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# Reversible ring opening and closure reactions of the triazine ligands derived from 1-phenylazo-2-naphthylamine and pyridine-2-aldehyde or quinoline-2-aldehyde – structure and reactivity of the palladium(II) complexes

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#### Abstract

New ligands containing a heterocyclic ring, L<sup>1</sup> (1-anilino-2-(2-pyridyl)-naphth[1,2-d]imidazol-1-io-3-ide), L<sup>2</sup> (2-phenyl-3-(2-pyridyl)-3,4-dihydro-naphtho[2,1-e][1,2,4]triazin-1-io-4-ide), and L<sup>3</sup> (1-anilino-2-(2-quinolyl)-naphth[1,2-d]imidazol-1-io-3-ide), and their palladium (II) complexes have been prepared. Structures of the ligands and the complexes were determined by X-ray crystal-lography. The mononuclear square-planar complexes of  $[PdCl_2(L^n)]$  (n = 1 (1), n = 2 (2) and n = 3 (3)) had didentate L<sup>n</sup> (n = 1-3) ligands. The L<sup>n</sup> (n = 1-3) ligands were stable and their absorption spectra did not change in dichloromethane and methanol. On the other hand, the absorption spectrum of  $[PdCl_2(L^2)]$  (2) in dichloromethane changed rapidly when methanol was added to the solution, and  $[PdCl(L^{4b})]$  (5) (L<sup>4b</sup> = *N*-[methoxy(2-pyridyl)methyl]-1-(phenylazo)-2-naphthylamide) was obtained from the concentrated reaction mixture. In this reaction, the dihydrotriazine ring of the didentate L<sup>2</sup> ligand in complex **2** opened and the resulting tridentate L<sup>4b</sup> ligand coordinated to the Pd atom in complex **5**. When an excess amount of ("Bu)<sub>4</sub>NCl was added to complex **5** in dichloromethane, the absorption spectrum reverted to that of complex **2**. Thus, the reversible ring opening and closure reactions of the coordinating dihydrotriazine ligand were observed. We also prepared  $[PdCl_2(L^5)]$  (9) (L<sup>5</sup> = 1-(phenylazo)-*N*-[1-(2-pyridyl)ethy-lidene]-2-naphthylamine) and determined the structure. It is noted that neither the ring closure reaction nor the coordination of the date the structure of the diacon reaction nor the coordination of the date that resulting the result in complex **9**.

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Keywords: Palladium (II) complex; Ring opening and closure reaction; Crystal structure; Triazine; Imidazole; Azo ligand

### 1. Introduction

Azoaromatic compounds are highly colored and have long been used as dyes and pigments. It is well known that the azo group is photoreactive and isomerizes between *trans* and *cis* conformers by irradiation of

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the  $\pi$ - $\pi^*$  and n- $\pi^*$  bands with UV or visible light. They are also redox active and could be reduced stepwise to a radical anion and a hydrazido(2–) species. Recently, transition metal complexes containing various kinds of azo ligands have attracted increasing attention because of their interesting electronic and geometrical features in connection with their application for photo-switching devices, molecular memory storage, etc. The structure and reactivity [1], redox chemistry [2], and photochemical properties [3] of

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various azo complexes have been reported. It is expected that the reactivity and properties of azo functions will be controlled in conjunction with the electronic state of the metal ions. For example, the *trans-cis* photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization of azobenzene–bipyridine ligands was controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization controlled with the Co(III)/Co(II) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with the Co(III) [4] or the trans-cis photoisomerization controlled with trans-cis photoisomerization controlled with trans-cis photo

to metal ions in these complexes. This work arose from our current research interest in the preparation of photo- and thermal-responsive metal complexes incorporating an azo functional group whose nitrogen atom coordinates to the metal ions. We expect that the electronic state of the metal ions would clearly affect the properties and reactivities of the coordinating azo functional group. In a previous paper, we reported the preparation, structures, and properties of the mono-, di-, and trinuclear palladium (II) and platinum (II) complexes with the ligands derived from 1-phenylazo-2-naphthylamine and 2-(diphenylphosphino)benzaldehyde or 2-(tert-butylthio)benzaldehyde [6]. In this paper, the related triazine and imidazole ligands were successfully isolated, and their palladium (II) complexes were prepared (Fig. 1). We determined the structures of the ligands and complexes, and investigated the ring opening and closure reactions of the triazine skeleton.

Cu(II)/Cu(I) [5] redox reactions, although the nitrogen

atom of the azo functional group does not coordinate



Fig. 1. Schematic representation of the ligands.

#### 2. Experimental

#### 2.1. General procedures

[PdCl<sub>2</sub>(PhCN)<sub>2</sub>] was prepared according to the literature procedure [7]. <sup>1</sup>H NMR spectra were recorded at 400 MHz on a JEOL JNM LA-400 spectrometer with TMS as the internal reference. IR spectra were obtained on a KBr disk using a Perkin–Elmer Spectrum 2000 spectrophotometer. UV–Vis spectra were measured on a Shimadzu UV-2500PC or UV-1650PC spectrophotometer.

# 2.2. Preparations

# 2.2.1. $L^1$ and $L^2$ ligands

1-Phenylazo-2-naphthylamine (0.294 g, 1.19 mmol) was added to the methanol solution (30 cm<sup>3</sup>) of pyridine-2-aldehyde (0.129 g, 1.20 mmol). The reaction mixture was refluxed for 5 h and evaporated to dryness. The red oily residue was then dissolved in diethyl ether (2  $cm^3$ ) and the solution was cooled in an ice bath for 30 min to yield a pale orange precipitate of  $L^1$ , which was filtered and washed with a small amount of hexane. The precipitate was dissolved in a small amount of THF and n-hexane was added slowly. The mixture was left at room temperature for several days to yield pale yellow crystals of L<sup>1</sup>. Yield: 0.113 g, 28.2%. Anal. Calc. for  $L^1 = C_{22}H_{16}N_4$ : C, 78.55; H, 4.79; N, 16.66. Found: C, 78.45; H, 4.60; N, 16.71%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 10.12$  (s, 1H), 8.83 (m, 1H), 8.61 (m, 1H), 8.35 (d, 1H), 7.98 (m, 1H), 7.92 (d, 1H), 7.79 (m, 2H), 7.49 (m, 2H), 7.28 (m, 1H), 7.10 (m, 2H), 6.86 (m, 1H), 6.60 (dd, 2H). UV–Vis {dichloromethane,  $\sigma/10^3$  $cm^{-1} (\log \varepsilon / M^{-1} cm^{-1})$  28.1 (4.20), 28.9 (4.21), 31.7 (4.11), 33.1 (4.14), 35.2 (4.42), 42.8 (4.56). The filtrate and the washings were combined and evaporated. The resulting red oily residue was dissolved in dichloromethane and charged on top of a silica gel column (20  $cm \times 10$  mm ID). Upon elution with a 1:1 mixture of *n*-hexane and diethyl ether, several bands were developed. Red crystals of  $L^2$  were obtained from the eluate containing the red band. Yield: 0.151 g, 37.9%. Anal. Calc. for  $L^2 = C_{22}H_{16}N_4$ : C, 78.55; H, 4.79; N, 16.66. Found: C, 78.33; H, 4.54; N, 16.64%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 8.63$  (m, 1H), 8.09 (m, 1H), 7.60 (m, 3H), 7.31-7.42 (m, 6H), 7.27 (s, 1H), 7.24-7.17 (m, 3H), 6.85 (d, 1H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup>  $(\log \varepsilon/M^{-1} \text{ cm}^{-1})$  20.1 (4.02), 26.4 (3.47), 32.3 (4.19), 40.9 (4.57).

# 2.2.2. $L^3$ ligand

1-Phenylazo-2-naphthylamine (0.191 g, 0.77 mmol) was added to the methanol solution ( $30 \text{ cm}^3$ ) of quinoline-2-aldehyde (0.122 g, 0.78 mmol) and the reaction mixture was refluxed for 2 h to yield a pale yellow precipitate. The precipitate was filtered and dissolved in a small amount of dichloromethane. *n*-Hexane was added slowly to the solution, which was left at room temperature for several days to yield pale yellow crystals of L<sup>3</sup>. Yield: 0.218 g, 73.0%. *Anal.* Calc. for L<sup>3</sup> = C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.37; H, 4.41; N, 14.40%. The triazine ligand corresponding to L<sup>2</sup> could be in the filtrate but was not isolated. <sup>1</sup>H NMR (chloroform-d)  $\delta$  = 10.53 (s, 1H), 8.88 (m, 1H), 8.51 (d, 1H), 8.26 (d, 1H), 8.13 (d, 1H), 8.00 (m, 1H), 7.96 (d, 1H), 7.84–7.75 (m, 3H), 7.60–7.47 (m, 3H), 7.09 (dd, 2H), 6.83 (t, 1H), 6.70 (d, 2H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/M^{-1}$  cm<sup>-1</sup>)} 26.9 (4.48), 30.9 (4.09), 36.2 (4.68).

# 2.2.3. $[PdCl_2(L^1)]$ (1)

An acetonitrile solution  $(10 \text{ cm}^3)$  of  $[PdCl_2(PhCN)_2]$ (0.016 g, 0.042 mmol) was added to dichloromethane– acetonitrile (1:4 v/v) solution (25 cm<sup>3</sup>) of L<sup>1</sup> (0.014 g, 0.042 mmol) with stirring. The reaction mixture was warmed at 60 °C in an oil bath for 2 h to yield a yellow precipitate, which was filtered and air-dried. Yield: 0.018 g, 83.6%. *Anal.* Calc. for  $[PdCl_2(L^1)] = C_{22}H_{16}Cl_2N_4Pd$ : C, 51.44; H, 3.14; N, 10.91. Found: C, 51.15; H, 2.73; N, 10.87%. The complex is almost insoluble in common organic solvents.

# 2.2.4. $[PdCl_2(L^2)]$ (2)

*Method A:* [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.033 g, 0.086 mmol) was added to a dichloromethane solution of L<sup>2</sup> (0.032 g, 0.096 mmol). The reaction mixture was refluxed for 7 h and evaporated to 5 cm<sup>3</sup>. *n*-Hexane (20 cm<sup>3</sup>) was added slowly and the solution was left overnight to yield dark red crystals. Yield: 0.037 g, 83.4%. *Anal.* Calc. for [PdCl<sub>2</sub>(L<sup>2</sup>)]·0.67CH<sub>2</sub>Cl<sub>2</sub> = C<sub>22.66</sub>H<sub>17.33</sub>Cl<sub>3.33</sub>N<sub>4</sub>Pd: C, 47.72; H, 3.06; N, 9.82. Found: C, 47.94; H, 2.91; N, 9.77%. Alternatively, the complex was also conveniently prepared according to the following procedure.

Method B: The methanol solution (40 cm<sup>3</sup>) of pyridine-2-aldehyde (0.090 g, 0.842 mmol) and 1-phenylazo-2-naphthylamine (0.205 g, 0.828 mmol) was refluxed for 2.5 h, and evaporated to dryness. The dark red residue was dissolved in dichloromethane (40 cm<sup>3</sup>) and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.303 g, 0.789 mmol) was added. The reaction mixture was refluxed for 9 h, filtered, and evaporated to a small amount. *n*-Hexane (20 cm<sup>3</sup>) was added slowly and the solution was left overnight to yield dark red crystals. Yield: 0.307 g, 75.6%. <sup>1</sup>H NMR (chloroform-d)  $\delta$  = 9.24 (d, 1H), 8.14 (d, 1H), 7.95 (d, 1H), 7.90 (td, 1H), 7.55–7.30 (m, 12H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/M^{-1}$  cm<sup>-1</sup>)} 17.6 (3.82), 22.4 (3.94), 32.3 (4.11), 41.1 (4.69).

# 2.2.5. $[PdCl_2(L^3)]$ (3)

 $[PdCl_2(PhCN)_2]$  (0.022 g, 0.058 mmol) was added to a dichloromethane solution (10 cm<sup>3</sup>) of L<sup>3</sup> (0.023 g, 0.060 mmol). The reaction mixture was refluxed for 2 h to

yield a yellow precipitate, which was filtered and airdried. Yield: 0.030 g, 92.4%. *Anal.* Calc. for  $[PdCl_2(L^3)] = C_{26}H_{17}Cl_2N_4Pd$ : C, 55.49; H, 3.04; N, 9.96. Found: C, 55.32; H, 2.94; N, 9.86%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 10.36$  (s, 1H), 8.86 (m, 1H), 8.49 (d, 1H), 8.41 (d, 1H), 8.16–8.09 (m, 2H), 8.01–7.95 (m, 2H), 7.89–7.80 (m, 2H), 7.65 (td, 1H), 7.58–7.55 (m, 2H), 7.11 (t, 2H), 6.75 (t, 1H), 6.63 (d, 2H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/M^{-1}$  cm<sup>-1</sup>)} 23.5 (3.70 sh), 24.8 (3.74), 32.6 (3.57 sh), 36.2 (4.07).

# 2.2.6. $[PdCl(L^{4a})]$ (4)

Complex 2 (0.030 g, 0.059 mmol) was suspended in dichloromethane  $(30 \text{ cm}^3)$ -acetone  $(20 \text{ cm}^3)$  and water (4 cm<sup>3</sup>) was added. The reaction mixture was stirred for 10 min. and evaporated to dryness. The residue was dissolved in a small amount of dichloromethane. *n*-Hexane was added slowly to the solution, which was left at room temperature for several days to yield brown crystals. Yield: 0.014 g, 47.9%. Anal. Calc. for  $[PdCl(L^{4a})] = C_{22}H_{17}ClN_4OPd: C, 53.35; H, 3.46; N,$ 11.31. Found: C, 53.67; H, 3.48; N, 11.17%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 9.26$  (dd, 1H), 8.40 (d, 1H), 7.95 (m, 1H), 7.80 (d, 1H), 7.74 (d, 1H), 7.61 (m, 4H), 7.54-7.41 (m, 2H), 7.40-7.28 (m, 4H), 6.60 (d, 1H), 2.96 (d, 1H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup>  $(\log \varepsilon/M^{-1} \text{ cm}^{-1})$ } 18.5 (3.88), 20.0 (3.62 sh), 26.4 (3.97), 31.3 (4.13 sh), 33.8 (4.26 sh), 39.6 (4.68).

# 2.2.7. $[PdCl(L^{4b})]$ (5), $[PdCl(L^{4c})]$ (6), and $[PdCl(L^{4d})]$ (7)

The following procedure is described for  $[PdCl(L^{4b})]$  (5), as an example.

Method A: Methanol (20 cm<sup>3</sup>) was added to a suspension of complex 2 (0.101 g, 0.197 mmol) in dichloromethane (20  $\text{cm}^3$ ). After the reaction mixture was stirred for several minutes, the reddish purple solution was filtered and evaporated to dryness. The residue was dissolved in a small amount of dichloromethane. Methanol was added slowly to the solution, which was left at room temperature for several days to yield reddish-purple crystals. Yield: 0.086 g, 85.7%. Anal. Calc. for  $[PdCl(L^{4b})] = C_{23}H_{19}ClN_4OPd$ : C, 54.24; H, 3.76; N, 11.00. Found: C, 54.10; H, 3.64; N, 10.91%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 9.36$  (dd, 1H), 8.43 (d, 1H), 7.97 (td, 1H), 7.78 (d, 1H), 7.70 (d, 1H), 7.66–7.60 (m, 4H), 7.49 (m, 1H), 7.46–7.41 (m, 3H), 7.33 (m, 2H), 6.70 (s, 1H), 3.18 (s, 3H). UV-Vis {dichloromethane,  $\sigma/10^3 \text{ cm}^{-1} (\log \epsilon/\text{M}^{-1} \text{ cm}^{-1})$  18.5 (3.74), 20.0 (3.51) sh), 26.4 (3.85), 31.3 (4.03 sh), 33.8 (4.16 sh), 39.9 (4.58). Alternatively, the complex was also conveniently prepared according to the following procedure.

*Method B:* The methanol solution (40 cm<sup>3</sup>) of pyridine-2-aldehyde (0.034 g, 0.321 mmol) and 1-phenylazo-2-naphthylamine (0.078 g, 0.317 mmol) was refluxed for 2 h. [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.113 g, 0.293 mmol) was then added to the solution, which was refluxed for 8 h to yield fine reddish-purple crystals. The crystals were filtered, washed with a small amount of diethyl ether, and air-dried. Yield: 0.120 g, 80.3%.

A similar procedure (Method A) was also applied for the synthesis of [PdCl(L<sup>4c</sup>)] (Yield: 79.8%. Anal. Calc. for  $[PdCl(L^{4c})] = C_{24}H_{21}ClN_4OPd$ : C, 55.08; H, 4.04; N, 10.71. Found: C, 54.91; H, 3.89; N, 10.66%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 9.67$  (d, 1H), 8.43 (d, 1H), 8.00-7.94 (m, 2H), 7.72 (d, 1H), 7.64 (d, 1H), 7.54-7.28 (m, 9H), 6.76 (s, 1H), 3.75-3.66 (m, 1H), 3.12-3.04 (m, 1H), 1.94 (s, 3H). UV-Vis {dichloromethane,  $\sigma/10^3 \text{ cm}^{-1} (\log e/M^{-1} \text{ cm}^{-1})$  18.5 (3.86), 20.0 (3.63) sh), 26.4 (3.95), 29.8 (4.03 sh), 31.5 (4.11), 39.5 (4.66).) and  $[PdCl(L^{4d})]$  (Yield: 46.2%. Anal. Calc. for  $[PdCl(L^{4d})] = C_{26}H_{25}ClN_4OPd: C, 56.64; H, 4.57; N,$ 10.16. Found: C, 56.36; H, 4.40; N, 10.09%. <sup>1</sup>H NMR (chloroform-d)  $\delta = 9.35$  (dd, 1H), 8.43 (d, 1H), 7.96 (td, 1H), 7.77 (d, 1H), 7.71-7.60 (m, 5H), 7.52-7.40 (m, 4H), 7.32 (m, 2H), 6.70 (s, 1H), 3.74–3.67 (m, 1H), 3.14-3.07 (m, 1H), 1.42 (m, 2H), 1.22 (m, 2H), 0.75 (t, 3H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/$  $M^{-1} cm^{-1}$  = 18.5 (3.79), 20.0 (3.56 sh), 26.4 (3.87), 29.9 (3.98 sh), 31.4 (4.04), 39.5 (4.59).) using EtOH and "BuOH, respectively, instead of MeOH.

# 2.2.8. $[PdCl(L^{4e})]$ (8)

Complex 2 (0.030 g, 0.058 mmol) was dissolved in acetone (100  $\text{cm}^3$ ) and the solution was left in the dark at room temperature for 20 days. After the solution was filtered, the filtrate was evaporated to dryness. The brown residue was dissolved in THF  $(1 \text{ cm}^3)$  and *n*-hexane (20 cm<sup>3</sup>) was added slowly to yield fine reddish-purple crystals, which were filtered and air-dried. Yield: 0.014 g, 45.2%. Anal. Calc. for  $[PdCl(L^{4e})] =$ C<sub>25</sub>H<sub>21</sub>ClN<sub>4</sub>OPd: C, 56.09; H, 3.95; N, 10.47. Found: C, 56.01; H, 3.79; N, 10.40%. <sup>1</sup>H NMR (chloroformd)  $\delta = 9.33$  (ddd, 1H), 8.41 (d, 1H), 7.83 (td, 1H), 7.72-7.64 (m, 4H), 7.56 (d, 1H), 7.48 (m, 1H), 7.42 (m, 2H), 7.35 (m, 1H), 7.32-7.27 (m, 2H), 7.18 (d, 1H), 6.13 (dd, 1H), 3.28 (dd, 1H), 3.06 (dd, 1H), 2.18 (s, 3H). UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/$  $M^{-1} cm^{-1}$  = 18.3 (3.88), 20.0 (3.65 sh), 26.3 (3.91 sh), 29.6 (4.12), 31.0 (4.09 sh), 38.8 (4.66).

# 2.2.9. $[PdCl_2(L^5)]$ (9)

2-Acetylpyridine (0.041 g, 0.338 mmol) and 1-phenylazo-2-naphthylamine (0.080 g, 0.322 mmol) were dissolved in acetonitrile (30 cm<sup>3</sup>), and the solution was refluxed for 2 h. The acetonitrile solution (20 cm<sup>3</sup>) of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.130 g, 0.340 mmol) was added and the reaction mixture was evaporated to about 15 cm<sup>3</sup>. After the solution was left at room temperature for one day, the red crystals were filtered, washed with diethyl ether, and air-dried. Yield: 0.065 g, 34.8%. *Anal.* Calc. for [PdCl<sub>2</sub>(L<sup>5</sup>)]·0.5H<sub>2</sub>O = C<sub>24</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>0.5</sub>Pd: C, 52.53; H, 3.49; N, 10.21. Found: C, 52.39; H, 3.20; N, 10.58%. UV–Vis {dichloromethane,  $\sigma/10^3$  cm<sup>-1</sup> (log  $\varepsilon/M^{-1}$  cm<sup>-1</sup>)} 16.9 (3.91), 24.8 (3.83), 30.3 (4.23), 38.4 (4.62). The complex is almost insoluble in common organic solvents.

# 2.3. X-ray crystallography

Crystallographic data and experimental details for ligand  $L^{n}$  (n = 1-3) and complexes 2, 3, 4, 5, 8, and 9 are summarized in Table 1. Each single crystal of the complexes except complex 4 was glued on a glass fiber, while that of complex 4 was sealed in a glass capillary with the mother liquor to prevent loss of the water of crystallization. X-ray diffraction data were collected on a Rigaku AFC7S diffractometer using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) for ligands L<sup>n</sup> (n = 1-3), a RAXIS-RAPID diffractometer using graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) for complexes 2, 4, 5, and 9, and an MSC Mercury CCD diffractometer using graphite-monochromated Mo Ka radiation ( $\lambda = 0.71069$  Å) for complexes 3 and 8. A numerical absorption correction using the program NUMABS [8] was applied to the intensity data. The structures were solved by direct methods (SIR92 [9]) and expanded using Fourier techniques (DIRDIF94 [10]). The structures were refined by full-matrix least-squares based on  $F(L^{n}, n = 1-3 \text{ and } 2, 4, 5, \text{ and } 9)$  and  $F^{2}(3)$ and 8) with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and included in the refinement but were not refined. All calculations were performed using the teXsan [11] crystallographic software package of Molecular Structure Corporation.

#### 3. Results and discussion

## 3.1. Structures of ligands $L^1$ , $L^2$ , and $L^3$

Ligands  $L^1$  and  $L^2$  were obtained from the reaction of 1-phenylazo-2-naphthylamine with pyridine-2-aldehyde. 1-Phenylazo-2-naphthylamine was added to the methanol solution of pyridine-2-aldehyde and the reaction mixture was evaporated to dryness. The residue was dissolved in ether and pale orange crystals of the  $L^1$  ligand were isolated from the solution. When chromatographic separation of the reaction mixture was carried out on a column of silica gel, several eluates of the products were obtained. However, only the  $L^1$  and  $L^2$  ligands were isolated as major products, and other minor components were not isolated. Although we expected that the reaction of 1-phenylazo-2-naphthylamine with pyridine-2-aldehyde would produce a tridentate Schiff base ligand  $(L^{6})$  $(L^6 = 1-(phenylazo)-N-(2-pyridylmethylidene)-2$ naphthylamine), the L<sup>6</sup> ligand was not identified. We

Table 1	
Crystallographic data and experimental details	

Compound	$L^1$	$L^2$	$L^3$	2	3	<b>4</b> · 2.5H <sub>2</sub> O	5	8	9
Formula	C22H16N4	C22H16N4	C26H18N4	C <sub>22</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>4</sub> Pd	C <sub>26</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>4</sub> Pd	C <sub>22</sub> H <sub>16</sub> ClN <sub>4</sub> O <sub>3.5</sub> Pd	C23H19ClN4OPd	C <sub>25</sub> H <sub>21</sub> ClN <sub>4</sub> OPd	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> Cl <sub>2</sub> Pd
М	336.40	336.40	386.45	513.70	563.76	534.25	509.28	535.32	527.73
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	$P\bar{1}$	Pa	$P2_{1}/c$	Pbca	Pccn	$P2_{1}/c$	$P2_1/n$	$P2_{1}/c$
a (Å)	31.061(2)	10.1427(8)	20.341(2)	10.8969(3)	10.609(3)	13.991(1)	13.1173 (5)	12.203(2)	11.4571(5)
b (Å)	11.474(1)	10.3580(9)	13.445(1)	13.9359(3)	16.408(4)	16.801(1)	10.3936(5)	8.909(2)	12.3142(4)
<i>c</i> (Å)	9.859(1)	9.418(1)	7.1923(6)	13.8534(3)	25.862(7)	20.438(1)	15.5499(7)	20.694(4)	15.7677(6)
α (°)		112.745(6)							
β (°)		101.636(7)	98.172(6)	108.827(1)			103.953(1)	93.062(5)	92.773(1)
γ (°)		70.531(6)							
$V(\text{\AA}^3)$	3513(1)	857.3(1)	1947.0(3)	1991.19(8)	4501(1)	4804.1(9)	2057.5(2)	2246.4(7)	2222.0(2)
Ζ	8	2	4	4	8	8	4	4	4
$\mu$ (cm <sup>-1</sup> )	6.10 (Cu Ka)	6.26 (Cu Ka)	6.25 (Cu Kα)	12.17 Mo Kα	10.85 Mo Kα	9.15 Mo Kα	10.55 Mo Kα	9.71 Mo Kα	10.93 Mo Kα
Transmission factor	0.8195-0.8985	0.9236-0.9998	0.9765-0.9997	0.7130-0.9312	0.8594-0.9759	0.9504-0.9614	0.6475-0.7799	0.8335-0.9774	0.7531-0.8926
Crystal color	colorless	red	colorless	purple	orange	red	purple	orange	brown
Crystal habit	prism	prism	prism	plate	needle	prism	prism	needle	prism
Crystal size (mm <sup>3</sup> )	$0.20 \times 0.30$	$0.25 \times 0.40$	$0.20 \times 0.30$	$0.06 \times 0.30$	$0.03 \times 0.03$	$0.20 \times 0.20$	$0.30 \times 0.30$	$0.05 \times 0.07$	$0.10 \times 0.20$
	$\times 0.40$	$\times 0.40$	$\times 0.40$	$\times 0.30$	$\times 0.20$	$\times 0.30$	$\times 0.30$	$\times 0.50$	$\times 0.40$
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.272	1.303	1.318	1.713	1.663	1.477	1.644	1.583	1.577
$2\theta_{\max}$ (°)	140.0	140.0	140.0	55.0	55.0	55.0	55.0	55.0	55.0
$R_1(R)^{\mathrm{a}}$	0.064	0.048	0.042	0.028	0.118 (0.180)	0.060	0.031	0.075 (0.092)	0.034
$R_{ m w}$	0.074 <sup>b</sup>	0.082 <sup>c</sup>	0.051 <sup>b</sup>	0.038 <sup>b</sup>	0.182	0.088 <sup>b</sup>	0.050 <sup>b</sup>	0.170 <sup>b</sup>	0.047 <sup>b</sup>
$S^{\mathrm{d}}$	1.97	1.99	1.53	1.12	1.10	1.47	1.57	1.36	1.27

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, R$  is obtained for all observed data. <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . <sup>c</sup>  $R_w = [\sum w(|F_o|^2 - |F_c|)^2 / \sum w(|F_o|^2)^2]^{1/2}$ . <sup>d</sup>  $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$  (*m* is the no. of used reflections, *n* is the no. of refined parameters).

Table 2

presume that the  $L^6$  ligand could be unstable and converted into the  $L^1$  and  $L^2$  ligands rapidly in the course of the reaction in methanol. The  $L^3$  ligand was also obtained in a similar manner by the reaction of 1-phenylazo-2-naphthylamine with quinoline-2-aldehyde; however, a ligand containing the six-membered ring of dihydrotriazine, the analogous compound with  $L^2$ , was not obtained. We determined the structures of the  $L^1$ ,  $L^2$ , and  $L^3$  ligands by X-ray crystallography (Fig. 2). These ligands had a six-membered ring of dihydrotriazine in  $L^2$ , and a five-membered ring of imidazole in  $L^1$  and  $L^3$ . The selected bond distances and angles of the ligands are summarized in Table 2.

In the L<sup>1</sup> ligand, the N(3) atom is attached to the C(6) atom, and an imidazole ring composed of C(6), N(2), C(7), C(16), and N(3) atoms is formed. The naphthoimidazole ring {N(2), N(3), and C(6)–C(16)} makes a dihedral angle of 25.75(9)° with the pyridine ring {N(1) and C(1)–C(5)}. The benzene ring {C(17)–C(22)} and the naphthoimidazole ring are almost perpendicular to each other (88.62(8)°). It is notable that a hydrogen atom is attached to N(4) and the bond length of N(3)–N(4) (1.396(3) Å) indicates an N–N single bond. Accordingly, the double bond character of the azo moiety of 1-phenylazo-2-naphthylamine was lost in the L<sup>1</sup> ligand.

In the L<sup>2</sup> ligand, on the other hand, the N(4) atom is attached to the C(6) atom, and a dihydrotriazine ring composed of C(6), N(2), C(7), C(16), N(3), and N(4) atoms is formed. The bond lengths of N(2)–C(6) (1.445(2) Å), N(4)–C(6) (1.482(2) Å), and C(5)–C(6) (1.532(2) Å) are in the range of common single bond lengths, and those of N(2)–C(7) (1.296(2) Å) and N(3)–C(16) (1.311(2) Å) indicate C=N double bond

· · ·	5	/ 0
1.313(3)	N(3)–C(6)	1.377(3)
1.380(3)	N(3)-C(16)	1.387(3)
1.396(3)	C(7)–C(16)	1.379(3)
105.2(2)	N(2)-C(6)-N(3)	111.7(2)
127.6(2)	N(2)-C(6)-C(5)	124.6(2)
124.3(2)	N(3)-C(6)-C(5)	123.7(2)
107.3(2)	N(2)-C(7)-C(16)	111.3(2)
116.0(2)	N(3)-C(16)-C(7)	104.4(2)
1.445(2)	N(3)–C(16)	1.311(2)
1.296(2)	N(4)–C(6)	1.482(2)
1.335(1)	C(7)–C(16)	1.464(2)
113.9(1)	N(2)-C(6)-N(4)	110.5(1)
116.8(1)	N(2)-C(6)-C(5)	113.0(1)
119.1(1)	N(4)-C(6)-C(5)	110.2(1)
116.9(1)	N(2)-C(7)-C(16)	122.3(1)
123.7(1)	N(3)-C(16)-C(7)	119.4(1)
1.307(5)	N(3)–C(10)	1.377(5)
1.355(5)	N(3)–C(20)	1.379(4)
1.406(4)	C(11)-C(20)	1.396(5)
107.6(3)	N(2)-C(10)-N(3)	110.2(3)
127.2(3)	N(2)-C(10)-C(9)	124.0(3)
124.8(3)	N(3)-C(10)-C(9)	125.7(3)
107.9(3)	N(2)-C(11)-C(20)	110.0(3)
115.7(3)	N(3)-C(20)-C(11)	104.3(3)
	1.313(3) 1.380(3) 1.396(3) 105.2(2) 127.6(2) 124.3(2) 107.3(2) 116.0(2) 1.445(2) 1.296(2) 1.335(1) 113.9(1) 116.8(1) 119.1(1) 116.9(1) 123.7(1) 1.307(5) 1.355(5) 1.406(4) 107.6(3) 127.2(3) 124.8(3) 107.9(3) 115.7(3)	1.313(3)         N(3)-C(6)           1.380(3)         N(3)-C(16)           1.396(3)         C(7)-C(16)           105.2(2)         N(2)-C(6)-N(3)           127.6(2)         N(2)-C(6)-C(5)           124.3(2)         N(3)-C(16)           116.0(2)         N(2)-C(7)-C(16)           116.0(2)         N(3)-C(16)           1.296(2)         N(4)-C(6)           1.335(1)         C(7)-C(16)           113.9(1)         N(2)-C(6)-N(4)           116.8(1)         N(2)-C(6)-N(4)           116.8(1)         N(2)-C(6)-C(5)           119.1(1)         N(4)-C(6)-C(5)           116.9(1)         N(2)-C(7)-C(16)           123.7(1)         N(3)-C(10)           1.355(5)         N(3)-C(10)           1.355(5)         N(3)-C(10)           1.355(5)         N(3)-C(10)           1.406(4)         C(11)-C(20)           107.6(3)         N(2)-C(10)-N(3)           127.2(3)         N(2)-C(10)-C(9)           124.8(3)         N(3)-C(10)-C(9)           125.7(3)         N(3)-C(20)-C(11)

character. The bond length of N(3)-N(4) (1.335(1) Å) is longer than those of uncoordinated N=N double bonds (the average N=N bond length of azo compounds; 1.25 Å [12]), however, the bond angles



Fig. 2. ORTEP drawings of ligands  $L^1-L^3$  with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

Selected bond distan	ices (Å) and angles (°	) for the $L^n$	(n = 1 - 3) ligands

Table 3

around the N(4) atom (116.9–123.7°) suggest that the N(4) atom is sp<sup>2</sup>-hybridized. Such a resonance hybrid of the ligand structure has been reported previously in the relevant Pd complexes [6]. The dihydrotriazine ring is not planar, and the plane 1 {N(2), C(7), C(16), N(3), and N(4) atoms} makes a dihedral angle of 40.91(4)° with the plane 2 {N(2), N(4), and C(6) atoms}. The C(6) atom is 0.563(2) Å out of the plane 1. The benzene ring {C(17)–C(22)} and the plane 1 make a dihedral angle of 39.85(5)°.

The L<sup>3</sup> ligand has a naphthoimidazole ring {N(2), N(3), and C(10)–C(20)}, which makes a small dihedral angle of 6.14(9)° with the quinoline ring {N(1) and C(1)–C(9)}. Thus, the two aromatic rings are conjugated and the bond length of C(9)–C(10) (1.486(5) Å) indicates some double bond character.

#### 3.2. Structures of the complexes

Complexes 1, 2, and 3 were prepared by treating  $[PdCl_2(PhCN)_2]$  with ligands  $L^1$ ,  $L^2$ , and  $L^3$  in dichloromethane or acetonitrile–dichloromethane. Complex 2 was also prepared in good yield by the reaction of  $[PdCl_2(PhCN)_2]$  with the reaction mixture of 1-phenylazo-2-naphthylamine and pyridine-2-aldehyde in dichloromethane, which suggests that the  $L^1$  ligand should be produced in preference to the  $L^2$  ligand. Complex 1 could not be recrystallized because the complex was almost insoluble in common organic solvents; however, complexes 2 and 3 were successfully recrystallized and good single crystals were obtained. We carried out the X-ray structure determination for complexes 2 and 3. The selected bond distances and angles of those complexes are summarized in Table 3.

Fig. 3 shows a perspective view of complex 2. The coordination geometry around the palladium atom is square planar. The difference in bond lengths in the dihydrotriazine ring was hardly discernible between the free  $L^2$  ligand and that of complex 2. However, the C(6) atom is 0.337(4) Å out of the plane 1 {N(2), C(7), C(16), N(3), and N(4) atoms}, and the dihedral angle  $(23.61(9)^\circ)$  between the plane 1 and the plane 2  $\{N(2), N(4), and C(6) atoms\}$  is considerably smaller than that of the free  $L^2$  ligand. The benzene ring  $\{C(17)-C(22)\}$  and the plane 1 show a small dihedral angle of 18.0(1)°. Accordingly, the naphthalene and benzene rings are conjugated via N(3) and N(4) atoms in complex 2. It seems that the coordinating  $L^2$  ligand has a longer conjugated system than the corresponding free  $L^2$  ligand. The conjugated plane, however, makes a large dihedral angle of  $64.5(1)^{\circ}$  with the coordination plane  $\{Pd(1), Cl(1), Cl(2), N(1), and N(2)\}$ .

Fig. 4 shows a perspective view of complex 3. The naphthoimidazole ring {N(2), N(3), and C(10)–C(20)} and the quinoline ring {N(1) and C(1)–C(9)} were almost in the same plane, and the chelate ring {N(1),

Selected bond distan	ices (A) and an	igles (°) for complexes 2	and 3
Complex 2			
Pd(1)-Cl(1)	2.2800(9)	N(2)–C(7)	1.301(4)
Pd(1)–Cl(2)	2.2887(8)	N(3)–N(4)	1.334(3)
Pd(1) - N(1)	2.053(2)	N(3)–C(16)	1.309(4)
Pd(1)–N(2)	2.027(3)	N(4)–C(6)	1.471(4)
N(2)-C(6)	1.468(3)	C(7)–C(16)	1.450(4)
Cl(1)-Pd(1)-Cl(2)	91.41(3)	N(3)-N(4)-C(6)	121.9(2)
Cl(1)-Pd(1)-N(1)	92.87(7)	N(3)-N(4)-C(17)	116.1(2)
Cl(1)-Pd(1)-N(2)	170.57(6)	C(6)-N(4)-C(17)	122.0(2)
Cl(2)-Pd(1)-N(1)	175.09(7)	N(2)-C(6)-N(4)	111.6(2)
Cl(2)-Pd(1)-N(2)	97.27(6)	N(2)-C(6)-C(5)	106.4(2)
N(1)-Pd(1)-N(2)	78.63(9)	N(4)-C(6)-C(5)	114.8(2)
C(6)-N(2)-C(7)	119.7(2)	N(2)-C(7)-C(16)	120.2(2)
N(4)-N(3)-C(16)	118.9(2)	N(3)-C(16)-C(7)	121.5(3)
Complex 3			
Pd(1)-Cl(1)	2.308(3)	N(2)–C(11)	1.38(1)
Pd(1)-Cl(2)	2.272(3)	N(3)–N(4)	1.40(1)
Pd(1)-N(1)	2.107(7)	N(3)-C(10)	1.36(1)
Pd(1)–N(2)	2.034(9)	N(3)-C(20)	1.40(1)
N(2)-C(10)	1.34(1)	C(11)-C(20)	1.36(2)
Cl(1)-Pd(1)-Cl(2)	85.6(1)	N(4)-N(3)-C(20)	127.6(9)
Cl(1)-Pd(1)-N(1)	100.0(3)	C(10)-N(3)-C(20)	107.4(9)
Cl(1)-Pd(1)-N(2)	165.5(3)	N(3)-N(4)-C(21)	116.5(8)
Cl(2)-Pd(1)-N(1)	173.4(2)	N(2)-C(10)-N(3)	111.0(9)
Cl(2)-Pd(1)-N(2)	95.2(2)	N(2)-C(10)-C(9)	119(1)
N(1)-Pd(1)-N(2)	80.3(3)	N(3)-C(10)-C(9)	129.9(9)
C(10)-N(2)-C(11)	105.2(9)	N(2)-C(11)-C(20)	111.4(9)
N(4)-N(3)-C(10)	124.9(8)	N(3)-C(20)-C(11)	105(1)



Fig. 3. An ORTEP drawing of  $[PdCl_2(L^2)]$  (2) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

N(2), C(9), and C(10)} has a small dihedral angle of  $17.9(2)^{\circ}$  with the plane defined by Pd(1), Cl(1), and Cl(2). Thus, the coordination plane around the Pd atom



Fig. 4. An ORTEP drawing of  $[PdCl_2(L^3)]$  (3) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

was slightly twisted towards tetrahedral, and close approaches between Cl(1) and the hydrogen atom H(1) attached to C(2), and between Cl(2) and H(7) attached to C(12) could be avoided. The calculated distances {2.50 Å for Cl(1)–H(1) and 2.60 Å for Cl(2)–H(7)} are, nevertheless, shorter than the sum of the van der Waals radii of 3.00 Å {1.20(H) + 1.80(Cl) Å}. The bond length of N(3)–N(4) (1.40(1) Å) is similar to that of the N(3)–N(4) single bond in ligand L<sup>3</sup>. A hydrogen atom attached to N(4) could not be observed by X-ray crystallography, but was confirmed by a measurement of the IR spectrum (vide infra). The most reasonable representation of complexes **2** and **3** is a resonance hybrid of the two structures, respectively (Fig. 5).

Figs. 6–8 show perspective views of complexes 4, 5, and 8, and selected bond distances and angles are summarized in Table 4. A tridentate ligand coordinates to the Pd atom with three nitrogen atoms (N(1), N(2), and N(4)) in each complex, and OH<sup>-</sup> (complex 4), CH<sub>3</sub>O<sup>-</sup> (complex 5) and CH<sub>3</sub>COCH<sub>2</sub><sup>-</sup> (complex 8) groups are attached to the sp<sup>3</sup>-C(6) atom. The bond length of N(2)–C(6) (1.48(1) (complex 4), 1.467(4) (complex 5), and 1.482(6) Å (complex 8)) indicates an N–C single bond, and the bond length of N(3)–N(4) (1.28(1) (complex 4), 1.268(4) (complex 5), and 1.287(7) Å (complex 8)) indicates an N–N double bond character of the azo moiety. These results are consistent with those of the expected structure, which is illustrated in Fig. 9(a). The coordinating azo group has the trans-



Fig. 5. A resonance hybrid of the two structures for  $[PdCl_2(L^2)]$  (2) and  $[PdCl_2(L^3)]$  (3).



Fig. 6. An ORTEP drawing of complex [PdCl( $L^{4a}$ )] (4) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

form. However, the bond lengths of N(2)–C(7) (1.32(1) (complex 4), 1.330(4) (complex 5), and 1.318(7) Å (complex 8)) and N(3)–C(16) (1.35(1) (complex 4), 1.359(4) (complex 5), and 1.296(7) Å (complex 8)) are considerably shorter than those of N–C single bonds. Accordingly, a resonance hybrid of the two structures (a) and (b) should be the most reasonable representation of the complexes, and the negative charge of the ligand is



Fig. 7. An ORTEP drawing of  $[PdCl(L^{4b})]$  (5) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.



Fig. 8. An ORTEP drawing of  $[PdCl(L^{4e})]$  (8) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

regarded as being spread over the conjugated system (c) (Fig. 9).

Fig. 10 shows a perspective view of complex 9. The selected bond distances and angles are summarized in Table 5. The complex contains a didentate Schiff base

Table 4 Selected bond distar	nces (Å) and an	gles (°) for complexes 4	I, 5, and 8
Complex 4 Pd(1)-Cl(1) Pd(1)-N(1) Pd(1)-N(2) Pd(1)-N(4) O(1)-C(6) N(2)-C(6)	2.325(3) 2.055(7) 1.975(7) 1.991(7) 1.39(1) 1.48(1)	N(2)–C(7) N(3)–N(4) N(3)–C(16) C(5)–C(6) C(7)–C(16)	1.32(1) 1.275(9) 1.35(1) 1.50(1) 1.44(1)
Cl(1)-Pd(1)-N(1) Cl(1)-Pd(1)-N(2) Cl(1)-Pd(1)-N(4) N(1)-Pd(1)-N(2) N(1)-Pd(1)-N(4) N(2)-Pd(1)-N(4) C(6)-N(2)-C(7)	92.5(3) 173.5(2) 94.9(2) 82.0(3) 172.6(3) 90.7(3) 119.5(8)	N(4)-N(3)-C(16) O(1)-C(6)-N(2) O(1)-C(6)-C(5) N(2)-C(6)-C(5) N(2)-C(7)-C(16) N(3)-C(16)-C(7)	125.7(8) 111.2(7) 112.9(9) 110.3(8) 122.4(8) 126.3(8)
Complex 5 Pd(1)-Cl(1) Pd(1)-N(1) Pd(1)-N(2) Pd(1)-N(4) O(1)-C(6) N(2)-C(6)	2.3392(7) 2.038(2) 1.979(2) 1.995(2) 1.408(4) 1.467(4)	N(2)-C(7) N(3)-N(4) N(3)-C(16) C(5)-C(6) C(7)-C(16)	1.330(4) 1.268(4) 1.359(4) 1.511(4) 1.441(4)
Cl(1)-Pd(1)-N(1) Cl(1)-Pd(1)-N(2) Cl(1)-Pd(1)-N(4) N(1)-Pd(1)-N(2) N(1)-Pd(1)-N(4) N(2)-Pd(1)-N(4) C(6)-N(2)-C(7)	93.09(7) 168.65(7) 94.83(7) 82.5(1) 171.10(9) 90.5(1) 118.3(2)	N(4)-N(3)-C(16) O(1)-C(6)-N(2) O(1)-C(6)-C(5) N(2)-C(6)-C(5) N(2)-C(7)-C(16) N(3)-C(16)-C(7)	124.9(2) 114.0(3) 111.3(3) 110.3(2) 122.8(3) 125.9(3)
Complex 8 Pd(1)-Cl(1) Pd(1)-N(1) Pd(1)-N(2) Pd(1)-N(4) N(2)-C(6) N(2)-C(7)	2.317(2) 2.046(5) 1.973(5) 1.978(5) 1.482(6) 1.318(7)	N(3)–N(4) N(3)–C(16) C(5)–C(6) C(6)–C(23) C(7)–C(16)	1.287(7) 1.296(7) 1.511(8) 1.521(8) 1.447(7)
Cl(1)-Pd(1)-N(1) Cl(1)-Pd(1)-N(2) Cl(1)-Pd(1)-N(4) N(1)-Pd(1)-N(2) N(1)-Pd(1)-N(4) N(2)-Pd(1)-N(4) C(6)-N(2)-C(7)	92.1(1) 174.3(1) 93.6(1) 82.9(2) 174.2(2) 91.3(2) 118.8(5)	N(4)–N(3)–C(16) N(2)–C(6)–C(5) N(2)–C(6)–C(23) C(5)–C(6)–C(23) N(2)–C(7)–C(16) N(3)–C(16)–C(7)	127.7(5) 110.6(4) 109.9(4) 110.4(5) 121.2(5) 127.1(5)

ligand  $L^5$ , whose azo group has the trans-form and the azo nitrogen atoms (N(3) and N(4)) are not coordinated to the Pd atom. The bond length of N(3)–N(4) (1.228(5) Å) is in the range of the common N–N double bond lengths and shorter than those of complexes **1**, **3–5** and **8**. The chelate ring {Pd(1), N(1), N(2), C(5), and C(6)} has a dihedral angle of 75.49(9)° with the naphthalene ring {C(8)–C(17)}. We suppose that these two rings could not be coplanar to each other because of the steric hindrance between the methyl protons attached to the C(7) atom and the aromatic proton attached to the C(9) atom. Therefore, coordination of the azo nitrogen atoms to the Pd atom did not occur.



Fig. 9. A resonance hybrid of the two structures ((a) and (b)) for  $[PdCl(L^{4a})]$  (4),  $[PdCl(L^{4b})]$  (5) and  $[PdCl(L^{4c})]$  (8), where the negative charge is spread over the conjugated system (c).



Fig. 10. An ORTEP drawing of  $[PdCl_2(L^5)]$  (9) with the atom labeling scheme. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids at 30% probability.

Table 5 Selected bond distances (Å) and angles (°) for complex 9					
Pd(1)-Cl(1)	2.280(1)	N(2)–C(8)	1.435(5)		
Pd(1)-Cl(2)	2.298(1)	N(3)–N(4)	1.228(5)		
Pd(1)–N(1)	2.024(3)	N(3)-C(17)	1.407(5)		
Pd(1)–N(2)	2.021(3)	C(5)–C(6)	1.471(5)		
N(2)-C(6)	1.285(5)	C(8)–C(17)	1.382(5)		
Cl(1)-Pd(1)-Cl(2)	92.23(4)	N(4)-N(3)-C(17)	117.1(3)		
Cl(1)-Pd(1)-N(1)	172.5(1)	N(2)-C(6)-C(5)	115.9(4)		
Cl(1)-Pd(1)-N(2)	94.05(9)	N(2)-C(6)-C(7)	124.4(4		
Cl(2)-Pd(1)-N(1)	94.0(1)	C(5)-C(6)-C(7)	119.7(3)		
Cl(2)-Pd(1)-N(2)	171.9(1)	N(2)-C(8)-C(17)	121.6(3		
N(1)-Pd(1)-N(2)	80.1(1)	N(3)-C(17)-C(8)	126.7(4		
C(6)-N(2)-C(8)	119.3(3)				

### 3.3. IR and UV-Vis spectra of the ligands and complexes

It has been reported that the  $v_{N=N}$  of 2-(phenylazo)aniline (H<sub>2</sub>L) is observed at 1460 cm<sup>-1</sup>, while that of Pd(HL)<sub>2</sub> is shifted to a lower wave number (1340  $cm^{-1}$ ) [13]. In the L<sup>2</sup> ligand, a strong band was observed at  $1382 \text{ cm}^{-1}$ , while the corresponding band was not detected in the  $L^1$  and  $L^3$  ligands. Accordingly, we assigned the band at 1382 cm<sup>-1</sup> as the  $v_{N=N}$ . On the other hand, the L<sup>1</sup> and L<sup>3</sup> ligands displayed a single band at 3303 and 3317 cm<sup>-1</sup>, characteristic of the NH group, respectively. These data are consistent with the structures of the  $L^1$  and  $L^3$  ligands that were determined by X-ray methods; that is, a hydrogen atom is attached to the N(4) atom and the N(3)–N(4) bond has a single bond character (Fig. 1). The  $v_{N=N}$  of complexes 2, 4, 5, 8, and 9 was not assigned because the spectra were complicated with many bands in the  $1200-1400 \text{ cm}^{-1}$  region. The complicated spectral aspect of this region is similar to those of palladium (II) and platinum (II) complexes with the ligands derived from 1-phenylazo-2-naphthylamine and 2-(diphenylphosphino)benzaldehyde or 2-(tert-butylthio)benzaldehyde that we reported in a previous paper [6]. Complexes 1 and 3 showed a broad stretching vibration band at 3240 and 3222  $cm^{-1}$ , respectively, and it was confirmed that a hydrogen remains attached to the N(4) atom.

Figs. 11 and 12 show the absorption spectra of the  $L^n$  (n = 1-3) ligands and complexes **2**, **6**, **8**, and **9** in dichloromethane. The  $L^2$  ligand has an N=N chromophore and the red solution of the  $L^2$  ligand exhibits an absorption band at 498 nm, while each solution of the  $L^1$  and  $L^3$  ligands is nearly colorless and no absorption band was observed in the visible region. The purple solution of complex **2** in dichloromethane exhibits an



Fig. 11. Absorption spectra of ligands  $L^1$  (----),  $L^2$  (----) and  $L^3$  (----) in dichloromethane.



Fig. 12. Absorption spectra of complexes  $[PdCl_2(L^2)]$  (2) (—),  $[PdCl(L^{4c})]$  (6) (---),  $[PdCl(L^{4e})]$  (8) (—·—) and  $[PdCl_2(L^5)]$  (9) (—··—) in dichloromethane.

absorption band at 570 nm. Thus, the absorption band of the visible region of complex 2 is shifted to a longer wavelength relative to the L<sup>2</sup> ligand. The absorption bands of complexes 6 and 8 appeared at 541 and 546 nm, respectively, and the spectral patterns were similar to each other in the wavelength region of 230-700 nm. The absorption spectral pattern of complexes 4, 5, and 7 also closely resembles these bands. On the other hand, the absorption band of complex 9 was observed at 592 nm. Unfortunately, the absorption spectra of pale yellow complexes 1 and 3 could not be measured quantitatively because of their poor solubility in common organic solvents; however, no absorption band was observed in the visible region. Accordingly, the absorption bands which were observed at 541-592 nm for complexes 2 and 4–9 could be identified as  $\pi - \pi$  \*or  $n - \pi^*$ transitions on the N=N chromophore.

## 3.4. Reactivity of the ligands and complexes

The absorption spectrum of ligand  $L^2$  remained unchanged for at least one day in dichloromethane or methanol, and those of ligands  $L^1$  and  $L^3$ , which were insoluble in methanol, were also invariant in dichloromethane.

The absorption spectrum of complex 2 in dichloromethane was invariant; however, the color of the solution changed from purple to reddish-purple rapidly when several drops of methanol or ethanol were added to the solution. The reaction of complex 2 with methanol proceeds faster than that with ethanol. Complexes 5 and 6 were obtained as reddish-purple crystals from each concentrated solution (vide supra, Method A for the preparation of complexes 5–7). Fig. 13 shows the change in the absorption spectrum of complex 2 in



Fig. 13. The change in absorption spectrum of  $[PdCl_2(L^2)]$  (2) (25 °C) in dichloromethane–ethanol (2:1 v/v) at 27 s intervals.

dichloromethane–ethanol (2:1 v/v) at regular time intervals. The absorption bands at 570 and 446 nm diminished with time, and new absorption bands at 541 and 379 nm grew. The converged spectrum was identical with that of complex 6. Complex 2 underwent a similar reaction with water and "BuOH to yield complexes 4 and 7, respectively. It is notable that complex 2 also reacted with acetone to yield complex 8, although the reaction was relatively slow at room temperature. Accordingly, alcohols and acetone undergo addition reactions for complex 2, and the ring opening reaction of the triazine skeleton occurs to produce the complexes containing azo ligands (Fig. 14).

On the other hand, the absorption spectrum of complex 5 (solid line) in dichloromethane changed as shown by the dashed line by an addition of excess amount of ("Bu)<sub>4</sub>NCl (Fig. 15). The absorption spectra of the product were exactly similar to that of complex 2. Complex 2 was recovered from the concentrated solution. Thus, it has become apparent that coordination of the Cl<sup>-</sup> ligand occurred and the triazine ring was formed by the subsequent ring closure to yield complex 2.



X = OH, OMe, OEt, O<sup>n</sup>Bu, CH<sub>2</sub>COCH<sub>3</sub>

Fig. 14. Schematic representation of a triazine ring opening reaction for  $[PdCl_2(L^2)]$  (2).



Fig. 15. An addition of  $({}^{n}Bu)_{4}NCl$  caused the change in absorption spectrum of  $[PdCl(L^{4b})]$  (5) (—) in dichloromethane and the spectrum represented by the dashed line was obtained.

Fig. 16 shows a possible mechanism for the ring opening and closure reactions. An addition reaction of the MeO<sup>-</sup> group to the C-3 atom of the triazine ring in complex **2** would cause the ring opening. Then, the following substitution reaction of a Cl<sup>-</sup> ligand by the azo nitrogen atom occurs to generate complex **5**. Unfortunately, we could not isolate the intermediate complex; however, we successfully determined the structure of complex **9**, where the azo nitrogen atom was not coordinated. We thus expected the intermediate as shown in Fig. 16. The reversible opening and closure reactions of the triazine ligand can be understood in terms of competition between the MeO<sup>-</sup> group and the Cl<sup>-</sup> ion.



Fig. 16. A presumable mechanism for the ring opening and closure reactions.

#### 4. Supplementary material

Tables of non-hydrogen atom coordinates and anisotropic thermal parameters, coordinates of the hydrogen atoms, and bond lengths and angles have been deposited as CIF files (Nos. 246824–246832 for ligands  $L^n$  (n = 1– 3) and complexes **2**, **3**, **4**, **5**, **8**, and **9**) at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

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