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Sugar-incorporated chelating bis-N-heterocyclic carbene palladium complexes. Synthesis, structures and catalytic ability for Suzuki-Miyaura cross-coupling reactions in water

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Abstract

Sugar-incorporated chelating bis-N-heterocyclic carbene ligand precursors 1,1'-bis(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-ethylene-diimidazolyl $[(\text{bisNHC-C2})\text{H}_2]^{2+}$ and 1,1'-bis(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-propylene-diimidazolyl $[(\text{bisNHC-C3})\text{H}_2]^{2+}$ were synthesized and used to prepare palladium complexes $[\text{Pd}(\text{bisNHC-C2})\text{Cl}_2]$ and $[\text{Pd}(\text{bisNHC-C3})\text{Cl}_2]$, respectively, by direct metallation reaction using dichlorobis(acetonitrile)palladium as a metal source. Catalytic abilities of the complexes for Suzuki-Miyaura coupling in aqueous media were examined and moderate TON (85,000) and TOF (170,000 h⁻¹) were obtained. Because the terminal chloro ligands in the complexes were substituted with solvent molecules or chloride anion and then ¹H NMR spectra of the chloro complexes were complicated, hydrosulfido complexes $[\text{Pd}(\text{bisNHC-Cn})(\text{SH})_2]$ (n = 2 and 3) were prepared to confirm structures in solution. Dynamic behavior of flapping-wing motion of the bisNHC ligand in $[\text{Pd}(\text{bisNHC-C3})(\text{SH})_2]$ in solution was evaluated using the signals of the SH protons, which are inequivalent in ¹H NMR spectra attributed to the chirality of the glucopyranosyl units.

1. Introduction

Most of organic reactions catalyzed by transition metal complexes were performed in organic solvents. However, most of organic solvents are volatile and/or combustible, and then their toxicity and risk are often problematic. On the other hand, water is a non-flammable, low toxic liquid and suitable for sustainable reactions. Use of water as a solvent for organic reactions brings other merits such as easy separation of organic products from catalysts and convenient reuse of catalysts.¹ Furthermore, water has unique character, which possibly derives peculiar reactivity,² for example, the second order rate constant for Diels-Alder reaction in water is three orders of magnitude larger than that in an organic solvent.³ This advantage is attributed to hydrophobic effects for substrates in water and suggests that utilization of water as a solvent for organic reactions leads novel reactivity on selectivity and high efficiency.³ For these reasons, catalytic organic reactions such

as Suzuki-Miyaura cross coupling⁵ and Mizoroki-Heck⁶ reaction in water were investigated using water-soluble palladium complexes. Introduction of sulfonate^{6a} and carboxylate^{1c} into ancillary ligands is one of the effective methods to obtain water-soluble complexes. Sugar groups were also good candidates to increase water-solubility of complexes. Sugar-incorporated phosphine⁷ and N-heterocyclic carbene (NHC)⁸ complexes were reported for asymmetric hydrogenation utilizing chirality of the sugar units^{7a} and Suzuki-Miyaura coupling in water,^{8a} respectively.

We previously synthesized iridium, nickel, and palladium complexes with sugar-incorporated monodentate or tridentate NHC ligands.⁹ We report here syntheses of chelated palladium complexes with bidentate bisNHC ligands with D-glucopyranosyl substituents and their catalytic ability for Suzuki-Miyaura coupling in aqueous media.

2. Results and Discussion

Syntheses and structure of sugar-incorporated bisNHC palladium complexes.

Bis-N-heterocyclic carbene ligand precursors 1,1'-bis(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-ethylene-diimidazolium bis(hexafluorophosphate) $[(\text{bisNHC-C2})\text{H}_2](\text{PF}_6)_2$ and 1,1'-bis(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-propylene-diimidazolium bis(hexafluorophosphate)

Scheme 1. Syntheses of ligand precursors.

Scheme 2. Syntheses of **1-C2**, **1-C3**, **2-C2**, and **2-C3**.

[[bisNHC-C3]H₂](PF₆)₂) were synthesized in two step (Scheme 1) because isolation of the ligand precursors from the reaction mixtures containing 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1*H*-imidazole (AcGlcIm) and the precursor, which were obtained by the reaction of 1,2-dibromoethane or 1,3-dibromopropane with excess AcGlcIm, was not succeeded. Palladium complexes [Pd(bisNHC-*Cn*)X₂] (*n* = 2, 3; X = halide, acetate, or coordinating solvent molecule) were obtained by the direct metallation reaction of the ligand precursors and [Pd(NCCH₃)₂Cl₂] in the presence of sodium acetate in DMSO. Electrospray mass spectrometry (ESI-MS) of the complexes showed signals for [Pd(bisNHC-*Cn*)(OAc)]⁺ exhibiting the coordination of the bisNHC ligands to the palladium ion. These complexes gave broad signals in ¹H NMR spectra due to substitution equilibrium of the terminal ligands and the signals

Figure 1. ORTEP drawing of one of the crystallographically independent molecules of **1-C3** with 30% probability of the ellipsoids. Hydrogen atoms are omitted for clarity. ORTEP drawing of another molecule was shown in Figure S1 in Supporting Information. Color codes: oxygen, red; nitrogen, blue; chlorine, green; palladium, purple.

Table 1. Selected bond lengths and angles for **1-C3**.

	1-C3^a		Me complex^b
Pd-Cl	2.378(3) Å	2.370(3) Å	2.3547(8) Å
	2.382(3) Å	2.381(3) Å	2.3615(8) Å
Pd-C	1.99(1) Å	2.01(1) Å	1.969(3) Å
	2.003(16) Å	2.039(9) Å	1.973(3) Å
Cl-Pd-Cl	94.45(9)°	94.38(9)°	92.68(3)°
C-Pd-C	87.0(4)°	86.3(4)°	87.63(12)°
Cl-Pd-C	87.5(3)°	88.3(3)°	88.8(8)°
	91.1(3)°	91.0(3)°	90.9(2)°
	172.3(3)°	173.4(3)°	176.2(1)°
	178.0(3)°	177.3(3)°	176.2(1)°

^a Two crystallographically independent molecules were observed. ^b Obtained from reference 10.

became sharp by the addition of excess tetraethylammonium chloride or sodium hydrosulfide owing to tightly coordinating nature of sulfur atoms to palladium.

Chloride complexes [Pd(bisNHC-*Cn*)Cl₂] (*n* = 2, **1-C2**; *n* = 3, **1-C3**) were obtained by treating the [Pd(bisNHC-*Cn*)X₂] complexes with tetraethylammonium chloride in chloroform. Single crystal X-ray diffraction study of **1-C3** (Figure 1) showed two independent complex molecules in the asymmetric unit and no significant differences were observed in their structures. The complex molecules have the C_s symmetry, if the acetyl-protected glucopyranosyl (AcGlc) groups are not taken into account, and the symmetry of the complex molecules are reduced to C₁ by incorporation of the chiral AcGlc groups. The bond lengths and angles around the Pd center in complex **1-C3** are similar to a corresponding bisNHC Pd complex with methyl N-substituents (Table 1). ¹H NMR spectrum for each chloro complex showed two sets of signals for the AcGlc-NHC moieties, reflecting the C₁ symmetry of the complexes.

Dynamic behavior of sugar-incorporated bisNHC palladium complexes

Corresponding bishydrosulfido complexes (**2-C2** and **2-C3**) were prepared by the addition of sodium hydrosulfide to solutions of **1-C2** and **1-C3** in DMSO-*d*₆. Because the bishydrosulfido complexes should have a similar structure of **1-C3**, two hydrosulfido ligands in each complex are inequivalent and two singlet signals appeared in between −1.5 and −2.1 ppm in ¹H NMR spectra. These SH signals should be affected by the surrounding chiral glucopyranosyl groups. This means that we can obtain the information of the environment around the coordination sites, which are used for catalytic reactions. The difference in the chemical shift of the two SH signals in each complex showed that the coordination sphere surrounded by the glucopyranosyl groups have asymmetric environment. Chelating bisNHC ligands in palladium complexes showed flapping wing motion (Figure 2) via Pd-C bond cleavage for the ethylene bridged bisNHC ligand and without the bond cleavage for the propylene bridged one.^{9d,e,11} The dynamic behavior of the bisNHC ligands in the complexes could affect selectivity of products and catalytic ability in

Figure 2. Flapping wing motion of the chelating bisNHC ligands in **2-C2**.

Figure 3. Temperature dependency of chemical shifts for SH protons in Pd complex (**2-C2**, left) and Pt complex (**3-C2**, right) in DMSO-*d*₆. The whole spectra were shown in Figure S20 and S21 in Supporting information.

Figure 4. Observed (left) and simulated (right) ^1H NMR signals of SH protons in (a) **2-C3** and (b) **3-C3** in $\text{DMSO-}d_6$. The whole spectra were shown in Figure S22 and S23 in Supporting information.

Figure 5. Eyring plots for $[\text{M}(\text{bisNHC-C3})(\text{SH})_2]$ ($\text{M} = \text{Pd}$ (**2-C3**), Pt (**3-C3**)) using kinetic constants obtained from line shape analyses.

Table 2. Activation parameters for dynamic behavior of **2-C3** and **3-C3**.^a

	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ ($\text{cal mol}^{-1} \text{K}^{-1}$)	$\Delta G^\ddagger_{298\text{K}}$ (kcal mol^{-1})
2-C3	14.7(3)	-6.7(10)	16.7(4)
3-C3	15.8(7)	-5.5(14)	17.4(8)

^a Values in parentheses represent standard deviations in the last figures of the activation parameters.

coupling reactions using the complexes as catalysts. For these reasons, variable temperature ^1H NMR (VT-NMR) spectroscopy and line shape analyses were performed for **2-C2** and **2-C3** using the SH signals. For comparison, VT-NMR measurements were also applied for the corresponding platinum complexes $[\text{Pt}(\text{bisNHC-C2})(\text{SH})_2]$ (**3-C2**) and $[\text{Pt}(\text{bisNHC-C3})(\text{SH})_2]$ (**3-C3**), as no Pt–C bond cleavage was reported for platinum complexes with bisNHC ligands.

^1H NMR spectra at 298–353 K of the complexes with the bisNHC-C2 ligand, **2-C2** and **3-C2**, exhibited no dynamic behavior attributed to the flapping wing motion. The $\{\text{Pd}(\text{bisNHC})\}$ unit with methyl N-substituents in a trinuclear complex $[(\text{MCP}^*)_2\{\text{Pd}(\text{bisNHC})\}(\mu\text{-S})_2]^{2+}$ showed dynamics

of the bisNHC ligand via Pd–C bond cleavage at higher temperature than 372 K.^{11a} For **2-C2** and **3-C2**, two signals of the SH protons for each complex showed different temperature dependency in their chemical shifts (Figure 3). The signals of the SH protons shifted to downfield as temperature increased and the rate of the shifts are different. As the complexes having the bisNHC-C2 ligand with the ethylene bridge do not exhibit the flapping-wing motion, two acetyl-protected glucopyranosyl groups in each complex are inequivalent. Then rotation or vibration of the acetyl-protected glucopyranosyl groups in each complex affords different contribution to the environment around the coordination sites, which appeared in the different temperature dependency of the chemical shifts for the SH protons in each complex.

On the other hand, Pd and Pt complexes with the bisNHC containing the propylene bridge, **2-C3** and **3-C3**, respectively, showed dynamic behavior attributed to the flapping wing motion (Figure 4). Activation parameters (Table 2) obtained from the Eyring plots (Figure 5) for **2-C3** and **3-C3** are very similar even they have different metal centers. These parameters are comparable to those reported for the Pd- or Pt-bisNHC units in the trinuclear complexes.

These results suggested that complexes with ethylene-bridged bisNHC ligands have more rigid frameworks to put their N-substituents in limited area around the metal center, while propylene-bridged bisNHC ligands are flexible to allow the N-substituents moving. This fact implies that higher selectivity of products in catalytic reactions is expected for the ethylene-bridged ligand. However, rotation and/or vibration of the N-substituents of the ethylene-bridged ligands are not negligible and slightly affected the environment of the coordination sites as observed for temperature dependency of the chemical shifts of the SH protons.

Catalytic ability of sugar-incorporated bisNHC palladium complexes in Suzuki-Miyaura cross-coupling in water

Catalytic ability of palladium complexes **1-C2** and **1-C3** in Suzuki-Miyaura cross-coupling in water was examined in the presence of potassium carbonate. Although water-solubility of **1-C2** and **1-C3** is low, the acetyl-protected glucopyranosyl units in **1-C2** and **1-C3** are deprotected under the condition affording water-soluble complexes¹². (See Figure S18 and S19 in Supporting Information)

Complexes **1-C2** and **1-C3** catalyzed reactions of 4'-bromoacetophenone and phenylboronic acid in the presence of potassium carbonate in water (Table 3). Turnover number (TON) and turnover frequency (TOF) for each of catalysts **1-C2** (entry 2) and **1-C3** (entry 6) reached to 85,000 and 170,000 h^{-1} , respectively. The catalytic ability of these complexes is relatively high but lower than those reported for palladium acetate with 1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-2,7-diphosphacyclooctane (TON 770,000 and TOF 390,000 h^{-1})^{1c} and for a sugar-incorporated NHC pincer palladium complex (TON 800,000 and TOF 50,000 h^{-1}).^{9c} The lower TON value is attributed to decomposition of the palladium complexes via irreversible protonation of the NHC ligand under the protic condition.^{9f} This result suggested that stabilization of the palladium complex by bisNHC ligands is not enough to prevent decomposition under the reaction condition. The addition of a drop of metallic mercury, which leads deactivation of catalytic ability of palladium nanoparticles,^{1c,13} did not affect the catalytic ability. This result suggests that the active species are the complexes (entries 4 and 8).

Reuse of the complexes for the catalysts in the Suzuki-Miyaura cross-coupling reaction was also examined.

Table 3. Suzuki-Miyaura cross-coupling reactions of 4'-bromoacetophenone and phenylboronic acid catalyzed by **1-C2** and **1-C3**.^a

Entry	Cat. (mol%)	Time (h)	Yield (%)	TON
1	1-C2 , 1.0×10^{-1}	0.5	96	960
2	1-C2 , 1.0×10^{-3}	0.5	85	85,000
3	1-C2 , 1.0×10^{-4}	3	0	0
4 ^b	1-C2 , 1.0×10^{-1}	0.5	90	900
5	1-C3 , 1.0×10^{-1}	0.5	98	980
6	1-C3 , 1.0×10^{-3}	0.5	85	85,000
7	1-C3 , 1.0×10^{-4}	3	0	0
8 ^b	1-C3 , 1.0×10^{-1}	0.5	84	840

^a Reaction condition: 4'-bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol) and K_2CO_3 (0.4 mmol) in water (1 mL), 100 °C. ^b A drop of Hg was added.

Table 4. Reuse of **1-C2** and **1-C3** in aqueous phase as catalysts for Suzuki-Miyaura cross-coupling reactions of 4'-bromoacetophenone and phenylboronic acid.^a

Entry	Catalyst	Cycle	Time (h)	Yield (%)
1	1-C2 ^b	1 st	0.5	96
2		2 nd	0.75	96
3		3 rd	0.75	79
4		4 th	0.75	25
5	1-C3 ^b	1 st	0.5	98
6		2 nd	0.75	89
7		3 rd	0.75	81
8		4 th	0.75	53

^a Reaction condition: 4'-bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol) and K_2CO_3 (0.4 mmol) in water (1 mL), 100 °C. ^b Initial concentration of catalysts: 0.1 mol%.

After the first catalytic reaction, the product and the remained starting materials were extracted with dichloromethane from the resulting reaction mixture. The separated aqueous phase, which contains the catalyst, was used for the other catalytic reaction of the freshly added substrates and base (Table 4). The second and third reactions (entries 2, 3, 6 and 7) afforded similar yields as those for the first reactions (entries 1 and 5). In the fourth reactions (entries 4 and 8), the yields remarkably decreased. These results showed that the complexes or their derivatives were remained in water phase, even though they decomposed after three times uses.

To investigate a scope of substrates for the complexes **1-C2** and **1-C3**, reactions of a variety of aryl halides with phenylboronic acid were examined (Table 5). The reactions of aryl bromides with an electron-withdrawing group such as NO_2 at the 4-position on the phenyl ring afforded biaryl products in high yields. The yields of the reactions were better in the order of the *p*-nitrobenzene with the electron-withdrawing NO_2 group (entries 1 and 2), bromobenzene (entries 3–6), and 4-bromoanisole with the electron-donating OMe group (entries 9–12). Generally, electron-withdrawing groups of aryl halides reduce the electron density on their C–X bonds and then oxidative addition of the C–X bonds to metal centers easily proceed.

Table 5. Suzuki-Miyaura cross-coupling reactions of a variety of aryl halides and phenylboronic acid catalyzed by **1-C2** and **1-C3**.^a

Entry	R	X	Cat.	Time (h)	Yield (%)	TON
1	NO_2	Br	1-C2	2	97	9,700
2	NO_2	Br	1-C3	2	98	9,800
3	H	Br	1-C2	2	56	5,600
4	H	Br	1-C3	2	66	6,600
5	H	Br	1-C2	6	80	8,000
6	H	Br	1-C3	6	81	8,100
7 ^b	H	Br	1-C2	2	69	6,900
8 ^b	H	Br	1-C3	2	89	8,900
9	OMe	Br	1-C2	2	28	2,800
10	OMe	Br	1-C3	2	41	4,100
11	OMe	Br	1-C2	6	64	6,400
12	OMe	Br	1-C3	6	63	6,300
13 ^b	OMe	Br	1-C2	2	74	7,400
14 ^b	OMe	Br	1-C3	2	83	8,300
15	Ac	Cl	1-C2	17	3	300
16 ^b	Ac	Cl	1-C2	17	57	5,700

^a Reaction condition: aryl halide (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol) and catalyst (10^{-2} mol%) in water (1 mL), 100 °C. ^b 0.3 mmol of nBu_4NBr was added.

For the reactions in water, solubility of organic substrates often affects the yields. To enhance the solubility of the arylhalide, tetrabutylammonium bromide is added as an additive. We also checked the effects of tetrabutylammonium bromide in the reactions (entries 7, 8, 13, 14) and observed improvement of the yields by the addition. Although the catalytic reaction of less reactive 4'-chloroacetophenone with phenylboronic acid afforded a low yield of the coupling product (entry 15), the addition of tetrabutylammonium bromide drastically improved the yield (entry 16).

3. Conclusion

Palladium complexes with chelating bis-NHC ligands having D-glucopyranosyl moieties were synthesized and their structures and dynamic behavior in solution were characterized. These palladium complexes exhibited moderate catalytic ability for Suzuki-Miyaura cross-coupling reactions in water. The complexes remained in retrieved water phases after extraction of the product from reaction mixtures and worked as a catalyst for the reactions.

4. Experimental

General procedures and materials. All chemicals were purchased from Aldrich, Nacalai Tesque, and Wako Pure Chemical. 1-(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)imidazole (AcGlcIm)^{9c} and $[Pd(NCCH_3)_2Cl_2]$ ¹⁴ were prepared by previously reported procedures. All reagents and solvents were used without purification. ¹H and ¹³C NMR spectra were recorded on a JEOL Lambda 300, Lambda 400, or Bruker AVANCE 300 FT-NMR spectrometer. Chemical shifts are expressed in ppm upfield from SiMe₄ and referenced to solvent peaks. Electrospray ionization (ESI) mass spectrometric measurements were performed on an Applied Biosystem

Mariner time-of-flight mass spectrometer using HPLC grade solvents. Elemental analyses were performed on a J-Science Lab JM-10 elemental analyser by the Analytical Research Center at Osaka City University.

Synthesis of 1-(2-bromoethyl)-3-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)imidazolium bromide

[AcGlcIm(CH₂)₂Br]Br. AcGlcIm (1.00 g, 2.52 mmol), 1,2-dibromoethane (6.0 mL, 70 mmol) and acetone (10 mL) were added into a sealed tube. The mixture was heated at 90 °C for 21 h to afford a white solid, which was collected by filtration (1.34 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ 11.29 (1H, s, 2-Im), 7.51 (1H, m, Im), 7.48 (1H, m, Im), 6.28 (1H, d, 2-Glc, ³J_{H-H} = 9.2 Hz), 5.45 (1H, t, Glc, ³J_{H-H} = 9.6 Hz), 5.26 (1H, t, Glc, ³J_{H-H} = 9.2 Hz), 5.24 (1H, t, Glc, ³J_{H-H} = 9.2 Hz), 5.03–4.88 (2H, m, Im-C₂H₄-Br), 4.35 (1H, dd, 6-Glc, ²J_{H-H} = 12.2 Hz, ³J_{H-H} = 4.8 Hz), 4.23 (1H, ddd, 5-Glc, ³J_{H-H} = 11.4 Hz, ³J_{H-H} = 4.9 Hz, ³J_{H-H} = 1.8 Hz), 4.17 (1H, dd, 6-Glc, ²J_{H-H} = 12.5 Hz, ³J_{H-H} = 1.7 Hz), 3.98 (1H, ddd, Im-C₂H₄-Br, ²J_{H-H} = 11.9 Hz, ³J_{H-H} = 6.4 Hz, ³J_{H-H} = 4.0 Hz), 3.88 (1H, ddd, Im-C₂H₄-Br, ²J_{H-H} = 12.2 Hz, ³J_{H-H} = 6.9 Hz, ³J_{H-H} = 4.1 Hz), 2.10 (3H, s, OAc), 2.08 (3H, s, OAc), 2.07 (3H, s, OAc), 2.01 (3H, s, OAc). ¹³C{¹H} NMR (75 MHz, DMSO-*d*₆): δ 170.5 (C=O), 169.8 (C=O), 169.7 (C=O), 169.1 (C=O), 137.3 (2-Im), 123.7 (4,5-Im), 120.9 (4,5-Im), 83.7 (1-Glc), 74.1 (Glc), 71.8 (Glc), 70.8 (Glc), 67.5 (Glc), 61.9 (Glc), 51.0 (Im-C₂H₄-Br), 31.6 (Im-C₂H₄-Br), 20.6 (CH₃-OAc), 20.4 (CH₃-OAc), 20.3 (CH₃-OAc), 20.2 (CH₃-OAc).

Synthesis of 1,1'-bis(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-ethylene-diimidazolium bis(hexafluorophosphate)

[(bisNHC-C2)H₂](PF₆)₂. AcGlcIm (0.853 g, 2.14 mmol), [AcGlcIm(CH₂)₂Br]Br (1.25 g, 2.14 mmol) and acetonitrile (20 mL) were placed into a sealed tube. After the mixture was heated at 110 °C for 72 h, the solvent was removed under reduced pressure to give a brown oil. Addition of diethyl ether afforded a white solid, which was collected by filtration. The solid was re-dissolved in water and an aqueous solution of ammonium hexafluorophosphate (1.76 g, 10.8 mmol) was added to the solution to give a white solid, which was collected by filtration and air-dried (1.93 g, 81%). ¹H NMR (400 MHz, CD₃CN): δ 8.67 (2H, t, 2-Im, *J*_{H-H} = 1.6 Hz), 7.67 (2H, t, 4,5-Im, *J*_{H-H} = 1.9 Hz), 7.49 (2H, t, 4,5-Im, *J*_{H-H} = 1.9 Hz), 5.74 (2H, d, 2-Glc, ³J_{H-H} = 8.9 Hz), 5.50 (2H, t, Glc, ³J_{H-H} = 9.7 Hz), 5.25 (2H, t, Glc, ³J_{H-H} = 9.8 Hz), 5.22 (2H, t, Glc, ³J_{H-H} = 9.8 Hz), 4.64 (4H, s, N-CH₂), 4.27–4.19 (4H, m, 6-Glc), 4.16 (2H, ddd, 5-Glc, ³J_{H-H} = 10.0 Hz, ³J_{H-H} = 5.0 Hz, ³J_{H-H} = 2.3 Hz), 2.02 (6H, s, OAc), 2.02 (6H, s, OAc), 1.99 (12H, s, OAc). ¹³C{¹H} NMR (75 MHz, acetone-*d*₆): δ 170.8 (C=O), 170.6 (C=O), 170.2 (C=O), 170.1 (C=O), 137.3 (2-Im), 124.5 (4,5-Im), 122.6 (4,5-Im), 85.9 (1-Glc), 75.9 (Glc), 72.6 (Glc), 72.2 (Glc), 68.1 (Glc), 62.4 (Glc), 50.5 (Im-C₂H₄-Im), 20.6 (CH₃-OAc), 20.54 (CH₃-OAc), 20.46 (CH₃-OAc), 20.4 (CH₃-OAc).

Synthesis of 1-(3-bromopropyl)-3-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)imidazolium hexafluorophosphate

[AcGlcIm(CH₂)₃Br](PF₆). AcGlcIm (0.527 g, 1.34 mmol), 1,3-dibromopropane (2.5 mL, 24 mmol) and acetone (10 mL) were added into a sealed tube. After the mixture was heated at 90 °C for 5 h, the solvent was removed under reduced pressure to give a brown oil. Addition of diethyl ether afforded a white solid, which was collected by filtration. The solid was re-dissolved in water and an aqueous solution of ammonium hexafluorophosphate (2.16 g, 13.3 mmol) was added to the solution to give a white solid, which was collected by filtration and air-dried (0.773 g, 88%). ¹H NMR (400 MHz, CD₃CN): δ 8.77 (1H, s, 2-Im), 7.63 (1H, s, Im), 7.49 (1H, s,

Im), 5.72 (1H, d, 1-Glc, ³J_{H-H} = 8.8 Hz), 5.48 (1H, t, Glc, ³J_{H-H} = 9.5 Hz), 5.31 (1H, t, Glc, ³J_{H-H} = 9.2 Hz), 5.27 (1H, t, Glc, ³J_{H-H} = 9.8 Hz), 4.44–4.28 (2H, m, Br-CH₂), 4.28–4.12 (3H, m, Glc), 3.51–3.39 (2H, m, Im-CH₂), 2.47–2.34 (2H, m, 2-(CH₂)₃), 2.03 (6H, s, OAc), 1.98 (3H, s, OAc), 1.99 (3H, s, OAc), 1.93 (3H, s, OAc). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 170.6 (C=O), 169.8 (C=O), 169.6 (C=O), 169.5 (C=O), 137.1 (2-Im), 123.5 (4,5-Im), 119.9 (4,5-Im), 84.0 (1-Glc), 74.8 (Glc), 72.0 (Glc), 70.9 (Glc), 67.4 (Glc), 61.4 (Glc), 48.8 (Im-C₃H₆-Br), 32.5 (Im-C₃H₆-Br), 29.0 (Im-C₃H₆-Br), 20.8 (CH₃-OAc), 20.7 (CH₃-OAc), 20.6 (CH₃-OAc), 20.5 (CH₃-OAc).

Synthesis of 1,1'-bis(2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl)-3,3'-propylene-diimidazolium bis(hexafluorophosphate)

[(bisNHC-C3)H₂](PF₆)₂. [(bisNHC-C3)H₂](PF₆)₂ was obtained analogously to [(bisNHC-C2)H₂](PF₆)₂ using AcGlcIm (0.419 g, 1.05 mmol), [AcGlcIm(CH₂)₃Br](PF₆) (0.699 g, 1.05 mmol) and acetonitrile (20 mL) with heating at 110 °C for 48 h and addition of ammonium hexafluorophosphate (0.703 g, 4.31 mmol) (1.07 g, 90%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.55 (2H, t, 2-Im, *J*_{H-H} = 1.3 Hz), 8.12 (2H, t, 4,5-Im, *J*_{H-H} = 1.7 Hz), 7.86 (2H, t, 4,5-Im, *J*_{H-H} = 1.7 Hz), 6.03 (2H, d, 2-Glc, ³J_{H-H} = 8.6 Hz), 5.59 (2H, t, Glc, ³J_{H-H} = 9.4 Hz), 5.51 (2H, t, Glc, ³J_{H-H} = 9.1 Hz), 5.25 (2H, t, Glc, ³J_{H-H} = 9.6 Hz), 4.40 (2H, ddd, 5-Glc, ³J_{H-H} = 10.1 Hz, ³J_{H-H} = 4.0 Hz, ³J_{H-H} = 4.0 Hz), 4.26 (4H, t, N-CH₂, ³J_{H-H} = 7.1 Hz), 4.15 (4H, d, 6-Glc, ³J_{H-H} = 3.8 Hz), 2.39 (2H, quin, 2-(CH₂)₃, ³J_{H-H} = 6.9 Hz), 2.04 (6H, s, OAc), 2.02 (6H, s, OAc), 1.98 (6H, s, OAc), 1.92 (6H, s, OAc). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 170.1 (C=O), 169.63 (C=O), 169.55 (C=O), 169.3 (C=O), 136.7 (2-Im), 123.4 (4,5-Im), 121.0 (4,5-Im), 83.7 (1-Glc), 73.8 (Glc), 71.3 (Glc), 71.0 (Glc), 67.2 (Glc), 61.8 (Glc), 46.5 (2-(CH₂)₃), 29.4 (N-CH₂), 20.6 (CH₃-OAc), 20.4 (CH₃-OAc), 20.2 (CH₃-OAc), 20.0 (CH₃-OAc).

Synthesis of [Pd(bisNHC-C2)Cl₂] (1-C2). A mixture of ligand precursor [(bisNHC-C2)H₂](PF₆)₂ (305 mg, 0.27 mmol), [Pd(NCCH₃)₂Cl₂] (71 mg, 0.27 mmol), sodium acetate (89 mg, 1.1 mmol) and DMSO (20 mL) was stirred overnight at room temperature. The solvent was removed under reduced pressure. The residue was triturated with water to afford [Pd(bisNHC-C2)X₂] (X = halide, acetate, or coordinating solvent molecules) as an insoluble solid, which was collected by filtration, washed with water and air-dried (208 mg). To a solution of [Pd(bisNHC-C2)X₂] (208 mg) in chloroform (10 mL), tetraethyl-ammonium chloride (344 mg, 2.08 mmol) was added and the mixture was stirred overnight. The resulting solution was washed with water (3 × 5 mL) and the separated organic layer was dried with magnesium sulfate. After magnesium sulfate was removed by filtration, the same procedure was repeated twice. After removal of the solvent under reduced pressure, the obtained solid was recrystallized from an acetone solution by slow addition of hexane to afford **1-C2** as a white solid (128 mg, 48%). ¹H NMR (300 MHz, acetone-*d*₆): δ 7.64 (1H, d, Im, ³J_{H-H} = 2.2 Hz), 7.47 (1H, d, Im, ³J_{H-H} = 2.2 Hz), 7.45 (1H, d, Im, ³J_{H-H} = 2.1 Hz), 7.32 (1H, d, Im, ³J_{H-H} = 2.2 Hz), 7.27 (1H, d, 1-Glc, ³J_{H-H} = 9.1 Hz), 6.44 (1H, d, 1-Glc, ³J_{H-H} = 9.6 Hz), 6.00 (1H, ddd, Im-C₂H₄-Im, ²J_{H-H} = 15.1 Hz, ³J_{H-H} = 11.4 Hz, ³J_{H-H} = 3.7 Hz), 5.75 (1H, t, Glc, ³J_{H-H} = 9.4 Hz), 5.58 (1H, t, Glc, ³J_{H-H} = 9.3 Hz), 5.47 (1H, t, Glc, ³J_{H-H} = 9.7 Hz), 5.46 (1H, t, Glc, ³J_{H-H} = 9.4 Hz), 5.29 (1H, t, Glc, ³J_{H-H} = 9.8 Hz), 5.14 (1H, t, Glc, ³J_{H-H} = 9.3 Hz), 4.97 (1H, dt, Im-C₂H₄-Im, ²J_{H-H} = 14.6 Hz, ³J_{H-H} = 3.9 Hz), 4.79 (1H, dt, Im-C₂H₄-Im, ²J_{H-H} = 15.0 Hz, ³J_{H-H} = 4.1 Hz), 4.67–4.55 (2H, m, Im-C₂H₄-Im and 5-Glc overlapping), 4.44 (1H, dd, 6-Glc, ²J_{H-H} = 13.0 Hz, ³J_{H-H} = 2.3 Hz), 4.34 (1H, dd, Glc, ²J_{H-H} = 12.9 Hz, ³J_{H-H} = 2.6 Hz), 4.26–4.14 (3H, m, Glc),

2.03 (3H, s, OAc), 2.02 (3H, s, OAc), 2.01 (3H, s, OAc), 2.00 (3H, s, OAc), 1.97 (3H, s, OAc), 1.93 (3H, s, OAc), 1.90 (3H, s, OAc), 1.33 (3H, s, OAc). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetone- d_6): δ 170.8 (C=O), 170.7 (C=O), 170.3 (C=O), 170.2 (two overlapped C=O), 170.04 (C=O), 170.01 (C=O), 169.9 (C=O), 164.0 (2-Im), 161.7 (2-Im), 124.4 (Im), 123.2 (Im), 121.3 (Im), 120.5 (Im), 86.7 (1-Glc), 86.6 (1-Glc), 75.2 (Glc), 75.0 (Glc), 74.3 (Glc), 73.4 (Glc), 70.8 (Glc), 70.1 (Glc), 70.0 (Glc), 68.7 (Glc), 62.5 (Glc), 62.2 (Glc), 50.0 (Im-C₂H₄-Im), 47.2 (Im-C₂H₄-Im), 20.88 (CH₃-OAc), 20.86 (CH₃-OAc), 20.78 (CH₃-OAc), 20.70 (CH₃-OAc), 20.66 (CH₃-OAc), 20.57 (CH₃-OAc), 20.52 (CH₃-OAc), 19.6 (CH₃-OAc). Anal. Calcd for C₃₅H₄₆Cl₂N₄O₁₈Pd•2H₂O: C, 41.43; H, 4.86; N, 5.41. Found: C, 41.80; H, 4.94; N, 5.35%. MS(ESI+) m/z = 965 ([M-Cl]⁺).

In-situ generation of [Pd(bisNHC-C2)(SH)₂] (2-C2). To a solution of [Pd(bisNHC-C2)X₂] (20 mg) in DMSO- d_6 (0.7 mL) in an NMR tube, sodium hydrosulfide (5.0 mg, 0.089 mmol) was added. ^1H NMR (300 MHz, DMSO- d_6): δ 7.60 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.2$ Hz), 7.51 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.1$ Hz), 7.47 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.1$ Hz), 7.30 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.0$ Hz), 7.10 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.4$ Hz), 6.16 (1H, d, 1-Glc, $J_{\text{H-H}} = 9.0$ Hz), 5.65 (1H, ddd, Im-C₂H₄-Im, $^2J_{\text{H-H}} = 14.4$ Hz, $^3J_{\text{H-H}} = 10.5$ Hz, $^3J_{\text{H-H}} = 3.8$ Hz), 5.62 (1H, t, Glc, $^3J_{\text{H-H}} = 9.4$ Hz), 5.55–5.45 (2H, m, Glc), 5.28 (1H, t, Glc, $^3J_{\text{H-H}} = 9.2$ Hz), 5.20 (1H, t, Glc, $^3J_{\text{H-H}} = 9.5$ Hz), 5.06 (1H, Glc, $^3J_{\text{H-H}} = 9.0$ Hz), 4.76 (1H, dt, Im-C₂H₄-Im, $^2J_{\text{H-H}} = 14.7$ Hz, $^3J_{\text{H-H}} = 4.0$ Hz), 4.55 (1H, dt, Im-C₂H₄-Im, $^2J_{\text{H-H}} = 14.6$ Hz, $^3J_{\text{H-H}} = 4.1$ Hz), 4.44 (1H, dt, 5-Glc, $^3J_{\text{H-H}} = 9.6$ Hz, $^3J_{\text{H-H}} = 2.2$ Hz), 4.38–4.26 (1H, m, Im-C₂H₄-Im), 4.31 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 12.9$ Hz, $^3J_{\text{H-H}} = 2.2$ Hz) 4.20–4.00 (4H, m, Glc), 2.014 (3H, s, OAc), 2.011 (3H, s, OAc), 2.00 (3H, s, OAc), 1.96 (3H, s, OAc), 1.95 (3H, s, OAc), 1.87 (3H, s, OAc), 1.86 (3H, s, OAc), 1.20 (3H, s, OAc), –1.82 (1H, s, SH), –1.83 (1H, s, SH).

Synthesis of [Pd(bisNHC-C3)Cl₂] (1-C3). A similar reaction for [Pd(bisNHC-C2)X₂] using [(bisNHC-C3)H₂](PF₆)₂ (307 mg, 0.27 mmol), [Pd(NCCH₃)₂Cl₂] (71 mg, 0.27 mmol), sodium acetate (87 mg, 1.1 mmol) and DMSO (20 mL) afforded [Pd(bisNHC-C3)X₂] (148 mg). A similar synthesis for **1-C2** using [Pd(bisNHC-C3)X₂] (130 mg) gave **1-C3** (20 mg, 7%). ^1H NMR (400 MHz, CD₃CN): δ 7.40 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.3$ Hz), 7.25 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 1.8$ Hz), 7.22 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.3$ Hz), 7.08 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.2$ Hz), 7.01 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.3$ Hz), 6.39 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.87 (1H, ddd, N-CH₂, $^2J_{\text{H-H}} = 15.1$ Hz, $^3J_{\text{H-H}} = 11.4$ Hz, $^3J_{\text{H-H}} = 3.7$ Hz), 5.54 (1H, t, Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.53 (1H, t, Glc, $^3J_{\text{H-H}} = 9.2$ Hz), 5.39 (1H, t, Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.35 (1H, t, Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.27 (1H, t, Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.10 (1H, t, Glc, $^3J_{\text{H-H}} = 10.1$ Hz), 4.76 (1H, dt, N-CH₂, $^2J_{\text{H-H}} = 14.6$ Hz, $^3J_{\text{H-H}} = 3.9$ Hz), 4.54 (1H, dt, N-CH₂, $^2J_{\text{H-H}} = 15.1$ Hz, $^3J_{\text{H-H}} = 4.1$ Hz), 4.37 (1H, ddd, N-CH₂, $^2J_{\text{H-H}} = 16.0$ Hz, $^3J_{\text{H-H}} = 11.0$ Hz, $^3J_{\text{H-H}} = 4.1$ Hz), 4.35 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 13.3$ Hz, $^3J_{\text{H-H}} = 2.3$ Hz), 4.25–4.05 (6H, m, 5-Glc, 6-Glc, and 2-(CH₂)₃ overlapping), 2.02 (9H, s, OAc), 2.01 (3H, s, OAc), 1.98 (6H, s, OAc), 1.891 (3H, s, OAc), 1.885 (3H, s, OAc). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetone- d_6): δ 170.8 (C=O), 170.7 (C=O), 170.3 (C=O), 170.2 (two overlapped C=O), 170.1 (C=O), 170.0 (C=O), 169.9 (C=O), 163.2 (2-Im), 160.8 (2-Im), 124.6 (4,5-Im), 123.5 (4,5-Im), 121.2 (4,5-Im), 120.5 (4,5-Im), 86.7 (1-Glc), 86.5 (1-Glc), 75.1 (Glc), 74.8 (Glc), 74.1 (Glc), 73.2 (Glc), 70.6 (Glc), 70.0 (Glc), 69.9 (Glc), 68.6 (Glc), 62.5 (Glc), 62.1 (Glc), 55.5 (Im-C₃H₆-Im) 50.0 (Im-C₃H₆-Im), 47.1 (Im-C₃H₆-Im), 20.92 (CH₃-OAc), 20.89 (CH₃-OAc), 20.74 (CH₃-OAc), 20.68 (CH₃-OAc), 20.6 (CH₃-OAc), 20.54 (CH₃-OAc), 20.51 (CH₃-OAc), 19.6 (CH₃-OAc). Anal. Calcd for C₃₇H₄₈Cl₂N₄O₁₈Pd•2H₂O•(CH₃)₂CO: C, 43.35; H, 5.28; N,

5.06. Found: C, 43.11; H, 5.23; N, 5.06%. MS(ESI+) m/z = 979 ([M-Cl]⁺).

In-situ generation of [Pd(bisNHC-C3)(SH)₂] (2-C3). To a solution of [Pd(bisNHC-C3)X₂] (17 mg) in DMSO- d_6 (0.7 mL) in an NMR tube, sodium hydrosulfide (5.0 mg, 0.089 mmol) was added. ^1H NMR (400 MHz, DMSO- d_6): δ 7.56 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 1.5$ Hz), 7.35 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 1.5$ Hz), 7.33 (2H, s, 4,5-Im), 6.58 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 8.8$ Hz), 6.18 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.0$ Hz), 5.62 (1H, t, Glc, $^3J_{\text{H-H}} = 9.5$ Hz), 5.56 (1H, t, Glc, $^3J_{\text{H-H}} = 9.1$ Hz), 5.52 (1H, t, Glc, $^3J_{\text{H-H}} = 9.8$ Hz), 5.37 (1H, t, Glc, $^3J_{\text{H-H}} = 8.7$ Hz), 5.32 (1H, t, Glc, $^3J_{\text{H-H}} = 9.7$ Hz), 5.07 (1H, t, Glc, $^3J_{\text{H-H}} = 9.3$ Hz), 4.95–4.80 (2H, m, N-CH₂), 4.80 (1H, d, 5-Glc, $^3J_{\text{H-H}} = 10.1$ Hz), 4.46 (1H, m, 5-Glc, $^3J_{\text{H-H}} = 9.6$ Hz, $^3J_{\text{H-H}} = 5.7$ Hz, $^3J_{\text{H-H}} = 2.4$ Hz), 4.29 (2H, dt, N-CH₂, $^2J_{\text{H-H}} = 13.8$ Hz, $^3J_{\text{H-H}} = 6.3$ Hz), 4.16–4.02 (1H, m, 2-(CH₂)₂), 4.14 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 12.3$ Hz, $^3J_{\text{H-H}} = 5.9$ Hz), 4.08 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 12.1$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz), 3.97 (1H, d, 6-Glc, $^2J_{\text{H-H}} = 12.0$ Hz), 3.91 (1H, d, 6-Glc, $^2J_{\text{H-H}} = 12.2$ Hz), 2.44–2.30 (1H, m, 2-(CH₂)₂), 2.02 (6H, s, OAc), 2.00 (3H, s, OAc), 1.97 (3H, s, OAc), 1.95 (3H, s, OAc), 1.91 (6H, s, OAc), 1.28 (3H, s, OAc), –2.02 (1H, s, SH), –2.08 (1H, s, SH).

In-situ generation of [Pt(bisNHC-C2)(SH)₂] (3-C2). A mixture of ligand precursor [(bisNHC-C2)H₂](PF₆)₂ (14.3 mg, 0.013 mmol), K₂[PtCl₄] (5.5 mg, 0.013 mmol) and sodium acetate (4.4 mg, 0.054 mmol) in DMSO- d_6 (0.7 mL) was heated in an NMR tube at 70 °C for 24 h, followed by the addition of sodium hydrosulfide (5.0 mg, 0.089 mmol). ^1H NMR (400 MHz, DMSO- d_6): δ 7.55 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.0$ Hz), 7.46 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.0$ Hz), 7.43 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 1.9$ Hz), 7.25 (1H, d, 4,5-Im, $^3J_{\text{H-H}} = 2.0$ Hz), 7.15 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.5$ Hz), 6.25 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.0$ Hz), 5.66 (1H, ddd, N-CH₂, $^2J_{\text{H-H}} = 14.3$ Hz, $^3J_{\text{H-H}} = 10.6$ Hz, $^3J_{\text{H-H}} = 3.5$ Hz), 5.59 (1H, t, Glc, $^3J_{\text{H-H}} = 9.4$ Hz), 5.55–5.45 (2H, m, Glc), 5.26 (1H, t, Glc, $^3J_{\text{H-H}} = 9.4$ Hz), 5.17 (1H, t, Glc, $^3J_{\text{H-H}} = 9.7$ Hz), 5.04 (1H, t, Glc, $^3J_{\text{H-H}} = 9.4$ Hz), 4.69 (1H, dt, N-CH₂, $^2J_{\text{H-H}} = 14.5$ Hz, $^3J_{\text{H-H}} = 3.7$ Hz), 4.44 (1H, dt, N-CH₂, $^2J_{\text{H-H}} = 14.6$ Hz, $^3J_{\text{H-H}} = 4.1$ Hz), 4.37 (1H, dt, 5-Glc, $^2J_{\text{H-H}} = 9.6$ Hz, $^3J_{\text{H-H}} = 2.2$ Hz), 4.30 (1H, ddd, N-CH₂, $^2J_{\text{H-H}} = 15.1$ Hz, $^3J_{\text{H-H}} = 11.1$ Hz, $^3J_{\text{H-H}} = 4.6$ Hz), 4.23 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 12.9$ Hz, $^3J_{\text{H-H}} = 1.8$ Hz), 4.16–3.98 (3H, m, Glc), 1.99 (6H, s, OAc), 1.98 (3H, s, OAc), 1.94 (3H, s, OAc), 1.92 (3H, s, OAc), 1.87 (3H, s, OAc), 1.84 (3H, s, OAc), 1.16 (3H, s, OAc), –1.50 (1H, s, SH), –1.53 (1H, s, SH).

In-situ generation of [Pt(bisNHC-C3)(SH)₂] (3-C3). A similar procedure for **3-C2** was applied to prepare **3-C3** using [(bisNHC-C3)H₂](PF₆)₂ (14.8 mg, 0.014 mmol), K₂[PtCl₄] (5.4 mg, 0.013 mmol) and sodium acetate (4.5 mg, 0.055 mmol) in DMSO- d_6 (0.7 mL) with heating at 70 °C for 4 h, followed by the addition of sodium hydrosulfide (5.0 mg, 0.089 mmol). ^1H NMR (400 MHz, DMSO- d_6): δ 7.53 (1H, s, 4,5-Im), 7.34 (1H, s, 4,5-Im), 7.27 (2H, s, 4,5-Im), 6.69 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 9.0$ Hz), 6.33 (1H, d, 1-Glc, $^3J_{\text{H-H}} = 8.8$ Hz), 5.76–5.60 (1H, m, N-CH₂), 5.58 (2H, t, Glc, $^3J_{\text{H-H}} = 9.0$ Hz), 5.51 (1H, t, Glc, $^3J_{\text{H-H}} = 9.6$ Hz), 5.36 (1H, t, Glc, $^3J_{\text{H-H}} = 9.5$ Hz), 5.31 (1H, t, Glc, $^3J_{\text{H-H}} = 10.0$ Hz), 5.06 (1H, t, Glc, $^3J_{\text{H-H}} = 9.1$ Hz), 4.83 (1H, t, Glc, $^3J_{\text{H-H}} = 11.0$ Hz), 4.90–4.70 (2H, m, N-CH₂), 4.43 (1H, ddd, 5-Glc, $^3J_{\text{H-H}} = 8.9$ Hz, $^3J_{\text{H-H}} = 5.4$ Hz, $^3J_{\text{H-H}} = 2.1$ Hz), 4.19 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 13.8$ Hz, $^3J_{\text{H-H}} = 7.0$ Hz), 4.18–4.09 (2H, m, N-CH₂; 1H, m, 2-(CH₂)₂), 4.07 (1H, dd, 6-Glc, $^2J_{\text{H-H}} = 12.2$ Hz, $^3J_{\text{H-H}} = 2.1$ Hz), 3.97 (1H, d, 6-Glc, $^3J_{\text{H-H}} = 12.4$ Hz), 3.91 (1H, d, 6-Glc, $^3J_{\text{H-H}} = 12.4$ Hz), 2.40–2.30 (1H, m, 2-(CH₂)₂), 2.02 (3H, s, OAc), 2.01 (3H, s, OAc), 1.99 (3H, s, OAc), 1.96 (6H, s, OAc), 1.944 (3H, s, OAc), 1.940 (3H, s, OAc), 1.90 (3H, s, OAc), –1.73 (1H, s, SH), –1.74 (1H, s, SH).

Elucidation of catalytic ability of the complexes for

Suzuki-Miyaura cross-coupling in water. A mixture of Pd complex **1-C2** or **1-C3**, aryl halide (0.2 mmol), phenylboronic acid (0.3 mmol), and potassium carbonate (0.4 mmol) in water (1 mL) was heated at 100 °C in a sealed tube. After a certain period, the reaction mixture was allowed to cool at room temperature and then extracted with dichloromethane (3 × 1 mL). The separated organic layer was dried with magnesium sulfate. After the solids were filtered off, the solvent of the filtrate was removed under reduced pressure. The yields of the coupling product were determined from integrated intensities of the signals in ¹H NMR spectra (Figure S2-S5 and S10-S17, Supporting Information) using 1,3,5-trimethoxybenzene as an internal standard. For detail, see Table S2 and S4 in Supporting Information.

Suzuki-Miyaura cross-coupling in water using recycled catalysts. After the first catalytic coupling reaction as mentioned above, 4'-bromoacetophenone (0.2 mmol) and phenylboronic acid (0.3 mmol) were added to the separated aqueous phase. The mixture was heated at 100 °C for 45 min. After cooling, the reaction mixture was extracted with dichloromethane (3 × 1 mL). The separated organic layer was dried with magnesium sulfate. After removal of the solids by filtration, the solvent of the filtrate was evaporated under reduced pressure. The yields of the product were determined from integrated intensities of ¹H NMR signals (Figure S6-S9, Supporting Information) using 1,3,5-trimethoxybenzene as an internal standard. The same procedure was repeated twice to evaluate the reuse of the catalysts. For detail, see Table S3 in Supporting Information.

Variable temperature ¹H NMR spectroscopy and line shape analyses. ¹H NMR spectra for the complexes in DMSO-*d*₆ at variable temperatures were obtained using a Bruker AVANCE 300 FT-NMR spectrometer. For lineshape analyses, ¹H NMR signals with various kinetic constants were simulated using a NMR simulation program in the NMRV4 program package.¹⁵ Activation parameters for the complexes were calculated using the obtained kinetic constants for various temperatures using the Microsoft Excel software.

X-ray crystallography. Crystallographic analysis was performed for the chloro complex **1-C3**. A single crystal was mounted on a loop using Pantone-N. Diffraction data were collected at 193(1) K on an VariMax Saturn diffractometer with graphite-monochromated Mo-*K*α radiation (λ = 0.7107 Å) using a rotation method. The data were integrated, scaled, sorted and averages using the CrystalClear¹⁶ software. Absorption corrections were applied using the multi-scan method. The structures were solved using SIR97¹⁷ expanded using Fourier techniques, and refined by using full matrix least-squares against *F*² with SHELXL97¹⁸ equipped in a CrystalStructure¹⁹ software. Crystallographic data are summarized in Table S1 in the Supporting Information. All hydrogen atoms except for the protons of the water molecule, which was disordered, were located at the calculated positions and refined as riding models. Full details for the analysis were documented in the CIF, which was deposited with the Cambridge Crystallographic Data Centre under CCDC 1535976.

Supporting Information

Crystallographic data for **1-C3**, detail of catalytic reactions, and deprotected reactions of **1-C2** and **1-C3**. This material is available electronically on J-STAGE.

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