

First Example of Monometallic Palladium(II) Compound with *Trans*-Chelating Tridentate Ligand: Synthesis, Crystal Structure, and Characterizations

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Abstract : The reaction of (COD)PdCl₂ with new C₃-symmetric tridentate **L** (COD = 1,5-cyclooctadien; **L** = 1,3,5-tris(picolinoyloxyethyl)cyanurate) in a mixture of acetone and dichloromethane produces single crystals consisting of unprecedented monometallacyclic [PdCl₂(**L**)]. This cyclic compound arises from *trans*-chelation of two of three donating pyridyl groups of **L**, while the third pyridyl group remains uncoordinated. Electrospray ionization mass spectrometry (ESI-MS) data on **L** exhibited the major peak corresponding to [C₂₇H₂₄N₆O₉ + H⁺]⁺. Fast atom bombardment mass spectrometry (FAB-MS) data on [PdCl₂(**L**)], however, showed the mass peak corresponding to the **L** instead of the present palladium(II) compound species, due to the insolubility and dissociation in solution. The physicochemical properties of the present palladium(II) compound were fully characterized by means of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, thermal analysis, single-crystal X-ray diffraction (SC-XRD) measurement.

Key words : Palladium(II) compound, metallacycle, 1,3,5-tris(picolinoyloxyethyl)cyanurate, X-ray diffractometry, MS analysis

Introduction

The interest in construction of coordination-driven discrete architectures that often require an appropriate balance of the coordinating geometry of a central metal ion and well-designed multi-dentate ligands¹⁻⁸ has increased during the past decades, as these desirable coordination materials have myriad applications such as to mixed-valence species, photo-induced electron or energy transfer, magnetic exchange between paramagnetic centers, and supramolecular weak interactions.⁹⁻¹⁵ Among the many coordination materials, preparation of task-specific palladium(II) and platinum(II) complexes has continued to receive considerable attention with respect to the promising structures that can be built, including rectangular building units and molecular polyhedrons, which can be used in extensive applications as catalysts, anticancer agents,

luminescent materials, and photophysical materials.¹⁶⁻²⁴ In construction of such tailor-made complexes, various polypyridyl *N*-donor ligands that can coordinate two or more remote palladium(II) central ions play an important role. In particular, introduction of tridentate *N*-donor ligands has been found to be useful for synthesis of coordination-driven cage complexes or C₃-symmetric discrete architectures, owing to their conformational non-rigidity, adjustability of spacer length, and manageable solubility.²⁵⁻³¹ Even though, to date, symmetric and discrete palladium(II) compounds containing tridentate *N*-donor ligands have been widely reported, synthesis of monometallic palladium(II) compounds by means of potential tridentate tectonics remains unexplored. In this paper, we report on the synthesis of a monometallic palladium(II) compound exhibiting the *trans* isomer by introduction of a potentially tridentate 1,3,5-tris(picolinoyloxyethyl)cyanurate (**L**) and characterizations by means of single-crystal X-ray diffraction (SC-XRD) measurement, elemental and thermal analyses, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies, and mass spectrometry (MS).

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Experimental

Materials and measurements

All chemicals including palladium(II) chloride (PdCl₂) and 1,3,5-tris(2-hydroxyethyl)cyanuric acid were purchased from Merck, and were used without further purification. (COD)PdCl₂ was prepared according to the procedure

in the literature.³² Infrared spectra were obtained on a Thermo Fisher Nicolet iS5 FT-IR spectrometer with samples prepared as KBr pellets. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Advance III HD 400 MHz FT-NMR spectrometer at ambient temperature. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TG-DSC 1600. Elemental microanalyses (C, H, N) were performed on samples in solid form using a Thermo Fisher Scientific IT/Flash 2000 installed at the Center for University-Wide Research Facilities (CURF) at Jeonbuk National University. Electrospray time of flight ionization mass spectrometry (ESI-TOF-MS) was carried out using a Synapt G2 mass spectrometer (WATERS) at the Ochang Center, KBSI. The mass samples were injected as a mixed solution of dimethyl sulfoxide and acetonitrile ($v/v = 1 : 250$). Fast atom bombardment mass spectrometry (Jeol LTD JMS-HX 110/110A) was performed by Seoul center, KBSI.

1,3,5-Tris(picolinoyloxyethyl)cyanurate (**L**)

Triethylamine (88 mmol, 12.27 mL) was added to a solution of a mixture of picolinoyl chloride hydrochloride (40 mmol, 7.1208 g) and 1,3,5-tris(2-hydroxyethyl)cyanuric acid (10 mmol, 2.6124 g) in toluene (150 mL) at room temperature, and the mixture was refluxed for 48 h. The precipitated quaternary ammonium salts were filtered off, and then the filtrate was cooled to room temperature to obtain the present **L**. Yield, 4.2662 g (74%). M.P. 276°C. Anal. Calcd. for C₂₇H₂₄N₆O₉: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.25; H, 4.21; N, 14.59. High-resolution ESI-TOF-MS: m/z 577.1686 (calcd for [C₂₇H₂₄N₆O₉ + H]⁺ = 577.1683). IR (KBr pellet, cm⁻¹): 2974, 1743, 1720, 1691, 1583, 1470, 1398, 1369, 1300, 1244, 1140, 1090, 1045, 993, 825, 764, 750, 706, 619, 580. ¹H NMR (400 MHz, CDCl₃, ppm): 8.73 (d, $J = 5.2$ Hz, 3H), 8.10 (d, $J = 8.0$ Hz, 3H), 7.84 (t, $J = 8.0$ Hz, 3H), 7.47 (dd, $J = 8.0$ and 5.2 Hz, 3H), 4.54 (t, $J = 5.6$ Hz, 6H), 4.28 (t, $J = 5.6$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): 164.95, 149.97, 149.20, 137.39, 128.48, 127.30, 125.53, 62.44, 41.90.

[PdCl₂(L)]·0.5Me₂CO·0.5CH₂Cl₂

An acetone solution (20 mL) of **L** (0.115 g, 0.2 mmol) was added to a dichloromethane solution of (COD)PdCl₂ (0.057 g, 0.2 mmol), and the mixture was stirred at room temperature for 5 h. Slow evaporation of the resulting solution yielded yellow crystalline product suitable for single crystal X-ray diffraction measurement. Yield: 87% (0.143 g). M.p. 229°C. Anal. Calcd. for C₂₉H₂₈N₆O_{9.5}Cl₃Pd: C, 42.20; H, 3.42; N, 10.18. Found: C, 42.15; H, 3.44; N, 10.15%. FAB-MS: m/z 577.1686 (calcd for [C₂₇H₂₄N₆O₉ + H]⁺ = 577.1683). IR (KBr pellet, cm⁻¹): 3618, 3080, 1747, 1720, 1963, 1599, 1460, 1367, 1306, 1292, 1250, 1146, 1105, 1065, 995, 868, 798, 762, 708, 690.

Crystal structure determination

X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a CCD detector at -25°C. Thirty-six frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The data reduction was performed by using the Bruker APEXII with SADABS packages.³³ The structure was solved by direct methods and refined by full-matrix least squares calculation using SHELX-2018/3.^{34,35} The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structural refinement are listed in Table 1, and their relevant bond lengths and angles are listed in Table 2. CCDC-2285319 contain the supplementary crystallographic data for this paper. These data can be obtained

Table 1. Crystal data and structural refinement for (**1**).

Empirical formula	2 C ₂₉ H ₂₈ N ₆ O _{9.5} Cl ₃ Pd
Weight (g mol ⁻¹)	1650.64
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	16.5862(4)
<i>b</i> (Å)	28.2894(6)
<i>c</i> (Å)	15.8233(4)
α (°)	90
β (°)	117.752(1)
γ (°)	90
Volume (Å ³)	6570.5(3)
<i>Z</i>	4
Density (Mg m ⁻³)	1.669
Absorption coefficient (cm ⁻¹)	0.873
<i>F</i> (000)	3336
Index ranges	-20 ≤ <i>h</i> ≤ 19 -32 ≤ <i>k</i> ≤ 35 -19 ≤ <i>l</i> ≤ 19
Reflections collected	103957
<i>R</i> _{int}	0.1402
Completeness to $\theta = 25.242^\circ$ (%)	100.0
Data / restraints / parameters	13606 / 10 / 874
GoF on <i>F</i> ²	1.047
<i>R</i> ₁ ^a	0.0630
<i>wR</i> ₂ ^b	0.1910

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$$

Table 2. Relevant bond lengths (Å) and angles (°) for **(1)**.

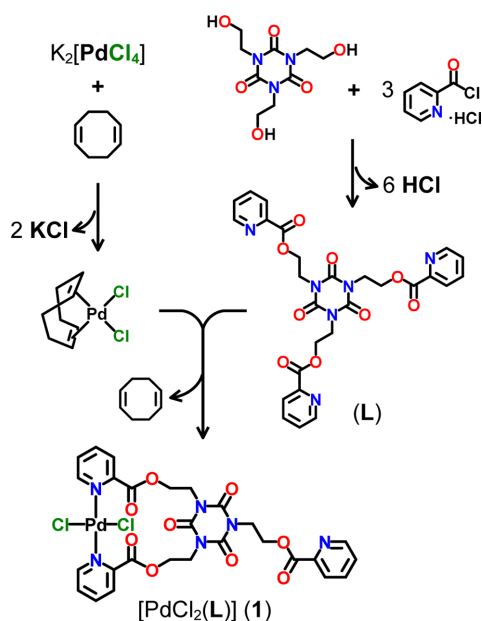
Pd(1)–N(1)	2.018(4)
Pd(1)–N(3)	2.038(5)
Pd(1)–Cl(1)	2.305(1)
Pd(1)–Cl(2)	2.297(1)
Pd(2)–N(7)	2.018(5)
Pd(2)–N(9)	2.038(5)
Pd(2)–Cl(3)	2.312(1)
Pd(2)–Cl(4)	2.294(2)
<hr/>	
N(1)–Pd(1)–N(3)	171.3(2)
Cl(1)–Pd(1)–Cl(2)	177.53(6)
N(1)–Pd(1)–Cl(1)	90.1(1)
N(1)–Pd(1)–Cl(2)	89.6(1)
N(7)–Pd(2)–N(9)	169.9(2)
Cl(3)–Pd(2)–Cl(4)	178.87(6)
N(7)–Pd(2)–Cl(3)	89.1(1)
N(7)–Pd(2)–Cl(4)	89.9(1)

free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthetic aspect

The strategy for construction of the monometallic palladium(II) compound is outlined in Scheme 1. C_3 -symmetric tridentate *N*-donor ligand is a key tectonic for self-



Scheme 1. Synthetic procedure for monometallicacyclic $[\text{PdCl}_2(\text{L})]$ (**1**).

assembly by coordination to palladium(II) metal ion. The new tridentate **L** with donating *ortho*-pyridyl groups was prepared from the reactions of 1,3,5-tris(2-hydroxyethyl)cyanuric acid with picolinoyl chloride in the presence of triethylamine in toluene. Its composition and structure were confirmed by elemental analyses, IR, ^1H and ^{13}C NMR, and electrospray ionization mass spectrometry (ESI-MS). The reaction of $(\text{COD})\text{PdCl}_2$ with **L** in a mixed acetone/ CH_2Cl_2 solution and, subsequently, slow evaporation of the solvents yielded yellow single crystals consisting of a discrete monometallic compound suitable for single-crystal X-ray diffractometry unlike cyclodimeric or cage palladium(II) compounds of general tripyridyl analogues.³⁶ The IR spectra (Figure 1) and elemental analyses were consistent with the proposed structure. The reactions were initially carried out at the mole ratio of 1 : 1, but the same compounds were obtained

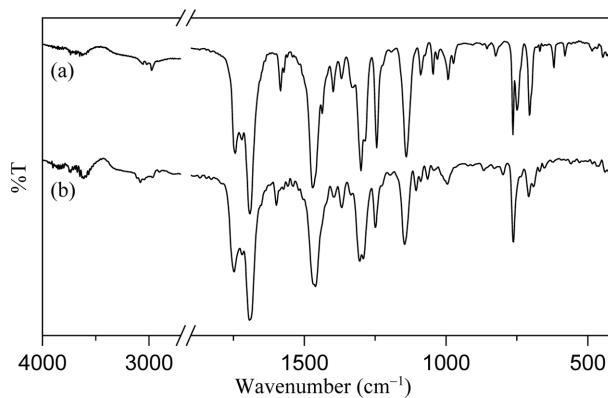


Figure 1. IR spectra (KBr pellet) for **L** (a) and **(1)** (b).

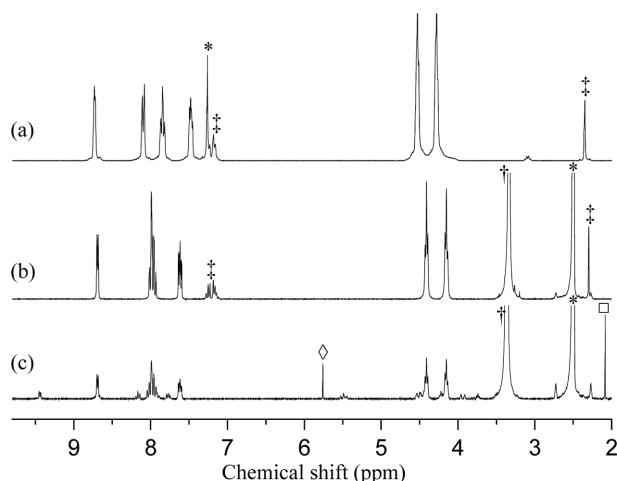


Figure 2. ^1H NMR spectra of **L** in CDCl_3 (a) and $\text{Me}_2\text{SO}-d_6$ (b), and **(1)** in $\text{Me}_2\text{SO}-d_6$ (c). The asterisks, dagger, double dagger, square, and rhombus designate the resonances corresponding to the NMR solvents, water, toluene, acetone, and dichloromethane molecules, respectively.

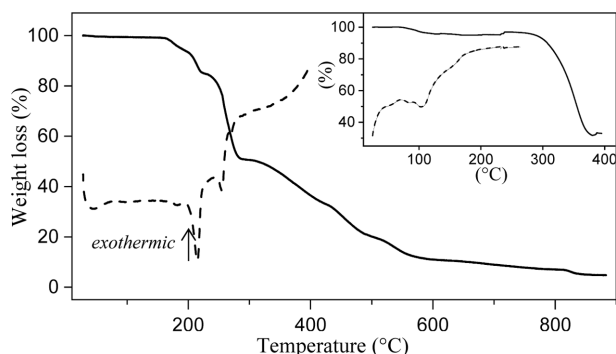


Figure 3. TGA (solid) and DSC (dashed line) curves for (**1**) and **L** (inset).

irrespective of the mole ratio. That is, the formation of the products was not significantly affected by the change of reactant mole ratio and concentration, indicating that the compound is a thermodynamically favorable species. The crystalline product is insoluble in water and common organic solvents such as acetone, acetonitrile, benzene, chloroform, diethyl ether, and tetrahydrofuran, but is dissociated in dimethyl sulfoxide and *N,N*-dimethylformamide. The ^1H NMR spectrum of the present palladium(II) compound in $\text{Me}_2\text{SO}-d_6$ is illustrated in Figure 2. The main peaks corresponding to the free **L** instead of the coordinating **L** were observed, indicating that the compound dissociates in $\text{Me}_2\text{SO}-d_6$ solution. That is, the present compound was not retained in solution. To confirm the thermal stability of the molecules in this system, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out. As plotted in Figure 3, the skeletal structures of **L** and the present palladium(II) compound were stable up to 276°C and 229°C, respectively.

X-ray crystal structure

Single-crystal X-ray diffraction measurement revealed that the single crystals of the present palladium(II) compound consist of $[\text{PdCl}_2(\text{L})]\cdot 0.5\text{Me}_2\text{CO}\cdot 0.5\text{CH}_2\text{Cl}_2$ (**1**). There are two $[\text{PdCl}_2(\text{L})]$ molecules in an asymmetric unit, namely one acetone and one dichloromethane solvate. As depicted in Figure 4, the local geometry around the palladium(II) ion approximates to a typical square-planar arrangement with two chlorides in the *trans* position ($\text{Pd}-\text{Cl} = 2.294(2)\text{--}2.312(1)$ Å; $\text{Cl}-\text{Pd}-\text{Cl} = 177.53(6), 178.87(6)^\circ$) and two nitrogen atoms from one **L** ($\text{Pd}-\text{N} = 2.018(4)\text{--}2.038(5)$ Å; $\text{N}-\text{Pd}-\text{N} = 169.9(2), 171.3(2)^\circ$). **L** acts as a chelated bidentate, and the third donating pyridyl group remains uncoordinated, resulting in the 16-membered metallacycle. To the best of our knowledge, this is the first reported example of a monometallacyclic palladium(II) compound with a *trans* coordinating environment. The dihedral angles between each of the coordinated pyridyl planes and the square plane of the palladium(II) ion were determined to be $56.1(2)\text{--}67.0(1)^\circ$. There existed intermolecular $\pi\cdots\pi$

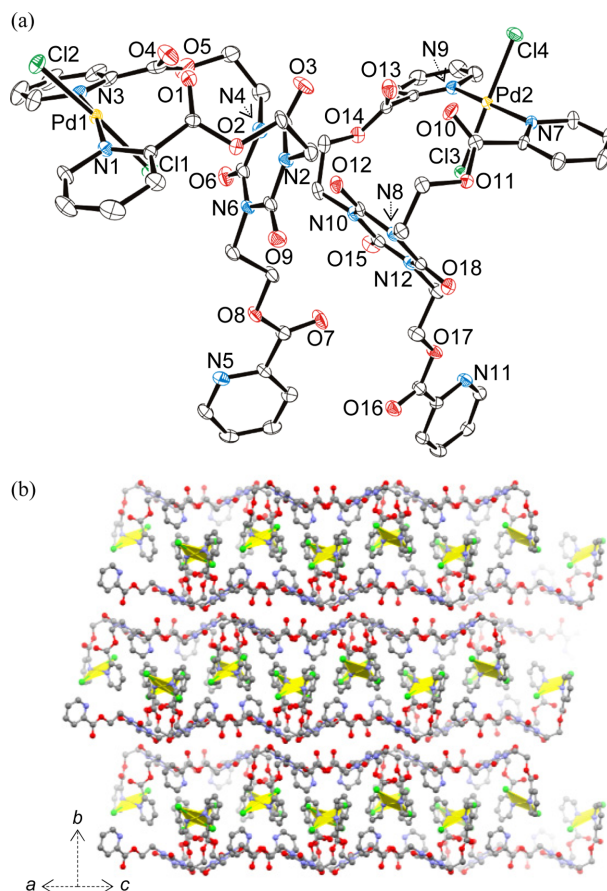


Figure 4. ORTEP drawings with anisotropic displacement parameters at 50% probability (a) and packing diagram (b) of (**1**). All hydrogen atoms and solvate molecules were omitted for clarity. The square planes in yellow color designate the coordinating environment around the palladium(II) center.

interactions between the two coordinating pyridyl groups having a dihedral angle and $\pi\cdots\pi$ distance of $4.8(3)^\circ$ and $3.4(1)$ Å, respectively, and between the coordinating pyridyl group and the adjacent free pyridyl moiety having a dihedral angle of $83.7(2)^\circ$, which arrangement could stabilize the uncoordinated pyridyl periphery of the present **L**. Solvate acetone and dichloromethane molecules were positioned in the vacant space in the unit cell.

Mass spectrometry (MS) data

MS data were obtained in order to characterize the chemical structures of the present **L** and (**1**). As depicted in Figure 5, high-resolution ESI-mass data on **L** showed that the major peaks (m/z) at 577.1686 and 599.1505 are consistent with $[\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_9 + \text{H}^+]^+$ (calcd. 577.1683) and $[\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_9 + \text{Na}^+]^+$ (calcd. 599.1502), respectively. The fast-atom bombardment (FAB)-mass data (matrix 3-nitrobenzyl alcohol) for the present palladium(II) compound (**1**) did not show a mass peak corresponding to the palladium(II)

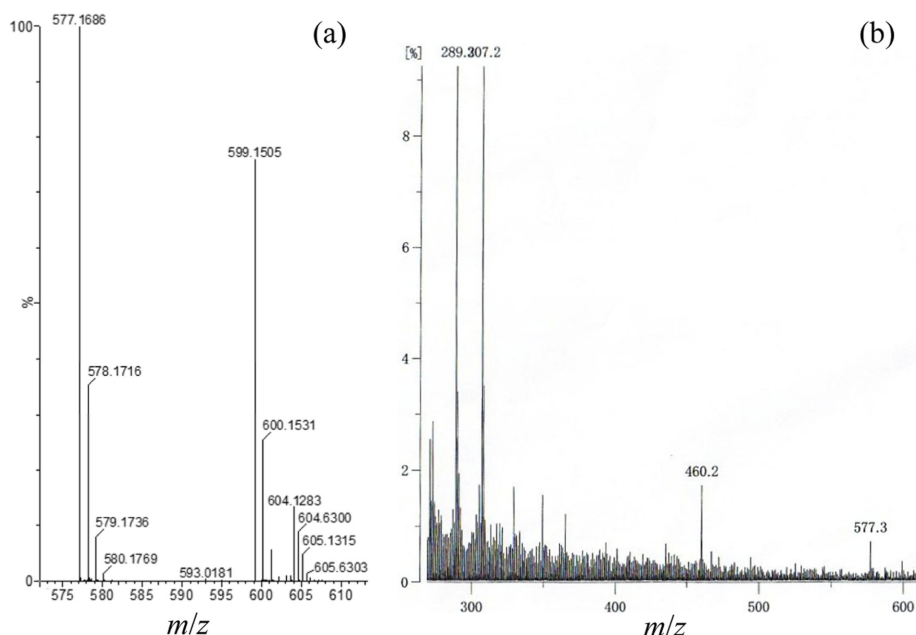


Figure 5. ESI-MS data for **L** (a) and FAB-MS data for **(I)** (b).

compound, presumably owing to the insolubility and dissociation in solution, but instead showed a mass peak corresponding to $[\mathbf{L} + 2\text{H}^+]^{2+}$ (obs. 289.2; calcd. 289.1) and $[\mathbf{L} + \text{H}^+]^+$ (obs. 577.3; calcd. 577.2).

Conclusions

We demonstrated the construction of a metallacyclic palladium(II) compound containing 1,3,5-tris(picolinoyloxyethyl)cyanurate (**L**) ligand, and then we fully characterized its crystal structure and physicochemical properties by means of IR and NMR spectroscopy, thermal analysis, and SC-XRD measurement. In spite of the potentially tridentate coordination of the present ligand, **L** acts as a chelated bidentate and the third donating pyridyl group remains uncoordinated, resulting in the unprecedented 16-membered monometallacycle along with the *trans* isomer around the palladium(II) center. High-resolution ESI-mass data on **L** exhibited the major peak corresponding to $[\text{C}_{27}\text{H}_{24}\text{N}_6\text{O}_9 + \text{H}^+]^+$. FAB-mass data on **(I)**, however, showed the mass peak corresponding to the **L** instead of the present palladium(II) compound species, due to the insolubility and dissociation in solution. Further experiments on the synthesis of bimetallic compounds by means of the uncoordinated pyridyl group as well as the compound's catalytic and photoluminescence properties are in progress.

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