Azaporphyrin Ligands

DOI: 10.1002/anie.201408852

A 3-Pyridyl-5,15-Diazaporphyrin Nickel(II) Complex as a Bidentate Metalloligand for Transition Metals**

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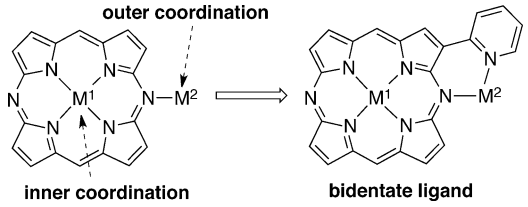
Abstract: *3-Pyridyl-5,15-diazaporphyrin nickel(II) serves as a bidentate metalloligand for platinum(II), ruthenium(II), and rhenium(I) metal centers. Single-crystal X-ray diffraction analysis of these metal complexes unambiguously reveals the presence of a dative bond between the outer metal center and the meso-nitrogen atom. The UV/Vis absorption spectra of the complexes show substantially red-shifted bands which are perturbed by outer-metal coordination. This is due to the contribution of metal-to-ligand charge transfer interactions.*



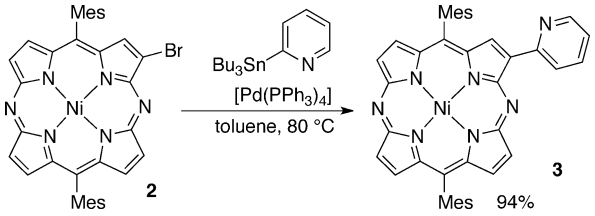
Scheme 1. Design of a 5,15-diazaporphyrin bidentate metalloligand.

Pyridine serves as an excellent ligand, in which the lone pair of the sp^2-hybridized nitrogen atom can be donated to a variety of metal ions to form strong bonds. Pyridine metal complexes are extremely important in organic synthesis as useful catalysts for reactions such as oxidative transformation, polymerization, and asymmetric induction.[1] Pyridine complexes are also key materials for light-emitting devices[2] and photovoltaic cells.[3] Furthermore, pyridine-based ligands are critical in the construction of supramolecular architectures[4] and metal–organic frameworks.[5]

In contrast to the rich chemistry of pyridine metal complexes, the coordination of the *meso*-nitrogen of azaporphyrins to metal centers has rarely been explored. Although azaporphyrins have an imine sp^2-hybridized nitrogen atom similar to that of pyridine, their outer-metal coordination ability has not been confirmed (Scheme 1). The coordination of *meso*-nitrogen atoms of a 5,15-diazaporphyrin ligand to Pd^{II} ions was previously proposed on the basis of elemental analysis.[6] However, such outer-metallated diazaporphyrin complexes are still elusive because of the lack of firm structural evidence. We have designed a new bidentate ligand bearing the 5,15-diazaporphyrin moiety and confirmed outer metal coordination to the *meso*-nitrogen atom on the basis of single-crystal X-ray diffraction analysis.

Coordination of metal ions to peripheral carbon atoms has been reported for regular porphyrins.[7] However, the formation of directly metallated porphyrin complexes requires C–H and C–Br bond cleavage at the porphyrin periphery, thus limiting the scope of available metals to only mercury, palladium, platinum, and iridium.[8–10] In this regard, a variety of metal ions could be coordinated to diazaporphyrins through a dative bond.

The pyridyldiazaporphyrin nickel(II) metalloligand **3** was readily prepared in 94% yield through a Stille coupling reaction between 2-(tributylstannyl)pyridine and a bromodiazaporphyrin Ni^{II} complex **2** (Scheme 2), which can be obtained by regioselective bromination of a 5,15-diazaporphyrin Ni^{II} complex with NBS (*N*-bromosuccinimide).[11] Single-crystal X-ray diffraction analysis of ligand **3** revealed



Scheme 2. Synthesis of pyridyldiazaporphyrin nickel(II) metalloligand **3** through a Stille coupling reaction. Mes = mesityl.

that the pyridyl group is almost coplanar to the diazaporphyrin core: the dihedral angle between the pyridine and pyrrole moieties is 6.86°.[12] Interestingly, the pyridine nitrogen atom points outward relative to the *meso*-nitrogen atom (Figure S16 in the Supporting Information). This orientation is probably due to a hydrogen-bonding interaction between the *meso*-nitrogen atom and the pyridyl proton. The distance between the *meso*-nitrogen atom and the carbon atom is 2.99 Å. Additionally, in the ^{1}H NMR spectrum of **3**, the signal which appears as a doublet attributed to the pyridyl proton is detected at $\delta = 9.9$ ppm in a substantially downfield region, which indicates that the *meso*-nitrogen in diazaporphyrins serves as a hydrogen-bonding acceptor.

Treatment of pyridyldiazaporphyrin Ni^{II} **3** with potassium tetrachloroplatinate in toluene/DMF at 100 °C afforded **4Pt**

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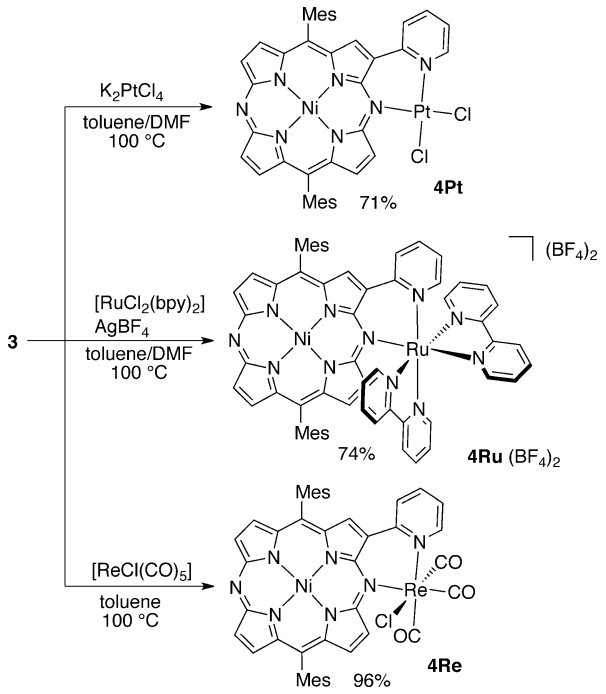
[**] This work was supported by Grants-in-Aid for Scientific Research (Numbers 24350023 and 26410042) and the Program for Leading Graduate Schools "Integrative Graduate Education and Research in Green Natural Sciences," MEXT (Japan). H.S. also acknowledges the Yazaki Science Foundation for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408852.

in 71% yield after purification by recrystallization (Scheme 3). Metallation of **3** with dichlorobis(2,2′-bipyridyl)-ruthenium in the presence of $AgBF_4$ provided the corresponding ruthenium complex **4Ru**$(BF_4)_2$ in 74% yield. The



Scheme 3. Platinum, ruthenium, and rhenium metallation of pyridyldiazaporphyrin Ni^{II} **3**. bpy = 2,2′-bipyridyl. DMF = dimethylformamide.

reaction of **3** with pentacarbonyl(chloro)rhenium also furnished tricarbonylrhenium complex **4Re** in almost quantitative yield. The formation of metal complexes **4Pt**, **4Ru**, and **4Re** was confirmed by analysis of their ^{1}H NMR spectra and high-resolution electrospray ionization time-of-flight mass spectra. ^{1}H NMR spectra of the metal complexes displayed signals for six methyl protons on mesityl groups because the molecular symmetry was lowered by complexation.

The single-crystal X-ray diffraction analysis unambiguously revealed the structures of these outer-metallated complexes **4**, confirming the existence of dative bonds between the *meso*-nitrogen atoms and the metal ions (Figure 1).[13] In the case of platinum complex **4Pt**, the diazaporphyrin metalloligand **3** is bound to a Pt^{II} center which has ideal square-planar geometry. The sum of the coordination angles around the Pt^{II} atom is 359.9° (Figure 1a,b). In **4Ru**, the Ru^{II} center adopts a typical octahedral geometry (Figure 1c,d).[14] The distance between the Ru^{II} center and the *meso*-nitrogen atom is 2.15 Å, which is slightly longer than other Ru–N bond lengths in **4Ru** (2.05–2.10 Å), probably because of the steric hindrance of the diazaporphyrin moiety. The preliminary X-ray structure of **4Re** is shown in Figure S17. The Re^{I} center in **4Re** also assumes an octahedral coordination geometry, in which three carbonyl ligands occupy facial positions. Upon outer coordination of **3** with metal centers, the diazaporphyrin skeleton is distorted whereas the diazaporphyrin core in **3** is highly planar: the

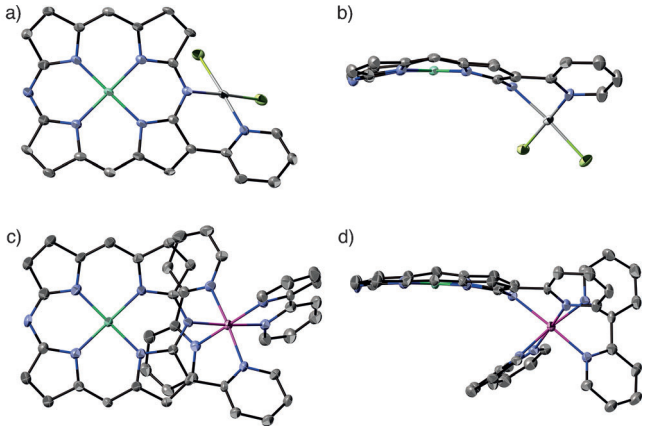


Figure 1. Crystal structures showing a) top and b) side views of **4Pt**, and c) top and d) side views of **4Ru**$(PF_6)_2$. Protons, counterions, and *meso*-mesityl groups have been omitted for clarity. Thermal ellipsoids were set at 50% probability.

mean-plane deviations of the macrocycle in **4Pt** and **4Ru** are 0.245 and 0.148 Å, respectively, and that in **3** is only 0.039 Å. This result indicates that the diazaporphyrin core has sufficient flexibility to adjust its conformation to accommodate the metal ions at the *meso*-nitrogen atom.

Figure 2 shows the UV/vis absorption spectra of **3**, **4Pt**, **4Ru**, and **4Re** in dichloromethane. Compared with the Soret and Q-bands in the spectrum of ligand **3**, the spectra of the outer-metallated complexes exhibit significant bathochromically shifted and broadened bands. In sharp contrast, the spectra of *meso*-platinoporphyrins retain typical porphyrin-like absorption features even after metallation at the *meso*-carbon atom.[9] To investigate the origin of the different absorption behaviors between the porphyrin and diazaporphyrin outer-metallated complexes, we conducted DFT calculations at the B3LYP/631SDD level. The frontier orbitals of **4Pt** clearly indicate the major contribution of metal-centered orbitals to the HOMO, which should impart substantial MLCT (metal-to-ligand charge transfer) character to the Soret and Q-bands (Figure S20). Involvement of d orbitals in the HOMOs of **4Ru** and **4Re** is also supported.

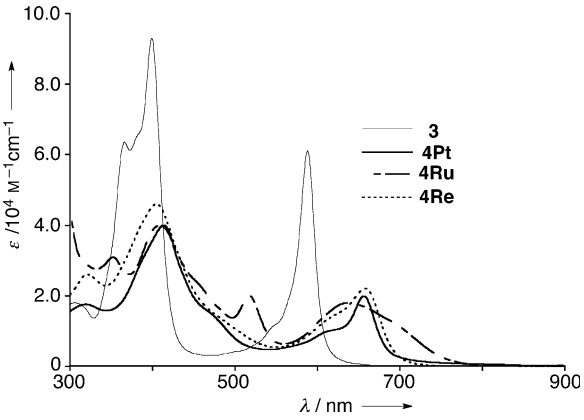


Figure 2. UV/vis absorption spectra of **3**, **4Pt**, **4Ru**, and **4Re** in dichloromethane.

In the case of *meso*-metallated porphyrins, both the HOMO and LUMO are π orbitals. This difference is explained by the lowering of the MO energy of the 5,15-diazaporphyrin ligand as a result of the electron-withdrawing imine-type nitrogen atoms. Stabilization of the ligand's π orbitals relative to the d orbitals leads to an increased contribution of the metal-centered HOMO, thus enhancing MLCT transitions for diazaporphyrin metal complexes. Bipyridyl metal complexes, such as $[Ru(bpy)_3]^{2+}$, often exhibit MLCT transitions and are used as sensitizers in many photocatalytic reactions.[15–17] Whereas $[Ru(bpy)_3]^{2+}$ complexes only utilize high-energy light with wavelengths shorter than $\lambda = 500$ nm, the absorption of pyridyldiazaporphyrin complexes **4** covers the entire visible region up to $\lambda = 800$ nm.

To gain deeper insight into the electronic structures of these complexes, the electrochemical properties were investigated using cyclic voltammetry (Table S1 and Figure S18). The cyclic voltammograms of the **4Pt**, **4Ru**, and **4Re** metal complexes showed reversible first reduction waves at −0.880, −0.858, and −0.962 V, respectively, which are considerably higher than that of **3** (−1.31 V). Additionally, the first oxidation potentials of these complexes were substantially shifted in the anodic direction, which reflects the tendency of the electron-withdrawing nature of each metal center to lower the electron density of ligand **3**.

In conclusion, we have prepared the metalloligand 3-pyridyldiazaporphyrin Ni^{II} and its function as a bidentate ligand to transition-metal ions has been clearly demonstrated by effective formation of its stable platinum, ruthenium, and rhenium complexes. Outer-metal coordination to *meso*-nitrogen induces a substantial red shift and broadening of the bands in the UV/Vis absorption spectra because the MLCT character enhances their visible-light-absorbing property. The present novel azaporphyrin-based ligand would be useful to render photofunctionality to various metal ions based on the high molecular absorptivity of diazaporphyrin. The preparation of other metal complexes of pyridyldiazaporphyrins and detailed studies of their photophysical properties are currently underway.

Received: September 5, 2014
Revised: September 27, 2014
Published online: October 22, 2014

Keywords: charge transfer · N ligands · platinum · porphyrinoids · ruthenium

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[12] Crystallographic data for **3**: $C_{42}H_{34}Cl_3N_7Ni$, $M_w = 800.81$, monoclinic, *Pc*, $a = 8.1902(6)$, $b = 14.1889(11)$, $c = 15.5044(12)$ Å, $\beta = 90.375(2)°$, $Z = 2$, $R = 0.0609$ ($I > 2.0\sigma(I)$), $R_w = 0.1686$ (all data), GOF = 1.012. CCDC-1021112 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Crystallographic data for **4Pt**: $C_{47}H_{38}Cl_3N_7NiPt$, $M_w = 1060.99$, monoclinic, $P2_1/c$, $a = 12.1397(15)$, $b = 22.625(2)$, $c = 15.1953(18)$ Å, $\beta = 103.828(6)°$, $Z = 4$, $R = 0.0381$ ($I > 2.0\sigma(I)$), $R_w = 0.0939$ (all data), GOF = 1.052. Crystallographic data for **4Ru**$[PF_6]_2$: $C_{64}H_{51.50}Cl_{7.50}F_{12}N_{11}NiOP_2Ru$, $M_w = 1706.26$, triclinic, $P\bar{1}$, $a = 13.8411(14)$, $b = 19.6345(19)$, $c = 26.829(3)$ Å, $\alpha = 77.107(2)°$, $\beta = 85.894(2)°$, $\gamma = 73.611(2)°$, $Z = 4$, $R = 0.0716$ ($I >$

2.0$\sigma(I)$), $R_w = 0.2101$ (all data), GOF = 1.048. CCDC-1021113 (**4Pt**) and 1022772 (**4Ru**$[PF_6]_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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