

## Formation of a palladium(II) complex of 2-(2-pyridinylmethyleamino)-2'-hydroxy-1,1'-binaphthyl with novel C<sub>σ</sub>-coordination and its theoretical investigation†

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Complexation of the NOBIN-derived Schiff base ligand **1** with Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> has been observed to result in a novel Pd–C bonding mode and theoretical calculations based on B3LYP density functional theory have been carried out to clarify the reaction mechanism.

As an analog of BINOL, chiral 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) is enjoying increasing application in the construction of chiral ligands for asymmetric catalysis.<sup>1–4</sup> Among the NOBIN-derived ligands, the Schiff bases have attracted additional interest owing to their intriguing features, such as their unique chiral biaryl structure, facile synthesis and easy modification. However, substantially less has been done about the organometallic features of these NOBIN-derived Schiff bases, and there has, to date, been no report on the well-characterized X-ray crystal structure of this kind of Schiff base complex. Herein we report interesting results of the formation of a novel C<sub>σ</sub>–Pd bonding mode in a Pd(II) complex of NOBIN-derived Schiff base **1** and a relevant mechanistic investigation with DFT calculations.

We began our investigation with the readily available racemic 2-(2-pyridinylmethyleamino)-2'-hydroxy-1,1'-binaphthyl **1**. The imine was prepared *in situ* by stirring a mixture of NOBIN and a slight excess of 2-pyridinecarbaldehyde (1.2 equivalents) in dichloromethane for one hour at ambient temperature in air.<sup>4a</sup> The *in situ* generated Schiff base ligand was treated with PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (1 equivalent).<sup>‡</sup> After stirring for 1 h, a mixture of yellow and red precipitate appeared, indicating that at least two kinds of compounds were formed in this reaction. The compounds are air-stable and display very low solubility for most of the solvents. Considering that 2-pyridinecarbaldehyde might function as both a reagent and a base, another experiment was conducted in dichloromethane with equimolar amounts of pure Schiff base **1** and Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> as reagents. After overnight stirring, only the yellow precipitate was observed. However, upon the addition of 1 equivalent of sodium acetate, the yellow precipitate became soluble and the yellow solution turned red in a few minutes. This observation confirmed our assumption that in the first experiment 2-pyridinecarbaldehyde has dual functions as both a reagent and a base. It also implied that the formation of the red compound involved a multi-step process: the formation of the yellow compound without the involvement of base followed by a base-promoted reaction generating the red compound. The red solution was allowed to stand for 3 days in air, and red crystals suitable for characterization *via* X-ray analysis formed.<sup>†</sup> Single crystals of the yellow compound suitable for X-ray diffraction study were obtained by dissolving the compound in warm DMSO followed by standing for over 1 week.

The yellow palladium complex **2**<sup>†</sup> crystallises in the monomeric form with two chloride atoms (C11 and C12) and two nitrogen atoms (N1 and N2) of the bidentate ligand forming the square-planar coordination sphere around the palladium center (see Fig. S1). The palladium atom is positioned in the coordination plane N1–N2–C11–C12 (0.0198 Å above the calculated plane) as the average off-plane deviation is 0.061 Å. The square-planar structure is slightly deformed due to the narrow N1–Pd–N2 angle [80.58(8)°]. The two naphthyl planes are perpendicular to each other, as indicated by a dihedral angle of 90.9°. As a result of the existence of a bulky binaphthyl ring on the N1 side, the palladium–imino bond Pd–N1 [2.038(2) Å] is slightly longer in comparison to Pd–N2 [2.035(2) Å].

The ORTEP plot of the structure of complex **3**<sup>†</sup> (red crystal) is shown in Fig. S2. Single crystal X-ray diffraction analysis revealed the existence of an unusual Pd–C bond and the loss of aromaticity of one ring. Obviously, this novel palladium coordination mode is a direct consequence of steric strain relief, allowing the ligand to avoid unfavorable steric interactions. The arrangement is evidenced by the bond distances of Pd–Cl, Pd–O1, C2–O1, C1–C2 and C3–C4 [2.133(4), 3.266(3), 1.244(5), 1.474(6) and 1.325(6) Å, respectively]. The metal adopts a distorted square-planar coordination geometry with C1, N1, N2 and C11 in a plane and Pd +0.0192 Å out of this plane. The N1–Pd–C1 angle of 82.98(14)° is smaller than the standard value of 90° for an ideal square planar complex, whereas the C1–Pd–C11 angle of 102.72(11)° is significantly greater than 90°. The Pd–C1 bond length of 2.133(4) Å is longer than the sum of the covalent radii (1.31 and 0.771 Å for palladium and carbon).<sup>5</sup> This lengthening is attributed to the existence of a bulky group on the imine side. The Pd–N2 bond length [2.100(4) Å] is longer than Pd–N1 [1.973(3) Å], reflecting the greater *trans* influence of the Pd–C1 bond. Pd–C1 and Pd–C2 distances of 2.133(4) and 2.709(5) Å rule out the formation of a η<sup>2</sup>-Pd coordination mode. The two binaphthyl rings are nearly perpendicular, as indicated by a dihedral angle of 78°.

It should be pointed out that whether cyclopalladation occurred or not proved to be strongly dependent on the presence of a weak base. This finding is similar to those obtained for the cyclopalladation or cycloplatination of thioimines and ferrocenyl Schiff bases.<sup>6</sup>

The unusual Pd–C<sub>σ</sub> bonding mode originates from the unique characteristics of both the ligand and the metal. The enolate character of the Schiff base ligand **1** leads to enol–keto tautomerization and high reactivity at C1, which has been observed in organic reactions with naphthyl-type substrates.<sup>7</sup> Considering the softness of the Pd(II) metal center,<sup>8</sup> which increases its carbophilicity relative to its oxophilicity, there is no doubt that the Pd(II) center readily coordinates to the softer benzyl enolate carbon. Consequently, the high electrophilicity of C1 coupled with the carbophilic nature of Pd(II) resulted in the five-membered palladacycle ring rather than larger metal–chelate rings, consistent with the known inclination of Pd(II).<sup>9</sup>

† Electronic supplementary information (ESI) available: ORTEP plots and crystal data for **2** and **3**. See <http://www.rsc.org/suppdata/cc/b3/b303477a/>

Similar phenomena have been observed in the coordination chemistry of Pd(II) or Pt(II).<sup>10–12</sup>

Since the yellow compound **2** can be converted to the red complex **3** in the presence of a weak base, it is of interest to examine whether the red complex **3** can be transformed to the yellow compound **2** when treated with acid. Indeed, upon addition of 1 equivalent of HCl solution to the mixture of complex **3** and dichloromethane at room temperature, the complex became soluble in the solvent after stirring, and the red color quickly changed to yellow followed by the appearance of a yellow precipitate, indicating the formation of yellow compound **2**.

On the basis of the experimental observations described above, it appears that the reaction of the NOBIN-derived Schiff base ligand **1** with palladium chloride initially gave the yellow dichloride complex **2** followed by a substitution reaction giving either complex **4a** or **4b**. Since complex **4a** is not expected to be formed in the absence of a strong base,<sup>13</sup> a plausible reaction mechanism is proposed in Scheme 1 involving the formation of complex **4b** followed by an enol–keto-like tautomerization process giving complex **5**. The base-promoted deprotonation of **5** leads to the formation of the red complex **3**.

To further examine the feasibility of the mechanism proposed in Scheme 1, we study the important enol–keto-like tautomerization step from complex **4b** to complex **5** with the aid of density functional theory calculations.<sup>14</sup> The result of this calculation indicates that the reaction from complex **4b** to **5** is energetically very favorable with a barrier of only 8.7 kcal mol<sup>-1</sup>, providing further support to the proposed reaction mechanism. We also calculated the structure of complex **3**, the deprotonation product of complex **5**. The experimental structure is well reproduced theoretically. The calculated structures of complexes **3** and **5** are quite similar to each other. Attempts to locate a transition state linking complex **4a** and **3** failed. This result suggests that the presence of a strong base may lead to the formation of **4a**, and may prevent the tautomerization process.

In conclusion, we have prepared and structurally characterized Pd(II) complexes **2** and **3** containing Schiff base ligand **1** derived from NOBIN. In the presence of a weak base, the novel Pd–C chelation mode was observed. The proposed pathway for the formation of the Pd–C bond is consistent with

DFT calculations. Further work to explore the application of these complexes in catalysis and the examination of the coordination chemistry of NOBIN-derived Schiff bases is in progress.

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## Notes and references

‡ Selected data for **2**: ESIMS: *m/z* (%), 551(4) [M<sup>+</sup>], 515 (22) [M<sup>+</sup> – Cl], 479 (12) [M<sup>+</sup> – 2Cl]; Anal. calc. for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>OCl<sub>2</sub>Pd: C, 56.60; H, 3.29; N, 5.08. Found: C, 56.51; H, 3.36; N, 5.14%. FTIR (KBr pellet, cm<sup>-1</sup>): ν(OH) 3288 (s), ν(C=N) 1622(s).

Selected data for **3**: ESIMS: *m/z* (%), 515 (13) [M<sup>+</sup>], 479 (38) [M<sup>+</sup> – Cl]; Anal. calc. for C<sub>26</sub>H<sub>17</sub>N<sub>2</sub>OClPd: C, 60.60; H, 3.33; N, 5.44. Found: C, 60.50; H, 3.41; N, 5.47%. FTIR (KBr pellet, cm<sup>-1</sup>): ν(C=O) 1703 (s), ν(C=N) 1614(s).

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- In the B3LYP calculations, the Lan2dz basis set was used for Pd, and Cl while 6-31G was used for all other atoms. Polarization functions were added for N, the OH group, Cl and the two carbon atoms which are directly involved in the bond breaking/formation process [ $\zeta_d(N) = 0.864$ ;  $\zeta_d(O) = 1.154$ ;  $\zeta_d(Cl) = 0.514$ ;  $\zeta_d(C) = 0.6$ ;  $\zeta_p(H) = 1.1$ ]. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency).

