

(4-Nitro-benzylidene)-(3-nitro-phenyl)-amine 및 *trans*-Dichlorobis(3-nitroaniline)palladium(II)의 구조

이희근 · 이순원*
성균관대학교 화학과

Structures of (4-Nitro-benzylidene)-(3-nitro-phenyl)-amine and *trans*-Dichlorobis(3-nitroaniline)palladium(II)

Hee K. Lee and Soon W. Lee*

Department of Chemistry (BK21), Sungkyunkwan University, Suwon 440-746, Korea

요 약

4-Nitrobenzaldehyde와 3-nitroaniline의 Schiff-base 축합 반응으로 잠재적 연결 리간드 (4-Nitro-benzylidene)-(3-nitro-phenyl)-amine (**1**)이 합성되었다. 리간드 **1**과 PdCl₂(NCPh)₂의 반응에서 가수 분해로 인한 예상 밖의 생성물 *trans*-PdCl₂(NO₂-C₆H₄-NH₂)₂ (**2**)가 분리되었다. X-ray 회절법으로 화합물 **1**과 **2**가 구조적으로 규명되었다. 화합물 **2**에서 3-nitroaniline의 NH₂ 수소 원자들은 Cl 원자와 분자간 N-H...Cl 수소 결합에 참여하고 있다.

Abstract

A novel potential linking ligand (4-nitro-benzylidene)-(3-nitro-phenyl)-amine (**1**) was prepared from 4-nitrobenzaldehyde and 3-nitroaniline by the Schiff-base condensation. From the reaction between **1** and dichlorobis(benzonitrile)palladium (II) (PdCl₂(NCPh)₂), an unexpected product *trans*-PdCl₂(NO₂-C₆H₄-NH₂)₂ (**2**) was isolated. Compounds **1** and **2** were structurally characterized by X-ray diffraction. In compound **2**, the NH₂ hydrogen atoms in the 3-nitroaniline ligand participate in intermolecular N-H...Cl hydrogen bonds.

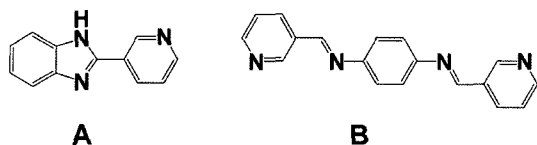
1. Introduction

The field of coordination polymers, also known as metal-organic frameworks, has been expanded enormously for the past decade. These compounds would probably further continue to receive attraction for the years to come, due to their desirable applications, such as catalysis, chirality, conductivity, luminescence, magnetism, nonlinear optics, and porosity.^{1,2)} In the preparation of 1-D, 2-D, or 3-D coordination polymers, selection of appropriate linking ligands is crucial in determining topologies of resulting polymers. Multifunctional ligands containing N- and O-donor atoms are employed typically

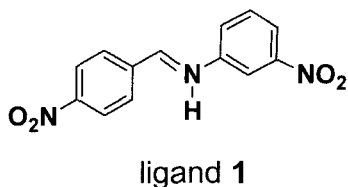
for the construction of coordination polymers.¹⁻⁴⁾ For example, dicarboxylates and bipyridyls have been employed extensively in preparing these polymers.⁵⁻⁸⁾

For synthetic strategies, it would be desirable to vary ligands in systematic and predictable ways, in terms of relative orientations of donor atoms, intervening fragments between donor atoms, and steric and electronic properties of ligands. Recently, we utilized the Schiff-base condensation reaction to prepare novel bipyridyl-type ligands (**A** and **B**), in which ligands **A** and **B** have been derived from 1,2-phenylenediamine and 1,4-phenylenediamine, respectively. Ligand **A** existed as a hydrogen-bonded

tetramer, whereas ligand **B** reacted with zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) under various conditions to give one discrete molecule, $\text{trans}[\text{Zn}(\text{H}_2\text{O})_4(\text{B})_2] \cdot (\text{NO}_3)_2 \cdot (\text{MeOH})_2$, and two 1-D zinc polymers, $[\text{Zn}(\text{NO}_3)(\text{H}_2\text{O})_2(\text{B})] \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})_2$ and $[\text{Zn}(\text{B})(\text{OBC})(\text{H}_2\text{O})](\text{OBC}=4,4'\text{-oxybis(benzoate)})$.⁹⁾



As a continuation of our research, we decided to expand the Schiff-base condensation to prepare novel ligands that have two terminal nitro groups as coordinating sites. We succeeded to prepare one such ligand (**1**) from 3-nitroaniline and 4-nitrobenzaldehyde in ethanol. When ligand **1** was treated with $\text{PdCl}_2(\text{NPh}_2)_2$ to prepare a Pd coordination polymer by replacing benzonitrile groups, an unexpected molecular product, $\text{trans-PdCl}_2(\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2)_2$ (**2**), was isolated from this reaction. Herein, we report the preparation and structures of ligand **1** and compound **2**.



2. Experimental Section

3-Nitroaniline, 4-nitrobenzaldehyde, formic acid, diethyl ether, dichloromethane, and ethanol were purchased from Aldrich company. Dichlorobis(benzonitrile)palladium(II) was prepared as described in the literature.¹⁰⁾ IR spectra were recorded with a Bruker IFS-66/S FTIR spectrophotometer.

Preparation of $(\text{O}_2\text{N-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-NO}_2)$ (**1**).

At room temperature, two drops of formic acid were added to a solution containing 3-nitroaniline (0.503 g, 3.64 mmol) and 4-nitrobenzaldehyde (0.544 g, 3.60 mmol) in ethanol (30 mL). The resulting

mixture was stirred for 6 h at room temperature, and the solvent was removed under vacuum. The resultant yellow solids were washed with diethyl ether (10 mL \times 2), and then crystallized from dichloromethane and diethyl ether to give ligand **1** (0.963 g, 3.55 mmol, 98.6%). mp: 139-141°C. IR (KBr, cm^{-1}): 1630, 1596, 1516, 1344, 1189, 843, 685 cm^{-1} .

Preparation of $[\text{PdCl}_2(\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2)_2]$ (**2**).

Compound **2** was prepared by layer-diffusion methods. An acetonitrile (5 mL) solution of $\text{PdCl}_2(\text{NPh}_2)_2$ (0.058 g, 0.151 mmol) was carefully layered onto the top of a dichloromethane (5 mL) solution of **1** (0.046 g, 0.170 mmol) at room temperature. Red crystals of **2** were grown in 2 days, which were isolated by filtration and air-dried to give compound **2** (0.040 g, 0.088 mmol, 58.3% yield). mp: 238-240°C.

Table 1. X-ray data collection and structure refinement details

	1	2
formula	$\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4$	$\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}_4\text{Pd}$
fw	271.23	453.56
temp, K	293(2)	293(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
<i>a</i> , Å	12.403(5)	13.031(2)
<i>b</i> , Å	3.927(1)	8.182(1)
<i>c</i> , Å	24.776(9)	7.782(2)
β , deg	92.35(2)	102.34(2)
<i>V</i> , Å ³	1205.8(7)	810.5(3)
<i>Z</i>	4	2
<i>d</i> _{calc} , g cm ⁻³	1.494	1.859
μ , mm ⁻¹	0.114	1.498
<i>F</i> (000)	560	448
<i>T</i> _{min}		0.2896
<i>T</i> _{max}		0.3529
2 θ range (°)	3.5-50	3.5-50
no. of reflns measured	2194	1537
no. of reflns unique	2108	1422
no. of reflns with <i>I</i> > 2 σ (<i>I</i>)	1115	1239
no. of params refined	218	131
max in $\Delta\rho$ (eÅ ⁻³)	0.205	0.591
min in $\Delta\rho$ (eÅ ⁻³)	?0.306	?0.510
<i>GOF</i> on <i>F</i> ²	1.024	1.036
<i>R</i> 1 ^a	0.0680	0.0312
<i>wR</i> 2 ^b	0.1552	0.0843

$$^a\text{R1} = \frac{\sum ||F_o| - |F||}{\sum |F_o|}$$

$$^b\text{wR2} = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

IR (KBr, cm^{-1}): 3189, 3108, 1586, 1532, 1351, 801, 808, 671, cm^{-1} .

X-ray Structure Determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Orientation matrices and unit-cell parameters were determined by least-squares analyses of the setting angles of 25 (for **1**) or 22 reflections (for **2**) in the range of $10.0^\circ < 2\theta < 25.0^\circ$. No absorption corrections were made for the organic compound (ligand **1**), but empirical absorption corrections were made with ψ -scan data for the palladium complex **2**. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and refined isotropically. All calculations were carried out with the use of SHELXTL programs.¹¹⁾

A pale yellow crystal of **1**, shaped as a rod of approximate dimensions $0.60 \times 0.14 \times 0.08 \text{ mm}^3$, was used for crystal- and intensity-data collection. A red crystal of **2**, shaped as a plate of approximate dimen-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor**

	x	y	z	$U(\text{eq})$
O1	6732(3)	-393(12)	6014(1)	87(1)
O2	5607(3)	2756(11)	5566(1)	85(1)
O3	4774(3)	10191(12)	1278(1)	90(1)
O4	3236(3)	10386(12)	1631(2)	91(1)
N1	6425(3)	1015(11)	5601(1)	57(1)
N2	6926(2)	2991(10)	3668(1)	52(1)
N3	4187(3)	9601(11)	1645(2)	59(1)
C1	7076(3)	673(11)	5117(2)	47(1)
C2	6671(3)	1990(12)	4638(2)	47(1)
C3	7262(3)	1654(11)	4180(2)	44(1)
C4	8257(3)	-34(13)	4222(2)	53(1)
C5	8643(4)	-1268(14)	4704(2)	59(1)
C6	8062(4)	-996(13)	5168(2)	57(1)
C7	5922(3)	3245(12)	3546(2)	49(1)
C8	5499(3)	4850(11)	3053(2)	44(1)
C9	6172(3)	6058(12)	2658(2)	49(1)
C10	5751(3)	7571(13)	2193(2)	49(1)
C11	4640(3)	7958(11)	2128(2)	44(1)
C12	3959(3)	6782(12)	2520(2)	49(1)
C13	4383(3)	5230(12)	2975(2)	51(1)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor**

	x	y	z	$U(\text{eq})$
Pd1	5000	5000	5000	38(1)
Cl1	5454(1)	7717(1)	5119(1)	51(1)
O1	7699(4)	-902(5)	4053(8)	124(2)
O2	9105(4)	-600(7)	5995(8)	129(2)
N1	5968(3)	4588(4)	3278(4)	47(1)
N2	8337(4)	-43(5)	5075(9)	80(2)
C1	6991(3)	3940(4)	4110(5)	44(1)
C2	7788(4)	5006(5)	4853(8)	64(1)
C3	8757(4)	4385(7)	5674(8)	79(1)
C4	8943(4)	2763(7)	5771(7)	73(1)
C5	8136(3)	1712(5)	4988(6)	55(1)
C6	7161(3)	2278(4)	4154(5)	47(1)

Table 4. Selected bond distances (\AA) and bond angles ($^\circ$) in **1 and **2****

	1	2	
O1-N1	1.210(5)	Pd1-N1	2.054(3)
O2-N1	1.223(5)	Pd1-Cl1	2.2971(9)
O3-N3	1.210(5)	O1-N2	1.238(7)
O4-N3	1.218(4)	O2-N2	1.190(7)
N1-C1	1.480(5)	N1-C1	1.452(5)
N2-C7	1.274(5)	N2-C5	1.459(5)
N2-C3	1.420(5)	N1-Pd1-Cl1	89.8(1)
N3-C11	1.453(5)	N1#1-Pd1-Cl1	90.2(1)
O1-N1-O2	123.2(4)	Cl1-Pd1-Cl1#1	180.0
O1-N1-C1	118.7(4)	C1-N1-Pd1	113.7(2)
O2-N1-C1	118.1(4)	O2-N2-O1	122.1(5)
C7-N2-C3	119.3(3)	O2-N2-C5	121.6(6)
O3-N3-O4	122.9(4)	O1-N2-C5	116.1(5)
O3-N3-C11	118.6(4)		
O4-N3-C11	118.5(4)		
N2-C7-C8	123.3(4)		

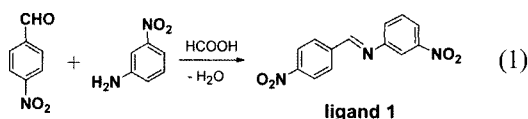
Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1, -y + 1, -z + 1$

sions $0.44 \times 0.42 \times 0.08 \text{ mm}^3$, was used. Details on crystal data, intensity collection, and refinement details are given in Table 1. Final atomic coordinates for **1** and **2** are given in Tables 2, and 3 respectively. Selected bond lengths and angles are given in Table 4.

3. Results and Discussion

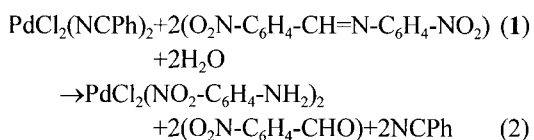
Preparation. Schiff-bases are imine species that

contain a C=N bond in which the carbon atom is bonded to at least one aryl group. These compounds are usually prepared by condensation of primary amines and ketones or aldehydes.¹²⁾ Ligand **1** was readily prepared from an aldehyde (4-nitrobenzaldehyde) and a primary amine (3-nitroaniline) by the Schiff-base condensation in high yield (eq. 1). A great number of Schiff-base type ligands have been prepared by this type of condensation.¹²⁾ In this reaction, formic acid was used as an acid catalyst, which activates the carbonyl group of aldehyde to be more susceptible to attack by amine.



The C=N stretching frequencies of Schiff bases are known to appear in the range 1680-1603 cm^{-1} , and therefore the absorption band at 1630 cm^{-1} in the IR spectrum of ligand **1** can be assigned to the C=N bond.¹²⁻¹⁴⁾

The *trans*-bis(ammine) complex of Pd(II), $\text{trans-PdCl}_2(\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2)_2$ (**2**), was isolated from the reaction of $\text{PdCl}_2(\text{NPh})_2$ with **1** (eq. 2). The formulation of compound **2** tells us that hydrolysis probably occurred during the reaction, which led to the decomposition of ligand **1** to its starting compounds, 3-nitroaniline and 4-nitrobenzaldehyde. In a subsequent step, the amino nitrogen atom of 3-nitroaniline binds to the palladium metal to give a molecular compound **2**, rather than a desired Pd polymer. The IR spectrum of compound **2** displays two N-H absorption bands at 3189 and 3108 cm^{-1} .



Structure. The molecular structure of compound **1** with the atom-numbering scheme is shown in Fig. 1. The entire molecule is not planar, and two benzene rings are twisted from each other with a dihedral angle of 27.8(2)°. The N1...N3 separation between two nitrobenzene rings is 10.627 Å.

The molecular structure of compound **2** is pre-

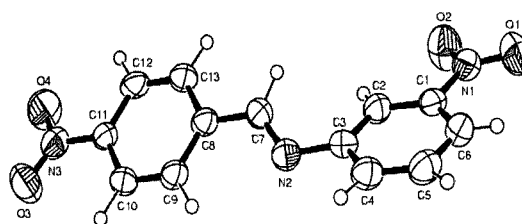


Fig. 1. ORTEP drawing of ligand **1** with 50% probability thermal ellipsoids.

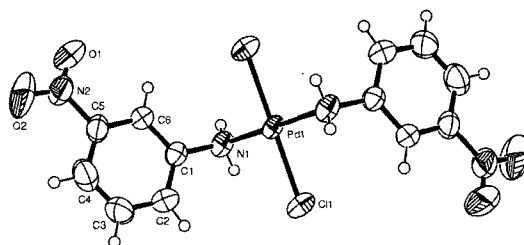


Fig. 2. ORTEP drawing of compound **2**. Unlabeled atoms are related to labeled atoms by the crystallographic inversion.

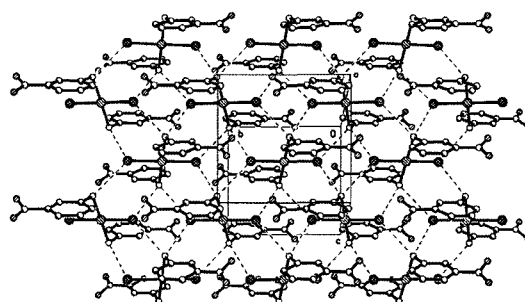


Fig. 3. Projection of compound **2** in the [100] direction, in which dotted bonds represent hydrogen bonds.

sented in Fig. 2. The coordination sphere of Pd metal can be described as a square plane, which consists of two *trans* Cl ligands and also two *trans* 3-nitroaniline ligands. The Pd metal lies on the crystallographic center of symmetry, which explains the *Z* value of this compound to be 2 instead of 4. The formal oxidation state of the Pd metal is +2 (d^8). All of the NH_2 hydrogen atoms in the 3-nitroaniline ligands participate in intermolecular hydrogen bonds of the type N-H...Cl (Fig 3).

In summary, we have prepared a novel potential linking ligand possessing two terminal nitro groups,

O₂N-C₆H₄-CH=N-C₆H₄-NO₂ (**1**), from 4-nitrobenzaldehyde and 3-nitroaniline by the Schiff-base condensation. A molecular compound *trans*-PdCl₂(NO₂-C₆H₄-NH₂)₂ (**2**) was isolated from the reaction of PdCl₂(NPh)₂ with **1**, during which **1** appeared to have undergone hydrolysis with the trace amount of water present in the reaction mixture. Both compounds were structurally characterized by X-ray diffraction.

Acknowledgement

This work was supported by the 63 Research Fund of Sungkyunkwan University (2004-2005).

References

- 1) Janiak, C., *Dalton Trans.*, 2781 (2003).
- 2) Moulton, B. and Zaworotko, M. J., *Chem. Rev.*, **101**, 1629 (2001).
- 3) Rosi, N. L., Kim, J., Eddaoudi, M., Chen, B., O'Keeffe, M. and Yaghi, O. M., *J. Am. Chem. Soc.*, **127**, 1504 (2005).
- 4) Barnett, S. A. and Champness, N. R., *Coord. Chem. Rev.*, **246**, 145 (2003).
- 5) Kesanli, B. and Lin, W., *Coord. Chem. Rev.*, **246**, 305 (2003).
- 6) Ye, B. H., Tong, M. L. and Chen, X. M., *Coord. Chem. Rev.*, **249**, 545 (2005).
- 7) Min, D. and Lee, S. W., *Inorg. Chem. Commun.*, **5**, 978 (2002).
- 8) Lee, Y. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **24**, 906 (2003).
- 9) Kim, H. N., Lee, H. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **26**, 892 (2005).
- 10) Anderson, G. K. and Minren, L., *Inorg. Synth.*, **28**, 61 (1990).
- 11) Bruker, SHELXTL, *Structure Determination Software Programs*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1997).
- 12) Vigato, P. A. and Tanburini, S., *Coord. Chem. Rev.* **248**, 1717 (2004) and references therein.
- 13) Calligaris, M. and Randaccio, L., In Schiff Bases as Acyclic Polydentate Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G, Gillard, R. D. and McCleverty, J. A. Eds.; Pergamon Press: New York, **2**, 715 (1987).
- 14) Hernandez-Molina, R. and Mederos, A., In Acyclic and Macrocyclic Schiff Base Ligands. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A. and Meyer, T. J. Eds.; Pergamon Press: New York, **2**, 411 (2004).