for clarity. Selected bond lengths (Å): Ru1–Cl1, 2.3995(9); Ru1–Cl2, 2.4128(9); Ru1–P1, 2.3185(9); Ru1–Cl4, 2.214(4); P1–O3, 1.635(2); P1–C1, 1.824(3); P1–C7, 1.817(3). Selected bond angles (°): Cl1–Ru1–Cl2, 86.27(3); Cl1–Ru1–P1, 87.59(3); Cl1–Ru1–Cl4, 152.30(10); Cl1–Ru1–Cl7, 90.27(8) Cl2–Ru1–P1, 90.74(3); P1–O3–C23, 123.8(2).



**Fig. 5.** Perspective view of molecular structure of **6**. Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms and the solvated dichloromethane molecules were omitted for clarity. Selected bond lengths (Å): Rh1–C11, 2.3609(8); Rh1–C31, 1.812(3); Rh1–P1, 2.2977(9); Rh1–P2, 2.3032(9); P1–O1, 1.644(2); P1–C1, 1.824(3); P1–C7, 1.812(3); P2–O2, 1.640(2); P2–C22, 1.812(3); P2–C16, 1.813(3). Selected bond angles (°): Cl1–Rh1–C31, 175.76(11); Cl1–Rh1–P1, 89.97(3); Cl1–Rh1–P2, 88.91(3); P1–Rh1–C31, 92.27(11); P1–Rh1–C31, 88.50(11).

Cl<sub>2</sub>Ru<sub>2</sub>] [44], and [AuCl(SMe<sub>2</sub>)] [45] were prepared according to the published procedures.

# 4.2. Spectroscopy

The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$  in ppm) spectra were obtained on a Varian VXR 400 spectrometer operating at frequencies of 400 and 162 MHz respectively. The tetramethylsilane and 85% H<sub>3</sub>PO<sub>4</sub> were used as an internal and external standards for <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR respectively. Positive shifts lie downfield of the standard in all the cases. Electro-spray ionization (EI) mass spectrometry experiments were carried out by using Waters Q-Tof micro-YA-105. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as a KBr disc. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected.

# 4.2.1. Synthesis of $[Ph_2POC_6H_4OPPh_2]$ (1)

The chloro diphenylphosphine (2.49 g, 11.285 mmol) in diethyl ether (10 mL) was added dropwise to mixture of 1,4-dihydroxy benzene (0.621 g, 5.642 mmol) and triethylamine (1.142 g, 11.285 mmol) in 30 mL of diethyl ether over a period of 15 min with constant stirring at 0 °C. The reaction mixture was allowed to warm to room temperature and the stirring was continued for 16 h. The hydrochloride salt formed was filtered through frite containing celite and all volatiles were removed under vacuum and recrystallized from dichloromethane and petroleum ether to afford **1** as white crystalline compound. Yield: 76% (2.052 g, 4.288 mmol). Mp: 128–130 °C. Anal. Calcd. for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>P<sub>2</sub>: C, 75.31; H, 5.06%. Found: C. 75.49; H, 5.22%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.58–7.37 (m, *phenyl*, 20H), 6.99 (s,  $-C_6H_4$ –, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 110.5 (s).

# 4.2.2. Synthesis of [Ph<sub>2</sub>(S)POC<sub>6</sub>H<sub>4</sub>OP(S)Ph<sub>2</sub>] (2)

A mixture of **1** (0.192 g, 0.401 mmol) and elemental sulfur (0.026 g, 0.802 mmol) in 10 mL of toluene was heated under reflux for 16 h. The reaction mixture was allowed to cool to room temperature and all the volatiles were removed under vacuum. The

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Crystallographic Data	for <b>1–4</b> ,	and	6.

	1	2	3	4	6
Formula	C <sub>30</sub> H <sub>24</sub> O <sub>2</sub> P <sub>2</sub>	C <sub>30</sub> H <sub>24</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub>	$C_{30}H_{24}O_2P_2Se_2$	C51H54Cl6O2P2Ru2	C64H52Cl6O6P4Rh2
fw	478.43	542.55	636.35	1175.72	1459.46
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1 (No. 2)	P21/c (No. 14)	P21/c (No. 14)	P21/c (No. 14)	P1 (No. 1)
a, Å	10.261(3)	9.0992(6)	9.1027(6)	22.5307(9)	9.0041(8)
<i>b</i> , Å	10.883(3)	10.3873(7)	10.4872(7)	16.0097(7)	11.7680(10)
<i>c</i> , Å	11.917(3)	14.3560(10)	14.4430(10)	14.3400(6)	15.3110(10)
$\alpha$ , deg	87.926(4)	90	90	90	74.3880(10)
$\beta$ , deg	87.763(4)	104.2660(10)	104.6350(10)	107.8950(10)	88.3540(10)
γ, deg	65.648(4)	90	90	90	77.0890(10)
<i>V</i> , Å <sup>3</sup>	1211.2(6)	1315.03(15)	1334.02(16)	4922.3(4)	1522.2(2)
Ζ	2	2	2	4	1
$\rho_{\rm calc}$ , g cm <sup>-3</sup>	1.312	1.370	1.584	1.587	0.796
$\mu$ (MoKa), mm $^{-1}$	0.206	0.351	2.918	1.044	0.963
F (000)	500	564	636	2384	368
Crystal size (mm)	$0.08 \times 0.12 \times 0.27$	$0.08\times0.15\times0.17$	$0.09\times0.13\times0.14$	$0.03 \times 0.09 \times 0.09$	$0.05 \times 0.09 \times 0.09$
Т, К	100	100	100	100	100
$2\theta$ range, deg	2.0, 27.8	2.3-28.4	2.3–28.8	1.6-28.0	2.6-28.0
Total no. reflns	36,029	22,413	23,229	43,065	26,380
No. of indep. Reflns	10,681 $[R_{int} = 0.028]$	$3274 [R_{int} = 0.028]$	3449 $[R_{int} = 0.034]$	11,619 $[R_{int} = 0.050]$	7276 $[R_{int} = 0.042]$
R1 <sup>a</sup>	0.0614	0.0333	0.0220	0.0402	0.0392
wR <sub>2</sub> <sup>b</sup>	0.1967	0.0926	0.0595	0.0886	0.1007
GOF (F <sup>2</sup> )	1.48	1.023	1.072	1.016	1.04

<sup>a</sup>  $R = \Sigma ||F_0| - |F_0|/\Sigma |F_0|.$ 

<sup>b</sup>  $wR_2 = \{ \sum w(F_0^2 - F_c^2) / \sum w(F_0^2)^2 \}^{1/2}; w = 1 / [\sigma^2(F_0^2 + (xP)^2)] \text{ where } P = (F_0^2 + 2F_c^2) / 3.$ 

residue was extracted with dichloromethane (10 mL) and filtered off. The filtrate was concentrated to 4 mL and layered with petroleum ether (2 mL); kept at room temperature for a day to give **2** as white crystalline compound. Yield: 94% (0.205 g, 0.377 mmol). Mp: 184–186 °C. Anal. Calcd. for  $C_{30}H_{24}O_2P_2S_2$ : C, 66.41; H, 4.46; S, 11.82%. Found: C. 66.53; H, 4.22; S, 11.95%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.68–7.15 (m, *phenyl*, 20H), 6.78 (s,  $-C_6H_4$ –, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 80.3 (s).

#### 4.2.3. Synthesis of $[Ph_2(Se)POC_6H_4OP(Se)Ph_2]$ (3)

This was synthesized by a procedure similar to that of **2**, using **1** (0.192 g, 0.401 mmol) and elemental selenium powder (0.063 mg, 0.802 mmol). Yield: 88% (0.224 g, 0.353 mmol). Mp: 196–198 °C. Anal. Calcd. for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>: C, 56.62; H,3.80%. Found: C. 56.49; H, 3.72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.55–7.17 (m, *phenyl*, 20H),



**Fig. 6.** The molecular structure of  $[{(PPh_2O)Pd(\mu-Cl)(PPh_2OH)}_2]$  (7). All hydrogen atoms and the solvated dichloromethane molecules were omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

6.85 (s,  $-C_6H_4$ -, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 85.1 (s), <sup>1</sup>J<sub>P-Se</sub> = 824 Hz.

# 4.2.4. Synthesis of $[{(\eta^6-p-cymene)Cl_2Ru}_2(Ph_2POC_6H_4OPPh_2)]$ (4)

A dichloromethane (5 mL) solution of  $[Cl_2Ru(\eta^6-p-cymene)]_2$ (0.033 g, 0.054 mmol) was added dropwise to **1** (0.026 g, 0.054 mmol) in dichloromethane (5 mL) for about 2 min. The reaction mixture was stirred for 6 h at room temperature. The clear red colored solution was concentrated to 6 mL, layered with 3 mL of petroleum ether and kept at room temperature for 2 days to afford **4** as red crystalline compound. Yield: 83% (0.049 g, 0.045 mmol). Mp: 164–166 °C (dec). Anal. Calcd. for C<sub>50</sub>H<sub>52</sub>  $O_2P_2Ru_2Cl_4$ : C, 55.05; H,4.80%. Found: C. 55.28; H, 4.69%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.95–7.32 (m, *phenyl*, 20H), 6.72 (s,  $-C_6H_4-$ , 4H), 5.25 (d,  $J_{HH} = 6.0$  Hz, *Cymene phenyl*, 4H), 5.16 (d,  $J_{HH} = 6.0$  Hz, *Cymene phenyl*, 4H), 2.75 (septet, *CH*, 2H), 2.15 (s, *CH*<sub>3</sub>, 6H), 1.59 (d,  $J_{HH} = 12.8$  Hz, *CH*<sub>3</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 113.6 (s).

# 4.2.5. Synthesis of [{Rh(COD)Cl}<sub>2</sub>(Ph<sub>2</sub>POC<sub>6</sub>H<sub>4</sub>OPPh<sub>2</sub>)] (**5**)

To a solution of **1** (0.018 g, 0.037 mmol) in dichloromethane (5 mL) added dropwise a solution of  $[Rh(COD)Cl]_2$  (0.018 g, 0.037 mmol) also in dichloromethane (5 mL) at room temperature. The stirring was continued for further 6 h. The yellow colored solution was concentrated to 4 mL, layered with 2 mL of petroleum ether and kept at -25 °C to afford **5** as yellow crystalline compound. Yield: 73% (0.026 g, 0.026 mmol). Mp: 140–142 °C (dec). Anal. Cal. for C<sub>46</sub>H<sub>48</sub>O<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>Cl<sub>2</sub>: C, 56.86; H, 4.98%. Found: C. 56.55; H, 4.82%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.86–6.94 (m, *phenyl*, 20H), 6.69 (s,  $-C_6H_4$ -, 4H), 5.59 (br s, *CH*, 4H), 2.35 (d, *J*<sub>HH</sub> = 18.8 Hz, *CH*<sub>2</sub>, 8H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 122.9 (d, <sup>1</sup>*J*<sub>RhP</sub> = 180.6 Hz).

# 4.2.6. Synthesis of $[{(Rh(CO)Cl)}(Ph_2POC_6H_4OPPh_2)]_2$ (6)

A dichloromethane (5 mL) solution of  $[RhCl(CO)_2]_2$  (0.014 g, 0.035 mmol) was added dropwise to a well-stirred dichloromethane solution (5 mL) of **1** (0.034 g, 0.071 mmol) at room temperature. The reaction mixture was stirred for 4 h. The solution was concentrated to 5 mL under reduced pressure, layered with

3 mL of petroleum ether, and placed at room temperature to get **6** as pale yellow crystalline compound. Yield: 82% (0.037 g, 0.057 mmol). Mp: 232–234 °C (dec). Anal. Cal. for C<sub>31</sub>H<sub>24</sub>O<sub>3</sub>PRhCl: C, 60.65; H, 3.94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): Found: C. 60.48; H, 3.62%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.86–7.84 (m, *phenyl*, 10H), 7.41–7.40 (m, *phenyl*, 10H), 6.71 (s,  $-C_6H_4$ –, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 121.1 (d, <sup>1</sup>J<sub>RhP</sub> = 140.4 Hz).

# 4.2.7. Synthesis of $[{(Ph_2PO)Pd(\mu-Cl)(PPh_2OH)}_2]$ (7)

The pale yellow colored solution of  $[Pd(COD)Cl_2]$  (0.030 g, 0.105 mmol) in dichloromethane (5 mL) was added dropwise to **1** (0.050 g, 0.105 mmol) also in dichloromethane (5 mL) for about 3 min. The reaction mixture was stirred for 4 h at room temperature. The clear yellow colored reaction mixture was concentrated to 5 mL, layered with 2 mL of petroleum ether and kept at room temperature for a day to afford compound **7** as yellow crystals. Yield: 73% (0.038 g, 0.034 mmol). Mp: 188–190 °C (dec). Anal. Cal. for C<sub>48</sub>H<sub>42</sub>O<sub>4</sub>P<sub>4</sub>Pd<sub>2</sub>Cl<sub>2</sub>: C, 52.87; H, 3.88%. Found: C. 52.68; H, 3.79%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.92–7.22 (m, *phenyl*, 20H), 6.71 (s,  $-C_6H_4-$ , 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 76.7(s).

#### 4.2.8. Synthesis of copper $[Cu_2I_2(Ph_2POC_6H_4OPPh_2)]$ (8)

To a solution of **1** (0.031 g, 0.065 mmol) in dichloromethane (5 mL) added dropwise CuI (0.024 g, 0.129 mmol) in acetonitrile (5 mL) at room temperature. The reaction mixture was stirred for further 4 h. During which time the product get precipitated and separated by filtration. The product was washed several times with diethyl ether and dried under vacuum to afford **8** as white crystalline solids. Yield: 68% (0.45 g, 0.034 mmol). Mp: >250 °C (dec). Anal. Cal. for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>P<sub>2</sub>Cu<sub>2</sub>I<sub>2</sub>: C, 41.92; H, 2.81%. Found: C. 41.63; H, 2.75%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.79–7.27 (m, *phenyl*, 20H), 6.69 (s,  $-C_6H_4-$ , 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 90.8 (br s).

#### 4.2.9. Synthesis of gold [ $\{AuCl\}_2(\mu-Ph_2POC_6H_4OPPh_2)$ ] (9)

A dichloromethane (5 mL) solution of [AuCl(SMe<sub>2</sub>)] (0.027 g, 0.092 mmol) was added dropwise to a well-stirred dichloromethane solution (5 mL) of **1** (0.022 g, 0.046 mmol) for about 2 min. The reaction mixture was stirred for 4 h at room temperature. The solution was concentrated to 5 mL under reduced pressure, layered with 3 mL of petroleum ether and placed at room temperature to get **9** as white crystalline compound. Yield: 95% (0.041 g, 0.044 mmol). Mp: 178–180 °C (dec). Anal. Cal. for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>P<sub>2</sub>Au<sub>2</sub>Cl<sub>2</sub>: C. 38.19; H, 2.55%. Found: C. 38.35; H, 2.62%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.83–7.77 (m, *phenyl*, 10H), 7.61–7.53 (m, *phenyl*, 10H), 6.99 (s,  $-C_6H_4-$ , 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 112.9 (s).

# 4.3. X-ray crystallography

Crystals of **1**−**4** and **6** were mounted in a CryoLoop<sup>™</sup> with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex<sup>™</sup> attachment of the Bruker APEX CCD diffractometer. For each, a full sphere of data was collected using 400–606 scans in  $\omega$  $(0.3-0.5^{\circ} \text{ per scan})$  at  $\phi = 0,90$  and  $180^{\circ}$  (for **3**,  $\phi = 0,120$  and  $240^{\circ}$ ) using the SMART software package [46]. The raw data were reduced to  $F^2$  values using the SAINT+ [47] software and global refinements of unit cell parameters employing 3274-11,158 reflections chosen from the full data set were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS) [48]. The structure of 7 was solved by Patterson method, while the remaining structures were solved by direct methods and all were refined by full-matrix leastsquares procedures using the SHELXTL program package [49]. Hydrogen atoms attached to carbon were placed in calculated positions (C–H = 0.95 Å (aromatic rings) or 0.98 Å (methyl groups)) and included as riding contributions with isotropic displacement parameters 1.2 (aromatic rings) or 1.5 (methyl groups) times those of the attached non-hydrogen atoms.

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#### Appendix A. Supplementary material

CCDC 830366, 830367, 830368, 830369 and 830370 contain the supplementary crystallographic data for **1–4** and **6**. These 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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