

# Synthesis and characterization of nickel and palladium complexes containing hetero-multidentate PNO ligands

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## Abstract

Formation of mono- and dinuclear complexes containing ligands stemmed from the condensation of 2,6-diformyl-4-methylphenol derivatives with 2-(diphenylphosphino)aniline ( $P\sim N$ ) was investigated. Condensation of  $P\sim N$  with 2,6-diformyl-4-methylanisole yielded the desired bis(imine-phosphine)  $L_3$ , but provided the cyclized benzoazaphospholium compound with 2,6-diformyl-4-methylphenol. Complexation of  $L_3$  with  $(COD)PdCl_2$  gave the dinuclear complex **4**. On the other hand,  $L_3$  underwent the intramolecular cyclization in the presence of  $(DME)NiCl_2$  via the formation of benzoazaphospholium rings. Template condensation of 2,6-diformyl-4-methylphenol with  $P\sim N$  in the presence of metal ions yielded the mononuclear nickel(II) and palladium(II) complexes, respectively.

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## 1. Introduction

There is a considerable interest in the design and synthesis of ligands consisting of both soft and hard donors to accommodate metal ions for fine-tuning their properties [1]. Accordingly, unsymmetrical bidentate ligands with a nitrogen and a phosphorus donor atoms [referred to as  $PN$  ligands] have received much attention recently, due to the distinct *trans* effect of these donors [2]. Furthermore, heterotridentate  $PNO$  ligands resulted from the combination of  $PN$  with an extra oxygen donor displaying unique features in manipulating the catalytic activity on polymerization [3,4]. Several other known  $PNO$  ligands involving an *o*-phenylene  $PN$  frame are appeared in Chart 1. Ligand  $L_A$  was studied for the coordination toward  $Fe(III)$ ,  $Co(III)$  and  $Re(V)$  ions [5],

whereas ligand  $L_B$  demonstrated the versatility in the formation of  $Ni(II)$  [6a],  $Pd(II)$  [4,6],  $Pt(II)$  [6], and  $Ru(II)$  [7] complexes as a tridentate. The binuclear  $Rh(I)$  complexes of ligand  $L_C$  were studied for hydrosilylation of ketones [8]. In our laboratory, the coordination behavior of ligand  $L_D$  toward palladium(II) was investigated [9,10]. Continuing this trend, we pursue to synthesize new multi-chelating ligands  $L_n$  (Scheme 1) from 2,6-diformyl-4-methylphenol and study the coordination ability of these related multidentates toward  $Pd(II)$  and  $Ni(II)$  ions.

## 2. Results and discussion

### 2.1. Preparation of ligands

In an attempt to synthesize the ligand  $L_2$  by the condensation of 2,6-diformyl-4-methylphenol with 2-(diphenylphosphino)aniline ( $P\sim N$ ) (1:2) in the presence of a

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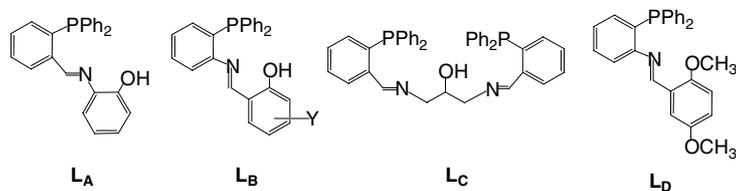
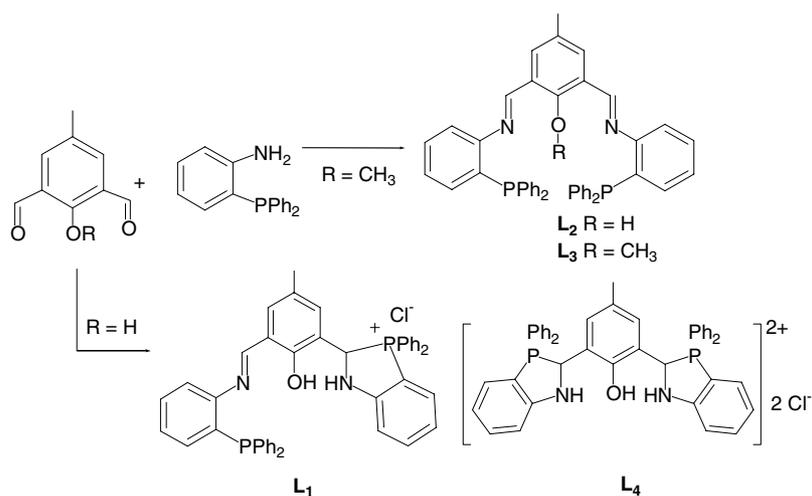


Chart 1. Various PNO ligands.



Scheme 1. Ligand synthesis.

trace amount of conc. HCl in toluene under nitrogen atmosphere afforded the one side cyclized benzoazaphospholium schiff base ligand **L<sub>1</sub>** instead of the anticipated ligand **L<sub>2</sub>** (Scheme 1). The <sup>31</sup>P NMR spectrum showed two absorptions at –14.8 and 36.8 ppm, which were corresponding to the *tert*-phosphine and the cyclized benzoazaphospholium group [11], respectively. The infrared spectrum showed a strong absorption at 1624 cm<sup>–1</sup> manifesting the formation of imine functionality, which was also evidenced by the <sup>1</sup>H NMR signal at 8.32 ppm for the imino proton. Interestingly, the bis-benzoazaphospholium compound **L<sub>4</sub>** was obtained when the reaction was carried out in a polar solvent such as dichloromethane (see below).

Under similar conditions, reaction of 2,6-diformyl-4-methylanisole with **P~N** in a molar ratio of 1:2 afforded the bis-imine ligand **L<sub>3</sub>** in good yield (70%). Crystallization from dichloromethane and hexane gave lemon yellow crystals. IR spectrum shows a strong characteristic absorption for imine group at 1617 cm<sup>–1</sup>. The <sup>31</sup>P NMR spectrum exhibits one signal at –16.1 ppm corresponding to the presence of a *tert*-diphenylphosphino group. All spectral data including <sup>1</sup>H, <sup>13</sup>C NMR as well as FAB mass spectrum and elemental analysis of **L<sub>3</sub>** are consistent with the structure proposed. From the above observation, it is assumed that the phenolic proton readily facilitates the cyclization of benzoazaphospholium

ring. It has been known that condensation of **P~N** with a carbonyl compound in the presence of acid could provide the cyclized benzoazaphospholium products [11].

## 2.2. Nickel(II) complexes

Reaction of **L<sub>3</sub>** with Ni(DME)Cl<sub>2</sub> (1:2) in dichloromethane resulted in the cyclization of ligand to form the azaphospholium **1** in 28% isolated yield. (Eq. (1)) Recrystallization from dichloromethane and hexane gave light blue crystals. The <sup>31</sup>P NMR spectrum of the compound shows only one singlet absorption at 41.2 ppm, which is typical for the phosphonium group. The X-ray structural characterization of the complex shows the formation of bis-benzoazaphospholium ring of the ligand with the [NiCl<sub>4</sub>]<sup>–2</sup> as counter anion (Fig. 1). It appeared that the phosphorus and nitrogen donors do not bound to the metal ion. Distances of C(9)–N(2) [1.464(6) Å] and C(28)–N(1) [1.476(6) Å] are typical for a C–N single bond, indicating that the molecule does not include any imine functionality. Examination of the carbon to phosphorus distances and the associated bond angle clearly shows that the phosphorus atom is seated in a tetrahedral geometry, a typical phosphonium salt. It appears that the nickel ions act as Lewis acid to catalyze the cyclization of the phospholium ions and undergo the disproportionation to yield [NiCl<sub>4</sub>]<sup>2–</sup>, which

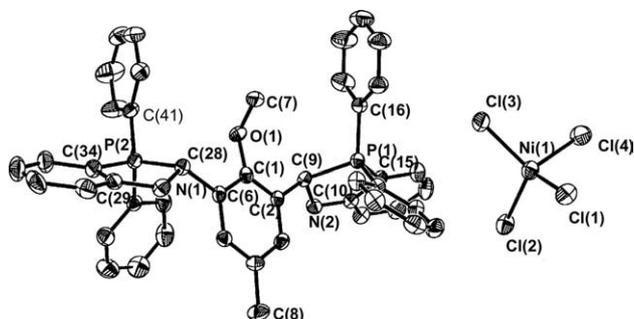
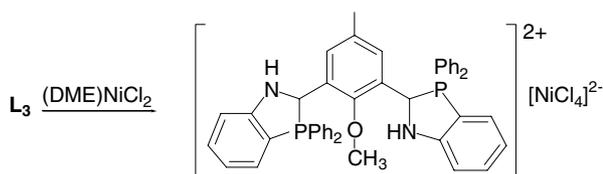


Fig. 1. ORTEP plot of complex **1**. Average Ni–Cl 2.257 Å, C(2)–C(9) 1.518(7) Å; C(9)–N(2) 1.464(6) Å; P(1)–C(9) 1.872(5) Å; N(2)–C(10) 1.369(7) Å; C(15)–P(1) 1.772(5) Å; N(1)–C(28) 1.476(6) Å; C(28)–P(2) 1.857(5) Å; P(2)–C(34) 1.759(6) Å; N(1)–C(29) 1.391(7) Å.

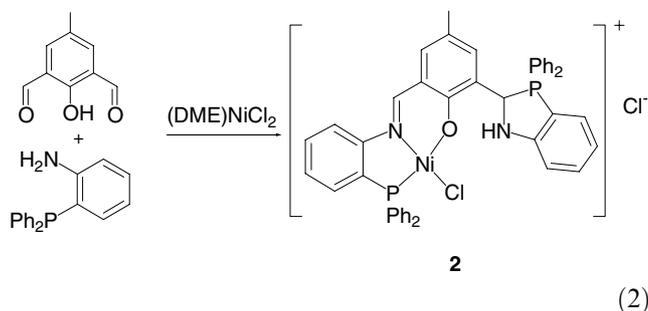
provides the appropriate anions to form the single crystal of **1**. In fact, some of the starting nickel(II) complex was recovered.



1

(1)

On the other hand, template condensation method, a common approach to construct the oxo-bridge bimetallic species, was employed to synthesize the phenoxo bridged dinuclear nickel complex. Thus, a mixture of 2,6-diformyl-4-methylphenol, P~N, (DME)NiCl<sub>2</sub> and triethylamine (molar ratio = 1:2:2:1) in dry methanol under nitrogen at 55 °C resulted in the formation of the corresponding Schiff base-phosphine mono nickel complex **2** instead of the anticipated dinuclear nickel complex (Eq. (2)). Recrystallization of the crude product from dichloromethane and hexane gave complex **2** in the crystalline form. The chemical shift at 39.7 ppm of complex **2** in <sup>31</sup>P NMR was determined due to the phosphonium group. The formation of benzo-azaphospholium ring might be due to the Lewis acid nature of nickel ion. No <sup>31</sup>P NMR signal was observed for the phosphorus coordinated to the nickel center, which might be due to the paramagnetic nature of nickel ion. This is in agreement with the literature known mononuclear nickel complexes of PNO donor ligands [6a]. The NH proton was observed as a doublet at 8.76 ppm (*J*<sub>P–H</sub> = 2.4 Hz) and was confirmed by the D<sub>2</sub>O exchange. The imino proton appeared to be a singlet at 8.41 ppm. The two aromatic protons of the phenol are observed as doublets at 8.22 (0.8 Hz) and 8.19 (0.8 Hz) ppm. The proton on the carbon of aza-phosphonium ring was observed as a doublet at 6.32 ppm (1.2 Hz) due to the phosphorus coupling. FAB mass spectrum shows the isotope pattern at *m/z* 775 for the cation part of the complex **2**.



2

(2)

ORTEP plot of **2** with partial atom labeling is presented in Fig. 2. Selected bond distances and bond angles are summarized in Table 1. The charge of nickel ion was neutralized with ligand phenoxide group and chloride anion, whereas the positive charge was located at phosphorus center of the phosphazolum group. The nickel(II) center was seated in a slightly distorted square planar geometry by the coordination of ligand PNO donors and a chloride. The chloride group bound *trans* to the imine nitrogen. Angles of O–Ni–P [175.19(9)°] and N–Ni–Cl [174.96(9)°] are less than 180° presumably due to steric arrangement of the P~N~O donors. Bond distance of the newly formed C(9)–P(2) [1.853(4) Å] is

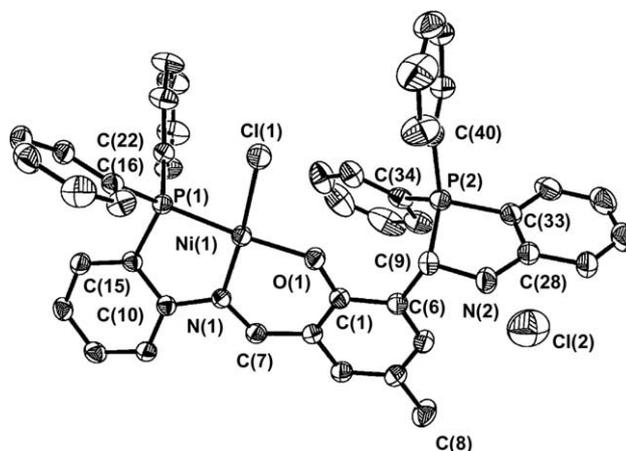


Fig. 2. Molecular structure of complex **2**.

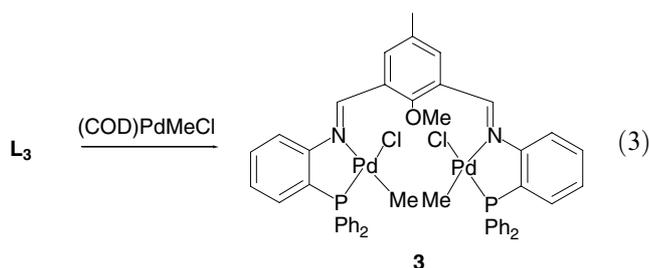
Table 1  
Selected bond lengths (Å) and bond angles (°) of **2**

Ni(1)–O(1)	1.866(3)
Ni(1)–P(1)	2.1262(10)
C(7)–N(1)	1.316(5)
P(2)–C(9)	1.853(4)
Ni(1)–N(1)	1.885(3)
Ni(1)–Cl(1)	2.1861(11)
C(9)–N(2)	1.460(5)
O(1)–Ni(1)–N(1)	95.83(12)
N(1)–Ni(1)–P(1)	87.63(9)
N(1)–Ni(1)–Cl(1)	174.96(9)
O(1)–Ni(1)–P(1)	175.19(9)
O(1)–Ni(1)–Cl(1)	89.20(9)
P(1)–Ni(1)–Cl(1)	87.33(4)

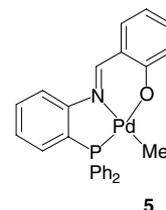
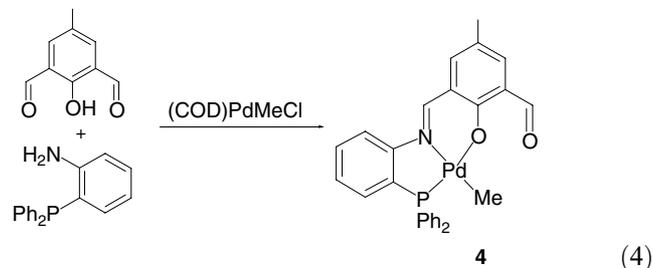
longer than all other P–C bonds in the complex. The distance of C(9)–N(2) [1.46(5) Å] determines the single bond nature of that bonding, compared to the imine C(7)–N(1) distance [1.316(5) Å]. It is interesting to note that even though the N–H···O interactions are very strong, the steric bulky benzo-azaphospholium group is arranged towards the nickel complex instead of NH group.

### 2.3. Palladium(II) complexes

In contrast to the nickel complex, the di-palladium complex **3** can be easily obtained by the substitution of COD from (COD)PdMeCl with **L**<sub>3</sub> in a dichloromethane/hexane solution. Recrystallization of **3** from dichloromethane/hexane gave the resulting complex as an air-stable, light yellowish crystalline complex. The <sup>31</sup>P NMR spectrum showed a singlet absorption at 34.31 ppm corresponding to the coordination of phosphine toward palladium center. The <sup>1</sup>H NMR spectrum exhibited a doublet at 0.76 (1.6 Hz) ppm corresponding to the CH<sub>3</sub> group bonded to the palladium metal ion in *trans* arrangement to the imine donor. The <sup>13</sup>C NMR absorption at –1.47 ppm is in agreement with Pd–CH<sub>3</sub> moiety, consistent to the literature known complexes [4]. Owing to the influence of chloride groups on the palladium, the aryl protons of the phenol group shift to downfield from 7.72 to 8.86 ppm.



Interestingly, condensation of 2,6-diformyl-4-methylphenol with 2-(diphenylphosphino)-aniline in the presence of Pd(COD)MeCl in dry methanol under basic conditions at 55 °C provided the one side Schiff base complex **4** in low yields. The FT-IR spectral absorptions at 1660 and 1616 cm<sup>-1</sup> show clearly the presence of both the aldehyde and imine functional groups, respectively, in the complex along with the support of <sup>1</sup>H NMR signals at 10.75 and 8.85 ppm. The <sup>1</sup>H NMR spectrum showed the Pd–CH<sub>3</sub> absorption at 0.7 ppm corresponding to the *trans* arrangement of the methyl group to the imine functionality. The <sup>31</sup>P NMR show the coordinated phosphorus signal at 43.71 ppm. Overall, the spectral data of **4** are quite similar to that of **5** [4], which allow us to assign the structure of **4** properly. Further reaction of **4** with P~N provided the complicated product distribution, from which we have not isolated any pure form.



### 3. Conclusion

Through this study, it was found that the imino-phosphine readily underwent cyclization to form the benzo-azaphospholium moiety via the nucleophilic attack of phosphine toward imine functionality under acidic conditions. Although donor atoms of ligand **L**<sub>3</sub> are ready for coordination of two metal ions to form the dinuclear species, the cyclization still takes place prior to the complexation with the use of nickel ions, indicating the Lewis acidic character of nickel ions. In contrast to nickel complexes, the coordination of (COD)PdMeCl toward **L**<sub>3</sub> allows to yield the desired bi-metallic species. The construction of multi-metal complexes with PNO-donors is currently under investigation.

### 4. Experimental

#### 4.1. General

All reactions, manipulations and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried with CaH<sub>2</sub> and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. 2,6-Diformyl-4-methylphenol [12] and 2-(diphenylphosphino)aniline [13] were synthesized from the reported procedures.

Nuclear magnetic resonance spectra were recorded in CDCl<sub>3</sub> on either a Bruker AM-300 or AVANCE-400 spectrometer. Chemical shifts are given in parts per million relative to Me<sub>4</sub>Si for <sup>1</sup>H and relative to 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR. Mass spectra were obtained from a Joel JMSD-300 instrument. FT-IR spectra were recorded on Nicolet Magna-IR 550 spectrometer (series II) as KBr pellets. Elemental analyses were carried out using

Perkin–Elmer 240C instrument. FAB mass spectra were recorded using Jeol JMSD-300 spectrometer.

#### 4.2. Synthesis and characterization

##### 4.2.1. Preparation of $L_1$ and $L_4$

A dry toluene (10 ml) solution of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol) was added to 2-(diphenylphosphino)aniline (0.553 g, 2 mmol), and 1 drop of conc. HCl under dry nitrogen atmosphere and stirred at room temperature for about 3 h. The reaction is monitored by  $^{31}\text{P}$  NMR spectra. The resulting orange solution was concentrated and washed with hexane several times. Yield: 0.38 g, 53%. FT-IR (KBr,  $\text{cm}^{-1}$ ): ( $\nu_{\text{C}=\text{N}}$ ) 1624;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.04 (s, 3H, Ar-CH<sub>3</sub>), 6.77–7.67 (m, Ar), 8.32 (s, 1H, C=N);  $^{31}\text{P}$  NMR  $\delta$ : –14.8, 36.8 ppm. *Anal.* Calc. for  $\text{C}_{45}\text{H}_{37}\text{ClN}_2\text{OP}_2$ : C, 75.15; H, 5.19; N, 3.90. Found: C, 74.89; H, 5.01; N, 3.66%.

$L_4$  was obtained via the similar procedure by running the reaction in dichloromethane: (31%):  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CD}_3\text{OD}$ )  $\delta$ : 1.40 (s, 3H, Ar-CH<sub>3</sub>), 6.43 (s, 2H, CH), 6.67 (m, 1H, CH), 6.75 (m, 2H, Ar), 6.93 (m, 2H, Ar), 7.19 (s, 4H, Ar), 7.30 (m, 8H, Ar), 7.50 (m, 8H, Ar), 7.72 (m, 2H, Ar), 7.89 (m, 4H, Ar);  $^{31}\text{P}$  NMR  $\delta$ : 38.9; *Anal.* Calc. for  $\text{C}_{45}\text{H}_{38}\text{Cl}_2\text{N}_2\text{OP}_2$ : C, 71.53; H, 5.07; N, 3.71. Found: C, 71.22; H, 4.67; N, 3.52%.

##### 4.2.2. Synthesis of 2,6-bis[*o*-diphenylphosphino]-benzeneimino]-4-methylanisole ( $L_3$ )

A dry toluene (10 ml) solution of 2,6-diformyl-4-methylanisole (0.656 g, 4 mmol) was added to 2-(diphenylphosphino)aniline (2.21 g, 8 mmol), and 1 drop of conc. HCl under dry nitrogen atmosphere and stirred at room temperature for about 6 h. The resulting lemon yellow solution was diluted with dichloromethane and treated with aq.  $\text{NaHCO}_3$  solution. The organic layer was dried over  $\text{MgSO}_4$  and concentrated. Recrystallization from  $\text{CH}_2\text{Cl}_2$  and hexane afford to the desired compound as lemon yellow crystals. Yield: 2.00 g, 70%. FT-IR (KBr,  $\text{cm}^{-1}$ ): ( $\nu_{\text{HC}=\text{N}}$ ) 1617;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.28 (s, 3H, Ar-CH<sub>3</sub>), 3.35 (s, 3H, OCH<sub>3</sub>), 6.86 (q,  $J = 7.6$  Hz, 2H, Ar-*H*), 7.02 (q,  $J = 7.6$  Hz, 2H, Ar), 7.14 (t,  $J = 7.6$  Hz, 2H, Ar-*H*), 7.28–7.40 (m, 22H, Ar), 7.72 (s, 2H, Ar), 8.43 (s, 2H, C=N);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C)  $\delta$ : 20.6 (Ar-CH<sub>3</sub>), 64.8 (OCH<sub>3</sub>), 117.1, 125.9, 128.2, 128.3, 128.5, 128.7, 129.7, 131.6, 132.5, 132.5, 132.6, 134.0, 134.2, 136.7, 136.8, 154.3, 154.5 (C=O), 154.8 (C=N), 159.1 (C=N);  $^{31}\text{P}$  NMR  $\delta$ : –16.11 ppm; FAB mass:  $m/z$ , 697.3  $[\text{M}]^+$ . *Anal.* Calc. for  $\text{C}_{46}\text{H}_{38}\text{N}_2\text{OP}_2$ : C, 79.30; H, 5.50; N, 4.02. Found: C, 79.25; H, 5.77; N, 3.93%.

##### 4.2.3. Complex 1

(DME)NiCl<sub>2</sub> (0.220 g, 1 mmol) was added to a solution of  $L_3$  (0.348 g, 0.5 mmol) in dry dichloromethane (10 ml) under nitrogen and the mixture was stirred at

room temperature for 1.5 h. The resulting light orange solution was concentrated under vacuum and the solid obtained was washed with hexane. Recrystallization from dichloromethane and hexane obtained light blue crystals and orange crystals. Spectral characterization of the orange crystals shows Ni(DME)Cl<sub>2</sub> compound, while the blue crystals showed the formation of the complex **1**. Yield: 0.160 g, 28%.  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CD}_3\text{OD}$ )  $\delta$ : 1.42 (s, 3H, Ar-CH<sub>3</sub>), 3.11 (s, 3H, OCH<sub>3</sub>), 6.32 (s, 1H, CH), 6.50 (m, 1H, CH), 6.69 (m, 1H, Ar), 6.87 (s, 1H, Ar), 7.06 (s, 4H, Ar), 7.20 (m, 8H, Ar), 7.51 (m, 8H, Ar), 7.69 (m, 2H, Ar), 7.82 (m, 4H);  $^{31}\text{P}$  NMR  $\delta$ : 41.2; *Anal.* Calc. for  $\text{C}_{46}\text{H}_{40}\text{Cl}_4\text{N}_2\text{OP}_2\text{Ni}$ : C, 61.44; H, 4.48; N, 3.12. Found: C, 61.84; H, 4.57; N, 3.00%.

##### 4.2.4. Complex 2

2,6-Diformyl-4-methylphenol (0.082 g, 0.5 mmol) in 20 ml dry methanol was added to anhydrous (DME)-NiCl<sub>2</sub> (0.220 g, 1 mmol) and 2-(diphenylphosphino)aniline (0.277 g, 1 mmol), Et<sub>3</sub>N (0.050 mg, 0.5 mmol) and the reaction mixture was heated to 55 °C for 2 h. The resulting solution was concentrated and the solid was washed with ether, dried under vacuum. Recrystallization from dichloromethane and hexane gave the crystals suitable for X-ray analysis. Yield: 0.300 g, 52%. FT-IR (KBr,  $\text{cm}^{-1}$ ): ( $\nu_{\text{C}=\text{N}}$ ) 1623;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.04 (s, 3H, Ar-CH<sub>3</sub>), 6.29 (d,  $J = 1.2$  Hz, 1H, CH), 6.91 (t,  $J = 4$  Hz, 2H, Ar), 7.07 (t,  $J = 4$  Hz, 2H, Ar), 7.22 (m,  $J = 8$  Hz, 2H, Ar), 7.36 (m, 8H, Ar), 7.53 (q,  $J = 8$  Hz, 8H, Ar), 7.65 (q,  $J = 8$  Hz, 2H, Ar), 7.84 (d,  $J = 8$  Hz, 4H, Ar), 8.17 (q,  $J = 8$  Hz, 2H, Ar), 8.41 (s, 1H, HC=N), 8.70 (d,  $J_{\text{NH-P}} = 2.4$  Hz, NH);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 39.41; FAB mass:  $m/z$  775  $[\text{Ni}(\text{L}^4)\text{Cl}]^+$ . *Anal.* Calc. for  $\text{C}_{45}\text{H}_{35}\text{N}_2\text{O}_2\text{P}_2\text{NiCl}_2$ : C, 66.68; H, 4.48; N, 3.46. Found: C, 66.44; H, 4.68; N, 2.99%.

##### 4.2.5. Complex 3

Pd(COD)MeCl (0.265 g, 1 mmol) was added to a solution of  $L_3$  (0.348 g, 0.5 mmol) in dry dichloromethane (10 ml) under nitrogen and the mixture was stirred at room temperature for 1 h. The resulting light yellow solid was filtered and washed repeatedly with hexane and ether and dried under vacuum. Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane gave **3** as crystalline solids. Yield: 0.545 g, 89%. FT-IR (KBr,  $\text{cm}^{-1}$ ): ( $\nu_{\text{C}=\text{N}}$ ) 1624;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{CD}_3\text{OD}$ )  $\delta$ : 0.76 (d, 6H,  $J = 1.6$  Hz, Pd-CH<sub>3</sub>), 2.49 (s, 3H, Ar-CH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 7.11 (t,  $J = 2$  Hz, 2H, Ar-*H*), 7.31 (t,  $J = 2$  Hz, 2H, Ar-*H*), 7.33–7.52 (m, 22H, Ar), 7.57 (t,  $J = 2$  Hz, 2H, Ar-*H*), 8.87 (s, 2H, Ar-*H*), 8.92 (s, 2H, C=N);  $^{13}\text{C}$  NMR  $\delta$ : –1.47 (Pd-CH<sub>3</sub>), 20.9 (Ar-CH<sub>3</sub>), 65.3 (OCH<sub>3</sub>), 118.9, 119.0, 127.0, 128.2, 128.7, 129.0, 129.4, 129.5, 131.2, 131.7, 131.9, 132.9, 132.9, 133.0, 133.6, 133.8, 133.9, 136.3, 156.3, 164.7 (C=N);  $^{31}\text{P}$  NMR  $\delta$ : 34.3. FAB mass:  $m/z$  1018  $[\text{M}]^+$ . *Anal.* Calc. for  $\text{C}_{48}\text{H}_{44}\text{Cl}_2\text{N}_2\text{OP}_2\text{Pd}_2$ : C, 57.05; H, 4.39; N, 2.77. Found: C, 56.89; H, 4.41; N, 2.94%.

#### 4.2.6. Complex 4

A mixture of 2,6-diformyl-4-methylphenol (0.082 g, 0.5 mmol), (COD)PdMeCl (0.265 g, 1 mmol), and 2-(diphenylphosphino)aniline (0.277 g, 1 mmol) in 20 ml dry methanol and Et<sub>3</sub>N (0.5 mmol) was heated to 55 °C with stirring for 2 h. The resulting solution was concentrated and the solid was washed with ether, dried under vacuum. Recrystallization from dichloromethane and hexane gave **4** as light yellow crystalline solids. Yield: 0.080 g, 13%. FT-IR (KBr, cm<sup>-1</sup>): (ν<sub>C=O</sub>) 1660, (ν<sub>C=N</sub>) 1623. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.70 (s, 3H, Pd-CH<sub>3</sub>) 2.24 (s, 3H, Ar-CH<sub>3</sub>), 7.26 (m, 1H, Ar), 7.32 (s, 1H, Ar), 7.33–7.55 (m, 8H, Ar), 7.61–7.66 (m, 4H, Ar), 7.73–7.76 (m, 1H, Ar), 7.80 (s, 1H, Ar), 8.85 (s, 1H, HC=N), 10.75 (s, 1H, HC=O). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: -0.80 (d, J = 1.2 Hz, Pd-CH<sub>3</sub>), 19.95 (Ar-CH<sub>3</sub>), 115.81, 122.67, 123.46, 127.69, 127.79, 128.74, 128.85, 129.05, 129.84, 130.39, 130.93, 131.09, 131.12, 132.67, 133.22, 133.64, 133.86, 136.58, 144.04, 153.81, 154.00, 157.57, 169.61 (C=N), 192.03 (C=O); <sup>31</sup>P NMR δ: 43.71; FAB mass: *m/z* 543.0 [M]<sup>+</sup>. Anal. Calc. for C<sub>28</sub>H<sub>24</sub>NO<sub>2</sub> PPd: C, 61.83; H, 4.45; N, 2.58. Found: C, 61.91; H, 4.62; N, 2.60%.

#### 4.3. X-ray crystallographic analysis

Crystals suitable for X-ray determination were obtained for **1** and **2** · CH<sub>3</sub>OH · 2H<sub>2</sub>O by the slow diffusion of the hexane into the dichloromethane/methanol solution of the complexes at room temperature. The cell parameters were determined at 298 K using a Nonius

Table 2  
Crystallographic data of complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>46</sub> H <sub>40</sub> Cl <sub>4</sub> N <sub>2</sub> OP <sub>2</sub> Ni	C <sub>46</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> P <sub>2</sub> Ni
Formula weight	899.27	888.33
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub>	P2 <sub>1</sub> /n
<i>a</i> (Å)	11.8110(2)	14.2020(10)
<i>b</i> (Å)	15.8030(2)	19.2730(10)
<i>c</i> (Å)	12.0330(2)	15.9530(10)
α (°)	90	90
β (°)	106.1280(10)	102.7460(10)
γ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2157.56(6)	4258.97(5)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.384	1.385
<i>F</i> (000)	928	1832
Crystal size (mm)	0.20 × 0.15 × 0.10	0.30 × 0.25 × 0.20
θ Range (°)	2.14–25.07	1.68–25.00
Number of reflections collected	12 849	83 163
Number of independent reflections	7115	7479
Refined method	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]	0.0506	0.0643
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.120	1.076

kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.071073 Å). All the structures were solved by direct methods (SHELXTL) and all of the non-hydrogen atoms refined anisotropically. Structural refinements were done by full-matrix least-squares methods on *F*<sup>2</sup>. Absorption corrections were done using multi-scan methods. Crystal data for complexes are listed in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Center: CCDC-250230 for **1** and CCDC-250231 for **2**. Copies of this information can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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