

η^2 -Porphyrin Ru(II) π ComplexesShigeru Yamaguchi,[†] Hiroshi Shinokubo,^{*,‡} and Atsuhiko Osuka^{*,†}

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Abstract: Highly stable η^2 -porphyrin Ru(II) π complexes have been synthesized. The formation of the η^2 π bond has been facilitated through π – π stacking interactions between the porphyrin and the planar ligand on Ru. π coordination of ruthenium to porphyrin results in dramatic changes in the aromaticity and electronic properties. These properties are controllable via fine-tuning of the ligand on ruthenium.

Porphyrins are an important and extensively investigated class of ligands in which the central cavity is employed as the coordination site. In contrast, research on metal coordination at the porphyrin periphery is an emerging area.¹ One of the characteristic features of a porphyrin is strong π – π stacking interactions with another π -conjugated molecule due to their extended π -conjugated framework.

Metal– π -arene complexes have received much attention in organometallic chemistry. However, there are few examples of porphyrins bearing a π -coordinated metal on the core.² Among the metal– π -arene complexes, creation of η^2 coordination is particularly difficult. Precise design of the metal center in terms of electron density and coordination environment is required for synthesis of η^2 π -arene complexes.³ Not surprisingly, no example of an η^2 -porphyrin metal π complex has been reported to date. One of the serious problems is instability of η^2 π coordination. Here we report the synthesis of η^2 -porphyrin metal π complexes through stabilization by π – π stacking interactions between the porphyrin and the planar ligand on the metal.

We serendipitously achieved the synthesis of highly stable η^2 -porphyrin metal π complexes in the course of our investigation of peripherally cyclometalated porphyrins.⁴ According to the known procedure for cyclometalation of 2-phenylpyridine derivatives,⁵ β -(2-pyridyl)porphyrin **1H**⁴ was reacted with Ru(terpyridyl) cation in toluene/*n*-BuOH solution at 100 °C. To our surprise, the product was found to be the η^2 -porphyrin Ru(II) π complex **2H**, which was obtained in 57% yield as a brown solid after separation by silica gel column chromatography under ambient conditions. This is quite unusual because η^2 π -arene complexes are generally unstable except with electron-rich metals.³ The structure was unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 1). The Ru(II) atom is bound to both a meso carbon atom and an adjacent α -carbon of the porphyrin in a distinct η^2 manner.⁶ Remarkably, the terpyridyl moiety and the porphyrin macrocycle are almost parallel, and the interplanar distance between them is quite close (~ 3.3 Å), suggesting that the structure is stabilized by π – π stacking interactions. The bond lengths of the Ru(II)–C bonds are 2.294 and 2.342 Å, respectively, which are slightly longer than those of an η^2 π -alkene Ru(II) complex (2.196 and 2.260 Å).⁷ Because of the π complexation, the deviations of the meso and α -carbons from the mean plane are relatively large (Figure

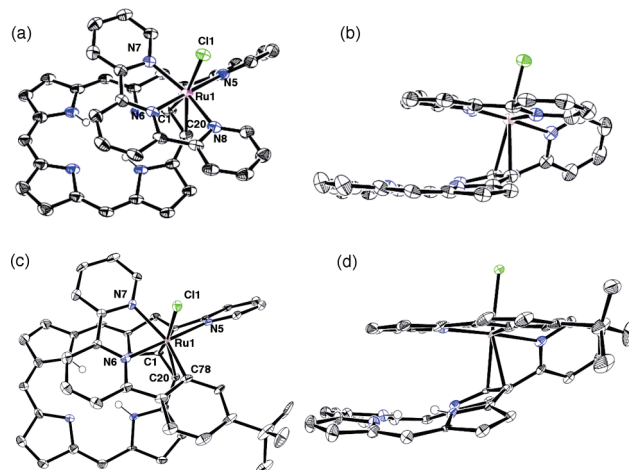


Figure 1. X-ray crystal structures of **2H** [(a) top view and (b) side view] and **7** [(c) top view and (d) side view]. The counteranion of **2H**, the meso-aryl substituents, and hydrogen atoms have been omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

S15 in the Supporting Information). Importantly, none of the expected σ complexes of **1H** were detected in the reaction mixture. This is probably because such cyclometalated σ complexes would lose stabilization by π -stacking interactions.

In the ¹H NMR spectrum of **2H**, a set of three peaks at δ = 6.60, 5.47, and 4.62 ppm was assigned to the central pyridine moiety of the terpyridine. These signals were substantially upfield-shifted by the shielding effect of the aromatic ring current of the porphyrin. Generally, π complexation induces some degree of dearomatization of an arene. In fact, the nucleus-independent chemical shift (NICS) value of **2H** at the center of the porphyrin was calculated to be δ = –11.2 ppm, which is slightly larger than that of porphine (δ = –15.5 ppm).⁸ The meso proton at δ = 6.60 ppm exhibited an upfield shift relative to that of **1H** (10.67 ppm) due to the electron donation from the Ru center, the decrease in aromaticity of the porphyrin ring, and the shielding effect of the terpyridyl moiety.

The π complexation on the macrocycle largely influences the UV–vis absorption spectrum (Figure 2). The Soret band of **2H** is ill-defined, and the Q band exhibits a substantial red shift relative to that of **1H**.

The unusual stability of the η^2 π bonds is also highlighted by the central metalation of **2H**. Metalation of the central cavity of **2H** with Zn(OAc)₂ and Cu(OAc)₂ afforded **2Zn** and **2Cu** in high yields without decomposition of the η^2 π coordination (Scheme 1).

This procedure allows the introduction of functionalized terpyridyl moieties into the η^2 π complex. As shown in Scheme 1, π complexes bearing electron-donating and electron-withdrawing groups on terpyridyl were successfully synthesized (**3**, 62% yield; **4**, 73% yield; **5**, 29% yield). In the cyclic voltammograms, two reversible oxidation waves were observed, and the first oxidation potentials of **1H**, **2H**, **3**,

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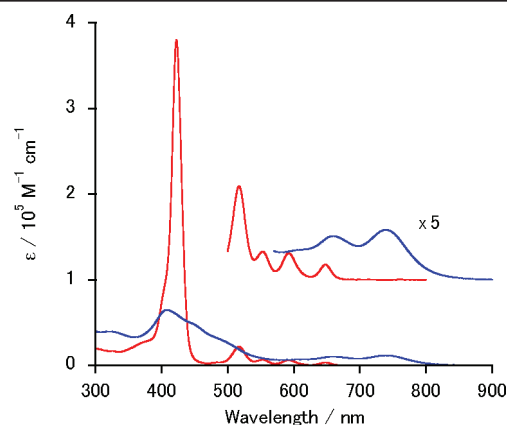
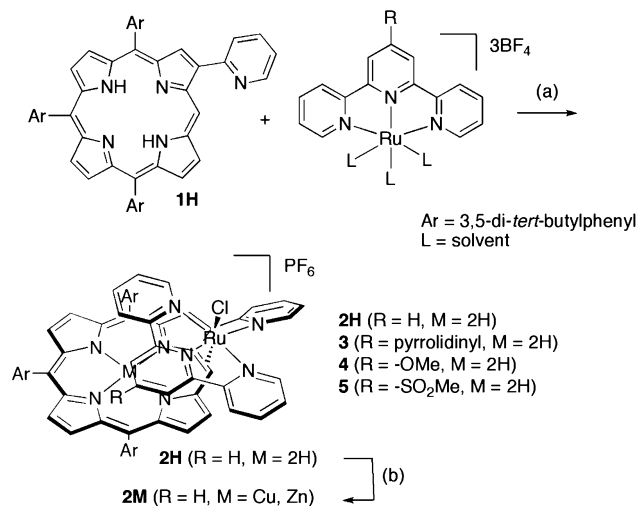


Figure 2. UV-vis absorption spectra of **1H** (red) and **2H** (blue) in CH_2Cl_2 .

Scheme 1. Synthesis of η^2 -Porphyrin Ru π Complexes^a

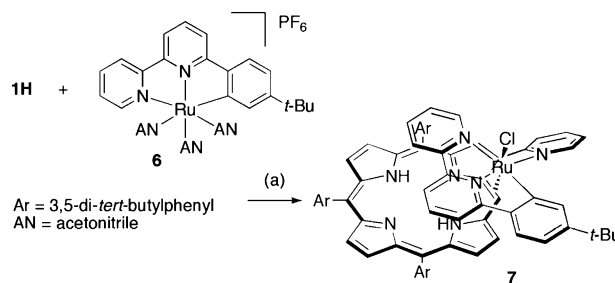


^a (a) (i) *n*-BuOH/toluene, 100 °C; (ii) KPF_6 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, rt. (b) $\text{M}(\text{OAc})_2$ ($\text{M} = \text{Cu}, \text{Zn}$), MeOH , rt.

4, and **5**, were at 0.44, 0.38, 0.32, 0.35, and 0.40 V (vs the ferrocene/ferrocenium ion couple), respectively.⁹ These data indicate that the HOMO energies of the complexes were destabilized by the Ru coordination. These potentials were plotted versus the Hammett σ parameter, and the reaction constant ρ was calculated to be 0.054 V, which is slightly lower than that of para-substituted *meso*-tetraarylporphyrins ($\rho = 0.065$ V).¹⁰ Consequently, the electronic properties of a porphyrin can be manipulated through π coordination.

To demonstrate the generality of this strategy, we then attempted to use other planar ligands. Gratifyingly, the reaction of **1H** with dipyrrolylbenzene Ru complex **6** provided the stable neutral π complex **7** in 39% yield (Scheme 2). The η^2 π coordination in **7** was confirmed by X-ray diffraction analysis (Figure 1c,d). Generally, the carbon–metal σ bond substantially increases the electron density of the metal center. In the cyclic voltammogram of **7**, the first oxidation wave was observed at -0.08 V, which is a much lower potential than that of **2H** ($E_{\text{ox1}} = 0.38$ V). In the ^1H NMR spectrum of **7**, the meso proton at 5.27 ppm exhibited a substantial upfield shift relative to that of **2H** ($\delta = 6.60$ ppm) due to the higher donation ability of the Ru center of **7**. The higher electron density also results in stronger back-donation of the Ru center to the macrocycle, and consequently, the π -bond lengths in **7** (2.223 and 2.198 Å) are shorter than those in **2H** (2.294 and 2.342 Å). The stronger back-donation significantly weakens the aromaticity of the porphyrin in **7**. The signals of the inner NH protons of **7** appear

Scheme 2. Synthesis of an η^2 -Porphyrin Ru π Complex Bearing a Carbon–Metal σ Bond^a



^a (a) LiCl , 1,2-dichloroethane/methanol, 80 °C.

at 3.22 and 2.70 ppm (vs 0.59 ppm for **2H**). The NICS value for **7** was calculated to be -8.6 ppm, supporting the weaker aromaticity of **7** than **2H** (NICS = -11.2 ppm).

In summary, we have established a novel strategy for the synthesis of highly stable η^2 -porphyrin metal π complexes. The formation of these π complexes is facilitated through π – π interactions between the porphyrinic macrocycle and the planar Ru complexes. π coordination of ruthenium to porphyrin results in dramatic changes in the aromaticity and electronic properties. Importantly, these properties are controllable via modification of the ligand on the Ru center. Further extension of the chemistry of η^2 -porphyrin metal π complexes is currently underway.

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Supporting Information Available: General procedures, spectral data for compounds, absorption spectra, and CIF files from the X-ray analyses of **2H** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Klein Gebank, R. J. M.; Suijkerbuijk, B. M. J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7396.
- (2) (a) Cuesta, L.; Karnas, E.; Lynch, V. M.; Sessler, J. L.; Kajonkijya, W.; Zhu, W.; Zhang, M.; Ou, Z.; Kadish, K. M.; Ohkubo, K.; Fukuzumi, S. *Chem.–Eur. J.* **2008**, *14*, 10206. (b) Cuesta, L.; Karnas, E.; Lynch, V. M.; Chen, P.; Shen, J.; Kadish, K. M.; Ohkubo, K.; Fukuzumi, S.; Sessler, J. L. *J. Am. Chem. Soc.* **2009**, *131*, 13538. (c) Dailey, K. K.; Yap, G. P. A.; Rheingold, A. L.; Rauchfuss, T. B. *Angew. Chem., Int. Ed.* **1996**, *35*, 1833. (d) Dailey, K. K.; Rauchfuss, T. B. *Polyhedron* **1997**, *16*, 3129. (e) Wang, H. J. H.; Jaquinod, L.; Olmstead, M. M.; Vicente, M. G. H.; Kadish, K. M.; Ou, Z.; Smith, K. M. *Inorg. Chem.* **2007**, *46*, 2898.
- (3) (a) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953. (b) Winemiller, M. D. B.; Kelsch, A.; Harman, W. D. *Organometallics* **1997**, *16*, 3672. (c) Keane, J. M.; Harman, W. D. *Organometallics* **2005**, *24*, 1786. (d) Harrison, D. P.; Welch, K. D.; Nichols-Niellander, A. C.; Sabat, M.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 16844.
- (4) (a) Yamaguchi, S.; Katoh, T.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 6392. (b) Yamaguchi, S.; Katoh, T.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 14440. (c) Yamaguchi, S.; Shinokubo, H.; Osuka, A. *Inorg. Chem.* **2009**, *48*, 795.
- (5) (a) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521. (b) Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1993**, *32*, 4539.
- (6) For other examples of η^2 -arene Ru(II) π complexes, see: (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555. (b) Chen, Y.; Shepard, R. E. *Inorg. Chem.* **1998**, *37*, 1249.
- (7) Huang, Y.-H.; Huang, W.-W.; Lin, Y.-C.; Huang, S.-L. *Organometallics* **2010**, *29*, 38.
- (8) The NICS value was obtained by a single-point calculation on the X-ray structure of **2H**. The structure optimization of **2H** by the DFT method failed, but the MP2 method nicely reproduced the face-to-face structure. This fact emphasizes the importance of π – π interactions in stabilizing the complex.
- (9) The reduction potentials of the complexes could not be obtained because of the instability of the complexes in the reduced states.
- (10) Kadish, K. M.; Morrison, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 3326.

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