Development of palladium complexes bearing multidentate N-heterocyclic carbene ligands with sugar units and their application in catalysis in cross-coupling reactions in water

（糖修飾多座 N-ヘテロ環カルベンパラジウム錯体の合成と水中での鈴木−宮浦カップリング反応の研究）

理学研究科

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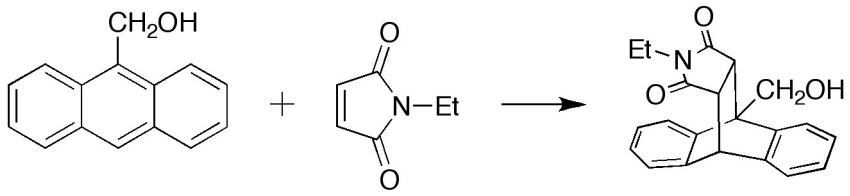
1. Introduction

1-1. Organic Reaction in Aqueous Media

Catalysts for organic reactions in water have been studied concerning development of environmentally friendly chemical processes because water is a nontoxic and unexplosive liquid.[1] Using water as a solvent for organic syntheses leads to some advantages for separation of products and reuse of homogeneous catalysts. Using water as a solvent provides special environment for substrates by the hydrophobic effect.[2] For the Diels-Alder reaction between anthracene-9-carbinol and N-ethylmaleimide, the second-order rate constant in water was two orders of magnitude larger than those in organic solvents (Scheme 1-1).[2b]



$k_2 / (10^{-5}\ M^{-1}\ s^{-1}) =$ { 796 ± 71 (isooctane); 666 ± 23 (1-butanol); 344 ± 25 (methanol); 107 ± 8 (CH_3CN); 22600 ± 700 (water) }

Scheme 1-1. Hydrophobic acceleration of Diels-Alder reactions in water

Water-soluble transition-metal catalysts are applied for a variety of organic reactions. For example, the Suzuki-Miyaura cross-coupling reactions between arylboronic acids and aryl halides were widely studied.[3] This reaction is one of the most widely used protocols for the formation of carbon-carbon bonds, due to the good tolerance of various functional groups and easy handling. The reactions are generally catalyzed by palladium complexes with supporting ligands such as phosphorus ligands.

In order to conduct the reaction in aqueous media, water-soluble moieties, such as carboxylates, sulfonates, ammonium ions, and sugar groups were incorporated into ligands of complexes. The Suzuki-Miyaura cross-coupling reaction in neat water is applicable for the reaction on a protein surface.[4] Covalent modification of biomolecules, such as proteins and peptides, by catalytic reactions is one of promising approaches in the field of bioengineering. For this purpose, catalysts that operate in neat water are necessary for avoiding undesirable denaturation of the biomolecules by organic solvents, and for *in vivo* applications.

1-2. N-Heterocyclic Carbene Ligands

After the first application of a palladium complex containing an N-heterocyclic carbene (NHC) ligand to catalysis,[5] NHC ligands have been often utilized as a spectator ligand of a transition-metal catalyst due to their strong ligation ability and strong σ-donating ability.[6] Many palladium and ruthenium complexes with NHC ligands effectively catalyze C-C coupling reactions[6c] and olefin metathesis,[6d] respectively. In C-C coupling reactions, strong σ-donating ability of NHC ligands activates a zerovalent palladium center toward oxidative addition of organic halides. Furthermore, N-substituents of NHC ligands can be readily modified in order to modulate electronic and steric character of the ligands. For example, hydrophilic moieties such as carboxylate, sulfonate, ammonium, alcohol, and ether functionalities were incorporated for the purpose of aqueous application of their metal complexes.[7]

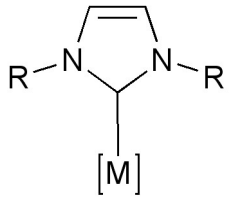
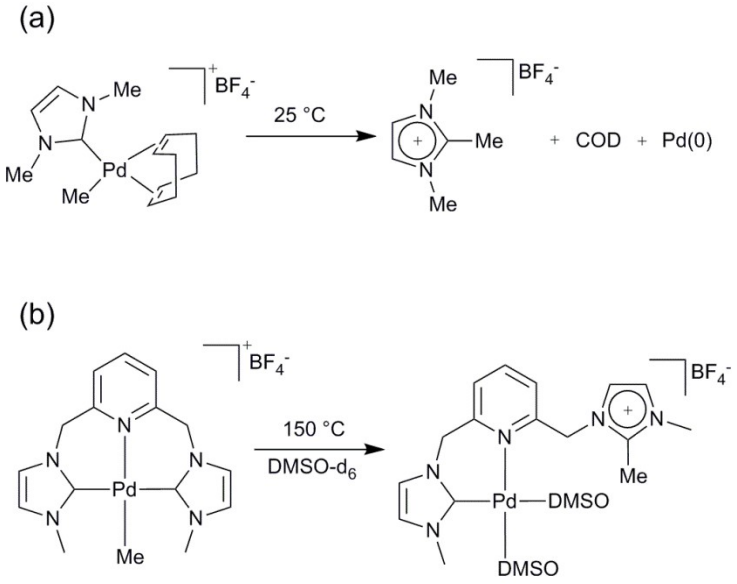


Figure 1-1. N-heterocyclic carbene complex

The multidentated ligands constituted of more than two NHC units were also synthesized, not only for stabilization of their metal complexes, but also for tuning of topological properties such as steric hindrance, chirality, and fluxional behaviors.[8] One of the most remarkable features of such multidentate NHC ligands is highly stabilizing their metal complexes. In some cases, NHC complexes exhibit decomposition via reductive elimination reactions, displacement by other ligands, and C-H and C-C insertions.[9] Relative to metal complexes with monodentate NHC ligands, those with

chelating NHC ligands hardly decompose via these decomposition processes.[10] A cationic palladium methyl complex with monodentate NHC and cyclooctadiene (cod) ligands underwent immediate reductive elimination at room temperature generating a 1,2,3-trimethyl-imidazolium salt and free cod accompanied by the formation of palladium metal (Scheme 1-2(a)).[11] For the counterpart with a tridentate pincer ligand, which is composed of two NHCs connected with a pyridine donor, heating at 150 ºC for 15-18 hours in DMSO-d_6 is required for completely removal of the methyl group from the Pd center (Scheme 1-2(b)).[12] This fact is attributed to the restricted geometries of the chelated NHC ligands, which are not suitable for reductive elimination with overlap of the relevant molecular orbitals. In addition, chelated NHC ligands allow direct control of geometries of their complexes.



Scheme 1-2. Decomposition pathway for palladium methyl complexes with (a) a monodentate NHC ligand, and (b) a tridentate ligand.

Chapter 2. Synthesis, Structure, and Dynamic Behavior of Palladium Complexes Containing Multidentate N-Heterocyclic Carbene Ligands with Sugar Units

2-1. Introduction

Sugar is one of the most available bio-resources in nature and has many advanced properties such as chirality, water-solubility, steric bulk, and stereochemical diversity. Incorporation of sugar units into metal complexes gives them some advanced features such as high water-solubility and molecular recognition abilities, which are utilized for sustainable catalysts,[13] sensors,[14] and drug delivery system.[15] Many researchers have reported syntheses of metal complexes containing sugar units and their application to catalysis. For example, a rhodium complex bearing an α,α-trehalose-derived phosphine-phosphinite ligand was reported as a catalyst for enantioselective hydrogenation of enamides in aqueous media.[13g] This example suggests that sugars are the promising building blocks of catalysts.

NHC complexes bearing sugar units as N-substituents also have been studied.[16] An iridium complex bearing a sugar-incorporated NHC ligand catalyzed H/D exchange reactions of 2-propanol and cyclohexanol in D_2O in the presence of AgOTf.[16a] In addition, a Ru complex with a sugar-containing NHC ligand was reported as a catalyst for asymmetric ring-opening cross-metathesis (AROCM), despite the modest levels of enantioselectivity.[32] Suzuki-Miyaura coupling reaction in water have been also achieved by a metal complex catalyst with a water-soluble sugar unit.[16d]

Use of multidentate NHC ligand is a promising approach for structural control of their metal complexes.[17] However, to the best of my knowledge, metal complexes with a multidentate NHC ligand bearing a sugar unit have not been reported, except for

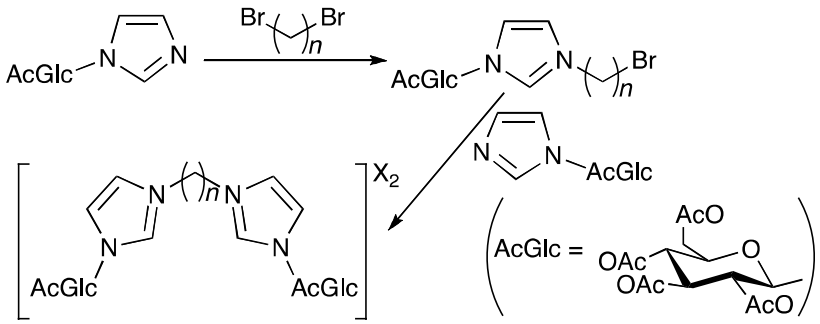
rhodium and iridium complexes having NHC ligands with picolyl group and acetyl-protected D-glucopyranosyl unit reported from our research group.[16h] In the previous report, *S* and *R* configurations of chiral-at-metal Ir(III) and Rh(III) complexes were selectively obtained by using chelate-type NHC ligands with α- and β-glucopyranosyl units, respectively.

In this chapter, the sugar units were introduced into bidentate or tridentate NHC ligands in palladium complexes, in order to prepare complexes soluble in water and to control their whole structures.

2-2. Sugar-Incorporated Bis-NHC 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) ([(bisNHC-C2)H_2](PF_6)$_2$) and 1,1'-bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3,3'-propylene-diimidazolium bis(hexafluorophosphate) ([(bisNHC-C3)H_2](PF_6)$_2$) were synthesized in two steps (Scheme 2-1) because isolation of the ligand precursors from the reaction mixture containing 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1H-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. Direct metallation reactions of the ligand precursors with [Pd($NCCH_3$)$_2$$Cl_2$] in the presence of NaOAc in DMSO afforded palladium complexes [Pd(bisNHC-C*n*)X_2] (n = 2,3; X = halide, acetate, or coordinating solvent molecule). Electrospray mass spectrometry (ESI-MS) of the complexes showed signals for [Pd(bisNHC-C*n*)(OAc)]$^+$ exhibiting the coordination of the bisNHC ligands to the palladium ions. These complexes gave broad signals in the ^{1}H NMR spectra due to substitution equilibrium of

the terminal ligands and the signals became sharp by the addition of excess tetraethylammonium chloride or sodium hydrosulfide owing to tightly coordinating nature of sulfur atoms to a palladium ion.



Scheme 2-1. Syntheses of ligand precursors.

Chloride complexes [Pd(bisNHC-C*n*)Cl_2] (n = 2, 3) were obtained by treating the [Pd(bisNHC-C*n*)X_2] complexes with tetraethylammonium chloride in $CHCl_3$. Single crystal X-ray diffraction study of [Pd(bisNHC-C3)Cl_2] (Figure 2-1) 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 is reduced to C_1 by incorporation of the chiral AcGlc groups. The bond lengths and angles around the Pd center in complex [Pd(bisNHC-C3)Cl_2] are similar to the corresponding bisNHC Pd complex with methyl N-substituents (Table 2-1). The ^{1}H NMR spectrum for each chloro complex showed two sets of signals for the AcGlc-NHC moieties, reflecting the C_1 symmetry of the complexes.

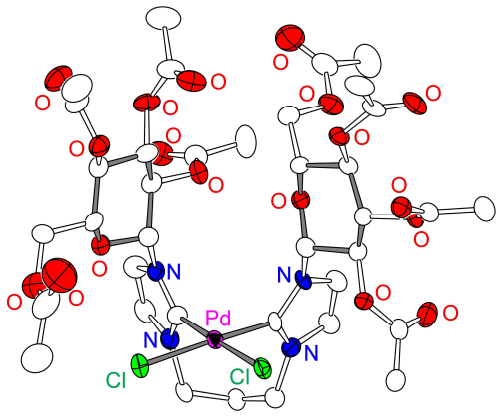


Figure 2-1. ORTEP drawing of one of the crystallographically independent molecules of [Pd(bisNHC-C3)Cl_2] with 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2-1. Selected bond lengths and angles for [Pd(bisNHC-C3)Cl_2].

	[Pd(bisNHC-C3)Cl_2][a]		Me complex [b]
Pd–Cl	2.378(3) Å 2.382(3) Å	2.370(3) Å 2.381(3) Å	2.3547(8) Å 2.3615(8) Å
Pd–C	1.99(1) Å 2.003(16) Å	2.01(1) Å 2.039(9) Å	1.969(3) 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)° 91.1(3) ° 172.3(3)° 178.0(3)°	88.3(3)° 91.0(3)° 173.4(3)° 177.3(3)°	88.8(8)° 90.9(2)° 176.2(1) ° 176.2(1)°

[a] Two crystallographically independent molecules were observed. [b] Obtained from reference 18.

Corresponding bishydrosulfido complexes ([Pd(bisNHC-C2)$(SH)_2$] and [Pd(bisNHC-C3)$(SH)_2$]) were prepared by the addition of sodium hydrosulfide to solutions of [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] in DMSO-d_6. Because the bishydrosulfido complexes should have a similar structure of [Pd(bisNHC-C3)Cl_2], two hydrosulfido ligands in each complex are inequivalent and two singlet signals appeared between –1.5 and –2.1 ppm in the ^{1}H NMR spectra. These SH signals should be affected by the surrounding chiral glucopyranosyl groups. This means that we can obtain the information about the environment around the coordination sites, which are used for catalytic reactions. Chelating bisNHC ligands in the palladium complexes showed flapping wing motion. The dynamic behavior of the bisNHC ligands in the complexes could affect the selectivity of products and catalytic ability in coupling reactions using the complexes as catalysts. For these reasons, variable temperature ^{1}H NMR (VT-NMR) spectroscopy and line shape analyses of the SH signals were performed for [Pd(bisNHC-C2)$(SH)_2$] and [Pd(bisNHC-C3)$(SH)_2$]. For comparison, VT-NMR measurements were also applied for the corresponding platinum complexes [Pt(bisNHC-C2)$(SH)_2$] and [Pt(bisNHC-C3)$(SH)_2$].

^{1}H NMR spectra of the complexes with the bisNHC-C2 ligand, [Pd(bisNHC-C2)$(SH)_2$] and [Pt(bisNHC-C2)$(SH)_2$], at 298–353 K exhibited no dynamic behavior attributed to the flapping wing motion. The {Pd(bisNHC)} unit with methyl N-substituents in a trinuclear complex $[(MCp^*)_2\{Pd(bisNHC)\}(\mu_3\text{-}S)_2]^{2+}$ showed dynamics of the bisNHC ligand via Pd–C bond cleavage at higher temperature than 372 K.[19a] For [Pd(bisNHC-C2)$(SH)_2$] and [Pt(bisNHC-C2)$(SH)_2$], two signals of the SH protons for each complex showed different temperature dependency in their chemical shifts (Figure 2-2). The signals of the SH protons shifted to downfield as

temperature increased and the rate of the shifts are different. This result suggests that rotation or vibration of the acetyl-protected glucopyranosyl groups in each complex with the fixed conformation of the bisNHC-C2 ligand affords different contribution to the environment around the coordination sites.

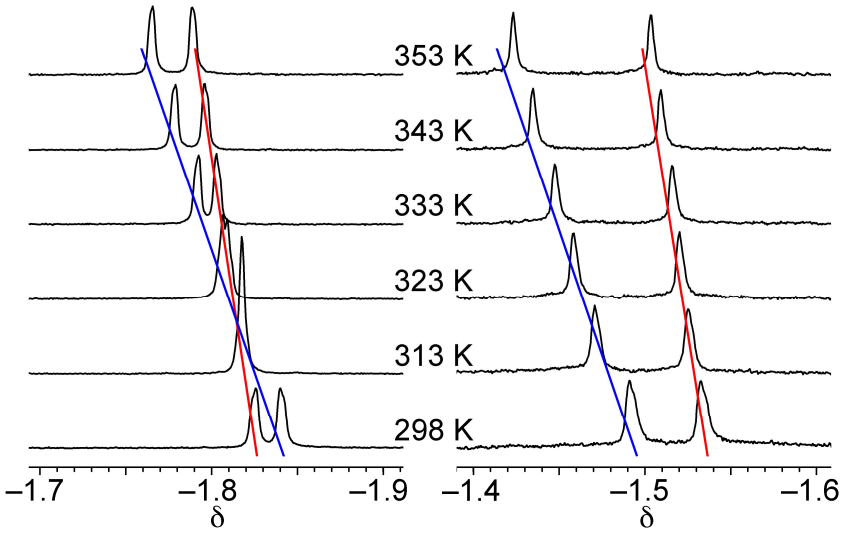


Figure 2-2. Temperature dependency of chemical shifts for SH protons in Pd complex ([Pd(bisNHC-C2)$(SH)_2$], left) and Pt complex ([Pt(bisNHC-C2)$(SH)_2$], right).

On the other hand, Pd and Pt complexes with the bisNHC containing the propylene bridge, [Pd(bisNHC-C3)$(SH)_2$] and [Pd(bisNHC-C3)$(SH)_2$], respectively, showed dynamic behavior attributed to the flapping wing motion (Figure 2-3). Activation parameters (Table 2-2) obtained from the Eyring plots (Figure 2-4) for [Pd(bisNHC-C3)$(SH)_2$] and [Pt(bisNHC-C3)$(SH)_2$] are very similar even they have different metal centers. These parameters are comparable to those reported for the Pd- or Pt-bisNHC units in trinuclear complexes.

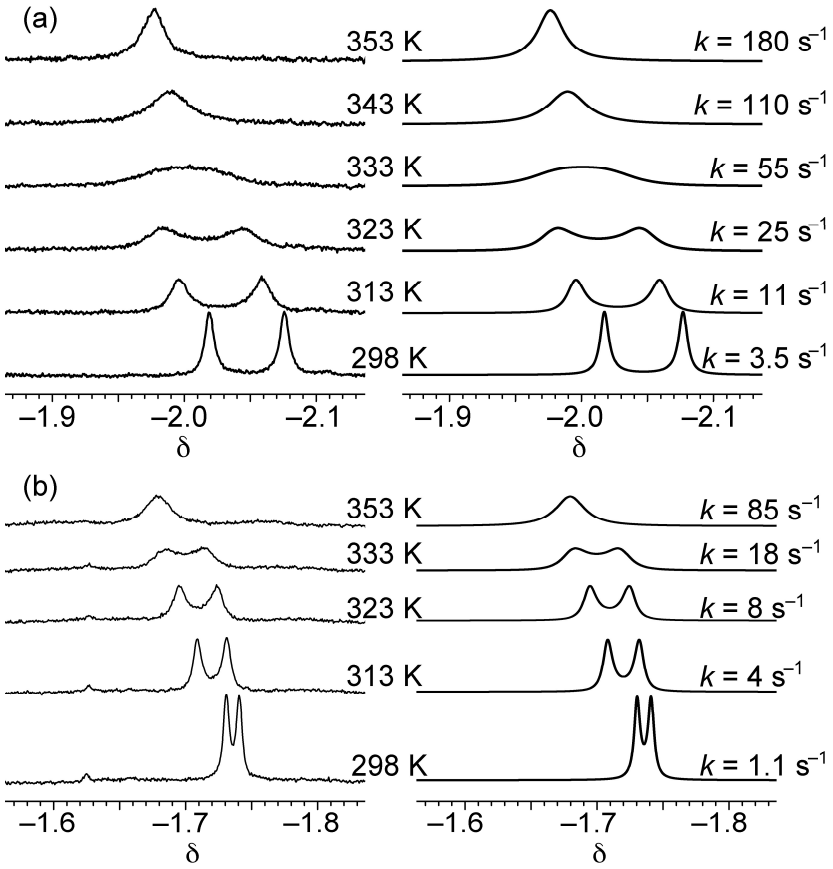


Figure 2-3 Observed (left) and simulated (right) ^{1}H NMR signals of SH protons in (a) [Pd(bisNHC-C3)(SH)$_2$] and (b) [Pt(bisNHC-C3)(SH)$_2$].

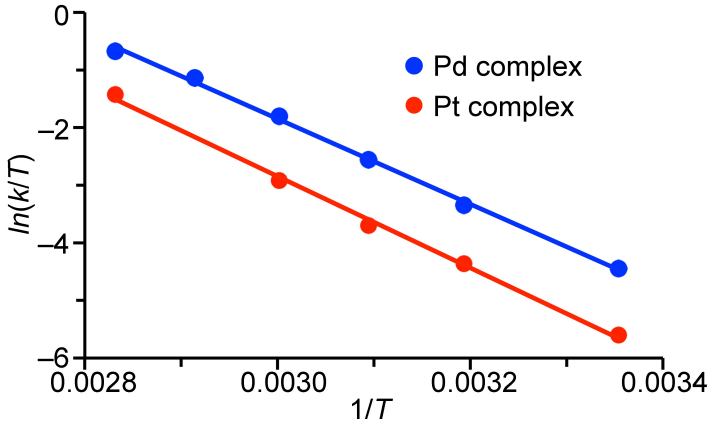


Figure 2-4 Eyring plots for [M(bisNHC-C3)(SH)$_2$] (M = Pd, Pt) using kinetic constants obtained from line shape analyses.

Table 2-2 Activation parameters for dynamic behaviour of [M(bisNHC-C3)$(SH)_2$].[a]

	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{298K}$ (kJ mol^{-1})
Pd complex	62(1)	–28 (4)	70 (2)
Pt complex	66(3)	–23 (6)	73 (3)

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

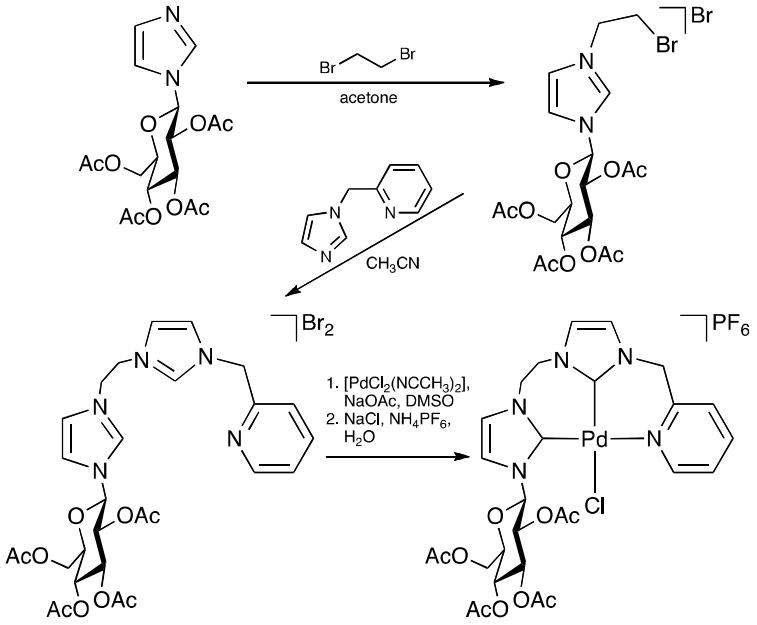
These results suggest that the complexes with the ethylene-bridged bisNHC ligands have more rigid frameworks to place their N-substituents in a limited area around the metal center, while the propylene-bridged bisNHC ligands are flexible to allow the N-substituents moving. This fact implies that higher 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 the temperature dependency of the chemical shifts of the SH protons.

2-3. Palladium Complexes with Sugar-Incorporated C-N-C or C-C-N Pincer Ligand Containing Two NHC Units and One Pyridyl Unit

As well as the bidentate NHC ligands, pincer ligands containing two NHC units have been developed to stabilize their metal complexes and to control the coordination geometry. In this section, palladium complexes having sugar-incorporated C-N-C or C-C-N pincer ligand constituted of two NHC units and one pyridine unit.

The C-C-N ligand precursor containing bis-imidazolium bearing a pyridyl group and an acetyl-protected β-D-glucopyranosyl unit as N-substituents

([(CCN-AcGlc)H_2]Br_2) was used to prepare a C-C-N pincer palladium complex [Pd(CCN-AcGlc)Cl](PF_6) via the direct metallation method using NaOAc as a base in 10% yield after purification (Scheme 2-2). The structure of [Pd(CCN-AcGlc)Cl](PF_6) in the solid state was analyzed by using X-ray crystallography (Figure 2-5). The distance between the Pd and pyridine N atoms (2.109(3) Å) is significantly longer than those found in an N-C-N Pd complex having a pincer ligand constituted of a central NHC unit with two 2-picolyl groups as N-substituents of the central NHC unit (2.047(4) and 2.058(4) Å).[20] This elongation observed in [Pd(CCN-AcGlc)Cl](PF_6) is attributed to *trans*-influence of the terminal NHC moiety. The C-C-N pincer ligand is twisted by coordination and then there are two possible *P*- and *M*-isomers, which are not enantiomers but diastereomers due to the chiral D-glucopyranosyl unit. In the crystal, only the *P*-isomer was observed (Figure 2-5(b)). On the other hand, the ^{1}H NMR spectrum of [Pd(CCN-AcGlc)Cl](PF_6) in acetone-d_6 (Figure 2-6) showed small signals corresponding to the other isomer. Ratios of the two isomers varied between 3.4:1 (in CH_3OH) and 10:1 (in acetone) depending on solvents (Figure 2-7). DFT calculations suggested that the *P*-isomer is more stable thermodynamically than the *M*-isomer is (Figure 2-8). The solid-state structure obtained from crystallography is also of the *P*-isomer, although the orientations of the acetyl-protected groups in the D-glucopyranosyl unit were different from those obtained by using DFT calculations. These results imply that the *P*-isomer is dominant in solution, and the *P*- and *M*-isomers are in equilibrium.



Scheme 2-2. Synthesis of [Pd(CCN-AcGlc)Cl](PF$_6$).

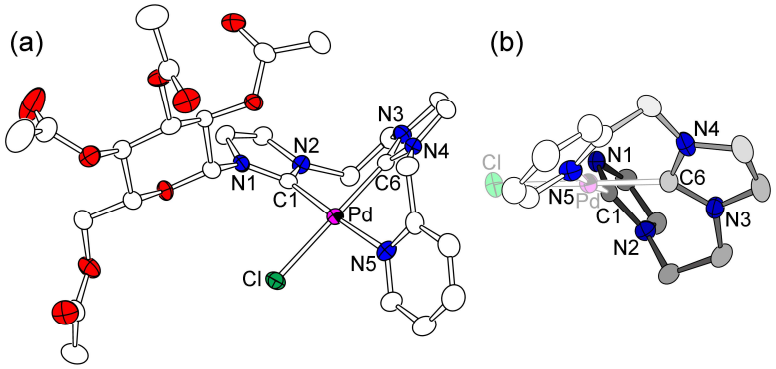


Figure 2-5. (a) Structure of the cationic part of [Pd(CCN-AcGlc)Cl](PF$_6$) with 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. (b) Side view of the cationic part of [Pd(CCN-AcGlc)Cl](PF$_6$). The acetyl-protected β-D-glucopyranosyl unit is also omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–Cl, 2.3388(9); Pd–N5, 2.109(3); Pd–C1, 1.981(3); Pd–C6, 1.987(4); Cl–Pd–N5, 91.99(9); Cl–Pd–C1, 90.58(10); Cl–Pd–C6, 179.54(10); N5–Pd–C1, 176.80(12); N5–Pd–C6, 87.83(13); C1–Pd–C6, 89.58(14).

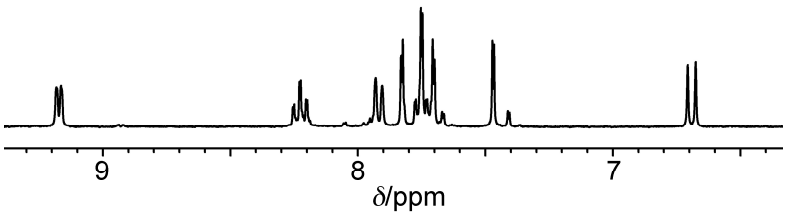


Figure. 2-6 ^{1}H NMR spectrum of [Pd(CCN-AcGlc)Cl](PF$_6$) in acetone-d_6.

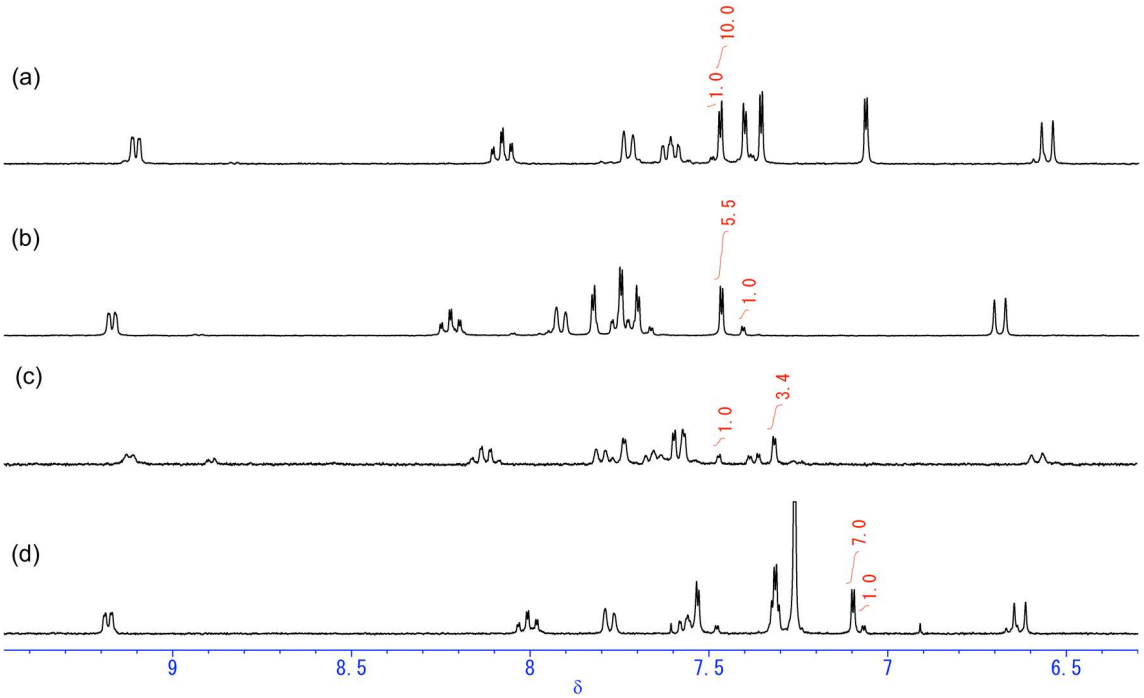


Figure 2-7. ^{1}H NMR spectra for C-C-N complex [Pd(CCN-AcGlc)Cl](PF$_6$) in (a) CD_3CN (b) acetone-d_6 (c) CD_3OD, and (d) $CDCl_3$ (300 MHz).

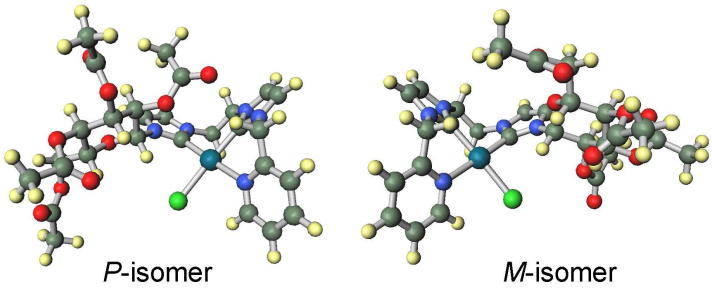
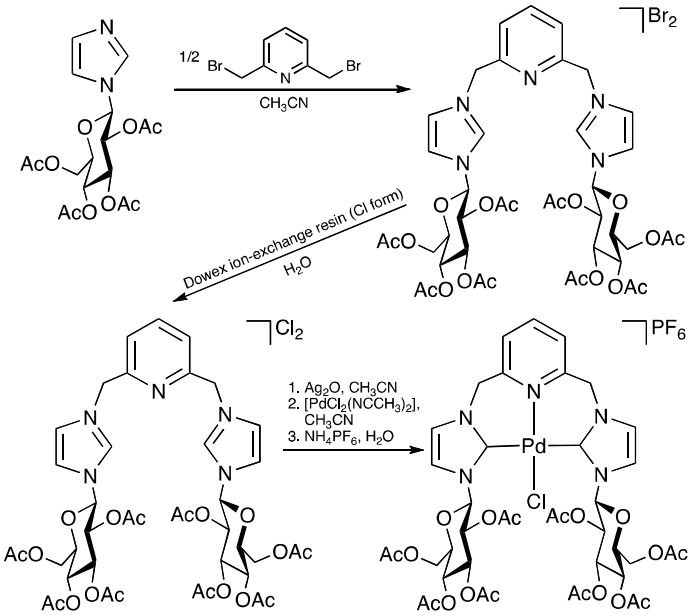


Figure 2-8. Optimized structures of *P*- and *M*-isomers of $[Pd(CCN\text{-}AcGlc)Cl]^+$.

A C-N-C pincer palladium complex, $[Pd(CNC\text{-}AcGlc)Cl](PF_6)$, was synthesized via a carbene transfer method[21] using $[PdCl_2(NCCH_3)_2]$ and a corresponding silver complex, which was prepared by the reaction of the C-N-C ligand precursor with Ag_2O (Scheme 3-3). Several palladium complexes with the same N-C-N pincer ligand framework with different N-substituents were reported and they exhibit dynamic behavior in solution attributed to the inversion of the axial chirality between *P*- and *M*-enantiomers due to the flapping motion of the methylene bridging parts of the twisted pincer ligands.[22] In the case of $[Pd(CNC\text{-}AcGlc)Cl](PF_6)$, there are two possible diastereomers attributed to the twist of the ligand and the chiral D-glucopyranosyl units similar to the C-C-N complex $[Pd(CCN\text{-}AcGlc)Cl](PF_6)$. Results of DFT calculations show that the *P*-diastereomer of $[Pd(CNC\text{-}AcGlc)Cl](PF_6)$ is thermodynamically more stable than the *M*-diastereomer is. The difference in the Gibbs free energies between the diastereomers with the optimized structures (Figure 2-9) was 4.9 kJ mol^{-1}, suggesting that the diastereomers exist in ca. 7:1 ratio in solution when they are in equilibrium. However, the ^1H NMR spectrum of $[Pd(CNC\text{-}AcGlc)Cl](PF_6)$ exhibited only one set of signals for the pincer ligand (Figure 2-10) and two sharp signals with geminal coupling for the protons of the methylene bridges. Thus, only one of the diastereomers selectively

forms, and no isomerization occurs. Our group has reported the kinetically selective formation of an iridium complex having an NHC ligand with picolyl and acetyl-protected D-glucopyranosyl units in carbene transfer reaction using a corresponding silver complex.[16i] Although isomerization was observed for the iridium complex, the two bulky acetyl-protected D-glucopyranosyl units in [Pd(CNC-AcGlc)Cl](PF$_6$) inhibited isomerization.



Scheme 3-3. Synthesis of [Pd(CNC-AcGlc)Cl](PF$_6$).

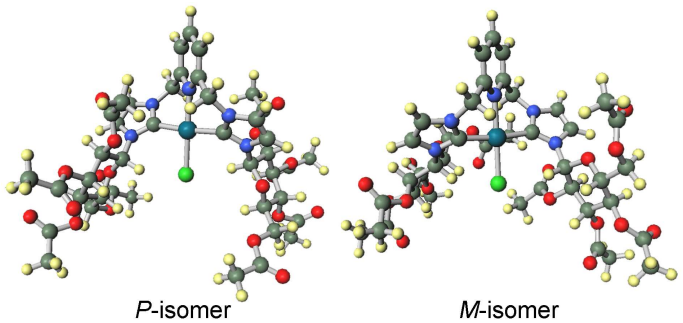


Figure 2-9. Optimized structures of *P*- and *M*-diastereomers of [Pd(CNC-AcGlc)Cl]$^+$.

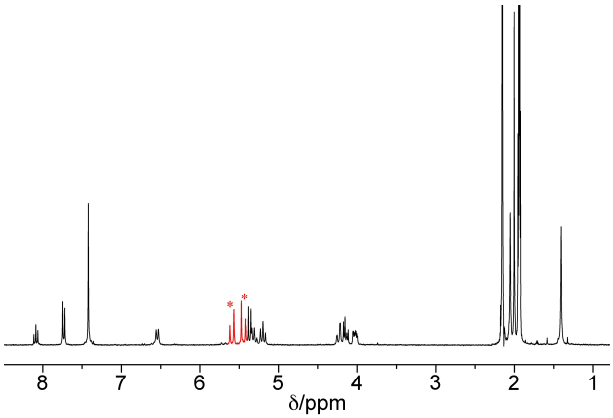
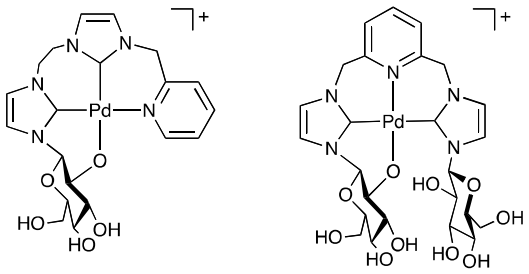


Figure 2-10. ^{1}H NMR spectrum of [Pd(CNC-AcGlc)Cl](PF$_6$) in CD$_3$CN. The asterisks (*) represent the signals for the protons of the methylene bridges.

The acetyl-protected groups in the pincer ligands of the complexes were removed in order to obtain highly water-soluble complexes. Although the deprotected complexes could not be isolated, the ^{1}H NMR and mass spectra clearly showed the deprotection of the complexes. The reaction of [Pd(CCN-AcGlc)Cl](PF$_6$) with potassium carbonate in CH$_3$OH at room temperature afforded the deprotected C-C-N complex, whose ^{1}H NMR spectrum showed one set of signals for the C-C-N ligand framework and the unprotected D-glucopyranosyl unit. The signal for the anomeric proton appeared at the higher magnetic field (ca. 5 ppm). In the ESI mass spectrum for the deprotected C-C-N complex (Figure 2-12(a)), signals corresponding to the monocation losing H^+ and Cl^- ions from $[Pd(CCN\text{-}Glc)Cl]^+$, which is obtained by simple replacement of the acetyl groups of $[Pd(CCN\text{-}AcGlc)Cl]^+$ with protons, were observed. Deprotection of [Pd(CNC-AcGlc)Cl](PF$_6$) was carried out using the same conditions for the C-C-N complex. In the ^{1}H NMR spectrum for deprotected [Pd(CNC-AcGlc)Cl](PF$_6$) (Figure 2-11(b)), two sets of the signals for imidazolylidene and D-glucopyranosyl moieties were observed. One of the signals for the anomeric

protons appeared at the higher magnetic field (ca. 5 ppm) than the other did (ca. 6 ppm). ESI mass spectrum of deprotected [Pd(CNC-AcGlc)Cl](PF$_6$) also exhibited signals for a monocation losing H^+ and Cl^- ions from the complex having two D-glucopyranosyl units with a C_2 axis, $[PdCl(CNC\text{-}Glc)]^+$ were observed (Figure 2-12(c)). These results suggest that one of the OH groups in the D-glucopyranosyl unit of each deprotected complex coordinates to the metal center as the deprotonated form (Scheme 2-4). The coordination of the D-glucopyranosyl unit in the deprotected C-C-N complex and one of those in the deprotected C-N-C complex brings their ^{1}H NMR signals appearing at the higher magnetic field. From the results of the DFT calculations for the glucopyranosyl-coordinated complexes and uncoordinated complexes, the signals for the anomeric protons of the coordinated D-glucopyranosyl units appear around 5 ppm and those of the uncoordinated ones appear around 7 ppm. These results support the coordination of the D-glucopyranosyl units during the deprotection reactions. The stability of the deprotected C-C-N and C-N-C complexes in CD_3OD were evaluated by using ^{1}H NMR spectroscopy. The deprotected C-N-C complex decomposed slowly to unidentified products in a few weeks at room temperature, during which time a light-yellow precipitate formed. On the other hand, decomposition of the deprotected C-C-N complex in CD_3OD at room temperature was not observed. The difference in stability is attributed to the strong *trans*-influence from each NHC units to the other in [Pd(CNC-Glc)Cl](PF$_6$), due to the strong σ-donating ability of the NHC ligands. Furthermore, a protic solvent promotes irreversible dissociation of the NHC moieties via protonation.



Scheme 2-4. Proposed structures of deprotected C-C-N and C-N-C complexes.

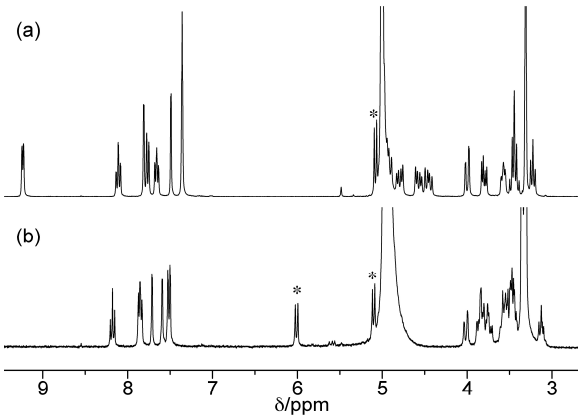


Figure 2-11. ^{1}H NMR spectra in CD_3OD of deprotected (a) C-C-N and (b) C-N-C. The asterisks (*) represent the signals for the anomeric protons.

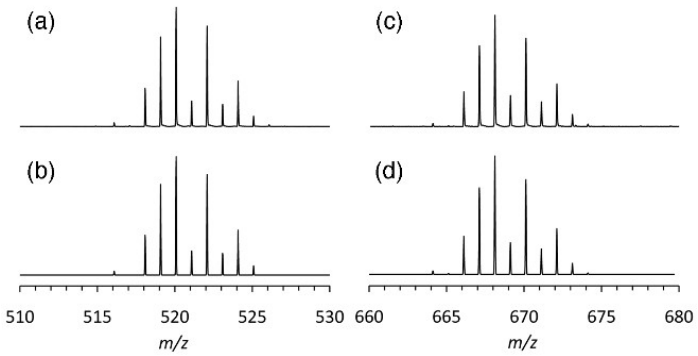
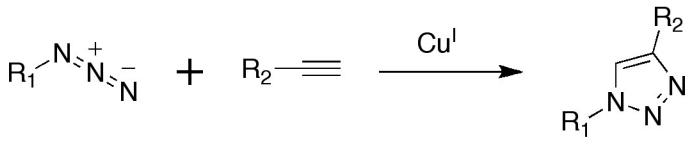


Figure 2-12. (a) Observed and (b) simulated ESI-mass spectra in CH_3OH for [Pd(CCN-Glc)Cl](PF_6) minus Cl^- and H^+ and (c) observed and (d) simulated spectra for [Pd(CNC-Glc)Cl](PF_6) minus Cl^- and H^+.

2-4. Incorporation of Sugar Units Using the Click Chemistry

In this section, “click chemistry” was utilized for the incorporation of a D-glucopyranosyl unit into bisNHC units to generate a C-C-N pincer ligand. A representative example of the click chemistry is the Cu-catalyzed azide-alkyne cycloaddition, known as the Huisgen reaction (Scheme 2-5). It is widely used in many different areas of chemistry, due to their wide substrate scope and easy handling. The Huisgen reaction can be used for general preparation of many kinds of sugar-incorporated metal complexes, because a variety of sugar-azides are avalable.[23]



Scheme 2-5. The Huisgen reaction

An important point for ligand design is the coordination ability of 1,2,3-triazole moiety generated by the Huisgen reaction. Coordination through N(3) and N(2) of 1,2,3-triazole was reported (Figure 2-13), and N(3) is a better donor than N(2) is.[24] In this section, incorporation of a sugar unit into C-C-N pincer Pd complexes using the “click to chelate” approach and its dynamic behavior in solution were described.

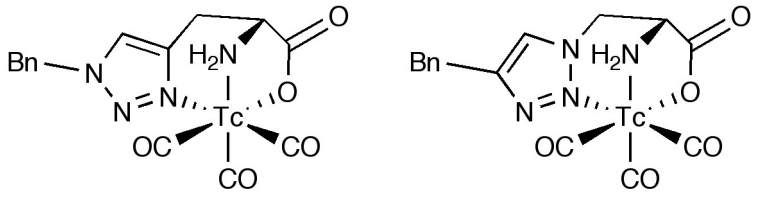
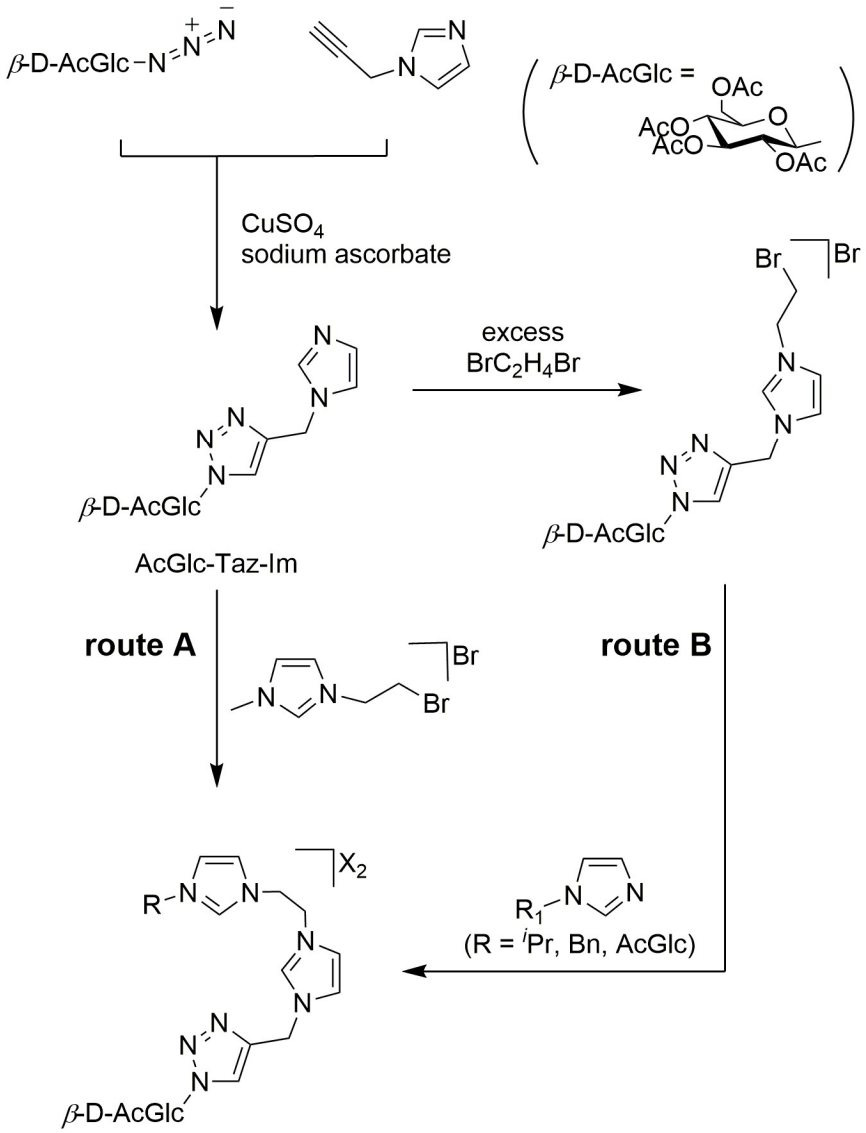


Figure 2-13. Complexes with a 1,2,3-triazole ligand coordinating through N(3) and N(2)

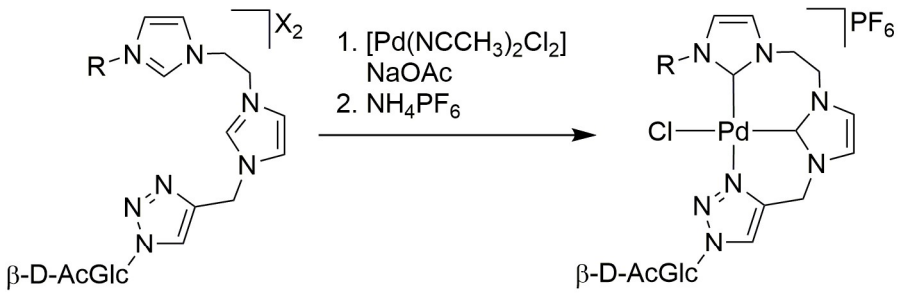
A series of the C-C-N pincer complexes were prepared using bis-imidazolium salts bearing sugar triazolyl units as ligand precursors. The ligand precursors were synthesized via two synthetic routes (Scheme 2-6). The Huisgen reaction of tetra-*O*-acetyl-*β*-D-glucopyranosyl azide with 1-(prop-2-ynyl)-1*H*-imidazole afforded an N-substituted imidazole bearing a sugar triazolyl unit (AcGlc-Taz-Im). For the preparation of the ligand precursor possessing a methyl group ([(Taz-bisNHC-Me)H_2]Br_2), AcGlc-Taz-Im was reacted with imidazolylakyl bromide (route A). However, in some cases, preparation of imidazolylalkyl bromide by the reaction of N-substituted imidazole and 1,2-dibromoethane was not suitable, because the corresponding 1,2-diimidazolylethane was also obtained as a side product. For this reason, the other ligand precursor was prepared by another route (route B). AcGlc-Taz-Im was reacted with an excess amount of 1,2-dibromoethane, followed by the addition of the N-substituted imidazole derivative to afford the C-C-N pincer ligand precursors possessing isopropyl, benzyl, or sugar units ([(Taz-bisNHC-R)H_2]$(PF_6)_2$, R = ^{i}Pr, Bn, AcGlc, respectively).



Scheme 2-6. Preparation of the C-C-N pincer ligand precursors.

The reactions of the ligand precursors with $[Pd(NCCH_3)_2Cl_2]$ and NaOAc in dimethylsulfoxide (DMSO) afforded C-C-N pincer palladium complexes $[Pd(Taz\text{-}bisNHC\text{-}R)Cl](PF_6)$ (Scheme 2-7). These complexes were isolated as PF_6 salts.

These complexes were characterized by elemental analyses, electrospray (ESI) mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy.



[(Taz-bisNHC-Me)H_2]Br_2	[Pd(Taz-bisNHC-Me)Cl](PF_6)	: R = methyl
[(Taz-bisNHC-^{i}Pr)H_2](PF_6)$_2$	[Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6)	: R = isopropyl
[(Taz-bisNHC-Bn)H_2](PF_6)$_2$	[Pd(Taz-bisNHC-Bn)Cl](PF_6)	: R = benzyl
[(Taz-bisNHC-AcGlc)H_2](PF_6)$_2$	[Pd(Taz-bisNHC-AcGlc)Cl](PF_6)	: R = β-D-AcGlc

Scheme 2-7. Preparation of the C-C-N pincer Pd complexes.

Similar to the case for [Pd(CCN-Glc)Cl](PF_6) and [Pd(CNC-Glc)Cl](PF_6), complexes [Pd(Taz-bisNHC-R)Cl](PF_6) possibly adopt two diastereomeric structures derived from the combinations of the chiral D-glucopyranosyl group and the *P*- or *M*-helical framework of the tridentate ligands as shown in Figure 2-14. For [Pd(Taz-bisNHC-Me)Cl](PF_6), two sets of the ^{1}H NMR signals for the two diastereomers appeared in DMSO-d_6 and the ratio of the diastereomers was 1:1.3 (Figure 2-15(b)). Variable temperature (VT) ^{1}H NMR spectroscopy exhibited equilibrium between the diastereomers. The signals for the two diastereomers observed at room temperature were going to merge at higher temperatures and the averaged signals were observed at 150 °C (Figure 2-15(a)). Similar equilibrium between the two diastereomers was also observed for [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6). In previously reported Re complexes containing methylene- or ethylene-bridged bisNHC ligands

(Figure 2-16(a)), flipping motion was observed only for those with the methylene-bridged ligands.[19a] In previously reported trinuclear complexes containing a platinum moiety with bisNHC ligands having methylene- or ethylene-bridges (Figure 2-16(b)), a similar flipping motion was observed, except for those containing platinum moiety with the ethylene-bridged bisNHC ligand.[19b] In these cases, only the complexes with the methylene-bridged bisNHC ligand exhibited flipping motion, because simultaneous inversion of two CH_2 at the ethylene bridge is hard to occur. These examples imply that a similar flipping motion is allowed only for the methylene bridge between the triazole and NHC moieties but prohibited for the ethylene bridge between the two NHC moieties for [Pd(Taz-bisNHC-R)Cl](PF_6) (R = Me, ^{i}Pr). The inversion of the whole ligand-framework is prevented by this conformational restriction around the ethylene bridge, even if dissociation of the triazole moiety from the metal center occurs. Line shape analyses of the signals for the 5-H protons of the triazole groups in the VT-^{1}H NMR spectra afforded $\Delta S^{\ddagger}$ = –74(1) J•mol^{-1}•K^{-1} for [Pd(Taz-bisNHC-Me)Cl](PF_6), and –52(2) J•mol^{-1}•K^{-1} for [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) (Figures 2-18 − 2-21 and Table 2-3). These negative $\Delta S^{\ddagger}$ values suggest dissociation of one of the NHC moieties from the metal center and coordination of the solvent molecule.

Additionally, the ratio of the diastereomers of [Pd(Taz-bisNHC-Me)Cl](PF_6) in DMSO-d_6 afforded the small ΔG value (0.65 kJ•mol^{-1} at 298.15 K) between the diastereomers, due to the position of the D-glucopyranosyl moiety far from the metal center in the complex giving only small influence on the stability of the diastereomers. Replacement of the methyl group with the D-glucopyranosyl moiety on the terminal NHC unit leads a significant influence on the ratio of the diastereomers, though that of the achiral substituents affords less impact. From the ^{1}H NMR spectroscopy (Figure

2-22), the ratios of the diastereomers for [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$) or [Pd(Taz-bisNHC-Bn)Cl](PF$_6$) in CD_3CN are 1:1.4 or 1:1.3 respectively, which are similar to that for [Pd(Taz-bisNHC-Me)Cl](PF$_6$) in DMSO-d_6. In contrast, the ratio of the diastereomers for [Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$) in CD_3CN are 1:13.1, and the ΔG value of these diastereomers is 6.4 kJ•mol^{-1} at 298.15 K. The DFT calculations of the both diastereomers for [Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$) suggest that the *P*-isomer is more stable than the *M*-isomer is, and the ΔG value of these diastereomers is 27.2 kJ•mol^{-1} at 298.15 K. The large ΔG value of the diastereomers for [Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$) is attributed to the location of the chiral sugar unit near the metal center. This result suggests that the chiral nature of the sugar unit induces the helical chirality of the pincer ligand, which should be applicable to an asymmetric catalyst.

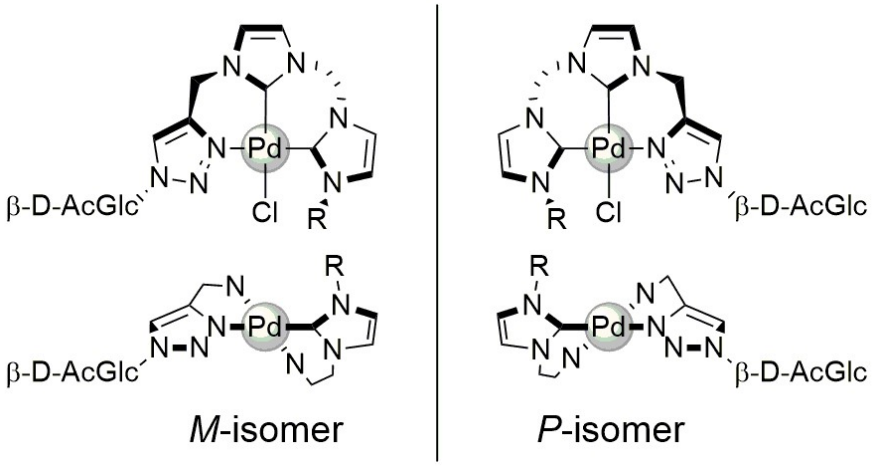


Figure 2-14. Top and side views of possible *P*- and *M*-isomers for each of Pd complexes [Pd(Taz-bisNHC-R)Cl](PF$_6$).

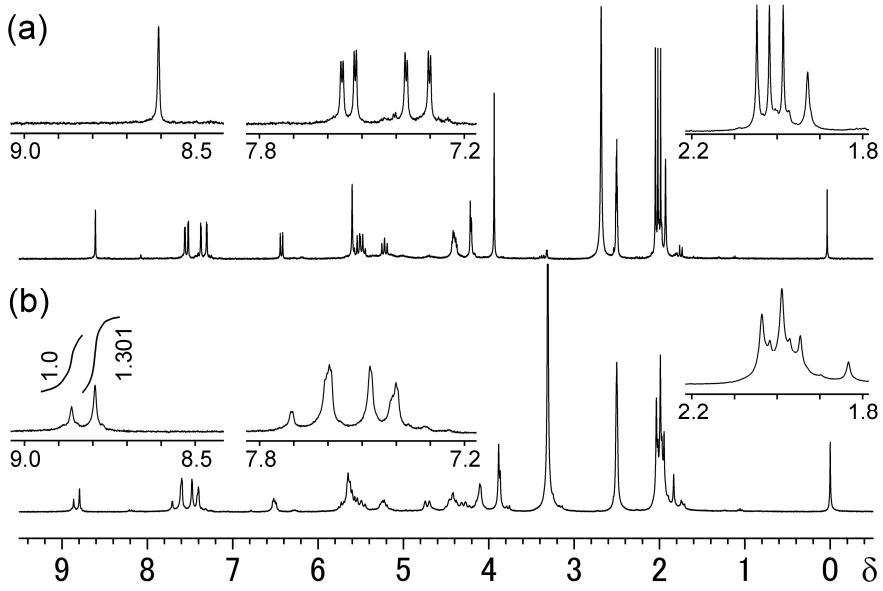


Figure 2-15. ^{1}H NMR spectra of complex [Pd(Taz-bisNHC-Me)Cl](PF$_6$) in DMSO-d_6 (a) at 150 °C and (b) at 25 °C.

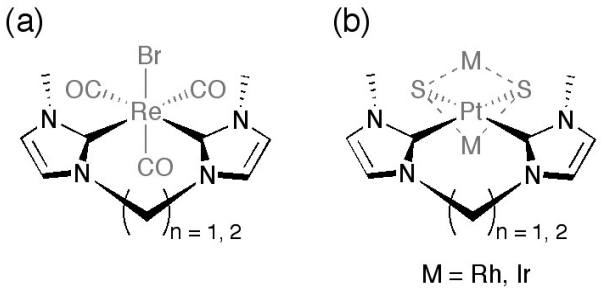


Figure 2-16. (a) Previously reported Re complexes containing methylene- or ethylene-bridged bisNHC ligands and (b) previously reported trinuclear complexes containing a platinum moiety with methylene- or ethylene-bridged bisNHC ligands.

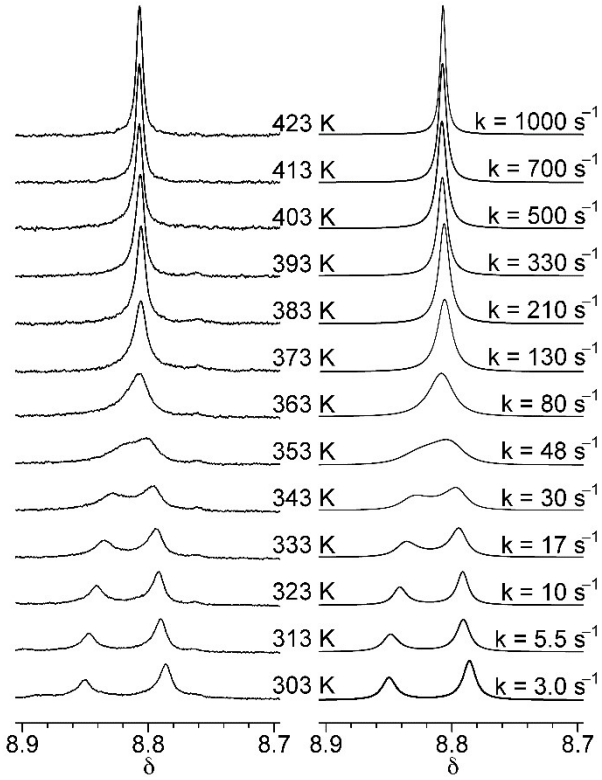


Figure 2-18. Observed (left) and simulated (right) signals of the 5-triazole proton in VT-NMR spectra of [Pd(Taz-bisNHC-Me)Cl](PF$_6$) in DMSO-d_6

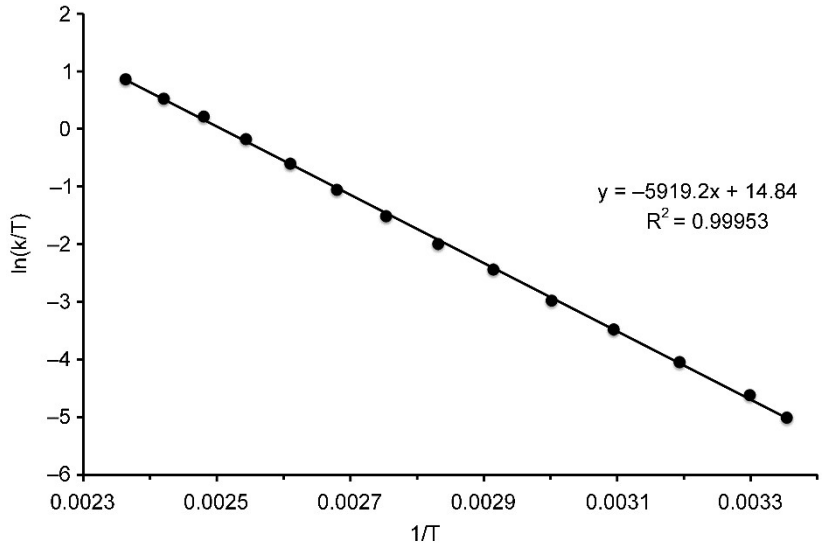


Figure 2-19. Eyring plots for line shape analyses of [Pd(Taz-bisNHC-Me)Cl](PF$_6$)

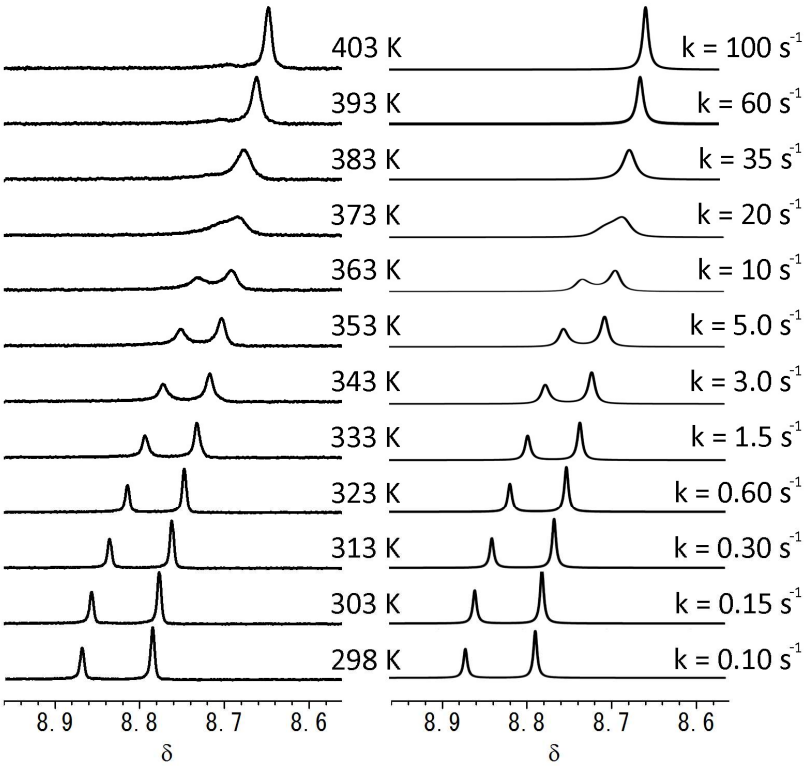


Figure 2-20. Observed (left) and simulated (right) signals of the 5-triazole proton in VT-NMR spectra of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$) in DMSO-d_6

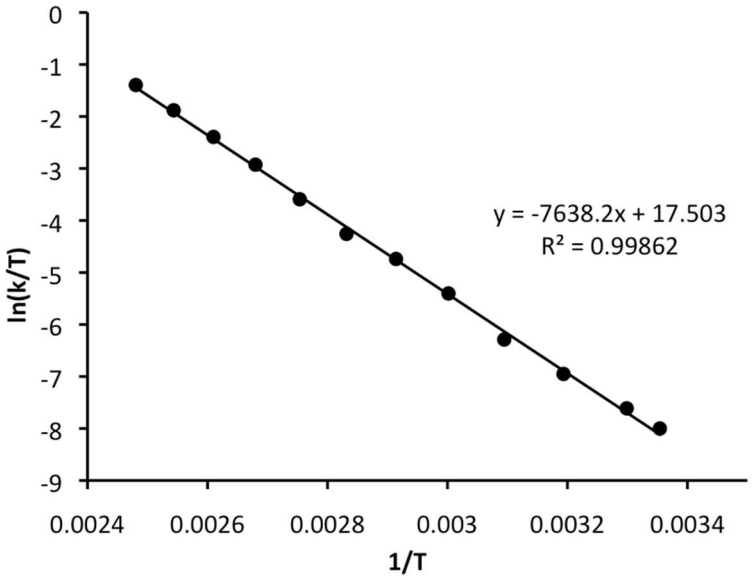


Figure 2-21. Eyring plots for line shape analyses of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$)

Table 2-3. Activation parameters for dynamic behavior of [Pd(Taz-bisNHC-Me)Cl](PF$_6$) and [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$).[a]

	$\Delta H^{\ddagger}$ (kJ•mol^{-1})	$\Delta S^{\ddagger}$ (J•mol^{-1}•K^{-1})	$\Delta G^{\ddagger}_{298K}$ (kJ•mol^{-1})
[Pd(Taz-bisNHC-Me)Cl](PF$_6$)	49.3(4)	–74(1)	71.3(7)
[Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$)	63.5(7)	–52(2)	79(1)

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

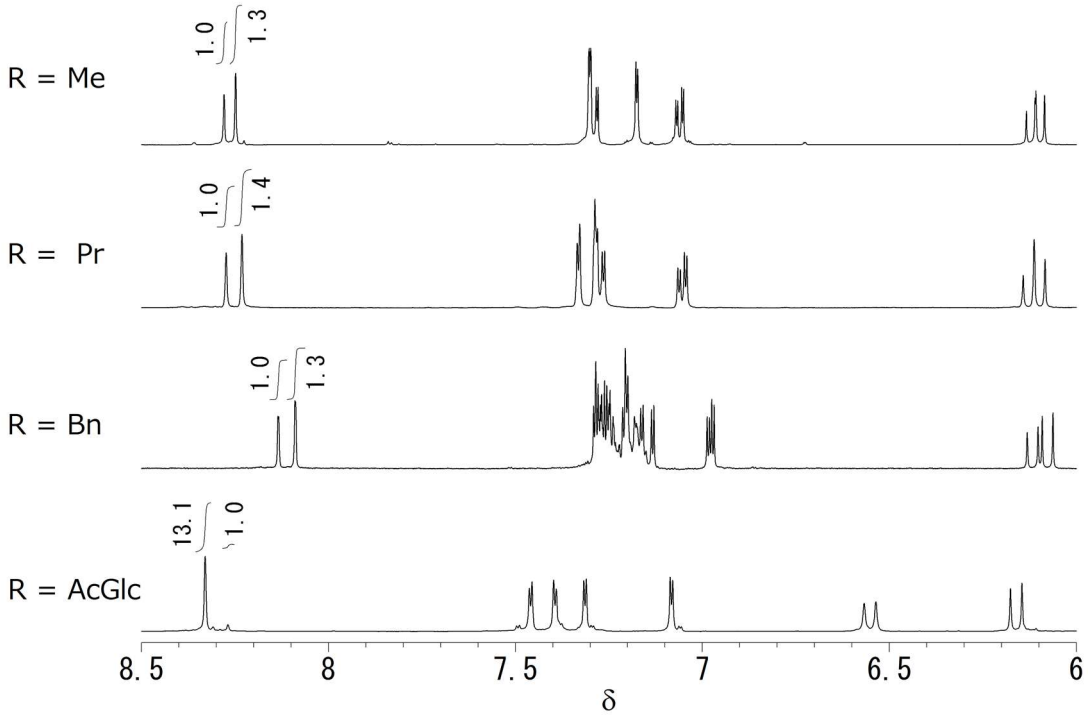
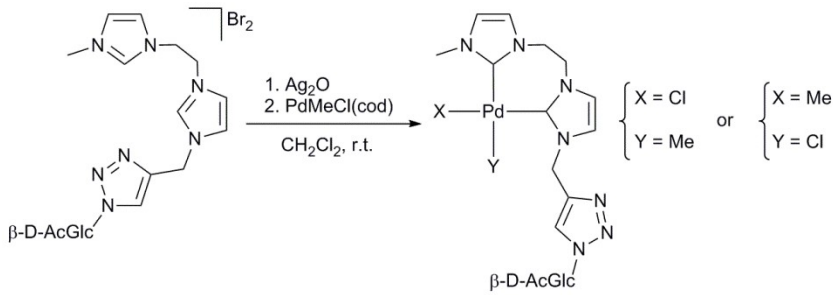


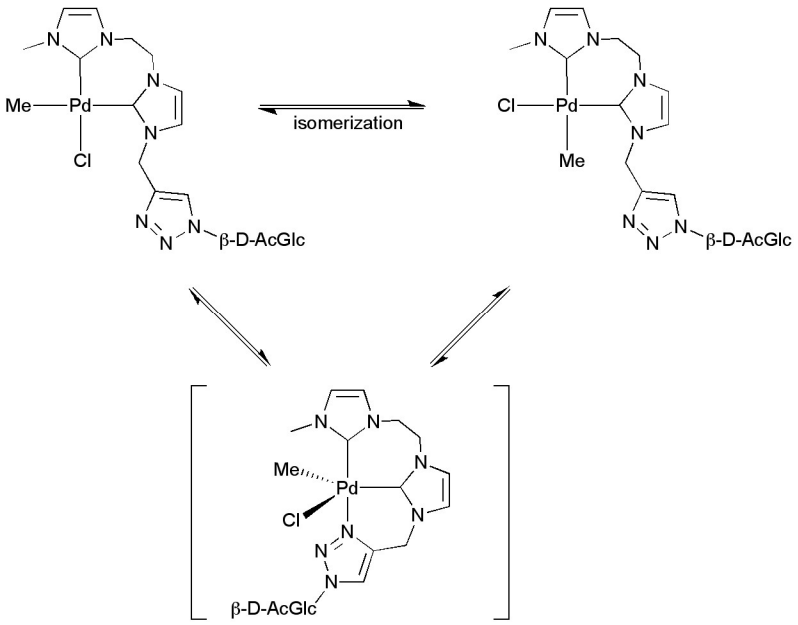
Figure 2-22. ^{1}H NMR spectra of [Pd(Taz-bisNHC-R)Cl](PF$_6$) (R = Me, ^{i}Pr, Bn, AcGlc) in CD_3CN.

A palladium complex bearing chloro and methyl ligands was also synthesized using ligand precursor $[(Taz\text{-}bisNHC\text{-}Me)H_2]Br_2$. The chloro methyl complex [Pd(Taz-bisNHC-Me)(Me)Cl] was prepared by the carbene transfer method using the corresponding silver NHC complexes. Because silver NHC complexes react smoothly with a various palladium precursors even at room temperature, this carbene transfer method is appropriate for the synthesis of a relatively unstable methyl palladium complex.[21] [Pd(Taz-bisNHC-Me)(Me)Cl] was obtained by the transmetalation reaction of [Pd(cod)(Me)Cl] and the silver complex, which was generated in situ by the reaction of $[(Taz\text{-}bisNHC\text{-}Me)H_2]Br_2$ with Ag_2O in CH_2Cl_2 (Scheme 2-8).



Scheme 2-8. Synthesis of methyl palladium complex

The ^1H NMR spectra of [Pd(Taz-bisNHC-Me)(Me)Cl] in CD_3CN or $CDCl_3$ show broad signals, suggesting tautomerization of the complex having methyl and chloro ligands. The isomerization may proceed by an associative mechanism involving the 5-coordinate intermediate[25] with binding the triazole donor (Scheme 2-9), because no tautomerization was observed for $[Pd(bis\text{-}NHC)(Me)(py)]^+$ or [Pd(bis-NHC)(Me)(OAc)] complex, where the bis-NHC ligands have no sidearm donors.[26]



Scheme 2-9. Associative mechanism for the transformation between isomers having methyl and chloro ligands in different positions.

Prolonged incubation of [Pd(Taz-bisNHC-Me)(Me)Cl] in CD_3CN at room temperature resulted in the transformation of the broad signals of the ^1H NMR spectrum into two sets of sharp signals for the ligand (Figure 2-23). It is attributed to dissociation of the chloro ligand to generate the cationic complex with the tridentate C-C-N pincer ligand (Scheme 2-10), which has two diastereomers as described for [Pd(Taz-bisNHC-Me)Cl](PF_6) (Figure 2-14). Complete conversion into the sharp signals required addition of D_2O to the CD_3CN solution, probably due to stabilization of the chloride counter anion by hydrogen bonding.[27] On the other hand, no change in the signal shape was observed in a $CDCl_3$ solution.

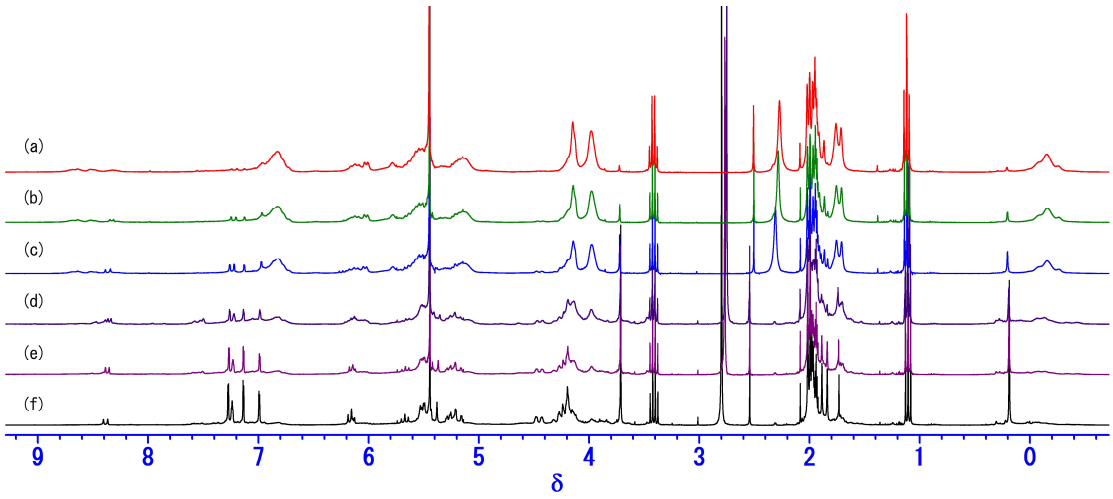
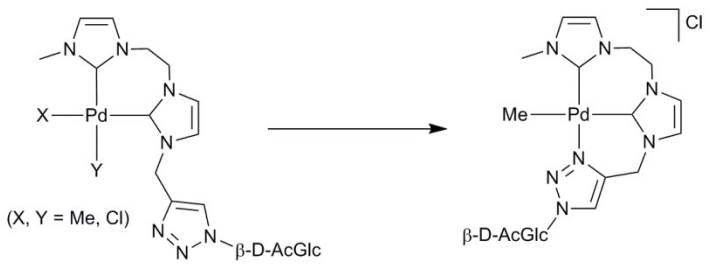


Figure 2-23. ^{1}H NMR spectra of [Pd(Taz-bisNHC-Me)(Me)Cl] in CD_3CN (a) shortly after, (b) 1 day after, and (c) 3 days after preparation of the sample. ^{1}H NMR spectra of the complex in CD_3CN (d) shortly after, (e) 1 day after, and (f) 4 days after addition of D_2O.



Scheme 2-10. Dissociation of the chloro ligand of [Pd(Taz-bisNHC-Me)(Me)Cl] to generate the cationic complex [Pd(Taz-bisNHC-Me)(Me)]Cl.

In the ESI mass spectrum of [Pd(Taz-bisNHC-Me)(Me)Cl], two sets of intense signals at m/z 708 and 728 for $[M-Cl]^+$ and $[M-CH_3]^+$, respectively, were observed in CH_2Cl_2, while only one set of the signals for $[M-Cl]^+$ was observed in CH_3CN (Figure 2-24). These results indicate that the Pd complex has both chloro and methyl ligands in CH_2Cl_2, and no transformation into [Pd(Taz-bisNHC-Me)(Me)]Cl

occurs. On the other hand, the cationic complex without the chloro ligand [Pd(Taz-bisNHC-Me)(Me)]Cl was formed in a CH_3CN solution. These observations indicate that the formation of the cationic complexes alters in different solvents, implying a hemilabile character of the bisNHC-triazole ligand.

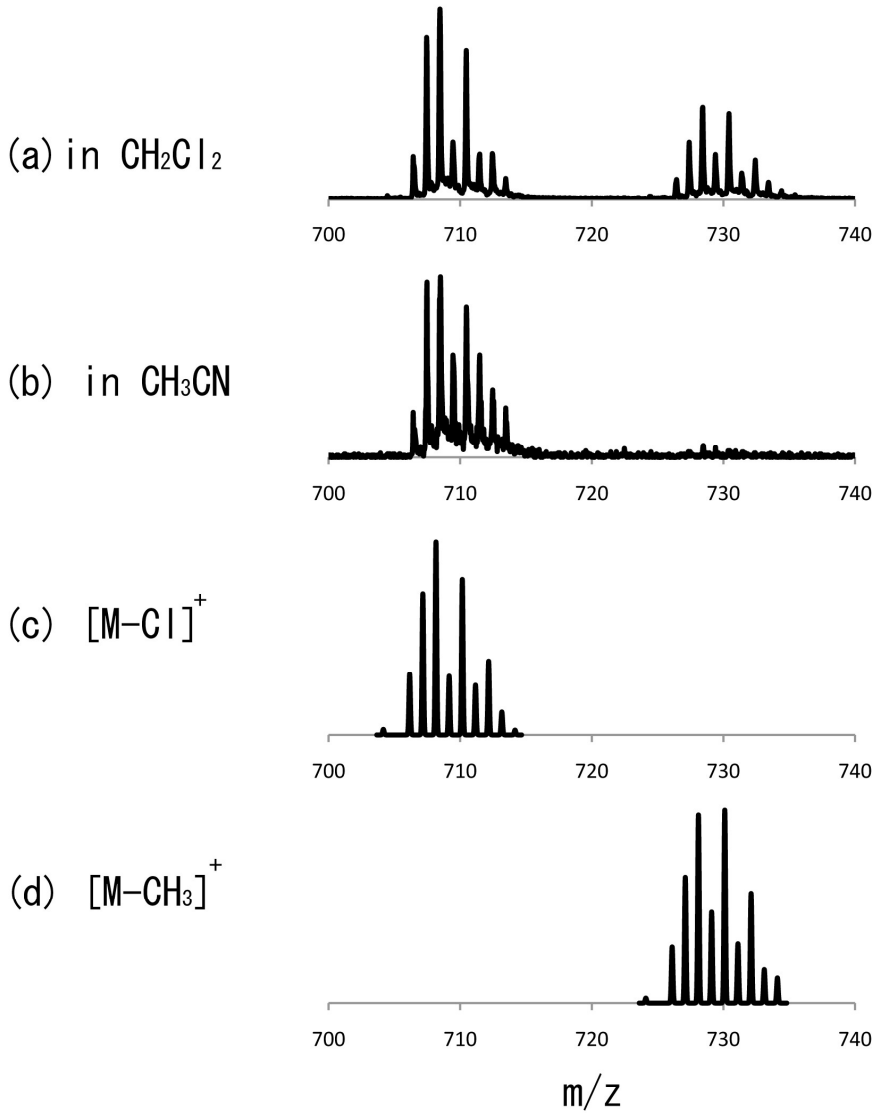


Figure 2-24. Electrospray ionization mass spectrum of [Pd(Taz-bisNHC-Me)(Me)Cl] in (a) CH_2Cl_2 and (b) CH_3CN, and simulated for (c) $[M-Cl]^+$ and (d) $[M-CH_3]^+$.

Chapter 3. Suzuki-Miyaura Cross-Coupling Reactions in Water

3-1. Introduction

C-C coupling catalyzed by palladium complexes is one of the most important reactions in organic syntheses.[28] The coupling reactions are generally performed in organic solvents, most of which are toxic, flammable, and explosive. Thus, use of water would resolve these problems[29] and render the facile separation of products and recovery of catalysts from reaction mixtures. To develop active catalysts in water, the ligand of metal complexes with water-soluble units, such as carboxylates,[30] sulfonates[31] and ammoniums,[31a] are preferable. Water-soluble complexes for transfer hydrogenation,[16a] coupling reactions[16c,d] and olefin methathesis[32] have been prepared by incorporating sugar groups as water-soluble units into N-heterocyclic carbene (NHC) ligands. NHC palladium complexes are known as useful catalysts for coupling reactions due to strong σ-donating ability of the NHC ligands.[6,33,34]

In the previous chapter, synthesis, structure, and dynamic behavior of various palladium complexes with multidentate ligands containing two NHC coordination moieties and D-glucopyranosyl unit were described. In this section, the catalytic activity of these complexes toward the Suzuki-Miyaura cross-coupling reactions in water will be discussed.

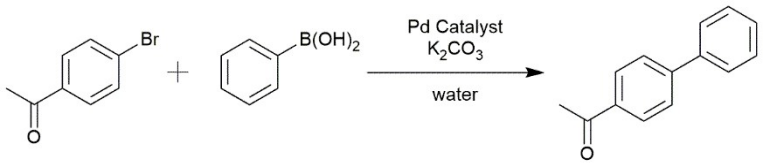
3-2. Catalytic Ability of Sugar-Incorporated BisNHC Palladium Complexes in Suzuki-Miyaura Cross-Coupling in Water

Catalytic ability of palladium complexes [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] in Suzuki-Miyaura cross-coupling in water was examined in the

presence of potassium carbonate. Although water-solubility of these complexes is low, the acetyl-protected glucopyranosyl units in [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] are deprotected under the conditions affording water-soluble complexes.

Complexes [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] catalyzed reactions of 4'-bromoacetophenone and phenylboronic acid in the presence of potassium carbonate in water (Table 3-1). 4'-Bromoacetophenone is generally used to study catalytic activities towards Suzuki-Miyaura coupling reactions in water because of its high reactivity and water solubility. All of the reactions were carried out in air. Turnover number (TON) and turnover frequency (TOF) for each of catalysts [Pd(bisNHC-C2)Cl_2] (entry 2) and [Pd(bisNHC-C2)Cl_2] (entry 6) reached to 85,000 and 170,000, 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}).[3e] The addition of a drop of metallic mercury, which leads deactivation of catalytic ability of palladium nanoparticles, did not affect the catalytic ability of [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] suggesting that the Pd complexes are involved in the catalytic reaction (entries 4 and 8).

Table 3-1. Suzuki-Miyaura cross-coupling reactions of 4'-bromoacetophenone and phenylboronic acid catalyzed by [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2].[a]



Entry	Catalyst	Loading (mol%)	Time (h)	Yield (%)	TON	TOF (h^{-1})
1	[Pd(bisNHC-C2)Cl_2]	10^{-1}	0.5	96	960	1,920
2	[Pd(bisNHC-C2)Cl_2]	10^{-3}	0.5	85	85,000	170,000
3	[Pd(bisNHC-C2)Cl_2]	10^{-4}	3	0	0	0
4[b]	[Pd(bisNHC-C2)Cl_2]	10^{-1}	0.5	90	900	1,800
5	[Pd(bisNHC-C3)Cl_2]	10^{-1}	0.5	98	980	1,960
6	[Pd(bisNHC-C3)Cl_2]	10^{-3}	0.5	85	85,000	170,000
7	[Pd(bisNHC-C3)Cl_2]	10^{-4}	3	0	0	0
8[b]	[Pd(bisNHC-C3)Cl_2]	10^{-1}	0.5	84	840	1,680

[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.

Reuse of the complexes for the catalysts in the Suzuki-Miyaura cross-coupling reaction was also examined. After the first catalytic reaction, the product and the remained starting materials were extracted with CH_2Cl_2 from the resulting reaction mixture. The separated aqueous phase, which contained the catalyst, was used for the other catalytic reaction of the freshly added substrates and base (Table 3-2). The second and third reactions (entries 10, 11, 14 and 15) afforded similar yields to those for

the first reactions (entries 9 and 13). In the fourth reactions (entries 12 and 16), 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.

Table 3-2. Reuse of [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2] in aqueous phase as catalysts for Suzuki-Miyaura cross-coupling reactions of 4'-bromoacetophenone and phenylboronic acid.[a]

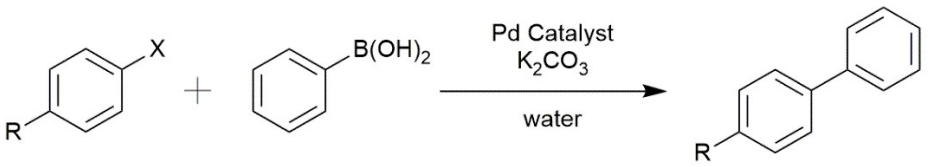
Entry	Catalyst	Cycle	Time (h)	Yield (%)
9	[Pd(bisNHC-C2)Cl_2][b]	1st	0.5	96
10		2nd	0.75	96
11		3rd	0.75	79
12		4th	0.75	25
13	[Pd(bisNHC-C3)Cl_2][b]	1st	0.5	98
14		2nd	0.75	89
15		3rd	0.75	81
16		4th	0.75	53

[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%.

To investigate a scope of substrates for complexes [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2], reactions of a variety of aryl halides with phenylboronic acid were examined (Table 3-3). The reactions of aryl bromides bearing 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 19 and 20), bromobenzene (entries 21–24), and 4-bromoanisole with the electron-donating OMe group (entries 27–30). Electron-withdrawing groups of aryl halides generally reduce the electron density on their C–X bonds and then oxidative addition of the C–X bonds to metal centers readily proceeds. Additionally, solubility of organic substrate often affected the yield of the reactions in water. To solve the problem, tetrabutylammonium bromide is added as an additive. The effects of tetrabutylammonium bromide in the reactions were also checked (entries 25, 26, 31, 32) and improvement of the yields by the addition was observed. Although the catalytic reaction of less reactive 4'-chloroacetophenone with phenylboronic acid afforded a low yield of the coupling product (entry 33), the addition of tetrabutylammonium bromide drastically improved the yield (entry 34).

Table 3-3. Suzuki-Mataura cross-coupling reactions of a variety of aryl halides and phenylboronic acid catalyzed by [Pd(bisNHC-C2)Cl_2] and [Pd(bisNHC-C3)Cl_2].[a]

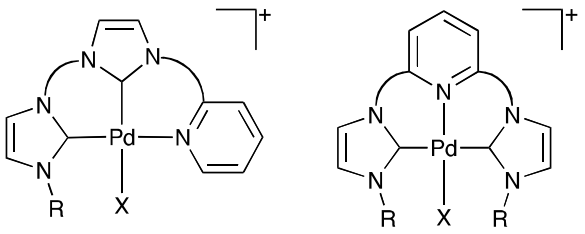


Entry	R	X	Catalyst precursor	Additive	Time (h)	Yield (%)	TON
17[b]	Ac	Br	[Pd(bisNHC-C2)Cl_2]	–	0.5	85	85,000
18[b]	Ac	Br	[Pd(bisNHC-C3)Cl_2]	–	0.5	85	85,000
19	NO_2	Br	[Pd(bisNHC-C2)Cl_2]	–	2	97	9,700
20	NO_2	Br	[Pd(bisNHC-C3)Cl_2]	–	2	98	9,800
21	H	Br	[Pd(bisNHC-C2)Cl_2]	–	2	56	5,600
22	H	Br	[Pd(bisNHC-C3)Cl_2]	–	2	66	6,600
23	H	Br	[Pd(bisNHC-C2)Cl_2]	–	6	80	8,000
24	H	Br	[Pd(bisNHC-C3)Cl_2]	–	6	81	8,100
25	H	Br	[Pd(bisNHC-C2)Cl_2]	$^{n}BuN_4Br$	2	69	6,900
26	H	Br	[Pd(bisNHC-C3)Cl_2]	$^{n}BuN_4Br$	2	89	8,900
27	OMe	Br	[Pd(bisNHC-C2)Cl_2]	–	2	28	2,800
28	OMe	Br	[Pd(bisNHC-C3)Cl_2]	–	2	41	4,100
29	OMe	Br	[Pd(bisNHC-C2)Cl_2]	–	6	64	6,400
30	OMe	Br	[Pd(bisNHC-C3)Cl_2]	–	6	63	6,300
31	OMe	Br	[Pd(bisNHC-C2)Cl_2]	$^{n}BuN_4Br$	2	74	7,400
32	OMe	Br	[Pd(bisNHC-C3)Cl_2]	$^{n}BuN_4Br$	2	83	8,300
33	Ac	Cl	[Pd(bisNHC-C2)Cl_2]	–	17	3	300
34	Ac	Cl	[Pd(bisNHC-C2)Cl_2]	$^{n}BuN_4Br$	17	57	5,700

[a] Reaction condition: aryl halide (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol), catalyst (10^{-2} mol%) and $^{n}Bu_4NBr$ (0.3 mmol if added) in water (1 mL), 100 °C. [b] 10^{-3} mol% catalyst.

3-3. Effect of the Arrangement of Two N-Heterocyclic Carbene Moieties in Palladium Pincer Complexes on Their Catalytic Activity Towards Suzuki-Miyaura Cross-Coupling Reactions in Water

As well as bidentate ligands, pincer ligands have been used to stabilize their complexes via chelate effects. The donor atoms and substituents on the pincer ligands can be varied to control the electron densities on the metal ions.[35] Pincer complexes having a C-Y-C donor atoms with two NHC side arms have been widely investigated due to their high catalytic activities.[22] Palladium pincer complexes with *trans*-arrangement of the two NHC units have been reported to exhibit catalytic activity toward Suzuki-Miyaura cross-coupling reactions in water, while it has been suggested that the active species in the reactions are palladium nanoparticles generated by decomposition of the palladium complexes.[3c] As described in the section 2-3, *trans*-arrangement of two NHC units in a pincer ligand causes strong *trans*-influence from each NHC unit to the other due to strong σ-donating ability of the NHC ligands. Furthermore, a protic solvent, such as water, promotes irreversible dissociation of the NHC moieties via protonation. In this section, the palladium complex [Pd(CCN-AcGlc)Cl](PF_6) having the pincer ligand constituted of two *cis*-arranged NHC units with a terminal pyridyl group (C-C-N pincer ligand) was applied to the Suzuki-Miyaura cross-coupling reaction in water. The pincer palladium complex [Pd(CNC-AcGlc)Cl](PF_6) having two *trans*-arranged NHC units with a central pyridine donor atom (C-N-C pincer ligand) was examined for comparison.

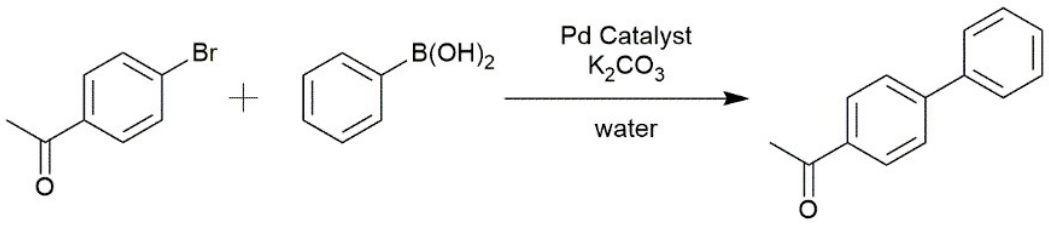


Scheme 3-1. *Cis*- (C-C-N, left) and *trans*- (C-N-C, right) arrangements of NHC ligand moieties in pincer complexes containing two NHC and pyridine units.

Although acetyl-protected complexes [Pd(CCN-AcGlc)Cl](PF_6) and [Pd(CNC-AcGlc)Cl](PF_6) are hardly soluble in water, deprotection of the acetyl groups in the complexes [Pd(CCN-AcGlc)Cl](PF_6) and [Pd(CCN-AcGlc)Cl](PF_6) improve the solubility. Therefore, the activities of *in-situ* deprotected complexes towards Suzuki-Miyaura cross-coupling reactions in water were examined.

The Suzuki-Miyaura cross-coupling reaction of 4'-bromoacetophenone and phenylboronic acid in water was performed in the presence of potassium carbonate as a base. The reaction using 1.0×10^{-3} mol% of the precatalyst [Pd(CNC-AcGlc)Cl](PF_6) afforded the product in 5% yield (Table 3-3, entry 5), whereas the reaction using the same quantity of [Pd(CCN-AcGlc)Cl](PF_6) gave the biaryl product in 75% yield with a TON value of 75,000 (Table 3-3, entry 2). The TON value for [Pd(CCN-AcGlc) Cl](PF_6) is relatively high but still lower than the reported values of 770,000 for similar reactions in water.[3e] A smaller amount of [Pd(CCN-AcGlc)Cl](PF_6) (1.0×10^{-4} mol%) caused the yield to drop to 6% (Table 3-3, entry 3).

Table 3-3. Suzuki-Miyaura cross-coupling reaction of 4'-bromoacetophenone and phenylboronic acid using [Pd(CCN-AcGlc)Cl](PF_6) and [Pd(CNC-AcGlc)Cl](PF_6) complexes as catalyst precursors.



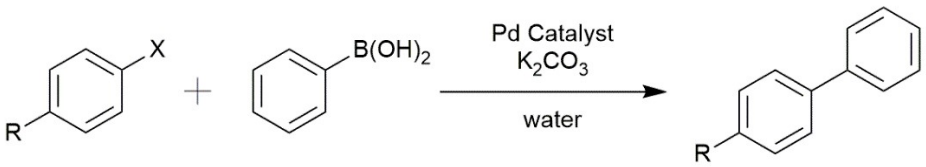
Entry	Catalyst, loading (mol%)	Yield (%)	TON
1	[Pd(CCN-AcGlc)Cl](PF_6), 1.0×10^{-2}	98	9,800
2	[Pd(CCN-AcGlc)Cl](PF_6), 1.0×10^{-3}	75	75,000
3	[Pd(CCN-AcGlc)Cl](PF_6), 1.0×10^{-4}	6	60,000
4	[Pd(CNC-AcGlc)Cl](PF_6), 1.0×10^{-2}	89	8,900
5	[Pd(CNC-AcGlc)Cl](PF_6), 1.0×10^{-3}	5	5,000

Reaction conditions: 4'-bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol), and catalyst in 1 mL of H_2O at 100 °C for 16 h.

Substrate scope for the Suzuki-Miyaura cross-coupling reaction in water using [Pd(CCN-AcGlc)Cl](PF_6) or [Pd(CNC-AcGlc)Cl](PF_6) as catalyst precursors was examined using different aryl halides (Table 3-4). They showed similar catalytic ability for bromobenzene (entries 11–15) and 2-bromo-1,3-dimethylbenzene (entries 16–20). On the other hand, [Pd(CCN-AcGlc)Cl](PF_6) is a better precatalyst in the reaction with 4-bromoanisole (entries 6–10) or 4'-chloroacetophenone (entries 21–24) than [Pd(CNC-AcGlc)Cl](PF_6). The yields of the coupling reactions using 4-bromoanisole, bromobenzene, 2-bromo-1,3-dimethylbenzene, and 4'-chloroacetophenone were lower

than those using 4'-bromoacetophenone (Table 3-3, entries 1–5). The lower yields are attributed to the lower solubility of the aryl halides in water than that of 4'-bromoacetophenone. The ^{1}H NMR spectrum of the reaction mixture of 2-bromo-1,3-dimethylbenzene and phenylboronic acid, showed signals for benzene, which formed by the competitive protodeboronation of boronic acid.[36] This competitive reaction also affects the yields of the coupling reactions.

Table 3-4. Suzuki-Miyaura cross-coupling reaction of aryl halides and phenylboronic acid using [Pd(CCN-AcGlc)Cl](PF$_6$) and [Pd(CNC-AcGlc)Cl](PF$_6$) complexes as catalyst precursors.



Entry	R, X	Catalyst, loading (mol%)	Yield (%)	TON
6	4-OMe, Br	[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	75	750
7		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	63	6,300
8		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-3}	39	39,000
9	4-OMe, Br	[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	70	700
10		[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	18	1,800
11	H, Br	[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	49	490
12		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	21	2,100
13		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-3}	4	4,000
14	H, Br	[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	88	880
15		[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	24	2,400
16	1,3-Me$_2$, Br	[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	9	90
17		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	3	300
18		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-3}	2	2,000
19	1,3-Me$_2$, Br	[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	9	90
20		[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	4	400
21	4-Ac, Cl	[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	10	100
22		[Pd(CCN-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	0.7	70
23	4-Ac, Cl	[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-1}	4	40
24		[Pd(CNC-AcGlc)Cl](PF$_6$), 1.0×10^{-2}	0.3	30

Reaction conditions: aryl halides (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol), and catalyst in 1 mL of H_2O at 100 °C for 16 h.

A Hg drop test is widely used to distinguish between homogeneous and heterogeneous catalysis.3b,[3c,3f,37] Metallic Hg deactivates heterogeneous catalysts, such as Pd nanoparticles, by amalgamation with the surface of heterogeneous catalysts, whereas it does not poison homogeneous palladium complexes in which ancillary ligands are tightly bound to the metal centers. To get an insight into the catalytically active species of the reaction using the C-C-N and C-N-C complexes as catalyst precursors, the coupling reactions with 4'-bromoacetophenone and phenylboronic acid were performed in the presence or absence of metallic Hg. In the absence of metallic Hg, both complexes started to work as catalysts after a brief induction period, and almost quantitative conversions were observed after 90 min for [Pd(CCN-AcGlc)Cl](PF_6) and 20 min for [Pd(CNC-AcGlc)Cl](PF_6) (Figure 3-1(a)). For the reaction in the absence of Hg with relatively higher catalyst loading, [Pd(CNC-AcGlc)Cl](PF_6) exhibited a higher catalytic activity. It is in contrast to the previously mentioned results that [Pd(CCN-AcGlc)Cl](PF_6) exhibited higher catalytic activity than [Pd(CNC-AcGlc)Cl](PF_6) did when 1.0×10^{-3} mol% of the precatalysts were used. The higher stability of the catalytically active species generated from [Pd(CCN-AcGlc)Cl](PF_6), which brings a higher TON value at lower catalyst loadings, may causes the difference. On the other hand, [Pd(CCN-AcGlc)Cl](PF_6) and [Pd(CNC-AcGlc)Cl](PF_6) exhibited completely different activity for the coupling reactions in the presence of excess metallic Hg (Figure 3-1(b)). Metallic Hg afford little effect on the coupling reaction using [Pd(CCN-AcGlc)Cl](PF_6), although the induction period was slightly longer in the presence of Hg. In the case of [Pd(CNC-AcGlc)Cl](PF_6), metallic Hg depressed the catalytic reaction, indicating that the active species in the coupling reactions using [Pd(CNC-AcGlc)Cl](PF_6) is a

heterogeneous catalyst, such as Pd nanoparticles. Generation of Pd nanoparticles from Pd complexes in coupling reactions was reported for pincer complexes with C-N-C, P-C-P, or S-C-S ligands.[10,38]

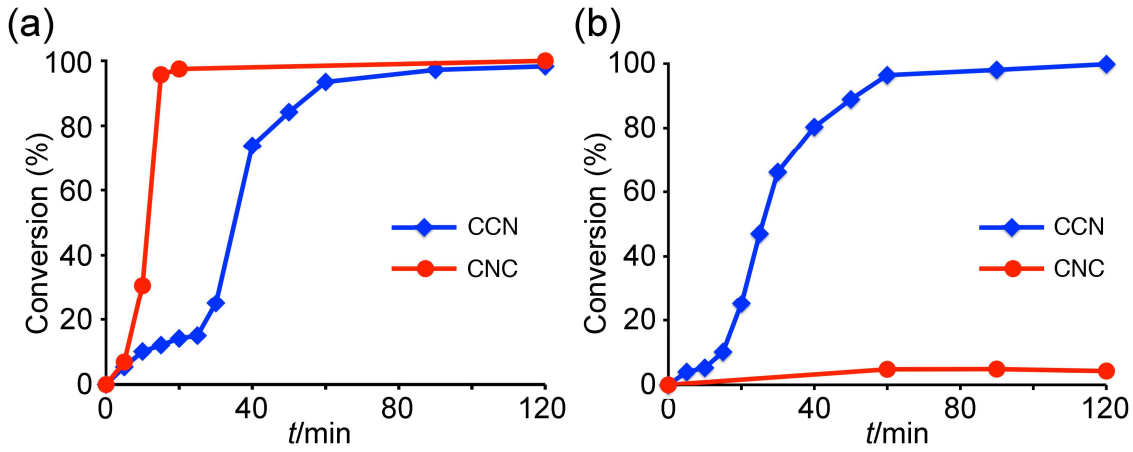


Figure 3-1. Suzuki-Miyaura coupling reactions of 4'-bromoacetophenone and phenylboronic acid in water using [Pd(CCN-AcGlc)Cl](PF$_6$) (blue) or [Pd(CNC-AcGlc)Cl](PF$_6$) (red) as a catalyst (0.02 mol%) (a) in the absence and (b) in the presence of excess Hg.

In summary, [Pd(CCN-AcGlc)Cl](PF$_6$), which transforms to the deprotected form under the conditions used for the catalytic reactions, acts as a homogeneous catalyst, whereas a heterogeneous species, such as nanoparticles, is the active species for the reaction using [Pd(CNC-AcGlc)Cl](PF$_6$) as a catalyst precursor. For complexes with C-N-C pincer ligands, one of the NHC moieties readily dissociates due to the large *trans*-influence of the NHC moieties. Moreover, the terminal NHC moiety in the C-N-C complexes often irreversibly dissociates from the metal center when protonation occurs under protic conditions.[39]

3-3. Catalytic Ability of the Palladium Complex with C-C-N Pincer Ligand Containing Sugar Triazolyl Unit

For development of the homogeneous molecular catalyst, “ligand design” is one of the most important strategies to improve performance as catalysts. In the previous section, the Pd complex with the C-C-N pincer ligand revealed to act as a homogeneous molecular catalyst in the Suzuki-Miyaura cross-coupling reaction. However, regulation of steric and/or electronic properties by introducing various substituents into the C-C-N pincer ligand constituted of two NHC moieties and one pyridine moiety is relatively difficult, because of difficulty in the modification of the pyridyl group. Therefore, the palladium complexes with the C-C-N ligands synthesized using the click chemistry were utilized for the Suzuki-Miyaura cross-coupling reaction in water, and the effects of the N-substituents on the catalytic ability were discussed.

The catalytic activity of the Pd complexes was investigated for the Suzuki-Miyaura cross-coupling reaction of phenylboronic acid and 4’-bromoacetophenone (Table 3-5).

The acetyl-protected glucopyranosyl groups in [Pd(Taz-bisNHC-R)Cl](PF_6), which is hardly soluble in water, are deprotected in the presence of K_2CO_3 used in the coupling reaction affording the water-soluble deprotected complexes. This deprotection reaction was confirmed by the *in-situ* reaction of [Pd(Taz-bisNHC-Me)Cl](PF_6) and K_2CO_3 in D_2O with heating at 100 °C for 1 hour in an NMR tube.

The ^1H NMR spectrum of the resulting solution and ESI-mass spectrum of the sample, which was prepared by dilution of the reaction mixture in D_2O with CH_3OH, were shown in Figure 3-2 and 3-3. The ^1H NMR spectrum revealed the signals for the deprotected ligand showing the deprotection reaction successfully proceeded, though

the signal of the 5-H of the triazole moiety was not observed because of the deuteration. Under the basic condition in D_2O, the 5-H of the triazole was deuterated due to the higher acidity of the proton. The mass spectrum, which exhibited signals at the molecular weight of $[M–PF_6]^+$ plus one, also supports the deuteration of the triazole moiety. These results agree with the deprotection of the complex and guarantee the solubility of the complex in water during the catalytic reaction.

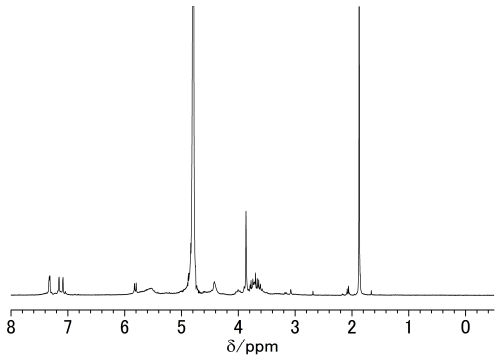


Figure 3-2. ^1H NMR spectrum of *in-situ* generated deprotected [Pd(Taz-bisNHC-Me)Cl](PF_6) in D_2O.

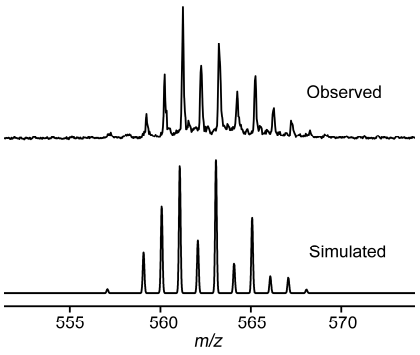


Figure 3-3. ESI-mass spectrum of diluted sample in MeOH of *in-situ* generated deprotected [Pd(Taz-bisNHC-Me)Cl](PF_6) in D_2O.

Among the complexes [Pd(Taz-bisNHC-R)Cl](PF_6) with various N-substituents R, [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) showed the best catalytic activity (Table

3-5). In the reaction using 1 mol ppm of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) as the catalyst precursor, the product was obtained in 80% yield, corresponding to the TON value of 800,000. To the best of our knowledge, this TON value is comparable to the best one that was reported for the similar reactions in water.[3e] However, reduction of the amount of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) to 0.1 mol ppm led a significant decrease of the yield (3.3%). On the other hand, the use of 1 mol ppm of [Pd(Taz-bisNHC- R)Cl](PF_6) (R = Me, Bn, AcGlc) as precatalysts exhibited low yields, though the TON values are relatively high. Higher catalyst loading such as 10 mol ppm was required to obtain the product in moderate yields. The catalytic reactions using [Pd(Taz-bisNHC-Me)Cl](PF_6) and [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) were also examined in the presence of metallic Hg to confirm the nature of active catalysts. The reactions proceeded even in the presence of metallic Hg, indicating that molecular Pd species are active catalysts. For these reactions, no side-reactions such as a homo-coupling reaction were observed.

High efficiency of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF_6) as the catalyst can be explained by the higher electron donating ability and the larger steric hindrance of the isopropyl group. Although the steric hindrance of the benzyl and sugar units is significant, those functionalities have the electron-withdrawing phenyl group and the oxygen atoms, which decrease the electron density on the palladium centers.[24] For the palladium-catalyzed C-C coupling reactions, high electron density on the palladium center and large steric hindrance, which is induced by the N-substituents of the NHC ligands, improves the catalytic ability.[40]

The effect of the methyl ligand, which was reported to improve the catalytic activity for the Heck reaction, was examined.[11,41] When using [Pd(Taz-bisNHC-Me)Cl(CH_3)] as a catalyst precursor, the higher loading level of the

catalyst such as 10 mol ppm was required to obtain the product in moderate yields, revealing that the presence of the methyl ligand is not effective in the Suzuki-Miyaura reaction in aqueous media.

Table 3-5. Catalyst Screening for the Suzuki-Miyaura coupling reaction in water[a]

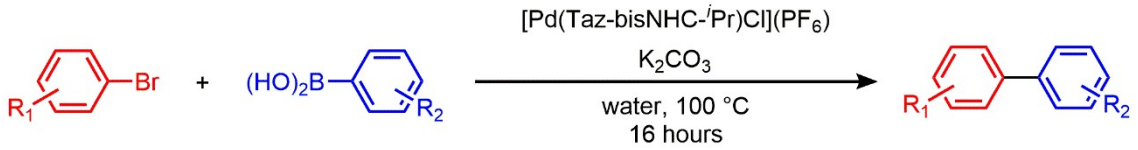
Entry	Catalyst	Cat.(mol ppm)	Yield[b] (%)	TON[c]
1	[Pd(Taz-bisNHC-Me)Cl](PF$_6$)	10	76	76000
2	[Pd(Taz-bisNHC-Me)Cl](PF$_6$)	1	6.5	65000
3	[Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$)	1	80	800,000
4	[Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$)	0.1	3.3	330,000
5	[Pd(Taz-bisNHC-Bn)Cl](PF$_6$)	10	76	76,000
6	[Pd(Taz-bisNHC-Bn)Cl](PF$_6$)	1	11	110,000
7	[Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$)	10	77	77,000
8	[Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$)	1	4.2	42,000
9	[Pd(Taz-bisNHC-Me)Cl(CH$_3$)]	10	84	84000
10	[Pd(Taz-bisNHC-Me)Cl(CH$_3$)]	1	0.0	0

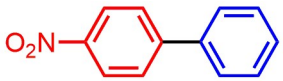
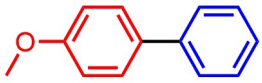
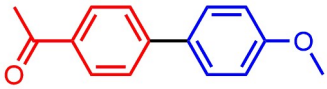
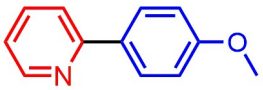
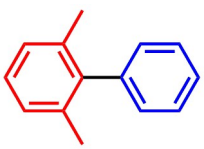
[a]Reaction conditions: 4'-bromoacetophenone, phenylboronic acid, K_2CO_3, and catalyst in 1 mL of water at 100 °C for 16 h. [b]The yields were determined by the ^{1}H NMR integral intensities using 1,3,5-trimethoxybenzene as an internal standard. [c]TON = (mmol of the isolated product)/(mmol of the catalyst).

The dependency of the catalytic ability of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$) on the properties of substrates and solvent was examined (Table 3-6). In the reaction using electron-withdrawing NO_2 or donating OMe at the 4-position on the phenyl rings of the

aryl bromides afforded biaryl products in high yields both in water and in toluene (entry 1-4). Use of 4-methoxyphenylboronic acid also afforded the biaryl product in high yields in water and in toluene (entry 5, 6). On the other hand, catalytic ability for the reaction using 2-bromopyridine or 2,6-dimethylbromobenzene largely depended on the solvents used. Using water as a solvent resulted in relatively low yields (entry 7, 10, 13), although the reactions in toluene afforded biaryl products in moderate yields (entry 9, 12, 15). In the aqueous reactions, side-products such as hydrolysis products of aryl boronic acids were obtained, implying the competitive reactions of the cross-coupling and hydrolysis of aryl boronic acid. Accordingly, use of excess amount of aryl boronic acids resulted in increase in yields of the biaryl products (entry 8, 11, 14).

Table 3-6. Catalytic activities of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$) towards Suzuki-Miyaura cross-coupling of aryl halides and phenylboronic acid in water.



Entry	Product	solvent	ArB(OH)$_2$ (equiv.)	Catalyst (mol%)	Yield (%)	TON
1		water	1.5	1.0×10^{-1}	87	870
2		toluene	1.5	1.0×10^{-1}	87	870
3		water	1.5	1.0×10^{-1}	79	790
4		Toluene	1.5	1.0×10^{-1}	83	830
5		water	1.5	1.0×10^{-1}	92	920
6		toluene	1.5	1.0×10^{-1}	100	1000
7		water	1.5	1.0×10^{-1}	10	100
8			7.5	1.0×10^{-1}	97	970
9		toluene	1.5	1.0×10^{-1}	97	970
10		water	1.5	1.0×10^{-1}	38	380
11			7.5	1.0×10^{-1}	94	940
12		toluene	1.5	1.0×10^{-1}	62	620
13		water	1.5	1.0	22	22
14			7.5	1.0	80	80
15		toluene	1.5	1.0	78	78

Reaction conditions: aryl halides (0.2 mmol), arylboronic acids, K_2CO_3 (0.4 mmol), and catalyst in 1 mL of H_2O or toluene at 100 °C for 16 h.

Conclusions

In this thesis, a series of sugar-incorporated palladium complexes with bidentate or tridentate ligands containing two N-Heterocyclic carbene (NHC) units were successfully synthesized, which allowed detailed discussion on their structures, dynamic behavior in solution, and catalytic ability for the Suzuki-Miyaura cross-coupling reactions in water. Each of these ligands is constituted of two NHC and N-donor units, namely pyridyl or triazolyl units, as a tridentate ligand. To the best of our knowledge, these are the first example of metal complexes with sugar-incorporated poly-NHC ligands.

The C-C-N complex showed higher catalytic activity than the C-N-C complex did and was not deactivated by the addition of metallic Hg, indicating that the C-C-N complex framework remains intact and serves as an active catalyst. On the other hand, the C-N-C complex exhibited no catalytic activity for the coupling reactions in the presence of metallic Hg, exhibiting that the active species are heterogeneous catalysts, such as Pd nanoparticles. This difference is attributed to the *cis*- and *trans*-arrangements of the two NHC moieties in the complexes. The NHC moieties in the C-N-C complex, which are strong σ-donors, cause a large *trans*-influence, resulting in the dissociation of one of the NHC moieties upon protonation especially under protic conditions. This irreversible dissociation of the NHC moiety triggers the decomposition of the C-N-C complex, affording Pd nanoparticles. In the case of the C-C-N complex, the NHC moiety *trans* to the terminal pyridine enhances dissociation of the pyridine to generate a vacant site for catalytic reactions on the metal center. These results suggest that the *cis*-arrangement of the two NHC units in pincer ligands results in a robust homogeneous catalyst with activity towards coupling reactions in water.

Modification of the structures of the palladium complexes with the C-C-N ligands, each of which is constituted of two NHC units and a sugar troazolyl unit, leads the improvement of the catalytic ability toward the Suzuki-Miyaura reactions. The TON values reached to 800,000, which is comparable to the best value reported for the similar reactions. All of the reactions were carried out without degassing process. These results would provide useful information to develop homogeneous catalysts in water not only for the C-C coupling reactions but also for generation of carbon-heteroatom bonds such as C-N, C-O, and C-S bonds.

Furthermore, the pincer ligands adopt screw structures by coordination, and in some cases, the orientations could be controlled by the chirality of the sugar D-glucopyranosyl unit. This can be applied for asymmetric catalysis using the chiral nature of the earth-abundant sugars. Because many complexes containing multidentate ligands with the screw structure that work as asymmetric catalysts[42] have been reported, complexes with a C-C-N pincer ligand having a sugar unit are promising candidates for asymmetric catalysts.

Experimental Section

Materials and methods. All chemicals were purchased from Aldrich, Nacalai Tesque, and Wako Pure Chemical. All reagents and solvents were used without further purification. 1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)imidazole,[16h] 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl azide,[23a] 1-(prop-2-ynyl)imidazole,[43a] 3-(2-bromoehtyl)-1-methylimidazolium bromide,[43b] N-isopropylimidazole,[43c] N-benzylimidazole,[43c] and $[PdCl_2(NCCH_3)_2]$[43d] were prepared according to the reported procedures. ^1H and ^{13}C 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 $SiMe_4$ (^1H) and referenced to solvent peaks (^{13}C). 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 or FISONS Instrument EA108 elemental analyzer by the Analytical Research Center at Osaka City University. For line shape analyses, ^1H NMR signals with various kinetic constants were simulated using an NMR simulation program in the NMRV4 program pakage.[44]

Synthesis of 1-(2-bromoethyl)-3-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl) imidazolium bromide ([AcGlcIm(CH$_2$)$_2$Br]Br). A solution of 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)imidazole (1.0 g, 2.52 mmol) and 1,2-dibromoethane (5 mL) in acetone (10 mL) was heated at 90 °C for 21 h in a sealed tube. After cooling the reaction mixture to room temperature, a white powder was collected by suction filtration. Yield: 1.2 g (80%). Anal. Calcd for $C_{19}H_{26}Br_2N_2O_9$ (586.23 g mol^{-1}): C, 38.93; H, 4.47; N, 4.78. Found: C, 38.94; H, 4.49; N, 4.79. ^1H NMR (300 MHz,

$CDCl_3$): δ 11.29 (1H, s, 2-Im), 7.50 (1H, s, 4,5-Im), 7.47 (1H, s, 4,5-Im), 6.27 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.45 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.26 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.24 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.03–4.89 (2H, m, Im-$C_2\underline{H}_4$-Br), 4.35 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 4.9 Hz), 4.22 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 9.9 Hz, $^3J_{H\text{-}H}$ = 4.9 Hz, $^3J_{H\text{-}H}$ = 1.8 Hz), 4.18 (1H, 6-Glc, dd, $^2J_{H\text{-}H}$ = 12.4 Hz, $^3J_{H\text{-}H}$ = 1.7 Hz), 3.98 (1H, ddd, Im-$C_2\underline{H}_4$-Br, $^2J_{H\text{-}H}$ = 11.5 Hz, $^3J_{H\text{-}H}$ = 6.4 Hz, $^3J_{H\text{-}H}$ = 3.9 Hz), 3.88 (1H, ddd, Im-$C_2\underline{H}_4$-Br, $^2J_{H\text{-}H}$ = 12.1 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz, $^3J_{H\text{-}H}$ = 4.0 Hz), 2.11 (3H, s, OAc), 2.08 (3H, s, OAc), 2.07 (3H, s, OAc), 2.01 (3H, s, OAc). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 170.4 (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 (5-Glc), 71.8 (3-Glc), 70.8 (2-Glc), 67.5 (4-Glc), 61.9 (6-Glc), 50.9 (Im-$\underline{C}H_2$), 31.6 (Br-$\underline{C}H_2$), 20.6 ($\underline{C}H_3$-OAc), 20.4 ($\underline{C}H_3$-OAc), 20.3 ($\underline{C}H_3$-OAc), 20.2 ($\underline{C}H_3$-OAc).

Synthesis of 1,1'-bis(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-3,3'-ethylene-diimidazolium bis(hexafluoro-phosphate) ([(bisNHC-C2)H$_2$](PF$_6$)$_2$). 1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-imidazole (0.853 g, 2.14 mmol), [AcGlcIm$(CH_2)_2$Br]Br (1.25 g, 2.14 mmol), and CH_3CN (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 Et_2O afforded a white solid, which was collected by filtration. The solid was re-dissolved in water and an aqueous solution of NH_4PF_6 (1.76 g, 10.8 mmol) was added to the solution to give a white solid, which was collected by filtration and air-died (1.93 g, 81%). ^1H NMR (400 MHz, CD_3CN): δ8.67 (2H, t, 2-Im, $J_{H\text{-}H}$ = 1.6 Hz), 7.67 (2H, t, 4,5-Im, $J_{H\text{-}H}$ = 1.9 Hz), 7.49 (2H, t, 4,5-Im, $J_{H\text{-}H}$ = 1.9 Hz), 5.74 (2H, d, 2-Glc, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.50 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.25 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 5.22 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.64 (4H s, N-$C\underline{H}_2$),

4.27-4.19 (4H, m, 6-Glc), 4.16 (2H, ddd, 5-Glc, $^{3}J_{H\text{-}H}$ = 10.0 Hz, $^{3}J_{H\text{-}H}$ = 5.0 Hz, $^{3}J_{H\text{-}H}$ = 2.3 Hz), 2.02 (6H, s, OAc), 2.02 (6H, s, OAc), 1.99 (12H, s, OAc). $^{13}C\{^{1}H\}$ 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-$\underline{C}_2H_4$-Im), 20.6 ($\underline{C}H_3$-OAc), 20.54 ($\underline{C}H_3$-OAc), 20.46 ($\underline{C}H_3$-OAc), 20.4 ($\underline{C}H_3$-OAc).

Synthesis of 1-(3-bromopropyl)-3-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl) imidazolium hexafluorophosphate ([AcGlcIm(CH$_2$)$_3$Br](PF$_6$)). 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 Et_2O afforded a white solid, which was collected by filtration. The solid was re-dissolved in water and an aqueous solution of NH_4PF_6 (2.16 g, 13.3 mmol) was added to the solution to give a white solid, which was collected by filtration and air-died (0.773 g, 88%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.77 (1H, s, 2-Im), 7.63 (1H, s, Im), 7.49 (1H, s, Im), 5.72 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 5.48 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 5.31 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.2 Hz), 5.27 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.8 Hz), 4.44−4.28 (2H, m, Br-$\underline{C}H_2$), 4.28−4.12 (3H, m, Glc), 3.51−3.39 (2H, m, Im-$\underline{C}H_2$), 2.47−2.34 (2H, m, 2-$(CH_2)_3$), 2.03 (6H, s, OAc), 1.98 (3H, s, OAc), 1.99 (3H, s, OAc), 1.93 (3H, s, OAc). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 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-$\underline{C}_3H_6$-Br), 32.5 (Im-$\underline{C}_3H_6$-Br), 29.0 (Im-$\underline{C}_3H_6$-Br), 20.8 ($\underline{C}H_3$-OAc), 20.7 ($\underline{C}H_3$-OAc), 20.6 ($\underline{C}H_3$-OAc), 20.5 ($\underline{C}H_3$-OAc).

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

diimidazolium bis(hexafluorophos-phate) ([(bisNHC-C3)H$_2$](PF$_6$)$_2$). [(bisNHC-C3)H$_2$](PF$_6$)$_2$ was obtained analogously to [(bisNHC-C2)H$_2$](PF$_6$)$_2$ using AcGlcIm (0.419 g, 1.05 mmol), [AcGlcIm(CH$_2$)$_3$Br](PF$_6$) (0.699 g, 1.05 mmol), and CH$_3$CN (20 mL) with heating at 110 °C for 48 h and addition of NH$_4$PF$_6$ (0.703 g, 4.31 mmol) (1.07 g, 90%). ^{1}H NMR (300 MHz, DMSO-d_6): δ9.55 (2H, t, 2-Im, $J_{H\text{-}H}$ = 1.3 Hz), 8.12 (2H, t, 4,5-Im, $J_{H\text{-}H}$ = 1.7 Hz), 7.86 (2H, t, 4,5-Im, $J_{H\text{-}H}$ = 1.7 Hz), 6.03 (2H, d, 2-Glc, $^3J_{H\text{-}H}$ = 8.6 Hz), 5.59 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.51 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.1 Hz), 5.25 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 4.40 (2H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 10.1 Hz, $^3J_{H\text{-}H}$ = 4.0 Hz, $^3J_{H\text{-}H}$ = 4.0 Hz), 4.26 (4H, t, N-C$\underline{H}_2$, $^3J_{H\text{-}H}$ = 7.1 Hz), 4.15 (4H, d, 6-Glc, $^3J_{H\text{-}H}$ = 3.8 Hz), 2.39 (2H, quin, 2-(CH$_2$)$_3$, $^3J_{H\text{-}H}$ = 6.9 Hz), 2.04 (6H, s, OAc), 2.02 (6H, s, OAc), 1.98 (6H, s, OAc), 1.92 (6H, s, OAc). ^{13}C{^{1}H} 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-(CH$_2$)$_3$), 29.4 (N-$\underline{C}$H$_2$), 20.6 ($\underline{C}$H$_3$-OAc), 20.4 ($\underline{C}$H$_3$-OAc), 20.2 ($\underline{C}$H$_3$-OAc), 20.0 ($\underline{C}$H$_3$-OAc).

Synthesis of [Pd(bisNHC-C2)Cl$_2$]. A mixture of ligand precursor [(bisNHC-C2)H$_2$](PF$_6$)$_2$ (305 mg, 0.27 mmol), [Pd(NCCH$_3$)$_2$Cl$_2$] (71 mg, 0.27 mmol), NaOAc (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)X$_2$] as an insoluble solid, which was collected by filtration, washed with water and air-dried (208 mg). To a solution of [Pd(bisNHC-C2)X$_2$] (208 mg) in CHCl$_3$ (10 mL), tetraethylammonium 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 recrystallised from an acetone solution by slow addition of hexane to afford **1-C2** as a white solid (128 mg, 48%). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.64 (1H, d, Im, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 7.47 (1H, d, Im, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 7.45 (1H, d, Im, $^{3}J_{H\text{-}H}$ = 2.1 Hz), 7.32 (1H, d, Im, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 7.27 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.1 Hz), 6.44 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 6.00 (1H, ddd, Im-$C_2\underline{H}_4$-Im, $^{2}J_{H\text{-}H}$ = 15.1 Hz, $^{3}J_{H\text{-}H}$ = 11.4 Hz, $^{3}J_{H\text{-}H}$ = 3.7 Hz), 5.75 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 5.58 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 5.47 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.7 Hz), 5.46 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 5.29 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.8 Hz), 5.14 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 4.97 (1H, dt, Im-$C_2\underline{H}_4$-Im , $^{2}J_{H\text{-}H}$ = 14.6 Hz, $^{3}J_{H\text{-}H}$ = 3.9 Hz), 4.79 (1H, dt, Im-$C_2\underline{H}_4$-Im, $^{2}J_{H\text{-}H}$ = 15.0 Hz, $^{3}J_{H\text{-}H}$ = 4.1 Hz), 4.67-4.55 (2H, m, Im-$C_2\underline{H}_4$-Im and 5-Glc overlapping), 4.44 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 13.0 Hz, $^{3}J_{H\text{-}H}$ = 2.3 Hz), 4.34 (1H, dd, Glc, $^{2}J_{H\text{-}H}$ = 12.9 Hz, $^{3}J_{H\text{-}H}$ = 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}C{^{1}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-$\underline{C}_2H_4$-Im), 47.2 (Im-$\underline{C}_2H_4$-Im), 20.88 ($\underline{C}H_3$-OAc), 20.86 ($\underline{C}H_3$-OAc), 20.78 ($\underline{C}H_3$-OAc), 20.70 ($\underline{C}H_3$-OAc), 20.66 ($\underline{C}H_3$-OAc), 20.57 ($\underline{C}H_3$-OAc), 20.52 ($\underline{C}H_3$-OAc), 19.6 ($\underline{C}H_3$-OAc). Anal. Calcd for $C_{35}H_{46}Cl_2N_4O_{18}Pd{\bullet}2H_2O$: 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)$_2$]. To a solution of [Pd(bisNHC-C2)X_2]

(20 mg) in DMSO-d_6 (0.7 mL) in an NMR tube, sodium hydrosulfide (5.0 mg, 0.089 mmol) was added. ^{1}H NMR (300 MHz, DMSO-d_6): δ7.60 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.51 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.47 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.30 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.10 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 6.16 (1H, d, 1-Glc, $J_{H\text{-}H}$ = 9.0 Hz), 5.65 (1H, ddd, Im-C$_2$H$_4$-Im, $^2J_{H\text{-}H}$ = 14.4 Hz, $^3J_{H\text{-}H}$ = 10.5 Hz, $^3J_{H\text{-}H}$ = 3.8 Hz), 5.62 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.55–5.45 (2H, m, Glc), 5.28 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 5.20 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.06 (1H, Glc, $^3J_{H\text{-}H}$ = 9.0 Hz), 4.76 (1H, dt, Im-C$_2$H$_4$-Im, $^2J_{H\text{-}H}$ = 14.7 Hz, $^3J_{H\text{-}H}$ = 4.0 Hz), 4.55 (1H, dt, Im-C$_2$H$_4$-Im, $^2J_{H\text{-}H}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 4.1 Hz), 4.44 (1H, dt, 5-Glc, $^3J_{H\text{-}H}$ = 9.6 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz), 4.38−4.26 (1H, m, Im-C$_2$H$_4$-Im), 4.31(1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.9 Hz, $^3J_{H\text{-}H}$ = 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)Cl$_2$]. A similar reaction for [Pd(bisNHC-C2)X$_2$] using [(bisNHC-C3)H$_2$](PF$_6$)$_2$ (307 mg, 0.27 mmol), [Pd(NCCH$_3$)$_2$Cl$_2$] (71 mg, 0.27 mmol), NaOAc (87 mg, 1.1 mmol), and DMSO (20 mL) afforded [Pd(bisNHC-C3)X$_2$] (148 mg). A similar synthesis for **1-C2** using [Pd(bisNHC-C3)X$_2$] (130 mg) gave **1-C3** (20 mg, 7%). ^{1}H NMR (400 MHz, CD$_3$CN): δ7.40 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.25 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.22 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ =2.3 Hz), 7.08 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 7.01 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.3 Hz), 6.39 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.87 (1H, ddd, N-CH$_2$, $^2J_{H\text{-}H}$ = 15.1 Hz, $^3J_{H\text{-}H}$ = 11.4 Hz, $^3J_{H\text{-}H}$ = 3.7 Hz), 5.54 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.53 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 5.39 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.35 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.27 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.10 (1H, t, Glc, $^3J_{H\text{-}H}$ = 10.1 Hz), 4.76 (1H, dt, N-CH$_2$, $^2J_{H\text{-}H}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 3.9 Hz), 4.54 (1H, dt, N-CH$_2$,

$^{2}J_{H\text{-}H}$ = 15.1 Hz, $^{3}J_{H\text{-}H}$ = 4.1 Hz), 4.37 (1H, ddd, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 16.0 Hz, $^{3}J_{H\text{-}H}$ = 11.0 Hz, $^{3}J_{H\text{-}H}$ = 4.1 Hz), 4.35 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 13.3 Hz, $^{3}J_{H\text{-}H}$ = 2.3 Hz), 4.25-4.05 (6H, m, 5-Glc, 6-Glc, and 2-$(CH_2)_3$ 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). $^{13}C\{^{1}H\}$ 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-$\underline{C}_3H_6$-Im) 50.0 (Im-$\underline{C}_3H_6$-Im), 47.1 (Im-$\underline{C}_3H_6$-Im), 20.92 ($\underline{C}H_3$-OAc), 20.89 ($\underline{C}H_3$-OAc), 20.74 ($\underline{C}H_3$-OAc), 20.68 ($\underline{C}H_3$-OAc), 20.6 ($\underline{C}H_3$-OAc), 20.54 ($\underline{C}H_3$-OAc), 20.51 ($\underline{C}H_3$-OAc), 19.6 ($\underline{C}H_3$-OAc). Anal. Calcd for $C_{37}H_{48}Cl_2N_4O_{18}Pd•2H_2O•(CH_3)_2CO$: 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)$_2$]. To a solution of [Pd(bisNHC-C3)X_2] (17 mg) in DMSO-d_6 (0.7 mL) in an NMR tube, sodium hydrosulfide (5.0 mg, 0.089 mmol) was added. ^{1}H NMR (400 MHz, DMSO-d_6): δ7.56 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 1.5 Hz), 7.35 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 1.5 Hz), 7.33 (2H, s, 4,5-Im), 6.58 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 8.8 Hz), 6.18 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.0 Hz), 5.62 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 5.56 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.1 Hz), 5.52 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.8 Hz), 5.37 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 8.7 Hz), 5.32 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.7 Hz), 5.07 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 4.95−4.80 (2H, m, N-C$\underline{H}_2$), 4.80 (1H, d, 5-Glc, $^{3}J_{H\text{-}H}$ = 10.1 Hz), 4.46 (1H, m, 5-Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz, $^{3}J_{H\text{-}H}$ = 5.7 Hz, $^{3}J_{H\text{-}H}$ = 2.4 Hz), 4.29 (2H, dt, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 13.8 Hz, $^{3}J_{H\text{-}H}$ = 6.3 Hz), 4.16-4.02 (1H, m, 2-$(CH_2)_2$), 4.14 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ =12.3 Hz, $^{3}J_{H\text{-}H}$ =5.9 Hz), 4.08 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.1 Hz, $^{3}J_{H\text{-}H}$ = 1.8 Hz), 3.97 (1H, d, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.0

Hz), 3.91 (1H, d, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.2 Hz), 2.44−2.30 (1H, m, 2-$(CH_2)_2$), 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)$_2$]. A mixture of ligand precursor [(bisNHC-C2)H_2]$(PF_6)_2$ (14.3 mg, 0.013 mmol), $K_2[PtCl_4]$ (5.5 mg, 0.013 mmol), and NaOAc (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). ^{1}H NMR (400 MHz, DMSO-d_6): δ7.55 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 2.0 Hz), 7.46 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 2.0 Hz), 7.43 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 1.9 Hz), 7.25 (1H, d, 4,5-Im, $^{3}J_{H\text{-}H}$ = 2.0 Hz), 7.15 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 6.25 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.0 Hz), 5.66 (1H, ddd, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 14.3 Hz, $^{3}J_{H\text{-}H}$ = 10.6 Hz, $^{3}J_{H\text{-}H}$ = 3.5 Hz), 5.59 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 5.55–5.45 (2H, m, Glc), 5.26 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 5.17 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.7 Hz), 5.04 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 4.69 (1H, dt, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 14.5 Hz, $^{3}J_{H\text{-}H}$ = 3.7 Hz), 4.44 (1H, dt, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 14.6 Hz, $^{3}J_{H\text{-}H}$ = 4.1 Hz), 4.37 (1H, dt, 5-Glc, $^{2}J_{H\text{-}H}$ = 9.6 Hz, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 4.30 (1H, ddd, N-C$\underline{H}_2$, $^{2}J_{H\text{-}H}$ = 15.1 Hz, $^{3}J_{H\text{-}H}$ = 11.1 Hz, $^{3}J_{H\text{-}H}$ = 4.6 Hz), 4.23 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.9 Hz, $^{3}J_{H\text{-}H}$ = 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)$_2$]. A similar procedure for [Pt(bisNHC-C2)$(SH)_2$] was applied to prepare [Pt(bisNHC-C3)$(SH)_2$] using [(bisNHC-C3)H_2]$(PF_6)_2$ (14.8 mg, 0.014 mmol), $K_2[PtCl_4]$ (5.4 mg, 0.013 mmol), and NaOAc (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). ^{1}H 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, $^3J_{H\text{-}H}$ = 9.0 Hz), 6.33 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.8 Hz), 5.76-5.60 (1H, m, N-C$\underline{H}_2$), 5.58 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.0 Hz), 5.51 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 5.36 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.31 (1H, t, Glc, $^3J_{H\text{-}H}$ = 10.0 Hz), 5.06 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.1 Hz), 4.83 (1H, t, Glc, $^3J_{H\text{-}H}$ = 11.0 Hz), 4.90−4.70 (2H, m, N-C$\underline{H}_2$), 4.43 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 8.9 Hz, $^3J_{H\text{-}H}$ = 5.4 Hz, $^3J_{H\text{-}H}$ = 2.1 Hz), 4.19 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 13.8 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz), 4,18-4.09 (2H, m, N-C$\underline{H}_2$; 1H, m, 2-$(CH_2)_2$), 4.07 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 2.1 Hz), 3.97 (1H, d, 6-Glc, $^3J_{H\text{-}H}$ = 12.4 Hz), 3.91 (1H, d, 6-Glc, $^3J_{H\text{-}H}$ = 12.4 Hz), 2.40−2.30 (1H, m, 2-$(CH_2)_2$), 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).

Synthesis of the sugar-incorporated C-C-N ligand precursor [(CCN-AcGlc)H$_2$]Br$_2$.

A solution of 1-(2-bromoethyl)-3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) imidazolium bromide (1.0 g, 1.7 mmol) and 2-(1*H*-imidazol-1-ylmethyl)pyridine (0.56 g, 3.4 mmol) in CH_3CN (30 mL) was heated at 90 °C for 29 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in water (30 mL), and the aqueous solution was washed three times with CH_2Cl_2 (20 mL) to remove the unreacted starting materials. The solvent of the separated aqueous layer was removed under reduced pressure to give a yellow oily material, which was dissolved in CH_2Cl_2 (20 mL). After the solution to remove insoluble solids was filtered, the solvent of the filtrate was removed under reduced pressure. The residue was dissolved in acetone (10 mL) and added Et_2O (50 mL) to afford a yellow powder, which was collected by filtration and dried in air. Yield: 1.4 g (75%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.56 (1H, s, 2-Im), 9.25 (1H, s, 2-Im),

8.55 (1H, d, 6-Py, $^{3}J_{H\text{-}H}$ = 4.2 Hz), 8.12 (1H, s, 4,5-Im), 7.90 (1H, td, 4-Py, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}H}$ = 1.8 Hz), 7.84 (1H, s, 4,5-Im), 7.77 (1H, s, 4,5-Im), 7.70 (1H, s, 4,5-Im), 7.48 (1H, d, 3-Py, $^{3}J_{H\text{-}H}$ = 7.8 Hz), 7.47 (1H, dd, 5-Py, $^{3}J_{H\text{-}H}$ = 7.4 Hz, $^{3}J_{H\text{-}H}$ = 4.1 Hz), 6.07 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 8.7 Hz), 5.57 (2H, s, Py-C$\underline{H}_2$-Im), 5.56 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 5.44 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 5.23 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 4.87-4.71 (4H, m, Im−$C_2\underline{H}_4$−Im), 4.38 (1H, m, 5-Glc), 4.12-4.07 (2H, m, 6-Glc), 2.04 (3H, s, OAc), 2.01 (3H, s, OAc), 1.98 (3H, s, OAc), 1.90 (3H, s, OAc). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6): δ 170.0 (C=O), 169.5 (C=O), 169.4 (C=O), 169.2 (C=O), 153.2 (Py), 149.4 (Py), 137.8 (Py), 137.5 (2-Im), 137.1 (2-Im), 123.8 (4,5-Im), 123.6 (4,5-Im), 123.4 (4,5-Im), 122.7 (Py), 122.4 (Py), 120.8 (4,5-Im), 83.5 (1-Glc), 73.6 (5-Glc), 71.3 (3-Glc), 67.1 (2-Glc), 61.7 (4-Glc), 53.1 (6-Glc), 49.9 (Im-$\underline{C}H_2$-Py), 48.9 (Im−$\underline{C}H_2CH_2$−Im), 48.1 (Im−$CH_2\underline{C}H_2$−Im), 20.6 ($\underline{C}H_3$-OAc), 20.4 ($\underline{C}H_3$-OAc), 20.2 ($\underline{C}H_3$-OAc), 20.1 ($\underline{C}H_3$-OAc). HRMS (ESI+, CH_3CN): *m/z* calcd for $[C_{28}H_{35}BrN_5O_9]^+$: 664.1618, found: 664.1618.

Synthesis of [Pd(CCN-AcGlc)Cl](PF$_6$). A solution of the C-C-N ligand precursor (0.65 g, 0.87 mmol), $[PdCl_2(NCCH_3)_2]$ (0.23 g, 0.87 mmol), and NaOAc (0.21g, 2.4 mmol) in DMSO (30 mL) was stirred overnight at room temperature. The solvent of the reaction mixture was evaporated under reduced pressure to give an orange residue, which was dissolved in water (30 mL). The aqueous solution was washed with CH_2Cl_2 (20 mL) three times. An aqueous solution of NaCl was added to the separated aqueous phase, and the mixture was stirred for 1 h at room temperature. An aqueous solution of NH_4PF_6 was added to the mixture to afford a light-yellow powder, which was collected by suction filtration. After the light yellow powder was dissolved in CH_2Cl_2 (30 mL), the insoluble solids were removed by filtration. The solvent was evaporated under

reduced pressure to give a yellow solid, which was recrystallized from CH_3CN to afford a white powder. Yield: 69 mg (10%). Single crystals suitable for X-ray crystallography were obtained from a solution in a mixed solvent of CH_3OH and acetone with diffusion of Et_2O. Anal. Calcd for [Pd(CCN-AcGlc)Cl]$PF_6 \cdot H_2O$ ($C_{28}H_{35}ClF_6N_5O_{10}P$ Pd) (888.44 g mol^{-1}): C, 37.85; H, 3.97; N, 7.88. Found: C, 37.87; H, 3.91; N, 7.92%. ^{1}H NMR (300 MHz, CD_3CN): Major isomer: δ 9.10 (1H, dd, 6-Py, $^3J_{H\text{-}H}$ = 5.8 Hz, $^4J_{H\text{-}H}$ = 1.0 Hz), 8.09 (1H, td, 4-Py, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz), 7.73 (1H, d, 3-Py, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.60 (1H, ddd, 5-Py, $^3J_{H\text{-}H}$ = 7.7 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz), 7.48 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.41 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.36 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.08 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 6.56 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.70—5.58 (1H, m, Im−$C_2\underline{H}_4$−Im), 5.63 (1H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 15.3 Hz), 5.50 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.41 (1H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 15.3 Hz), 5.31 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.18 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.60 (1H, ddd, Im−$C_2\underline{H}_4$−Im, $^2J_{H\text{-}H}$ = 15.4 Hz, $^3J_{H\text{-}H}$ = 2.9 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz), 4.44-4.25 (2H, m, Im−$C_2\underline{H}_4$−Im), 4.22 (1H, 6-Glc, dd, $^2J_{H\text{-}H}$ = 12.4 Hz, $^3J_{H\text{-}H}$ = 2.3 Hz), 4.12 (1H, 6-Glc, dd, $^3J_{H\text{-}H}$ = 12.4 Hz, $^3J_{H\text{-}H}$ = 5.5 Hz), 4.00 (1H, 5-Glc, ddd, $^3J_{H\text{-}H}$ = 10.3 Hz, $^3J_{H\text{-}H}$ = 5.8 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz), 2.02 (3H, s, OAc), 2.00 (3H, s, OAc), 1.94 (3H, s, OAc), 1.28 (3H, s, OAc). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): Major isomer: δ 170.8 (C=O), 170.22 (C=O), 170.17 (C=O), 169.4 (C=O), 158.9 (2-Im), 153.9 (Py), 153.1 (Py), 152.5 (2-Im), 141.7 (Py), 126.1 (Py), 125.8 (Py), 124.8 (4,5-Im), 123.8 (4,5-Im), 123.8 (4,5-Im), 121.6 (4,5-Im), 86.4 (1-Glc), 75.4 (5-Glc), 73.4 (3-Glc), 72.3 (2-Glc), 69.1 (4-Glc), 62.5 (6-Glc), 56.0 (Py−$\underline{C}H_2$−Im), 51.1 (Im−$\underline{C}H_2CH_2$−Im), 47.5 (Im−$CH_2\underline{C}H_2$−Im), 20.7 ($\underline{C}H_3$-OAc), 20.6 ($\underline{C}H_3$-OAc), 20.5 ($\underline{C}H_3$-OAc), 19.3 ($\underline{C}H_3$-OAc). ^{1}H and $^{13}C\{^1H\}$ NMR signals of the minor isomer were too small for assignments.

Synthesis of the sugar-incorporated C-N-C ligand precursor ([(CNC-AcGlc)H$_2$]Br$_2$). A solution of 2,6-bis(bromomethyl)pyridine (0.25 g, 1.0 mmol) and 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) imidazole (0.80 g, 2.0 mmol) in CH_3CN (30 mL) was refluxed for 5 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure to afford a white residue, which was dissolved in water (30 mL). The aqueous solution was washed with $CHCl_3$ three times. After the solvent of the aqueous solution was evaporated, the residue was dissolved in $CHCl_3$ (30 mL). The solution was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to give a white powder. Yield: 0.83 g (75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.7 (2H, s, 2-Im), 8.04 (2H, s, 4,5-Im), 7.70 (1H, t, 4-Py, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.64 (2H, d, 3,5-Py, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.52 (2H, s, 4,5-Im), 6.78 (2H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 6.07 (2H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 14.5 Hz), 5.75 (2H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 14.5 Hz), 5.47 (2H, t, 3-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.34 (2H, t, 2-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.29 (2H, t, 4-Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.39 (2H, d, 5-Glc, $^3J_{H\text{-}H}$ = 10.1 Hz), 4.30 (2H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 3.7 Hz), 4.25 (2H, d, 6-Glc, $^2J_{H\text{-}H}$ = 11.5 Hz), 2.07 (6H, s, OAc), 2.04 (6H, s, OAc), 2.03 (6H, s, OAc), 2.00 (6H, s, OAc). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 170.5 (C=O), 169.7 (C=O), 169.54 (C=O), 169.47 (C=O), 152.8 (2-Py), 139.1 (4-Py), 137.8 (2-Im), 124.3 (4-Im), 123.7 (3-Py), 118.6 (5-Im), 83.9 (1-Glc), 74.9 (5-Glc), 72.5 (3-Glc), 70.4 (2-Glc), 67.4 (4-Glc), 61.2 (6-Glc), 53.8 (Py-$\underline{C}H_2$-Im), 20.8 ($\underline{C}H_3$-OAc, overlapped), 20.5 ($\underline{C}H_3$-OAc), 20.4 ($\underline{C}H_3$-OAc). HRMS (ESI+, CH_3CN): *m/z* calcd for $[C_{41}H_{51}BrN_5O_{18}]^+$: 980.2413, found: 980.2418.

Synthesis of [Pd(CNC-AcGlc)Cl](PF$_6$). [(CNC-AcGlc)H$_2$]Br$_2$ (1.0 g, 0.94 mmol) and Dowex ion-exchange resin (Cl form, 10 g) in water were stirred for 3 h. After the Dowex was removed by filtration, the solvent was removed under reduced pressure.

The residue was dissolved in $CHCl_3$ (30 mL), and the solution dried over $MgSO_4$. The solvent was evaporated to give a white powder. A mixture of the white powder (0.80 g, 0.82 mmol) and Ag_2O (0.19 g, 0.83 mmol) in CH_3CN (30 mL) was stirred for 3 h at room temperature. $[PdCl_2(NCCH_3)_2]$ (0.22 g, 0.82 mmol) was added, and the mixture was stirred for 3 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in $CHCl_3$ (30 mL), and the insoluble solids were removed by filtration through Celite. The solvent of the filtrate was removed under reduced pressure. The residue was dissolved in CH_3OH (30 mL) and the insoluble solid was removed by filtration through Celite. The solvent was evaporated, and the residue was dissolved in water. An aqueous solution of NaCl was added to the solution, and the mixture was stirred for 30 min. An aqueous solution of NH_4PF_6 was added to the solution to afford a light yellow solid, which was collected by suction filtration. Yield: 138 mg (14%). Anal. Calcd for $[Pd(CNC\text{-}AcGlc)Cl]PF_6 \cdot 2H_2O$ ($C_{41}H_{53}ClF_6N_5O_{20}PPd$) (1222.72 g mol^{-1}): C, 40.27; H, 4.37; N, 5.73, Found: C, 39.99; H, 4.24; N, 5.74. ^1H NMR (300 MHz, CD_3CN): δ 8.09 (1H, t, 4-Py, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.74 (2H, d, 3,5-Py, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.42 (4H, s, 4,5-Im), 6.54 (2H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.8 Hz), 5.60 (2H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 15.3 Hz), 5.45 (2H, d, Py−C$\underline{H}_2$−Im, $^2J_{H\text{-}H}$ = 15.4 Hz), 5.38 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.31 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.20 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 4.24 (2H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 10.5 Hz, $^3J_{H\text{-}H}$ = 1.9 Hz), 4.14 (2H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.3 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz), 4.03 (2H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 9.9 Hz, $^3J_{H\text{-}H}$ = 5.2 Hz, $^3J_{H\text{-}H}$ = 2.1 Hz), 2.05 (6H, s, OAc), 2.00 (6H, s, OAc), 1.93 (6H, s, OAc), 1.41 (6H, s, OAc). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ 171.3 (C=O), 170.7 (C=O), 170.7 (C=O), 169.7 (C=O), 168.3 (2-Im), 155.7 (2,6-Py), 143.1 (4-Py), 127.3 (3,5-Py), 124.2 (4,5-Im), 120.1 (4,5-Im), 85.7 (1-Glc), 75.3 (5-Glc), 73.4 (3-Glc), 71.8 (2-Glc), 68.9 (4-Glc), 62.7 (6-Glc), 56.3 (Py−$\underline{C}H_2$−Im),

21.0 ($\underline{C}H_3$-OAc), 20.9 ($\underline{C}H_3$-OAc), 20.8 ($\underline{C}H_3$-OAc), 20.2 ($\underline{C}H_3$-OAc).

Deprotection of D-glucopyranosyl units of [Pd(CCN-AcGlc)Cl](PF$_6$) and [Pd(CNC-AcGlc)Cl](PF$_6$) affording water-soluble complexes [Pd(CCN-Glc)Cl](PF$_6$) and [Pd(CNC-Glc)Cl](PF$_6$). A mixture of [Pd(CCN-AcGlc)Cl](PF$_6$) (18.5 mg, 0.021 mmol) or [Pd(CNC-AcGlc)Cl](PF$_6$) (25.0 mg, 0.23 mmol) and potassium carbonate (50 mg, 0.36 mmol) in CD_3OD (1 mL) was stirred for an hour. Insoluble solids were removed by filtration. Samples for MS analysis were prepared by using an analogous procedure with CH_3OH instead of CD_3OD. [Pd(CCN-Glc)Cl](PF$_6$): ^{1}H NMR (600 MHz, CD_3OD): δ 9.24 (1H, dd, 6-Py, $^3J_{H\text{-}H}$ = 5.5 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 8.11 (1H, td, 4-Py, $^3J_{H\text{-}H}$ = 7.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz), 7.81 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.76 (1H, d, 3-Py, $^3J_{H\text{-}H}$ = 7.3 Hz), 7.66 (1H, ddd, 5-Py, $^3J_{H\text{-}H}$ = 7.3 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz), 7.49 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.36 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.35 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 5.08 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.4 Hz), 4.93 (1H, dd, Im−$C_2\underline{H}_4$−Im, $^2J_{H\text{-}H}$ = 15.4 Hz, $^3J_{H\text{-}H}$ = 9.2 Hz), 4.79 (1H, dd, Im−$C_2\underline{H}_4$−Im, $^2J_{H\text{-}H}$ = 15.2 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz), 4.57 (1H, dd, Im−$C_2\underline{H}_4$−Im, $^2J_{H\text{-}H}$ = 15.3 Hz, $^3J_{H\text{-}H}$ = 6.9 Hz), 4.46 (1H, dd, Im−$C_2\underline{H}_4$−Im, $^2J_{H\text{-}H}$ = 15.2 Hz, $^3J_{H\text{-}H}$ = 9.1 Hz), 4.00 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz), 3.80 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.3 Hz, $^3J_{H\text{-}H}$ = 6.0 Hz), 3.57 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 8.4 Hz, $^3J_{H\text{-}H}$ = 6.4 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz), 3.46 (1H, t, 3-Glc, $^3J_{H\text{-}H}$ = 8.9 Hz), 3.41 (1H, t, 4-Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 3.23 (1H, t, 2-Glc, $^3J_{H\text{-}H}$ = 8.4 Hz). (The absence of ^{1}H NMR signals of the methylene bridges between the NHC and the pyridine moieties is attributed to H/D exchange reaction in CD_3OD under basic conditions) $^{13}C\{^1H\}$ NMR (150 MHz, CD_3OD): δ 158.8 (2-Im), 153.6 (2-Py), 152.6 (6-Py), 150.8 (2-Im), 141.7 (4-Py), 126.4 (5-Py), 125.0 (3-Py), 124.5 (4,5-Im), 123.5 (4,5-Im), 123.4 (4,5-Im), 120.1 (4,5-Im), 92.5 (1-Glc), 81.0 (5-Glc), 80.0 (3-Glc), 79.0 (2-Glc), 71.1 (4-Glc), 62.8

(6-Glc), 52.5 (Py-C$\underline{D}_2$-Im, quintet, $^1J_{H\text{-}D}$ = 23 Hz), 52.0 (Im−$\underline{C}_2H_4$−Im), 49.04 (Im−$\underline{C}_2H_4$−Im). HRMS (ESI+, CH_3OH): *m/z* calcd for $[C_{20}H_{24}N_5O_5Pd]^+$: 520.0812, found: 520.0823.

[Pd(CNC-Glc)Cl](PF_6): ^{1}H NMR (600 MHz, CD_3OD): δ 8.17 (1H, t, 4-Py, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.87 (1H, dd, 3,5-Py, $^3J_{H\text{-}H}$ = 7.7 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz), 7.85 (1H, dd, 3,5-Py, $^3J_{H\text{-}H}$ = 7.8 Hz, $^4J_{H\text{-}H}$ = 1.3 Hz), 7.69 (4,5-Im, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.58 (4,5-Im, d, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.53 (4,5-Im, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.51 (4,5-Im, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.00 (1-Glc, d, $^3J_{H\text{-}H}$ = 9.0 Hz), 5.07 (1-Glc, d, $^3J_{H\text{-}H}$ = 8.3 Hz), 4.00 (6-Glc, dd, $^2J_{H\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 1.8 Hz), 3.85 (6-Glc, dd, $^2J_{H\text{-}H}$ = 11.5 Hz, $^3J_{H\text{-}H}$ = 2.1 Hz), 3.83 (2-Glc, t, $^3J_{H\text{-}H}$ = 9.3 Hz), 3.79 (6-Glc, dd, $^2J_{H\text{-}H}$ = 12.3 Hz, $^3J_{H\text{-}H}$ = 5.9 Hz), 3.77 (6-Glc, dd, $^2J_{H\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 5.0 Hz), 3.58-3.44 (6H, m, Glc), 3.11 (2-Glc, t, $^3J_{H\text{-}H}$ = 8.2 Hz). (The absence of ^{1}H NMR signals of the methylene bridges between the NHC and the pyridine moieties is attributed to H/D exchange reaction in CD_3OD under basic conditions) $^{13}C\{^1H\}$ NMR (150 MHz, CD_3OD): δ 173.9 (2-Im), 163.19 (2-Im), 157.2 (2,6-Py), 156.5 (2,6-Py), 142.6 (4-Py), 127.9 (3,5-Py), 127.6 (3,5-Py), 122.9 (4,5-Im), 121.8 (4,5-Im), 119.5 (4,5-Im), 119.2 (4,5-Im), 91.6 (1-Glc), 88.7 (1-Glc), 81.5 (2-Glc), 81.3 (5-Glc), 80.9 (5-Glc), 79.0 (3-Glc), 77.6 (2-Glc), 75.3 (3-Glc), 71.3 (4-Glc), 71.1 (4-Glc), 62.8 (6-Glc), 62.5 (6-Glc), 52.6 (Py-$\underline{C}D_2$-Im, quintet, $^1J_{H\text{-}HD}$ = 23 Hz), 51.5 (Py-$\underline{C}D_2$-Im, quintet, $^1J_{H\text{-}D}$ = 25 Hz). HRMS (ESI+, CH_3OH): *m/z* calcd for $[C_{25}H_{32}N_5O_{10}Pd]^+$: 668.1179, found: 668.1186.

Synthesis of 1-(2,3,4,6-tetra-*O*-acetyl-β-glucopyranosyl)-4-(1*H*-imidazol-1-ylmethyl)-1*H*-1,2,3-triazole. To a solution of 1-(prop-2-ynyl)imidazole (0.96 g, 9.1 mmol) and 2,3,4,6-tetra-*O*-acetyl-*β*-glucopyranosyl azide (1.99 g, 5.3 mmol) in 25 mL of dimethylformamide (DMF) was added a solution of $CuSO_4$•$5H_2O$ (72 mg, 0.29

mmol) and sodium ascorbate (0.95 g, 4.8 mmol) in 5 mL of distilled water. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with 50 mL of water, and a small amount of an aqueous solution of NH_3 (14%) was added to the solution. The mixture was extracted with ethyl acetate (50 mL × 3). The separated organic layer was concentrated under reduced pressure, washed with an aqueous solution of NH_3 (14%, 20 mL × 2) and brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the product as a light yellow solid (1.58 g, 62%). ^{1}H NMR (600 MHz, acetone-d_6): δ 8.25 (1H, s, 5-Taz), 7.62 (1H, s, 2-Im), 7.09 (1H, s, 5-Im), 6.91 (1H, s, 4-Im), 6.23 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.59 (1H, t, 2-Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.53 (1H, t, 3-Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.36 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 16.0 Hz), 5.33 (1H, d, Taz-C$\underline{H}_2$-Im), 5.25 (1H, t, 4-Glc, $^3J_{H\text{-}H}$ = 9.6 Hz), 4.34 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 10.1 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz), 4.24 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.5 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz), 4.16 (1H, dd, 6-Glc, $^2J_{H\text{-}H}$ = 12.6 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz), 2.02 (3H, s, 4-C$\underline{H}_3$-OAc), 1.97 (3H, s, 6-C$\underline{H}_3$-OAc), 1.96 (3H, s, 3-C$\underline{H}_3$-OAc), 1.77 (3H, s, 2-C$\underline{H}_3$-OAc). ^{13}C NMR (150 MHz, acetone-d_6): δ 170.6 (C=O), 170.2 (C=O), 170.0 (C=O), 169.3 (C=O), 145.0 (4-Taz), 138.0 (2-Im), 129.9 (4-Im), 122.9 (5-Taz), 119.9 (5-Im), 85.9 (1-Glc), 75.3 (5-Glc), 73.2 (3-Glc), 71.4 (2-Glc), 68.7 (4-Glc), 62.6 (6-Glc), 42.2 (Taz-$\underline{C}H_2$-Im), 20.5 (overlapped two $\underline{C}H_3$-OAc), 20.4 ($\underline{C}H_3$-OAc), 20.1 ($\underline{C}H_3$-OAc).

Synthesis of AcGlc-Taz-Im-C2Br. 1-(2,3,4,6-Tetra-*O*-acetyl-β-glucopyranosyl)-4-(1*H*-imidazol-1-ylmethyl)-1*H*-1,2,3-triazole (1.58 g, 3.30 mmol) and 1,2-dibromoethane (18.5 mL, 220 mmol, 66 equiv.) in 40 mL of acetone were stirred for 23 hours at 80 °C. The solvent of the mixture was removed under reduced pressure. The resulting residue was dissolved in a small amount of acetone, and then Et_2O was added

to afford a precipitate, which was collected by filtration. Additional two re-precipitation operations afforded a light brown powder. (1.88 g, 90%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (1H, s, 2-Im), 8.67 (1H, s, 5-Taz), 7.66 (1H, t, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 1.7 Hz), 7.55 (1H, t, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 1.7 Hz), 5.93 (1H, d, Taz-C$\underline{H}_2$-Im, $^{2}J_{H\text{-}H}$ = 15.0 Hz), 5.89 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 8.9 Hz), 5.80 (1H, d, Taz-C$\underline{H}_2$-Im, $^{2}J_{H\text{-}H}$ = 15.0 Hz), 5.52 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.2 Hz), 5.43 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 5.28 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 4.83 (2H, t, Im-C$_2\underline{H}_4$Br, $^{3}J_{H\text{-}H}$ = 5.5 Hz), 4.30 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.7 Hz, $^{3}J_{H\text{-}H}$ = 4.8 Hz), 4.19 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.7 Hz, $^{3}J_{H\text{-}H}$ = 2.1 Hz), 4.06 (1H, ddd, 5-Glc, $^{3}J_{H\text{-}H}$ = 10.1 Hz, $^{3}J_{H\text{-}H}$ = 4.7 Hz, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 3.88 (2H, t, Im-C$_2\underline{H}_4$Br, $^{3}J_{H\text{-}H}$ = 5.5 Hz), 2.10 (3H, s, OAc), 2.09 (3H, s, OAc), 2.04 (3H, s, OAc), 1.88 (3H, s, OAc). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8 (C=O), 170.1 (C=O), 169.5 (C=O), 169.1 (C=O), 140.5 (4-Taz), 137.4 (2-Im), 125.2 (5-Taz), 122.8 (4 or 5-Im), 122.4 (4 or 5-Im), 85.8 (1-Glc), 75.3 (Glc), 72.7 (Glc), 70.8 (Glc), 67.7 (Glc), 61.6 (Glc), 51.7 (Taz-$\underline{C}H_2$-Im), 44.6 (Im-$\underline{C}_2H_4$-Im), 30.4 (Im-$\underline{C}_2H_4$-Im), 20.9 ($\underline{C}H_3$-OAc), 20.69 ($\underline{C}H_3$-OAc), 20.66 ($\underline{C}H_3$-OAc), 20.5 ($\underline{C}H_3$-OAc).

Synthesis of [(Taz-bisNHC-Me)H$_2$](PF$_6$)$_2$. 1-(2,3,4,6-Tetra-*O*-acetyl-β-glucopyranosyl)-4-(1*H*-imidazol-1-ylmethyl)-1*H*-1,2,3-triazole (1.01 g, 2.1 mmol) and 3-(2-bromoethyl)-1-methylimidazolium bromide (0.56 g, 2.1 mmol) were dissolved in 20 mL of CH_3CN. After the mixture was heated in a sealed tube for 6 days at 111 °C, the solvent was evaporated under reduced pressure. The obtained crude product was washed with acetone to give a gray solid, which was collected by filtration. (1.29 g, 81%) ^{1}H NMR (600 MHz, CD_3CN): δ 9.69 (1H, s, 2-Im), 9.51 (1H, s, 2-Im), 8.52 (1H, s, 5-Taz), 7.88 (1H, s, 4-Im), 7.77 (1H, s, 5-Im), 7.54 (1H, s, 5-Im), 7.40 (1H, s, 4-Im), 6.25 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 9.3 Hz), 5.61 (2H, s, Taz-C$\underline{H}_2$-Im), 5.60 (1H, t, 2-Glc, $^{3}J_{H\text{-}H}$

= 9.5 Hz), 5.49 (1H, t, 3-Glc, $^{3}J_{H\text{-}H}$ = 9.6 Hz), 5.26 (1H, t, 4-Glc, $^{3}J_{H\text{-}H}$ = 9.8 Hz), 4.94 (4H, s, Im-$C_2\underline{H}_4$-Im), 4.28 (1H, ddd, 5-Glc, $^{3}J_{H\text{-}H}$ = 10.1 Hz, $^{3}J_{H\text{-}H}$ = 5.0 Hz, $^{3}J_{H\text{-}H}$ = 2.3 Hz), 4.20 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.6 Hz, $^{3}J_{H\text{-}H}$ = 5.0 Hz), 4.14 (1H, dd, 6-Glc, $^{2}J_{H\text{-}H}$ = 12.6 Hz, $^{3}J_{H\text{-}H}$ = 2.2 Hz), 3.88 (3H, s, C$\underline{H}_3$-Im), 2.00 (3H, s, OAc), 1.98 (3H, s, OAc), 1.95 (3H, s, OAc), 1.79 (3H, s, OAc). ^{13}C NMR (150 MHz, CD_3CN): δ 171.2 (C=O), 170.7 (C=O), 170.5 (C=O), 169.9 (C=O), 141.8 (4-Taz), 138.4 (2-Im), 138.1 (2-Im), 125.4 (5-Taz), 124.7 (4-Im), 124.1 (4-Im), 123.7 (5-Im), 123.4 (5-Im), 85.7 (1-Glc), 75.3 (5-Glc), 73.2 (3-Glc), 71.2 (2-Glc), 68.61 (4-Glc), 62.49 (6-Glc), 49.54 (Im-$\underline{C}H_2$), 49.22 (Im-$\underline{C}H_2$), 45.21 (Im-$\underline{C}H_2$-Taz), 37.2 (Im-$\underline{C}H_3$), 20.9 ($\underline{C}H_3$-OAc), 20.82 ($\underline{C}H_3$-OAc), 20.78 ($\underline{C}H_3$-OAc), 20.6 ($\underline{C}H_3$-OAc).

Synthesis of [(Taz-bisNHC-^{i}Pr)H$_2$](PF$_6$)$_2$. AcGlc-Taz-Im-C2Br (1.14 g, 1.71 mmol) and N-isopropylimidazole (1.0 equiv.) in 20 mL of CH_3CN were stirred for 40 hours at 110 °C. The solvent of the mixture was removed under reduced pressure to afford a light brown powder. After the powder was dissolved in water, insoluble solids were removed by filtration. An aqueous solution of NH_4PF_6 was added to the filtrate to afford a light brown powder, which was collected by filtration. The powder was recrystallized from CH_3OH to afford a light brown powder. (0.925 mg, 60%) ^{1}H NMR (300 MHz, CD_3CN): δ 8.51 (1H, t, 2-Im, $^{4}J_{H\text{-}H}$ = 1.6 Hz), 8.39 (1H, t, 2-Im, $^{4}J_{H\text{-}H}$ = 1.6 Hz), 8.16 (1H, s, 5-Taz), 7.49 (1H, dd, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 2.2 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz), 7.47 (1H, dd, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 2.3 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz), 7.30 (1H, dd, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 2.1 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz), 7.29 (1H, dd, 4 or 5-Im, $^{3}J_{H\text{-}H}$ = 2.0 Hz, $^{4}J_{H\text{-}H}$ = 1.7 Hz), 6.04 (1H, d, 1-Glc, $^{3}J_{H\text{-}H}$ = 8.9 Hz), 5.56 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 5.50 (2H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.4 Hz), 5.45 (2H, s, Taz-CH_2-Im), 5.26 (1H, t, Glc, $^{3}J_{H\text{-}H}$ = 9.5 Hz), 4.57 (1H, sep, C$\underline{H}$-^{i}Pr, $^{3}J_{H\text{-}H}$ = 6.5 Hz), 4.61–4.50 (4H, m, Im-$C_2\underline{H}_4$Br), 4.25–4.12(3H, m, 5,6-Glc), 2.03 (3H, s, OAc),

2.00 (3H, s, OAc), 1.98 (3H, s, OAc), 1.81 (3H, s, OAc), 1.49 (6H, d, (C$\underline{H}_3$)$_2$-*i*Pr, $^3J_{H\text{-}H}$ = 6.7 Hz). ^{13}C NMR (75 MHz, CD_3CN): δ 171.5 (C=O), 171.0 (C=O), 170.7 (C=O), 170.2 (C=O), 141.5 (4-Taz), 137.3 (2-Im), 135,6 (2-Im), 125.1 (5-Taz), 124.4 (4-Im), 123.8 (4-Im), 123.6 (5-Im), 122.5 (5-Im), 86.0 (1-Glc), 74.4 (5-Glc), 73.2 (3-Glc), 71.4 (2-Glc), 68.6 (4-Glc), 62.6 (6-Glc), 54.6 (C$\underline{H}$-*i*Pr), 49.8 (Im-$\underline{C}_2H_4$-Im), 49.6 (Im-$\underline{C}_2H_4$-Im), 45.3 (Taz-$\underline{C}H_2$-Im), 22.7 (overlapped two $\underline{C}H_3$-^{i}Pr), 20.95 ($\underline{C}H_3$-OAc), 20.92 ($\underline{C}H_3$-OAc), 20.89 ($\underline{C}H_3$-OAc), 20.5 ($\underline{C}H_3$-OAc).

Synthesis of [(Taz-bisNHC-Bn)H$_2$](PF$_6$)$_2$. [(Taz-bisNHC-Bn)H$_2$](PF$_6$)$_2$ was prepared analogously to [(Taz-bisNHC-^{i}Pr)H$_2$](PF$_6$)$_2$. Yield: 0.897 g, 55%. ^{1}H NMR (300 MHz, CD_3CN): δ 8.49 (1H, t, 2-Im, $^4J_{H\text{-}H}$ = 1.6 Hz), 8.36 (1H, t, 2-Im, $^4J_{H\text{-}H}$ = 1.6 Hz), 8.16 (1H, s, 5-Taz), 7.49–7.43 (4H, m, three $C_6\underline{H}_5$-Bn, one 4 or 5-Im), 7.41 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 2.2 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.40–7.35 (2H, m, two $C_6\underline{H}_5$-Bn), 7.31 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 2.2 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.29 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 6.04 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.1 Hz), 5.57 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.50 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.44 (2H, s, Taz-C$\underline{H}_2$-Im), 5.32 (2H, s, C$\underline{H}_2$-Bn), 5.26 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.61–4.49 (4H, m, Im-$C_2\underline{H}_4$Br), 4.26–4.10 (3H, m, 5,6-Glc), 2.02 (3H, s, OAc), 1.99 (3H, s, OAc), 1.97 (3H, s, OAc), 1.80 (3H, s, OAc). ^{13}C NMR (75 MHz, CD_3CN): δ 171.5 (C=O), 171.0 (C=O), 170.8 (C=O), 170.3 (C=O), 141.5 (4-Taz), 137.3 (2-Im), 130.0 (2-Im), 134.3 (1-$\underline{C}_6H_5$), 130.4 (4-$\underline{C}_6H_5$), 130.3 (4- or 5-$\underline{C}_6H_5$), 129.8 (4- or 5-$\underline{C}_6H_5$), 125.1 (5-Taz), 124.3 (overlapped two 4- or 5-Im), 123.8 (4- or 5-Im), 123.7 (4- or 5-Im), 86.0 (1-Glc), 75.5 (Glc), 73.2 (Glc), 71.4 (Glc), 68.6 (Glc), 62.6 (6-Glc), 54.6 ($\underline{C}H_2$-Bn), 49.8 (overlapped two Im-$\underline{C}_2H_4$-Im), 45.3 (Taz-$\underline{C}H_2$-Im), 20.95 ($\underline{C}H_3$-OAc), 20.91 ($\underline{C}H_3$-OAc), 20.90 ($\underline{C}H_3$-OAc), 20.5 ($\underline{C}H_3$-OAc).

Synthesis of [(Taz-bisNHC-AcGlc)H$_2$](PF$_6$)$_2$. [(Taz-bisNHC-AcGlc)H$_2$](PF$_6$)$_2$ was

prepared analogously to [(Taz-bisNHC-^{i}Pr)H$_2$](PF$_6$)$_2$ Yield: 1.08 g, 53%. ^{1}H NMR (300 MHz, CD$_3$CN): δ 8.66 (1H, t, 2-Im, $^4J_{H\text{-}H}$ = 1.6 Hz), 8.54 (1H, t, 2-Im, $^4J_{H\text{-}H}$ = 1.7 Hz), 8.17 (1H, s, 5-Taz), 7.65 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 7.48 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.41 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 7.36 (1H, dd, 4 or 5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 6.05 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.8 Hz), 5.74 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.8 Hz), 5.73 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.57 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.50 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 5.505 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 5.497 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 5.45 (2H, s, Taz-C$\underline{H}_2$-Im), 5.28 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.26 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 4.66–4.54 (4H, m, Im-C$_2\underline{H}_4$Br), 4.26–4.12 (6H, m, 5,6-Glc), 2.04 (3H, s, OAc), 2.03 (3H, s, OAc), 2.02 (3H, s, OAc), 2.00 (3H, s, OAc), 1.99 (3H, s, OAc), 1.98 (3H, s, OAc), 1.94 (3H, s, OAc), 1.81 (3H, s, OAc). ^{13}C NMR (75 MHz, CD$_3$CN): δ 171.63 (C=O), 171.61 (C=O), 171.1 (C=O), 171.00 (C=O), 170.96 (C=O), 170.8 (overlapped two C=O), 170.3 (C=O), 141.5 (4-Taz), 137.4 (2-Im), 136.9 (2-Im), 125.1 (5-Taz), 124.4 (4- or 5-Im), 124.3 (4- or 5-Im), 123.7 (4- or 5-Im), 122.4 (4- or 5-Im), 86.0 (1-Glc), 85.7 (1-Glc), 75.8 (Glc), 75.5 (Glc), 73.2 (Glc), 72.4 (Glc), 72.3 (Glc), 71.4 (Glc), 68.6 (Glc), 68.3 (Glc), 62.6 (6-Glc), 62.4 (6-Glc), 50.3 (Im-$\underline{C}_2$H$_4$-Im), 49.5 (Im-$\underline{C}_2$H$_4$-Im), 45.3 (Taz-$\underline{C}$H$_2$-Im), 21.0–20.8 (overlapped six $\underline{C}$H$_3$-OAc), 20.6 ($\underline{C}$H$_3$-OAc), 20.5 ($\underline{C}$H$_3$-OAc).

Synthesis of [Pd(Taz-bisNHC-Me)Cl](PF$_6$). Ligand precursor [(Taz-bisNHC-Me)H$_2$](PF$_6$)$_2$ (500 mg, 0.67 mmol), [PdCl$_2$(NCCH$_3$)$_2$] (174 mg, 0.67 mmol), and NaOAc (128 mg, 1.6 mmol) were dissolved in 15 mL of DMSO. After the mixture was stirred for 8 hours at 60 °C, the solvent of the mixture was removed under reduced pressure. The residue was dissolved in CH$_3$CN and the insoluble solids were filtered off. Addition of Et$_2$O into the filtrate gave a light yellow precipitate, which was collected by

filtration. The solid was re-dissolved in CH_3OH and the insoluble solid was removed by filtration. The solvent of the filtrate was evaporated to give a light yellow solid. The PF_6 salt was obtained by addition of a solution of KPF_6 in water into an aqueous solution of the light yellow solid, collected by filtration, and washed with water. (325 mg, 57%) ^{1}H NMR (600 MHz, CD_3CN): Major isomer: δ 8.25 (1H, s, 5-Taz), 7.30 (1H, s, 4,5-Im), 7.28 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.17 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.05 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.10 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 5.65–5.58 (1H, m, Im-$C_2\underline{H}_4$-Im), 5.53 (1H, t, 3-Glc, 9.5 Hz), 5.45–5.38 (2H, m, Taz-$C\underline{H}_2$-Im), 5.43 (1H, t, 2-Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.28 (1H, t, 4-Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 4.59–4.53 (1H, m, Im-$C_2\underline{H}_4$), 4.39–4.32 (1H, m, Im-$C_2\underline{H}_4$), 4.31–4.24 (1H, m, Im-$C_2\underline{H}_4$), 4.23–4.16 (3H, m, 5,6-Glc), 3.90 (3H, s, Im-$C\underline{H}_3$), 2.03 (3H, s, OAc), 2.00 (3H, s, OAc), 1.99 (3H, s, OAc), 1.97 (3H, s, OAc). Minor isomer: δ 8.28 (1H, s, 5-Taz), 7.30 (2H, s, 4,5-Im), 7.17 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.17 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.07 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 6.12 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.65–5.58 (1H, m, Im-$C_2\underline{H}_4$-Im), 5.58 (1H, t, 2-Glc, 9.4 Hz), 5.49 (1H, t, 3-Glc, 9.5 Hz), 5.45–5.38 (2H, s, Taz-$C\underline{H}_2$-Im), 5.28 (1H, t, 4-Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 4.59–4.53 (1H, m, Im-$C_2\underline{H}_4$), 4.39–4.32 (1H, m, Im-$C_2\underline{H}_4$), 4.31–4.24 (1H, m, Im-$C_2\underline{H}_4$), 4.23–4.16 (3H, m, 5,6-Glc), 3.90 (3H, s, Im-$C\underline{H}_3$), 2.02 (3H, s, OAc), 2.01 (3H, s, OAc), 1.97 (3H, s, OAc), 1.85 (3H, s, OAc). ^{13}C NMR (150 MHz, CD_3CN): Major isomer: δ 171.2 (C=O), 170.8 (C=O), 170.6 (C=O), 170.2 (C=O), 155.3 (2-Im), 153.3 (2-Im), 141.9 (4-Taz), 125.9 (4,5-Im), 124.3 (4,5-Im), 124.0 (4,5-Im), 123.1 (5-Taz), 122.2 (4,5-Im), 87.3 (1-Glc), 75.9 (5-Glc), 72.7 (3-Glc), 71.5 (2-Glc), 68.5 (4-Glc), 62.3 (6-Glc), 51.5 (Im-$\underline{C}_2H_4$-Im), 47.2 (Im-$\underline{C}_2H_4$-Im), 45.7 (Taz-$\underline{C}H_2$-Im), 39.3 (Im-$\underline{C}H_3$), 21.0–20.6 ($\underline{C}H_3$-OAc). Minor isomer: δ 171.2 (C=O), 170.8 (C=O), 170.6 (C=O), 169.9 (C=O), 155.3 (2-Im), 153.3

(2-Im), 142.0 (4-Taz), 125.9 (4,5-Im), 124.4 (4,5-Im), 123.9 (4,5-Im), 123.8 (5-Taz), 122.2 (4,5-Im), 87.0 (1-Glc), 75.9 (5-Glc), 73.2 (3-Glc), 70.9 (2-Glc), 68.4 (4-Glc), 62.3 (6-Glc), 51.5 (Im-$\underline{C}_2H_4$-Im), 47.2 (Im-$\underline{C}_2H_4$-Im), 45.7 (Taz-$\underline{C}H_2$-Im), 39.3 (Im-$\underline{C}H_3$), 21.0–20.6 ($\underline{C}H_3$-OAc). ESI-MS: *m/z* 730 ($[M\text{-}PF_6]^+$). Anal. Calcd for $C_{26}H_{33}ClF_6N_7O_9PPd\bullet 2H_2O$: C, 34.30; H, 4.10; N, 10.77, Found: C, 34.21; H, 3.89; N, 10.73% (The integrated intensity of the signal of H_2O in the ^1H NMR spectrum of the complex in dry $CDCl_3$ was 3.19 (1.6 equiv. of H_2O) relative to the sum of the integrated intensity of the 5-H of the triazole in the complex.)

Synthesis of [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$). Ligand precursor [(Taz-bisNHC-^{i}Pr)H_2]$(PF_6)_2$ (384 mg, 0.423 mmol), $[PdCl_2(NCCH_3)_2]$ (120 mg, 0.462 mmol), and NaOAc (80 mg, 0.975 mmol) were dissolved in 25 mL of DMSO. After the mixture was stirred for 8 hours at 60 °C, the solvent of the mixture was removed under reduced pressure. The residue was dissolved in acetone, and insoluble solid were filtered off. The solvent of the solution was removed, and an aqueous solution of NH_4PF_6 was added to afford a light yellow precipitate, which was collected by filtration. (183 mg, 48%). ^1H NMR (300 MHz, acetone-d_6): Major isomer: δ 8.65 (1H, s, 5-Taz), 7.63 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.62 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.58 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.37 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 6.38 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.0 Hz), 5.82 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 16.0 Hz), 5.78–5.74 (1H, m, Im-$C_2\underline{H}_4$-Im), 5.70 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 15.8 Hz), 5.63 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.52 (1H, t, Glc, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.49 (1H, sep, C$\underline{H}$-^{i}Pr, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.31 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 4.87 (1H, ddd, Im-$C_2\underline{H}_4$-Im, $^2J_{H\text{-}H}$ = 15.3 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz), 4.73-4.62 (1H, m, Im-$C_2\underline{H}_4$-Im), 4.57 (1H, dd, Im-$C_2\underline{H}_4$-Im, $^2J_{H\text{-}H}$ = 12.1 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz), 4.48–4.40 (1H, m, 5-Glc), 4.32-4.17 (2H, m, 6-Glc), 2.05 (3H, s, C$\underline{H}_3$-OAc), 2.01 (6H, s,

C$\underline{H}_3$-OAc), 2.00 (3H, s, C$\underline{H}_3$-OAc). Minor isomer: δ 8.70 (1H, s, 5-Taz), 7.60 (2H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.57 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.38 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 6.42 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.82 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 16.0 Hz), 5.78-5.74 (1H, m, Im-$C_2\underline{H}_4$-Im), 5.70 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 15.8 Hz), 5.70 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.57 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.49 (1H, sep, C$\underline{H}$-^{i}Pr, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.29 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 4.87 (1H, ddd, Im-$C_2\underline{H}_4$-Im, $^2J_{H\text{-}H}$ = 15.3 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz), 4.73–4.62 (1H, m, Im-$C_2\underline{H}_4$-Im), 4.52 (1H, dd, Im-$C_2\underline{H}_4$-Im, $^2J_{H\text{-}H}$ = 12.0 Hz, $^3J_{H\text{-}H}$ = 2.6 Hz), 4.48–4.40 (1H, m, 5-Glc), 4.32-4.17 (2H, m, 6-Glc), 2.05 (3H, s, C$\underline{H}_3$-OAc), 2.02 (3H, s, C$\underline{H}_3$-OAc), 1.98 (6H, s, C$\underline{H}_3$-OAc), 1.87 (3H, s, C$\underline{H}_3$-OAc). ^{13}C NMR (75 MHz, CD_3CN): Major isomer: δ 171.3 (C=O), 170.8 (C=O), 170.6 (C=O), 170.3 (C=O), 154.4 (2-Im), 151.6 (2-Im), 141.8 (4-Taz), 124.4 (4,5-Im), 124.1 (4,5-Im), 123.2 (4,5-Im), 122.8 (5-Taz), 120.5 (4,5-Im), 87.22 (1-Glc), 75.8 (5-Glc), 72.7 (3-Glc), 71.4 (2-Glc), 68.4 (4-Glc), 62.3 (6-Glc), 53.6 (C$\underline{H}$-^{i}Pr), 51.5 (Im-$\underline{C}_2H_4$-Im), 47.3 (Im-$\underline{C}_2H_4$-Im), 45.7 (Taz-$\underline{C}H_2$-Im), 24.1 ($\underline{C}H_3$-^{i}Pr), 22.9 ($\underline{C}H_3$-^{i}Pr), 21.0–20.6 ($\underline{C}H_3$-OAc). Minor isomers: δ 171.3 (C=O), 170.9 (C=O), 170.6 (C=O), 170.0 (C=O), 154.4 (2-Im), 151.6 (2-Im), 141.9 (4-Taz), 124.5 (4,5-Im), 124.1 (4,5-Im), 123.8 (4,5-Im), 122.8 (5-Taz), 120.5 (4,5-Im), 87.0 (1-Glc), 75.7 (5-Glc), 73.1 (3-Glc), 70.9 (2-Glc), 68.3 (4-Glc), 62.3 (6-Glc), 53.6 (C$\underline{H}$-^{i}Pr), 51.5 (Im-$\underline{C}_2H_4$-Im), 47.3 (Im-$\underline{C}_2H_4$-Im), 45.7 (Taz-$\underline{C}H_2$-Im), 24.1 ($\underline{C}H_3$-^{i}Pr), 22.8 ($\underline{C}H_3$-^{i}Pr), 21.0–20.6 ($\underline{C}H_3$-OAc). ESI-MS: *m/z* 758 ([M-PF_6]$^+$). Anal. Calcd for $C_{28}H_{37}ClF_6N_7O_9PPd•H_2O$: C, 36.54; H, 4.27; N, 10.65, Found: C, 36.42; H, 4.28; N, 10.52% (The integrated intensity of the signal of H_2O in the ^{1}H NMR spectrum of the complex in dry $CDCl_3$ was 1.91 (1.0 equiv. of H_2O) relative to the sum of the integrated intensity of the 5-H of the triazole in the complex.)

Synthesis of [Pd(Taz-bisNHC-Bn)Cl](PF$_6$). [Pd(Taz-bisNHC-Bn)Cl](PF$_6$) was prepared analogously to [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$). Yield: 241 mg, 60%. ^{1}H NMR (300 MHz, acetone-d$_6$): Major isomer: δ 8.61 (1H, s, 5-Taz), 7.64 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.53 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.51 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.42-7.31 (6H, m, 4,5-Im, C$_6$H$_5$-Bn), 6.36 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.1 Hz), 5.96 (1H, d, CH$_2$-Bn, $^2J_{H\text{-}H}$ = 14.7 Hz), 5.90–5.76 (1H, m, Im-C$_2$H$_4$-Im), 5.65 (1H, d, Taz-CH$_2$-Im, $^2J_{H\text{-}H}$ = 15.6 Hz), 5.63 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.472 (1H, d, Taz-CH$_2$-Im, $^2J_{H\text{-}H}$ = 14.6 Hz), 5.465 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.30 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.93 (1H, d, CH$_2$-Bn, $^2J_{H\text{-}H}$ = 15.7 Hz), 4.91 (1H, ddd, Im-C$_2$H$_4$-Im, $^2J_{H\text{-}H}$ = 15.3 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz), 4.73–4.52 (2H, m, Im-C$_2$H$_4$-Im), 4.49–4.39 (1H, m, 5-Glc), 4.33–4.17 (2H, m, 6-Glc), 2.05 (3H, s, CH$_3$-OAc), 2.04 (6H, s, CH$_3$-OAc), 2.00 (3H, s, CH$_3$-OAc), 1.99 (6H, s, CH$_3$-OAc). Minor isomer: δ 8.66 (1H, s, 5-Taz), 7.64 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.56 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.52 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.4 Hz), 7.42–7.31 (6H, m, 4,5-Im, C$_6$H$_5$-Bn), 6.41 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 6.03 (1H, d, CH$_2$-Bn, $^2J_{H\text{-}H}$ = 14.9 Hz), 5.90–5.76 (1H, m, Im-C$_2$H$_4$-Im), 5.662 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.658 (1H, d, Taz-CH$_2$-Im, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.57 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.45 (1H, d, Taz-CH$_2$-Im, $^2J_{H\text{-}H}$ = 14.8 Hz), 5.27 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.01 (1H, d, CH$_2$-Bn, $^2J_{H\text{-}H}$ = 15.8 Hz), 4.91 (1H, ddd, Im-C$_2$H$_4$-Im, $^2J_{H\text{-}H}$ = 15.3 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz), 4.73–4.52 (2H, m, Im-C$_2$H$_4$-Im), 4.49–4.39 (1H, m, 5-Glc), 4.33–4.17 (2H, m, 6-Glc), 2.05 (3H, s, CH$_3$-OAc), 2.01 (6H, s, CH$_3$-OAc), 1.97 (3H, s, CH$_3$-OAc), 1.84 (6H, s, CH$_3$-OAc). ^{13}C NMR (75 MHz, CD$_3$CN): Major isomer: δ 171.3 (C=O), 170.8 (C=O), 170.6 (C=O), 170.2 (C=O), 156.3 (2-Im), 151.2 (2-Im), 141.5 (4-Taz), 138.3 (CH$_2$-Bn), 129.7-129.0 (C$_6$H$_5$-Bn), 125.5 (4,5-Im), 124.4 (4,5-Im), 123.9 (4,5-Im),

123.3 (5-Taz), 122.2 (4,5-Im), 87.2 (1-Glc), 75.8 (5-Glc), 72.6 (3-Glc), 71.3 (2-Glc), 68.4 (4-Glc), 62.3 (6-Glc), 51.4 (Im-$\underline{C}_2H_4$-Im), 47.4 (Im-$\underline{C}_2H_4$-Im), 45.3 (Taz-$\underline{C}H_2$-Im), 21.0–20.6 ($\underline{C}H_3$-OAc). Minor isomer: δ 171.3 (C=O), 170.9 (C=O), 170.6 (C=O), 170.0 (C=O), 156.3 (2-Im), 151.3 (2-Im), 141.6 (4-Taz), 138.3 ($\underline{C}H_2$-Bn), 129.7–129.0 ($\underline{C}_6H_5$-Bn), 125.4 (4,5-Im), 124.5 (4,5-Im), 123.9 (4,5-Im), 123.7 (5-Taz), 122.2 (4,5-Im), 86.9 (1-Glc), 75.7 (5-Glc), 73.1 (3-Glc), 70.8 (2-Glc), 68.2 (4-Glc), 62.3 (6-Glc), 51.4 (Im-$\underline{C}_2H_4$-Im), 47.4 (Im-$\underline{C}_2H_4$-Im), 45.3 (Taz-$\underline{C}H_2$-Im), 21.0–20.6 ($\underline{C}H_3$-OAc). ESI-MS: *m/z* 806 ($[M\text{-}PF_6]^+$). Anal. Calcd for $C_{32}H_{37}ClF_6N_7O_9PPd\bullet 0.7H_2O$: C, 39.91; H, 4.02; N, 10.09, Found: C, 40.07; H, 4.08; N, 10.09% (The integrated intensity of the signal of H_2O in the ^1H NMR spectrum of the complex in dry $CDCl_3$ was 1.36 (0.7 equiv. of H_2O) relative to the sum of the integrated intensity of the 5-H of the triazole in the complex.)

Synthesis of [Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$). [Pd(Taz-bisNHC-AcGlc)Cl](PF$_6$) was prepared analogously to [Pd(Taz-bisNHC-^{i}Pr)Cl](PF$_6$). Yield: 284 mg, 57%. ^1H NMR (300 MHz, acetone-d_6): Major isomer: δ 8.73 (1H, s, 5-Taz), 7.80 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.68 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.67 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.45 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.1 Hz), 6.71 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 6.43 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.3 Hz), 5.91 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.92–5.75 (1H, m, Im-C$_2\underline{H}_4$-Im), 5.72 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.65 (1H, d, Taz-C$\underline{H}_2$-Im, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.57 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.37 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.29 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 5.20 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 4.94 (1H, d, Im-C$_2\underline{H}_4$-Im, $^2J_{H\text{-}H}$ = 15.4 Hz), 4.78–4.50 (2H, m, Im-C$_2\underline{H}_4$-Im), 4.44 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 10.1 Hz, $^3J_{H\text{-}H}$ = 5.1 Hz, $^3J_{H\text{-}H}$ = 2.5 Hz), 4.34–4.12 (2H, m, 6-Glc), 4.12–4.02 (1H, m, 5-Glc), 2.06 (3H, s, C$\underline{H}_3$-OAc), 2.03 (6H, s, C$\underline{H}_3$-OAc), 2.024 (3H, s, C$\underline{H}_3$-OAc), 2.018 (6H, s,

C<u>H</u>$_3$-OAc), 1.98 (3H, s, C<u>H</u>$_3$-OAc), 1.94 (6H, s, C<u>H</u>$_3$-OAc), 1.88 (3H, s, C<u>H</u>$_3$-OAc), 1.35 (6H, s, C<u>H</u>$_3$-OAc). Minor isomer: δ 8.67 (1H, s, 5-Taz), 7.82 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.4 Hz), 7.67 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.61 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.38 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.71 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 6.40 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.2 Hz), 5.91 (1H, d, Taz-C<u>H</u>$_2$-Im, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.92–5.75 (1H, m, Im-C$_2$<u>H</u>$_4$-Im), 5.74 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.2 Hz), 5.65 (1H, d, Taz-C<u>H</u>$_2$-Im, $^2J_{H\text{-}H}$ = 15.9 Hz), 5.57 (2H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.46 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.31 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.5 Hz), 5.18 (1H, t, Glc, $^3J_{H\text{-}H}$ = 9.7 Hz), 4.94 (1H, d, Im-C$_2$<u>H</u>$_4$-Im, $^2J_{H\text{-}H}$ = 15.4 Hz), 4.78–4.50 (2H, m, Im-C$_2$<u>H</u>$_4$-Im), 4.37 (1H, ddd, 5-Glc, $^3J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 4.9 Hz, $^3J_{H\text{-}H}$ = 2.5 Hz), 4.34–4.12 (2H, m, 6-Glc), 4.12–4.02 (1H, m, 5-Glc), 2.06 (3H, s, C<u>H</u>$_3$-OAc), 2.02 (6H, s, C<u>H</u>$_3$-OAc), 2.01 (3H, s, C<u>H</u>$_3$-OAc), 2.00 (6H, s, C<u>H</u>$_3$-OAc), 1.99 (3H, s, C<u>H</u>$_3$-OAc), 1.95 (6H, s, C<u>H</u>$_3$-OAc), 1.94 (3H, s, C<u>H</u>$_3$-OAc), 1.35 (6H, s, C<u>H</u>$_3$-OAc). ^{13}C NMR (75 MHz, CD_3CN): δ 171.4 (C=O), 171.3 (C=O), 170.9 (C=O), 170.8 (overlapped two C=O), 170.6 (C=O), 170.1 (C=O), 169.9 (C=O), 158.5 (2-Im), 156.7 (2-Im), 141.6 (4-Taz), 125.5 (4,5-Im or 5-Taz), 124.3 (4,5-Im or 5-Taz), 124.0 (4,5-Im or 5-Taz), 123.9 (4,5-Im or 5-Taz), 121.3 (4,5-Im or 5-Taz), 86.9 (1-Glc), 86.4 (1-Glc), 75.6 (Glc), 75.3 (Glc), 73.3 (Glc), 73.1 (Glc), 72.0 (Glc), 70.7 (Glc), 69.1 (Glc), 68.2 (Glc), 62.7 (6-Glc), 62.3 (6-Glc), 51.3 (Im-<u>C</u>$_2$H$_4$-Im), 47.5 (Im-<u>C</u>$_2$H$_4$-Im), 45.8 (Taz-<u>C</u>H$_2$-Im), 21.1 (<u>C</u>H$_3$-OAc), 20.89 (overlapped three <u>C</u>H$_3$-OAc), 20.84 (<u>C</u>H$_3$-OAc), 20.83 (<u>C</u>H$_3$-OAc), 20.6 (<u>C</u>H$_3$-OAc), 19.6 (<u>C</u>H$_3$-OAc). ESI-MS: *m/z* 1046 ([M-PF_6]$^+$). Anal. Calcd for $C_{39}H_{49}ClF_6N_7O_{18}PPd \cdot H_2O$: C, 38.76; H, 4.25; N, 8.11, Found: C, 38.50; H, 4.37; N, 8.22% (The integrated intensity of the signal of H_2O in the ^{1}H NMR spectrum of the complex in dry $CDCl_3$ was 1.81 (0.9 equiv. of H_2O) relative to the sum of the integrated intensity of the 5-H of the triazole in the

complex.)

Synthesis of [Pd(Taz-bisNHC-Me)(Me)Cl]. A suspension of Ag_2O (318 mg, 1.37 mmol) and $[(Taz\text{-}bisNHC\text{-}Me)H_2]Br_2$ (936 mg, 1.24 mmol) in 40 mL of CH_2Cl_2 was stirred for 4 hours at room temperature to give a colorless solution. [Pd(cod)(Me)Cl] was added to the solution, and the mixture was stirred for 16 hours at room temperature. Insoluble solid was filtered off, and the filtrate was concentrated under reduced pressure. Addition of Et_2O into the concentrated filtrate gave a brown precipitate, which was collected by filtration. (514.9 mg, 56%) An analytically pure product was obtained by fractional precipitation with Et_2O from the solution of the crude product in CH_2Cl_2. (79.9 mg, 8.6%) ^{1}H NMR (300 MHz, CD_3CN, 4 days after addition of D_2O): Major isomer: δ 8.41 (1H, s, 5-Taz), 7.27 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.24 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.14 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.99 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz), 6.17 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 9.0 Hz), 5.67 (1H, d, Glc, $^3J_{H\text{-}H}$ = 9.4 Hz), 5.58-5.35 (3H, m, Glc, Taz-C$\underline{H}_2$-Im), 5.31-5.14 (2H, m, Im-$C_2\underline{H}_4$, 4-Glc), 4.46 (1H, d, Im-$C_2\underline{H}_4$, $^3J_{H\text{-}H}$ = 15.4 Hz), 4.35-4.07 (4H, m, Im-$C_2\underline{H}_4$, 5,6-Glc), 3.71 (3H, s, N-C$\underline{H}_3$), 2.08-1.72 (12H, m, OAc). Minor isomer: d 8.37 (1H, s, 5-Taz), 7.27 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.24 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.14 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.99 (1H, d, 4,5-Im, $^3J_{H\text{-}H}$ = 1.7 Hz), 6.14 (1H, d, 1-Glc, $^3J_{H\text{-}H}$ = 8.5 Hz), 5.58-5.35 (4H, m, 2,3-Glc, Taz-C$\underline{H}_2$-Im), 5.28 (1H, d, Im-$C_2\underline{H}_4$, $^3J_{H\text{-}H}$ = 8.9 Hz), 5.31-5.14 (2H, m, Im-$C_2\underline{H}_4$, 4-Glc), 4.46 (1H, d, Im-$C_2\underline{H}_4$, $^3J_{H\text{-}H}$ = 15.4 Hz) 4.35-4.07 (4H, m, two Im-$C_2\underline{H}_4$, 5,6-Glc), 3.71 (3H, s, N-C$\underline{H}_3$), 2.08-1.72 (12H, m, OAc). ESI-MS: *m/z* = 708 ($[M-Cl]^+$) in CH_3CN; m/z = 708 ($[M-Cl]^+$), 728 ($[M-Me]^+$) in CH_2Cl_2. Anal. Calcd for $C_{27}H_{36}ClN_7O_9Pd\bullet H_2O\bullet 0.5CH_2Cl_2$: C, 41.03; H, 4.88; N, 12.18, Found: C, 41.06; H, 4.91; N, 12.41%.

X-ray crystallography. 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 CrystalClear[45] software. Absorption corrections were applied using the multi-scan method. The structures were solved using SIR97[46] expanded using Fourier techniques, and refined by using full matrix least-squares against F^2 with SHELXL97[47] equipped in a CrystalStructure[48] software. Crystallographic data are summarised in 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 ridding models.

DFT Calculations.

DFT caluculations were carried out using Gaussian03.[49] Atomic coordinates were optimized at the level of B3LYP/LanL2DZ for the Pd and 6-31G(d,p) for the others. Vibrational frequencies were calculated for all converged structures, and no imaginary frequencies were determined showing that these structures lie on minima.

Elucidation of catalytic ability of the complexes for Suzuki-Miyaura cross-coupling in water

Suzuki-Miyaura cross-coupling in water. A mixture of Pd complex, 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 CH_2Cl_2 (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 ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard.

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 CH_2Cl_2 (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 ^{1}H NMR signals using 1,3,5-trimethoxybenzene as an internal standard. The same procedure was repeated twice to evaluate the reuse of the catalysts.

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List of Achievements

【学術論文】

Yosuke Imanaka, Hideki Hashimoto, Isamu Kinoshita, Takanori Nishioka, "Incorporation of a Sugar Unit into a C-C-N Pincer Pd Complex Using Click Chemistry and Its Dynamic Behavior in Solution and Catalytic Ability toward the Suzuki-Miyaura Coupling in Water", *Chem. Lett.*, 2014, **43**, 687.

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