

## Porphyrin Pincer Complexes: Peripherally Cyclometalated Porphyrins and Their Catalytic Activities Controlled by Central Metals

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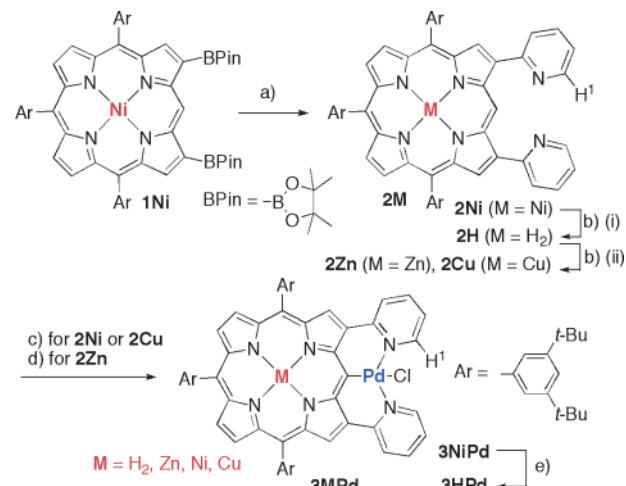
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Porphyrin metal complexes generally employ the inner cavity as the coordination site. The central metal often plays a critical role to dominate electronic and structural properties of a metal-porphyrin. In contrast, transition metal porphyrin complexes that have a carbon–metal  $\sigma$ -bond at the porphyrin periphery are still rare.<sup>1</sup> Nevertheless, peripherally metalated porphyrins should offer a nice scaffold to investigate electronic and steric effects of the inner metal and porphyrin core onto the outer metal. Such effects likely influence physical and chemical properties such as magnetism, photophysics, and reactivity in metal-catalyzed reactions of the complexes.

Pincer type organometallic complexes have received much attention as highly active and stable catalysts in a number of organic transformations, as well as light emitting materials.<sup>2</sup> The tridentate ligand strongly supports a metal to prevent ligand dissociation, achieving high thermal stability. Although there have been numerous pincer complexes reported, heterobimetallic pincer complexes are not well-precedented.<sup>3</sup> More importantly, the effect of one metal upon the other catalytic center has not been investigated.

We undertook the synthesis of a heterobimetallic porphyrin pincer complex, namely, a hybrid of a peripherally metalated porphyrin and a pincer type complex (Scheme 1).<sup>4</sup> Two 2-pyridyl groups were introduced at the  $\beta$ -positions adjacent to the unsubstituted *meso*-position of 5,10,15-triarylporphyrin to set up the outer coordination site, starting from  $\beta,\beta'$ -diborylporphyrin **1Ni** via Suzuki–Miyaura cross-coupling with 2-iodopyridine.  $\beta,\beta'$ -Difunctionalized porphyrins have been difficult to prepare but have now become readily available through iridium-catalyzed borylation of porphyrins.<sup>5</sup> Metalation of nickel porphyrin **2Ni** with  $K_2PdCl_4$  in toluene–DMF at 100 °C proceeded efficiently with vivid color change from purple to green via smooth C–H bond cleavage to furnish heterobimetallic complex **3NiPd** as an air- and moisture-stable solid in 92% yield after recrystallization. Its parent mass ion peak was observed at  $m/z = 1191.4577$  (calcd for  $(C_{72}H_{77}N_6NiPd)^+ = 1191.4600 [(M - Cl)^+]$ ) in its high-resolution electrospray-ionization time-of-flight (HR ESI-TOF) mass spectrum. Accordingly, disappearance of the *meso*-proton in the  $^1H$  NMR spectrum of **3NiPd** supported the formation of a carbon–metal bond. Upon metalation, the proton  $H^1$  on the pyridyl group exhibited substantial downfield shift (from  $\delta = 9.01$  to 9.84). Palladation of **2Cu** also proceeded smoothly to provide **3CuPd** in 72% yield, and **3ZnPd** was obtained under milder conditions at 60 °C in 83% yield. Interestingly, treatment of **3NiPd** with sulfuric acid in refluxing trifluoroacetic acid (TFA) induced preferential demetalation of the inner nickel ion to provide free base porphyrin **3HPd** in 71% yield, thus highlighting the strength of the C–Pd bond. X-ray crystallographic analyses of **3NiPd**, **3CuPd**, and **3HPd** unambiguously elucidated their structures. Interestingly, the structure of the porphyrin macrocycle is highly distorted to take a saddle conformation, while the outer palladium exhibits almost ideal square planar coordination (Figure

Scheme 1<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) 2-iodopyridine,  $Pd_2(dba)_3$ ,  $PPh_3$ ,  $Cs_2CO_3$ ,  $CsF$ , toluene/DMF/ $H_2O$ , reflux; (b) (i) concd  $H_2SO_4/CH_2Cl_2$ , (ii)  $Zn(OAc)_2 \cdot 2H_2O$  or  $Cu(OAc)_2 \cdot H_2O$ ,  $CHCl_3/MeOH$ ; (c)  $K_2PdCl_4$ , toluene/DMF, 100 °C; (d)  $K_2PdCl_4$ ,  $NaOAc$ , DMF, 60 °C; (e) concd  $H_2SO_4/TFA$ , reflux.

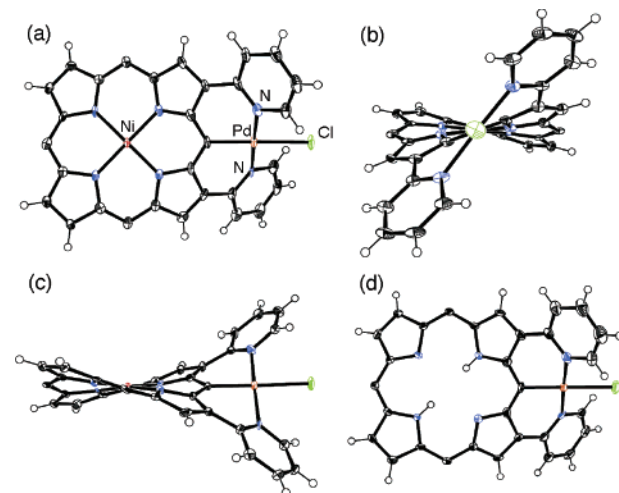
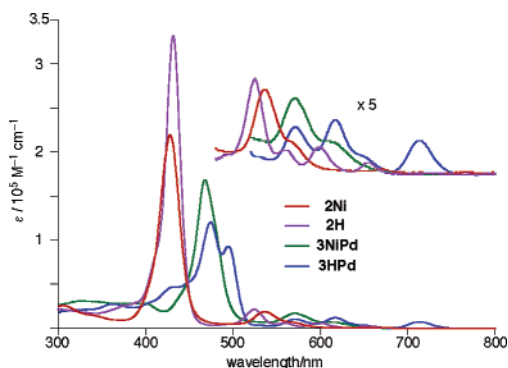
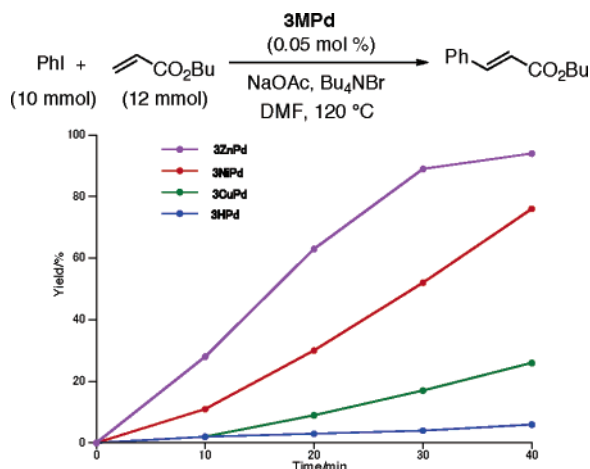


Figure 1. X-ray structures of porphyrin pincer complexes. Top view (a), front view (b), side view (c) of **3NiPd**, and top view (d) of **3HPd**. The thermal ellipsoids are scaled to the 50% probability level. *meso*-Aryl substituents are omitted for clarity.

1 and Supporting Information).<sup>6</sup> Maximum displacements of the  $\beta$ -carbon from the 4N plane are 1.067 Å for **3NiPd**, 0.982 Å for **3CuPd**, and 1.054 Å for **3HPd**, and the mean plane deviations are 0.436 Å for **3NiPd**, 0.384 Å for **3CuPd**, and 0.380 Å for **3HPd**. The bond lengths of C–Pd are 1.977(7) Å for **3NiPd**, 1.972(6) Å for **3HPd**, and 1.969(6) Å for **3CuPd**. The pyridyl groups are rather coplanar (ca. 6–9°) to the adjacent pyrrole units in the deformed



**Figure 2.** UV/vis absorption spectra of **2Ni**, **2H**, **3NiPd**, and **3HPd** in  $\text{CH}_2\text{Cl}_2$ .



**Figure 3.** Reaction profile of the Heck reaction with **3MPd**.

porphyrin core. The outer metalation also induced lowering of dihedral angles (ca.  $46\text{--}57^\circ$ ) between the aromatic substituents and the core. These structural analyses revealed that the environment of the palladium center in these complexes is almost identical, while the distortion of the porphyrin cores varies depending on the central metals.

Figure 2 shows UV/vis absorption spectra of **3** along with **2**, which exhibit substantial red shift (for the Soret band,  $\Delta\lambda = 41$  nm from **2Ni** to **3NiPd** and  $\Delta\lambda = 42$  nm from **2H** to **3HPd**) due to deformation of the porphyrin skeleton as well as expansion of conjugation by the coplanar pyridyl groups.<sup>7</sup> Soret bands of porphyrin pincer complex **3** are broadened (**3NiPd**) or split (**3HPd**). Absorption spectra of **3ZnPd** and **3CuPd** are quite similar as those of **3HPd** and **3NiPd**, respectively (Supporting Information). No emission was observed for **3HPd** and **3ZnPd** upon excitation at their Soret bands.

The attractive feature of porphyrins is that their structural and electronic properties are susceptible to the central metal. With several porphyrin pincer palladium complexes in hand, we carried out preliminary experiments to elucidate metal dependence of the catalytic activity in the typical Heck reaction.<sup>8</sup> All of the pincer complexes exhibited catalytic activity, but comparative experiments revealed notable differences in the initial reaction profile (Figure 3). Although the mechanism of the present Heck system is unclear, it is clear that the inner metal significantly influences the property of the active site of the catalyst.

In conclusion, we have achieved the synthesis of heterobimetallic porphyrin pincer complexes. Highly distorted structures of them have been revealed by X-ray analyses. These complexes exhibit markedly different catalytic activity in the typical Heck reaction depending on the central metals. Highly tunable nature of porphyrins by central metals and peripheral substituents should allow further creation of effective complexes for various transition-metal-catalyzed reactions.

**Acknowledgment.** This paper is dedicated to the memory of Professor Yoshihiko Ito. This work was supported by a Grant-in-Aid for Scientific Research (No. 18685013) from MEXT. H.S. acknowledges Asahi Glass Foundation and Mitsubishi Chemical Corporation Fund for financial support.

**Supporting Information Available:** General procedures, spectral data for compounds, crystal structures, and CIF files for **2Zn**, **3NiPd**, **3CuPd**, and **3HPd**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA072218S