

단 신

말단 퓨란 고리에 산소 원자를 함유한 리간드와 그것의 팔라듐 화합물

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A Novel Ligand Containing Oxygen Atoms in the Terminal Furan Rings and Its Palladium Compound

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Coordination polymers (or metal–organic frameworks) have continually received attraction due to their useful properties applicable to various fields such as catalysis, conductivity, magnetism, luminescence, and fuel storage.^{1–10} In designing these polymers, properties of linking ligands such as various coordination modes, variable lengths, and relative orientation of donor atoms play a fundamental role in determining the structural outcomes of target polymers.

We have recently prepared several long bipyridine-type linking ligands by Schiff-base condensation (Chart 1).^{11–15} We decided to expand this synthetic strategy to synthesize potential novel link-

ing ligands that contains group 16 elements. In this study, we prepared a potential linking ligand, 1,2-bis(furan-2-ylmethylene)hydrazine (**L**), which contains terminal heteroaromatic rings with oxygen atoms. Herein, we report the preparation of this ligand and its Pd complex.

EXPERIMENTAL SECTION

All chemicals were purchased and purified. All solvents were distilled and stored over molecular sieves. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute. $[PdCl_2(NCPh)_2]$ was prepared by the literature method.¹⁴

Preparation of 1,2-bis(furan-2-ylmethylene)hydrazine (L**).** To an ethanol solution (30 mL) containing hydrazine (35 wt% solution in H₂O) (0.916 mL, 10 mmol) and 2-furaldehyde (1.660 g, 20 mmol) was added a dichloromethane solution (30 mL) containing formic acid (0.2 mL), and the solution was stirred for 4 h. The resulting brown slurry was filtered, washed with hexane (25 mL×2), and dried

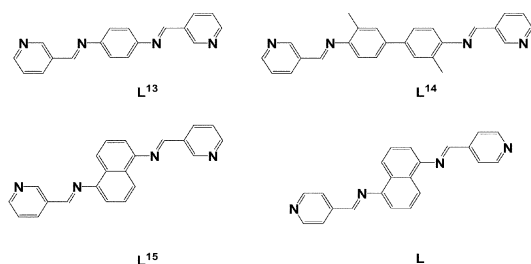


Chart 1.

under vacuum to give a yellow solid of **L**¹. 96% yield. mp: 134–136°C. IR (KBr, cm⁻¹): 1613, 1414, 728. Anal. Calcd for C₁₀H₈N₂O₂ (*M*_r = 188.18): C, 63.83; H, 4.29; N, 14.89. Found: C, 63.81; H, 4.29; N, 14.88.

Preparation of [PdL₂Cl₂] (1). At room temperature, a benzene solution (3 mL) containing PdCl₂(NCPPh)₂ (0.054 g, 0.14 mmol) was layered onto the top of a dichloromethane solution (3 mL) containing **L** (0.029 g, 0.15 mmol) in a test tube. After 3 days, the resulting solution was filtered, washed with diethyl ether (25 mL × 2), and then air-dried to give brown needle crystals of **1**. 58% yield. mp: 176–178 °C (decom). IR (KBr, cm⁻¹): 3098, 1522, 1388, 725. Anal. Calcd for C₃₀H₁₆Cl₂N₄O₄Pd (*M*_r = 553.67):

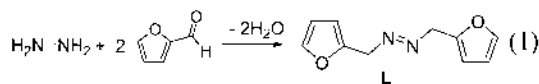
C, 43.39; H, 4.29; N, 10.12. Found: C, 43.44; H, 3.80; N, 9.98.

X-ray Structure Determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data for compound **1** were empirically corrected for absorption with ψ -scan data. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Whereas hydrogen atoms in ligand **L** were located and refined isotropically, those in compound **1** were generated in idealized positions and refined in a riding model. All calculations were carried out with the SHELXTL programs.¹⁵ Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 619283 (**L**) and 619284 (**1**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Preparation of a ligand. A novel potential linking ligands (**L**) containing oxygen donor atoms in two terminal heteroaromatic (furan) rings has been prepared in 96% isolation yield by the simple and straightforward Schiff-base condensation. Hydrazine reacted with 2-furaldehyde to give 1,2-bis(furan-2-ylmethylene)hydrazine (**L**) at room temperature under slightly acidic conditions (pH = 5–6) (eq 1).



This ligand was characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. The IR spectrum of ligand **L** displays an absorption bands at 1613 cm⁻¹ assignable to the C–N bond, consistent with the fact that C–N stretching frequencies of Schiff bases appear in the range 1680–1603 cm⁻¹.^{16–18}

Table 1. X-ray Data Collection and Structure Refinement Details

	L	1
formula	C ₁₀ H ₈ N ₂ O ₂	C ₃₀ H ₁₆ Cl ₂ N ₄ O ₄ Pd
fw	188.18	553.67
temp, K	293(2)	293(2)
crystal size	0.66×0.50×0.46	0.18×0.16×0.06
color	yellow	yellow
cryst syst	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> , Å	6.897(1)	8.644(1)
<i>b</i> , Å	9.019(1)	13.334(3)
<i>c</i> , Å	15.231(1)	9.416(3)
β , deg	s	92.82(2)
<i>V</i> , Å ³	947.3(2)	1084.0(4)
<i>Z</i>	4	2
<i>D</i> _{calc} , g cm ⁻³	1.319	1.696
μ , mm ⁻¹	0.095	1.137
<i>F</i> (000)	392	552
<i>T</i> _{min}		0.6823
<i>T</i> _{max}		0.8917
2 θ range (°)	2.67–24.99	2.36–25.00
no. of reflns measured	763	2038
no. of reflns unique	763	1906
no. of reflns with <i>I</i> > 2 σ (<i>I</i>)	1272	1307
no. of params refined	81	143
max. in $\Delta\rho$ (e Å ⁻³)	0.122	0.520
min. in $\Delta\rho$ (e Å ⁻³)	-0.143	-0.412
GOF on <i>F</i> ²	1.110	1.042
<i>R</i> 1 ^a	0.0427	0.0410
<i>wR</i> 2 ^b	0.1007	0.0849

^a*R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, ^b*wR*2 = $\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

Table 2. Selected Bond Lengths (Å) and Angles (deg)

L					
O1–C4	1.367(3)	O1–C1	1.372(2)	N1–C5	1.275(3)
N1–N1#1	1.409(3)	C1–C2	1.339(3)	C1–C5	1.431(3)
C4–O1–C1	105.6(2)	C5–N1–N1#1	111.3(2)	C2–C1–O1	109.5(2)
C2–C1–C5	131.5(2)	O1–C1–C5	119.0(2)	C1–C2–C3	107.5(2)
C4–C3–C2	106.0(2)	C3–C4–O1	111.5(2)	N1–C5–C1	123.1(2)
Compound 1					
Pd1–N1	2.036(4)	Pd1–N1#2	2.036(4)	Pd1–Cl1	2.311(2)
N1–C5	1.281(6)	N1–N2	1.413(5)	N2–C6	1.273(6)
O1–C1	1.355(7)	O1–C4	1.384(7)	O2–C10	1.374(7)
C9–C10	1.310(9)	N1–Pd1–Cl1	91.7(1)	N1#2–Pd1–Cl1	88.3(1)
Cl1–Pd1–Cl1#2	180.00(7)	C5–N1–N2	112.8(4)	C5–N1–Pd1	125.5(4)
C6–N2–N1	115.2(4)	C1–O1–C4	105.5(4)	C2–C1–O1	111.9(5)
C4–C3–C2	107.9(6)	C3–C4–O1	108.8(5)	O1–C4–C5	120.8(4)
N1–C5–C4	126.7(5)	N2–C6–C7	123.9(5)	O2–C7–C6	119.0(5)

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1, -y + 1, -z + 1$; #2 = $-x, -y, -z$

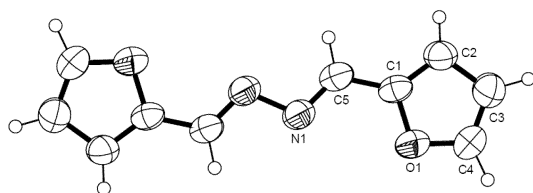


Fig. 1. ORTEP drawing of of L with 50% probability thermal ellipsoids. Unlabeled atoms are related to labeled ones by the crystallographic inversion.

The structure of ligand **L** is shown in Fig. 1. The central N–N bond length is 1.409(3) Å. The O···O distance between two terminal furan rings is 6.988 Å, and the whole molecule is conjugated.

Molecular palladium compound. We tried to prepare palladium coordination polymers by employing ligand **L**. For this purpose, PdCl₂(NCPh)₂ was selected, because it possesses labile benzonitrile (NCPh) ligands. Inconsistent with our expectation, however, ligand **L** produced a molecular Pd compound from the reactions with PdCl₂(NCPh)₂, in which the Pd metal is bound to the nitrogen atoms in the Schiff-base imine groups, not to the oxygen atoms in the terminal heteroaromatic rings to give a polymeric species (eq 2).

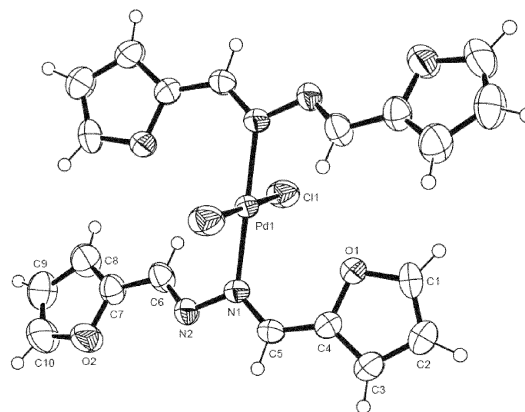
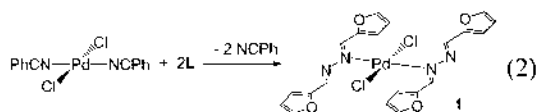


Fig. 2. ORTEP drawing of compound **1**. Unlabeled atoms are related to labeled ones by the crystallographic inversion.

The molecular structure of compound **1** is presented in Fig. 2, which clearly shows that the Pd metal is bonded to the nitrogen atom in the Schiff-base imine groups, not to the oxygen atoms in the terminal furan rings. The coordination sphere of the Pd metal can be described as square planar. The Pd–N bond lengths (2.036(4) Å for **1** and 2.040(3) Å for **2**) indicate a single Pd–N bond.

In summary, we prepared a novel potential linking ligand, 1,2-bis(furan-2-ylmethylene)hydrazine (**L**) that contains oxygen atoms in the terminal furan rings. Ligand **L** reacted with [PdCl₂(NCPh)₂] to produce a molecular Pd compound, [PdL₂Cl₂] (**1**),

in which the Pd metal is bound to the nitrogen atoms in the Schiff-base imine groups, not oxygen atoms to give polymers.

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