Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 1683–1689
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Large bite bisphosphite, 2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$: Synthesis, derivatization, transition metal chemistry and application towards hydrogenation of olefins

Benudhar Punji, Maravanji S. Balakrishna *

Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India

Received 20 October 2006; received in revised form 19 December 2006; accepted 19 December 2006
Available online 10 January 2007

Abstract

Large bite bisphosphite ligand, 2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$ (**2**), is obtained by reacting chlorophosphite, $\{\text{-}OC_{10}H_6(\mu\text{-}S)C_{10}H_6O\text{-}\}PCl$ (**1**) with 2,6-pyridinedimethanol in presence of triethylamine. Treatment of **2** with aqueous solution of H_2O_2 or elemental sulfur resulted in the formation of bis(oxide) or bis(sulfide) derivatives, 2,6-$C_5H_3N\{CH_2OP(E)(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$ (**3**, E = O; **4**, E = S) in quantitative yield. The 10-membered cationic chelate complex, $[RuCl(\eta^6\text{-}C_{10}H_{14})\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2\text{-}\kappa P,\kappa P]Cl$ (**5**) is produced in the reaction between $[Ru(p\text{-cymene})(\mu\text{-}Cl)(Cl)]_2$ and bisphosphite **2**, whereas the neutral chelate complex, *cis*-$[Rh(CO)Cl\{2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)\}_2\}\text{-}\kappa P,\kappa P]$ (**6**) is isolated in the reaction of **2** with 0.5 equiv. of $[Rh(CO)_2Cl]_2$. Compound **2** on treatment with $M(COD)Cl_2$ (M = Pd, Pt) produce the chelate complexes, $[MCl_2\{\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2\}\text{-}\kappa P,\kappa P]$ (**7**, M = Pd; **10**, M = Pt). Similarly the reaction of bisphosphite **2** with Pd(COD)MeCl affords *cis*-$[PdMe(Cl)\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2\text{-}\kappa P,\kappa P]$ (**8**). Treatment of **2** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in the presence of $AgClO_4$ furnish the cationic complex, $[Pd(\eta^3\text{-}C_3H_5)\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2\text{-}\kappa P,\kappa P]ClO_4$ (**9**). The binuclear complex, $[Au_2Cl_2\{2,6\text{-}C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2\}\text{-}\kappa P,\kappa P]$ (**11**) is obtained in the reaction of compound **2** with two equiv. of $AuCl(SMe_2)$, where the ligand exhibits bridged bidentate mode of coordination. All the complexes are characterized by the ^1H NMR, ^{31}P NMR, elemental analysis and mass spectroscopy data. The cationic ruthenium complex **5** is proved to be an active catalyst for the hydrogenation of styrene and α-methyl styrene.

Keywords: Bisphosphite; Chalcogen derivatives; Chelate complexes; Binuclear complex; Platinum metals; Hydrogenation reactions

1. Introduction

The design and synthesis of new bidentate phosphorus-based ligand systems for transition metal catalyzed reactions has become one of the most intense areas of investigation. The influence of the steric and electronic properties of these ligands on catalytic activity is well understood, however, some other specific effects of the ligands are yet to be rationalized [1]. This limitation made several chemists to synthesize new ligands on the basis of trial and error. The bisphosphines have been extensively used in the optimization of catalytic process and found to be the most useful and versatile ligands for metal catalyzed reactions. In contrast to the bisphosphines, the use of bisphosphites in catalysis is less extensive, though some of them are proved to be very efficient [2]. Several bisphosphite ligands have been developed by tuning their steric and electronic properties and used for rhodium- and iridium-catalyzed hydrogenation [3], nickel-catalyzed olefin hydrocyanation [4], rhodium- and platinum-catalyzed hydroformylation [5], rhodium-catalyzed hydrosilylation of ketones [6] and cobalt-catalyzed Pauson–Khand reaction [2d]. van Leeuwen et al. suggested that the large natural bite angle in such ligands has a pronounced effect on rate

* Corresponding author. Tel.: +91 22 2576 7181; fax: +91 22 2576 7152/2572 3480.
E-mail address: krishna@chem.iitb.ac.in (M.S. Balakrishna).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.12.037

and selectivity during the catalytic reactions [1,7]. In this context, we have designed and synthesized a large bite bisphosphite ligand **2** having the bulky thioether backbone with moderate stability. As a part of our interest in organometallic chemistry [8] and their catalytic investigation [9], we report here the synthesis, chalcogen derivatives and transition metal complexes (Ru^{II}, Rh^{I}, Pd^{II}, Pt^{II} and Au^{I}) of bisphosphite **2**. As will be seen, the ruthenium (II) complex (**5**) exhibits a significant catalytic activity in the hydrogenation reaction of styrene and α-methyl styrene.

2. Results and discussion

2.1. Synthesis of ligand and its chalcogen derivatives

The chlorophosphite, **1**, was synthesized previously from the reaction of thiobis(2,2′-naphthol) with an excess of PCl_3 in the presence of an excess of triethylamine [9d]. Treatment of 2,6-pyridinedimethanol with two equiv. of chlorophosphite, **1**, followed by the addition of triethylamine at −78 °C gives the bisphosphite, 2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$ (**2**) as white crystalline solid (Scheme 1). The ^{31}P NMR spectrum of **2** shows a single resonance at 120.7 ppm. In ^{1}H NMR spectrum, a doublet is observed at 5.45 ppm for the methylene protons (–CH_2–), because of the coupling with phosphorus center. The mass spectrum of compound **2** shows molecular ion peak (M^+) as the base peak at *m*/*z* 832.0. Formation of product **2** is also supported by elemental analysis data.

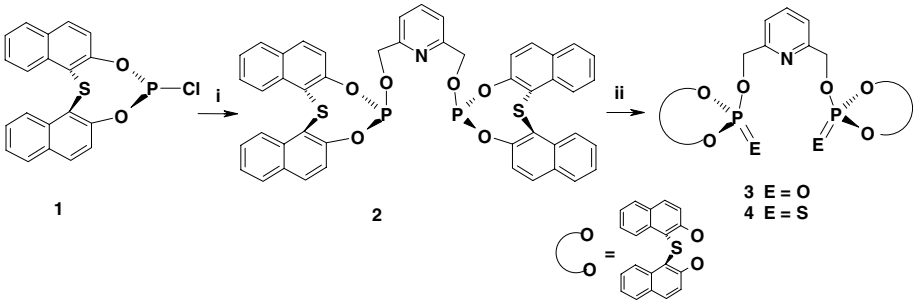
In order to asses the reactivity of the phosphorus (III) centers and their steric and electronic attributes, the oxidation reactions were carried out with oxidizing agents such as hydrogen peroxide and elemental sulfur.

The reaction of bisphosphite **2** with aqueous solution of hydrogen peroxide or elemental sulfur in THF or toluene gives the bisoxide or bissulfide derivatives, 2,6-$C_5H_3N\{CH_2OP(E)(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$ (**3**, E = O;**4**, E = S) in good yield. The ^{31}P NMR spectra of **3** and **4** show single resonance at −13.5 and 55.4 ppm, respectively. In ^{1}H NMR spectrum of each compound a doublet is observed in the region 5.48–5.52 ppm for the –CH_2 protons. The mass spectrum of **3** shows a peak at *m*/*z* 864.1 (100%) corresponding to the molecular ion. Similarly, the mass spectrum of bissulfide derivative **4** shows peaks at *m*/*z* 896.1 and 518.1 correspond to the ion M^+ and M^+-(–O,O–P═S) fragment, respectively.

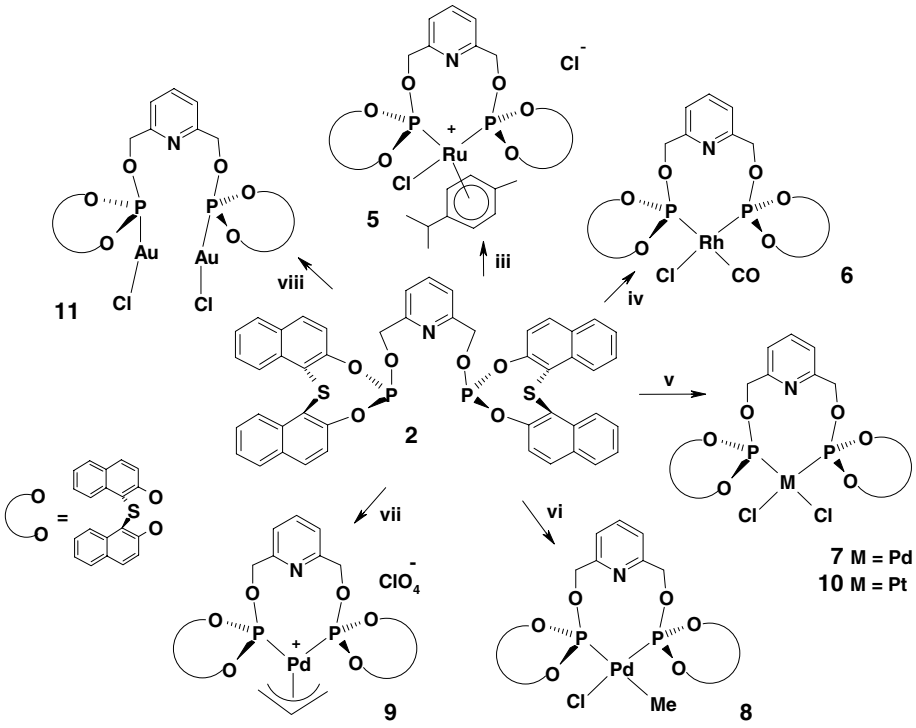
The bisphosphite ligand **2** with five potential donor atoms (two tervalent phosphorus centers, two sulfur atoms and a pyridinic nitrogen center) can act as $2e^-(\eta^1)$, $4e^-(\eta^2)$, $6e^-(\eta^3)$, $8e^-(\eta^4)$ or $10e^-(\eta^5)$ donors depending upon the metal reagents, the stoichiometry, and the reaction conditions. However, it is less likely that the sulfur centers participate in coordination due to the strong bonding interactions between S and P atoms which makes the mesocyclic phosphonate rings less flexible [8a,9d]. In the present investigation due to the sterically demanding phosphorus substituents and their preference to form *cis* complexes, participation of nitrogen coordination was not anticipated. The complexation reactions of ligand **2** was carried out with low-valent transition metals to understand its coordination behavior which in turn gives vital information about its catalytic utility in homogeneous catalysis.

2.2. Ruthenium and rhodium derivatives

The reaction of [Ru(*p*-cymene)(μ-Cl)(Cl)]$_2$ with an excess of bisphosphite **2** in ethanol at 50 °C afforded the cationic complex, [RuCl(η^6-$C_{10}H_{14}$)η^2-2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O-)\}_2$-κ*P*,κ*P*]Cl (**5**) in good yield. A large excess of bisphosphite was used to avoid the formation of phosphite bridged bimetallic complex and the reaction was not carried out under refluxing conditions to prevent the loss of arene on ruthenium precursor [10]. The ^{31}P NMR spectrum of complex **5** shows a singlet at 81.4 ppm. In ^{1}H NMR spectrum, a doublet is observed at 5.65 ppm for the –CH_2 protons of bisphosphite, whereas signals at 3.09 (m), 1.92 (s) and 1.25 (d) ppm confirm the presence of *p*-cymene moiety. Treatment of **2** with [Rh(CO)$_2$Cl]$_2$ in a 2:1 molar ratio in dichloromethane gives the 10-membered chelate complex, *cis*-[Rh(CO)Cl{2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)\}_2$}-κ*P*,κ*P*] (**6**) in quantitative yield (Scheme 2). The IR spectrum of complex **6** exhibits a strong CO absorption at 2009 cm^{-1} suggesting the *trans* disposition of CO ligand to one of the phosphorus centers rather than to chlorine [11]. The ^{13}P NMR spectrum shows two doublet of doublets centered at 111.7 and 93.7 ppm due to the presence of two magnetically non-equivalent phosphorus centers. The corresponding



Scheme 1. Conditions: (i) 2,6-Pyridinedimethanol, Et_3N, THF, −78 °C; (ii) H_2O_2 or S_8, toluene.



Scheme 2. Conditions: (iii) $[Ru(p\text{-cymene})(\mu\text{-Cl})Cl]_2$, EtOH, 50 °C; (iv) $[Rh(CO)_2Cl]_2$, toluene, r.t.; (v) $Pd(COD)Cl_2$ or $Pt(COD)Cl_2$, CH_2Cl_2, r.t.; (vi) Pd(COD)MeCl, toluene, 70 °C; (vii) $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $AgClO_4$, CH_2Cl_2, r.t.; (viii) $AuCl(SMe_2)$, CH_2Cl_2, r.t.

$^1J_{RhP}$ coupling constants are 210 and 153 Hz, respectively, with a $^2J_{PP}$ coupling of 38 Hz. The low field chemical shift with large $^1J_{RhP}$ is assigned to P-atom *trans* to Cl, whereas the upfield shift with comparatively low $^1J_{RhP}$ coupling (153 Hz) is assigned to P-atom *trans* to carbonyl group [11]. The mass spectrum of this complex shows a peak at *m/z* 935, which corresponds to the ion $[M^+ - (CO+Cl)]$.

2.3. Palladium and platinum derivatives

The reactions of bisphosphite **2** with $M(COD)Cl_2$ (M = Pd, Pt) in dichloromethane at room temperature give the corresponding chelate complexes, $[MCl_2\{\eta^2\text{-}2,6\text{-}C_5H_3N\text{-}\{CH_2OP(\text{–}OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O\text{–})\}_2\}\text{-}\kappa P,\kappa P]$ (M = Pd, **7**; M = Pt, **10**) in good yield. The ^{31}P NMR spectrum of **7** and **10** shows single resonance at 90.9 and 88.1 ppm, respectively, with later showing a large $^1J_{PtP}$ coupling of 3227 Hz, which is consistent with the proposed *cis* geometry for similar platinum complexes [8g,8i]. In the mass spectrum of complex **10**, a peak at *m/z* 1062.1 is observed for the ion $(M^+ - Cl)$. In order to know the preferred coordination mode of bisphosphite towards platinum metals, ligand **2** was treated with [Pd(COD)MeCl] in toluene at 70 °C, which gives the chelate complex, $[PdMe(Cl)\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(\text{–}OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O\text{–})\}_2\text{-}\kappa P,\kappa P]$ (**8**) in quantitative yield. The ^{31}P NMR spectrum of complex **8** shows two doublets centered at 108.3 and 69.1 ppm with a $^2J_{PP}$ coupling of 57 Hz. The two doublets confirm *cis*-chelating mode of coordination of bisphosphite **2** to the palladium center. The cationic chelate complex, $[Pd(\eta^3\text{-}C_3H_5)\eta^2\text{-}2,6\text{-}C_5H_3N\{CH_2OP(\text{–}OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O\text{–})\}_2\text{-}\kappa P,\kappa P]ClO_4$ (**9**) is synthesized by the treatment of **2** with 0.5 equiv. of allyl-palladium dimer, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in the presence of two equiv. of $AgClO_4$. The ^{31}P NMR spectrum of complex **9** shows a single resonance at 139.5 ppm. The ^1H NMR spectrum and the microanalysis of complex **9** agree well with the proposed molecular composition.

2.4. Gold derivative

The reaction of compound **2** with two equiv. of $AuCl(SMe_2)$ in dichloromethane at room temperature affords the binuclear complex, $[Au_2Cl_2\{2,6\text{-}C_5H_3N\text{-}\{CH_2OP(\text{–}OC_{10}H_6)(\mu\text{-}S)(C_{10}H_6O\text{–})\}_2\}\text{-}\kappa P,\kappa P]$ (**11**) with ligand exhibiting the bridged bidentate mode of coordination (Scheme 2). The ^{31}P NMR spectrum of complex **11** shows a single resonance at 110.5 ppm and the mass spectrum shows a peak at *m/z* 1260.0 corresponding to $(M^+ - Cl)$ ion. Further evidence for the molecular composition of complex **11** comes from elemental analysis and ^1H NMR data. Attempts to grow single crystals of these complexes suitable for X-ray studies have been unsuccessful.

3. Catalytic activity of ruthenium complex 5

The ruthenium complex **5** is employed for the catalytic hydrogenation of styrene and α-methyl styrene with molecular hydrogen (4 atm) in THF solution at 80 °C to yield ethyl benzene and isopropyl benzene (cumene), respectively. Catalytic studies have been performed without the addition

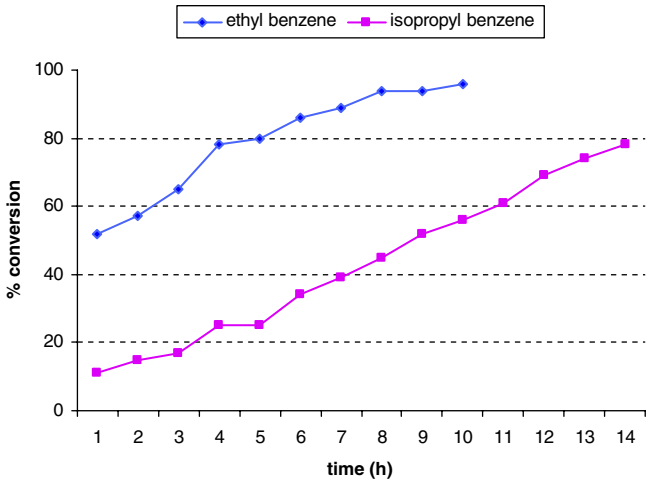


Fig. 1. The hydrogenation of styrene and α-methyl styrene using complex **5**. Styrene (or α-methyl styrene):catalyst **5** = 500:1; solvent, THF (20 ml); 4 atm H_2; 80 °C.

of an organic base, which is usually added when the ruthenium (II) complexes are used.

Using milder conditions that Bennet et al. applied with the catalyst [RuClH(C_6H_6)(PPh_3)] [12], we detected 96% conversion of styrene to ethyl benzene using 0.2 mol% of the catalyst **5** at 80 °C after 10 h (Fig. 1). The hydrogenation of α-methyl styrene to cumene is very slow and gives maximum conversion of 78% even after 14 h under similar reaction conditions. This catalyst precursor is found to be much better than the similar catalyst [RuCl(p-cymene)(PPh_2Py)]$^+$ used by Moldes et al. [13], where they observed 94% conversion of styrene to ethyl benzene with 0.5 mol% of catalyst after 24 h. The homogeneous nature of the catalysis was checked by the classical mercury test [14]. Addition of a drop of mercury to the reaction mixtures did not affect the yields of the hydrogenations thus showing them to be truly homogeneous systems.

4. Conclusion

A new large bite bisphosphite ligand **2** and its chalcogenide derivatives were synthesized. The bisphosphite ligand **2** mostly prefers chelating mode of coordination. With rhodium (I), palladium (II) and platinum (II) derivatives it forms 10-membered neutral chelated complexes, whereas cationic chelate complexes were synthesized with ruthenium (II) and palladium–allyl metal derivatives. Binuclear gold complex **11** was synthesized from the reaction of **2** with gold (I) precursor. Surprisingly, in the present investigation, the pyridyl-nitrogen coordination to the metal centers was not observed mainly due to the bulky substituents on phosphorus centers. The ligands of the type **2** containing mesocyuclic thiophosphonates are known to show bonding interactions between P and S making the mesocyclic rings less flexible. As a result the sulfur atoms may not have participated in coordination. By choosing less bulky phosphorus substituents, the coordination of nitrogen can be envisaged making it more flexible and versatile ligand. However, the nitrogen coordination can be anticipated in an octahedral complex wherein a facial isomer can be formed if the ligand acts as a six-electron donor tridentate ligand. The ruthenium complex **5** shows excellent activity for the hydrogenation of styrene and α-methyl styrene. Further coordination chemistry and the utility of this ligand in other catalytic processes like hydroformylation of olefins, hydrosilylation of ketones, hydrocyanation of olefins is under active investigation in our laboratory.

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. Chlorophosphite, **1** was synthesized previously from thiobis(2,2′-naphthol) and PCl_3 [9d]. The metal precursors [Ru(η^6-cymene)(μ-Cl)Cl]$_2$ [15], [Rh(CO)$_2$-Cl]$_2$ [16], M(COD)Cl_2 (M = Pd, Pt) [17], Pd(COD)MeCl [18], [Pd(η^3-C_3H_5)Cl]$_2$ [19] and AuCl(SMe_2) [20] were prepared according to the published procedures. Other reagents were used as obtained from commercial sources. The ^{1}H and ^{31}P{^{1}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 spectra were recorded in $CDCl_3$ (or DMSO-d_6) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^{1}H and ^{31}P{^{1}H} NMR, respectively. Positive shifts lie downfield of the standard in all of the cases. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as a KBr disk. 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 were uncorrected. GC analyses were performed on a Perkin–Elmer Clarus 500 GC fitted with FID detector and packed column.

5.1. Synthesis of Bisphosphite 2,6-Py{$CH_2OP(-OC_{10}H_6$-(μ-S)$C_{10}H_6O-)$}$_2$ (2)

A solution of chlorophosphite **1** (1.5 g, 3.92 mmol) in THF (20 ml) was added dropwise to a solution of 2,6-pyridinedimethanol (0.27 g, 1.96 mmol) in THF (20 ml) at −78 °C. After 10 min of continuous stirring, Et_3N (0.59 ml, 4.31 mmol) in THF (10 ml) was added dropwise to the reaction solution at same temperature. After the completion of addition, the solution was warmed to room temperature and stirred for 14 h. The solvent was removed under reduced pressure and the white residue obtained was dissolved in 40 ml of toluene and the triethylamine hydrochloride salt was removed by filtration. The clear solution was concentrated and cooled to −25 °C to give analytically pure product of **2**. Yield: 90% (1.45 g). m.p.: 134–136 °C.

Anal. Calc. for $C_{47}H_{31}O_6NP_2S_2$: C, 67.86; H, 3.76; N, 1.68; S, 7.71. Found: C, 67.72; H, 3.69; N, 1.63; S, 7.65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 4H, Ar, $^3J_{HH} = 8.0$ Hz), 7.95 (t, 1H, Py, $^3J_{HH} = 8.0$ Hz), 7.26–7.72 (m, 2H, Py, 16H, Ar), 7.14 (d, 4H, Ar, $^3J_{HH} = 8.8$ Hz), 5.45 (d, 4H, CH_2, $^3J_{PH} = 6.4$ Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 120.7 (s). MS (EI): *m/z* 832.0 (M^+).

5.2. Synthesis of 2,6-$C_5H_3N\{CH_2OP(O)(-OC_{10}H_6)$-$(\mu$-$S)(C_{10}H_6O-)\}_2$ (3)

An aqueous solution (30%) of H_2O_2 (0.027 ml, 0.24 mmol) in THF (5 ml) was added dropwise to a solution of bisphosphite **2** (0.1 g, 0.12 mmol) in THF (8 ml) at room temperature. After stirring for 3 h, the solvent was removed under vacuum. The white residual product obtained was recrystallized from CH_2Cl_2/petroleum ether mixture to give pure product **3**. Yield: 83% (0.086 g). m.p.: 148–150 °C. Anal. Calc. for $C_{47}H_{31}NO_8P_2S_2$: C, 65.35; H, 3.62; N, 1.62; S, 7.42. Found: C, 65.26; H, 3.56; N, 1.60; S, 7.32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, 4H, Ar, $^3J_{HH} = 8.8$ Hz), 7.89 (t, 1H, Py, $^3J_{HH} = 8.0$ Hz), 7.25–7.79 (m, 2H, Py, 16H, Ar), 7.24 (d, 4H, Ar, $^3J_{HH} = 8.0$ Hz), 5.52 (d, 4H, CH_2, $^3J_{PH} = 9.20$ Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −13.5 (s). MS (EI): *m/z* 864.1 (M^+).

5.3. Synthesis of 2,6-$C_5H_3N\{CH_2OP(S)(-OC_{10}H_6)$-$(\mu$-$S)(C_{10}H_6O-)\}_2$ (4)

A mixture of bisphosphite **2** (0.1 g, 0.12 mmol) and elemental sulfur (0.008 g, 0.24 mmol) in toluene (10 ml) was heated at 90 °C for 4 h. The reaction mixture was allowed to attain the room temperature and the solvent was removed under vacuum. The resulted white residue was recrystallized from CH_2Cl_2/petroleum ether to give the white crystalline product **3**. Yield: 78% (0.084 g). m.p.: 170–172 °C. Anal. Calc. for $C_{47}H_{31}NO_6P_2S_4$: C, 63.01; H, 3.49; N, 1.56; S, 14.32. Found: C, 62.89; H, 3.42; N, 1.49; S, 14.23%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, 4H, Ar, $^3J_{HH} = 8.0$ Hz), 7.84 (t, 1H, Py), 7.19–7.73 (m, 2H, Py, 20H, Ar), 5.48 (d, 4H, CH_2, $^3J_{PH} = 9.20$ Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 55.4 (s). MS (EI): *m/z* 896.1 (M^+), 518.1 ($M^+-O_2P(S)$).

5.4. Synthesis of $[RuCl(\eta^6$-$C_{10}H_{14})\eta^2$-2,6-$C_5H_3N\{CH_2OP$-$(-OC_{10}H_6)(\mu$-$S)(C_{10}H_6O-)\}_2$-$\kappa P,\kappa P][Cl]$ (5)

A mixture of bisphosphite **2** (0.108 g, 0.13 mmol) and [Ru(p-cymene)(μ-Cl)Cl]$_2$ (0.02 g, 0.033 mmol) in ethanol (12 ml) was heated at 50 °C for 18 h. The reaction mixture was allowed to attain the room temperature, filtered with celite and the volatile was removed under reduced pressure. The resulted crude product was recrystallized in acetone to give the pure desired product **5**. Yield: 88% (0.065 g). m.p.: 134 °C (dec.). Anal. Calc. for $C_{57}H_{45}Cl_2NO_6P_2S_2Ru$: C, 60.16; H, 3.99; N, 1.23; S, 5.64. Found: C, 60.01; H, 3.83; N, 1.02; S, 5.58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, 4H, Ar, $^3J_{HH} = 8.4$ Hz), 7.21–7.75 (m, 3H, Py, 20H, Ar, 4H, cymene), 5.65 (d, 4H, CH_2, $^3J_{PH} = 9.20$ Hz), 3.09 (m, 1H, cymene), 1.92 (s, 3H, CH_3), 1.25 (d, 6H, $C(CH_3)_2$, $^3J_{HH} = 6.8$ Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ 81.4 (s).

5.5. Synthesis of $[Rh(CO)Cl\{2,6$-$C_5H_3N\{CH_2OP$-$(-OC_{10}H_6(\mu$-$S)C_{10}H_6O-)\}_2\}$-$\kappa P,\kappa P]$ (6)

A solution of $[Rh(CO)_2Cl]_2$(0.015 g, 0.038 mmol) in toluene (5 ml) was added dropwise to a solution of bisphosphite **2** (0.064 g, 0.077 mmol) in toluene (8 ml) and the reaction mixture was stirred for 4 h. The resulting yellow suspension was filtered and dried to get the pure product **5**. The filtrate was also concentrated to give the same product at −25 °C. Yield: 68% (0.052 g). m.p.: 178–180 °C (dec.). Anal. Calc. for $C_{48}H_{31}ClNO_7P_2S_2Rh$: C, 57.76; H, 3.13; N, 1.40; S, 6.42. Found: C, 57.61; H, 3.05; N, 1.38; S, 6.33%. FT IR (KBr disk) cm^{-1}: ν(CO): 2009 vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 4H, Ar, $^3J_{HH} = 8.4$ Hz), 7.14–7.95 (m, 3H, Py, 20H, Ar), 5.45 (d, 4H, CH_2, $^3J_{PH} = 6.4$ Hz). ^{13}P{^{1}H} NMR (121.4 MHz, DMSO-d_6): δ 111.7 (dd, $^1J_{Rh-P} = 210$ Hz), 93.7 (dd, $^1J_{Rh-P} = 153$ Hz), ($^2J_{P-P} = 38$ Hz). MS (EI): *m/z* 935 (M^+-(CO+Cl)).

5.6. Synthesis of $[PdCl_2\{\eta^2$-2,6-$C_5H_3N\{CH_2OP(-OC_{10}H_6)$ $(\mu$-$S)(C_{10}H_6O-)\}_2\}$-$\kappa P,\kappa P]$ (7)

A solution of bisphosphite **2** (0.073 g, 0.088 mmol) in CH_2Cl_2 (8 ml) was added dropwise to a solution of Pd(COD)Cl_2 (0.025 g, 0.088 mmol) in CH_2Cl_2(6 ml) at room temperature and the reaction mixture was stirred for 3 h. The precipitate formed was filtered, washed with Et_2O and dried. Yield: 66% (0.058 g). m.p.: 168 °C (dec.). Anal. Calc. for $C_{47}H_{31}Cl_2NO_6P_2S_2Pd$: C, 55.94; H, 3.09; N, 1.39; S, 6.36. Found: C, 55.86; H, 2.99; N, 1.32; S, 6.21%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 (d, 4H, Ar, $^3J_{HH} = 8.4$ Hz), 7.21–8.15 (m, 3H, Py, 20H, Ar), 5.64 (br s, 4H, CH_2). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ 90.9 (s).

5.7. Synthesis of $[PdMe(Cl)\{\eta^2$-2,6-$C_5H_3N\{CH_2OP$-$(-OC_{10}H_6)$ $(\mu$-$S)(C_{10}H_6O-)\}_2\}$-$\kappa P,\kappa P]$ (8)

A suspension of bisphosphite **2** (0.078 g, 0.094 mmol) and Pd(COD)MeCl (0.025 g, 0.094 mmol) in toluene (10 ml) was heated at 70 °C for 12 h. The reaction mixture was allowed to attain the room temperature and was filtered through celite. The solvent was removed under reduced pressure and the resulted residue was recrystallized from CH_2Cl_2 and diethyl ether mixture to give crystalline product of **8**. Yield: 70% (0.065 g). m.p.:162 °C (dec.). Anal. Calc. for $C_{48}H_{34}ClNO_6P_2S_2Pd$: C, 58.31; H, 3.47; N, 1.42; S, 6.49. Found: C, 58.22; H, 3.39; N, 1.38; S, 6.37%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 (d, 4H,

Ar, $^3J_{HH} = 8.8$ Hz), 7.10–8.51 (m, 3H, Py, 20H, Ar), 5.62 (s, 4H, CH_2), 1.17 (t, 3H, CH_3, $^3J_{PH} = 7.2$ Hz). $^{13}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 108.3 (d, $^2J_{P-P} = 57$ Hz), 69.1 (d, $^2J_{P-P} = 57$ Hz).

5.8. Synthesis of [Pd(η^3-C_3H_5)η^2-2,6-C_5H_3N{CH_2OP-($-OC_{10}H_6$)(μ-S)($C_{10}H_6O-$)}$_2$-$\kappa P,\kappa P$]ClO_4 (9)

A solution of [Pd(η^3-C_3H_5)Cl]$_2$ (0.02 g, 0.055 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a solution of bisphosphite **2** (0.091 g, 0.109 mmol) in CH_2Cl_2 (6 ml) at room temperature. After 2 h, $AgClO_4$ (0.025 g, 0.109 mmol) was added and the reaction mixture was stirred for additional 30 min. The suspension was filtered through celite to separate AgCl salt. The solution obtained was concentrated to 2 ml and layered with petroleum ether, which gives yellow crystalline product of **9**. Yield: 75% (0.089 g). m.p.: 184 °C (dec.). Anal. Calc. for $C_{50}H_{36}ClNO_{10}P_2S_2Pd$: C, 55.67; H, 3.36; N, 1.29; S, 5.94. Found: C, 55.62; H, 3.31; N, 1.25; S, 5.88%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, 4H, Ar, $^3J_{HH} = 8.8$ Hz), 7.22–7.75 (m, 3H, Py, 12H, Ar), 7.18 (d, 8H, Ar, $^3J_{HH} = 8.8$ Hz), 5.63 (s, 4H, CH_2), 5.14–5.27 (m, 1H, *allyl*), 4.84 (br s, 2H, *allyl*), 4.04 (br s, 2H, *allyl*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 139.5 (s).

5.9. Synthesis of [$PtCl_2${η^2-2,6-C_5H_3N{CH_2OP-($-OC_{10}H_6$)(μ-S)($C_{10}H_6O-$)}$_2$}-$\kappa P,\kappa P$] (10)

A solution of bisphosphite **2** (0.058 g, 0.07 mmol) in CH_2Cl_2 (8 ml) was added dropwise to a solution of Pt(COD)Cl_2 (0.025 g, 0.067 mmol) in CH_2Cl_2(6 ml) at room temperature and stirred for 3 h. The white precipitate formed was filtered and was dried under vacuum to the desired product. Yield: 66% (0.048 g). m.p.: 186 °C (dec). Anal. Calc. for $C_{47}H_{31}Cl_2NO_6P_2S_2Pt$: C, 51.42; H, 2.85; N, 1.27; S, 5.84. Found: C, 51.36; H, 2.56; N, 1.23; S, 5.59%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.52 (d, 4H, Ar, $^3J_{HH} = 8.4$ Hz), 7.18–8.31 (m, 3H, Py, 20H, Ar), 5.75 (br s, 4H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 88.1 (s, $^1J_{Pt-P} = 3227$ Hz). MS (EI): m/z 1062.1 (M^+-Cl).

5.10. Synthesis of [Au_2Cl_2{2,6-C_5H_3N{$CH_2OP(-OC_{10}H_6)$-(μ-S)($C_{10}H_6O-$)}$_2$}-$\kappa P,\kappa P$] (11)

A solution of bisphosphite **2** (0.042 g, 0.051 mmol) in CH_2Cl_2 (8 ml) was added dropwise to a solution of AuCl(SMe_2) (0.03 g, 0.102 mmol) in CH_2Cl_2 (6 ml) and was stirred at room temperature for 4 h. The resulting solution was concentrated to 3 ml and was layered with petroleum ether, which on cooling to −25 °C gives the desired product. Yield: 88% (0.058 g). m.p.: 176 °C (dec). Anal. Calc. for $C_{47}H_{31}Cl_2NO_6P_2S_2Au_2$: C, 43.53; H, 2.41; N, 1.08; S, 4.95. Found: C, 43.29; H, 2.28; N, 1.02; S, 4.76%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, 4H, Ar, $^3J_{HH} = 8.4$ Hz), 7.21–7.82 (m, 3H, Py, 20H, Ar), 5.56 (d, 4H, CH_2, $^3J_{PH} = 11.2$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 110.5 (s). MS (EI): m/z 1260.0 (M^+-Cl).

5.11. Catalytic hydrogenation reactions

All catalytic experiments were performed in a 50 ml stainless steel autoclave at 80 °C pressurized with hydrogen. In a typical experiment, a solution of the catalyst precursor **5** (9.92×10^{-4} g, 8.72×10^{-4} mmol) and the organic substrate (styrene or α-methyl styrene) (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 4 atmosphere of hydrogen. The reaction mixture was stirred at 80 °C and the extent of conversion was determined by periodic GC analysis.

Acknowledgements

We are grateful to the Department of Science and Technology (DST), New Delhi for funding through Grant SR/S1/IC-05/2003. B.P. thanks CSIR for Senior Research Fellowship (SRF). We also thank SAIF, Mumbai, Department of Chemistry Instrumentation Facilities, Bombay, for spectral and analytical data.

Appendix A. Supplementary material

Important spectroscopic data of compounds **2**–**4**, **6**, **8**, **10** and **11**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.037.

References

[1] Z. Freixa, P.W.N.M. van Leeuwen, Dalton Trans. (2003) 1890–1901, and references there in.
[2] (a) J.R. Briggs, J. Klosin, G.T. Whiteker, Org. Lett. 7 (2005) 4795–4798;
(b) C.J. Cobley, K. Gardner, J. Klosin, C. Praquin, C. Hill, G.T. Whiteker, A. Zanotti-Gerosa, J.L. Petersen, K.A. Abboud, J. Org. Chem. 69 (2004) 4031–4040;
(c) G.T. Whiteker, J.R. Briggs, J.E. Babin, B.A. Barner, Chemical Industries, Catalysis of Organic Reactions, vol. 89, Marcel Dekker, New York, 2003, pp. 359–367;
(d) S.J. Sturla, S.L. Buchwald, J. Org. Chem. 67 (2002) 3398–3403;
(e) J.R. Briggs, G.T. Whiteker, Chem. Commun. (2001) 2174–2175;
(f) Z. Freixa, J.C. Baýon, J. Chem. Soc., Dalton Trans. (2001) 2067–2068;
(g) P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation (Catalysis by Metal Complexes), vol. 22, Kluwer Academic Press, Dordrecht, The Netherlands, 2000, p. 284.
[3] (a) O. Pàmies, G. Net, A. Ruiz, C. Claver, Eur. J. Inorg. Chem. (2000) 1287–1294;
(b) M.T. Reetz, T. Neugebauer, Angew. Chem., Int. Ed. 38 (1999) 179–181.
[4] M. Yan, Q.Y. Xu, A.S.C. Chan, Tetrahedron: Asymmetry 11 (2000) 845–849.
[5] (a) G.J.H. Buisman, L.A. van der Veen, A. Klootwijk, W.G.J. de Lange, P.C.J. Kamer, P.W.N.M. van Leewen, D. Vogt, Organometallics 16 (1997) 2929–2939;

(b) R. Kadyrov, D. Heller, R. Selke, Tetrahedron: Asymmetry 9 (1998) 329–340;
(c) S. Cserépi-Szűcs, G. Huttner, L. Zsolnai, A. Szölősy, C. Hegedüs, J. Bakos, Inorg. Chim. Acta 296 (1999) 222–230.
[6] (a) A.R. Smith, J.W. Bruno, S.D. Pastor, Phosphorus, Sulfur Silicon Relat. Elem. 177 (2002) 479–485;
(b) J. Sakaki, W.B. Schweizer, D. Seebach, Helv. Chim. Acta 76 (1993) 2654–2665.
[7] (a) R.P.J. Bronger, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 22 (2003) 5358–5369;
(b) P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, Acc. Chem. Res. 34 (2001) 895–904;
(c) P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, P. Dierkes, Chem. Rev. 100 (2000) 2741–2770;
(d) L.A. van der Veen, P.H. Keeven, G.C. Schoemaker, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Lutz, A.L. Spek, Organometallics 19 (2000) 872–883.
[8] (a) B. Punji, J.T. Mague, M.S. Balakrishna, Eur. J. Inorg. Chem. (2007) 720–731;
(b) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 45 (2006) 5893–5897;
(c) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 45 (2006) 6678–6683;
(d) B. Punji, M.S. Balakrishna, Indian J. Chem. A 45 (2006) 1390–1394;
(e) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 44 (2005) 7925–7932;
(f) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Organometallics 24 (2005) 3780–3783;
(g) S. Priya, M.S. Balakrishna, J.T. Mague, S.M. Mobin, Inorg. Chem. 42 (2003) 1272–1281;
(h) M.S. Balakrishna, R. Panda, J.T. Mague, J. Chem. Soc., Dalton Trans. (2002) 4617–4621;
(i) M.S. Balakrishna, R. Panda, J.T. Mague, Inorg. Chem. 40 (2001) 5620–5625;
(j) M.S. Balakrishna, R.M. Abhyankar, J.T. Mague, J. Chem. Soc., Dalton Trans. (1999) 1407–1412.
[9] (a) B. Punji, J.T. Mague, M.S. Balakrishna, Dalton Trans. (2006) 1322–1330;
(b) B. Punji, C. Ganesamoorthy, M.S. Balakrishna, J. Mol. Catal. A 259 (2006) 78–83;
(c) B. Punji, J.T. Mague, M.S. Balakrishna, J. Organomet. Chem. 691 (2006) 4265–4272;
(d) B. Punji, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 45 (2006) 9454–9464;
(e) S. Mohanty, B. Punji, M.S. Balakrishna, Polyhedron 25 (2006) 815–820;
(f) S. Priya, M.S. Balakrishna, S.M. Mobin, R. McDonald, J. Organomet. Chem. 688 (2003) 227–235.
[10] C. Daguenet, R. Scopelliti, P.J. Dyson, Organometallics 23 (2004) 4849–4857.
[11] E.K. van den Beuken, W.G.J. de Lange, P.W.N.M. van Leeuwen, N. Veldman, A.L. Spek, B.L. Feringa, J. Chem. Soc., Dalton Trans. (1996) 3561–3569.
[12] M.A. Bennett, T.N. Huang, A.K. Smith, T.W. Turney, J. Chem. Soc., Chem. Commun. (1978) 582–583.
[13] I. Moldes, E. de la Encarnacion, J. Ros, A. Alvarez-Larena, J.F. Piniella, J. Organomet. Chem. 566 (1998) 165–174.
[14] (a) J.A. Widegren, M.A. Bennett, R.G. Finke, J. Am. Chem. Soc. 125 (2003) 10301–10310;
(b) J.A. Widegren, R.G. Finke, J. Mol. Catal. A 198 (2003) 317–341.
[15] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74–78.
[16] J.A. McCleverty, G. Wilkinson, Inorg. Synth. 28 (1990) 84–86.
[17] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1990) 346–349.
[18] B.S. Heinz, W. Heitz, S.A. Krugel, F. Raubacher, J.H. Wendorff, Acta Polym. 48 (1997) 385–391.
[19] Y. Tatsuno, T. Yoshida, S. Otsuka, Inorg. Synth. 28 (1990) 342–343.
[20] M.C. Brandys, M.C. Jennings, R.J. Puddephatt, J. Chem. Soc., Dalton Trans. (2000) 4601–4606.