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Association of *trans*-[$PdCl_2$(NH=CPh_2-κN)$_2$] via Intermolecular N–H···Cl Hydrogen Bonding in the Solid State and in Solution

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The crystal structure of a new complex, *trans*-[$PdCl_2$(NH=CPh_2-κN)$_2$], shows an association of the two molecules via intermolecular N–H···Cl hydrogen bonds. The ^{1}H NMR signal of the N–H hydrogen in $CDCl_3$ changes its position depending on the concentration and temperature of the solution.

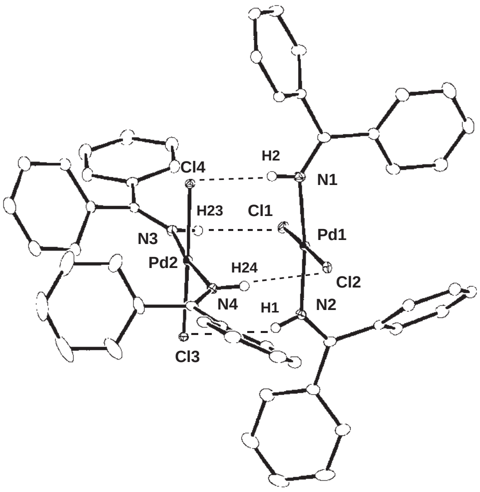
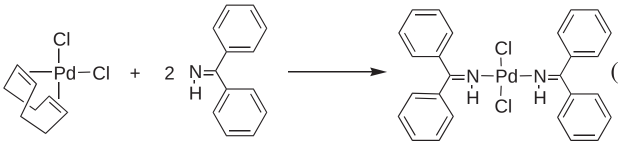


Fig. 1. ORTEP drawing of **1** at the 30% ellipsoidal level. Selected bond distances (Å) and angles (deg) are as follows: Pd1–Cl1, 2.3311(6); Pd1–Cl2, 2.3355(6); Pd1–N1, 1.997(2); Pd1–N2, 2.009(2); Pd1–Pd2, 3.4240(3); Cl1···N3, 3.399(2); Cl2···N4, 3.290(2); Cl3···N1, 3.375(3); Cl4···N2, 3.328(2); Cl1···H23, 2.54(3); Cl2···H24, 2.43(4); Cl3···H1, 2.59(4); Cl4···H2, 2.53(4); Cl1–Pd1–N1, 86.91(6); Cl2–Pd1–N1, 90.91(7); Cl1–Pd1–N2, 91.59(7); Cl2–Pd1–N2, 90.59(7); Cl1–Pd1–Cl2, 177.81(2); N1–Pd1–N2, 172.6(1).

Intermolecular O–H···O, N–H···O, and O–H···N hydrogen bonding between the organic groups coordinating to transition metals[1,2] form linear multinuclear complexes,[3] a sheet-type aggregation of a metal complex,[4] and double-strand assemblies of metal complexes.[5] Although N–H···Cl hydrogen bonding between organic molecules is much less stable than N–H···O and N–H···N hydrogen bonding, Cl ligand bonding to a transition metal is a good hydrogen-bond acceptor to form stable N–H···Cl–M bonding (M = transition metal).[6] Several Pt complexes having such coordination-driven N–H···Cl bonding were found in the literature.[7–9] The number of Pd complexes with N–H···Cl bonding is much smaller than that of the Pt complex; intramolecular hydrogen bonding was observed in the crystal structure of [$PdCl_2$(NNHC(*t*-Bu)CHCCH$_2$CH$_2$PPh$_2$-κN,κP)].[10] The crystal structure of *trans*-[PdCl(Me)(NH=CPh_2-κN)$_2$] in our previous paper does not show a short contact between the NH group with the Cl ligand.[11] In this paper we report on the intermolecular N–H···Cl hydrogen bonding of *trans*-[$PdCl_2$(NH=CPh_2-κN)$_2$].

The reaction of benzophenoneimine with [$PdCl_2$(cod)] produces *trans*-[$PdCl_2$(NH=CPh_2-κN)$_2$] (**1**), similarly to the reaction with [PdCl(Me)(cod)], to give *trans*-[PdCl(Me)(NH=CPh_2-κN)$_2$][11] (**2**) (Eq. 1).



(1)

Figure 1 depicts the structures of two crystallographically independent molecules. Both molecules have a slightly distorted square-planar coordination around the Pd center. Cl atoms bonded to a Pd center have close contact with NH groups coordinating to the other Pd center; the Cl···N distances are in the range of 2.987(2)–3.399(2) Å. N–H bonds direct to Cl atoms with H···Cl distances of 2.43(4)–2.59(4) Å. These lengths are smaller than the sum of the van der Waals radii for H and Cl (2.95 Å), and are within the ordinary range of the hydrogen-bond length of N–H···Cl–M.[6] The four N–H···Cl hydrogen bonds form an aggregate of two molecules of Pd complexes whose coordination planes are parallel to each other. Although complex **2** also contains two benzophenone imine ligands at trans positions, its crystal structure does not show either stacking of the coordination planes or intermolecular N–H···Cl hydrogen bonding.[11]

Hydrogen bonding in solution is often discussed based on the ^{1}H NMR spectra of the compounds because peak position of the hydrogen included in the hydrogen bonding changes depending on concentration or temperature of the solution. Figure 2 shows the ^{1}H NMR signals of the NH hydrogen of **1** and **2**. Complex **1** showed a downfield shift of the NH signal by ca 0.44 ppm upon cooling from 25 °C to −50 °C (Fig. 2(a) 10 mM $CDCl_3$ solution). A solution with 2 mM showed the NH signal at δ 9.10, while that with 8 mM showed the signal at δ 9.43 at 25 °C (Fig. 2(b)). The NH signal of **2** changed the position to a smaller extent than **1** under the same conditions. From these observations, complex **1** is suggested to have N–H···Cl bonds in solution. A plausible major species is a dimer of the molecules linked by four N–H···Cl bonds, similar to the dimer observed in the crystal structure. It generated a mononuclear complex partly in solution via reversible dissociation and the formation of a dimer. A Pt complex with imine-containing ligands, *trans*-[PtCl{(C_6H_4)PhC=NH-κN,κC}(NH=CPh_2-κN)], also showed two N–H···Cl–Pt bonds between the ligands

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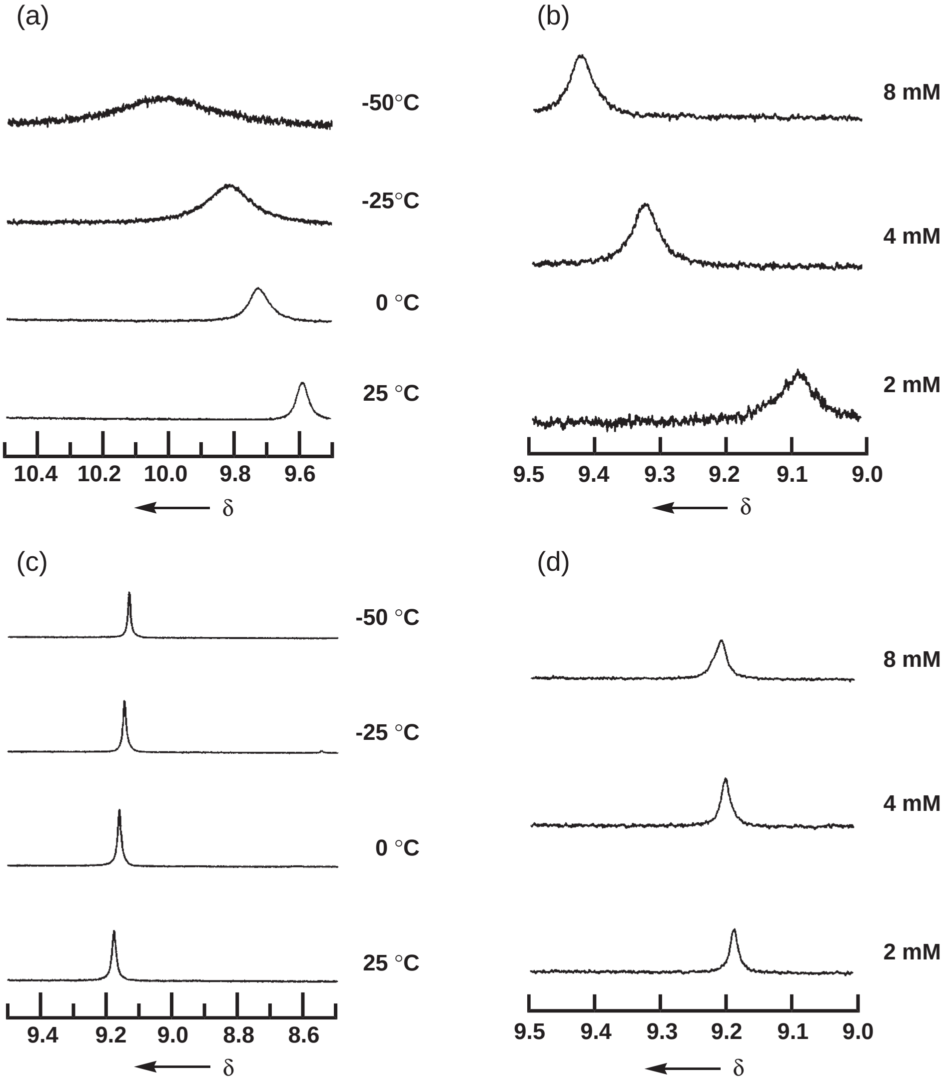


Fig. 2. ^{1}H NMR spectra ($CDCl_3$) of the NH region of (a) **1** at different temperature (−50 °C to 25 °C, 10 mM), (b) **1** at different concentration (2–8 mM, 25 °C), (c) **2** at different temperature (−50 °C to 25 °C, 10 mM), and (d) **2** at different concentration (2–8 mM, 25 °C).

of two molecules in the solid state and in solution.[9] Scheme 1 compares the dimeric structures of the Pd complex **1** in this study and the above Pt complex.

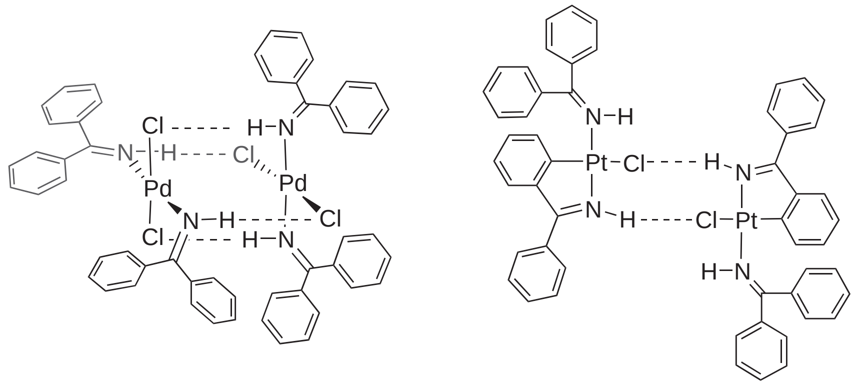
The IR spectrum of **2** shows sharp absorption of N–H stretching at 3285 cm^{-1} in the solid state. In contrast, the spectrum of single crystals of **1** contains broad absorption of N–H vibration at lower frequency (3193, 3240 cm^{-1}) due to the N–H···Cl hydrogen bond. The sharp peak of **2** was observed at 3295 cm^{-1} in a CH_2Cl_2 solution (2 mM), while a solution of **1** exhibited a sharp peak in a weak intensity at 3301 cm^{-1} and a strong broadened peak at 3191 cm^{-1}. The two ν(NH) peaks of **1** in the solution were assigned to monomeric and associated complexes. The association constant of **1** in a $CDCl_3$ solution was tentatively estimated as 7 (M^{-1}) at 27 °C from the dependence of the NH peak positions on the concentration of the complex in the ^{1}H NMR spectra.[9]

In summary, complex **1** exists as a dimer in a single-crystalline state. A solution of **1** also contains the dimer as a major species at low temperature (−50 °C) and high concentration. Complex **2** does not show any evidence for such a dimer, both in the solid state and in solution.

Experimental

General Procedure, Materials, and Measurement. All of the manipulations of the air unstable complexes were carried out under nitrogen or argon using standard Schlenk techniques. CH_2Cl_2 and $CDCl_3$ were distilled from CaH_2 and stored under nitrogen. Benzophenoneimine and other chemicals were used as received from commercial suppliers. **2**,[11] [$PdCl_2$(cod)],[12] and [PdCl(Me)(cod)],[13] were prepared according to the literature. The NMR spectra (^{1}H, and ^{13}C) were recorded on a Varian Mercury 300 spectrometer and a JEOL EX-400 spectrometer. The IR spectra were measured using a Shimazu FTIR-8100A. Elemental analysis was carried out on a Yanaco MT-5 CHN autocorder.

Preparation of *trans*-[$PdCl_2(NH{=}CPh_2\text{-}\kappa N)_2$] (1). To a solution of [$PdCl_2$(cod)] (104 mg, 0.36 mmol) in CH_2Cl_2 (45 mL) was added $NH{=}CPh_2$ (0.14 mL, 0.86 mmol). After stirring at room temperature for 12 h, the solution was concentrated at re-



1

trans-[PtCl(C_6H_4PhC=NH-κ*C*,κ*N*)(NH=CPh$_2$-κ*N*)]

Scheme 1.

duced pressure. Hexane was added to the solution to cause the separation of **1** as a pale-yellow solid (175 mg, 90%). Anal. Calcd for $C_{26}H_{22}Cl_2N_2Pd$: C, 57.85; H, 4.11; N, 5.19; Cl, 13.14%. Found: C, 57.60; H, 3.88; N, 5.25; Cl, 12.71%. ^{1}H NMR (300 MHz, at 25 °C in $CDCl_3$) δ 9.59 (br, 2H, NH), 8.10 (d, 4H, $J = 8$ Hz, C_6H_5 ortho), 7.64 (t, 2H, $J = 8$ Hz, C_6H_5 para), 7.47 (t, 4H, $J = 8$ Hz, C_6H_5 meta), 7.45 (t, 2H, $J = 8$ Hz, C_6H_5 para), 7.43 (d, 4H, $J = 8$ Hz, C_6H_5 ortho), 7.35 (t, 4H, $J = 8$ Hz, C_6H_5 meta). The positions of the NH hydrogen peak in $CDCl_3$ vary depending on the concentration; δ 9.48 (6.4 mM), 9.40 (5.2 mM), 9.26 (3.3 mM), 9.15 (1.9 mM), and 9.005 (0.98 mM). $^{13}C\{^1H\}$ NMR (75 MHz, at 25 °C in $CDCl_3$) δ 182.9 (C=N), 137.6 (C_6H_5 ipso), 137.0 (C_6H_5 ipso), 131.9 (C_6H_5 para), 131.1 (C_6H_5 para), 130.6, 129.4, 128.4, 128.2 (C_6H_5 ortho and meta).

X-ray Crystallography. A crystal of **1** suitable for an X-ray diffraction study was obtained by recrystallization from CH_2Cl_2/hexane and mounted in glass capillary tube. The data for **1** were collected at a temperature of -160 ± 1 °C to a maximum 2θ value of 55.0° on a Rigaku Saturn CCD area detector. Calculations were carried out by using a program package CrystalStructure for Windows. The structure was solved by a direct method and expanded using Fourier techniques. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Atomic scattering factors were obtained from the literature.[14] Crystal data of **1**: $C_{26}H_{22}Cl_2N_2Pd$; Crystal size $0.4 \times 0.3 \times 0.3$ mm^3; M_r, 539.78; monoclinic; space group $P2_1/n$ (No. 14); a 20.439(3), b 10.956(2), c 22.587(4) Å; β 108.155(2)°; V 4806(1) Å^3; Z 8; μ(Mo Kα) 1.010 mm^{-1}; F(000) 2176; D_{calcd} 1.492 g cm^{-3}; unique reflections ($2\theta < 55°$) 11213; used reflections ($I < 3\sigma(I)$) 9388; number of variables 735; $R(F_o)$ 0.032; $R_w(F_o)$ 0.043, GOF 0.936. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 249486.

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References

1 D. Braga, F. Grepioni, and G. R. Desiraju, *Chem. Rev.*, **98**, 1375 (1998).

2 J. C. M. Rivas and L. Brammer, *Coord. Chem. Rev.*, **183**, 43 (1999).

3 C. S. A. Fraser, H. A. Jenkins, M. C. Jennings, and R. J. Puddephatt, *Organometallics*, **19**, 1635 (2000).

4 C. B. Aakeröy, A. M. Beatty, and D. S. Leinen, *J. Am. Chem. Soc.*, **120**, 7383 (1998).

5 C. J. Kuehl, F. M. Tabellion, A. M. Arif, and P. J. Stang, *Organometallics*, **20**, 1956 (2001).

6 G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton, and A. G. Orpen, *Chem. Commun.*, **1998**, 653.

7 G. R. Lewis and A. G. Orpen, *Chem. Commun.*, **1998**, 1873.

8 J. C. M. Rivas and L. Brammer, *Inorg. Chem.*, **37**, 4756 (1998).

9 L. Grøndahl, J. Josephsen, R. M. Bruun, and S. Larsen, *Acta Chem. Scand.*, **53**, 1069 (1999).

10 D. B. Grotjahn, S. Van, D. Combs, D. A. Lev, C. Schneider, C. D. Incarvito, K. Lam, G. Rossi, A. L. Rheingold, M. Rideout, C. Meyer, G. Hernandez, and L. Mejorado, *Inorg. Chem.*, **42**, 3347 (2003).

11 J. Kuwabara, D. Takeuchi, and K. Osakada, *Organometallics*, **23**, 5092 (2004).

12 D. Drew and J. R. Doyle, *Inorg. Synth.*, **13**, 52 (1972).

13 R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, and K. Vrieze, *Inorg. Chem.*, **32**, 5769 (1993).

14 "International Tables for X-ray Crystallography," Kynoch, Birmingham, England (1974), Vol. IV.