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A 1D palladium coordination polymer and its catalytic activity in microwave-assisted Sonogashira reactions

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ABSTRACT

A palladium coordination polymer, $[Pd(dppp)(L)](OTf)_2 (H_2O)]$ (1) (dppp = 1,3-bis(diphenylphosphino) propane), was prepared from a bipyridine-type ligand (L = (4-py)-CH = N-C₁₀H₆-N = CH-(4-py)) and $[Pd(dppp)](OTf)_2$. An X-ray diffraction study showed that it has a one-dimensional zigzag chain structure and the triflate ions act as counterions. Compound **1** exhibited Sonogashira coupling reactivity in air under microwave conditions.

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1. Introduction

Coordination polymers (CPs) and metal–organic frameworks (MOFs) of transition metals have received continuous attention due to their desirable properties and potential application in catalysis, gas storage and photoluminescence [1–10]. According to IUPAC's definitions in 2013, CPs are coordination compounds with repeating coordination entities extending in 1, 2 or 3 dimensions, and MOFs are coordination networks with potential voids [11]. However, the crystal structures of such species with heavy metals, except cadmium, are relatively rare.

Palladium-catalyzed Sonogashira coupling reactions are of considerable importance in organic chemistry for the preparation of pharmaceuticals, natural products, fine chemicals and polymers. Recently, microwave irradiation has been utilized in organic synthesis, including the Sonogashira coupling reaction, because it is an efficient heating method [12-15]. A wide range of molecular palladium compounds and palladium nanoparticles have been extensively employed in catalytic carbon-carbon coupling reactions, with industrial and academic interest. On the other hand, studies of heterogeneous catalysis using the palladium CPs and MOFs, especially for carbon-carbon coupling, are rather limited [16–26]. The limited use of palladium CPs and MOFs is related to the small number of crystal structures [16–18]. In this paper, we report the preparation and structure of a one-dimensional palladium coordination polymer, as well as its catalytic activity under microwave irradiation in Sonogashira coupling reactions. We also attempted to investigate the catalytic activity in the Suzuki coupling reaction, but our palladium polymer did not exhibit any activity at all.

2. Experimental

2.1. Materials and measurements

All solid chemicals were purified by recrystallization and solvents were vacuum-distilled and stored over 4Å molecular sieves under argon. Triethylamine was distilled over calcium hydride and stored under argon. Activation of molecular sieves was performed under vacuum by heating and then purging with nitrogen gas [27]. The ligand (L) and [Pd(dppp)(OTf)₂] (dppp = 1,3-bis (diphenylphosphino)propane, $OTf = CF_3SO_3^-$) were prepared by the literature methods [28,29]. The microwave heating experiments were conducted with a Monowave 300 (Anton Paar, 300 W). IR spectra were obtained in the range 400–4000 cm^{-1} on a Nicolet 320 FT-IR spectrophotometer. ¹H and ¹³C NMR spectra in the supporting information were obtained with a Bruker 500 MHz spectrometer. Melting points were measured with a 1201D MEL-TEMP apparatus. Elemental analyses were carried out by the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University.

2.2. Preparation of the Pd coordination polymer (1)

A mixture of $[Pd(dppp)(OTf)_2]$ (0.0082 g, 0.010 mmol), the ligand (0.0034 g, 0.010 mmol) and dichloromethane (20 mL) was stirred at room temperature for 6 h. The resulting solution was fil-





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tered and then concentrated by slow evaporation. The crystals formed were filtered, washed with dichloromethane (2 × 2 mL) and air-dried to give brown crystals of compound **1** (0.0075 g, 0.0064 mmol, yield: 64%). IR (KBr, cm⁻¹): 638, 693, 746, 789, 832, 923, 972, 1029 (v_sSO_3), 1102, 1154 (v_sCF), 1254 ($v_{as}CF$), 1432, 1616 (C=N). Anal Calcd for C₅₁H₄₂F₆N₄O₇P₂PdS₂: C, 52.38; H, 3.62; N, 4.79. Found: C, 53.02; H, 4.12; N, 4.52%.

2.3. Microwave-assisted optimization of the Sonogashira crosscoupling reaction of iodobenzene with phenylacetylene

A mixture of iodobenzene (1.0 mmol), phenylacetylene (1.0 mmol), TEA (triethylamine, 1.2 mmol), compound **1** (5 mol %), copper(I) iodide (7 mol%) and H₂O (5 mL) in a 10 mL microwave reaction vial was heated under microwave conditions (40, 60, 80 and 100 °C) in air for an appropriate time. After the mixture was cooled to room temperature, the crude product was extracted with ether (3 × 10 mL), the combined organic phases were dried over sodium sulfate and then concentrated by rotary evaporation. The desired product was isolated by silica gel column chromatography.

2.4. Microwave-assisted Sonogashira cross-coupling reaction of aryl halides with phenylacetylene

A mixture of the aryl halide (1 mmol), phenylacetylene (1 mmol), copper(I) iodide (7 mol%), compound **1** (5 mol%), TEA (1.2 mmol) and H₂O (5 mL) in a microwave reaction vial was heated under microwave conditions in air at 100 °C for 2 h and then cooled to room temperature. The crude product was purified by column chromatography. All coupled products were treated by a similar workup (for the NMR spectra and melting points of the products, see the supporting information).

2.5. X-ray structure determination

X-ray data for compound **1** was collected with a Bruker Smart APEX2 diffractometer (Madison, WI, USA) equipped with a Mo Xray tube at the Korea Basic Science Institute (KBSI). The reflection data were absorption-corrected with sADABS based upon the Laue symmetry by using equivalent reflections [30]. All calculations were carried out with SHELXTL programs [31].

A brown crystal of $1\cdot({\rm H_2O})$ of approximate dimensions $0.20\times0.17\times0.13$ mm, shaped as a block, was used for crystal and intensity data collection. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model, except those in the lattice water molecules, which could not be located. Details of the crystal data, intensity collection and refinement details are given in Table 1. Selected bond lengths and angles are shown in Table 2.

3. Results and discussion

3.1. Synthesis and structure of the Pd coordination polymer (1)

The one-dimensional palladium coordination polymer [Pd (dppp)(L)](OTf)₂·(H₂O) (**1**) was prepared from a 4,4'-bipyridinetype ligand (L) and [Pd(dppp)(OTf)₂] in dichloromethane (Scheme 1). The product was characterized by IR and X-ray crystallography. Compound **1** is insoluble in common organic solvents, such as dichloromethane, acetonitrile, toluene and acetone. The IR spectrum of compound **1** displays a C=N stretch at 1616 cm⁻¹, a CF₃ asymmetric stretch at 1254 cm⁻¹, a CF₃ symmetric stretch at 1029 cm⁻¹. As a com-

Та	bl	le	1

X-ray data collection and structure refinement.

	Compound $1(H_2O)$
Empirical formula	$C_{51}H_{42}F_6N_4O_7P_2PdS_2$
Formula weight	1169.34
Temperature (K)	223(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.276(3)
b (Å)	23.777(5)
<i>c</i> (Å)	21.451(4)
α (°)	90
β (°)	105.92(3)
γ (°)	90
$V(Å^3)$	6512(2)
Ζ	4
ho (g cm ⁻³)	1.193
$\mu (\mathrm{mm}^{-1})$	0.459
F(000)	2376
No. of reflections collected	188,371
No. of independent reflections	16,248
No. of reflections with $I > 2\sigma(I)$	9774
T _{maximum}	0.7457
T _{minimum}	0.6178
No. of parameters	658
Goodness-of-fit on F ²	1.029
R1 ^a	0.0643
wR2 ^b	0.1639
Maximum in $\Delta \rho$ (e Å ⁻³)	2.583
Minimum in $\Delta \rho$ (e Å ⁻³)	-1.069

^a $R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$, ^b $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

parison, the IR spectrum of the ligand shows a C=N bond stretch at 1625 cm⁻¹ [27].

Fig. 1 shows the asymmetric unit of compound **1**, which consists of a Pd^{2+} ion, a 4,4'-bipyridine-type ligand (L), a dppp ligand, an aqua ligand (a lattice water), as well as two triflate counterions. The local coordination environment around the central Pd atom is presented in Fig. 2, in which the Pd metal is 4-coordinated. The Pd (dppp) units are linked by the L ligands in the [010] direction to form a one-dimensional zigzag chain (Fig. 3). As discussed in the introduction, crystal structures of the Pd CPs and MOFs are currently limited and only a few structures have been reported. Pud-dephatt and coworkers reported the 1D structures of *trans*-[PdCl₂(2-Ph-NC₉H₅COOH)₂] [16]. In addition, Jain's group reported the 1D structure of [Pd₂(SeCH₂CH₂CH₂CH₂MMe₂)₂(CH₃COO)](OTf) [17]. A third example, which closely resembles our compound (1), is a 1D zigzag chain reported by Sara and coworkers [18].

3.2. Microwave-assisted optimization for the Sonogashira crosscoupling reaction

To determine the optimum conditions, we performed the coupling reactions of iodobenzene with phenylacetylene under aerobic conditions. Under the conditions in which the product is diphenylacetylene, the solvent was water, the amount of catalyst (compound 1) was 5 mol% and the reaction time was 2 h, whilst the reactions were carried out at various temperatures (40-100 °C, Scheme 2). The results (entries 1-4 in Table 3) revealed that the yield increases with increasing temperature and the highest yield (60%) was obtained at 100 °C. Consequently, subsequent reactions were performed at this temperature. Next, we performed the reactions for various reaction times (0.5-10 h) and found the optimum time to be 2 h (entries 5–15 in Table 3). Finally, the reactions were carried out at 100 °C for 2 h using various catalyst concentrations (1-10 mol%) and the optimum catalyst concentration was found to be 5 mol% (entries 16-25 in Table 3). Hence, from entries 1–25 in Table 3, the optimum reaction conditions can be summaGang Min Lee and S.W. Lee

Table 2

Selected bond lengths (Å) and bond angles (°).

Pd1–N4A	2.115(3)	Pd1-N1	2.121(3)	Pd1-P2	2.2683(12)
Pd1–P1 N4A–Pd1–N1 N4A–Pd1–P1 C33–N2–C34	2.2710(12) 84.8(1) 177.2(1) 115.8(4)	N2-C33 N4A-Pd1-P2 N1-Pd1-P1 C44-N3-C39	1.265(6) 91.1(1) 92.9(1) 118.8(4)	N3-C44 N1-Pd1-P2 P2-Pd1-P1	1.266(6) 176.0(1) 91.1(1)

Symmetry transformations used to generate equivalent atoms: A = -x + 1/2, y + 1/2, -z + 1/2.



Scheme 1. Synthesis of compound 1.



Fig. 1. The asymmetric unit of compound $1(H_2O)$ showing the atomic numbering and 30% probability displacement ellipsoids.

rized as 100 °C (reaction temperature), 2 h (reaction time) and 5 mol% of the catalyst.

3.3. Microwave-assisted Sonogashira cross-coupling reaction of aryl halides with phenylacetylene

Under the optimum conditions determined for the reaction between iodobenzene and phenylacetylene, we performed the coupling reactions of several aryl halides and phenylacetylene under microwave heating at 100 °C (Scheme 3). All microwaveassisted catalytic reactions were performed in air. Ortho-, metaand *para*-methyl-substituted iodobenzenes (entries 2–4 in Table 4) exhibit yields of 41, 36 and 49%, respectively. In terms of substrates, I–C₆H₄–X (entries 1–7 in Tables 4), the highest yield (60%) comes from iodobenzene (X = H), and the lowest yield comes from 1 to iodo-4-nitrobenzene, which contains an electron-withdrawing group (X = NO₂). Although compound **1** shows a relatively low Sonogashira reactivity compared with those employing palla-



Fig. 2. Coordination environment around the Pd metal in compound 1 (H₂O).

dium compounds [32–35], it seems to be worth trying heterogeneous catalysis using palladium coordination polymers.



Fig. 3. Packing diagram of compound 1.(H₂O) down the *c*-axis.



Scheme 2. Optimization of the coupling of iodobenzene with phenylacetylene.

4. Conclusions

In summary, we prepared a one-dimensional palladium coordination polymer, $[Pd(dppp)(L)](OTf)_2 \cdot (H_2O)$ (1), from a bipyridinetype ligand (L = (4-py)-CH = N-C₁₀H₆-N = CH-(4-py)) and [Pd (dppp)](OTf)₂. Compound 1 has a zigzag chain structure, with triflate ions acting as counterions, and is a rare example of a structurally characterized palladium coordination polymer. Compound 1 exhibits relatively low Sonogashira reactivity under microwave conditions, but, unfortunately, we cannot provide a plausible explanation for this activity. The catalytic results revealed that

 Table 3

 Microwave-assisted optimization experiments for the Sonogashira cross-coupling reaction in air.

any substituent on the ArI phenyl ring, whether electron withdrawing or not, lowers the yield with respect to the non-substituted ring.

CRediT authorship contribution statement

Gang Min Lee: Methodology, Validation, Writing - original draft. **Soon W. Lee:** Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115229.

	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield (%)
1	5	40	2	30
2	5	60	2	38
3	5	80	2	45
4	5	100	2	60
5	5	100	0.5	16
6	5	100	0.75	28
7	5	100	1	35
8	5	100	1.25	40
9	5	100	1.5	46
10	5	100	1.75	55
11	5	100	2	60
12	5	100	4	60
13	5	100	6	60
14	5	100	8	61
15	5	100	10	61
16	1	100	2	15
17	2	100	2	25
18	3	100	2	35
19	4	100	2	48
20	5	100	2	60
21	6	100	2	63
22	7	100	2	65
23	8	100	2	66
24	9	100	2	68
25	10	100	2	70



Scheme 3. Microwave-assisted catalytic reaction of arvl halides with phenylacetylene.

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Table 4

Microwave-assisted Sonogashira cross-coupling reaction of aryl halides and phenylacetylene in air.



Gang Min Lee and S.W. Lee

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