

# Ruthenium(II), copper(I) and silver(I) complexes of large bite bisphosphinite, bis(2-diphenylphosphinoxynaphthalen-1-yl)methane: Application of Ru(II) complexes towards the hydrogenation of styrene and phenylacetylene

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## Abstract

Ruthenium(II), copper(I) and silver(I) complexes of large bite bisphosphinite  $\text{Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2$  (**1**) are described. Reactions of bisphosphinite **1** with  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})\text{Cl}]_2$  and  $\text{RuCl}_2(\text{PPh}_3)_3$  afford mono- and bis-chelate complexes  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]_2\text{Cl}$  (**2**) and *trans*- $[\text{RuCl}_2\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]_2$  (**3**), respectively. Treatment of **1** with  $\text{CuX}$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) furnish 10-membered chelate complexes of the type  $[\text{Cu}(\text{X})\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]$  (**4**,  $\text{X} = \text{Cl}$ ; **5**,  $\text{X} = \text{Br}$ ; **6**,  $\text{X} = \text{I}$ ), whereas  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  affords a bis-chelated cationic complex  $[\text{Cu}\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]_2[\text{PF}_6]$  (**7**). Reaction between **1** and  $\text{AgOTf}$  produce both mono- and bis-chelated complexes  $[\text{Ag}\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}(\text{SO}_3\text{CF}_3)]$  (**8**) and  $[\text{Ag}\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]_2[\text{SO}_3\text{CF}_3]$  (**9**), respectively; whereas the similar reaction of **1** with  $[\text{Ag}(\text{OTf})\text{PPh}_3]$  affords chelate complex of the type  $[\text{Ag}\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}(\text{PPh}_3)(\text{SO}_3\text{CF}_3)]$  (**10**). All the complexes were characterized by  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, elemental analysis and mass spectrometry, including low-temperature NMR studies in the case of silver complexes. The molecular structures of **4** and **6** are determined by X-ray diffraction studies. Ruthenium complexes **2** and **3** promote catalytic hydrogenation of styrene and phenylacetylene with good turnover numbers.

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**Keywords:** Bisphosphinite; Chelate complexes; Ruthenium(II), copper(I) and silver(I) complexes; Crystal structures; Hydrogenation reactions

## 1. Introduction

Synthesis of novel bisphosphine ligand systems to stabilize transition metal chelates in low valent states is considered to be a most challenging task in view of their potential usefulness in a variety of metal-mediated organic transformations [1]. Most of these phosphine ligands bear the bulky substituents, where both the steric and electronic factors play a vital role for imposing regioselectivity during

the catalytic process. Transition metal complexes containing bulky mono- and bisphosphines as catalyst in organic transformation are well documented. Surprisingly, the utilization of analogous bisphosphinite ligands in such reactions are sparse although some of them are proved to be efficient catalysts [2]. In this context, recently we have synthesized an inexpensive large bite bisphosphinite, bis(2-diphenylphosphinoxynaphthalen-1-yl)methane (**1**) and explored its ligating behavior and catalytic properties toward coupling reactions [3,4]. Since, the group 10 metal precursors containing bisphosphines are known to give interesting halide-bridged metal clusters and bimetallic complexes, which inturn show metallophilic interactions

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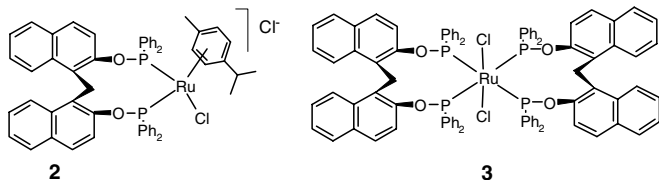
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and are rich in luminescence properties [5], we sought to examine the reactivity of this large bite bisphosphinite **1** with the group 10 metals. As a part of interest in organometallic chemistry and catalytic investigations [6], we describe here the ruthenium(II), copper(I) and silver(I) complexes of the bisphosphinite **1**. The catalytic activity of ruthenium(II)–bisphosphinite complexes towards hydrogenation of styrene and phenylacetylene is also described.

## 2. Results and discussion

### 2.1. Ruthenium derivatives

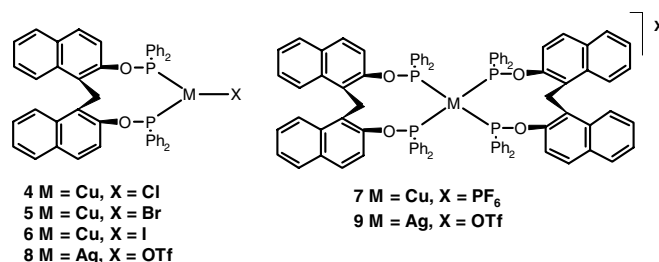
The reaction of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})\text{Cl}]_2$  with excess of bisphosphinite  $\text{Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2$  (**1**) in ethanol at 50 °C afforded the cationic complex  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}\text{Cl}]$  (**2**) in good yield. A large excess of bisphosphinite was used to avoid the formation of phosphinite bridged bimetallic complex and lower temperature was applied to prevent the loss of the arene [7]. The  $^{31}\text{P}$  NMR spectrum of complex **2** shows a single resonance at 122.1 ppm. In  $^1\text{H}$  NMR spectrum, a singlet at 4.66 ppm is observed for the  $\text{CH}_2$  protons of bisphosphinite, whereas signals at 2.46 (septet), 1.49 (s) and 0.84 (d) ppm confirm the presence of *p*-cymene moiety. In the mass spectrum, the base peak appear at  $m/z$  828.2 correspond to the ion  $[\{\text{M}^+(\text{cymene}+\text{Cl})\}+\text{Na}]$ . Treatment of  $\text{RuCl}_2(\text{PPh}_3)_3$  with two equivalents of bisphosphinite **1** in dichloromethane at room temperature resulted in the formation of a bis-chelated *trans* complex  $[\text{RuCl}_2\{\eta^2\text{-Ph}_2\text{P}\{(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\}\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}_2]$  (**3**). In the  $^{31}\text{P}$  NMR spectrum, a singlet is observed at 137.5 ppm, which indicates the presence of only one type of phosphorus environment confirming the *trans* arrangement. The mass spectrum of complex **3** shows the isotopic pattern at  $m/z$  805.3 and 807.3 for the ion  $(\text{M}^+(\text{1}+\text{Cl}))$ . Similarly, another set of peak appears at  $m/z$  769.3 corresponds to the ion  $(\text{M}^+(\text{1}+\text{Cl}_2))$ . Further support for the molecular composition and structure comes from the  $^1\text{H}$  NMR and elemental analysis data.



### 2.2. Copper derivatives

The reactions of bisphosphinite **1** with  $\text{CuX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are independent of stoichiometry and the reaction conditions and afford exclusively the mononuclear 10-member chelated complexes  $[\text{Cu}(\text{X})\{\eta^2\text{-Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)$

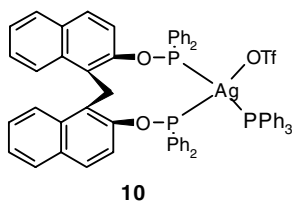
$(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]$  (**4**,  $\text{X} = \text{Cl}$ ; **5**,  $\text{X} = \text{Br}$ ; **6**,  $\text{X} = \text{I}$ ). However, this is not true for the reactions of **1** with  $\text{Ag}(\text{I})$  and  $\text{Au}(\text{I})$  metal precursors. For example, reaction of **1** with  $\text{AuCl}(\text{SMe}_2)$  gives either mononuclear chelate complex  $[\text{Au}(\text{Cl})\{\eta^2\text{-Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]$  or bridged binuclear complex  $[\text{Au}(\text{Cl})\{\mu\text{-Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}\text{Au}(\text{Cl})]$  depending upon the stoichiometry, as we have reported previously [4]. The  $^{31}\text{P}$  NMR spectra of the complexes **4–6** exhibit single resonance at 92.6, 94.6 and 96.9 ppm, respectively. Although, the reaction of **1** with  $\text{CuX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) produced only the mononuclear uni-chelate complexes, the reaction with 0.5 equiv. of  $[\text{Cu}(\text{MeCN})_4\text{PF}_6]$  afforded the cationic bis-chelated complex  $[\text{Cu}\{\eta^2\text{-Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}_2][\text{PF}_6]$  (**7**) in good yield. Since the copper has high tendency to adopt higher coordination numbers than the  $\text{Ag}(\text{I})$  or  $\text{Au}(\text{I})$ , we propose a tetrahedral geometry for complex **7**. The  $^{31}\text{P}$  NMR spectrum of the complex **7** shows a singlet at 97.3 ppm and the chemical shift due to  $\text{PF}_6$  appears as a septet at  $-146.0$  ppm with  $^1J_{\text{PF}}$  coupling of 713 Hz. In the mass spectrum, peak appears at  $m/z$  1401.5 and 731.2 for the cation  $(\text{M}^+(\text{1}+\text{PF}_6))$  and  $\text{M}^+(\text{1}+\text{PF}_6)$ , respectively. Further structural composition of complexes **4–7** comes from  $^1\text{H}$  NMR and microanalytical data. The structures of complexes **4** and **6** have been confirmed by single crystal X-ray analysis.



### 2.3. Silver derivatives

The reaction of **1** with  $\text{AgOTf}$  in 1:1 molar ratio provides a complex with composition  $[\text{Ag}(\text{OTf})(\text{1})]$  (**8**). The  $^{31}\text{P}$  NMR spectrum of complex **8** at  $-50$  °C shows two doublets centered at 117.7 ppm, because of the coupling with the two silver nuclei,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ . The  $\text{Ag-P}$  coupling constants are  $^1J(^{109}\text{AgP})$  564 and  $^1J(^{107}\text{AgP})$  486 Hz. In the mass spectrum, the molecular peak due to the cation appears at  $m/z = 776.9$  for  $(\text{M}^+(\text{1}+\text{OTf}))$ . This suggests that the complex **8** is bisphosphinite-chelated complex. Generally, 1:1 reaction of  $\text{AgOTf}$  with bisphosphine ligands can afford two types of binuclear tetrahedral complexes: (i) ligand chelate to silver with the two anionic groups bridge the silver centers, for example  $[\text{Ag}_2(\mu\text{-SCN})_2(\text{dppf})_2]$  or (ii) ligand as well as anionic groups bridge between the two silver centers, example  $[\text{Ag}_2(\mu\text{-CN})_2(\mu\text{-dppf})_2]$  [8]. As the mass spectroscopy data indicates the chelation of ligand to silver center, we propose trifluoromethanesulfonate bridge binuclear

tetrahedral geometry for the complex **8**. Similarly, the reaction of **1** with AgOTf in a molar ratio 2:1 gives the cationic complex  $[\text{Ag}\{\eta^2\text{-Ph}_2\text{P}(\text{-OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}_2][\text{SO}_3\text{CF}_3]$  (**9**). The  $^{31}\text{P}$  NMR spectrum of complex **9** recorded at  $-50^\circ\text{C}$  shows two doublets centered at 111.7 ppm with Ag–P coupling of  $^1J(^{109}\text{AgP})$  489 and  $^1J(^{107}\text{AgP})$  423 Hz. In the mass spectrum, a peak due to cation appears at  $m/z = 775.2$  ( $\text{M}^+ - (\text{I} + \text{OTf})$ ). The treatment of **1** with  $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$  in dichloromethane at room temperature leads to the formation of air stable complex  $[\text{Ag}\{\eta^2\text{-Ph}_2\text{P}(\text{-OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}(\text{PPh}_3)(\text{SO}_3\text{CF}_3)]$  (**10**) in excellent yield. The  $^{31}\text{P}$  NMR spectrum of **10** exhibits four broad signals, two each at 113.3 ppm and 3.8 ppm, respectively, for bisphosphinite and  $\text{PPh}_3$  centers. Even the low temperature NMR studies ( $-50^\circ\text{C}$ ) did not resolve the signals to show the proper couplings with  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  and also the  $^2J_{\text{PP}}$  couplings. In the mass spectrum, a peak at  $m/z = 774.8$  is observed for the ion ( $\text{M}^+ - (\text{PPh}_3 + \text{OTf})$ ). Further support for the molecular composition and structural assignments came from  $^1\text{H}$  NMR and microanalytical data.



#### 2.4. The crystal and molecular structures of complexes **4** and **6**

Perspective views of the molecular structures of complexes **4** and **6** with atom numbering schemes are shown

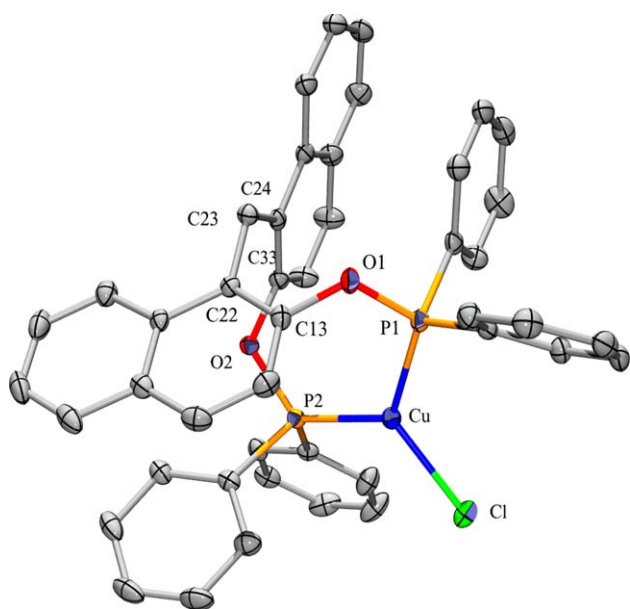


Fig. 1. Molecular structure of  $[\text{Cu}(\text{Cl})\{\eta^2\text{-Ph}_2\text{P}(\text{-OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]$  (**4**) (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity).

in Figs. 1 and 2, respectively. The crystallographic data and the details of the structure determination are given in Table 1, while the selected bond lengths and bond angles appear in Table 2.

In the structures of **4** and **6**, the copper centers adopt almost trigonal planar geometry with the bite angles of  $122.21(2)^\circ$  and  $119.93(2)^\circ$ , respectively. The structure of complex **4** is similar to that of  $(\text{PPh}_3)_2\text{CuCl}$  [9]. The P1–Cu–P2 bite angle in complex **4** is very large compared to

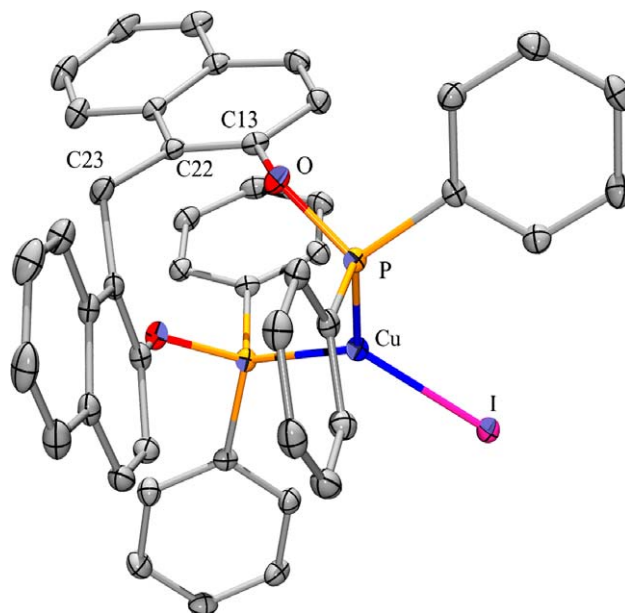


Fig. 2. Molecular structure of  $[\text{Cu}(\text{I})\{\eta^2\text{-Ph}_2\text{P}(\text{-OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O-})\text{PPh}_2\text{-}\kappa\text{P},\kappa\text{P}\}]$  (**6**) (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity).

Table 1  
Crystallographic data for complexes **4** and **6**

Compound	<b>4</b>	<b>6</b>
Formula	$\text{C}_{45}\text{H}_{34}\text{ClCuO}_2\text{P}_2$	$\text{C}_{45}\text{H}_{34}\text{CuIO}_2\text{P}_2$
Molecular weight	767.66	859.11
Crystal system	Monoclinic	Monoclinic
Crystal size (mm)	$0.12 \times 0.14 \times 0.14$	$0.09 \times 0.14 \times 0.18$
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
$a$ (Å)	17.4180(10)	14.8040(10)
$b$ (Å)	12.4200(9)	20.851(2)
$c$ (Å)	17.4730(10)	12.4140(10)
$\alpha$ (°)	90	90
$\beta$ (°)	90.0450(10)	110.0930(10)
$\gamma$ (°)	90	90
$V$ (Å <sup>3</sup> )	3780.0(4)	3598.7(5)
$Z$	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.349	1.586
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.771	1.593
$F(000)$	1584	1728
Temperature (K)	100	100
$\theta_{\text{min-max}}$ (°)	1.6–28.3	1.8–28.2
Goodness-of-fit on $F^2$	1.04	1.05
$R_1^a$	0.0370	0.0246
$wR_2^b$	0.0938	0.0624

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum w[(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2}$$

Table 2  
Selected bond distances (Å) and bond angles (°) for **4** and **6**

Bond distances (Å)		Bond angles (°)	
<i>Complex 4</i>			
Cu–Cl	2.209(1)	Cl–Cu–P1	117.55(2)
Cu–P1	2.219(1)	Cl–Cu–P2	120.23(2)
Cu–P2	2.220(1)	P1–Cu–P2	122.21(2)
P1–O1	1.637(1)	Cu–P1–O1	114.68(4)
P2–O2	1.645(1)	Cu–P1–C1	121.83(6)
P1–C1	1.812(2)	Cu–P1–C7	112.11(6)
P1–C7	1.807(2)	O1–P1–C1	100.33(7)
P2–C34	1.807(2)	O1–P1–C7	102.66(7)
P2–C40	1.821(2)	C1–P1–C7	102.82(8)
		C22–C23–C24	121.28(13)
<i>Complex 6</i>			
Cu–I	2.517(1)	I–Cu–P	120.04(1)
Cu–P	2.230(1)	I–Cu–P <sub>a</sub>	120.04(1)
Cu–P <sub>a</sub>	2.230(1)	P–Cu–P <sub>a</sub>	119.93(2)
P–O	1.646(1)	Cu–P–O	115.22(5)
P–C1	1.812(2)	Cu–P–C1	119.70(6)
P–C7	1.806(2)	Cu–P–C7	113.58(6)
O–C13	1.400(2)	O–P–C1	102.85(8)
		O–P–C7	100.45(7)
		C1–P–C7	102.51(9)
		C22–C23–C22 <sub>a</sub>	119.82(19)

the same in the chloro-bridged complex  $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]$  [10]. Similarly, the bite angle in complex **6** is large compared to the same in the iodo-bridged complex  $[\text{Cu}_2(\mu\text{-I})_2(\kappa^2\text{-P,P-dppf})_2]$  [11]. Generally, copper complexes of bisphosphine form halide-bridged chelate complexes with tetrahedral geometry; however, chelate complexes of copper with trigonal planar geometry are rare. To the best of our knowledge, chelated copper complexes of bisphosphine with such a large bite angle is not seen in the literature. Because of these large bite angles of complexes **4** and **6**, the angles at the bridgehead methylene carbon ( $121.28(13)^\circ$  and  $119.82(19)^\circ$ ) are approximately  $2\text{--}4^\circ$  greater than those found in the other chelate complexes of **1** (see Table 3). Interestingly, in both the complexes the bisphosphinite makes a twisted 10-membered chelate ring with one of the naphthyl rings oriented almost orthogonal to the plane of the ring. There are no significant differences between the Cu–P1 (2.2193(4) Å) and Cu–P2 (2.2203(4) Å) bond lengths of complex **4**, whereas it is exactly the same (Cu–P = Cu–P<sub>a</sub> = 2.2305(5) Å) in the

Table 3  
Bite angles and bridgehead methylene angles in chelate complexes of **1** (L–L)

Complexes	(P–M–P) bite angles (°)	Bridgehead methylene angles (°)	Reference
$\text{Mo}(\text{CO})_4(\text{L-L})$	95.06(3)	114.2(3)	[4]
$\text{CpRuCl}(\text{L-L})$	93.94(7)	114.7(6)	[3]
$\text{NiCl}_2(\text{L-L})$	95.96(2)	117.04(17)	[4]
$[(\text{C}_3\text{H}_5)_2\text{Pd}(\text{L-L})]\text{BF}_4$	98.95(3)	114.5(3)	[4]
$\text{PtCl}_2(\text{L-L})$	95.37(9)	116.9(8)	[3]
$\text{CuCl}(\text{L-L})$	122.21(2)	121.28(13)	<sup>a</sup>
$\text{CuI}(\text{L-L})$	119.93(2)	119.82(19)	<sup>a</sup>
$\text{AuCl}(\text{L-L})$	132.56(4)	122.2(3)	[4]

<sup>a</sup> This work.

complex **6**. The Cu–P bond lengths in complexes **4** and **6** are significantly shorter than the corresponding Cu–P bond lengths of trigonal planar complex,  $[(\text{PPh}_3)_2\text{CuCl}]$  (Cu–P1, 2.272(2); Cu–P2, 2.260(2) Å) and  $[(\text{PPh}_3)_2\text{CuI}]$  (Cu–P, 2.273(2) Å), respectively [12]. This would suggest the significant  $\pi$ -accepting capacity of bisphosphinite ligand in both the complexes. The Cu–Cl and Cu–I bond distances in **4** and **6** are 2.2097(5) Å and 2.5175(4) Å, respectively.

### 3. Catalytic properties of compounds **2** and **3**

Complexes **2** and **3** are tested for the catalytic hydrogenation of styrene and phenylacetylene with molecular hydrogen in THF solution at  $80^\circ\text{C}$ . Catalytic studies have been performed without addition of organic bases, which increases the catalytic activity of Ru(II) complexes [13]. We have studied the catalytic activity of the cationic complex **2** and the neutral complex **3**, both at 20 atm as well as 45-atm hydrogen pressure.

Using milder conditions than Bennet applied with the catalyst  $[\text{RuCl}(\text{C}_6\text{H}_6)(\text{PPh}_3)]$  [14], we detected 98% conversion of styrene to ethylbenzene using 0.05 mol% of the catalyst **2** at  $80^\circ\text{C}$  after 6 h (Fig. 3). The neutral complex **3** is slightly less active which shows about 95% conversion after 7 h under similar reaction conditions. An increase in the  $\text{H}_2$  pressure from 20 to 45 atm, resulted in 96% conversion of styrene to ethylbenzene within 2.5 h with the catalyst **2**, whereas no significant improvement was observed in the performance of catalyst **3**. These catalyst precursors are much better than the similar catalysts  $[\text{RuCl}(p\text{-cymene})(\text{PPh}_2\text{Py})]^+$  used by Moldes et al. [15], where they observed 94% conversion of styrene to ethylbenzene with 0.5 mol% of catalyst after 24 h.

Complexes **2** and **3** are also active species for hydrogenation of phenylacetylene to styrene and ethylbenzene. The

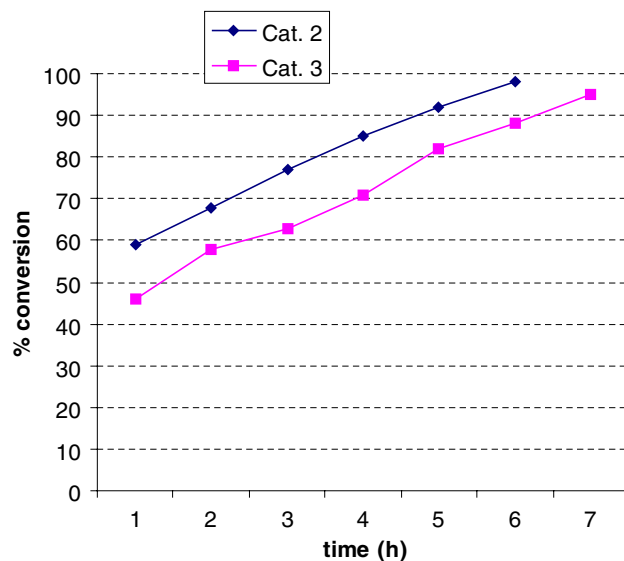


Fig. 3. The hydrogenation of styrene using complexes **2** and **3**. Styrene/complex = 2000; solvent, THF (20 ml); 20 atm  $\text{H}_2$ ;  $80^\circ\text{C}$ .

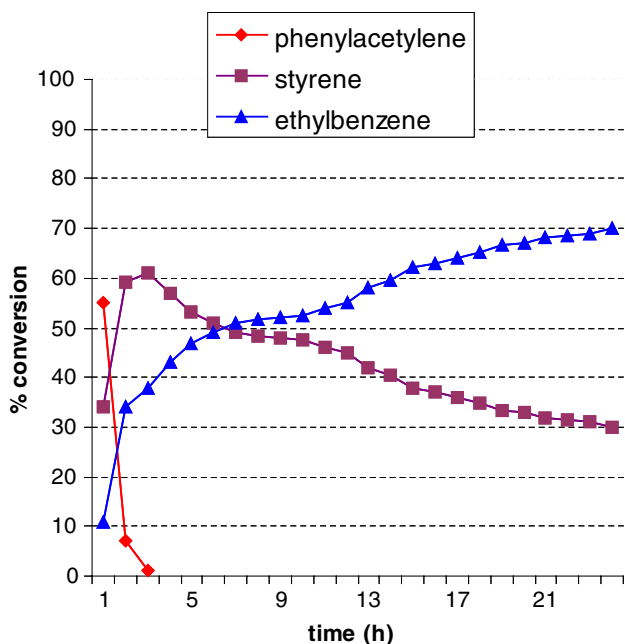


Fig. 4. The hydrogenation of phenylacetylene using complex **2**. Phenylacetylene/complex = 2000; solvent, THF (20 ml); 20 atm H<sub>2</sub>; 80 °C.

reaction profile of a run with complex **2** at 20 atm and 80 °C is shown in Fig. 4. Using the catalyst **2** (0.05 mol%, 80 °C) at 20 atm of H<sub>2</sub> pressure, phenylacetylene is hydrogenated to 30% of styrene and 70% of ethylbenzene after 24 h. The alkyne hydrogenation is completed with in 3 h, whereas styrene hydrogenation proceeded very slowly. With increase in the H<sub>2</sub> pressure from 20 to 45 atm, the phenylacetylene was hydrogenated to 98% of ethylbenzene after 8 h. The activity of the catalyst **3** was poor for the hydrogenation of phenylacetylene at 20 atm, whereas its performance is same as that of catalyst **2** at 45 atm of H<sub>2</sub> pressure.

#### 4. Conclusion

The bisphosphinite **1** forms mainly chelate complexes with most of the transition metals. With copper(I) derivatives it forms both chelated trigonal planar as well as bis-chelated tetrahedral complexes, the former type of copper complexes are very rare with bisphosphine systems. The reactions with ruthenium derivatives produce both cationic uni-chelated and neutral bis-chelated complexes under different reaction conditions. The reactions of **1** with silver precursor exclusively form chelated tetrahedral complexes. The ruthenium complexes **2** and **3** show excellent activity for the hydrogenation of styrene and phenylacetylene.

#### 5. Experimental

All experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. Solvents were dried and distilled prior to use by conventional methods. Bis(phosphinite) **1** [3], [Ru(η<sup>6</sup>-cym-

ene)(μ-Cl)Cl]<sub>2</sub> [16], RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> [17], CuCl, CuBr [18], [Cu(MeCN)<sub>4</sub>PF<sub>6</sub>] [19] and Ag(PPh<sub>3</sub>)OTf [20] were prepared according to the published procedures. Other reagents were used as obtained from commercial sources. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR (δ in ppm) spectra were obtained on a Varian VXR 300 or VRX 400 spectrometer operating at frequencies of 300 or 400 and 121 or 162 MHz, respectively. The NMR spectra were recorded in CDCl<sub>3</sub> solutions with CDCl<sub>3</sub> as an internal lock; TMS and 85% H<sub>3</sub>PO<sub>4</sub> were used as 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 cases. Microanalyses were carried out on a Carlo Erba (Model 1106) elemental analyzer. Mass spectra were recorded using Waters Q-ToF micro(YA-105) instrument. Melting points of all compounds were determined on Veego melting point apparatus and are uncorrected. GC analyses were performed on a Perkin-Elmer Clarus 500 GC fitted with packed column.

##### 5.1. Synthesis of [RuCl(η<sup>6</sup>-*p*-cymene){η<sup>2</sup>-Ph<sub>2</sub>P{-OC<sub>10</sub>H<sub>6</sub>}(μ-CH<sub>2</sub>)(C<sub>10</sub>H<sub>6</sub>O-)}PPh<sub>2</sub>-κP,κP}]Cl (**2**)

A suspension of ligand **1** (0.094 g, 0.14 mmol) and [Ru(η<sup>6</sup>-*p*-cymene)(μ-Cl)Cl]<sub>2</sub> (0.02 g, 0.033 mmol) in ethanol (10 ml) was heated at 50 °C for 16 h to get a clear orange color solution. The solvent was removed under reduced pressure to get oily liquid, which was redissolved in acetone and was cooled to -25 °C to get yellow crystalline product **2**. Yield: 91% (0.058 g), m.p.: 122–124 °C. Anal. Calc. for C<sub>55</sub>H<sub>48</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 67.76; H, 4.96. Found: C, 67.44; H, 4.89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.17 (d, 2H, Ar), 8.05 (t, 2H, Ar), 7.65 (d, 2H, Ar), 7.50–7.18 (m, 4H, cymene, 6H, Ar, 20H, OPPh<sub>2</sub>), 4.66 (s, 2H, Ar-CH<sub>2</sub>-Ar), 2.46 (septet, 1H, CH), 1.49 (s, 3H, CH<sub>3</sub>), 0.84 (d, 6H, C(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>): δ 122.1 (s). MS (EI): 828.2 [(M<sup>+</sup>-(cymene+Cl))+Na].

##### 5.2. Synthesis of trans-[RuCl<sub>2</sub>{η<sup>2</sup>-Ph<sub>2</sub>P{-OC<sub>10</sub>H<sub>6</sub>}(μ-CH<sub>2</sub>)(C<sub>10</sub>H<sub>6</sub>O-)}PPh<sub>2</sub>-κP,κP}]<sub>2</sub> (**3**)

A solution of the ligand **1** (0.057 g, 0.085 mmol) in 8 ml of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the 6 ml dichloromethane solution of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.041 g, 0.042 mmol) at room temperature and the reaction mixture was stirred for 6 h. The solvent was evaporated under reduced pressure and the residue obtained was washed with diethyl ether (3 × 5 ml). The cream color residue was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (b.p. 60–80 °C) in (2:1) mixture to get the product **3** of analytical purity at -25 °C. Yield: 86% (0.055 g), m.p.: 188–190 °C (dec.). Anal. Calc. for C<sub>90</sub>H<sub>68</sub>Cl<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Ru: C, 71.62; H, 4.54. Found: C, 71.46; H, 4.49%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.25 (d, 4H, Ar), 7.08–7.92 (m, 16H, Ar, 40H, OPPh<sub>2</sub>), 6.55 (d, 4H, Ar), 4.74 (s, 4H, Ar-CH<sub>2</sub>-Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>): δ 137.5 (s). MS (EI): 805.3 (M<sup>+</sup>-(L+Cl)), 769.3 (M<sup>+</sup>-(L+Cl<sub>2</sub>)).

5.3. Synthesis of  $[Cu(Cl)\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}]$  (**4**)

A solution of CuCl (0.011 g, 0.111 mmol) in acetonitrile (6 ml) was added dropwise to the 8 ml dichloromethane solution of **1** (0.074 g, 0.111 mmol) at room temperature. After 30 min of slow stirring, the resulted suspension was filtered to get a clear solution. Then, the reaction solution was concentrated to 8 ml under reduced pressure, which gave colorless crystalline product of **4** at  $-30^\circ\text{C}$ . Yield: 76% (0.065 g), m.p.:  $224^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{45}H_{34}ClO_2\text{-}P_2Cu$ : C, 70.40; H, 4.46. Found: C, 70.32; H, 4.41%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.17 (d, 2H, Ar), 8.01 (br s, 2H, Ar), 7.52 (t, 2H, Ar), 7.26–7.49 (m, 20H, OPPh<sub>2</sub>, 2H, Ar), 7.05 (d, 2H, Ar), 6.72 (d, 2H, Ar), 4.95 (s, 2H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (161.9 MHz,  $CDCl_3$ ):  $\delta$  92.6 (s).

5.4. Synthesis of  $[Cu(Br)\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}]$  (**5**)

This was synthesized by the procedure similar to that for **4**, using CuBr (0.015 g, 0.104 mmol) and **1** (0.07 g, 0.104 mmol). Yield: 81% (0.069 g), m.p.:  $240^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{45}H_{34}BrO_2\text{-}P_2Cu$ : C, 66.55; H, 4.22. Found: C, 66.49; H, 4.19%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.17 (d, 2H, Ar), 8.03 (br s, 2H, Ar), 7.51 (t, 2H, Ar), 7.26–7.48 (m, 20H, OPPh<sub>2</sub>, 2H, Ar), 7.04 (d, 2H, Ar), 6.71 (d, 2H, Ar), 4.95 (s, 2H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (161.9 MHz,  $CDCl_3$ ):  $\delta$  94.6 (s).

5.5. Synthesis of  $[Cu(I)\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}]$  (**6**)

This was synthesized by the procedure similar to that for **4**, using CuI (0.025 g, 0.13 mmol) and **1** (0.088 g, 0.13 mmol). Yield: 81% (0.091 g), m.p.:  $242^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{45}H_{34}IO_2\text{-}P_2Cu$ : C, 62.91; H, 3.99. Found: C, 62.89; H, 3.92%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.16 (d, 2H, Ar), 8.06 (br s, 2H, Ar), 7.50 (t, 2H, Ar), 7.29–7.38 (m, 20H, OPPh<sub>2</sub>, 2H, Ar), 7.06 (d, 2H, Ar), 6.71 (d, 2H, Ar), 4.96 (s, 2H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (161.9 MHz,  $CDCl_3$ ):  $\delta$  96.9 (s).

5.6. Synthesis of  $[Cu\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}_2][PF_6]$  (**7**)

To the solution of ligand **1** (0.073 g, 0.109 mmol) in 12 ml of dichloromethane  $[Cu(MeCN)_4PF_6]$  (0.02 g, 0.054 mmol) was added and the reaction mixture was stirred for 2 h. The suspension was filtered through celite to remove insoluble impurities and the clear solution was concentrated to 3 ml, which on slow evaporation gave white crystalline product of **7**. Yield: 95% (0.079 g), m.p.:  $112^\circ\text{C}$ . Anal. Calc. for  $C_{90}H_{68}F_6O_4\text{-}P_5Cu$ : C, 69.92; H, 4.43. Found: C, 69.65; H, 4.46%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.21 (d, 4H, Ar), 7.92 (d, 4H, Ar), 7.11–7.82 (m, 12H, Ar, 40H, OPPh<sub>2</sub>), 6.68 (d, 4H, Ar), 4.91 (s, 4H,

Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (161.9 MHz,  $CDCl_3$ ):  $\delta$  97.3 (s, 4P),  $-146.0$  (septet, 1P,  $PF_6$ ),  $^1J_{PF} = 713$  Hz. MS (EI): 1401.5, ( $M^+ - PF_6$ ); 731.2,  $M^+ - (L + PF_6)$ .

5.7. Synthesis of  $[Ag\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}(SO_3CF_3)]$  (**8**)

To the 12 ml dichloromethane solution of ligand **1** (0.078 g, 0.117 mmol), AgOTf (0.03 g, 0.117 mmol) was added and stirred the reaction mixture for 2 h. The clear solution obtained was concentrated to 2 ml, diethyl ether was added to precipitate out white stuff, which was filtered and dried to obtain analytically pure product of **8**. Yield: 82% (0.089 g), m.p.:  $158\text{--}160^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{46}H_{34}F_3O_5\text{-}P_2SAg$ : C, 59.69; H, 3.70; S, 3.46. Found: C, 59.36; H, 3.68; S, 3.39%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.16 (d, 2H, Ar), 7.18–7.68 (m, 8H, Ar, 20H, OPPh<sub>2</sub>), 6.69 (br s, 2H, Ar), 4.92 (s, 2H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (121.4 MHz,  $CDCl_3$  ( $-50^\circ\text{C}$ )):  $\delta$  117.7 (2d, 2P, OPPh<sub>2</sub>,  $^1J(^{109}AgP) 564$ ,  $^1J(^{107}AgP) 486$  Hz) ppm. MS (EI): 776.9, ( $M^+ - OTf$ ).

5.8. Synthesis of  $[Ag\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}_2][SO_3CF_3]$  (**9**)

To a solution of the ligand **1** (0.106 g, 0.159 mmol) in 15 ml of  $CH_2Cl_2$  was added AgOTf (0.02 g, 0.078 mmol) and the reaction mixture was stirred for 3 h. The clear solution obtained was concentrated to 2 ml, added petroleum ether to precipitate out white stuff, which was filtered and dried to obtain analytically pure product of **9**. Yield: 77% (0.095 g), m.p.:  $170\text{--}172^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{91}H_{68}F_3O_7\text{-}P_4SAg$ : C, 68.55; H, 4.29; S, 2.01. Found: C, 68.13; H, 4.19; S, 1.98%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.22 (d, 4H, Ar), 8.13 (d, 4H, Ar), 6.78–7.87 (m, 12H, Ar, 40H, OPPh<sub>2</sub>), 6.71 (d, 4H, Ar), 4.91 (s, 4H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (121.4 MHz,  $CDCl_3$  ( $-50^\circ\text{C}$ )):  $\delta$  111.7 (2d, 4P, OPPh<sub>2</sub>,  $^1J(^{109}AgP) 489$ ,  $^1J(^{107}AgP) 423$  Hz) ppm. MS (EI): 775.2, ( $M^+ - (L + OTf)$ ).

5.9. Synthesis of  $[Ag\{\eta^2\text{-}Ph_2P(-OC_{10}H_6)-(\mu\text{-}CH_2)(C_{10}H_6O\text{-})PPh_2\text{-}\kappa P, \kappa P\}(PPh_3)(SO_3CF_3)]$  (**10**)

To a solution of the ligand **1** (0.053 g, 0.08 mmol) in 15 ml of  $CH_2Cl_2$  was added  $Ag(PPh_3)OTf$  (0.04 g, 0.077 mmol) and the reaction mixture was stirred for 2 h. The solution was concentrated to 2 ml, added petroleum ether to precipitate out white stuff, which was filtered and dried to obtain analytically pure product of **10**. It was recrystallized from  $CH_2Cl_2$ /petroleum ether mixture to give colorless crystalline product at room temperature. Yield: 91% (0.083 g), m.p.:  $132^\circ\text{C}$  (dec.). Anal. Calc. for  $C_{64}H_{49}F_3O_5\text{-}P_3SAg$ : C, 64.71; H, 4.16; S, 2.69. Found: C, 64.63; H, 4.09; S, 2.58%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.21 (d, 2H, Ar), 8.05 (d, 2H, Ar), 7.13–7.73 (m, 6H, Ar, 20H, OPPh<sub>2</sub>, 15H, PPh<sub>3</sub>), 6.79 (d, 2H, Ar), 4.73 (s, 2H, Ar–CH<sub>2</sub>–Ar).  $^{31}P\{^1H\}$  NMR (121.4 MHz,  $CDCl_3$

(−50 °C):  $\delta$  113.3 (2d br, 2P, OPPh<sub>2</sub>,  $J(\text{AgP})$  342 Hz), 3.8 (2d br, 1P, PPh<sub>3</sub>,  $J(\text{AgP})$  228 Hz). MS (EI): 774.8, ( $\text{M}^+$ −(PPh<sub>3</sub>+OTf)).

### 5.10. Catalytic hydrogenation reactions

All catalytic experiments were performed in a 50 ml or 100 ml stainless steel autoclave at 80 °C pressurized with hydrogen. In a typical experiment, a solution of the catalyst precursor **2** or **3** ( $2.18 \times 10^{-4}$  mmol) and the organic substrate (styrene or phenylacetylene) (0.436 mmol) in 20 ml of THF was placed into the reactor and was sealed. The vessel was purged three times with hydrogen and then the autoclave was pressurized with 20 or 45 atm of hydrogen. The reaction mixture was stirred at 80 °C and the extent of conversion was determined by periodic GC analysis.

## 6. X-ray crystallography

Crystals of **4** and **6** were mounted in a Cryoloop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. A full sphere of data were collected using 606 scans in  $\omega$  (0.3° per scan) at  $\phi = 0^\circ$ , 120° and 240° using the SMART software package [21]. The raw data were reduced to  $F^2$  values using the SAINT+ software [22], and a global refinement of unit cell parameters using 5340–8700 reflections chosen from the full data set was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS [23]). The structure was solved by direct method for **4** or the position of the metal atom was obtained from a sharpened Patterson function for **6** and refined by full-matrix least-squares procedures using the SHELXTL program package [24]. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

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### Appendix A. Supporting information

Full details of data collection and structure refinement for compounds **4** and **6** have been deposited with the Cambridge Crystallography Data Centre, CCDC Nos. 608254

and 608253. CCDC and copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: [www://http.ccdc.cam.ac.uk](http://www://http.ccdc.cam.ac.uk)). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.040.

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