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 tetradeinate 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 pyridine5 and a diboranyl isophlorin complex [B2(TTP); TTP: tetraanion of tetrap-tolytporphyrin],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 unexplored 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 isophlorins 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,N2-hybrid porphyrin with zerovalent group 10 metals, and the structure and aromaticity of their 20π systems.

In this study, we used P,S,N2-hybrid 11 and S2,N2-hybrid 2 as core-modified porphyrin free bases. Compound 2 was newly prepared via BF3-promoted [3 + 1] condensation of a 2,5-bis(hydroxymethyl)thiophene with a thiatripyrrane12 (Scheme S1 in Supporting Information). When treated with 1 equiv of Pd(dba)2 (dba = dibenzylidenacetone) in CH2Cl2 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,N2 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 1H 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 observed at δ 6.01 (JHH = 37.6 Hz), 5.58−6.13, and 7.65−8.37, respectively, and they are upfield-shifted (∆δ = −4.4 to −2.5 for meso, β) or downfield-shifted (∆δ = +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 31P{1H} NMR spectra, a singlet (3Ni and 3Pd) or doublet (3Pt, JF−P = 3190 Hz) peak appears at δ 35.1−61.9, and it is deshielded relative to the 31P 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−P,S,N2 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 P−X (X = N, S) bond lengths are very close to those observed for a square planar Pd(II)−P,S,N2-hybrid calixphyrin complex,15 and the peripheral C−C bond alternation well explains the 20π valence-bond structure for the P,S,N2-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)2,5e and Ge(TPP)(py)2,7 and planar meso-pentafluorophenyl core-modified O2− and O2S2-isophlorins,13,14,16 all of which were reported to be antiaromatic. Variable-temperature 1H measurement of 3Pd in CDCl3 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 λmax = 375−414 nm and no detectable Q bands (Figure S2), which is characteristic of highly ruffled, nonaromatic 4π-ring porphyrinoids.1,3,4,16 The electrochemical oxidation processes of 3Pd occurred reversibly at −0.26 and +0.06 V vs Fe/Fe+ (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.
The Pt complex 3Pt exhibited similar optical and electrochemical properties (\( \lambda_{\text{max}} 312\text{--}407 \text{ nm; } E_{\text{pa}} = -0.24 \) and +0.07 V).

To gain a deeper insight into the aromaticity of the P,S,N-isophlorin ring in 3M–m, 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. As indicated in Figures S4 and S5, the optimized geometry and 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 heterocyclic 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-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, 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 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).

Theoretical calculations of Pd–m and Pt–m by the DFT method. As shown in Scheme S2, formation of 3Pd–m and dba from 1–m and Pd(dbta)2 yields a negative energy (\( \Delta \mu = -7.1 \text{ kcal mol}^{-1} \)), suggesting that the Pd-complexation of 1–m is thermodynamically favorable. On the other hand, the Pd-complexation of S2N2-free base model 2–m yields a positive energy (\( \Delta \mu = +9.1 \text{ kcal mol}^{-1} \)). Evidently, the core-photosphorus 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-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 reveal that the P,S,N-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 4π porphyrinoids.

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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.