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Synthesis and characterization of cyclopalladated complexes of oximes by ligand-exchange method

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Abstract—The ligand-exchange reaction between $\{Pd(dmba)Cl\}_2$ (dmba = *N*,*N*-dimethylbenzylamine) and various oximes such as 3,4-$(Me)_2C_6H_3C(CH_3)$=NOH (**1**), 4-$OMeC_6H_4C(CH_3)$=NOH (**2**), 4-$BrC_6H_4C(CH_3)$=NOH (**3**) and α-tetralone oxime (**4**) was studied. The products obtained were found to be chloro-bridged complexes. The reactions of these complexes were investigated with triphenylphosphine and acetylacetone. The resulting complexes were analysed by IR, ^1H NMR and ^{13}C NMR methods. For one of the complexes, $[\{Pd(4,5\text{-}(CH_3)_2C_6H_2C(CH_3)=NOH)(Cl)\}_2]$ (**1a**), the structure was investigated by single crystal XRD.

Keywords: cyclopalladation; ligand-exchange reaction; oximes; triphenylphosphine; acetylacetone.

Cyclopalladation is an important class of reaction in organometallic chemistry and has been well reviewed [1]. Cyclopalladated complexes play a vital role in organic synthesis [2], photochemistry [3], homogeneous catalysis [4], optical resolution [5], liquid crystals [6] and antitumor agents [7]. Onoue *et al.* first reported the preparation of cyclopalladated complexes of oximes by electrophilic substitution reactions using lithium tetrachloropalladate as starting material in the presence of sodium acetate [8]. The formation of side products and the impurity of cyclopalladated complexes are the main disadvantages associated with this method. Ryabov *et al.* simplified the procedure for the synthesis of cyclopalladated complexes of oximes [9]. This procedure involves the exchange of cyclopalladated ligand and free ligand during the course of the reaction. The ligand-exchange method has been successfully used to synthesize cyclopalladated complexes of nitrogen containing ligands like azobenzene, *p*-nitro-*N*,*N*-dimethylbenzylamine and Schiff bases [10]. This method is also used to synthesize cyclopalladated sulfur-containing ligands such as 4,4′-dimethoxythiobenzophenone and *N*,*N*,*N*′,*N*′-tetramethylthiourea [11].

It is proposed that the presence of acetic acid is essential for the ligand-exchange reaction. The mechanism of the ligand-exchange reaction involves the initial coordination of the incoming ligand to palladium followed by acidolysis of the Pd—C bond of the leaving ligand. Moreover, the ligand-exchange reaction depends on the electron density of the coordinating atom of the incoming ligand and also the leaving ligand [12]. For the ligand-exchange reaction to occur, it is suggested that the incoming ligand should be electron poorer than the leaving ligand. Acetophenone oximes and benzaldehyde oximes were employed to synthesize cyclopalladated complexes under ligand-exchange reaction conditions. Moreover, it was observed that acetophenone oximes are more reactive than benzaldehyde oximes. No explanation has been offered for the high reactivity of the former than the latter. Continuing our interest in cyclopalladation chemistry [13], we report the synthesis of cyclopalladated complexes of various substituted acetophenone oximes, such as 3,4-$(Me)_2C_6H_3C(CH_3)$=NOH (**1**), 4-$OMeC_6H_4C(CH_3)$=NOH (**2**) and 4-$BrC_6H_4C(CH_3)$=NOH (**3**), by the ligand-exchange method in order to establish the effect of electron density of the oxime on the cyclopalladation reaction and also to find out regioselectivity changes, if any, under this condition. We

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have also carried out the synthesis of cyclopalladated complexes of α-tetralone oxime (**4**) in order to prove that the ligand-exchange reaction is superior to the conventional electrophilic substitution.

EXPERIMENTAL

Physical measurements

Elemental analyses were carried out in a Heraeus CHN-O rapid elemental analyser. IR spectra in the range 4000–400 cm^{-1} were recorded using a Shimadzu IR-470 spectrophotometer. IR spectra in the range 400–180 cm^{-1} were recorded as polyethylene discs using a Perkin–Elmer 983G spectrophotometer. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ solution with TMS as internal standard and ^{31}P NMR spectra were taken in CH_2Cl_2 solution with 85% H_3PO_4 as external standard using a JEOL-JNM-GSX 400 spectrometer.

X-ray structure determination

A crystal with approximate size $0.30 \times 0.40 \times 0.10$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite-monochromated Mo-K_α X-ray source ($\lambda = 0.710\,73$Å) for the data collection. The unit-cell parameters were obtained by using the method of short vectors followed by least-squares refinement of 25 reflections with $15 < \theta < 20°$. Two check reflection intensities monitored every hour showed less than three percentage variations during the data collections. After Lorentz and polarization corrections, an empirical absorption correction was carried out using ψ-scan data. Space group $P\bar{1}$ could be assigned for the complex using crystallographic statistics. There are two molecules in the unit cell. The structure was solved by direct methods and refined using MolEN (MolEN, structure determination system, Enraf–Nonius, Delft, 1990). The complex was refined to $R(F) = 0.033$ with anisotropic parameters for all nonhydrogen atoms by using 4383 unique reflections with $I > 2.5 > (I)$. All the hydrogen atoms were fixed and refined isotropically.

Synthesis

Solvents were purified by standard methods [14]. The cyclopalladated chloro-bridged dimer of *N,N*-dimethylbenzylamine, $\{Pd(dmba)Cl\}_2$, was prepared by the standard method [15]. The oximes were prepared by refluxing 1 equiv. of ketone with 1 equiv. of hydroxylamine hydrochloride in the presence of 1 equiv. of pyridine in ethanol for 3 h. Commercial samples of triphenylphosphine, acetylacetone and ketones were used as received.

Synthesis of $[\{Pd(4,5\text{-}(CH_3)_2C_6H_2C(CH_3)=NOH)(Cl)\}_2]$ (**1a**)

The chloro-bridged cyclopalladated dimer of *N,N*-dimethylbenzylamine, $\{Pd(dmba)Cl\}_2$ (55.2 mg, 0.1 mmol), was stirred with 3,4-dimethylacetophenone oxime (32.6 mg, 0.2 mmol) in a 1 : 1 mixture of chloroform and acetic acid (8 cm^3) at 55°C for 5 h. The solution was cooled, the complex formed was filtered, washed with methanol and dried *in vacuo* (55 mg, 90%). Other chloro-bridged complexes (**2a–4a**) were prepared similarly.

Synthesis of $[\{Pd(4,5\text{-}(CH_3)_2C_6H_2C(CH_3)=NOH)(Cl)(PPh_3)\}]$ (**1b**)

The chloro-bridged dimer **1a** (61 mg, 0.1 mmol) was stirred with triphenylphosphine (52 mg, 0.2 mmol) in dichloromethane (5 cm^3) for 1 h. The resultant solution was filtered and concentrated. The pale-yellow product **1b** obtained was recrystallized from dichloromethane/methanol (105 mg, 93%). Other complexes **2b** and **3b** were similarly prepared.

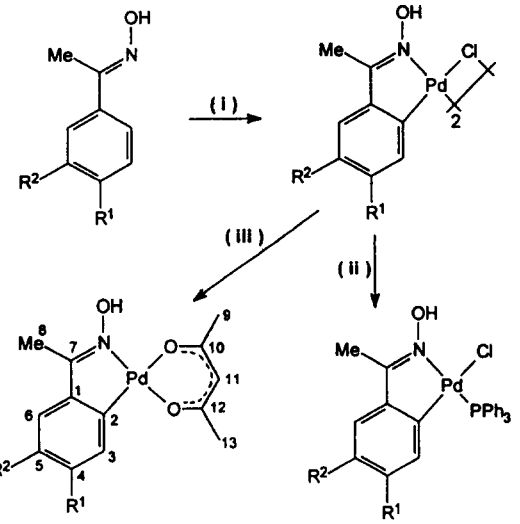
Synthesis of $[Pd(4,5\text{-}(CH_3)_2C_6H_2C(CH_3)=NOH)(acac)]$ (**1c**)

The chloro-bridged dimer **1a** (61 mg, 0.1 mmol) was added to a clear solution of acetylacetone (20 mg, 0.2 mmol) and sodium hydroxide (8 mg, 0.2 mmol) in methanol (5 cm^3) with stirring. Stirring was continued for 10 h. The white precipitate **1c** formed was filtered, washed with methanol and recrystallized from dichloromethane/methanol (60 mg, 81%). Other complexes (**2c–4c**) were similarly prepared.

RESULTS AND DISCUSSION

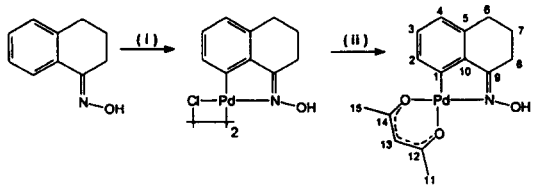
Synthesis and spectroscopic investigations

The acetophenone oximes $3,4\text{-}(Me)_2C_6H_3C(CH_3)=NOH$ (**1**), $4\text{-}OMeC_6H_4C(CH_3)=NOH$ (**2**), $4\text{-}BrC_6H_4C(CH_3)=NOH$ (**3**) and α-tetralone oxime (**4**) upon treatment with the cyclopalladated chloro-bridged dimer of *N,N*-dimethylbenzylamine, $\{Pd(dmba)Cl\}_2$, in chloroform : acetic acid mixture (1 : 1) at 55°C gave cyclopalladated chloro-bridged complexes of oximes (**1a–4a** Scheme 1). The oxime **3** is more reactive to give the product within 2 h. The other two acetophenone oximes **1** and **2** took more than 4 h for complete conversion. This high reactivity of the oxime **3** could be due to the poor electron density on the coordinating nitrogen. Nielson was the first to report the synthesis of cyclopalladated complexes of α-tetralone oxime (**4a**) [16]. Cyclopalladated complexes of oximes were prepared by stirring equimolar quantities of oxime and lithium tetrachloropalladate in the presence of a base in methanol.



Scheme 1. (i) $\{Pd(dmba)Cl\}_2$ in AcOH and $CHCl_3$ (1 : 1); (ii) PPh_3 in CH_2Cl_2; (iii) acetylacetone and NaOH in methanol. **1**: $R^1 = R^2 = CH_3$; **2**: $R^1 = OCH_3$, $R^2 = H$; **3**: $R^1 = Br$, $R^2 = H$.

Under these conditions, the ligand α-tetralone oxime (**4**) gave the cyclopalladated complex (**4a**) and a simple coordination complex of the type $PdCl_2L_2$. To avoid the formation of a simple coordination complex, Nielson used 2 equiv. of lithium tetrachloropalladate instead of 1 equiv. The α-tetralone oxime (**4**) readily gave the cyclopalladated complex **4a** with **1a** under ligand-exchange conditions (Scheme 2). This suggests that the ligand-exchange method is a better choice than the substitution reaction.



Scheme 2. (i) $\{Pd(dmba)Cl\}_2$ in AcOH and $CHCl_3$ (1 : 1); (ii) acetylacetone and NaOH in methanol.

The IR spectra of these complexes exhibit a strong band at *ca* 3400 cm^{-1}, corresponding to the O—H group of cyclopalladated oximes. The O—H stretching frequency of the free ligands is around 3200 cm^{-1}, suggesting the formation of cyclopalladated complexes of oxime [8]. The far-IR spectra of the complexes **1a–4a** exhibit two strong bands at *ca* 275 and 320 cm^{-1}, suggesting that these complexes are chloro-bridged dimers [17] (Table 1). The C=N stretching frequency of the complexes was absent in the IR spectra. The solubility of these complexes was found to be poor in common organic solvents; hence, the bridge-splitting reaction of these complexes was studied with triphenylphosphine and acetylacetone. With triphenylphosphine, the complexes **1a–3a** gave **1b–3b** in dichloromethane. The far-IR spectra of these complexes exhibit one strong band at *ca* 310 cm^{-1}, suggesting that the chlorine is *trans* to the palladated carbon atom [17]. The ^{31}P NMR spectrum of complex **1b** exhibits only one peak at 40.32 ppm, suggesting that only one isomer was formed from the reaction of **1a** and triphenylphosphine. Single-crystal XRD studies of one of the complexes (**1b**) was carried out and

Table 1. Elemental and IR spectral data of complexes[a]

Complexes	C	H	N	IR data (cm^{-1})
1a	39.4 (39.5)	4.0 (4.0)	4.7 (4.6)	3408,[b] 258,[c] 325[c]
2a	35.4 (35.3)	3.3 (3.3)	4.5 (4.6)	3424,[b] 265,[c] 323[c]
3a	27.2 (27.1)	1.9 (2.0)	3.9 (4.0)	3440,[b] 290,[c] 345[c]
4a	39.7 (39.8)	3.4 (3.3)	4.7 (4.6)	3380,[b] 260,[c] 330[c]
1b	59.5 (59.4)	4.9 (4.8)	2.5 (2.5)	3216,[b] 300[d]
2b	57.2 (57.1)	4.5 (4.4)	2.4 (2.5)	3320,[b] 310[d]
3b	50.5 (50.6)	3.6 (3.6)	2.3 (2.3)	3440,[b] 322[d]
1c	49.1 (49.0)	5.3 (5.2)	3.9 (3.8)	3408,[b] 1584,[e] 1510[e]
2c	45.6 (45.5)	4.7 (4.6)	3.8 (3.8)	3420,[b] 1577,[e] 1516[e]
3c	37.3 (37.3)	3.4 (3.4)	3.4 (3.4)	3392,[b] 1577,[e] 1513[e]
4c	49.3 (49.3)	4.7 (4.7)	3.9 (3.8)	3435,[b] 1600,[e] 1520[e]

[a]Calculated values are given in the parenthesis.
[b]O—H stretching frequency.
[c]Stretching frequency corresponds to bridging Pd—Cl bonds.
[d]Stretching frequency corresponds to terminal Pd—Cl bond.
[e]Stretching frequencies corresponding to the chelated acetylacetonato moiety.

Table 2. ^{1}H, ^{13}C and ^{31}P NMR data of complexes

1b	^{1}H NMR: δ 1.58 (s, 3H), 2.06 (s, 3H), 2.30 (s, 3H, H^{8}), 6.05 (d, 1H, H^{3}), 6.90 (s, 1H, H^{6}), 7.35 (m, 6H), 7.45 (m, 3H) 7.70 (m, 6H), 10.53 (d, 1H, OH). ^{13}C NMR: δ 11.13 (q, C^{8}), 19.14 (q); 19.46 (q), 126 (d, C^{6}), 128.23 [d, J(PC) = 10.6 Hz], 130.37 [s, J(PC) = 50.1 Hz], 130.92 (d), 132.23 (s, C^{1}), 135.25 [d, J(PC) = 12.1 Hz], 137.26 [s, J(PC) = 6.0 Hz], 139.09 [d, J(PC) = 10.6 Hz], 141.92 (s, C^{5}), 149.50 (s, C^{2}), 164.91 (s, C^{7}). ^{31}P NMR: δ 40.32.
1c	^{1}H NMR: δ 2.00 (s, 3H, H^{9}), 2.10 (s, 3H, H^{13}), 2.20 (s, 3H), 2.24 (s, 3H, H^{8}), 2.26 (s, 3H), 5.40 (s, H^{11}), 6.80 (s, H^{6}), 7.20 (s, H^{3}), 8.50 (s, OH). ^{13}C NMR: δ 10.73 (q, C^{8}), 19.49 (q), 19.99 (q), 27.67 (q, C^{9}), 27.96 (q, C^{13}), 101.03 (d, C^{11}), 125.97 (d, C^{6}), 131.62 (d, C^{3}), 132.26 (s, C^{5}), 137.55 (s, C^{4}), 140.18 (s, C^{1}), 148.72 (s, C^{2}), 165.49 (s, C^{7}), 187.08 (s, C^{10}), 188.29 (s, C^{12}).
2c	^{1}H NMR: δ 2.00 (s, 3H, H^{9}), 2.11 (s, 3H, H^{13}), 2.25 (s, 3H, H^{8}), 3.80 (s, 3H, OCH_3), 5.40 (s, 1H, H^{11}), 6.58 (dd, 1H, H^{5}), 6.95 (d, 1H, H^{3}), 7.02 (d, 1H, H^{6}, 8.40 (s, 1H, OH). ^{13}C NMR: δ 10.93 (q, C^{8}), 27.63 (q, C^{9}), 27.90 (q, C^{13}) 55.19 (q, OCH_3), 101.08 (d, C^{11}), 109.74 (d, C^{5}), 115.69 (d, C^{3}), 125.69 (d, C^{6}), 135.15 (s, C^{1}), 154.75 (s, C^{4}), 159.02 (s, C^{2}), 165.04 (s, C^{7}), 187.16 (s, C^{10}), 188.19 (s, C^{12}).
3c	^{1}H NMR: δ 2.00 (s, 3H, H^{9}), 2.10 (s, 3H, H^{13}), 2.20 (s, 3H, H^{8}), 5.38 (s, 1H, H^{11}), 6.90 (d, 1H, H^{6}), 7.20 (dd, H^{5}), 7.46 (d, H^{3}), 8.58 (s, OH). ^{13}C NMR: δ 10.92 (q, C^{8}), 27.52 (q, C^{9}), 27.84 (q, C^{13}), 101.21 (d, C^{11}), 123.10 (s, C^{4}), 125.64 (d, C^{6}), 127.38 (d, C^{5}), 132.86 (d, C^{3}), 141.38 (s, C^{1}), 154.66 (s, C^{2}), 164.89 (s, C^{7}), 188.04 (s, C^{10}), 188.37 (s, C^{12}).
4c	^{1}H NMR: δ 1.92 (m, 2H, H^{7}), 2.00 (s, 3H, H^{11}), 2.18 (s, 3H, H^{15}), 2.70 (t, 2H, H^{6}), 2.78 (t, 2H, H^{8}), 5.38 (s, 1H, H^{13}), 6.80 (d, 1H, H^{4}), 7.00 (t, 1H, H^{3}), 7.19 (d, 1H, H^{2}), 8.35 (s, 1H, OH). ^{13}C NMR: δ 22.28 (t, C^{8}), 24.35 (t, C^{7}), 28.26 (t, C^{6}), 27.67 (q, C^{11}), 27.85 (q, C^{15}), 100.99 (d, C^{13}), 124.09 (d, C^{4}), 128.35 (d, C^{3}), 128.63 (d, C^{2}), 138.65 (s, C^{10}), 139.53 (s, C^{5}), 152.2 (s, C^{1}), 166.38 (s, C^{9}), 187.11 (s, C^{12}), 188.16 (s, C^{14}).

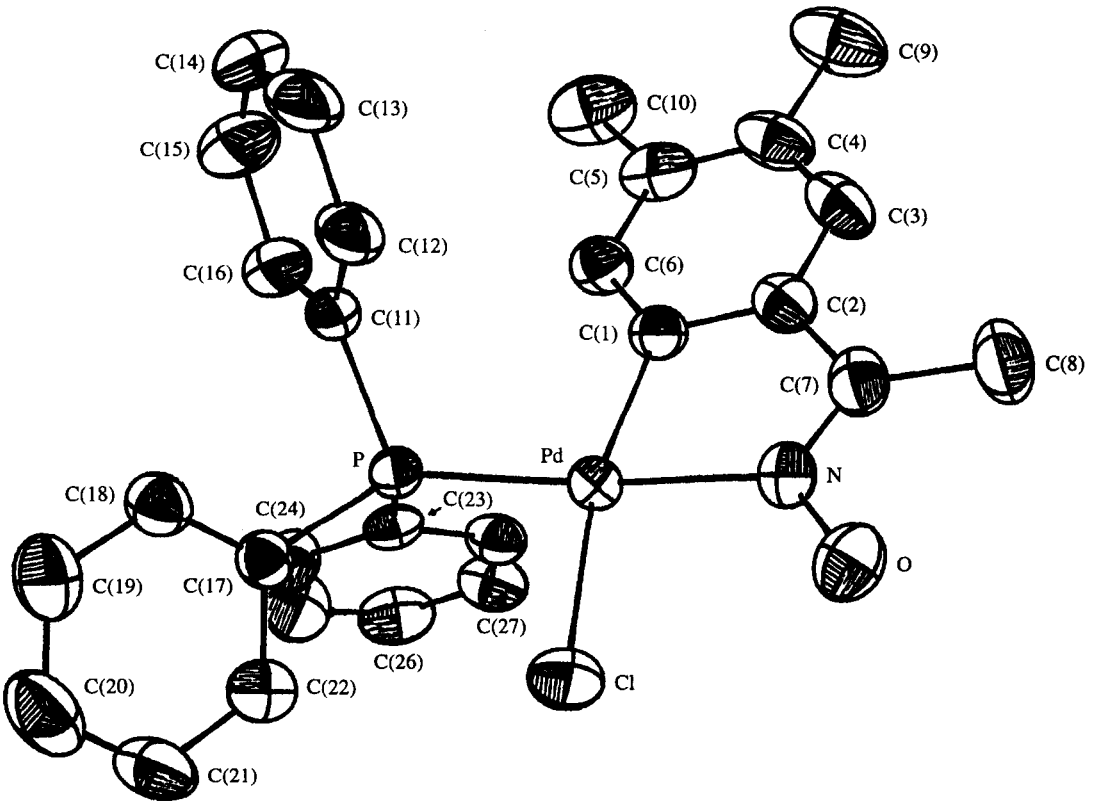


Fig. 1. ORTEP diagram of complex **1b**.

Table 3. Crystal data of complex **1b**

Chemical formula	$C_{28}H_{27}NOClPPd$
M	566.36
I (K)	298
Space group	$P\bar{1}$
Crystal system	Triclinic
a (Å)	9.084(1)
b (Å)	9.409(2)
c (Å)	16.141(3)
α (°)	92.07(2)
β (°)	103.52(3)
γ (°)	105.95(3)
V (Å)	1282.20(0)
Z	2
D_c (g cm^{-3})	1.467
F(000)	576
R	0.033
R'	0.047
No. of reflections	4806
No. of unique reflections	4383
No. of parameters refined	298
Goodness of fit	1.98
High peak in final difference map (eÅ^{-1})	0.51(11)
Low peak in final difference map (eÅ^{-1})	0.00(11)

Table 4. Bond distances (Å) and angles (°) of complex **1b**

Pd—Cl	2.4002(7)	Pd—P	2.2583(6)
Pd—N	2.050(2)	Pd—C(1)	2.027(3)
O—N	1.395(3)	N—C(7)	1.279(4)
Cl—Pd—P	96.82(2)	Cl—Pd—N	88.29(7)
Cl—Pd—C(1)	167.15(6)	P—Pd—N	174.50(7)
P—Pd—C(1)	95.82(6)	N—Pd—C(1)	79.17(9)
Pd—P—C(11)	112.68(8)	Pd—P—C(17)	117.79(7)
C(1)—C(2)—C(7)	117.9(2)	Pd—P—C(23)	112.03(8)
C(11)—P—C(17)	102.2(1)	C(11)—P—C(23)	108.9(1)
C(17)—P—C(23)	102.3(1)	Pd—N—O	123.6(2)
Pd—N—C(7)	119.3(2)	N—C(7)—C(2)	111.7(2)
O—N—C(7)	117.0(2)	N—C(7)—C(8)	124.5(2)
C(2)—C(7)—C(8)	123.8(3)		

the results are summarized below. The ^{1}H NMR spectrum of complex **1b** suggests that the proton adjacent to the metallated carbon atom is shielded and appears as a doublet at 6.05 ppm. This high-field shift suggests that the triphenylphosphine is *trans* to the nitrogen atom in the complex [13].

The bridge-splitting reaction of the chloro-bridged complexes **1a–4a** was also carried out with acetylacetone in the presence of a base. Complexes **1c–4c** obtained from **1a–4a** exhibit two strong bands at *ca* 1580 and 1515 cm^{-1} in the IR spectra, suggesting the presence of the chelated acetylacetonato moiety in these complexes [18]. The ^{1}H NMR spectra of complexes **1c–4c** show that both the methyl groups of acetylacetonato ligand are not magnetically equivalent. This could be due to the high *trans* influence of the carbon atom bonded to palladium (Table 2).

Regioselectivity is an important criterion in cyclopalladation chemistry. The regioselectivity depends on various factors such as reaction conditions, ring size, steric and electronic effects. The difference in reaction condition on regioselectivity of cyclopalladation is well known with ligands such as 3,4-dimethoxy-4′-nitro-*N*-methyldibenzylamine [19] and *N*-thiobenzoylpyrrolidine [20]. Steric effects on cyclopalladation of Schiff bases were well established by Vila *et al.* [21] We have carried out the cyclopalladation reaction of the oxime **1** by ligand exchange as well as the electrophilic substitution method in order to find any difference, in regioselectivity. The analysis of the products shows that only one product (**1a**) was formed under these conditions.

Crystal structure of complex **1b**

A dichloromethane : methanol (1 : 1) solution of complex **1b** gave pale yellow plate crystals on slow evaporation of the solvent at room temperature. Table 3 summarizes the experimental crystal data and Table 4 gives bond distances and bond angles of the complex **1b**. Figure 1 shows the ORTEP diagram of the complex. The palladium atom is coordinated to phosphorus, carbon, chlorine and imine nitrogen atoms. The geometry around the central metal atom is best represented as distorted square planar. The bond angle varies from 79.17(9) to 96.82(2)°. The coordinated bond distances are: Pd—Cl = 2.4002(7), Pd—P = 2.2583(6), Pd—N = 2.050(2) and Pd—C(1) = 2.027(3)Å. The palladium atom does not deviate appreciably from the mean plane determined by the four coordinated atoms. The phosphorus atom adopts a *trans* arrangement to the imine nitrogen atom. The smallest of the angles are those between the coordinated nitrogen and the palladated carbon atom. The palladium ligand distances are similar to those reported for the other cyclopalladated complexes [22] The atoms of the chelated ring do not deviate appreciably from the mean plane. The dihedral angle between the chelated ring and the palladated phenyl ring is 5.06°.

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