

## Synthesis of triethylphosphite complexes of nickel(II) and palladium(II) with tridentate Schiff base ligand for catalytic application in carbon–carbon coupling reactions

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### ABSTRACT

Air stable Ni(II) and Pd(II) complexes viz. [Ni(LS)(P(OEt)<sub>3</sub>)] (1), [Ni(LN)(P(OEt)<sub>3</sub>)] (2), [Pd(LS)(P(OEt)<sub>3</sub>)] (3) and [Pd(LN)(P(OEt)<sub>3</sub>)] (4) [where LS and LN are dianions of *N*-(2-mercaptophenyl)salicylideneimine and *N*-(2-mercaptophenyl)naphthylideneimine respectively] have been synthesized and characterized by analytical and spectral (electronic, FT-IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR) methods. The <sup>1</sup>H–<sup>31</sup>P HMBC spectrum established the coupling of phosphorus with the azomethine proton of the Schiff base and the aliphatic protons of triethylphosphite. Novel Ni(II) and Pd(II) complexes exhibited good catalytic activity in Kumada–Tamao–Corriu and Suzuki–Miyaura coupling reactions respectively.

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The chemistry of transition metal complexes with coordinated phosphorus ligands has been known for a long time [1]. A significant amount of work has been carried out on the syntheses and reactivity of phosphine complexes of transition metals, particularly with platinum group metals [2,3]. Alkyl phosphites are in some respects more tractable than the phosphines, but still only little attention has been paid to phosphite complexes [4]. Phosphite ligands possess good π-acceptor property owing to the availability of vacant 3dπ orbitals on the phosphorus atom, which makes possible back bonding with filled dπ orbitals of metal ions [5]. Phosphite complexes have been used as catalysts for hydrocyanation [6,7], hydroformylation [8], alkene oligomerization [9,10] and isomerization [11,12] reactions. Recently, Takeda *et al.* have applied Ni[P(OEt)<sub>3</sub>]<sub>4</sub> as catalyst for the transformations of (*E*)-alkenyl halides into sulphides [13] and allylic acetates into allylic sulphides [14].

Schiff base ligands which can accommodate various substituents play an important role in tuning the electronic property of metal ions in its complexes [15]. Many transition metal Schiff base complexes have been utilized as catalysts for important organic transformations [16,17]. Of which, considerable amount of Schiff base complexes contain tertiary phosphine as auxiliary ligand [18,19]. We could not find any report on Schiff base complexes incorporating phosphite ligand even though phosphite ligands are inexpensive compared to tertiary phosphines. Moreover, most of the homogeneous catalysts containing phosphite ligand exist in low valent state i.e. zero [13,14,20]. In this paper, we report the synthesis and characterization of Ni(II) and

Pd(II) complexes containing ONS donor tridentate Schiff base (Fig. 1) and triethylphosphite ligands. Carbon–carbon bond forming reactions involving aryl halides are important synthetic transformations in synthetic chemistry [21–26]. Interestingly, new air stable Ni(II) and Pd(II) complexes act as good catalysts for Kumada–Tamao–Corriu and Suzuki–Miyaura coupling reactions respectively.

As shown in Scheme 1, the reactions of tridentate Schiff base ligand (H<sub>2</sub>LS/H<sub>2</sub>LN) [27,28], metal salt (NiBr<sub>2</sub>/PdCl<sub>2</sub>) and triethylphosphite in presence of few drops of triethyl amine yielded the corresponding metal complexes in moderate yield [29]. All the prepared complexes were air stable and non-hygroscopic. They were found to be soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMSO and DMF. The Schiff bases behave as dianionic tridentate ligands using phenolic oxygen, azomethine nitrogen and thiolate sulfur atoms for bonding with Ni(II)/Pd(II).

The UV–Visible spectra of all the complexes in dichloromethane showed four bands in the region 231–446 nm. The bands appearing in the region 231–289 nm have been assigned to intraligand transitions. A less intense band in the region 322–336 nm corresponds to metal-to-ligand charge transfer transition (MLCT). The UV–Visible spectra of Ni(II) and Pd(II) complexes also showed d-d transition in the region 413–446 nm. The results are in accordance with the electronic spectra of other similar square planar Ni(II) and Pd(II) complexes [30,31].

The IR spectra of Ni(II) and Pd(II) complexes of the Schiff base are compared with that of the free Schiff base in order to determine the coordination sites. The spectra of ligands showed a strong band around 1614–1621 cm<sup>-1</sup> due to ν(C=N). As a result of coordination, this band has been shifted to a lower wave number (1605–1615 cm<sup>-1</sup>) in the complexes, indicating participation of the azomethine nitrogen in

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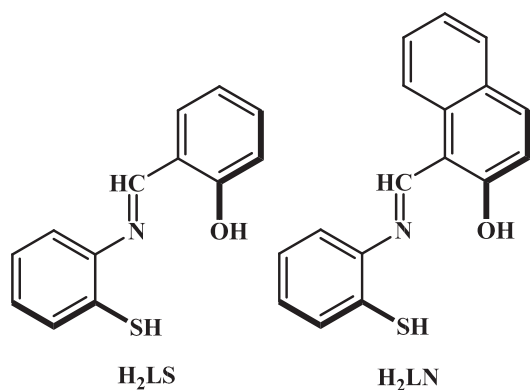
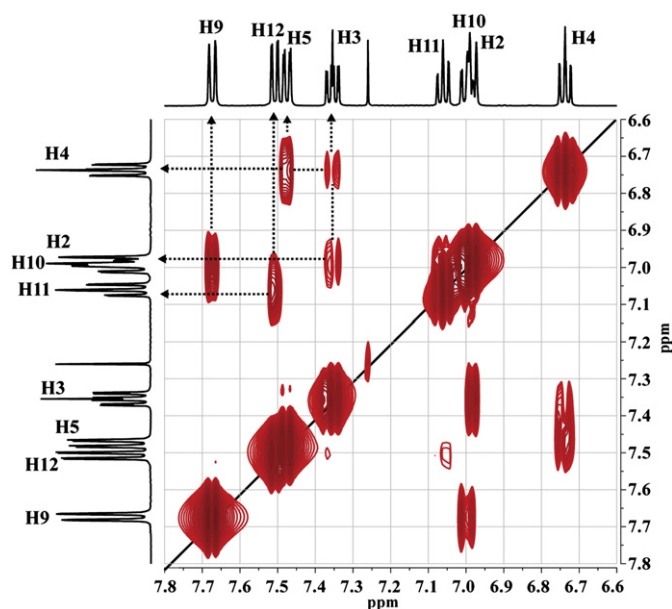


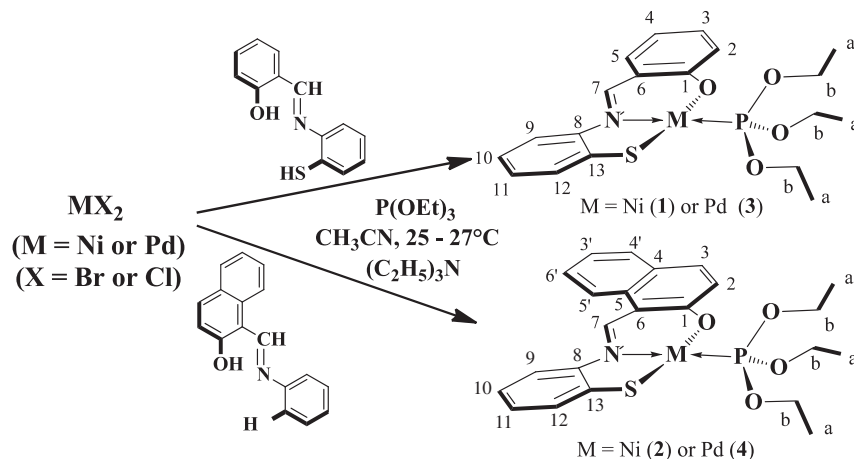
Fig. 1. Structure of ligands.

coordination [32,33]. The band in the region  $1304\text{--}1316\text{ cm}^{-1}$ , which is assigned to phenolic oxygen in the free ligand is shifted to a higher wave number ( $1310\text{--}1334\text{ cm}^{-1}$ ) in complexes, suggesting the coordination through phenolic oxygen to Pd(II) and Ni(II) ions [32,33]. However, participation of thiolato sulfur atom in coordination is ascertained from the negative shift of  $\nu(\text{C}\text{--}\text{S})$  in complexes by  $5\text{--}9\text{ cm}^{-1}$  compared to ligands [34–37]. Bands due to triethylphosphite are appeared in the expected region [38].

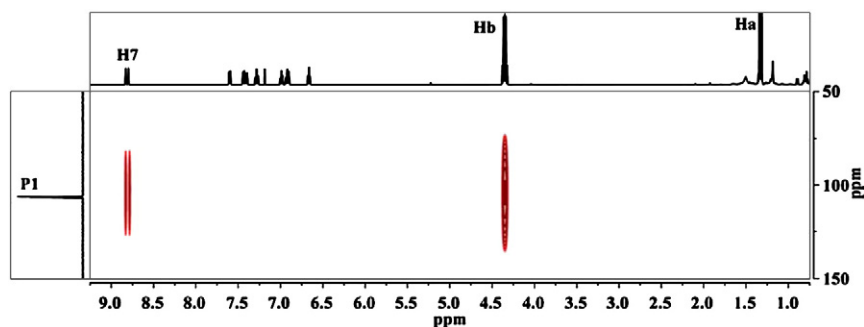
The disappearance of signals due to phenolic and thiolato hydrogen atoms in the  $^1\text{H}$  NMR spectra of all the Ni(II) and Pd(II) complexes indicates the deprotonation of these groups and the Schiff bases are coordinated to metal ions as dianionic ligands. A doublet observed in the  $^1\text{H}$  NMR spectra of all the complexes in the region  $8.87\text{--}9.88\text{ ppm}$  ( $^4J_{\text{P,H}} = 15.4\text{--}23.6\text{ Hz}$ ) has been assigned to the  $\text{HC}=\text{N}$

Fig. 3.  $^1\text{H}\text{--}^1\text{H}$  COSY spectrum of  $[\text{Ni}(\text{LS})(\text{P}(\text{OEt})_3)](\mathbf{1})$ .

resonance.  $^1\text{H}\text{--}^{31}\text{P}$  HMBC spectrum (Fig. 2) of  $\mathbf{1}$  revealed that this doublet is due to four bond coupling of phosphorus in triethylphosphite with the azomethine proton [39]. The strong coupling of azomethine proton in Pd(II) complexes ( $\sim 23\text{ Hz}$ ) compared to corresponding Ni(II) complexes ( $\sim 15\text{ Hz}$ ) is due to the fact that  $\pi$  electron cloud of azomethine group in Pd(II) complexes is attracted towards the large



Scheme 1. Synthesis of nickel(II) and palladium(II) complexes.

Fig. 2.  $^1\text{H}\text{--}^{31}\text{P}$  HMBC spectrum of  $[\text{Ni}(\text{LS})(\text{P}(\text{OEt})_3)](\mathbf{1})$ .

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