Redox-Coupled Complexation of 23-Phospha-21-thiaporphyrin with Group 10 Metals: A Convenient Access to Stable Core-Modified Isophlorin−Metal Complexes

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Isophlorins (*N,N′*-dihydroporphyrins) are a class of [20]annulenes, whose structure, optical/electrochemical properties, and aromaticity have received continuing interest in relation to the 18π porphyrin chemistry.[1−4] This class of compounds is also expected to show characteristic coordination behavior derived from tetradentate macrocyclic ligands. Vaid et al. and Brothers et al. recently succeeded in preparing silicon(IV) isophlorin complexes [Si(TPP)(L)$_2$; TPP: tetraanion of tetraphenylporphyrin; L = THF or pyridine][5] and a diboranyl isophlorin complex [B$_2$(TTP); TTP: tetraanion of tetra-*p*-tolylporphyrin],[6] respectively, by 2e-reduction of the corresponding metalloporphyrins and disclosed their antiaromatic character on the basis of experimental and theoretical results.[7,8] Except for these examples, however, the coordination chemistry of isophlorins still remains unveiled because of their intrinsic nature to undergo 2e-oxidation (aromatization to porphyrins) under ambient conditions.[9] We anticipated that replacement of pyrrole nitrogens with other heteroatoms, namely core-modification,[10] would bring chemical stability to isophlorin complexes by alternating the coordinating abilities, charges, and redox properties of their 20π macrocyclic platforms. Here, we report the first synthesis of core-modified isophlorin−metal complexes, which relies on the redox-coupled complexation of a P,S,N$_2$-hybrid porphyrin with zerovalent group 10 metals, and the structure and aromaticity of their 20π systems.

In this study, we used P,S,N$_2$-hybrid **1**[11] and S$_2$,N$_2$-hybrid **2** as core-modified porphyrin free bases. Compound **2** was newly prepared via BF$_3$-promoted [3 + 1] condensation of a 2,5-bis(hydroxymethyl)thiophene with a thiatripyrrane[12] (Scheme S1 in Supporting Information). When treated with 1 equiv of Pd(dba)$_2$ (dba = dibenzylideneacetone) in CH$_2$Cl$_2$ at room temperature, **1** was consumed completely within a minute (checked by TLC). After removal of the solvent, the residue was subjected to column chromatography on alumina to give Pd−P,S,N$_2$ complex **3Pd** as a dark green solid in 95% yield (Scheme 1). In sharp contrast, no complexation took place between **2** and Pd(dba)$_2$ even after refluxing in 1,2-dichlorobenzene for 5 h. This indicates that the core-phosphorus atom in **1** contributes significantly to the facile complexation with palladium. Treatment of **1** with Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) and excess Pt(dba)$_2$ under suitable reaction conditions produced **3Ni** and **3Pt**, respectively (Scheme 1). Complexes **3Pd** and **3Pt** were found to be stable in air, whereas **3Ni** gradually decomposed in solution.

The structures of **3M** were characterized by NMR and mass spectrometry. The salient feature of their ^{1}H spectra is negligible diatropic/paratropic ring current effects derived from the π electron circuit. For instance, *meso*, β, and P-phenyl protons of **3Pd** are

Scheme 1. Synthesis of P,S,N$_2$-Isophlorin−metal Complexes **3M**
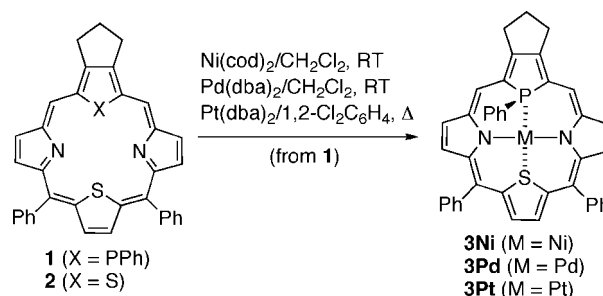
observed at δ 6.01 (J_{PH} = 37.6 Hz), 5.58−6.13, and 7.65−8.37, respectively, and they are upfield-shifted ($\Delta\delta$ = −4.4 to −2.5 for *meso*, β) or downfield-shifted ($\Delta\delta$ = +6.1 to +2.4 for P-phenyl) as compared to the corresponding protons of **1** (Figure S1b). The slight differences in chemical shifts among **3Ni**, **3Pd**, and **3Pt** imply that the central metal does not perturb the ring current effect in **3M** dramatically (Figure S1).[13] In the ^{31}P{^{1}H} NMR spectra, a singlet (**3Ni** and **3Pd**) or doublet (**3Pt**, $^1J_{P−Pt}$ = 3190 Hz) peak appears at δ 35.1−61.9, and it is deshielded relative to the ^{31}P peak of **1** (δ 18.6). These data show that **3M** essentially possesses nonaromatic character.

The crystal structure of **3Pd** was unambiguously elucidated by X-ray diffraction analysis.[14] As shown in Figure 1a, the palladium center adopts a square planar geometry with the sum of N−Pd−X (X = P, S) bond angles of 360°. Because of this coordination, the phosphorus and sulfur atoms are displaced by 0.95 and 0.93 Å, respectively, from the mean π plane composed of the peripheral 20 carbon atoms (Figure 1b). The Pd−X (X = N, S) bond lengths are very close to those observed for a square planar Pd(II)−P,S,N$_2$-hybrid calixphyrin complex,[15] and the peripheral C−C bond alternation well explains the 20π valence-bond structure for the P,S,N$_2$-hybrid ligand (Figure 1c). These data suggest that oxidation states of the metal center and the hybrid π ligand in **3Pd** are +2 and −2, respectively. The whole structure of **3Pd** differs considerably from the structures of ruffled Si(TPP)(THF)$_2$[5a] and Ge(TPP)(py)$_2$[7] and planar *meso*-pentafluorophenyl core-modified O$_4$- and O$_2$,S$_2$-isophlorins,[4] all of which were reported to be antiaromatic. Variable-temperature ^{1}H measurement of **3Pd** in CDCl$_3$ did not show noticeable spectral change between −50 and 50 °C, suggesting that the distorted structure of **3Pd** is basically maintained in solution. Indeed, the UV−vis absorption spectrum of **3Pd** shows broad Soret-like bands at λ_{max} 375−414 nm and no detectable Q bands (Figure S2), which is characteristic of highly ruffled, nonaromatic $4n\pi$ porphyrinoids.[1,3,4,16] The electrochemical oxidation processes of **3Pd** occurred reversibly at −0.26 and +0.06 V vs Fc/Fc$^+$ (Figure S3).[17] The Pd coordination shifts the first oxidation potentials of **1** to the negative side by 0.71 V, reflecting the 20π isophlorin structure of **3Pd**.

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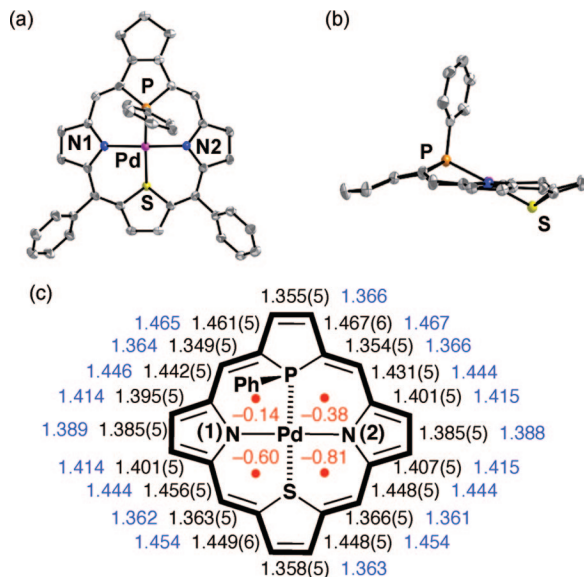∥ Fukui Institute for Fundamental Chemistry, Kyoto University.

Figure 1. (a) Top and (b) side views of **3Pd**. Hydrogen atoms and *meso*-phenyl groups (b) are omitted for clarity; bond lengths (Å) and bond angles (deg): Pd–P, 2.1830(11); Pd–N1, 2.060(3); Pd–N2, 2.070(3); Pd–S, 2.2664(11); P–Pd–N1, 88.14(9); P–Pd–N2, 90.65(9); S–Pd–N1, 90.02(9); S–Pd–N2, 91.15(9). (c) Bond lengths determined by X-ray (**3Pd**; black) and DFT calculation (**3Pd–m**; blue) and NICS values (red).

The Pt complex **3Pt** exhibited similar optical and electrochemical properties (λ_{max} 312–407 nm; $E_{ox} = -0.24$ and $+0.07$ V).

To gain a deeper insight into the aromaticity of the P,S,N$_2$-isophlorin ring in **3M**, we performed density functional theory (DFT) calculations of Pd and Pt model complexes (**3M–m**; M = Pd, Pt) at the B3LYP/6-31G(d,p)+LANL2DZ level (For details, see Supporting Information). As indicated in Figures S4 and S5, the optimized geometry and the bond lengths of **3Pd–m** are close to those of **3Pt–m**. The natural atomic orbital occupancies of d orbitals calculated for **3M–m** indicate that the formal oxidation state of their central metals is +2 (Table S1). The absolute values of nucleus-independent chemical shifts (NICS) at the center of two adjacent heterole rings of **3M–m** are much smaller than those of free-base model **1–m** (Figure S8c) and close to zero, suggesting that the 20π P,S,N$_2$-isophlorin ring in **3M–m** possesses nonaromatic character in terms of the magnetic criterion. Although the loss of paratropicity is ascribable to the distortion from planarity of the ring system,[18] other factors should also be taken into consideration. To reveal the effects of core elements and central metals on the paratropicity of isophlorin π circuit, we calculated NICS values of imaginary Pd–S$_2$,N$_2$ and Mg–P,S,N$_2$ complexes (**Pd–S$_2$,N$_2$–m** and **Mg–P,S,N$_2$–m**) as references (Figures S6 and S7). At the optimized structures, **Pd–S$_2$,N$_2$–m** shows a NICS value of -0.12, whereas **Mg–P,S,N$_2$–m** displays positive NICS values of $+2.66$ and $+3.03$.[19] These results imply that the lack of paratropic ring currents in the Ni–, Pd–, and Pt–P,S,N$_2$ complexes is due in a part to the central group 10 metals.

To evaluate the coordinating ability of **1**, we next calculated heat of formation of **3Pd–m** by the DFT method. As shown in Scheme S2, formation of **3Pd–m** and dba from **1–m** and Pd(dba)$_2$ yields a negative energy ($\Delta E^0 = -7.1$ kcal mol^{-1}), suggesting that the Pd-complexation of **1–m** is thermodynamically favorable. On the other hand, the Pd-complexation of S$_2$,N$_2$-free-base model **2–m** yields a positive energy ($\Delta E^0 = +9.1$ kcal mol^{-1}). Evidently, the core-phosphorus atom plays crucial roles in enhancing the electron-accepting ability of the 18π porphyrin ring and stabilizing the 20π isophlorin ring due to high P–M affinity.[20] It must be emphasized that incorporation

of P and S atoms changes the charge of fully anionic 20π system from -4 to -2. Thus, **3M** are regarded as neutral M(II) complexes.

In summary, we have revealed that isophlorin–metal complexes are readily accessible by redox-coupled complexation of P,S,N$_2$-hybrid porphyrin. Most importantly, group 10 metals, which are weakly reducing as compared to traditionally used Na/Hg, Mg, and Zn, have proven to reduce the 18π porphyrin ring efficiently. The experimental and theoretical results represent that the P,S,N$_2$-isophlorin complexes possess nonaromaticity in terms of both geometrical and magnetic criteria. The present study demonstrates that core-modification with phosphorus could be a promising methodology to develop coordination chemistry of 4$n\pi$ porphyrinoids.

Supporting Information Available: Experimental details, CIF file for **3Pd**, and DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) As descended from Ni to Pd to Pt, the peripheral protons of **3M** slightly shift to upfield ($\Delta\delta = 0.14–0.39$ ppm), and the P-phenyl-*ortho* protons slightly shift to downfield ($\Delta\delta = 0.27$ ppm).

(14) C$_{41}$H$_{29}$N$_2$PPdS, MW = 719.09, monoclinic, P2$_1$/n, $a = 9.352(3)$ Å, $b = 17.763(5)$ Å, $c = 18.934(6)$ Å, $\beta = 102.440(5)°$, $V = 3071.4(17)$ Å^3, $Z = 4$, $D_c = 1.555$ g cm^{-3}, 6950 obsd, 416 variables, $R_w = 0.1061$, $R = 0.0528$ ($I > 2\sigma(I)$), GOF = 1.010.

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(17) Redox potentials were measured in CH$_2$Cl$_2$ with 0.1 M nBu$_4$N$^+$PF$_6^-$; Ag/Ag$^+$ [0.01 M AgNO$_3$ (MeCN)].

(18) Conformation-induced loss of paratropicity was observed for a highly ruffled β-trifluoromethyl-substituted N$_4$-isophlorin (see ref. 3).

(19) The NICS values for the nonrelaxed geometry made by simply replacing Pd of the optimized **3Pd–m** geometry with Mg were $+4.55$ to $+6.41$ ppm.

(20) The difference in coordination behavior between **1** and **2** may be partly attributable to difference in their oxidizing abilities: the first and second reduction potentials of **1** (-1.36 and -1.56 V vs Fc/Fc$^+$) are more positive than the respective potentials of **2** (-1.43 and -1.77 V vs Fc/Fc$^+$).