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<td>Nakabuchi, Takashi</td>
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Kyoto University
Studies on the Fundamental Properties, Coordinating Ability, and Reactivity of Phosphole-Containing Macrocycles

Takashi Nakabuchi

2010
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1. Background

1.1. Porphyrin

Porphyrins, 18π aromatic macrocycles consisting of four pyrrole rings linked by \( sp^2 \) hybridized meso-carbon bridges, have attracted increasing attention in a wide range of research fields because of their characteristic optical, electrochemical, and coordinating properties (Figure 1a). For instance, UV-vis absorption spectra of porphyrins show an intense Soret band around 420 nm and a series of weak Q bands in 550–650 nm region (Figure 1b), which are promising for their applications in the areas such as photodynamic therapy (PDT)\(^1\) and organic solar cells.\(^2\) In addition, porphyrins behave as cyclic dianionic N\(_4\)-ligands, which can bind a variety of metals (M) at the core (Figure 1a).\(^3\)

![Figure 1](image1)

**Figure 1.** (a) Structure and characteristics of porphyrin. (b) UV-vis absorption spectrum of 5,10,15,20-tetraphenylporphyrin.

To perturb the fundamental and coordinating properties of porphyrins, several methods have been employed. Among them, attachment of various functionalities at the meso and pyrrole-\( \beta \) positions is the most widely employed (Figure 2a). For example, redox potentials of porphyrins are readily tunable by introducing electron-donating/−withdrawing groups at the meso and/or \( \beta \) positions.\(^4\) Furthermore, ring-expansion, namely adding the numbers of pyrrole

![Figure 2](image2)

**Figure 2.** (a) Meso and \( \beta \)-functionalized porphyrins. (b) Ring-expanded porphyrins (examples).
units and/or bridging carbon atoms is known to change the size of the cavity and the coordination sphere of π-systems (Figure 2b). Another potent method for altering the properties of porphyrins is core-modification.

1.2. Core-Modification of Porphyrins

The term “core-modification” means the replacement of one or more pyrrole rings by other heterocyclic or carbocyclic rings such as furan, thiophene, pyridine, and benzene. The chemistry of core-modified porphyrins started in late 1960s with a pioneering study by Broadhurst and co-workers. They prepared furan- and thiophene-containing β-alkylated porphyrins, 1 and 2, via [3+1]-type acid promoted condensation between functionalized tripyrrane diacids 3 and 2,5-diformylheteroles 4 followed by ring oxidation (Scheme 1a). These O,N3-, S,N3-, and O,S,N2-type core-modified porphyrins show 18π aromaticity and characteristic Soret and Q-type absorption bands similar to N4-porphyrins. On the other hand, from mid 1970s to early 1980s, Ulman and co-workers reported the synthesis and fundamental properties of a series of meso-arylated X,N3- and X,Y,N2-porphyrins 5 and 6 (X,Y = O, S, Se, Te: Scheme 1b). They used tripyrranes 7 and 2,5-bis[aryl(hydroxy)methyl]-heteroles 8 as the precursors for 5 and 6. Systematic comparison of the optical and redox properties of meso-arylated X,N3- and X,Y,N2-porphyrins (X,Y = O, S, Se, Te) with those of the corresponding N4-porphyrins revealed that replacement of one or two pyrrole rings with group 16 heteroles basically induces significant (i) bathochromic shifts of the Soret and Q bands and (ii) anodic shifts of the first oxidation and reduction potentials. For instance, the Soret/Q-type absorption maxima and the first oxidation/reduction potentials of

**Scheme 1. Synthesis of Core-Modified Porphyrins**

(a)

![Scheme 1a](image1)

(b)

![Scheme 1b](image2)
Scheme 2. Te–O Exchange Reaction and Oxidative Chlorination of Te,N3-Porphyrins

meso-tetraphenylated S2,N2-porphyrin are bathochromically and anodically shifted by $\Delta \lambda_{\text{max}} = 23–49$ nm and $\Delta E = 0.11–0.26$ V, respectively, relative to those of N4-porphyrin (H2TPP) (Figure 3). Considering the fact that these large bathochromic and anodic shifts are not easily achievable by conventional peripheral functionalizations, core-modifications can be regarded as a powerful tool for altering the optical and redox properties of porphyrin $\pi$-system. Another important consequence of the core-modification is that it affords X,N3- and X,Y,N2-type mixed-donor ligands (X,Y = O, S, Se, Te), which have different cavity sizes, charges, and electron-donating/-accepting abilities from those of conventional N4-porphyrins (Figure 4a). Since late 1980s, Latos-Grażyński's and other groups have extensively studied on the coordination chemistry of the X,N3- and X,Y,N2-porphyrins (X,Y = O, S, Se, Te), and revealed that these chalcogen-containing porphyrins can stabilize atypical oxidation states or unusual coordination geometries at the metal center (Figure 4b). The third interesting feature of core-modified porphyrins is the unique reactivity endowed by the core elements. For example, tellurium-containing porphyrins were reported to undergo the Te–O exchange reaction (Scheme 2) or oxidative chlorination at the tellurium center via Te-oxygenation.

Figure 3. Comparison of substitution effects on optical and redox properties between core-modification and peripheral functionalization.
1.3. Phosphole-Containing Porphyrinoids

Despite the encouraging findings on the core-modified porphyrins mentioned above, the types of heteroles introduced into the macrocyclic framework have been limited to group 16 heteroles (i.e. furan, thiophene, selenophene, tellurophene). Under these circumstances, the author decided to explore the chemistry of phosphole-containing porphyrins (phosphaporphyrins) shown in Figure 5a.

Phosphole, the phosphorus isologue of pyrrole, is known to possess totally different structural and electronic characters from those of pyrrole and group 16 heteroles (Figure 5b). First, phosphole shows very weak aromaticity because of the insufficient n–π orbital interaction between the trigonal pyramidal phosphorus center and the 1,3-dienic moiety. This is clearly demonstrated by the relatively small absolute nucleus-independent chemical shift (NICS) of phosphole (Table 1). Second, the LUMO of phosphole lies at a lower energy level, thus leading to the smaller HOMO–LUMO gap as compared with pyrrole, furan, and thiophene (Figure 6). This is a consequence of the effective σ*(P–R)–π*(1,3-diene) hyperconjugative interaction. Finally, the tricoordinate (σ₃) phosphorus center of phosphole can be converted to various tetracoordinate (σ₄) forms by simple chemical modifications such as P-oxygenation (to σ⁴-P=O), P-thioxygenation (to σ⁴-P=S), and P-metal coordination (to σ⁴-P–metal) with its active lone electron pair. In particular, the coordinating property as a
rigid cyclic P-ligand with reliable σ-donating and π-accepting abilities, has motivated many chemists to design various phosphole-based ligands.\textsuperscript{16}

<table>
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<th>Compound</th>
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<tr>
<td>phosphole</td>
<td>−5.5</td>
</tr>
<tr>
<td>pyrrole</td>
<td>−16.0</td>
</tr>
<tr>
<td>furan</td>
<td>−14.6</td>
</tr>
<tr>
<td>thiophene</td>
<td>−13.2</td>
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\textbf{Table 1. NICS Values of Heteroles}

Considering these characteristics of phosphole, the author envisioned that the core-modification with phosphorus would be a highly promising way to modify the optical, electrochemical, and coordinating properties of the porphyrin π-system.

In 2003, Delaere and Nguyen predicted the electronic structures and optical properties of phosphaporphyrins based on density functional theory (DFT) calculations and concluded that these phosphaporphyrins would exhibit reasonable aromaticity.\textsuperscript{17} However, the synthesis of phosphaporphyrins and other phosphole-containing porphyrinoids had not been reported, presumably due to the synthetic difficulties concerning the phosphole (\textit{vide infra}).

The author was also interested in the coordination chemistry of phosphole-containing calixpyrroles shown in Figure 7a. Calixpyrroles are a class of porphyrinoids wherein the pyrrole rings are linked by \textit{sp}^3 hybridized \textit{meso} carbons (Figure 7b).\textsuperscript{18} In contrast to porphyrins, calixpyrroles possess calix-like flexible framework. This structural property has proven to be beneficial for constructing anion receptors that can bind anions or anionic groups (X\textsuperscript{−}) through the corporate NH···X\textsuperscript{−} hydrogen-bonding interaction. The author expected that phosphole-containing calixpyrroles (phosphacalixpyrroles) would behave as unprecedented types of P ligands while maintaining the hosting functions that originate from the pyrrole subunits.

\textbf{Figure 6.} Energy levels of heteroles calculated at the HF/6-31G* level.

\textbf{Figure 7.} (a) Phosphacalixpyrroles. (b) Structure and anion binding of calixpyrroles.
2. Aims of This Thesis

The aims of this thesis are (1) to establish the synthetic method for the phosphole-containing porphyrins and calixpyrroles, and (2) to reveal their fundamental properties (e.g. structures, aromaticities, optical and electrochemical properties), coordinating behaviors, and reactivities.

2.1. Synthesis of Phosphole-Containing Porphyrinoids

The irony is that the above-mentioned attractive characters of phosphole are, at the same time, regarded as the drawbacks of synthesizing the phosphole-containing porphyrinoids: (i) Owing to the high nucleophilicity of the $\sigma^3$-phosphorus atom and the low aromaticity of the five-membered ring, conventional methods (Friedel-Crafts alkylation and direct lithiation) that have been widely used for the $\alpha$-functionalization of pyrrole and thiophene are not applicable to phosphole. (ii) The high reactivity of $\sigma^3$-phosphorus atom is not preferable also in the acidic and oxidizing reaction conditions used for constructing the porphyrin and calixpyrroles skeletons.

To overcome the first drawback, the author has developed a convenient method for the preparation of $\alpha,\alpha'$-difunctionalized phospholes (Scheme 2a). This method, which relies on Ti$^{III}$-mediated cyclization of terminally difunctionalized diyne (9), has allowed the author to prepare phospholes bearing ester groups at the both $\alpha$-positions (10) in gram scale. The ester groups of 10 can be modified by conventional methods to afford 2,5-bis[hydroxymethyl]-type phospholes (11), which are suitable starting materials of phosphaporphyrins and phosphacalixpyrroles.

Scheme 3. Solutions for the Synthetic Drawbacks

![Scheme 3](image)

To surmount the second drawback, the author adopted two different approaches. One
was P-masking/demasking technique wherein the $\sigma^3$-P atom was masked as the $\sigma^4$-P=S form throughout the construction of the macrocyclic frameworks (Scheme 3b: left). The other was an introduction of a highly electron-withdrawing perfluorophenyl group (C$_6$F$_5$) at the $\sigma^3$-P atom, which has been proven to remarkably enhance the tolerance of the $\sigma^3$-P atom against the acidic and oxidizing conditions (Scheme 3b: right).

2.2. Elucidation of the Fundamental Properties, Coordinating Behaviors, and Reactivities

The three important characteristics of phosphole pointed out in subsection 1.3 are “nonaromaticity”, “low-lying LUMO”, and “reactive $\sigma^3$-phosphorus atom”. It is of interest to reveal how these characters affect the fundamental properties, coordinating behaviors, and reactivities of the phosphole-containing porphyrins and calixpyrroles. The principal questions are following (Figure 8).

for phosphole-containing porphyrins:

(Q1) Is the aromaticity of the 18$\pi$ annulene circuit maintained after replacing the aromatic pyrrole ring with nonaromatic phosphole ring?

(Q2) How do the nonaromaticity and low-lying LUMO level of phosphole affect the optical and electrochemical properties of porphyrin $\pi$-system?

(Q3) What is caused by chemical modification on the phosphorus center (e.g. $\sigma^3$-P to $\sigma^4$-P=O) in the porphyrin core?

(Q4) Does the high metal affinity of the $\sigma^3$-phosphorus atom provide some unprecedented coordinating properties with the P,X,N$_2$-mixed donor ligand?

for phosphole-containing calixpyrroles:

(Q5) Is it possible to bind both the metal and anion concurrently through the P–M coordination and the cooperative NH•••X$^-$ hydrogen-bonding interactions?

Figure 8. Topics discussed in this thesis.
All of these topics are discussed in this thesis: Chapters 1 and 2 describe the synthesis, structure, and coordinating property of phosphacalixpyrroles (Q5). Chapters 3 and 4 describe the synthesis, structure, aromaticity, and optical and redox properties of phosphaporphyrins (Q1 and Q2). In Chapter 4, the reactivity of phosphaporphyrins is also discussed (Q3). In Chapter 5, the coordinating property of phosphaporphyrin is examined (Q4). Chapter 6 presents the synthesis and fundamental properties of the P-C₆F₅ type phosphaporphyrinoids including the ring-expanded analogue. It should be noted here that the topics Q1–Q4 are mutually dependent on one another. Specifically, chemical modification of the core-phosphorus atom triggers dramatic alteration of the aromaticity and/or optical and redox properties of the phosphaporphyrin π-system.
References and Footnotes


Chapter 1

Phosphole-Containing Hybrid Calixpyrroles: New Multifunctional Macrocyclic Ligands for Platinum(II) Ions

Abstract: Phosphole-containing hybrid calixpyrroles are prepared by the acid-promoted condensation reactions. The σ^3-calix[1]phosphole[1]thiophene[2]pyrrole reacts with PtCl₂(COD) to afford an unusual type of macrocyclic Pt(II)–monophosphine complex bearing a η^3-cyclooctadienyl ligand, in which the phosphole and pyrrole units bind the Pt–Cl moiety through cooperative, non-covalent bonding interactions.
1. Introduction

Calixpyrroles, first prepared by Baeyer in 1886, are of interest in supramolecular and coordination chemistry because of their functions as anion receptors and polyanionic \(N\)-ligands. A promising way of controlling the binding abilities of this class of compounds is to modify the components of the macrocyclic backbone, which induces changes in the size, shape and electronic properties of the cavities. In this respect, there is growing interest in the synthesis and host–guest chemistry of hybrid calixpyrroles containing non-pyrrolic arenes such as furan, thiophene\(^{-c-f}\) and pyridine. Despite this interest, however, no attempt has been made to incorporate phosphole, which is basically not aromatic and behaves as a neutral \(P\)-ligand for transition metals. The author expected that substitution of a nitrogen atom of calixpyrrole with a phosphorus atom, namely replacement of a pyrrole unit by phosphole, would provide an unexploited class of multifunctional macrocyclic phosphorus ligands capable of binding transition metals in the structurally well-defined cavity.

In this Chapter, the author describes the first examples of phosphole-containing hybrid calixpyrroles. The \(\sigma^3\)-phosphole-pyrrole-thiophene hybrid reacts with PtCl\(_2\)(COD) to afford an unusual type of macrocyclic Pt(II)–phosphine complex via allylic C–H bond activation of the ligated COD group. In particular, the coordination geometry at the platinum(II) center is defined by cooperative, non-covalent bonding interactions with the phosphole and pyrrole subunits.

2. Results and Discussion

*Scheme 1. Synthesis of the \(\sigma^4\)-P,S,N\(_2\)- and \(\sigma^4\)-P,O,N\(_2\)-Hybrids*

pyrrole, followed by silica gel column chromatography, gave a mixture of condensation products, from which compound 2 was isolated in 24% yield. The \(^{31}\text{P}\) NMR of 2 showed a single peak at \(\delta 69.3\) in CDCl\(_3\). The BF\(_3\)•OEt\(_2\)-promoted dehydrative condensation of 2 with 2,5-bis(1-hydroxy-1-methylethyl)thiophene (3)\(^{4c,9}\) and 2,5-bis(1-hydroxy-1-methylethyl)furan (4)\(^{4c,9}\) afforded the \(\sigma^4\)-P,S,N\(_2\)-hybrid 5 and the \(\sigma^4\)-P,O,N\(_2\)-hybrid 6, respectively.

Compounds 5 and 6 are yellow solids and were fully characterized by standard spectroscopic techniques. In their mass spectra, parent ion peaks were observed at \(m/z 609\) (for 5) and 595 (for 6), attributable to the 1:1 adduct between 2 and 3/4. The crystal structures of 5 and 6 were further elucidated by X-ray crystallography (Figure 1 for 5; Figure 2 for 6).\(^{10,11}\) The P,S,N\(_2\)-hybrid 5 has a partial cone conformation, whereas the P,O,N\(_2\)-hybrid 6 adopts a cone conformation. Both 5 and 6 provide a trapezoid-like cavity, which the P=S moiety is located inside. As shown in Figure 3, the cavity size of 5 is slightly larger than that of 6, mainly reflecting the difference in edge-to-edge distances between the thiophene and furan subunits. In both compounds, the pyrrole rings are tilted considerably, to direct their N–H group toward the sulfur atom of the P=S group. The observed N•••S distances of 3.34–3.62 Å imply that a hydrogen bonding interaction is present between the sulfur atom and the N–H protons in 5 and 6.\(^{12}\)

![Figure 1. ORTEP diagram of 5 (30% probability ellipsoids). Except for NH, hydrogen atoms are omitted for clarity. Selected bond lengths and distances (Å): S1–P1, 1.9724(5); C1–C2, 1.344(2); C2–C6, 1.485(2); C6–C7, 1.341(2); S1•••N1, 3.37; S1•••N2, 3.62.](image)

![Figure 2. ORTEP diagram of 6 (30% probability ellipsoids). Except for NH, hydrogen atoms are omitted for clarity. Selected bond lengths and distances (Å): S1–P1, 1.9746(6); C1–C2, 1.335(2); C2–C6, 1.481(2); C6–C7, 1.343(2); S1•••N1, 3.45; S1•••N2, 3.34.](image)
In order to prepare a $\sigma^3$-type of phosphole-containing calixpyrrole, reductive desulfurization of the $\sigma^4$-P,S,N$_2$-hybrid 5 was examined (Scheme 2). When heated with 2.8 equiv of P(NMe$_2$)$_3$ in refluxing toluene for 33 h, 5 was completely consumed to afford the $\sigma^3$-P,S,N$_2$-hybrid 7 in 92% yield. The $^1$H and $^{31}$P NMR spectra indicate that 7 exists as a mixture of two conformers. At 25 °C, two $^{31}$P peaks were observed at $\delta$ 31.4 and 32.1 ([D$_8$]toluene), suggesting that interconversion between the conformers occurs slowly on the NMR time scale at this temperature. At 70 °C, however, these two peaks coalesced.

Scheme 2. Synthesis of the $\sigma^3$-P,S,N$_2$-Hybrid and Pt(II) Complexes

With the $\sigma^3$-P,S,N$_2$-hybrid 7 in hand, the author set out to prepare a macrocyclic platinum(II)–phosphine complex. Thus, heating a mixture of 7 and an equimolar amount of PtCl$_2$(COD) (8) in toluene for 6 h, followed by silica gel column chromatography and GPC separation, gave the Pt(II)–monophosphine complex 9 in 62% yield as a pale yellow crystalline solid (Scheme 2). Besides 9, small amounts of trans-Pt(II)–bisphosphine complexes 10 and 11 were isolated as byproducts. In the $^{31}$P NMR spectra, the characteristic peaks with two $^{31}$P–$^{195}$Pt satellites were observed at $\delta$ 51.1 (for 9), $\delta$ 46.7 (for 10), and $\delta$ 45.5,
The coupling constants \( J_{P,P} \) observed for the bisphosphine complexes 10 and 11 are 2400–2560 Hz, implying that the two phosphine ligands are coordinated in a *trans* geometry.\(^{14}\) In the \(^1\)H NMR of 9, four olefinic resonances of the COD-derived ligand appeared separately in the range of \( \delta 5.50–6.56 \).

The structure of 9 was successfully elucidated by X-ray crystallography (Figure 4).\(^{15}\) The platinum center adopts a square planar geometry with the phosphorus and chlorine atoms in a *cis* orientation. The \( \sigma^3\)-P,S,N₂-macrocyle unit provides a trapezoid cavity with a cone conformation, in which the phosphole ring leans toward the outside, for binding the Pt(II) ion. It should be noted here that two pyrrole rings are tilted to direct the NH protons toward the chlorine atom bound to platinum. The observed Cl•••N distances of 3.34 and 3.40 Å are close to the reported values [3.264(7)–3.331(7) Å] for a chloride ion complex of *meso*-octamethylcalix[4]pyrrole.\(^{2a}\) Thus, there is a cooperative hydrogen bonding interaction between the Pt–Cl moiety and the two NH protons, which contributes to defining the coordination geometry at the platinum center in 9. The COD-like group coordinates as an anionic, 1,2-\( \eta^2 \)-6-\( \sigma \)-cyclocta-1,4-dienyl ligand, where the C38–C39 double bond is bound through \( \pi \)-coordination (\( \eta^2 \) mode) and the C42 atom is covalently bound to the Pt center (\( \sigma \) mode). This coordinative behavior is rare for group 10 chemistry and the first example for a Pt(II)–monophosphine complex,\(^{16}\) representing the unique binding ability of the \( \sigma^3\)-P,S,N₂-hybrid 7.

![Figure 4. ORTEP diagram of 9·(CHCl₃)₂ (30% probability ellipsoids). Two chloroform molecules and hydrogens (except for NH) are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt–Cl1, 2.4228(16); Pt–P, 2.2709(16); Pt–C38, 2.222(9); Pt–C39, 2.211(7); Pt–C42, 2.079(7); C38–C39, 1.353(14); Cl1–Pt–C42, 170.2(2); P–Pt–C42, 96.7(2).](image)

Plausible reaction pathways for the formation of 9–11 are illustrated in Scheme 3: the \( \sigma^3\)-P,S,N₂-hybrid 7 reacts with 8 to generate complex 12 or 13 as a transient species, from
which an allylic proton of the COD ligand is abstracted to produce 9 (path a) or the coordinated COD is substituted by the second phosphine 7 to produce 10 and 11 (path b). Large steric hindrance around the phosphorus center in 7 probably makes path b less favorable than path a, resulting in the higher yield of 9 relative to 10 and 11. From a mechanistic point of view, it is of interest that the allylic C–H bond is activated under neutral conditions with the assistance of the macrocyclic ligand 7: when triphenylphosphine (PPh₃) was used instead of 7, only half the amount of 8 was consumed, to yield cis-PtCl₂(PPh₃)₂¹⁸ as the sole Pt(II) product under the same reaction conditions.

**Scheme 3. Plausible Reaction Pathways for the Formation of 9–11**

3. Conclusion

In conclusion, the phosphole-containing hybrid calixpyrroles have been successfully prepared for the first time, and fully characterized their structures. The σ⁵-P,S,N₂ hybrid has been found to selectively activate the allylic C–H bond of PtCl₂(COD) under neutral conditions. The observed reactivity as well as the structure of the resulting Pt(II) complex demonstrates the potential utility of phosphole-containing hybrid calixpyrroles as a new class of multifunctional macrocyclic ligands.
Experimental Section

**General Procedures.** All melting points are uncorrected. $^{1}H$, $^{13}C$/$^{1}H$, and $^{31}P$/$^{1}H$ NMR spectra were recorded using CDCl$_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane ($^{1}H$ and $^{13}C$) and phosphoric acid ($^{31}P$). MALDI-TOF mass spectra were measured using CHCA as a matrix. IR spectra were observed as KBr pellets. All solvents were distilled from sodium benzophene ketyl (ether, THF), sodium (hexane), or calcium hydride (CH$_2$Cl$_2$, toluene) before use. All the reactions were performed under an argon or nitrogen atmosphere. Column chromatography was performed on silica gel or on a fast flow liquid chromatography system fitted with a silica gel column. Compound 1 was prepared by the reaction of the corresponding 2,5-diester with excess MeMgBr (Y. Matano, T. Miyajima, T. Nakabuchi, Y. Matsutani and H. Imahori, *J. Org. Chem.* 2006, 71, 5792.). Other chemicals were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted.

**Synthesis of Compound 2.** A solution of diol 1 (2.1 g, 6.0 mmol) in 60 mL (870 mmol) of pyrrole was bubbled with N$_2$ for 30 min, and BF$_3$•OEt$_2$ (0.77 mL, 6.0 mmol) was added to the solution. After stirring for 4 h at room temperature, CH$_2$Cl$_2$ (100 mL) and saturated NaHCO$_3$ solution (50 mL) were added. The water phase was extracted with CH$_2$Cl$_2$, and the organic extracts were combined, washed with brine, dried over Na$_2$SO$_4$ and evaporated. The products were subjected to silica gel column chromatography (CH$_2$Cl$_2$/EtOAc = 50/1) and the fraction of $R_f$ = 0.6 was collected and washed with MeOH to give 2 as a colorless solid (650 mg, 24%): Mp 154–155 °C; $^{1}H$ NMR δ 1.38 (s, 6H), 1.41 (s, 6H), 1.54–1.62 (m, 1H), 1.90–1.94 (m, 1H), 2.09–2.25 (m, 4H), 5.88–5.90 (m, 2H), 5.99–6.01 (m, 2H), 6.70–6.71 (m, 2H), 7.48–7.59 (m, 3H), 7.97 (m, 2H), 9.12 (br s, 2H); $^{13}C$/$^{1}H$ NMR δ 26.6, 27.6, 27.7, 27.9, 28.0, 28.7, 28.8, 37.7, 37.9, 102.5, 106.4, 117.2, 128.8, 129.8, 131.7, 131.8, 134.6, 135.0, 136.1, 138.3, 158.0, 158.4; $^{31}P$/$^{1}H$ NMR δ 69.3; MS (MALDI-TOF) m/z 447 (M$^+$). Anal. Calcd for C$_{27}$H$_{31}$N$_2$PS: C, 72.61; H, 7.00; N, 6.27; P, 6.94. Found: C, 72.60; H, 6.99; N, 6.27; P, 6.89.

**Synthesis of Compounds 5 and 6.** Compound 2 (50 mg, 0.11 mmol) and 3 (22 mg, 0.11 mmol) were dissolved in CH$_2$Cl$_2$ (80 mL), and the solution was bubbled with N$_2$ for 40 min. BF$_3$•OEt$_2$ (0.014 mL, 0.11 mmol) was added to the solution, and the mixture was then stirred for 3.5 h at room temperature. The resulting mixture was washed with distilled water (3 × 80 mL), dried over Na$_2$SO$_4$ and evaporated to give a pale yellow solid, which was subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1) to give the $\sigma^4$-P$_2$S$_2$N$_2$ hybrid 5 as a
yellow solid (Rt = 0.4; 41 mg, 61%). A similar treatment of 2 with 4 afforded the σ^4-P,O,N_2 hybrid 6 as a yellow solid (Rt = 0.4; 39%).

5: Mp 241–242 °C; 1H NMR δ 1.27 (m, 1H), 1.32 (s, 6H), 1.36 (s, 6H), 1.65 (s, 6H), 1.72 (s, 6H), 1.86 (m, 1H), 2.10 (m, 4H), 5.79 (s, 4H), 6.78 (s, 2H), 7.50 (m, 3H), 7.90 (m, 2H), 9.09 (s, 2H); 13C{1H} NMR δ 26.7, 27.2, 28.0, 28.2, 31.4, 31.7, 37.4, 37.6, 38.1, 99.8, 101.7, 101.8, 123.6, 128.6, 129.1, 129.5, 131.8, 135.5, 136.5, 137.0, 141.3, 152.0, 158.4, 158.7; 31P{1H} NMR (toluene-d_6) δ 69.6; MS (FAB) m/z 610 (M^+). Anal. Calc. for C_{17}H_{31}N_2PS_2: C, 72.75; H, 7.10; N, 4.59; P, 5.07. Found: , 72.85; H, 7.10; N, 4.47; P, 5.12.

6: Mp 177–178 °C; 1H NMR δ 1.27 (m, 1H), 1.39 (s, 6H), 1.40 (s, 6H), 1.60 (s, 6H), 1.67 (s, 6H), 1.82 (m, 1H), 2.11 (m, 4H), 5.76 (m, 2H), 5.78 (m, 2H), 6.05 (s, 2H), 7.51 (m, 3H), 7.96 (m, 2H), 9.57 (s, 2H); 13C{1H} NMR δ 22.6, 22.8, 23.3, 23.6, 23.7, 24.4, 24.6, 25.4, 25.7, 25.8, 25.9, 29.0, 29.2, 29.7, 29.8, 34.1, 36.0, 36.1, 37.6, 37.7, 60.2, 60.5, 100.2, 100.3, 100.9, 103.6, 103.8, 104.2, 130.1, 131.1, 131.2, 131.3, 133.5, 133.7, 134.4, 134.9, 137.9, 138.9, 139.2, 146.8, 147.0, 159.6, 159.7, 168.8, 169.0; 31P{1H} NMR δ 69.4; MS (MALDI-TOF) m/z 594 (M^+). Although spectroscopic data clearly supported a high state of purity of 6, we were not successful in obtaining satisfactory analytical data of an accuracy within ±0.4%.

**Synthesis of Compound 7.** To a toluene solution (5 mL) of 5 (47 mg, 0.077 mmol) was added P(NMe_2)_3 (0.040 mL, 0.22 mmol), and the mixture was then stirred under reflux for 33 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH_2Cl_2 = 2/1) to give 7 as a colorless solid (Rt = 0.5; 41 mg, 92%). The 1H NMR spectrum of 7 indicated that two conformers are present in a 4:1 ratio. Major conformer: 1H NMR δ 1.23 (s, 6H), 1.38 (s, 6H), 1.66 (s, 6H), 1.71 (s, 6H), 1.5–2.4 (m, 6H), 5.76 (m, 2H), 5.83 (m, 2H), 6.79 (s, 2H), 7.1–7.4 (m, 7H); 31P{1H} NMR (toluene-d_6) δ 32.1; Minor conformer: 1H NMR δ 1.16 (s, 6H), 1.52 (s, 6H), 1.66 (s, 12H), 1.5–2.4 (m, 6H), 5.65 (m, 2H), 5.79 (m, 2H), 6.84 (s, 2H), 7.1–7.4 (m, 7H); 31P{1H} NMR (toluene-d_6) δ 31.4; MS (MALDI-TOF) m/z 578 (M^+).

**Synthesis of Compounds 9, 10, and 11.** To a flask containing 7 (42 mg, 0.073 mmol) and PtCl_2(COD) (8, 27 mg, 0.073 mmol) was added toluene (2 mL), and the resulting mixture was heated under reflux for 6 h. The solution was concentrated under reduced pressure to give an oily residue, which was subjected to silica gel column chromatography (hexane/CH_2Cl_2 = 2/1) and GPC (CHCl_3), affording the platinum–phosphine complexes 9 (41 mg, 62%), 10 (2 mg, 4%) and 11 (3 mg, 5%).

9: Mp ca. 160 °C (decomp); 1H NMR δ 0.81 (m, 1H), 0.91 (s, 3H), 1.15 (m, 1H), 1.51–1.88 (m, 7H), 1.61 (s, 3H), 1.68 (s, 3H), 1.70 (s, 3H), 1.77 (s, 3H), 1.82 (s, 3H), 1.85 (s, 3H), 1.93 (s, 3H), 2.06–2.21 (m, 3H), 2.89 (m, 1H), 5.50–6.01 (m, 3H), 5.66 (m, 1H), 5.73 (m, 1H), 5.82 (s, 1H), 6.01 (m, 3H), 6.07 (s, 1H).
5.85 (m, 1H), 5.88 (m, 1H), 6.30–6.56 (m, 1H), 6.56 (s, 1H), 7.36–7.44 (m, 3H), 7.70–7.74 (m, 2H), 9.21 (s, 2H); $^{13}$C($^1$H) NMR δ 23.9, 25.5, 25.8, 25.9, 27.0, 27.1, 28.1, 29.8, 30.6, 31.1, 31.4, 31.7, 34.1, 36.2, 37.2, 37.4, 37.5, 37.7, 37.8, 40.5, 99.1, 99.8, 101.8, 102.3, 105.3, 105.5, 109.2, 109.3, 124.2, 124.4, 128.6, 128.9, 129.2, 129.5, 130.5, 131.6, 131.7, 134.1, 134.2, 134.8, 141.6, 141.7, 142.3, 142.5, 142.6, 143.2, 150.0, 151.0, 160.1, 160.3, 166.9, 167.1; $^{31}$P($^1$H) NMR δ 51.1 ($J_{Pt-P} = 4281$ Hz); MS (FAB) m/z 916 (M$^+$. Anal. Calcd for C$_{46}$H$_{55}$Cl$_4$N$_2$P$_2$S (9•CHCl$_3$): C, 53.34; H, 5.35; N, 2.70; P, 2.99. Found: C, 53.95; H, 5.57; N, 2.70; P, 2.72.

10: $^1$H NMR δ 0.92–1.04 (m, 4H), 1.23 (s, 12H), 1.60–1.72 (m, 28H), 1.88–2.05 (m, 4H), 2.09 (s, 12H), 5.76–5.79 (m, 8H), 6.41 (s, 4H), 7.34–7.38 (m, 4H), 7.45–7.49 (m, 2H), 7.86–7.90 (m, 4H), 8.85 (s, 4H); $^{31}$P($^1$H) NMR δ 46.7 ($J_{Pt-P} = 2476$ Hz); MS (MALDI-TOF) m/z 1388 (M$^+$–Cl).

11: $^1$H NMR δ 1.28 (s, 6H), 1.45 (s, 6H), 1.62 (s, 6H), 1.65 (s, 6H), 1.67 (s, 18H), 1.77–2.10 (m, 8H), 2.25 (s, 6H), 2.43–2.48 (m, 2H), 5.66–5.68 (m, 2H), 5.80–5.82 (m, 6H), 6.55 (s, 2H), 6.84 (s, 2H), 7.19–7.26 (m, 2H), 7.35–7.46 (m, 6H), 7.53 (m, 2H), 7.92 (s, 2H), 8.91 (s, 2H); $^{31}$P($^1$H) NMR δ 45.5 ($J_{Pt-P} = 2400$ Hz), 46.5 ($J_{Pt-P} = 2560$ Hz); MS (MALDI-TOF) m/z 1424 (M$^+$).

**X-ray Crystallography.** All X-ray crystallographic measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (0.71070 Å). The data were collected at a temperature of −150 °C to a maximum 2θ value of 55.0°. The data were corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, 27, 435) and refined by full-matrix least squares techniques against $F^2$ using SHELXL-97 (G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model, unless otherwise noted.
References and Footnotes


(10) Crystal data for 5: C\(_{74}\)H\(_{86}\)N\(_4\)P\(_2\)S\(_4\), \(M = 1221.7\), triclinic, \(a = 12.9517(19)\), \(b = 12.9645(19)\), \(c = 20.395(3)\) Å, \(\alpha = 82.092(4)\), \(\beta = 83.090(4)\), \(\gamma = 86.680(4)°\), \(V = 3364.4(8)\) Å\(^3\), space group P\(\overline{1}\), \(Z = 2\), \(\mu(\text{Mo-K}\alpha) = 2.333\) cm\(^{-1}\), 26815 reflections measured, 14641 unique, parameters 744, \(R_w = 0.1329\), \(R = 0.0493\) (\(I > 2.00\sigma(I)\)), gof = 1.076. One of the phenyl groups is disordered at two locations.

(11) Crystal data for 6: C\(_{37}\)H\(_{43}\)N\(_2\)OPS, \(M = 594.79\), orthorhombic, \(a = 11.2995(14)\), \(b = 16.673(2)\), \(c = 18.066(2)\) Å, \(V = 3403.7(7)\) Å\(^3\), space group P\(2_1\)\(2_1\)\(2_1\), \(Z = 4\), \(\mu(\text{Mo-K}\alpha) = 1.722\) cm\(^{-1}\), 276625 reflections measured, 7803 unique, parameters 380, \(R_w = 0.1042\), \(R = 0.0404\) (\(I > 2.00\sigma(I)\)), gof = 1.038.


(13) On the basis of the NMR spectra, they were assigned as the in-in and in-out types of complexes, where in and out denote that the Pt–Cl bond is located inside and outside the cavity, respectively.

(14) The trans stereochemistry as well as the in-in conformation of 10 was confirmed by X-ray crystallography, though the full refinement has been hampered by the presence of an unidentified peak.

(15) Crystal data for 9: C\(_{47}\)H\(_{56}\)Cl\(_7\)N\(_2\)PPtS, \(M = 1155.27\), monoclinic, \(a = 11.460(8)\), \(b = 18.498(13)\), \(c = 22.927(15)\) Å, \(\beta = 91.150(4)°\), \(V = 4859(6)\) Å\(^3\), space group P\(2_1/n\), \(Z = 4\), \(\mu(\text{Mo-K}\alpha) = 3.372\) cm\(^{-1}\), 38279 reflections measured, 10937 unique, parameters 533, \(R_w = 0.0578\), \(R = 0.0578\) (\(I > 2.00\sigma(I)\)), gof = 0.960.


(17) No intermediate was observed during the NMR monitoring of this reaction in [D\(_8\)]toluene.

Abstract: Symmetric and asymmetric hybrid calixpyrroles containing a $\sigma^4$-phosphole or $\sigma^4$-2,3-dihydroporphole unit (symmetric and asymmetric $\sigma^4$-P,X,N$_2$-hybrids: X = S, O) were prepared by using acid-promoted condensation reactions of the corresponding $\sigma^3$-phosphatripyrroles with 2,5-bis(1-hydroxy-1-methylethyl)heteroles. The X-ray crystallographic analyses of the symmetric and asymmetric $\sigma^4$-P,X,N$_2$-hybrids show that the cavity sizes of the $\sigma^4$-P,S,N$_2$-hybrids are larger than those of the $\sigma^4$-P,O,N$_2$-hybrids, mainly reflecting the difference in edge-to-edge distances of the thiophene and furan rings. The symmetric $\sigma^4$-P,X,N$_2$-hybrids and the asymmetric $\sigma^4$-P,S,N$_2$-hybrid were successfully converted to the corresponding $\sigma^3$ forms by reductive desulfurization at the phosphorus center. Each of the symmetric $\sigma^3$-P,X,N$_2$-hybrids was obtained as a mixture of two conformers, where the lone pair of the phosphorus atom is located inside (in) and outside (out) the cavity. While, the interconversion between the in and out type conformers of the asymmetric $\sigma^3$-P,S,N$_2$-hybrid was sufficiently slow to isolate each of them. The complexation reactions of the symmetric $\sigma^3$-P,S,N$_2$-hybrid with Au(I), Pt(II), and Pd(II) ions afforded both of the in and out type complexes, where the in type complexes were the thermodynamically favored products. In the complexation reactions of the asymmetric $\sigma^3$-P,S,N$_2$-hybrids, the stereochemistry at the phosphorus center was retained to give in or out type complex exclusively. In the in-in type trans-M(II)–bis(phosphine) complexes (M = Pt, Pd) derived from the symmetric and asymmetric $\sigma^3$-P,S,N$_2$-hybrids, the M–Cl fragment is bound above the cavities of the two macrocycles. The crystal structures and the $^1$H NMR spectra of these M(II) complexes reveal that the P,S,N$_2$-hybrid calixpyrroles bind the M–Cl fragments through the P–M coordination and the cooperative NH–Cl hydrogen-bonding interactions.
1. Introduction

Calix[4]pyrroles,\textsuperscript{12} which are regarded as the pyrrole analog of calix[4]arenes, have attracted growing interests in supramolecular chemistry, since the discovery by Sessler and co-workers that these macrocycles can bind anionic\textsuperscript{3} and neutral\textsuperscript{4} species by utilizing the pyrrole-NH groups as the multiple hydrogen-bonding donors. While, Floriani and co-workers extensively studied the coordination chemistry of calix[4]pyrroles, in which these macrocycles had been used as fully deprotonated, tetraanionic N\textsubscript{4} ligands for various metals.\textsuperscript{5} Inspired by these pioneering studies, many research groups have designed and prepared a wide variety of hybrid calixpyrroles containing non-pyrrolic arene units such as furan,\textsuperscript{6} thiophene,\textsuperscript{6c-f} pyridine,\textsuperscript{7,8} and benzene\textsuperscript{8} to modify the binding ability of the calixpyrrole platform. To my knowledge, however, no attempt has been made to incorporate phosphole into the calixpyrrole platform,\textsuperscript{9-11} despite its utility as neutral P-ligand for transition metals.\textsuperscript{12} The author expected that phosphole-containing hybrid calixpyrroles, formally obtained by incorporating a phosphole unit into the macrocyclic framework of the calixpyrrole, would exhibit some promising features as the structurally well-defined macrocyclic P-ligands while keeping the hosting function (Figure 1a).

![Figure 1](image_url)

**Figure 1.** Schematic views of metal complexes of the phosphole-containing hybrid calixpyrroles (a) and P(III)-functionalized calix[4]arenes (b, c).

The coordination chemistry of the calix[4]arene derivatives bearing P(III)-functionalities\textsuperscript{13} at the upper-\textsuperscript{14} or lower-rims\textsuperscript{15} has already been studied by several groups. For example, Matt and co-workers used an upper-rim bis(phosphine)-functionalized calix[4]arene as a bidentate P-ligand for Pt(II), Pd(II), and Ru(II) complexes, in which the M–R fragments were entrapped inside the macrocyclic cavity through the *trans*-P–M–P chelation (Figure 1b).\textsuperscript{14d} The phosphole-containing hybrid calixpyrroles are distinct from the P(III)-functionalized calix[4]arenes in three aspects. Firstly, as seen in the supramolecular chemistry of the parent calix[4]pyrroles, the macrocyclic platform of the phosphole-containing hybrid calixpyrroles provides the multiple hydrogen-bonding sites for negatively charged groups. Secondly, the size, shape, and binding ability of the hybrid...
platform are tunable by altering the combination of the heterole components (e.g., X in Figure 1a). Finally, the rigidity of the phosphole unit allows the coordinated metal to be located above the cavity without chelation, which is difficult for the mono-P(III)-functionalized calix[4]arenes owing to the C(calix)–P bond rotation (Figure 1c).14–16

This Chapter describes the synthesis, structures, and coordination behavior of the hybrid calixpyrroles 1S and 2S (Chart 1), which contain a phosphole unit and a 2,3-dihydrophosphole unit, respectively, as one of the heterocyclic components. The structures and thermal stabilities of the Au(I), Pt(II), and Pd(II) complexes are also reported.16 As expected, 1S and 2S have proven to behave as monodentate P ligands, whose macrocyclic frameworks provide hydrogen-bond-donating NH groups to the Pd–Cl and Pt–Cl fragments.

Chart 1. Structures of Phosphole-Containing Hybrid Calixpyrroles 1S and 2S

2. Results and Discussion

2.1. Synthesis of Hybrid Calixpyrroles Containing σ⁴-Phosphole or σ⁴-2,3-Dihydrophosphole Units

Scheme 1 outlines the synthesis of calix[1]phosphole[1]thiophene[2]pyrroles and calix[1]phosphole[1]furan[2]pyrroles (denoted hereafter as P,S,N₂- and P,O,N₂-hybrids). Treatment of 2,5-bis(1-hydroxy-1-methylethyl)phosphole P-sulfide (3)17 with BF₃•OEt₂ in pyrrole, followed by column chromatography on silica gel, gave an expected condensation product 4 in 32% yield together with unexpected products 5 and 6 in 26% and 27% yield, respectively. Presumably, the nonaromatic character of the phosphole ring allows the positive charge of carbenium intermediate 7 to delocalize onto the β-carbons (eq 1).18,19 The structures of 4, 5, and 6 were characterized by standard spectroscopic techniques. Judging from the ¹H and ³¹P NMR spectra, 5 and 6 were obtained as single diastereomers.20 The BF₃-promoted dehydrative condensation of 4 with 2,5-bis(1-hydroxy-1-methylethyl)thiophene (8S)⁶⁺,²¹ and 2,5-bis(1-hydroxy-1-methylethyl)furan (8O)⁶⁺,²¹ gave symmetric σ⁺-P,X,N₂-hybrids 9S (X = S) and 9O (X = O) in 61% and 39% yield, respectively. Similar condensations of 5 with 8S
Scheme 1. Synthesis of the $\sigma^4$-P,S,N$_2$ and $\sigma^4$-P,O,N$_2$ Hybrids

and 8O afforded the corresponding asymmetric $\sigma^4$-P,X,N$_2$-hybrids 10S and 10O in moderate yields. Compounds 9S, 9O, 10S, and 10O were characterized by spectroscopic methods. In their mass spectra, parent ion peaks were observed at $m/z$ 610 (for 9S and 10S) and $m/z$ 595 (for 9O and 10O), attributable to the 1:1 condensation products. In the $^{31}$P NMR spectra of 9S, 9O, 10S, and 10O, only one peak was observed at $\delta$ 69.6, 69.4, 62.3, and 63.1 ppm, respectively, indicating that a single diastereomer had been isolated in each reaction. In the $^1$H NMR spectra in CDCl$_3$, the NH protons appeared at considerably downfield ($\delta$ 7.84–9.32 ppm) relative to those of the $\sigma^3$-type compounds 1S, 1O, and 2S ($\delta$ 6.4–7.57 ppm), implying that the hydrogen-bonding interaction was present in solution (vide infra).

2.2. Crystal Structures of $\sigma^4$-Hybrids

Crystal structures of 9S, 9O, 10S, and 10O were elucidated by X-ray crystallography. The ORTEP diagrams of 10S and 10O are shown in Figures 2 and 3 (the ORTEP diagrams of 9S and 9O are shown in Figures 1 and 2 in Chapter 1), and those of. The crystallographic parameters are summarized in Table A1 (Appendix). In the symmetric hybrids 9S and 9O, the pyrrole rings are connected to the 2- and 5-positions of the phosphole ring through the $-\text{CMe}_2-$ bridge. On the other hand, in the asymmetric hybrids 10S and 10O, one of the pyrrole rings is directly connected to the 3-position of the 2,3-dihydrophosphole ring, producing two chiral centers at the phosphorus and $\beta$-carbon atoms. The P=S sulfur atom and
the pyrrole rings are located on the same side, suggesting that the stereochemistry of 5 was retained in the condensation with 8S and 8O (vide supra).

In the solid state, 9S, 10S, and 10O adopt a partial cone conformation, whereas 9O adopts a cone conformation. All of the hybrids possess a trapezoid-like cavity, where the P=S moiety is located inside. The phosphole, 2,3-dihydrophosphole, thiophene, and furan rings stand almost perpendicular to a plane formed by the four (9S and 9O) or three (10S and 10O) bridging meso carbon atoms, whereas the pyrrole rings are tilted considerably to direct their NH groups toward the sulfur atom of the P=S group (Table 1). The observed N•••S1 distances of 3.34–3.62 Å indicate that the hydrogen-bonding interaction is present between the sulfur atom and the NH protons in 9S, 9O, 10S, and 10O.

**Figure 2.** ORTEP diagram of 10S (30% probability ellipsoids). Except for NH, hydrogen atoms are omitted for clarity. Selected bond lengths and distances (Å): S1–P, 1.9772(14); C1–C2, 1.512(5); C1–C8, 1.334(5); C2–C6, 1.540(5); C6–C7, 1.337(4); S1•••N1, 3.60; S1•••N2, 3.58.

**Figure 3.** ORTEP diagram of 10O (30% probability ellipsoids). Except for NH, hydrogen atoms are omitted for clarity. Selected bond lengths and distances (Å): S1–P, 1.9738(6); C1–C2, 1.529(2); C1–C8, 1.3387(19); C2–C6, 1.5295(19); C6–C7, 1.341(2); S1•••N1, 3.58; S1•••N2, 3.61.

**Table 1.** Dihedral Angles and N•••S1 Distances

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dihedral Angles (°)</th>
<th>N•••S1 Distances (Å)</th>
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<tbody>
<tr>
<td></td>
<td>phosphole</td>
<td>thiophene/furan</td>
</tr>
<tr>
<td>9S</td>
<td>87.0</td>
<td>71.4</td>
</tr>
<tr>
<td>9O</td>
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<td>71.5</td>
</tr>
<tr>
<td>10S</td>
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<td>81.1</td>
</tr>
<tr>
<td>10O</td>
<td>82.2</td>
<td>88.7</td>
</tr>
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</table>

* Dihedral angles between the heterole ring and the mean plane of the four (three, in the case of 10S and 10O) bridging meso carbon atoms.
As shown in Table 2, the cavity sizes of 9S and 10S are larger than those of 9O and 10O, mainly reflecting the difference in edge-to-edge distances \( b \) between the thiophene (9S: 5.44 Å and 10S: 5.40 Å) and furan (9O: 4.94 Å and 10O: 4.91 Å) subunits. These data clearly show that the cavity size of hybrid calixpyrroles is tunable by simply changing the combination of the heterole subunits.

<table>
<thead>
<tr>
<th>Table 2. Edge-to-Edge Distances (Å) of 9S, 9O, 10S, and 10O</th>
</tr>
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<tbody>
<tr>
<td>9S (X = S)</td>
</tr>
<tr>
<td>( a )</td>
</tr>
<tr>
<td>( b )</td>
</tr>
<tr>
<td>( c )</td>
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<td>( d )</td>
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\( a \) Defined by the distances between the bridging carbon atom and the \( \beta \)-carbon atom of the dihydrophosphate unit (indicated by "•").

### 2.3. Synthesis of \( \sigma^2 \)-Hybrids

In order to prepare the \( \sigma^2 \)-type phosphole-containing calixpyrroles, reductive desulfurization of the symmetric \( \sigma^2 \)-P,X,N\(_2\)-hybrids 9S and 9O, and asymmetric \( \sigma^2 \)-P,S,N\(_2\)-hybrid 10S was examined. When heated with 2.8 equiv of \( \text{P(NMe}_2\text{)}_3 \) in refluxing toluene for 33 h, 9S was completely consumed to afford the symmetric \( \sigma^2 \)-P,S,N\(_2\)-hybrid 1S in 92% yield (eq 2). Similarly, 9O was converted to the symmetric \( \sigma^2 \)-P,O,N\(_2\)-hybrid 1O in 72% yield. The \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra indicate that each of 1S and 1O exists as a mixture of two conformers, in which the lone pair of the phosphorus atom is located inside and outside the cavity (\( 1\text{X}_{\text{in}} \) and \( 1\text{X}_{\text{out}} \) in eq 3; \( X = S, O \)). That is, two sets of \(^1\text{H}\) resonances and two \(^{31}\text{P}\) peaks (\( \delta \) 31.4 and 32.1 ppm for 1S; \( \delta \) 32.3 and 37.6 ppm for 1O) were observed at 25 °C in toluene-\( d_8 \), whereas they coalesced at 70 °C (Figure 3). Unfortunately, \( 1\text{X}_{\text{in}} \) and \( 1\text{X}_{\text{out}} \) could
not be separated at 25 °C, suggesting that interconversion between the two conformers takes place rapidly even at this temperature. It is well known that a pyramidal inversion barrier for phosphole (ca.16 kcal mol⁻¹) is smaller than those of the conventional triorganylphosphines (30–35 kcal mol⁻¹) due to the aromatic stabilization at the planar transition state.²³ The ratios of major/minor conformers in 1S and 1O at 25 °C were determined to be 4/1 and 5/1, respectively, based on the integral values.

In contrast to the desulfurization of the symmetric hybrids, a large excess amount of P(NMe₂)₃ (130 equiv) and a longer reaction time (60 h) were needed for the complete conversion of the asymmetric σ⁻⁻⁻⁻P₂S₅N₃-hybrid 10S to σ⁻⁻⁻⁻P₂S₅N₃-hybrid 2S (eq 4), which was obtained as a mixture of two conformers 2Sₕ and 2Sₗ. However, the rate of interconversion between 2Sₕ and 2Sₗ is so slow at room temperature that both of them could be isolated by column chromatography. The ³¹P NMR spectra of 2Sₕ and 2Sₗ in CDCl₃ showed only one peak at δ 29.5 and 17.7 ppm, respectively. The structures of these two conformers were confirmed by X-ray crystallographic analyses of their metal complexes (vide infra).

To assign the structures of the major and minor conformers in the symmetric hybrids 1X, we performed ¹H NMR titration measurements of 1X using dimethyl sulfoxide-δ₆ (DMSO-δ₆) as a guest, which were originally reported by Sessler and co-workers for evaluating the hydrogen-bonding ability of meso-octamethylcalix[4]pyrrole. These authors concluded that the observed downfield shift of the NH protons stems from the multiple hydrogen-bonding interaction between the pyrrolic NH groups and the S–oxo moiety of

Figure 3. Variable-temperature ¹H NMR spectra of (a) 1S and (b) 1O in toluene-δ₆. Filled circles: major conformer; open circles: minor conformer.
Figure 4. $^1$H NMR spectra of 1S, 1O, 2S$_{in}$ and 2S$_{out}$ in toluene-$d_8$ on addition of DMSO-$d_6$ at 25°C: (a) 1S (12 mM), DMSO-$d_6$(0, 0.12, and 0.24 M). (b) 1O (12 mM), DMSO-$d_6$(0, 0.12, and 0.24 M). Filled circles: major conformer; open circles: minor conformer. (c) 2S$_{in}$ (12 mM), DMSO-$d_6$(0 and 0.24 M). (d) 2S$_{out}$ (12 mM), DMSO-$d_6$(0 and 0.24 M).

DMSO. The results of the present system are summarized in Figure 4. As the amount of DMSO-$d_6$ increased, the NH peaks due to the major conformer in 1X shifted downfield [$\Delta \delta = 0.06$ ppm (10 eq), 0.11 ppm (20 eq) for 1S; $\Delta \delta = 0.09$ ppm (10 eq), 0.17 ppm (20 eq) for 1O]. By contrast, the addition of DMSO-$d_6$ caused no appreciable spectral change for the minor conformer. These observations suggest that the major and minor conformers in toluene-$d_8$ are 1X$_{in}$ and 1X$_{out}$, respectively. Namely, 1S$_{in}$ and 1O$_{in}$ are likely to bind DMSO-$d_6$ thorough the cooperative hydrogen-bonding interaction between two NH protons and the S=O group (Figure 5a), whereas 1S$_{out}$ and 1O$_{out}$ are unlikely to bind DMSO-$d_6$ at the core because the phenyl and trimethylene groups would protect the NH groups sterically (Figure 5b). This assignment was strongly supported by the results on similar titration measurements for the isolated asymmetric hybrids 2S$_{in}$ and 2S$_{out}$. On addition of DMSO-$d_6$(20 eq), the NH peaks of 2S$_{in}$ were shifted downfield considerably [$\Delta \delta > 0.6$ ppm] (Figure 4c), while 2S$_{out}$ displayed negligible spectral change (Figure 4d).

Figure 5. Schematic views of possible interaction of DMSO-$d_6$ with (a) 1X$_{in}$ and (b) 1X$_{out}$.
2.4. Synthesis of Au(I), Pt(II), and Pd(II) Complexes

With the $\sigma^{2}$-P,S,N$_{2}$-hybrids $1S$, $2S_{in}$, and $2S_{out}$ in hand, the author set out to examine their coordination behavior toward Au(I), Pt(II), and Pd(II) salts. As mentioned above, the symmetric hybrid $1S$ exists as an equilibrium mixture of two conformers $1S_{in}$ and $1S_{out}$ at room temperature. Hence, both in and out type coordination modes are conceivable in the complexation reactions (Figure 6a; hereafter in and out are used to indicate the conformation of the $\sigma^{2}$-P,N$_{2}$S-hybrids in metal complexes: in indicates $1S_{in}$ or $2S_{in}$, and out indicates $1S_{out}$ or $2S_{out}$). On the other hand, when the isolated asymmetric hybrids $2S_{in}$ and $2S_{out}$ are used as ligands, either in or out type coordination could be observed (Figure 6b). The structures of the metal complexes formed are summarized as simplified representations in Figure 7.

**Figure 6.** Coordination behavior of the (a) symmetric hybrid $1S$ and (b) asymmetric hybrids $2S_{in}$ and $2S_{out}$.

![Coordination behavior of the (a) symmetric hybrid 1S and (b) asymmetric hybrids 2S_in and 2S_out.](image)

**Figure 7.** Simplified representations of the metal complexes.

![Simplified representations of the metal complexes.](image)
Table 3. Reaction of 1S with AuCl(SMe₂)

<table>
<thead>
<tr>
<th>reaction conditions</th>
<th>relative ratio (^a) (yield/(%)(^b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT, 15 min</td>
<td>11_in/11_out (91/9) (80/-)</td>
</tr>
<tr>
<td>RT, 1 h</td>
<td>11_in/11_out (97/3) (86/-)</td>
</tr>
<tr>
<td>110 (^\circ)C, 2 h</td>
<td>11_in/11_out (97/3) (84/-)</td>
</tr>
</tbody>
</table>

\(^a\) Determined by \(^1\)H NMR spectra. \(^b\) Isolated yield.

As shown in Table 3, \(1S\) (a mixture of \(1S\)_in and \(1S\)_out) reacted with 1.1 equiv of AuCl(SMe₂) in toluene to give a mixture of the in type complex 11\_in and the out type complex 11\_out. In solution, 11\_out was gradually converted to 11\_in, indicating that 11\_in is thermodynamically more stable than the 11\_out. The conversion from 11\_out to 11\_in in toluene was almost complete within 1 h at room temperature. In contrast, \(2S\)_in and \(2S\)_out reacted with AuCl(SMe₂) to afford the in type complex 12\_in (eq 5) and the out type complex 12\_out (eq 6), respectively, with keeping the initial configuration at the phosphorus center. There was no sign of interconversion between 12\_in and 12\_out in CDCl₃ even after 10 h at room temperature. The in and out conformations of 11\_in and 12\_out were confirmed by X-ray crystallography (vide infra).

The complexation of the symmetric \(\alpha^3\)-P,N₂,S-hybrid \(1S\) with 0.5 equiv of PtCl₂ yielded three types of trans-Pt(II)-bis(phosphine) complexes 13\_\(t_i\), 13\_\(o_\alpha\), and 13\_\(o_o\) (Table 4), which are denoted as in-in,\(^{16}\) in-out,\(^{16}\) and out-out type, respectively. In refluxing toluene, the relative ratio of 13\_\(t_i/13\_\(o_\alpha/13\_\(o_o\) changed from 4/54/42 (after 45 min) to 9/70/21 (after 2 h), and finally reached an equilibrium value of 90/10/>0 \(^{24}\) (after 4 d). Similarly, the complexation of \(1S\) with PdCl₂ afforded the in-in type and in-out type complexes 14\_\(t_i\) and 14\_\(o_\alpha\) in a ratio of 92/8,\(^{25}\) In this reaction, the out-out type complex 14\_\(o_o\) was not observed during the reaction. The same equilibrium states were attained by heating the isolated in type complexes 13\_\(t_i\) and 14\_\(t_i\) in refluxing toluene \(13\_\(t_i/13\_\(o_\alpha/13\_\(o_o\) = 90/10/>0\) after 4 d; \(14\_\(t_i/14\_\(o_\alpha/14\_\(o_o\) = 92/8/>0\) after 2 h).
The two macrocyclic ligands isolated yield, respectively.

The complexes Pt, Pd were examined for their single peak was observed at δ 195.1 ppm, indicative of a trans geometry for all complexes. Determined by 31P–205Pt coupling constants of 2400, 2560 Hz; 31P–205Pt coupling constants of 2445 Hz; 31P–205Pt coupling constants of 2476 Hz. These results clearly indicate that the thermodynamic stability of 13 and 14 decreases in the order: in-in > in-out >> out-out. It should be noted that, at room temperature, the interconversion among the in-in, in-out, and out-out complexes in CDCl₃ does not occur even after 10 h. The 31P NMR spectra of 13₁₄, 13₁₆, and 1₃₈₀ displayed characteristic peaks at δ 46.7 ppm (1J₃₁₄₂₄ = 2476 Hz), δ 45.5, and 46.5 ppm (1J₃₁₄₂₄ = 2400, 2560 Hz; 1J₃₁₆₂₄ = 2445 Hz; ), respectively. The observed 31P–195Pt coupling constants of 2400–2560 Hz support are indicative of trans geometry of the two phosphine ligands are coordinated in a trans geometry for all complexes. In the 31P NMR spectrum of the Pd(II) complex 1₄₁₄, a single peak was observed at δ 49.4 ppm. The structures of 1₃₁₄, 1₄₁₄, and 1₃₁₆ were ultimately confirmed by X-ray crystallography (vide infra).

Finally, the reactions of the asymmetric α₃-P,S,N₂-hybrid 2S₈ with 0.5 equiv of MCl₂ (M = Pt, Pd) were examined (eq 7). In both cases, the in-in type trans-M(II)–bis(phosphine) complexes 1₅₁₄, (M = Pt) and 1₆₁₄ (M = Pd) were obtained as major products in 83% and 79% yield, respectively. The 31P NMR spectra of 1₅₁₄ and 1₆₁₄ showed only one resonance at δ 40.2 ppm (1J₃₁₄₂₄ = 2421 Hz) and δ 44.0 ppm, respectively, indicating that 1₅₁₄ and 1₆₁₄ had been isolated as single diastereomers. The X-ray diffraction analyses of 1₅₁₄ and 1₆₁₄ revealed that the two macrocyclic ligands have the same stereochemistry at the phosphorus and β-carbon

**Table 4.** Reaction of the Symmetric α₃-P,S,N₂-Hybrid 1S with MCl₂ (M = Pt, Pd)

<table>
<thead>
<tr>
<th>reaction time</th>
<th>relative ratio (yield/%)</th>
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</thead>
<tbody>
<tr>
<td>45 min</td>
<td>13₁₄/13₁₆/13₁₈₀</td>
</tr>
<tr>
<td>2 h</td>
<td>14₁₄/14₁₆/14₁₈₀</td>
</tr>
<tr>
<td>4 d</td>
<td>90/10/0 (85/–/–)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>reaction time</th>
<th>relative ratio (yield/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 min</td>
<td>4/54/42 (–/49/37)</td>
</tr>
<tr>
<td>2 h</td>
<td>9/70/21 (12/60/24)</td>
</tr>
<tr>
<td>4 d</td>
<td>92/8/–0 (45/–/–)</td>
</tr>
</tbody>
</table>

*a* Determined by 1H NMR spectra. *b* Isolated yields. *c* About 50% of free ligand 1S was recovered.
atoms. Although the data of $15_{i,i}$ are not at the publishable level (*vide infra*), the observed high diastereoselectivity represents that the asymmetric P,S,N$_2$-hybrid ligand $2S_{in}$ coordinated to the metal center discriminates the chirality of the second asymmetric ligand completely.

2.5. Crystal Structures of Au(I), Pt(II), and Pd(II) Complexes

The crystal structures of the Au(I) complexes $11_{in}$ (sym) and $12_{out}$ (asym), the Pt(II) complexes $13_{i,i}$ (sym) and $13_{as}$ (sym), and the Pd(II) complexes $14_{i,i}$ (sym) and $16_{i,i}$ (asym) were successfully elucidated by X-ray crystallography (Figures 8–13). In the Au(I) complexes $11_{in}$ and $12_{out}$, the gold center adopts a linear geometry with P–Au–Cl bond angles of 173.20(2)–176.24(2)° (Figures 8 and 9). The Au–P and Au–Cl bond lengths [2.2391(8) and 2.2892(8) Å] of $11_{in}$ are close to the respective values of $12_{out}$ [2.2381(4) and 2.2871(4) Å] and those reported for the Au(I)–phosphole complexes. In $11_{in}$, the Au–Cl moiety is located above the cavity provided by the symmetric σ$^2$-P,S,N$_3$ macrocycle with a cone conformation. On the other hand, the Au–Cl moiety in $12_{out}$ is located outside the cavity provided by the asymmetric σ$^2$-P,S,N$_2$ macrocycle with a partial cone conformation.

As shown in Figures 10–13, each metal center in the Pt(II) complexes $13_{i,i}$ and $13_{as}$ and the Pd(II) complexes $14_{i,i}$ and $16_{i,i}$ has a square planar geometry, and two phosphorus atoms are coordinated in a trans orientation. The Pt–P and Pt–Cl bond lengths in $13_{i,i}$ [2.3390(14), 2.3286(14) Å and 2.3035(12), 2.2992(11) Å] and $13_{as}$ [2.3218(6), 2.3375(5) Å and 2.3195(5), 2.3018(6) Å] are close to the values reported for a trans-Pt(II)–bis(2,5-dialkylphosphole) complex [2.309(3), 2.318(3) Å and 2.296(3), 2.301(3) Å]. Similarly, the Pd–P and Pd–Cl bond lengths of $14_{i,i}$ [2.3496(8), 2.3548(8) Å and 2.2990(6), 2.3034(6) Å] and $16_{i,i}$ [2.3488(10), 2.3343(8) Å and 2.2999(9), 2.3007(9) Å] are comparable to the values reported for a trans-Pd(II)–bis(2,5-dialkylphosphole)complex [2.325(7), 2.353(7) Å and 2.271(7), 2.280(7) Å].

In the in-out type Pt(II) complex $13_{as}$, one of the symmetric σ$^3$-P,S,N$_2$ ligands adopts a 1,2-alternate conformation and binds the platinum moiety outside the cavity, whereas the other adopts a cone conformation and binds the platinum moiety above the cavity. In the in-in type Pt(II) and Pd(II) complexes $13_{i,i}$ and $14_{i,i}$, the conformation of two symmetric σ$^3$-P,S,N$_2$ ligands is basically the same as that of the in type ligand of $13_{as}$. In these in-in type complexes, however, the whole structure has a $C_{2h}$ symmetry, and the metal center is located above the cavities of two macrocyclic ligands as though it is wrapped around. In the in-in type Pd(II) complex $16_{as}$, two asymmetric σ$^3$-P,S,N$_2$ ligands coordinating to one palladium center have the same stereochemistry and adopt partial cone conformation. The coordination mode of
16_{i-d} is similar to those of 13_{i-d} and 14_{i-d}.

**Figure 8.** ORTEP diagram of 11_{in} (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg):

Au–Cl, 2.2892(8); Au–P, 2.2391(8); C1–C2, 1.343(4); C2–C6, 1.469(4); C6–C7, 1.347(4); Cl–Au–P, 173.20(2).

**Figure 9.** ORTEP diagram of 12_{out} (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg):

Au–Cl, 2.2871(30); Au–P, 2.2381(4); C1–C2, 1.532(2); C1–C8, 1.343(3); C2–C6, 1.529(3); C6–C7, 1.343(3); Cl–Au–P, 176.24(2).

**Figure 10.** ORTEP diagram of 13_{i-t} (30% probability ellipsoids). meso-Me groups and hydrogen atoms except for NH, are omitted for clarity. Selected bond lengths (Å), angles (deg) and distances (Å):

Pt–Cl1, 2.3035(12); Pt–Cl2, 2.2992(11); Pt–P1, 2.3390(14); Pt–P2, 2.3286(14); Cl1–Pt–P1, 94.76(4); Cl1–Pt–P2, 86.99(4); Cl2–Pt–P1, 86.57(4); Cl2–Pt–P2, 93.36(4); Cl1⋯N3, 3.27; Cl1⋯N4, 3.52; Cl2⋯N1, 3.50; Cl2⋯N2, 3.23.

**Figure 11.** ORTEP diagram of 13_{p-o} (30% probability ellipsoids). meso-Me groups and hydrogen atoms except for NH, are omitted for clarity. Selected bond lengths (Å), angles (deg) and distances (Å):

Pt–Cl1, 2.3184(6); Pt–Cl2, 2.3018(6); Pt–P1, 2.3219(6); Pt–P2, 2.3375(6); Cl1–Pt–P1, 85.09(2); Cl1–Pt–P2, 88.89(2); Cl2–Pt–P1, 93.20(2); Cl2–Pt–P2, 93.08(2); Cl1⋯N1, 3.41; Cl1⋯N2, 3.40.
Harvey and co-workers reported that the metal fragments of Rh(III) complexes of the upper-rim monophosphinated calix[4]arenes were located outside the cavity in the crystalline state. In sharp contrast, the crystal structures of the present complexes $11_{in}$, $13_{i,i}$, $13_{o,o}$, $14_{i,i}$, and $16_{i,i}$ clearly show that the symmetric and asymmetric $\sigma^3$-P,S,N$_2$-hybrids $1S$ and $2S_{in}$ behave as monodentate P-ligands to bind the metal above the cavity. This is attributable to the

**Table 5. N···Cl Distances and NH Resonances in the Pt(II) and Pd(II) Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>N···Cl Distances (Å)</th>
<th>NH Resonances in CDCl$_3$ (ppm)</th>
<th>$\Delta\delta$ (ppm)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$13_{i,i}$</td>
<td>3.23, 3.27, 3.50, 3.52</td>
<td>8.85</td>
<td>1.5–1.8</td>
</tr>
<tr>
<td>$13_{o,o}$</td>
<td>3.40, 3.41$^b$</td>
<td>8.91$^b$, 7.19$^c$</td>
<td>1.5–1.8$^b$, -0.2–0.1$^c$</td>
</tr>
<tr>
<td>$13_{p,o}$</td>
<td>3.26, 3.27, 3.49, 3.50</td>
<td>8.98</td>
<td>-0.2–0.1</td>
</tr>
<tr>
<td>$14_{i,i}$</td>
<td>3.18, 3.23, 3.38, 3.51</td>
<td>8.37, 9.58</td>
<td>1.3–1.5, 2.6–2.7</td>
</tr>
</tbody>
</table>

$^a$ Differences in the NH resonances between the metal complexes ($\delta$(M)) and the free ligands ($\delta$(F)): $\Delta\delta = \delta$(M) – $\delta$(F). $^b$ Values for the $in$ type ligands. $^c$ Values for the $out$ type ligands.

**Figure 12.** ORTEP diagram of $14_{i,i}$ (30% probability ellipsoids). meso-Me groups and hydrogen atoms except for NH, are omitted for clarity. Selected bond lengths (Å), angles (deg) and distances (Å): Pd–Cl1, 2.2990(6); Pd–Cl2, 2.3034(6); Pd–P1, 2.3548(8); Pd–P2, 2.3496(8); Cl1–Pd–P1, 85.69(2); Cl1–Pd–P2, 95.46(2); Cl2–Pd–P1, 93.53(2); Cl2–Pd–P2, 85.54(2); Cl1···N1, 3.49; Cl1···N2, 3.26; Cl2···N3, 3.27; Cl2···N4, 3.50.

**Figure 13.** ORTEP diagram of $16_{i,i}$ (30% probability ellipsoids). meso-Me groups and hydrogen atoms except for NH, are omitted for clarity. Selected bond lengths (Å), angles (deg) and distances (Å): Pd–Cl1, 2.2999(9); Pd–Cl2, 2.3007(9); Pd–P1, 2.3488(10); Pd–P2, 2.3343(8); Cl1–Pd–P1, 89.13(3); Cl1–Pd–P2, 93.01(3); Cl2–Pd–P1, 94.85(3); Cl2–Pd–P2, 86.04(3); Cl1···N1, 3.38; Cl1···N2, 3.18; Cl2···N3, 3.51; Cl2···N4, 3.23.
difference in rigidity at the phosphorus center between the monophosphinated calix[4]arenes and the \( \sigma^3\text{-P,S,N}_2 \)-hybrids: the latter ligands are much more rigid than the former ones. Another interesting feature of the \( \sigma^3\text{-P,S,N}_2 \)-hybrid ligands stems from the pyrrole units, which behave as hydrogen-bonding donors. In the \(^1\text{H}\) NMR spectra of the Pt(II) and Pd(II) complexes \( 13_{\text{in}}, 13_{\text{ex}}, 14_{\text{in}}, 14_{\text{ex}}, 15_{\text{in}}, \) and \( 16_{\text{in}} \) in CDCl\(_3\), the NH resonances of the \textit{in} type ligands were observed at downfield relative to those of their free bases \( 1\text{S}_{\text{in}} \) and \( 2\text{S}_{\text{in}} \) (\( \Delta \delta = 1.2−2.7 \text{ ppm; Table 5} \)). In fact, in the crystal structures, two pyrrole rings of the \textit{in} type macrocyclic ligands of \( 13_{\text{in}}, 13_{\text{ex}}, 14_{\text{in}}, \) and \( 16_{\text{in}} \) are tilted to direct the NH protons toward the chlorine atom bound to the metal with N•••Cl distances of 3.18–3.52 Å, which are close to the reported values [3.264(7)–3.331(7) Å] of a chloride ion complex of \textit{meso}-octamethylcalix[4]pyrrole.\(^3\) These observations demonstrate the presence of cooperative hydrogen-bonding interaction between the M–Cl (M = Pt, Pd) fragment and the NH protons in these complexes.

### 3. Conclusion

Symmetric and asymmetric hybrid calixpyrroles containing a phosphole or a 2,3-dihydrophosphole unit (symmetric and asymmetric P,X,N\(_2\)-hybrids) were prepared for the first time via acid-promoted condensation reactions of the \( \sigma^4 \)-phosphatryptopyrroles with 2,5-difunctionalized heteroles. As clearly revealed by X-ray crystallographic analyses of the \( \sigma^4 \)-P,X,N\(_2\)-hybrids, the cavity size of the phosphole-containing hybrid calixpyrroles is tunable by exchanging the components of the macrocyclic backbone. The results on the complexation of the symmetric and asymmetric \( \sigma^3\text{-P,S,N}_2 \)-hybrid calixpyrroles with Au(I), Pd(II), and Pt(II) salts represent that both the symmetric and asymmetric \( \sigma^3\text{-P,S,N}_2 \)-hybrids behave as monodentate P-ligands. It is of particular interest that the pyrrole NH protons can be utilized as hydrogen-bonding donors to the metal-bound chlorine atoms. The present study demonstrates the potential utility of the phosphole-containing hybrid calixpyrroles as a new class of multifunctional macrocyclic P-ligands.
**Experimental Section**

**General.** All melting points are uncorrected. $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra were recorded using CDCl$_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane ($^1$H and $^{13}$C) and H$_2$PO$_4$ ($^{31}$P). MALDI-TOF and (HR-)FAB mass spectra were measured using CHCA and 3-nitrobenzyl alcohol as matrices. CH$_2$Cl$_2$ and toluene were distilled from calcium hydride before use. All the reactions were performed under an argon or nitrogen atmosphere. Column chromatography was performed on silica gel or on a fast flow liquid chromatography system fitted with a silica gel column. Compound 3 was prepared by the reaction of the corresponding 2,5-diester with excess MeMgBr.$^{17}$ Other chemicals were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Although spectroscopic data clearly supported high purity of all the isolated compounds, the author was not successful in obtaining satisfactory analytical data for some compounds with accuracy of ±0.4%.

**Synthesis of Compound 4, 5, and 6.** To a solution of diol 3 (2.2 g, 6.3 mmol) in 60 mL (870 mmol) of pyrrole, was added the 0.78 mL (6.3 mmol) of BF$_3$•OEt$_2$. After stirring for 5 h at room temperature, CH$_2$Cl$_2$ (50 mL) and saturated NaHCO$_3$ solution (30 mL) were added. The water phase was extracted with CH$_2$Cl$_2$, and the organic extracts were combined, washed with brine, dried over Na$_2$SO$_4$ and evaporated. Purification by silica gel column chromatography (CH$_2$Cl$_2$/EtOAc = 50/1) followed by recrystallization from EtOAc/hexane afforded compounds 4 (890 mg, 32%; $R_f$ = 0.6), 5 (740 mg, 26%; $R_f$ = 0.5), and 6 (670 mg, 27%; $R_f$ = 0.2) as colorless solids.

**4:** Mp 154–155 °C; $^1$H NMR δ 1.38 (s, 6H), 1.41 (s, 6H), 1.54–1.62 (m, 1H), 1.90–1.94 (m, 1H), 2.09–2.25 (m, 4H), 5.88–5.90 (m, 2H), 5.99–6.01 (m, 2H), 6.70–6.71 (m, 2H), 7.48–7.59 (m, 3H), 7.97 (m, 2H), 9.12 (br s, 2H); $^{13}$C{$^1$H} NMR δ 26.6, 26.6, 27.6, 27.7, 27.9, 28.1, 28.7, 28.8, 37.7, 37.8, 102.5, 106.4, 117.2, 128.8, 129.8, 131.7, 131.8, 135.0, 136.1, 138.3, 138.3, 158.0, 158.4; $^{31}$P{$^1$H} NMR δ 69.3; MS (MALDI-TOF) m/z 447 (M$^+$); Anal. Calcd for C$_{27}$H$_{31}$N$_2$PS: C, 72.61; H, 7.00; N, 6.27; P, 6.94. Found: C, 72.60; H, 6.99; N, 6.27; P, 6.89.

**5:** Mp 163–164 °C; $^1$H NMR δ 1.28 (s, 3H), 1.48 (s, 3H), 1.54 (d, 3H, $J$ = 2.4 Hz), 1.65–1.71 (m, 1H), 1.68 (d, 3H, $J$ = 2.0 Hz), 1.77–1.91 (m, 2H), 1.92–2.01 (m, 1H), 2.11–2.26 (m, 1H), 5.79–5.81 (m, 1H), 5.94–5.96 (m, 1H), 6.03–6.05 (m, 1H), 6.07–6.09 (m, 1H), 6.55–6.57 (m, 1H), 6.77–6.78 (m, 1H), 7–9 (br, 2H), 7.50–7.61 (m, 3H), 7.97 (br s, 1H), 9.60 (br s, 1H); $^{13}$C{$^1$H} NMR δ 22.8, 22.9, 23.5, 23.5, 23.6, 23.8, 23.9, 27.6, 27.6, 30.1, 30.1, 34.6, 34.7, 38.2, 38.3, 60.0, 60.2, 102.8, 102.9, 104.8, 106.7, 106.9, 116.8, 118.5, 128.6, 131.5, 131.5, 132.3,
was washed with distilled water (3 mL). After stirring for 3.5 h at room temperature, the resulting mixture was washed with distilled water (3 mL), dried over Na₂SO₄ and evaporated to give a pale yellow solid, which was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 2/1) to give the α²-P,S,N₅-hybrid 9S as a yellow solid (Rₛ = 0.4; 41 mg, 61%). A similar treatment of 4 with 8O afforded the α²-P,S,O,N₅-hybrid 9O as a yellow solid (Rₛ = 0.4; 39%).

**Synthesis of Compounds 9S and 9O.** Compound 4 (50 mg, 0.11 mmol) and 8S (22 mg, 0.11 mmol) were dissolved in CH₂Cl₂ (80 mL), and the solution was bubbled with N₂ for 40 min. BF₃•OEt₂ (0.014 mL, 0.11 mmol) was added to the solution, and the mixture was then stirred for 3.5 h at room temperature. The resulting mixture was washed with distilled water (3 × 80 mL), dried over Na₂SO₄ and evaporated to give a pale yellow solid, which was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 2/1) to give the α²-P,S,N₅-hybrid 9S as a yellow solid (Rₛ = 0.4; 41 mg, 61%). A similar treatment of 4 with 8O afforded the α²-P,S,O,N₅-hybrid 9O as a yellow solid (Rₛ = 0.4; 39%)

**9S:** Mp 241–242 °C; ¹H NMR δ 1.27 (m, 1H), 1.32 (s, 6H), 1.36 (s, 6H), 1.65 (s, 6H), 1.72 (s, 6H), 1.86 (m, 1H), 2.10 (m, 4H), 5.79 (m, 4H), 6.78 (s, 2H), 7.50 (m, 3H), 7.90 (m, 2H), 9.09 (s, 2H); ¹³C{¹H} NMR δ 26.7, 27.2, 28.0, 28.2, 31.4, 31.7, 37.4, 37.6, 38.1, 99.8, 101.7, 101.8, 123.6, 128.6, 129.1, 129.5, 131.8, 135.5, 136.5, 137.0, 141.3, 152.0, 158.4, 158.7; ³¹P{¹H} NMR (toluene-d₈) δ 69.6; MS (FAB) m/z 610 (M⁺); Anal. Calc. for C₃₁H₄₃N₂P₂S₂: C, 72.75; H, 7.10; N, 4.59; P, 5.07. Found: C, 72.85; H, 7.10; N, 4.47; P, 5.12.

**9O:** Mp 177–178 °C; ¹H NMR δ 1.27 (m, 1H), 1.39 (s, 6H), 1.40 (s, 6H), 1.60 (s, 6H), 1.67 (s, 6H), 1.82 (m, 1H), 2.11 (m, 4H), 5.76 (dd, 2H, J = 2.6, 2.6 Hz), 5.78 (dd, 2H, J = 2.6, 2.6 Hz), 6.05 (s, 2H), 7.51 (m, 3H), 7.96 (m, 2H), 9.57 (s, 2H); ¹³C{¹H} NMR δ 22.6, 22.8, 23.3, 23.6, 23.7, 24.4, 24.6, 25.4, 25.7, 25.8, 25.9, 29.0, 29.2, 29.7, 29.8, 34.1, 36.0, 36.1, 37.6, 37.7, 60.2, 60.5, 100.2, 100.3, 100.9, 103.6, 103.8, 104.2, 130.1, 131.1, 131.2, 131.3, 133.5, 133.7, 134.4, 134.9, 137.9, 138.9, 139.2, 146.8, 147.0, 159.6, 159.7, 168.8, 169.0; ³¹P{¹H} NMR δ 69.4; MS (MALDI-TOF) m/z 595 (M⁺).

**Synthesis of Compounds 10S and 10O.** Compound 5 (110 mg, 0.25 mmol) and 8S (50 mg, 0.25 mmol) were dissolved in CH₂Cl₂ (300 mL), and BF₃•OEt₂ (0.014 mL, 0.11 mmol) was added to the solution. After stirring for 3.5 h at room temperature. The resulting mixture was washed with distilled water (3 × 150 mL), dried over Na₂SO₄ and evaporated. The
products were subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 2/1) to give the asymmetric σ⁺-P,S,N₂-hybrid 10S as a colorless solid (Rᵢ = 0.3; 75 mg, 49%). A similar treatment of 5 with 8O afforded the asymmetric σ⁺-P,O,N₂-hybrid 10O as a colorless solid (Rᵢ = 0.3; 44%).

**10S**: Mp 252–253 °C; ¹H NMR δ 1.14 (s, 3H), 1.32 (s, 3H), 1.45 (d, 3H, J = 2.1 Hz), 1.64–1.75 (m, 17H), 1.80–2.02 (m, 1H), 2.10–2.26 (m, 1H), 2.40–2.55 (m, 1H), 2.73–2.79 (m, 1H), 5.63 (dd, 1H, J = 3.0, 3.0 Hz), 5.68 (dd, 1H, J = 3.0, 3.0 Hz), 5.82 (dd, 1H, J = 3.0, 3.0 Hz), 5.90 (dd, 1H, J = 3.0, 3.0 Hz), 6.85 (pseudo s, 2H), 7.26–7.60 (m, 4H), 7.84 (s, 1H), 8.40–8.52 (m, 1H), 8.93 (s, 1H); ¹³C{¹H} NMR δ 22.7, 22.8, 22.9, 23.4, 23.5, 24.1, 24.2, 26.4, 26.5, 29.5, 30.0, 30.2, 30.4, 34.1, 34.2, 37.4, 37.6, 38.2, 38.3, 39.5, 59.9, 99.6, 100.4, 101.0, 103.4, 120.9, 121.3, 130.9, 131.4, 131.4, 131.9, 133.1, 133.3, 134.2, 134.2, 135.3, 139.7, 139.7, 141.2, 142.1, 147.0, 147.2, 153.7, 155.7, 168.7, 169.0; ³¹P{¹H} NMR (toluene-d₈) δ 62.3; MS (MALDI-TOF) m/z 610 (M⁺); Anal. Calc. for C₅₇H₄₂N₂PS₂: C, 72.75; H, 7.10; N, 4.59; P, 5.07. Found: C, 72.99; H, 7.14; N, 4.53; P, 5.37.

**10O**: Mp ca. 240 °C (decomp); ¹H NMR δ 1.23 (s, 3H), 1.43 (s, 3H), 1.51 (d, 3H, J = 2.4 Hz), 1.61–1.79 (m, 17H), 1.89–1.99 (m, 1H), 2.12–2.26 (m, 1H), 2.48–2.56 (m, 1H), 2.77–2.82 (m, 1H), 5.63 (dd, 1H, J = 3.0, 3.0 Hz), 5.65 (dd, 1H, J = 3.0, 3.0 Hz), 5.75 (dd, 1H, J = 3.0, 3.0 Hz), 5.89 (dd, 1H, J = 3.0, 3.0 Hz), 6.04 (d, 1H, J = 2.8 Hz), 6.05 (d, 1H, J = 2.8 Hz), 7.3–7.7 (br, 4H), 8.4–8.7 (br, 1H), 9.00 (s, 1H), 9.32 (s, 1H); ¹³C{¹H} NMR δ 22.6, 22.8, 23.3, 23.6, 23.7, 24.4, 24.6, 25.4, 25.7, 25.9, 25.9, 29.0, 29.2, 29.7, 29.8, 34.1, 36.0, 36.1, 37.6, 37.7, 60.2, 60.5, 100.2, 100.3, 100.5, 100.9, 103.6, 103.8, 104.2, 130.1, 131.1, 131.3, 131.3, 131.4, 133.5, 133.7, 134.4, 137.9, 138.9, 138.9, 139.2, 146.8, 14.70, 159.7, 159.7, 168.8, 169.0; ³¹P{¹H} NMR δ 63.1; MS (MALDI-TOF) m/z 595 (M⁺).

**Synthesis of Compound 1X (X = S, O)**: To a degassed solution of 9S (47 mg, 0.077 mmol) in toluene (5 mL) was added P(NMe₂)₃ (0.040 mL, 0.22 mmol), and the mixture was then stirred under reflux for 3 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 2/1) to give the symmetric σ⁺-P,S,N₂-hybrid 1S as a colorless solid (Rᵢ = 0.5; 41 mg, 92%). A similar treatment of 9O with P(NMe₂)₃ afforded the symmetric σ⁺-P,O,N₂-hybrid 1O as a colorless solid (Rᵢ = 0.5; 72%).

**1S**: The ¹H NMR spectrum of 1 indicated that, in toluene-d₈, two conformers are present in about 4:1 ratio. Major conformer: ¹H NMR (toluene-d₈) δ 1.39 (s, 6H), 1.46 (s, 6H), 1.61 (s, 6H), 1.63 (s, 6H), 1.7–2.3 (m, 6H), 5.95 (m, 2H), 5.96 (m, 2H), 6.63 (s, 2H), 6.9–7.1 (m, 3H), 7.34 (m, 2H), 7.43 (br s, 2H); ³¹P{¹H} NMR (toluene-d₈) δ 32.1; Minor conformer: ¹H NMR (toluene-d₈) δ 1.30 (s, 6H), 1.57 (s, 6H), 1.58 (s, 6H), 1.61 (s, 6H), 1.7–2.3 (m, 6H), 5.79 (m,
When the reaction time was 15 min, a small amount of 11 was obtained at room temperature, the resulting mixture of 11 and 11 was subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1) to give 11 as a colorless solid ($R_f$ = 0.5; 66 mg, 86%).

When the reaction time was 15 min, a small amount of 11 was observed by $^1$H and $^{31}$P NMR spectra.
11<sub>in</sub>: Mp ca. 220 °C (decomp); <sup>1</sup>H NMR δ 1.34 (s, 6H), 1.54 (s, 6H), 1.55–1.69 (m, 3H), 1.67 (s, 6H), 1.75 (s, 6H), 1.85–1.97 (m, 1H), 2.14–2.26 (m, 2H), 5.82 (dd, 2H, J = 3.2, 3.2 Hz), 5.87 (dd, 2H, J = 3.2, 3.2 Hz), 6.98 (s, 2H), 7.43–7.49 (m, 2H), 7.51–7.57 (m, 3H), 7.64–7.72 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR δ 26.9, 26.9, 27.8, 27.9, 28.2, 28.2, 30.9, 31.5, 31.6, 31.8, 36.9, 37.1, 38.0, 100.1, 103.5, 103.5, 125.4, 125.9, 126.7, 129.5, 129.6, 132.5, 132.5, 133.4, 133.6, 135.4, 136.1, 137.3, 137.4, 140.8, 150.6, 161.6, 161.8; <sup>31</sup>P{<sup>1</sup>H} NMR δ 53.8; HR-FAB-MS: Calcd for C<sub>37</sub>H<sub>47</sub>N<sub>2</sub>CIP<sub>3</sub>Au(M<sup>+</sup>), 810.2239; Found, 810.2242.

11<sub>out</sub>: <sup>1</sup>H NMR δ 1.25 (s, 6H), 1.58 (s, 6H), 1.68 (s, 6H), 1.69 (s, 6H), 1.83–1.94 (m, 1H), 2.06–2.19 (m, 3H), 2.33–2.43 (m, 2H), 5.62 (dd, 2H, J = 3.0, 3.0 Hz), 5.76 (dd, 2H, J = 3.0, 3.0 Hz), 6.8–7.3 (br, 2H), 6.88 (s, 2H), 7.07 (br s, 2H), 7.30–7.33 (m, 2H), 7.42–7.46 (m, 1H); <sup>31</sup>P{<sup>1</sup>H} NMR δ 52.1.

**Synthesis of Compounds 12<sub>in</sub> and 12<sub>out</sub>.** To a Schlenk tube containing 2S<sub>in</sub> (8 mg, 0.014 mmol) and AuCl(SMe<sub>2</sub>) (4.5 mg, 0.015 mmol) was added 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 0.5 h at room temperature, the resulting mixture was evaporated and subjected to silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1/1) to give 12<sub>in</sub> as a pale yellow solid (R<sub>f</sub> = 0.4; 9 mg, 80%). A similar treatment of 2S<sub>out</sub> with AuCl(SMe<sub>2</sub>) afforded the complex 12<sub>out</sub> as a colorless solid (R<sub>f</sub> = 0.4; 92%).

12<sub>in</sub>: Mp ca. 240 °C (decomp); <sup>1</sup>H NMR δ 1.13 (s, 3H), 1.24–1.39 (m, 1H), 1.43 (s, 3H), 1.55 (s, 3H), 1.65 (pseudo s, 6H), 1.69 (s, 3H), 1.70–1.92 (m, 2H), 1.77 (s, 3H), 1.81 (s, 3H), 2.02–2.18 (m, 1H), 2.28–2.37 (m, 1H), 2.77–2.82 (m, 1H), 5.70–5.72 (m, 2H), 5.88 (dd, 1H, J = 3.0, 3.0 Hz), 5.93 (dd, 1H, J = 3.0, 3.0 Hz), 6.97 (br s, 1H), 6.98 (d, 1H, J = 3.6 Hz), 7.15 (d, 2H, J = 3.6 Hz), 7.30 (br s, 1H), 7.4–8.3 (br, 2H), 7.46–7.56 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR δ 22.5, 22.6, 23.8, 23.9, 26.5, 26.5, 26.6, 29.4, 29.7, 30.1, 30.5, 31.2, 31.3, 34.5, 37.2, 37.3, 38.4, 38.5, 62.7, 62.9, 99.6, 101.8, 102.9, 104.5, 122.5, 122.9, 128.4, 129.0, 129.2, 129.4, 129.9, 130.5, 131.3, 131.6, 131.6, 131.8, 132.3, 132.3, 138.2, 138.2, 141.0, 142.0, 148.4, 148.5, 153.2, 154.9, 168.4, 168.6; <sup>31</sup>P{<sup>1</sup>H} NMR δ 48.8; HR-FAB-MS: Calcd for C<sub>37</sub>H<sub>47</sub>N<sub>2</sub>CIP<sub>3</sub>Au(M<sup>+</sup>), 810.2239; Found, 810.2252.

12<sub>out</sub>: Mp 294–296 °C; <sup>1</sup>H NMR δ 1.20–1.37 (m, 1H), 1.28 (s, 3H), 1.58 (s, 3H), 1.63–1.75 (m, 10H), 1.78–1.93 (m, 2H), 1.85 (s, 3H), 1.89 (s, 3H), 2.03 (s, 3H), 2.18–2.32 (m, 1H), 2.55–2.65 (m, 1H), 5.80 (dd, 1H, J = 3.0, 3.0 Hz), 5.84 (dd, 1H, J = 3.0, 3.0 Hz), 5.87 (dd, 1H, J = 3.0, 3.0 Hz), 5.94 (dd, 1H, J = 3.0, 3.0 Hz), 6.73 (br s, 1H), 6.82 (d, 2H, J = 3.3 Hz), 6.88 (d, 2H, J = 3.3 Hz), 7.09 (br s, 1H), 7.43–7.48 (m, 2H), 7.52–7.64 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR δ 23.4, 23.6, 23.8, 24.4, 24.5, 26.0, 26.2, 27.1, 29.5, 29.6, 30.5, 30.9, 32.2, 32.3, 35.4, 37.9, 38.1, 38.3, 38.3, 62.9, 63.1, 100.7, 103.2, 103.9, 103.9, 106.5, 121.1, 121.5, 127.0, 127.9, 129.4, 129.5, 129.8, 130.5, 131.9, 131.9, 132.3, 132.4, 133.1, 133.2, 133.4, 138.5, 138.5,
140.4, 140.6, 149.7, 149.9, 154.1, 154.5, 169.4, 169.6; $^{31}$P{$^1$H} NMR δ 41.9; HR-FAB-MS: Calcd for C$_7$H$_{37}$N$_2$ClPSSAu (M$^+$), 810.2239; Found, 810.2240.

**Synthesis of Compounds 13$_{id}$, 13$_{io}$, and 13$_{ao}$.** To a Schlenk tube containing 1S (20 mg, 0.034 mmol) and PtCl$_2$ (4.5 mg, 0.017 mmol) was added 2.0 mL of toluene, and the resulting mixture was heated under reflux for 2 h. The solution was evaporated, and subjected to silica gel column chromatography (CH$_2$Cl$_2$/hexane = 2/1), affording the bisphosphine complexes 13$_{id}$ ($R_t = 0.5$; 3 mg, 12%), 13$_{io}$ ($R_t = 0.3$; 15 mg, 60%) and 13$_{ao}$ ($R_t = 0.2$; 6 mg, 24%) as a pale yellow solid, respectively. When the reaction time was 4 days, complex 13$_{id}$ was obtained exclusively (85%); small amounts of 13$_{io}$ (ca. 10%) and 13$_{ao}$ (trace) were also observed in the $^1$H NMR spectrum of the crude products.

13$_{id}$: Mp ca. 290 °C (decomp); $^1$H NMR δ 0.92–1.04 (m, 4H), 1.23 (s, 12H), 1.60–1.72 (m, 28H), 1.88–2.05 (m, 4H), 2.09 (s, 12H), 5.76–5.79 (m, 8H), 6.41 (s, 4H), 7.34–7.38 (m, 4H), 7.45–7.49 (m, 2H), 7.86–7.90 (m, 4H), 8.85 (s, 4H); $^{13}$C{$^1$H} NMR δ 26.1, 26.8, 30.7, 31.5, 34.4, 37.8, 38.0, 38.1, 99.4, 102.5, 124.7, 125.7, 125.9, 126.1, 128.2, 128.8, 128.3, 130.6, 132.8, 132.9, 138.4, 138.7, 138.9, 141.6, 142.1, 150.6, 163.5, 163.6, 163.7; $^{31}$P{$^1$H} NMR δ 46.7 ($J_{p,p}$ = 2476 Hz); HR-FAB-MS: Calcd for C$_{14}$H$_{60}$N$_2$Cl$_2$P$_2$S$_2$Pt (M$^+$), 1421.4794; Found, 1421.4780; Anal. Calcd for C$_{14}$H$_{60}$N$_2$Cl$_2$P$_2$S$_2$Pt: C, 62.43; H, 6.09; N, 3.94; Found: C, 62.09; H, 6.38; N, 3.51.

13$_{io}$: Mp ca. 230 °C (decomp); $^1$H NMR δ 1.28 (s, 6H), 1.45 (s, 6H), 1.62 (s, 6H), 1.65 (s, 6H), 1.67 (s, 18H), 1.77–2.10 (m, 8H), 2.25 (s, 6H), 2.43–2.48 (m, 2H), 5.67 (dd, 2H, $J = 3.0, 3.0$ Hz), 5.80–5.82 (m, 6H), 6.55 (s, 2H), 6.84 (s, 2H), 7.19 (s, 2H), 7.35–7.46 (m, 6H), 7.53 (m, 2H), 7.92 (m, 2H), 8.91 (s, 2H); $^{13}$C{$^1$H} NMR δ 14.1, 22.7, 25.7, 26.6, 26.7, 26.9, 26.9, 27.4, 28.3, 28.3, 28.4, 29.0, 30.3, 30.4, 30.5, 30.8, 31.3, 31.6, 31.6, 35.5, 35.5, 37.8, 37.9, 38.0, 38.4, 38.5, 38.6, 99.4, 101.5, 102.5, 103.1, 123.6, 124.4, 126.0, 126.7, 127.3, 127.9, 127.9, 128.0, 128.6, 128.7, 128.8, 130.3, 130.9, 132.8, 132.9, 132.9, 134.4, 134.5, 134.6, 138.1, 138.6, 138.8, 138.9, 139.0, 139.0, 139.2, 142.0, 142.1, 142.2, 151.0, 152.2, 159.3, 159.4, 163.2, 163.4, 163.5; $^{31}$P{$^1$H} NMR δ 45.5 ($J_{p,p}$ = 2400 Hz), 46.5 ($J_{p,p}$ = 2560 Hz); HR-FAB-MS: Calcd for C$_{14}$H$_{60}$N$_2$Cl$_2$P$_2$S$_2$Pt (M$^+$), 1421.4794; Found, 1421.4780.

13$_{ao}$: Mp ca. 220 °C (decomp); $^1$H NMR δ 1.51 (s, 12H), 1.66 (s, 12H), 1.68 (s, 12H), 1.69 (s, 12H), 1.75–2.05 (m, 8H), 2.35–2.46 (m, 4H), 5.70 (dd, 4H, $J = 3.0, 3.0$ Hz), 5.79 (dd, 4H, $J = 3.0, 3.0$ Hz), 6.85 (s, 4H), 7.16–7.28 (m, 4H), 7.22 (br s, 4H), 7.31–7.35 (m, 2H), 7.54–7.59 (m, 4H); $^{13}$C{$^1$H} NMR δ 27.4, 27.9, 28.0, 28.0, 28.7, 30.5, 30.7, 31.3, 37.9, 38.4, 38.5, 38.6, 101.2, 103.1, 123.8, 125.3, 125.6, 125.9, 128.4, 128.4, 128.5, 130.6, 134.5, 134.6, 134.7, 138.3, 138.7, 139.0, 139.2, 152.1, 159.6, 159.7, 159.8; $^{31}$P{$^1$H} NMR δ 45.7 ($J_{p,p}$ = 2445 Hz); HR-FAB-MS: Calcd for C$_{14}$H$_{60}$N$_2$Cl$_2$P$_2$S$_2$Pt (M$^+$), 1421.4794; Found, 1421.4816.
Synthesis of Compounds 14_{i,i}. To a Schlenk tube containing 1S (10 mg, 0.017 mmol) and PdCl$_2$ (1.5 mg, 0.0085 mmol) was added 1.5 mL of toluene, and the resulting mixture was heated under reflux for 2 h. The solution was evaporated, and subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1), affording the bisphosphine complex 14$_{i,i}$ ($R_i = 0.5$; 10 mg, 88%) as a yellow solid.

14$_{i,i}$: Mp ca. 240 °C (decomp); $^1$H NMR $\delta$ 0.93–1.02 (m, 4H), 1.22 (s, 12H), 1.55–1.77 (m, 28H), 1.89–2.01 (m, 4H), 2.09 (s, 12H), 5.75–5.78 (m, 8H), 6.43 (s, 4H), 7.33–7.37 (m, 4H), 7.45–7.49 (m, 2H), 7.86–7.90 (m, 4H), 8.98 (s, 4H); $^{13}$C($^1$H) NMR $\delta$ 25.9, 26.7, 26.7, 26.8, 27.0, 30.6, 31.5, 35.1, 35.2, 35.2, 37.8, 38.0, 38.1, 38.2, 38.2, 53.4, 99.4, 102.5, 124.8, 126.2, 126.5, 126.7, 128.2, 128.3, 128.4, 130.6, 133.0, 133.1, 134.3, 139.9, 140.1, 140.4, 141.4, 142.2, 150.6, 162.9, 163.0, 163.1; $^{31}$P($^1$H) NMR $\delta$ 49.4; HR-FAB-MS: Calcd for C$_{34}$H$_{68}$N$_4$Cl$_2$P$_2$S$_2$Pd (M$^+$), 1332.4181; Found, 1332.4198.

Synthesis of Compounds 15$_{i,i}$ and 16$_{i,i}$. To a suspension of PtCl$_2$ (2.3 mg, 0.0085 mmol) in MeOH (0.5 mL) was added a CH$_2$Cl$_2$ (1 mL) solution of 2S$_{i,i}$ (10 mg, 0.017 mmol). After stirring for 2 h at room temperature, the resulting mixture was evaporated. Purification with silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1) followed by recrystallization from CH$_2$Cl$_2$/MeOH gave 15$_{i,i}$ as a pale yellow solid ($R_i = 0.2$; 10 mg, 83%). A similar treatment of 2S$_{i,i}$ with PdCl$_2$ afforded the complex 16$_{i,i}$ as a yellow solid ($R_i = 0.2$; 79%).

15$_{i,i}$: Mp ca. 220 °C (decomp); $^1$H NMR $\delta$ 0.85 (s, 6H), 1.10–1.30 (m, 2H), 1.36 (s, 6H), 1.54 (s, 6H), 1.59 (s, 6H), 1.62–1.79 (m, 4H), 1.69 (s, 6H), 1.88 (s, 6H), 1.93 (s, 6H), 1.95–2.13 (m, 4H), 2.07 (s, 6H), 2.69–2.75 (m, 2H), 5.66 (dd, 2H, $J = 2.8, 2.8$ Hz), 5.71 (dd, 2H, $J = 2.8, 2.8$ Hz), 5.80 (dd, 2H, $J = 2.8, 2.8$ Hz), 5.92 (dd, 2H, $J = 2.8, 2.8$ Hz), 6.03 (d, 2H, $J = 3.6$ Hz), 6.47 (d, 2H, $J = 3.6$ Hz), 7.45–7.57 (m, 6H), 7.87–7.93 (m, 4H), 8.24 (s, 2H), 9.34 (s, 2H); $^{13}$C($^1$H) NMR $\delta$ 22.4, 22.6, 22.6, 22.7, 23.0, 23.1, 26.1, 27.9, 28.0, 28.1, 28.8, 30.8, 30.9, 31.5, 33.0, 33.1, 33.2, 33.2, 37.7, 37.8, 37.9, 38.0, 38.3, 61.8, 62.0, 62.1, 99.7, 101.4, 101.8, 104.6, 121.6, 121.9, 127.6, 127.6, 127.7, 127.7, 128.2, 128.4, 128.7, 129.4, 129.8, 130.1, 130.3, 133.6, 134.5, 134.5, 134.6, 141.1, 141.1, 141.1, 141.3, 142.0, 150.5, 152.3, 155.6, 166.0, 166.1, 166.2; $^{31}$P($^1$H) NMR $\delta$ 40.2 ($J_{P-P} = 2421$ Hz); HR-FAB-MS: Calcd for C$_{34}$H$_{68}$N$_4$Cl$_2$P$_2$S$_2$Pt (M$^+$), 1421.4794; Found, 1421.4819.

16$_{i,i}$: Mp ca. 220 °C (decomp); $^1$H NMR $\delta$ 0.86 (s, 6H), 1.10–1.25 (m, 2H), 1.35 (s, 6H), 1.54 (s, 6H), 1.60 (s, 6H), 1.62–1.79 (m, 4H), 1.70 (s, 6H), 1.86 (s, 6H), 1.91 (s, 6H), 1.95–2.13 (m, 4H), 2.06 (s, 6H), 2.68–2.74 (m, 2H), 5.67 (dd, 2H, $J = 3.0, 3.0$ Hz), 5.72 (dd, 2H, $J = 3.0, 3.0$ Hz), 5.81 (dd, 2H, $J = 3.0, 3.0$ Hz), 5.91 (dd, 2H, $J = 3.0, 3.0$ Hz), 6.05 (d, 2H, $J = 3.6$ Hz), 6.52 (d, 2H, $J = 3.6$ Hz), 7.45–7.57 (m, 6H), 7.85–7.91 (m, 4H), 8.37 (s, 2H), 9.58 (s, 2H); $^{13}$C($^1$H) NMR $\delta$ 22.5, 22.5, 22.6, 22.9, 23.0, 23.0, 26.1, 28.6, 28.6, 28.7, 28.8, 30.8, 31.1, 31.5,
X-ray Crystallography. Single crystals suitable for X-ray analyses were grown from CH₂Cl₂/MeOH (for 9S, 9O, 10S, 12_{out}, 13_{in} and 13_{out}), CH₂Cl₂/hexane (for 10O, 11_{in} and 14_{in}), or CH₂Cl₂/MeCN (for 15_{in} and 16_{in}). All X-ray crystallographic measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (0.71070 Å). The selected crystallographic data are summarized in Table A1 in Appendix. The structures were solved by using direct methods (SIR92\textsuperscript{28} for 9O, 11_{in}, 13_{in} and 16_{in}; SIR97\textsuperscript{29} for 9S, 10S, 10O, 13_{in} and 16_{in}; SHELXS97\textsuperscript{30} for 12_{out}). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model. All calculations were performed using CrystalStructure\textsuperscript{31} crystallographic software package except for refinement, which was performed using SHELXL-97.\textsuperscript{30}
### Appendix

**Table A1. X-Ray Parameters of Hybrid Calixpyrroles and Their Complexes**

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### Table A1. X-Ray Parameters of Hybrid Calixpyrroles and Their Complexes (continued)

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References and Footnotes


(18) Recently, Mathey and co-workers have reported that 2,5-bis(hydroxy(phenyl)methyl)phosphole P-sulfide reacts with a tripyrrane at one of the phosphole-β-positions under Friedel-Crafts conditions to produce a P-confused carbaporphyrinoid, which contains the 2,3-dihydro-3-pyrrolylphosphole subunit like 5 and 6. See ref 11e.

(19) When 6 was reacted with excess pyrrole for 5 h in the presence of BF₃•OEt₂, 5 was obtained as the main product (ca. 40%) with a substantial recovery of unreacted 6 (ca. 40%). Therefore, 6 is a possible precursor of 5.

(20) In the 'H NMR spectra, the NH protons of 5 and 6 appeared at the relatively downfield region (δ 7.97–9.46 ppm) comparable to those of 10S and 10O (δ 7.84–9.32 ppm), in which all the NH protons are hydrogen-bonded to the P=S moiety of the phosphole ring (*vide infra*). It is therefore likely that the pyrrole groups and the sulfur atom in 5 and 6 are located on the same side of the 2,3-dihydrophosphole ring similar to those in 10S and 10O.


also ref 11b,d.

(24) The preference for the in mode coordination was also found in a similar reaction in DMF (110 °C, 4 d: $13_{i}\text{p} / 13_{i}\text{p}= 92/8\sim 0$).

(25) Owing to the poor solubility of PdCl$_2$ in toluene, a large amount (ca. 50%) of free ligand 1S remained intact after 45 min.


Chapter 3

Synthesis of a Phosphorus-Containing Hybrid Porphyrin

Abstract: A phosphorus-containing hybrid porphyrin was successfully prepared via the BF₃-promoted dehydrative condensation between σ⁴-phosphatripyrrane and 2,5-bis[hydroxy(phenyl)methyl]-thiophene. The NMR and UV-Vis absorption spectra, electrochemical measurements, and DFT calculations have revealed that the σ³-P,S,N₂-hybrid porphyrin exhibits high aromaticity as an 18π-electron system in terms of both geometric and magnetic criteria.
1. Introduction

Porphyrs are one of the most widely studied aromatic macrocycles, because of their important roles in biological, materials, and coordination chemistry. Chemical modification of the core of porphyrins is a highly promising approach to developing new classes of dyes and catalysts, as the electronic structures and coordination environments of the porphyrin ring can be changed dramatically. In this respect, much attention has been paid to the chemistry of core-modified porphyrins, such as carbaporphyrins, N-confused porphyrins, chalcogen-containing porphyrins, and pyriporphyrins.

Incorporating a phosphorus atom at the core of the porphyrin ring, namely replacing a pyrrole ring with phosphole, seems quite promising for exhibiting characteristic optical, electrochemical, and coordinating properties derived from the phosphole subunit. In 2003, Delaere and Nguyen predicted the ground state electronic structures of unsubstituted monophospha- and diphosphaporphyrins based on density functional theory (DFT) calculations and concluded that these porphyrins would exhibit reasonable aromaticity. Experimentally, however, phosphorus-containing porphyrins have long been untouched. Recently, our group established a convenient method for the preparation of 2,5-difunctionalized phospholes, which have proven to be reliable starting materials for phosphorus-containing hybrid calixpyrroles and calixphyrins. This chapter describes the first example of a phosphorus-containing hybrid porphyrin as a new family of core-modified porphyrins. Both experimental and theoretical results clearly demonstrate that the $\sigma^3$-$\text{P,S,N}_2$-hybrid porphyrin possesses high aromaticity with a relatively narrow HOMO–LUMO gap.

Scheme 1. Synthesis of $\sigma^3$-$\text{P,S,N}_2$-Hybrid Porphyrin 6
2. Results and discussion

Scheme 1 illustrates the synthesis of $\sigma^3$-P,S,N$_2$-hybrid porphyrin 6. Treatment of 2,5-bis(hydroxymethyl)-1-phenyl-1-thiophosphole (1) with excess pyrrole in the presence of BF$_3$•OEt$_2$ afforded $\sigma^4$-phosphatryptyrane (2) in 14% yield. The BF$_3$-promoted dehydrative condensation of 2 with 2,5-bis[hydroxy(phenyl)methyl]thiophene (3) in CH$_2$Cl$_2$ gave $\sigma^4$-P,S,N$_2$-porphyrinogen (4) in 36% yield as a mixture of diastereomers. Desulfurization of 4 with excess P(NMe$_2$)$_3$ in refluxing toluene yielded $\sigma^3$-P,S,N$_2$-hybrid porphyrinogen (5), which was subsequently oxidized by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford the target compound 6 in 14% yield (from 4) as an air and thermally stable reddish purple solid.

The structure of $\sigma^3$-P,S,N$_2$-hybrid porphyrin 6 was fully characterized by mass spectrometry and NMR spectroscopy. In the HR-FAB-MS spectrum, the parent ion peak (M$^+$) was observed at m/z 612.1788 (calc for C$_{41}$H$_{29}$N$_2$PS: 612.1789). In the $^1$H NMR spectrum, the meso, pyrrole-β, and thiophene-β protons of 6 appeared at δ 10.44 (d, $^3$J$_{P-H}$ = 18.8 Hz), 8.67 and 8.93, and 9.22, respectively, whereas the P-phenyl ortho-, meta-, and para-protons appeared at δ 2.29, 5.27, and 5.66, respectively (Figure 2). The significant downfield and upfield appearances of these peaks are indicative of a ring current effect derived from the porphyrin π-circuit. The $^{31}$P peak of 6 (δ 18.6) was also very shielded as compared to that (δ 26.7) of $\sigma^3$-P,S,N$_2$-calixphyrin 7 (Figure 1) and those (δ 32.0–36.0) of 2,5-disubstituted 1-phenylphospholes bearing the same 3,4-C$_3$ bridge. Thus, the hybrid porphyrin 6 is likely to possess high aromatic character. It should be noted here that the upfield shift (Δδ/ppm) of the P-phenyl protons of 6 relative to the corresponding protons of 7 increases in the order: para (1.61) < meta (2.01) < ortho (5.27). This implies that the P-phenyl group in 6 stands above the porphyrin π-plane like the N-methyl group in N-methylporphyrins. As a consequence, the ortho protons of 6 and the 5/6 protons of 7 resonate at δ 8.22 and δ 8.30, respectively, in the $^1$H NMR spectrum of 6. The structure of $\sigma^3$-P,S,N$_2$-hybrid porphyrin 6 was fully characterized by

Figure 1. $\sigma^3$-P,S,N$_2$-Hybrid calixphyrin 7, porphyrins 8a,b, 21-thiaporphyrins 9a,b, and $\sigma^3$-P,S,N$_2$-Hybrid porphyrin 10.
Figure 2. $^1$H NMR spectrum of $6$ in CDCl$_3$ at 25 °C. Asterisks (*) indicate the residual solvent peaks.

mass spectrometry and NMR spectroscopy. In the HR-FAB-MS spectrum, the parent ion peak (M$^+$) was observed at m/z 612.1788 (calcd for C$_{41}$H$_{29}$N$_2$PS: 612.1789). In the $^1$H NMR spectrum, the meso, pyrrole-$\beta$, and thiophene-$\beta$ protons of $6$ appeared at $\delta$ 10.44 (d, $^3$J$_{P-H}$ = 18.8 Hz), 8.67 and 8.93, and 9.22, respectively, whereas the P-phenyl ortho-, meta-, and para-protons appeared at $\delta$ 2.29, 5.27, and 5.66, respectively (Figure 2). The significant downfield and upfield appearances of these peaks are indicative of a ring current effect derived from the porphyrin $\pi$-circuit. The $^{31}$P peak of $6$ ($\delta$ 18.6) was also very shielded as compared to that ($\delta$ 26.7) of $\sigma^3$-P,S,N$_2$-calixphyrin $7^{10}$ (Figure 1) and those ($\delta$ 32.0–36.0) of 2,5-disubstituted 1-phenylphospholes bearing the same 3,4-C$_3$ bridge.$^{15}$ Thus, the hybrid porphyrin $6$ is likely to possess high aromatic character. It should be noted here that the upfield shift ($\Delta\delta$/ppm) of the P-phenyl protons of $6$ relative to the corresponding protons of $7$ increases in the order; para (1.61) < meta (2.01) < ortho (5.27). This implies that the P-phenyl group in $6$ stands above the porphyrin $\pi$-plane like the N-methyl group in N-methylporphyrins.$^{16}$ As a consequence, the ortho protons of the meso-phenyl groups, which would be oriented at a slant against the porphyrin plane, were differentiated at 25 °C.$^{17}$

In the UV-Vis absorption spectrum of $6$ in CH$_2$Cl$_2$, the Soret band appeared at $\lambda_{\text{max}}$ 440 nm (Figure 3a), which was red-shifted as compared to those of 5,10,15,20-tetraphenylporphyrin (TPP) $8a$ ($\lambda_{\text{max}}$ 411 nm) and 21-thia-5,10,15,20-tetraphenylporphyrin $9a$ ($\lambda_{\text{max}}$ 425 nm). The Q-type transitions of $6$ were also observed at longer wavelengths, $\lambda_{\text{max}}$ 492, 518, 547, 647, and 718 nm. In contrast to $8a$, $\sigma^3$-P,S,N$_2$-hybrid $6$ was
not fluorescent.

All attempts to grow single crystals of 6 suitable for X-ray diffraction analysis were unsuccessful. Thus, DFT calculations were carried out to reveal the optimized structures of \( \sigma^3 \)-P,S,N\(_2\)-hybrid 10, parent porphyrin 8b, and 21-thiaporphyrin 9b as models for 6, 8a, and 9a, respectively.\(^{18}\) As shown in Figure 4, the porphyrin planes of 8b and 9b are completely planar, whereas that of 10 is nonplanar. Thus, replacement of the NH unit of thiaporphyrin with the PPh unit (from 9b to 10) induces a distortion of the porphyrin plane, where all the heterole subunits are slightly tilted to make a dish-like macrocyclic platform. Such a deviation is presumably caused by electrostatic repulsion between the phosphorus and sulfur atoms in 10.\(^{19}\)

The phosphorus center in 10 adopts a trigonal pyramidal geometry (\( \Sigma_{C-P-C} = 299.5^\circ \)), which prevents effective interaction between the phosphorus lone pair and the porphyrin \( 18\pi \)-circuit. Similar geometries at the phosphorus center (\( \Sigma_{C-P-X} = 292.4^\circ \sim 296.1^\circ ; \ X = C, H \)) were reported for the 21-phospha- and 21,23-diphosphaporphyrins bearing P–H bonds,\(^6\) suggesting that the phosphorus lone pair in \( \sigma^3 \lambda^3 \)-P-containing porphyrins essentially has an s character irrespective of the P substituents. The geometry of the P-phenyl group in 10 explains the \(^1\)H NMR observation for 6 well.

As the optimized structures were obtained, the aromaticity of 10 was evaluated by comparing it with those of 8b and 9b. Despite the nonplanarity, the P,S,N\(_2\)-hybrid 10 keeps high aromaticity in terms of a geometric criterion. The mean HOMA\(^{20}\) values for all 28 bonds of the porphyrin ring of 8b, 9b, and 10 were calculated to be 0.680, 0.645, and 0.550, respectively (Table 1). The rather low value of 10 as compared to those of 8b and 9b may be ascribed to distortion of the phosphole subunit.\(^{21}\) On the other hand, the HOMA values for the \( 18\pi \) circuit (18 bonds consisting of C and N atoms) of 8b, 9b, and 10 are 0.853, 0.877, and

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**Figure 3.** (a) UV-Vis absorption spectrum of 6 in CH\(_2\)Cl\(_2\). (b) Cyclic voltammogram of 6. 0.1 M \( n\)Bu\(_4\)NPF\(_6\), Ag\(^+\)/Ag (0.01 M AgNO\(_3\)). Scan rate 20 mV s\(^{-1}\).
0.879, respectively, implying high aromaticity of \( \text{10} \) as a bridged \([18]\)annulene derivative. To evaluate the degree of aromaticity of \( \text{10} \) on the basis of a magnetic criterion, we also calculated NICS\(^{22}\) values at the porphyrin ring and heterole ring centers (Table 1). The NICS values at the center of the core atoms of \( \text{8b, 9b, and 10} \) are \(-16.5, -16.2, \) and \(-15.6 \text{ ppm} \), respectively,\(^{23}\) indicating that the aromaticity of the P,S,N\(_2\)-hybrid \( \text{10} \) is slightly weaker than those of \( \text{8b and 9b} \). Interestingly, the NICS value at the phosphole ring center (\( \beta \)) in \( \text{10} \) (\(-16.7 \text{ ppm} \)) is much higher than that of the parent 1-phenylphosphole (\(-4.31 \text{ ppm} \)).\(^{24}\) This reflects that the cyclic 1,3-diene unit of the phosphole ring is included in an 18\(\pi\)-electron system. By contrast, the NICS value at the \( \gamma \) position in \( \text{10} \) (\(-1.96 \text{ ppm} \)) is much lower than the respective value of pyrrole, reflecting the strong 2-azafulvene character of the N-heterole rings.

To gain insight into the HOMO and LUMO energies of the P,S,N\(_2\)-hybrid porphyrin \( \text{6} \), redox potentials were measured by cyclic voltammetry (CV) and/or differential pulse voltammetry (DPV). As shown in Figure 3b, the electrochemical oxidation process of \( \text{6} \) is irreversible, and the first oxidation potential of \( \text{6} \) was determined by the DPV measurement to be \(+0.45 \text{ V (vs. Fc/Fc}) \),\(^{25}\) which is more cathodic than the reported values for \( \text{8a} (E_{1/2} +0.58 \text{ V}) \).

\[ \text{8b} \]
\[ \text{9b} \]
\[ \text{10} \]

**Figure 4.** Top (upper) and side (lower) views of the optimized structures of (a) \( \text{8b} \), (b) \( \text{9b} \), and (c) \( \text{10} \). The C, N, P, and S atoms are indicated as grey, blue, orange, and yellow balls, respectively.

\[ \text{8b} \]
\[ \text{9b} \]
\[ \text{10} \]

**Figure 5.** Bond lengths (Å) of the optimized structures of \( \text{8b, 9b, and 10} \).
V) and 9a (E_{1/2} = 0.62 V). On the other hand, electrochemical reduction of 6 occurred quasi-reversibly, and the first and second reduction potentials (E_{1/2}) were determined as −1.36 V and −1.56 V (vs. Fc/Fc^+), respectively, which are more anodic than those of 8a (−1.73 V and −2.06 V) and 9a (−1.55 V and −1.82 V). These data suggest that modification of the core of the porphyrin from an NH to a PPh unit basically narrows the HOMO–LUMO energy gap.26

Table 1. HOMA and NICS values for Model Compounds

<table>
<thead>
<tr>
<th>(X, Y)</th>
<th>8b (NH, NH)</th>
<th>9b (NH, S)</th>
<th>10 (PPh, S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMA</td>
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<tr>
<td>Total^a</td>
<td>0.680</td>
<td>0.645</td>
<td>0.550</td>
</tr>
<tr>
<td>18π^b</td>
<td>0.853</td>
<td>0.887</td>
<td>0.879</td>
</tr>
<tr>
<td>NICS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>−16.5</td>
<td>−16.2</td>
<td>−15.6</td>
</tr>
<tr>
<td>β</td>
<td>−15.3</td>
<td>−15.9</td>
<td>−16.7</td>
</tr>
<tr>
<td>γ</td>
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<td>−2.5</td>
<td>−2.0</td>
</tr>
<tr>
<td>δ</td>
<td>−19.0</td>
<td>−19.8</td>
<td></td>
</tr>
</tbody>
</table>

^a Calculated using all 28 bonds of the porphyrin ring.
^b Calculated using 18 bonds of the [18]annulene circuit.

3. Conclusion

In conclusion, a phosphorus-containing core-modified porphyrin was successfully prepared for the first time. It was found that the α^3-P,S,N_2-hybrid porphyrin is composed of a bridged [18]annulene π-system and displays high aromaticity in terms of both geometric and magnetic criteria. This class of compounds is expected to behave as macrocyclic, multidentate phosphorus ligands with characteristic optical properties. In this context, the coordination chemistry of phosphorus-containing porphyrins is worthy of further study.
Experimental Section

**General Procedures.** All melting points are uncorrected. $^1$H, $^{13}$C{$^{1}$H}, and $^{31}$P{$^{1}$H} NMR spectra were recorded using CDCl$_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane ({$^1$H} and $^{13}$C) and phosphoric acid ({$^{31}$P}). Mass spectra were measured using CHCA (MALDI-TOF), m-nitrobenzyl alcohol (FAB), or m-nitrophenyl octyl ether (HR-FAB) as a matrix. All solvents were distilled from sodium benzophenone ketyl (ether, THF) or calcium hydride (CH$_2$Cl$_2$, toluene) before use. All the reactions were performed under an argon or nitrogen atmosphere. Column chromatography was performed on silica gel or activated alumina. Compounds 1$^8$ and 3$^{11}$ were prepared according to the reported procedures.

**Synthesis of Compound 2.** To a mixture of 1 (1.9 g, 6.5 mmol) and pyrrole (35 mL, 510 mmol) was added BF$_3$•OEt$_2$ (4.2 mL, 33 mmol) at 80 °C. After stirring for 1.5 h at the same temperature, the second portion of BF$_3$•OEt$_2$ (4.9 mL, 39 mmol) was added, and the mixture was stirred for an additional 1 h. After cooling to room temperature, a saturated NaHCO$_3$ solution (20 mL) and CH$_2$Cl$_2$ (50 mL) were added. The organic phase was separated, dried over Na$_2$SO$_4$, and evaporated. The products were subjected to silica gel column chromatography (CH$_2$Cl$_2$) repeatedly and the fraction of $R_t = 0.3$ was collected and washed with MeOH to give 2 as a colorless solid (350 mg, 14%): Mp 141–143 °C; $^1$H NMR $\delta$ 1.98–2.05 (m, 2H), 2.25–2.40 (m, 4H), 3.48–3.53 (m, 4H), 5.85–5.87 (m, 2H), 5.96–5.98 (m, 2H), 6.57–6.58 (m, 2H), 7.39–7.43 (m, 2H), 7.48–7.50 (m, 1H), 7.71–7.75 (m, 2H), 8.77 (br, 2H); $^{13}$C{$^{1}$H} NMR $\delta$ 23.6, 23.8, 26.7, 26.7, 26.8, 26.9, 106.3, 107.7, 117.3, 126.7, 127.2, 127.3, 127.6, 127.7, 128.8, 128.9, 130.3, 130.4, 132.0, 132.0; $^{31}$P{$^{1}$H} NMR $\delta$ 72.2; MS (FAB) $m/z$ 391 (M$^+$). HR-FAB-MS: Calcd for C$_{25}$H$_{23}$N$_2$PS (M$^+$), 391.1398; Found, 391.1398.

**Synthesis of Compound 4.** A CH$_2$Cl$_2$ solution (530 mL) containing 2 (370 mg, 0.95 mmol) and 3 (280 mg, 0.95 mmol) was bubbled with N$_2$ for 30 min. BF$_3$•OEt$_2$ (0.12 mL, 0.95 mmol) was added to the solution, and the mixture was then stirred for 30 min at room temperature. The resulting mixture was washed with distilled water (2 × 500 mL), dried over Na$_2$SO$_4$, and evaporated. The crude products were subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 1/1) to give σ$^4$-porphyrinogen 4 as a mixture of three diastereomers ($R_t = 0.5–0.6$; 220 mg, 36%). The $^1$H and $^{31}$P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 6:5:3. $^1$H NMR Diastereomer A: $\delta$ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.37–5.39 (m, 1H), 5.46 (s, 1H), 5.54 (d, $^4$J = 1.6 Hz, 1H), 5.75–5.78 (m, 1H), 5.82–5.83 (m, 1H), 5.87–5.89 (m, 1H), 6.19 (dd, $J = 3.6$ Hz, $^4$J = 1.6 Hz, 1H), 6.82 (d, $J = 3.6$ Hz, 1H), 7.18–7.39 (m, 10H), 7.29 (dd, $J = 3.6$ Hz, 1H), 7.50 (m, 3H), 8.77 (br, 2H).
7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.38 (br, 1H), 9.74 (br, 1H); Diastereomer B: δ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.54 (s, 2H), 5.77–5.78 (m, 2H), 5.87–5.88 (m, 2H), 6.14 (s, 2H), 7.18–7.39 (m, 10H), 7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.61 (br, 2H); Diastereomer C: δ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.29–5.32 (m, 2H), 5.59 (s, 2H), 5.79–5.81 (m, 2H), 6.90 (s, 2H), 7.18–7.39 (m, 10H), 7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.51 (br, 2H); \(^{31}\)P\(\{^1\text{H}\}\) NMR δ 72.6, 72.7, 72.8; MS (MALDI-TOF) m/z 650 (M\(^+\)).

**Synthesis of Compound 5.** To a toluene solution (40 mL) of 4 (370 mg, 0.57 mmol) was added P(NMe\(_2\))\(_3\) (0.66 mL, 3.6 mmol), and the mixture was then stirred under reflux for 23 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH\(_2\)Cl\(_2\) = 2/1) to give 5 as a mixture of diastereomers (\(R_t = 0.3–0.4\); 330 mg, 93%): The ratio of the three diastereomers (A, B, C) was found to be 8:5:4. \(^1\)H NMR Diastereomer A: δ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.55 (s, 1H), 5.60 (s, 1H), 5.72–5.76 (m, 2H), 5.77–5.81 (m, 1H), 5.82–5.86 (m, 1H), 6.55 (d, \(J = 3.6\) Hz, 1H), 6.67 (d, \(J = 3.6\) Hz, 1H), 7.22–7.30 (m, 15H), 8.20 (br, 1H), 8.35 (br, 1H); Diastereomer B: δ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.60 (s, 2H), 5.65–5.69 (m, 2H), 5.78–5.82 (m, 2H), 6.67 (s, 2H), 7.22–7.30 (m, 15H), 8.27 (br, 2H); Diastereomer C: δ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.60–5.62 (m, 4H), 5.78–5.81 (m, 2H), 6.76 (s, 2H), 7.22–7.30 (m, 15H), 8.21 (br, 1H); \(^{31}\)P\(\{^1\text{H}\}\) NMR δ 32.7, 33.3, 33.5; MS (MALDI-TOF) m/z 618 (M\(^+\)).

**Synthesis of Compound 6.** To a solution of 5 (50 mg, 0.081 mmol) and P(NMe\(_2\))\(_3\) (0.060 mL, 0.32 mmol) in degassed toluene (3 mL), was added a toluene (2 mL) solution of DDQ (130 mg, 0.57 mmol) over 40 min at -78 °C, and the resulting mixture was directly subjected to a short alumina column (CH\(_2\)Cl\(_2\)). Further purification by alumina column chromatography, followed by recrystallization from CH\(_2\)Cl\(_2\)/MeOH, afforded 6 as a reddish purple solid (7 mg, 15%): Mp ca. 250 °C (decomp); \(^1\)H NMR δ 2.29 (dd, \(J = 7.6\) Hz, \(^3\)J\(_{P,H} = 4.5\) Hz, 2H), 2.90–3.00 (m, 1H), 3.20–3.31 (m, 1H), 3.53–3.59 (m, 2H), 4.40–4.51 (m, 2H), 5.27 (dd, \(J = 7.6\) Hz, 7.2 Hz, 2H), 5.66 (t, \(J = 7.2\) Hz, 1H), 7.75 (br, 6H), 7.91 (br, 2H), 8.33 (br, 2H), 8.67 (d, \(J = 4.4\) Hz, 2H), 8.93 (d, \(J = 4.4\) Hz, 2H), 9.22 (s, 2H), 10.44 (d, \(^3\)J\(_{P,H} = 18.8\) Hz, 2H); \(^{13}\)C\(\{^1\text{H}\}\) NMR (CD\(_2\)Cl\(_2\)) δ 29.3, 30.4 (d, \(J\_p\_C = 2.5\) Hz), 123.4 (d, \(J\_p\_C = 6.6\) Hz), 124.5, 125.0 (d, \(J\_p\_C = 4.2\) Hz), 127.6, 127.7 (d, \(J\_p\_C = 7.4\) Hz), 128.3, 132.3 (d, \(J\_p\_C = 9.9\) Hz), 133.7 (d, \(J\_p\_C = 3.3\) Hz), 134.4, 135.0, 135.6, 135.6, 141.3, 146.1 (d, \(J\_p\_C = 4.1\) Hz), 147.6 (d, \(J\_p\_C = 18.2\) Hz), 155.4, 159.1, 159.2 (d, \(J\_p\_C = 18.1\) Hz); \(^{31}\)P\(\{^1\text{H}\}\) NMR δ 18.6; UV/Vis (CH\(_2\)Cl\(_2\)) λ \((\varepsilon)\):
440 (141000), 492 (11600), 518 (7400), 547 (4900), 647 (1300), 718 (3100); MS (FAB) m/z 613 ([M+H]^+). HR-FAB-MS: Calcd for C_{41}H_{29}N_{2}PS (M^+), 612.1789; Found, 612.1788.

**Density Functional Theory (DFT) Calculations on Model Compounds.** The structures of σ\(^3\)-P,S,N\(^2\)-hybrid 10, parent porphyrin 8b, and 21-thiaporphyrin 9b, as models for 6, 8a, and 9a, respectively, were optimized using density functional theory (DFT). The basis set used was 6-311G(d,p).\(^{27}\) The functionals of DFT was the Becke 1988 exchange and Lee-Yang-Parr correlation functionals (B3LYP).\(^{28}\) The nucleus independent chemical shift (NICS) values\(^{29}\) were calculated at the Hartree-Fock level with gauge-including atomic orbitals (GIAOs) at the DFT optimized structures. The basis set used in the NICS value computations was 6-31+G(d).\(^{30}\) The optimized structures are depicted in Figure 4, and the bond lengths of the optimized structures are shown in Figure 5. All the calculations were carried out using the Gaussian 03 suite of programs.\(^{31}\)
References and Footnotes


2006, 71, 5792.


(12) The $^1$H and $^{31}$P NMR spectra of 4 and 5 indicated that three diastereomers were present. For details, see Supporting Information.


(14) It is known that the N-methyl protons in N-methylporphyrins are significantly shielded due to the ring current effect. For example, see: Lavallee, D. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, 104, 4707.


(16) It is known that the N-methyl protons in N-methylporphyrins are significantly shielded due to the ring current effect. For example, see: Lavallee, D. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, 104, 4707.

(17) These ortho protons (indicated as j in Figure 2) coalesced at 60 °C in Cl_2CDCl_2.

(18) The structures were optimized by the DFT method at the level of B3LYP/6–311G(d,p).

In the optimized structure of 10, the P-phenyl ring is vertical to the P–S axis. However, the difference in energy between the optimized structure and the structure in which the P-phenyl ring is rotated by 90 degrees (i.e., the P-phenyl ring is parallel to the P–S axis) is very small (1.87 kcal mol$^{-1}$). Thus, the binding for the P-phenyl ring rotation is considered to be very weak.

(19) It has been reported that substitution of an NH unit of 8b by a PH unit does not distort the carbon skeleton of the porphyrin ring. See, ref. 6.


(21) In the phosphole ring of 10, the phosphorus atom is slightly deviated from the 1,3-diene unit with a dihedral angle of 2.4°.

(22) NICS: Nuclear Independent Chemical Shift. The NICS values were calculated at the
level of GIAO-RHF/6–31+G(d) at the optimized geometries. For details, see Supporting Information.

(23) For the NICS values of porphyrins, see ref. 18d. See, also: Furuta, H.; Maeda, H.; Osuka, A. J. Org. Chem. 2001, 66, 8563.


(25) The second oxidation potential of 6 was determined to be 0.97 V (vs. Fc/Fc+) by the DPV measurement.

(26) The HOMO–LUMO energy gaps (eV) of 8b, 9b, and 10 were computed by the DFT method to be 2.94, 2.83, and 2.59, respectively.


Chapter 4

Synthesis and Reactions of Phosphaporphyrins: Reconstruction of \( \pi \)-Skeleton Triggered by Oxygenation of a Core-Phosphorus Atom

Abstract: The synthesis, structures, optical and redox properties, and reactivity of phosphaporphyrins are described. The 21-phosphaporphyrin (P,N\(_3\)-porphyrin) and 23-phospha-21-thiaporphyrin (P,S,N\(_2\)-porphyrin) were prepared via acid-promoted dehydrative condensation between a phosphatripyrrane and the corresponding 2,5-bis[hydroxy(phenyl)methyl]heteroles followed by 2,3-dichloro-5,6-dicyanobenzoquinone oxidation. Experimental (NMR, UV-vis, and X-ray analyses) and theoretical (DFT calculations) results suggest that the 18\( \pi \) aromatic character inherent in regular N\(_4\)-porphyrins was maintained in these phosphaporphyrins. X-ray crystallography revealed a slightly distorted 18\( \pi \) aromatic ring for the P,N\(_3\)-porphyrin with the phosphole and three pyrrole rings tilted from the 24-atoms mean plane by 9.6° and 3.8−15.4°, respectively. DFT calculations on model compounds showed that the P,X,N\(_2\)-porphyrins (X = N, S) possess considerably small HOMO−LUMO gaps as compared with N\(_4\) and S,N\(_3\)-porphyrins, which is reflected in the red-shifted absorptions, low oxidation potentials, and high reduction potentials of the phosphaporphyrins. The P-oxygenation of the P,X,N\(_2\)-porphyrins with H\(_2\)O\(_2\) has been found to lead to the formation of different types of products. The 18\( \pi \) P,N\(_3\)-porphyrin was transformed into the 22\( \pi \) aromatic P(O),N\(_3\)-porphyrin accompanied by the \( \pi \) extension at the peripheral C\(_3\) bridge, whereas the 18\( \pi \) P,S,N\(_2\)-porphyrin was converted to the isophlorin-type 20\( \pi \) antiaromatic P(O),S,N\(_2\)-porphyrin. In both of the reactions, simple P-oxygenated 18\( \pi \) P(O),X,N\(_2\)-porphyrins were formed as the initial products, which were subsequently transformed into the 22\( \pi \) or 20\( \pi \) porphyrins. The two reaction courses from 18\( \pi \) to 20\( \pi \)/22\( \pi \) are apparently determined by the combination of the core heteroatoms (i.e. P,N\(_3\) or P,S,N\(_2\)) and the structure of the peripherally fused carbocycles. The present results demonstrate that the incorporation of a phosphorus atom into the core is not only a highly promising way to modify the fundamental properties of the porphyrin 18\( \pi \) system but also a reliable tool to stabilize uncommon 22\( \pi \) and 20\( \pi \) systems through the chemical modifications at the core-phosphorus atom.
1. Introduction

Porphyrrins are one of the most widely studied macrocyclic heterocycles because of their important roles in biological and materials chemistry. To perturb optical, electrochemical, and coordinating properties of porphyrrins, chemical modifications of the macrocyclic platform have generally been employed. Core-modification, namely the replacement of one or more core-nitrogen atoms by other heteroatoms or carbon, is a highly promising chemical modification methodology.\textsuperscript{1-5} Recent extensive studies on the core-modified porphyrrins have disclosed that the electronic structures of their $\pi$ circuits differ significantly from those of regular porphyrrins (hereafter denoted as the N$_4$-porphyrrins). For instance, Soret and Q bands of 21-chalcogena- and 21,23-dichalcogenaporphyrins are red-shifted from those of N$_4$-porphyrrins, and the bathochromic shifts of these heteroporphyrins are strongly dependent on the relevant core-chalcogens (O, S, Se, Te).\textsuperscript{2f} The incorporation of four chalcogens (O, S) at the core has been successfully utilized to stabilize planar 20$\pi$ systems (isophlorin skeletons) that are difficult to construct with N$_4$-porphyrrins.\textsuperscript{6} An additional promising aspect of the core-modified porphyrrins is the unique reactivity endowed by the core elements. For example, the 21-telluraporphyrins undergo the Te–O exchange reaction\textsuperscript{7} or oxidative chlorination\textsuperscript{8} at the tellurium center via Te-oxygenation, and carbaporphyrinoids, typically in their metal complex forms, exhibit a variety of reactivities such as alkylation,\textsuperscript{9} cyanization,\textsuperscript{10} diphenylphosphanylation,\textsuperscript{11} halogenation,\textsuperscript{12} nitration,\textsuperscript{12} oxygenation,\textsuperscript{13} pyridination,\textsuperscript{14} and internal fusion.\textsuperscript{12} Despite these encouraging findings on the core-modified porphyrrins, the types of elements introduced into the core have been limited to carbon, silicon,\textsuperscript{15} and chalcogens. Under these circumstances, we were interested in the chemistry of phosphaporphyrin, a heavy analog of the parent N$_4$-porphyrrin, because the phosphole subunit provides unprecedented optical, electrochemical, and coordinating properties to the porphyrrin platform.

In sharp contrast to pyrrole, phosphole forms a trigonal pyramid structure at the phosphorus center and behaves basically as a neutral P ligand and as a highly conjugative cis-1,3-dienic $\pi$ system.\textsuperscript{16} Such structural and electronic properties of phosphole are beneficial for the construction of an unprecedented class of core-modified porphyrrins. Most importantly, the tricoordinate ($\sigma^3$) phosphorus center can be converted to various tetracoordinate ($\sigma^4$) forms by simple chemical modification such as P-oxygenation (to $\sigma^4$-P=O), P-thioxygenation (to $\sigma^4$-P=S), and P-metal coordination (to $\sigma^4$-P–metal) with its active lone electron pair.\textsuperscript{17} This implies that the electronic structure of a phosphaporphyrin $\pi$ system is readily tunable by the introduction of P substituents.
In 2003, Delaere and Nguyen predicted the electronic structures and optical properties of unsubstituted 21-phospha- and 21,23-diphosphaporphyrins based on density functional theory (DFT) calculations and concluded that these phosphaporphyrins would exhibit reasonable aromaticity. However, the synthesis of phosphaporphyrins has not been reported until recently, presumably due to the lack of their potential precursors. The reactivity of phosphole is well known to arise from the low aromaticity of the five-membered ring and the high nucleophility of the $\sigma^3$-phosphorus atom. Accordingly, conventional methods (Friedel-Crafts alkylation and direct lithiation) that have been widely used for the $\alpha$-functionalization of pyrrole and thiophene are not applicable to phosphole. Recently, Mathey’s group and our group independently reported convenient methods for the synthesis of 2,5-difunctionalized phospholes based on sequential [1,5]-sigmatropic shifts in P-functionalized phospholes and Ti$^{II}$-mediated cyclization of difunctionalized diynes, respectively. 2,5-Bis[hydroxymethyl]-type phospholes, suitable starting materials of phosphaporphyrins, are now readily available in gram scale.

In 2007, Mathey and co-workers reported an attempt to prepare a phosphaporphyrin via acid-promoted [3+1] condensation of a 2,5-bis[phenyl(hydroxy)methyl]phosphole, where the phosphorus atom was masked as the $\sigma^4$-P=S form, with a tripyrrane. However, this approach resulted in the formation of a small amount of “P-confused” carbaporphyrinoid (Chart 1).

In 2006, the author reported the first synthesis of a phosphaporphyrin of the P,S,N$_2$-type. This synthesis was achieved by using a different [3+1] condensation approach starting from a phosphatripyrrane (vide infra), and this method was later applied to the synthesis of a P,N$_2$-type phosphaporphyrin. With these encouraging results available, the author aimed to uncover the structures, aromaticity, and optical/electrochemical properties of phosphaporphyrins by comparison with those of known porphyrins. The author also aimed to clarify the reactivities of phosphaporphyrins, especially those at the core-phosphorus atom, as well as the fundamental properties of the resulting P-functionalized derivatives. The author envisioned that these comparative studies would highlight the characteristics of phosphorus in porphyrin chemistry and heteroatom chemistry.

In this Chapter, full details of the synthesis and reactions of 21-phosphaporphyrin (P,N$_2$-porphyrin) 1N and 23-phospha-21-thiaporphyrin (P,S,N$_2$-porphyrin) 1S (Chart 2) are described. The structures, aromaticity, and optical/electrochemical properties of 1N, 1S, and their P-functionalized derivatives are discussed in detail. The replacement of the N–H unit of the N$_4$-porphyrin with the P-Ph unit induced dramatic alternations in the fundamental properties and reactivity of the porphyrin ring. In particular, these 18$\pi$ phosphaporphyrins underwent unique $\pi$-reconstructions triggered by P-oxygenation, resulting in the formation of...
$22\pi$ or $20\pi$ systems depending on the combination of the core heteroatoms and the structure of the peripherally fused carbocycles.$^{25}$

**Chart 1.** (a) 21-Phospha- and 21,23-Diphosphaporphyrins Calculated by Delaere and Nguyen. (b) Mathey’s P-Confused Carbaporphyrinoid

![Chart 1](image)

**Chart 2.** Phosphaporphyrins 1N and 1S, and Thiaporphyrins 2N and 2S

![Chart 2](image)

2. Results and Discussion

2.1. Synthesis and Characterization of Phosphaporphyrins

2.1.1. Synthesis

Scheme 1 illustrates the synthesis of 21-phosphaporphyrin 1N and 23-phospha-21-thiaporphyrin 1S. The BF$_3$-promoted dehydrative condensation of P-masked phosphatripyrrane $^{33a}$ with 2,5-bis[hydroxy(phenyl)methyl]-pyrrole $^{4N}$,$^{26}$-thiophene $^{4S}$,$^{2b}$ or -furan $^{4O}$ afforded P-masked P,X,N$_2$-porphyrinogens 5X–S (X = N, S, O) in 9–43% yields as a mixture of two or three diastereomers. Desulfurization of 5X–S with excess P(NMe$_2$)$_3$ in refluxing toluene produced the corresponding σ$_3$-P,X,N$_2$-porphyrinogens 5X (X = N, S, O) in good yields. Compounds 5X were subsequently treated with 3.3 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature. In the DDQ oxidation of 5N, two major products were obtained. Flash column chromatography of the crude reaction
mixture on alumina (CH$_2$Cl$_2$/hexane = 1/1) followed by recrystallization from MeOH gave a reddish purple solid ($R_f = 0.9$) and a dark-purple solid ($R_f = 0.5$) in 17 and 8% yields, respectively. Based on the spectroscopic and crystallographic analyses (vide infra), the less polar compound was characterized as the expected 21-phosphaporphyrin 1N, whereas the more polar compound was found to be the P-oxo-type phosphaporphyrin 6-O. Under similar conditions, 5S reacted with DDQ to afford two major products. Flash column chromatography of the crude reaction mixture on alumina (CH$_2$Cl$_2$/hexane = 1/1) followed by recrystallization from MeOH gave reddish purple ($R_f = 0.7$) and dark-green ($R_f = 0.9$) solids in 5 and 1% yields, respectively. In this case, the more polar compound was found to be the expected 23-phospha-21-thiaporphyrin 1S and the less polar compound was the P-oxo derivative 7-O. Although the isolated yields of the products were low, the formation of 1X, 6-O, and 7-O was quite reproducible. Unfortunately, all attempts to prepare 21-phospha-23-oxaporphyrin 1O from 5O were unsuccessful; DDQ oxidation of 5O resulted in the formation of a complex mixture. Another P,N$_2$-porphyrin 1N', which bears a peripheral C$_3$-bridge at the phosphone ring, was also prepared from the corresponding precursors 3$'$ and 4N (Scheme 2). In this case, the P-oxo byproducts like 6-O were not obtained. All the phosphaporphyrins 1N,

Scheme 1. Synthesis of P,X,N$_2$-Porphyrins
**Scheme 2. Synthesis of P,N₃-Porphyrin Bearing a Peripheral C₄-Bridge**

1N' and 1S were observed to be stable in the solid state but slowly decomposed in solution under aerobic conditions and in room light. We assume that 6–O and 7–O were mainly formed by the P-oxidation of the corresponding P,X,N₂-porphyrins 1N and 1S during the reaction conditions employed. The details of these reactions will be discussed later.

To compare core-modification effects on the fundamental properties of porphyrin \( \pi \) systems, 21-thia- and 21,23-dithiaporphyrins, 2N and 2S, were newly prepared by a similar [3+1] type condensation of thiatripyrrane 2S with 4X (X = N, S) followed by DDQ oxidation. In the synthesis of 2X, no S-oxo (sulfoxide or sulfone) type byproducts were produced.

### 2.1.2. Characterization

The diagnostic spectral features of P,X,N₂-porphyrins 1N, 1N', and 1S are as follows. In the high-resolution FAB-MS (HR-FAB-MS) spectra, the parent ion peaks (M⁺) were observed at \( m/z \) 595.2182 for 1N (calcd for C₄₁H₃₀N₃P: 595.2177), 609.2335 for 1N' (calcd for C₄₂H₃₂N₃P: 609.2334), and 612.1788 for 1S (calcd for C₄₁H₂₉N₂PS: 612.1789). In the \(^1\)H NMR spectrum of 1N, meso and pyrrole-\( \beta \) protons appear at \( \delta \) 10.18 (d, \( ^3J_{PH} = 16.1 \) Hz) and 8.35–8.67 ppm, respectively, whereas the NH and P-phenyl protons appeared at \( \delta \) –0.59 and 2.43–5.68 ppm, respectively (Figure 1a; Table S1 in Supporting Information). It is apparent that the significant downfield and upfield positions of these peaks stem from ring current effects of the porphyrin 18\( \pi \)-electron circuit. In the \(^1\)H NMR spectra of 1N' and 1S (Figure 1b), similar diatropic ring current effects were observed. To evaluate and compare the ring current effects quantitatively, the difference in chemical shifts (\( \Delta \delta \)) of the heterole-\( \beta \) and P-phenyl protons between 1X (X = N, S) and calixphyrins 8X (X = N, S) was used as an index. As the \( \pi \) circuits in 8X are interrupted at the sp³-hybridized meso carbons, the positive/negative signs and the absolute values of \( \Delta \delta \) (Table 1) represent the diatropicity (paratropicity) and the degree of the aromaticity (antiaromaticity) of the \( \pi \)-circuits of 1X. The
downfield shifts of the heterole-β protons observed for the S,X,N₂-porphyrins 2X (X = N, S) versus the S,X,N₂-calixphyrins 9X (X = N, S)²⁸ are also summarized in Table 1.

The data for the heterole-β protons indicate that the ring current effects increase in the order: S₂,N₂-porphyrin > P,S,N₂-porphyrin ≈ S,N₃-porphyrin > P,N₃-porphyrin. The diminished ring current effects in the P,X,N₂-porphyrins as compared with the corresponding S,X,N₂-porphyrins may be ascribed to the slightly deviated π-planes in the phosphaporphyrins (vide infra). The upfield shifts of the P-phenyl protons of 1X versus 8X increase in the order: ortho > meta > para, implying that the P-phenyl group in 1X stands above the porphyrin π-plane. As summarized in Table 2, the ring current effects also emerged as upfield positions of the ³¹P peaks of 1N (δ –5.2 ppm), 1N’ (δ –32.6 ppm), and 1S (δ 18.6 ppm) relative to the ³¹P peaks of the respective precursors, 5N (δ 30.4–32.7 ppm), 5N’ (δ 2.6–4.1 ppm), and 5S (δ 32.7–33.5 ppm).²⁹ The structural and spectral properties of the P-oxo porphyrins 6–O and

![Figure 1](image-url)  
*Figure 1.* ¹H NMR spectra of phosphaporphyrins (a) 1N, (b) 1S, (c) 6-O, (d) 6-S, and (e) 7-O in CDCl₃. Asterisks (*) indicate the peaks of residual solvents.
7–O will be summarized later.

The structure of 1N was unambiguously determined by X-ray crystallography. The selected bond lengths and distances are summarized in Table 3. The porphyrin ring in 1N is slightly distorted, wherein the phosphole and three pyrrole rings are tilted from the 24-atom

\[ \text{Chart 3. P,X,Nc-Calixphyrins 8X, 8X–S, and 14 and S,X,Nc-Calixphyrins 9X (X = N, S)} \]

\[ 8N (X = NH, E = lone par) \]
\[ 8S (X = S, E = lone par) \]
\[ 8N–S (X = NH, E = S) \]
\[ 8S–S (X = S, E = S) \]

\[ \text{Table 1. Differences in the } ^1\text{H NMR Chemical Shifts (Δδ/ppm) between Porphyrins and Calixphyrins}^{a,b} \]

\[ \begin{array}{c|c|c}
\text{porphyrin/calixphyrin} & \text{heterole-β (β₁, β₂, β₃)} & \text{P-Ph (ortho, meta, para)} \\
\hline
1N/8N & +2.08, +1.79, +2.70 & −5.1, −2.0, −1.6 \\
1N’/8N & +1.93, +1.65, +2.53 & −5.0, −2.1, −2.0 \\
1S/8S & +2.29, +2.07, +2.62 & −5.3, −2.0, −1.6 \\
2N/9N & +2.29, +1.97, +2.89 & – \\
2S/9S & +2.35, +2.13, +3.10 & – \\
6–O/8N–S & +1.56, +1.48, +1.98 & −2.5, −0.9, −0.6 \\
6–S/8N–S & +0.90, +0.97, +1.42 & +0.1, +0.1, +0.1 \\
7–O/14 & −0.35, −0.97, −0.76 & +0.7, +0.5, +0.6 \\
\end{array} \]

\[ ^a \text{Measured in CDCl}_3. \quad ^b \text{Chemical shifts for the calixphyrin references were reported in ref. 24b,c (for 8X, 8X–S and 14) and ref. 28 (for 9X). Δδ = δ (porphyrin) – δ (calixphyrin). The plus sign indicates a downfield shift and the minus sign indicates an upfield shift.} \]
Table 2. $^1$H and $^{31}$P Chemical Shifts of Porphyrins and Porphyrinogens in CDCl$_3$

<table>
<thead>
<tr>
<th>porphyrins and porphyrinogens</th>
<th>δ$_i$/ppm</th>
<th>δ$_i$/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrrole-β</td>
<td>NH</td>
<td>P-Ph</td>
</tr>
<tr>
<td>1N</td>
<td>8.35–8.67</td>
<td>−0.59</td>
</tr>
<tr>
<td>1N'</td>
<td>8.21–8.52</td>
<td>−0.05</td>
</tr>
<tr>
<td>1S</td>
<td>8.67–8.93</td>
<td></td>
</tr>
<tr>
<td>6–O</td>
<td>8.02–8.19</td>
<td>5.40</td>
</tr>
<tr>
<td>6–S</td>
<td>7.38–7.53</td>
<td>4.35</td>
</tr>
<tr>
<td>7–O</td>
<td>4.99–5.68</td>
<td>18.0</td>
</tr>
<tr>
<td>2N</td>
<td>8.68–9.00</td>
<td>−2.82</td>
</tr>
<tr>
<td>2S</td>
<td>8.80–9.05</td>
<td></td>
</tr>
<tr>
<td>5N</td>
<td>5.65–6.00</td>
<td>7.79–8.35</td>
</tr>
<tr>
<td>5N'</td>
<td>5.63–6.04</td>
<td>7.80–8.32</td>
</tr>
<tr>
<td>5S</td>
<td>5.60–5.86</td>
<td>8.20–8.35</td>
</tr>
<tr>
<td>5N–O</td>
<td>5.46–6.19</td>
<td>7.89–10.40</td>
</tr>
<tr>
<td>5N–S</td>
<td>5.41–6.16</td>
<td>7.67–10.10</td>
</tr>
<tr>
<td>5S–O</td>
<td>5.34–5.89</td>
<td>10.11–10.15</td>
</tr>
</tbody>
</table>

mean plane with dihedral angles of 9.6 and 3.8–15.4°, respectively. The differences between the contiguous carbon(meso)–carbon(α) bond lengths (i.e. the absolute values of d–c and k–j in Table 3) are notably suppressed (0.03–0.04 Å), which indicates the efficient π-electron delocalization through the 18π circuit of 1N. In this regard, 1N possesses aromatic character in terms of the geometrical criterion. The phosphorus center adopts a trigonal pyramidal geometry with C–P–C bond angles of 91.2(13)–101.99(12)° ($\Sigma_{C-P-C} = 293.79°$), and the P-phenyl group is located above the porphyrin π-plane as suggested by the NMR observations. These structural features imply that the porphyrin π-circuit does not involve the lone electron pair on the phosphorus. The core of 1N provides a trapezoid cavity with $\text{N}_22–\text{N}_24$ and $\text{P}–\text{N}_23$ distances of 4.56 and 3.45 Å, respectively.

2.2. Optical and Electrochemical Properties

2.2.1. Optical Property

The UV-vis absorption spectra of P,X,N$_2$-porphyrins 1X and S,X,N$_2$-porphyrins 2X (X = N, S) in CH$_2$Cl$_2$ are displayed in Figure 2. The Soret bands of 1N and 1S appeared at $\lambda_{ab}$ 431
and 440 nm (Table 4), respectively, which are red-shifted compared with those of 2N (418 nm), 2S (426 nm), and 5,10,15,20-tetraphenylporphyrin (H$_2$TPP: 10) (411 nm)$^{29,31}$ The longest Q-type transitions of 1N ($\lambda_{ab}$ 698 nm) and 1S ($\lambda_{ab}$ 718 nm) were also observed at longer wavelengths relative to those of 2N ($\lambda_{ab}$ 660 nm), 2S ($\lambda_{ab}$ 682 nm), and 10 ($\lambda_{ab}$ 646 nm). Thus,

**Table 3.** Selected Bond Lengths$^a$ and Distances (Å) in the Crystal Structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\pi$ circuit</th>
<th>$6\cdots O$</th>
<th>$7\cdots O$</th>
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</thead>
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<td></td>
<td>$E, X, N$</td>
<td>$1N$</td>
<td>$6\cdots O$</td>
</tr>
<tr>
<td>$a$</td>
<td>lone pair, NH, N</td>
<td>1.38</td>
<td>1.48</td>
</tr>
<tr>
<td>$b$ ($b'$)</td>
<td>1.42</td>
<td>1.42</td>
<td>1.48</td>
</tr>
<tr>
<td>$c$ ($c'$)</td>
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<td>1.37</td>
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<tr>
<td>$d$ ($d'$)</td>
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<td>1.40</td>
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<td>1.39</td>
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<td>1.38</td>
<td>1.38</td>
</tr>
<tr>
<td>$i$ ($i'$)</td>
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<td>1.37</td>
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<td>$j$ ($j'$)</td>
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<td>$k$ ($k'$)</td>
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<td>$l$ ($l'$)</td>
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<td>$m$</td>
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<td>$n$ ($n'$)</td>
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<td>$p$ ($p'$)</td>
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<tr>
<td>N$_{24}$</td>
<td>4.56</td>
<td>4.47</td>
<td>4.69</td>
</tr>
<tr>
<td>P•••X</td>
<td>3.45</td>
<td>4.37</td>
<td>4.33</td>
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<tr>
<td>P=O•••N$_{24}$</td>
<td>–</td>
<td>2.65</td>
<td>2.73</td>
</tr>
</tbody>
</table>

$^a$ Average values between $y$ and $y'$ ($y$ denotes $b$–$l$ and $n$–$p$). $^b$ Average values.
the replacement of an N-H unit with a P-Ph unit shifts the Soret and Q bands to the longer wavelengths more strongly than does the replacement with a sulfur atom. The UV-vis absorption spectrum of 1N' (Soret: $\lambda_{ab}$ 431 nm, Q: $\lambda_{ab}$ 692 nm) was quite similar to the spectrum recorded on 1N. The S,X,N$_2$-porphyrins 2X were found to be fluorescent, whereas the P,X,N$_2$-porphyrins 1X were observed to be non-fluorescent.

**Table 4. Absorption and Fluorescence Properties in CH$_2$Cl$_2$**

| Compound | $\lambda_{ab}$/nm ($\varepsilon$/10$^3$ M$^{-1}$cm$^{-1}$) | $\lambda_{em}$/nm$^a$ ($\Phi_F$/%)
| Soret band | Q band$^b$ | $\lambda_{em}$/nm$^a$ ($\Phi_F$/%)
|-----------|-------------|-------------
| 1N        | 431 (177)   | 698 (3.1)   | n.f.$^c$
| 1N'       | 431 (172)   | 692 (3.2)   | n.f.$^c$
| 1S        | 440 (164)   | 718 (3.1)   | n.f.$^c$
| 2N        | 418 (218)   | 660 (3.2)   | 665, 735 (0.94)$^d$
| 2S        | 426 (188)   | 682 (3.4)   | 685, 760 (0.46)$^e$
| 6–O       | 422 (42.1), 494 (77.2) | 964 (2.5) | –
| 6–S       | 424 (25.7), 485 (29.4) | 750–1200 (sh) | –
| 7–O       | 394 (66.1)  | 1130 (0.8)  | –

$^a$ Excited at 506 nm for 2N and 2S. $^b$ The longest absorption maxima. $^c$ Non-fluorescent. $^d$ Fluorescence quantum yield relative to $\Phi_F$ of 2S. $^e$ Absolute fluorescence quantum yield determined by a calibrated integrating sphere system.

**Table 5. Redox Potentials vs Fc/Fc$^+$ (V) in CH$_2$Cl$_2$**

| Compound | oxidation | reduction | $\Delta E$ $^b$
|-----------|-----------|-----------|-----------
|           | $E_{ox,1}$ | $E_{ox,2}$ | $E_{red,1}$ | $E_{red,2}$ |
| 1N        | +0.38$^c$  | -         | −1.51      | −1.74      | 1.89       |
| 1N'       | +0.41$^c$  | -         | −1.52      | −1.72      | 1.93       |
| 1S        | +0.45$^c$  | +0.97$^c$ | −1.36      | −1.56      | 1.81       |
| 2N        | +0.62$^c$  | +1.11$^c$ | −1.56      | −1.92      | 2.18       |
| 2S        | +0.70$^c$  | +1.20$^c$ | −1.43      | −1.77      | 2.13       |
| 6–O       | +0.10$^c$  | +0.44$^c$ | −1.21      | −1.61      | 1.31       |
| 6–S       | +0.21$^c$  | -         | −1.13      | −1.56$^c$  | 1.34       |
| 7–O       | −0.29      | −0.02     | −1.92$^c$  | −2.08$^c$  | 1.63       |

$^a$ 0.1 M nBu$_4$NPF$_6$, Ag$^+/Ag$ (0.01 M AgNO$_3$). Scan rate 20 mV s$^{-1}$. $^b$ $\Delta E = E_{ox,1} - E_{red,1}$.

Determined by DPV.
Figure 2. UV-vis absorption spectra of (a) 1N (red) and 2N (black), and (b) 1S (red) and 2S (black) in CH₂Cl₂.

2.2.2. Electrochemical Property

Redox potentials of 1X were measured by cyclic voltammetry (CV) and/or differential pulse voltammetry (DPV), and are compared with the potentials of 2X and 10 (Figures 3 and 4 and Table 5). The electrochemical oxidation processes of 1N and 1S were found to be irreversible, and the first oxidation potentials (E_{ox,1}) of 1N and 1S, determined by DPV, were +0.38 and +0.45 V (vs Fc/Fc⁺), respectively, both of which are more cathodic than E_{ox,1} of 2N (+0.62 V) and 2S (+0.70 V). On the other hand, the electrochemical reduction of 1N and 1S occurred reversibly or quasi-reversibly, and the first reduction potentials (E_{red,1}) of 1N and 1S were −1.51 and −1.36 V, respectively, which are more anodic than those of 2N (−1.56

Figure 3. Cyclic voltammograms of 1N (red, upper), 2N (black, upper), 1S (red, lower) and 2S (black, lower) in CH₂Cl₂; 0.1 M nBu₄NPF₆, Ag⁺/Ag (0.01 M AgNO₃). Scan rate 20 mV s⁻¹. Asterisk (*) indicates ferrocene/ferrocnium couple.
V) and 2S (−1.43 V). As a result, the differences in the redox potentials (ΔE: Ɛ_{ox,i} - Ɛ_{red,i}) of 1N (1.89 V) and 1S (1.81 V) are significantly smaller than those of 2N (2.18 V) and 2S (2.13 V). The redox behavior of 1N’ (Ɛ_{ox,i}: +0.41 V, Ɛ_{red,i}: −1.52 V, ΔE: 1.93 V) is quite similar to that of 1N. All of the P,X,N-porphyrins 1X showed more negative Ɛ_{ox,i} and more positive Ɛ_{red,i} than H_{2}TPP 10 (Ɛ_{ox,i}: +0.58 V, Ɛ_{red,i}: −1.73 V, ΔE: 2.31 V).

Figure 4. First oxidation (Ɛ_{ox,i}) and reduction (Ɛ_{red,i}) potentials for (a) 1N, (b) 1N’, (c) 1S, (d) 2N, (e) 2S, (f) 6-O, (g) 6-S, and (h) 7-O.

2.3. DFT Calculations

Chart 4. Model Compounds

To gain more insight into the structure, aromaticity, and optical and electrochemical properties of P,X,N_{2}-porphyrins 1X and S,X,N_{2}-porphyrins 2X, DFT calculations on a series of model compounds 1N-m, 1S-m, 1N(H)-m, 2N-m, 10-m, and 11-m (Chart 4) at the B3LYP/6-311G(d,p) level were carried out. The optimized structures are shown in Figure 5,
and selected bond lengths and distances are summarized in Table 6. The differences between the contiguous carbon(meso)–carbon(α) bond lengths (i.e. the absolute values of $d-c$ and $k-j$ in Table 6) of $1N-m$ (0.01–0.03 Å) and $1S-m$ (0.01–0.02 Å) are comparable to those of $10-m$ (0.01 Å). In the structures of P,X,N$_2$-models $1X-m$, each phosphorus atom forms a pyramidal geometry ($\Sigma_{C,P,C} = 299.5^\circ$ for both $1N-m$ and $1S-m$), and the P-phenyl group is located above the macrocyclic plane (Figures 5a and 5b). These theoretical results are in good agreement with the experimental results (NMR and X-ray) observed for $1N$ and $1S$. In contrast to the completely planar S,N$_3$-model $2N-m$, P,N$_3$-models $1N-m$ and $1N(H)-m$ possess slightly distorted π planes. The porphyrin π plane of $1S-m$ deviates more than that of $1N-m$, probably due to the electrostatic repulsion between the two relatively large heteroatoms, P and S, making a dish-like macrocyclic platform with a slightly deeper bottom. The comparison of the optimized structure of the P-phenyl model $1N-m$ with that of the P-H model $1N(H)-m$ confirmed that the phenyl group attached to the phosphorus causes a slightly larger distortion of the macrocyclic framework (Figures 5a versus 5c; dihedral angles between the phosphole ring and the 24-atom mean plane for $1N-m$ and $1N(H)-m$ are 12.1 and 2.7°, respectively). However, the deviation caused by the introduction of the phenyl group is considerably smaller than that observed for N$_4$-porphyrins; the π planes of the N-alkyl and -aryl porphyrins have been reported to deviate substantially from planarity.$^{33}$ The N-phenyl pyrrole ring of $11-m$ is tilted from the 24-atom mean plane with a dihedral angle of 34.9°, and the phenyl-bound nitrogen atom takes a flattened pyramidal geometry with the sum of the bond angles of $\Sigma_{C,N,C} = 342.9^\circ$ (Figure 5f). This is because the core nitrogen atom in $11-m$ aptly retains the sp$^3$ hybridization, even when it is phenylated.

![Figure 5.](image)

Figure 5. Top (upper) and side (lower) views of the optimized structures for (a) $1N-m$, (b) $1S-m$, (c) $1N(H)-m$, (d) $2N-m$, (e) $10-m$, and (f) $11-m$. The C, H, N, P and S atoms are indicated as grey, light blue, blue, orange, and yellow balls, respectively.
Table 6. Selected Bond Lengths and Distances (Å), and Angles (deg) in Optimized Structures

![Diagram]

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<th>6–S-m</th>
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\(^a\) LP = lone pair. \(^b\) Distance between the phosphorus atom and the porphyrin mean plane. \(^c\) Slant of the P-R bond axis against the porphyrin mean plane (deg).
Table 6. Selected Bond Lengths, Distances (Å), and Angles (deg) in Optimized Structures (continued)

![Diagram](image)

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*Distance between the 23-heteroatom X (X = N, P) and the porphyrin mean plane. $^b$ Slant of the X-R bond axis (X = N, P) against the porphyrin mean plane (deg).
Nucleus-independent chemical shifts (NICS) have been used as indices for evaluating the aromaticity of the porphyrin rings.\(^{34}\) The NICS values at the center of the four heteroatoms of 1\textbf{N}-\textit{m} and 1\textbf{S}-\textit{m} were determined as \(-13.8\) and \(-15.7\) ppm, respectively (Table 7). The absolute NICS values of 1\textbf{N}-\textit{m} and 1\textbf{S}-\textit{m} are somewhat smaller than those of the N\(_4\)-porphyrin 10\textbf{-m} (\(-16.5\) ppm) and S,N\(_2\)-porphyrin 2\textbf{N}-\textit{m} (\(-16.2\) ppm), but are sufficiently large enough to maintain aromaticity. On the basis of these theoretical results, together with the above-mentioned experimental data, we can conclude that the inherent aromatic character is maintained in the P,X,N\(_2\)-porphyrin 18\(\pi\) systems.

The frontier orbitals of the model compounds are depicted in Figure 6. The replacement of a core-nitrogen atom of porphyrin with a chalcogen atom is well known to stabilize LUMOs more largely than HOMOs. This is commonly explained by the inductive or electron-withdrawing effect that the heteroarom has on the frontier orbitals.\(^{11,5}\) Indeed, in our calculations, HOMO and one of the nearly degenerated LUMOs of the S,N\(_2\)-model 2\textbf{N}-\textit{m} are stabilized by 0.10 and 0.18 eV, respectively, relative to those of the N\(_4\)-model 10\textbf{-m}. As a result, the HOMO–LUMO gap of 2\textbf{N}-\textit{m} becomes narrower by 0.08 eV than that of 10\textbf{-m}.

\textbf{Table 7.} NICS Values for Model Compounds

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</tr>
<tr>
<td>1\textbf{S}-\textit{m} (X = PPh, Y = S)</td>
<td>(-15.7^a)</td>
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<tr>
<td>2\textbf{N}-\textit{m} (X = S, Y = NH)</td>
<td>(-16.2^a)</td>
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<tr>
<td>10\textbf{-m} (X,Y = NH)</td>
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<td>\textit{Type C} (20(\pi))</td>
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<tr>
<td>7\textbf{-O}-\textit{m}</td>
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\(^{a}\)Calculated at the center of the four heteroatoms. \(^{b}\)Calculated at the center of the two facing nitrogen atoms.
DFT calculations on the P–H model 1N(H)-m \textsuperscript{12} showed that the replacement of an N–H group with a P–H group stabilizes the HOMO and LUMO by 0.17 and 0.29 eV, respectively, and the HOMO–LUMO gap of 1N(H)-m becomes narrower by 0.12 eV than that of 10-m. Therefore, the core-modification with phosphorus has more significant impacts on the frontier orbitals than that with sulfur.

Phosphaporphyrins contain three high-energy HOMOs due to the involvement of a lone electron pair and a substituent (Ph, H) at the phosphorus atom. In the P-Ph porphyrin 1N-m, the lone electron pair orbital at the phosphorus effectively mixes into one of the two inherent HOMOs of porphyrin (the one which has large orbital coefficients at the core and meso positions), thus giving rise to significantly destabilized HOMO and HOMO–2 (by 0.17 and 0.33 eV) in comparison with those of 1N(H)-m. Presumably, the σ–π anti-bonding interaction between the P–C(Ph) σ orbital and the porphyrin π orbital in 1N-m leads to the destabilization of these HOMOs. Similar orbital interactions appear in the P,S,N\textsubscript{2}-porphyrin 1S-m. The large contribution of the phosphorus lone pair to the HOMO explains the unique
reactivity of $\text{1X}$ (vide infra). As seen in Figure 6f, the HOMOs of $\text{11-m}$ are destabilized by 0.07–0.14 eV relative to those of the N–H counterpart $\text{10-m}$, which is attributable to a steric factor rather than an orbital interaction.

Overall, the HOMO levels of $\text{1N-m}$ (−5.42 eV) and $\text{1S-m}$ (−5.39 eV) are comparable to the HOMO level of the N$_r$-porphyrin $\text{10-m}$ (−5.42 eV), whereas the LUMO levels of $\text{1N-m}$ (−2.78 eV) and $\text{1S-m}$ (−2.90 eV) are largely stabilized by 0.28 and 0.40 eV relative to that of $\text{10-m}$ (−2.50 eV). As a consequence, the HOMO–LUMO gaps of $\text{1N-m}$ (2.64 eV) and $\text{1S-m}$ (2.49 eV) are considerably smaller than the gap calculated for $\text{10-m}$ (2.92 eV). These DFT results are in good agreement with the above-mentioned experimental results in that the core-modification of porphyrin from the N–H unit or the S atom basically narrows the HOMO-LUMO gap.

2.4. P-Functionalized Phosphaporphyrins

2.4.1. Chemical Functionalization of a Core-Phosphorus Atom

The electronic structures of phosphole-containing $\pi$-conjugated systems are well known to be effectively altered by the chemical functionalization of the phosphorus atom.$^{17}$ We anticipated that oxidation of the core phosphorus atom would produce new $\pi$ systems with different electronic structures. Moreover, the formation of byproducts $\text{6–O}$ and $\text{7–O}$ suggested to us that the P-oxygenation pathway would be involved in the synthesis of $\text{1X}$. With these concepts in mind, we examined the reactions of $\text{1N}$, $\text{1N'}$, and $\text{1S}$ with H$_2$O$_2$ (Scheme 3).

Initially, the reaction of the C$_4$-bridge type P,N$_3$-porphyrin $\text{1N'}$ with H$_2$O$_2$ in CDCl$_3$ was monitored by $^1$H NMR spectroscopy at several intervals (Figure 7a). After 5 min, $\text{1N'}$ was consumed completely, and P–oxo P,N$_3$-porphyrin $\text{1N'–O}^{35}$ was formed in 94% NMR yield with a small amount (6%) of its tautomer $\text{12'}$. The structures of $\text{1N'–O}$ and $\text{12'}$ were characterized based only on the NMR spectra because of their instability in solution (For detailed $^1$H NMR peak assignments of the intermediates presented in this section, see Figures A1 and A2 in Appendix). The $^{31}$P resonances of $\text{1N'–O}$ ($\delta_p$ 21.8 ppm) and $\text{12'}$ ($\delta_p$ 39.2 ppm) appeared at the significantly downfield region in the spectra when compared with the $^{31}$P resonance of $\text{1N'}$ ($\delta_p$ −32.6 ppm); supporting the notion that the phosphorus atom was oxygenated. The tautomer $\text{12'}$ shows an asymmetric $^1$H peak pattern with two NH protons ($\delta$ 13.8; 12.4), two meso protons ($\delta$ 5.60, d, $^3J_{P,H} = 25.8$ Hz; $\delta$ 7.12, d, $^3J_{P,H} = 35.6$ Hz), and an olefinic proton of the peripheral cyclohexene ring ($\delta$ 6.09, pseudo t, $J = 4.0$ Hz). Most of
1N’–O was converted into 12’ within 60 min,\textsuperscript{36} whereas 12’ slowly decomposed to afford a complex mixture after 3 h. Next, the reaction of the C₂-bridge type P,N₂-porphyrin 1N with H₂O₂ was monitored (Figure 7b). Within 5 min, 1N (δP -5.2 ppm) was quantitatively converted to P–oxo P,N₂-porphyrin 1N–O (δP 36.4 ppm), which was then tautomerized into 12 (δP 48.2 ppm). The spectral features of 1N–O and 12 are very close to those of 1N’–O and 12’. In contrast to the reaction of 1N’; however, the mixture of 1N–O and 12 was ultimately (after 3 h) transformed into 6–O, which was isolated in 77% yield. Finally, the reaction of the P,S,N₂-porphyrin 1S with H₂O₂ was monitored (Figure 7c). After 10 min, 1S (δP 18.6 ppm) was consumed to generate two types of P–oxo porphyrins 1S–O (δP 43.8 ppm) and 7–O in 76 and 17% NMR yields, respectively. On standing the solution for 48 h, 1S–O decomposed completely, while 7–O was obtained as the sole isolated product in 16% yield. The above results imply that the P-oxidation of 1N and 1S is one of the most plausible pathways leading to 6–O and 7–O in Scheme 1.

*Scheme 3.* Reactions of P,X,N₂-Porphyrins 1N’, 1N and 1S with H₂O₂
Figure 7. $^1$H NMR monitoring experiments of the reactions between P,X,N$_2$-porphyrins (3.3 mmol) and H$_2$O$_2$ (30 wt%, 3.6 mmol) in CDCl$_3$/THF-d$_8$ (total 0.64 mL; v/v = 14/1) with 1,1,2,2-tetrachloroethane as an internal standard. (a) The reaction of 1N' (open red circle); 1N'-O (pink circle), 12' (brown circle). (b) The reaction of 1N (open red circle); 1N-O (pink circle), 12 (brown circle), 6-O (purple circle). (c) The reaction of 1S (open red circle); 1S-O (pink circle), 7-O (green circle). Asterisk (*) indicates the peaks of residual solvents.
**Scheme 4.** DDQ Oxidation of P-Functionalized Porphyrinogens 5N–O, 5N–S, 5S–O, and 5S–S

From the viewpoint of the syntheses of 6–O and 7–O, it seemed convenient to oxidize the macrocyclic rings of 5N–O and 5S–O, which were readily available from the corresponding $\sigma^3$-P.X.N$_2$-porphyrinogens 5X in high yields (for details, see Experimental Section). In this context, the reactions of 5X–O with DDQ were examined (Scheme 4). To understand the substituent effects on the reactivity, DDQ oxidations of 5X–S were also examined. Treatment of the P,N$_2$-porphyrinogens, 5N–O and 5N–S, with DDQ afforded 6–O and 6–S as the sole isolable products in 26 and 17% yields, respectively (Scheme 4). Hence, 5N–O is also likely to be a precursor of 6–O in the DDQ oxidation of 5N depicted in Scheme 1. The overall yield of the conversion from 5N to 6–O via 5N–O (25%) was better than the yield via 1N (13%). The P–thioxo substituent in 5N–S appreciably retarded the efficiency of the ring oxidation; however, the first P=S phosphaporphyrin 6–S could be isolated as a dark brown solid. On the other hand, the DDQ oxidations of 5S–O and 5S–S gave complex mixtures and the expected 20$\pi$ porphyrins 7–O and 7–S were not obtained.37

As discussed below, both of the isolated P-oxo porphyrins 6–O and 7–O no longer possess ordinary 18$\pi$ aromatic structures; the $\pi$ system of 6–O is extended to an unprecedented type of aromatic 22$\pi$ system through the peripherally fused C$_5$-bridge, whereas 7–O possesses an isophlorin-type antiaromatic 20$\pi$ structure. Despite containing the isophlorin-type 20$\pi$ structure, 7–O is stable in air.38 The formation of different types of $\pi$ systems, 6–O and 7–O, can be reasonably explained by considering the following factors; (i) the steric congestion at the core, (ii) the electrostatic and hydrogen-bonding interactions
among the core components, and (iii) the redox properties of the macrocyclic \( \pi \) systems (Scheme 5). Since the P-oxidation increases the steric congestion at the core, factor (i) is basically important for all the reactions in Scheme 3. Consequently, it is likely that factors (ii) and (iii) mainly determine the reaction pathways. In the simple P-oxygenated 18\( \pi \) porphyrins 1N–O and 1S–O, there must be electrostatic repulsion between the P=O moiety and the two adjacent nitrogen lone pairs at the core. By contrast, in 6–O and 7–O, there are two hydrogen bonds between the NH protons and the P=O moiety (vide infra). The reconstruction of the 18\( \pi \) structure of 1X–O into the 22\( \pi \) (6–O) or 20\( \pi \) (7–O) structure arises to apparently relieve the “stress” and gain the attractive hydrogen-bonding interaction at the core. The intermediate 12, in which the \( \pi \) circuit is interrupted at the peripheral five-membered ring, undergoes 2e-oxidation to gain the aromatic stabilization, giving 6–O as the final product.\(^{39}\) In contrast, in the case of 1S–O, the formation of a tautomer like 13 is inhibited probably because such an intermediate is not stabilized sufficiently by one hydrogen-bond at the core (Scheme 3). Instead, the 2e-reduction of 1S–O proceeds rapidly to afford the 20\( \pi \) porphyrin 7–O\(^{40,41}\) and the overall reaction from 1S to 7–O is formally regarded as a hydration. It should be emphasized that the core-phosphorus atom of 1N and 1S acts as a kind of switch, which realizes a dramatic alteration of the \( \pi \)-electronic structure by a simple chemical modification.\(^{42}\)

**Scheme 5.** Reconstruction of \( \pi \) Systems via P-Oxidation

2.4.2. Structures, Aromaticity, and Optical and Electrochemical Properties of P-Functionalized Phosphaporphyrins

Single crystals of 6–O and 7–O were grown from CH\(_2\)Cl\(_2\)--MeOH at room temperature (for 6–O)\(^{23b}\) or from CH\(_2\)Cl\(_2\) at –10 °C (for 7–O). Top and side views of 7–O are depicted in Figures 8, and selected bond lengths and distances of 6–O and 7–O are summarized in Table 3. Unfortunately, we could not obtain high-quality single crystals of 6–S. In the crystal structures of 6–O and 7–O, each core-phosphorus atom adopts a tetrahedral geometry with
C–P–C/C–P–O angles of 94.3(3)–107.5(2)°/108.1(3)–119.09(18)° and 94.3(3)–107.5(2)°/108.1(3)–119.09(18)°, respectively. To avoid the steric congestion at the core, the phosphole rings lean substantially outwards. As a consequence, the phosphorus atom deviates from the 24-atom mean plane by 1.20 Å (for 6–O) and 1.22 Å (for 7–O), and the P–C(Ph) bond axis tilts against the mean plane by 114.5° (for 6–O) and 115.1° (for 7–O). These values are larger than those observed for P,N₄-porphyrin 1N (0.34 Å and 82.5°), indicating that the π circuits in the P–oxo derivatives 6–O and 7–O are distorted considerably as compared with the 18π circuit of 1N. The 22π aromatic character of 6–O is well corroborated by the significantly diminished carbon–carbon bond length alternation through the 22π-circuit including the exocyclic C₃-bridge. The differences between the contiguous carbon( meso)–carbon(α) and carbon(C₃-bridge)–carbon(C₃-bridge) bond lengths of 6–O (i.e. the absolute values of d–c and k–j, and o–o’ in Table 3) are 0.00–0.03 Å and 0.00 Å, respectively. In contrast, notable bond length alternation is observed for 7–O, in which the differences between the contiguous carbon( meso)–carbon(α) bond lengths are 0.07–0.09 Å. This indicates that the aromaticity is lost for the 20π-circuit of 7–O (Table 3). The relatively short P=O•••N₂₂/₂₄ distances (2.65 Å for 6–O and 2.73 Å for 7–O) clearly display the presence of intramolecular hydrogen-bonds between the P–oxo group and the two adjacent NH protons. This interaction is likely to play a crucial role in stabilizing the novel 22π and 20π systems.

To obtain more information on the structures and the aromaticity of 6–O, 6–S, and 7–O, DFT calculations on their model compounds 6–O-m, 6–S-m, and 7–O-m (Chart 4) were performed at the level of B3LYP/6-311G(d,p). The optimized structures of these models are

![Image](image_url)

**Figure 8.** Top (upper) and side (lower) views of 7–O (30% probability ellipsoids). Hydrogen atoms (except for NH) and solvent molecules are omitted for clarity.
depicted in Figure 9, and selected bond lengths, distances, and angles are listed in Table 6. The bond parameters of the optimized structures of 6−O-m and 7−O-m are very close to those of the crystal structures of 6−O and 7−O. As shown in Figure 9, the phosphole ring of 6−S-m is tilted more than the phosphole rings of 6−O-m and 7−O-m to accommodate the bulky P=S moiety in the core.44 The P=S•••N distances (each 3.13 Å) calculated for 6−S-m suggest the presence of intramolecular hydrogen-bonding interaction between the P−thioxo group and the two adjacent NH protons.45

![Figure 9](image)

Figure 9. Top (upper) and side (lower) views of the optimized structures for (a) 6−O-m, (b) 6−S-m, and (c) 7−O-m: gray (C), light blue (H), blue (N), red (O), orange (P), yellow (S).

In the HR-FAB-MS spectra, 6−O, 6−S, and 7−O clearly show parent ion peaks (M+) at m/z 609.1975 (calcd for C41H28N3OP: 609.1975 for 6−O), 625.1742 (calcd for C41H28N3PS: 625.1738 for 6−S), and 630.1895 (calcd for C41H31N2OPS: 630.1895 for 7−O). In the 1H NMR spectrum of 6−O, meso, pyrrole-β, NH, and P-phenyl protons appear at δ 9.21 (d, 3J_P,H = 35.6 Hz), 7.94–8.19, 5.40, and 5.60–6.92 ppm, respectively (Figure 1c). Additionally, the peripheral protons that originate from a C3-bridge of the phosphole backbone are observed at δ 8.16 (d, J = 3.9 Hz, 2H) and 9.06 (dt, J = 3.9 Hz, 5J_P,H = 5.4 Hz, 1H) ppm, indicating that the π-circuit goes through the five-membered fused ring in 6−O. The 31P peak of 6−O appears at δ 28.6 ppm, which is considerably shielded when compared with that of the P-oxo P,N3-porphyrinogen 5N−O (δ 59.2–59.6 ppm, Table 2). These NMR data obviously reflect diatropic ring-current effects induced by the aromatic 22π circuit of 6−O; however, both shielding and deshielding effects are somewhat diminished in comparison with 1N. This reduction in shielding and deshielding is due to the deviated structure of 6−O. The 1H NMR spectrum of 6−S (Figure 1d) is quite different from that of 6−O. The C3-bridge protons appear at δ 3.80 (d, J = 3.4 Hz, 2H) and 5.70 (dt, J = 3.4 Hz, 5J_P,H = 5.4 Hz, 1H) ppm,
respectively, which are significantly upfield-shifted by 4.36 and 3.36 ppm from those of 6–O. In contrast, the P-phenyl protons of 6–S (δ 7.5–8.23 ppm) are downfield-shifted by 0.6–2.63 ppm from those of 6–O. As mentioned above, the phosphole ring of 6–S (6–S–m) is considerably tilted from the mean π plane and the P-Ph moiety leans outwards from the cavity. Due to this large deviation, the C–bridge and P-Ph moieties in 6–S are located in regions where the diatropic ring-current effect is weak. However, the highly distorted 22π circuit of 6–S retains moderate aromaticity; significant upfield shifts (Δδ = 0.84–0.99 ppm) are seen for the pyrrole-β protons of 6–S as compared with those of the corresponding calixphyrin 8N–S24b,c (Table 1). Indeed, the NICS value at the center of the two facing nitrogen atoms of 6–S–m (–8.8) is only slightly positive relative to that of 6–O–m (–9.9) (Table 7).

In contrast to 6–E (E = O, S), 7–O displays weakly paratropic ring current effects in the 1H NMR spectrum (Figure 1e). Specifically, the pyrrole-β and P-phenyl protons of 7–O appear at δ 4.99–5.68 and 7.75–8.64 ppm, respectively, which are slightly upfield shifted (Δδ = −0.35 to −0.97 ppm) or downfield shifted (Δδ = 0.41–0.69 ppm) when compared with the chemical shifts of the protons in the corresponding calixphyrin 1424b,c (Chart 3 and Table 1). Small, positive NICS values (+2.4) at the center of 7–O–m support that 7–O has weakly antiaromatic character in terms of magnetic criterion (Table 7).

In the UV-vis absorption spectra of 6–E (E = O, S), split Soret-like bands (6–O: λab 422 and 494 nm; 6–S: λab 424 and 485 nm) and a remarkably broad, low-energy band reaching into a near-infrared region were observed (Figure 10a and Table 4). The absorption coefficients of 6–S are considerably smaller than that of 6–O. This is presumably due to the structural deviation of 6–S. The UV-vis absorption spectrum of 7–O shows a broad Soret-like band at the high-energy region (λab 394 nm) and no detectable Q bands, which is characteristic of highly ruffled, nonaromatic 4nπ porphyrinoids (Figure 10b).25,46

**Figure 10.** UV-vis absorption spectra of (a) 6–O (reddish-purple) and 6–S (bluish-purple), and (b) 7–O (green) in CH2Cl2. The spectra of corresponding 18π porphyrins 1N and 1S are shown by black line in each spectrum.
The electrochemical oxidation processes of 6−E (E = O, S) were found to be irreversible, whereas the reduction processes were reversible or quasi-reversible (Figure 11). The first oxidation and reduction potentials of 6−O ($E_{\text{ox},1} = +0.10$ V; $E_{\text{red},1} = -1.21$ V, vs Fc/Fc$^+$) and 6−S ($E_{\text{ox},1} = +0.21$ V; $E_{\text{red},1} = -1.13$ V, vs Fc/Fc$^+$) are more cathodic and more anodic as compared with the respective values of 1N (Figure 4). As a result, this yields very small HOMO-LUMO gaps for 6−O ($\Delta E = 1.31$ V) and 6−S ($\Delta E = 1.34$ V) in comparison with 1N ($\Delta E = 1.89$ V). The electrochemical oxidation processes of 7−O occurred reversibly at −0.29 and +0.02 V (vs Fc/Fc$^+$). The first oxidation and reduction potentials of 7−O ($E_{\text{ox},1} = -0.29$ V; $E_{\text{red},1} = -1.92$ V, vs Fc/Fc$^+$) are considerably cathodically shifted when compared with the respective values of 1S (Figure 4), which exhibits the isophlorin character of the π system of 7−O. As a whole, the calculated HOMO and LUMO levels of the model compounds 6−O-m (−4.96 and −3.03 eV), 6−S-m (−5.00 and −3.12 eV), and 7−O-m (−4.47 and −2.41 eV) are in good agreement with the observed redox potentials (Figure 12). It is noteworthy that the HOMO–LUMO gaps of the P-oxidized derivatives 6−O, 6−S, and 7−O are much narrower than those of the 18π σ3-P,X,N2 porphyrins 1X. Most importantly, the optical and electrochemical properties of the P,X,N2-porphyrin π systems are readily tunable by simple P-oxidation reactions.

**Figure 12.** HOMOs and LUMOs of (a) 6−O-m, (b) 6−S-m, and (c) 7−O-m.
Figure 11. Cyclic voltammograms of 6−O (reddish-purple), 6−S (bluish-purple) and 7−O (green) in CH₂Cl₂; 0.1 M nBu₄NPF₆, Ag⁺/Ag (0.01 M AgNO₃). Scan rate 20 mV s⁻¹. Asterisk (*) indicates decamethylferrocene/decamethylferrocenium couple.

3. Conclusion

The 18π P,X,N₂-porphyrins 1N, 1N’, and 1S have been successfully prepared via an acid-promoted [3+1] condensation approach using phosphatripyrranes and 2,5-bis[hydroxy(phenyl)methyl]heteroles. Both experimental (NMR, UV-vis, and X-ray) and theoretical (DFT calculations) results have revealed that these P,X,N₂-porphyrins possess reasonably high aromatic characters that stem from the slightly deviated 18π-annulene circuit. The UV-vis and CV/DPV measurements as well as the DFT calculations have also revealed that these P,X,N₂-porphyrins possess considerably narrow HOMO−LUMO gaps. It is of particular interest that the simple P-oxygenation of σ₃-P,X,N₂-porphyrins with H₂O₂ causes unprecedented types of π-reconstruction from 18π into peripherally extended 22π or isophlorin-type 20π circuits. Notably, the reaction modes and the structures of the resulting P-oxygenated porphyrins strongly depend on the combination of the core heteroatoms and the structure of the peripherally fused carbocycles. The present results demonstrate for the first time that the introduction of a phosphorus atom into the core is a highly promising methodology to modify the fundamental properties and reactivities of porphyrin π systems.
Experimental Section

**General.** $^1$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR spectra were measured in CDCl$_3$. Chemical shifts are reported as the relative value vs tetramethylsilane ($^1$H, $^{13}$C) and H$_3$PO$_4$ ($^{31}$P), respectively. MALDI-TOF and HR-FAB-MS mass spectra were measured using CHCA and 3-nitrobenzyl alcohol as matrices, respectively. Electrochemical measurements were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^{+}$ [0.01 M AgNO$_3$, 0.1 M nBu$_4$NPf$_6$ (MeCN)] reference electrode. The potentials were calibrated with ferrocenium/ferrocene [$E_{\text{mid}} = +0.20 \text{ V vs Ag/AgNO}_3$]. Dichloromethane (CH$_2$Cl$_2$) and toluene and THF were distilled from CaH$_2$ (CH$_2$Cl$_2$, toluene) or sodium benzophenone ketyl (THF) before use. Other chemicals and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F$_{254}$ (Merck). Gravity column chromatography was carried out using Silica gel or Alumina in open air. Starting materials 4N, 4S, 4O, S1, S3, and S3$^*$ were prepared according to the reported procedures. Phosphatripyrrane 3 and P,X,N$_2$-porphyrins 1X (X = N, S) were prepared by slightly modified method from the preliminary report.$^{23}$

**Scheme E1.** Synthesis of S,X,N$_2$-Porphyrins 2N and 2S

**Synthesis of S,X,N$_2$-Porphyrins 2X (X = N, S).** To a solution of diol S1 (330 mg, 1.8 mmol) in 10 mL (140 mmol) of pyrrole, was added 100 µL (0.80 mmol) of BF$_3$•OEt$_2$. After stirring for 30 min at room temperature, CH$_2$Cl$_2$ (30 mL) and saturated NaHCO$_3$ solution (20 mL) were added. The water phase was extracted with CH$_2$Cl$_2$, and the organic extracts were combined, washed with brine, dried over Na$_2$SO$_4$ and evaporated. The crude mixture was filtered through a short silica gel column (CH$_2$Cl$_2$/EtOAc = 50/1) to afforded crude S2 (ca. 390 mg, ca. 1.4 mmol, ca. 80%; $R_f = 0.9$) as beige solids. The crude S2 was dissolved in CH$_2$Cl$_2$ solution (430 mL) containing 4N (ca. 390 mg, ca. 1.4 mmol), followed by addition of BF$_3$•OEt$_2$ (160 µL, 1.3 mmol). After stirring for 30 min, DDQ (950 mg, 4.2 mmol) was added
to the mixture. After stirring for an additional 15 min at room temperature, the reaction mixture was condensed, and subjected to an alumina column chromatography (CH₂Cl₂). A greenish yellow band was collected, evaporated, and recrystallized from CH₂Cl₂/MeOH to afford 2N as a purple solid (170 mg, 20% from S1); A similar treatment of S1 with 4S gave 2S as a purple solid (88 mg, 10% from S1).

2N: Mp > 300 °C; ¹H NMR (CDCl₃, 400 MHz) δ −2.82 (s, 1H), 3.33 (quin, J = 8.0 Hz, 2H), 4.33 (t, J = 8.0 Hz, 4H), 7.72–7.78 (m, 6H), 8.18–8.20 (m, 4H), 8.68 (d, J = 4.4 Hz, 2H), 8.91 (d, J = 1.5 Hz, 2H), 9.00 (d, J = 4.4 Hz, 2H), 10.45 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 29.4 (s), 30.1 (s), 113.7 (s), 124.1 (s), 126.5 (s), 127.8 (s), 128.4 (s), 132.7 (s), 134.4 (s), 135.8 (s), 138.4 (s), 141.2 (s), 142.5 (s), 153.7 (s), 154.5 (s), 157.2 (s); UV-vis (CH₂Cl₂): λₓ max (ε) 418 (218000), 472 (3700), 503 (24700), 533 (4100), 601 (3500), 660 nm (3200); HR-FAB-MS: Calcd for C₁₃H₂₄N₂S (M⁺), 519.1769; Found, 519.1776.

2S: Mp > 300 °C; ¹H NMR (CDCl₃, 400 MHz) δ 3.34 (quin, J = 7.3 Hz, 2H), 4.32 (t, J = 7.3 Hz, 4H), 7.80–7.81 (m, 6H), 8.24–8.25 (m, 4H), 8.80 (d, J = 4.4 Hz, 2H), 9.05 (d, J = 4.4 Hz, 2H), 9.71 (s, 2H), 10.54 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 29.3 (s), 30.2 (s), 115.9 (s), 127.4 (s), 128.0 (s), 133.99 (s), 134.04 (s), 134.2 (s), 135.01 (s), 135.04 (s), 141.3 (s), 141.4 (s), 147.6 (s), 155.5 (s), 156.2 (s); UV-vis (CH₂Cl₂): λₓ max (ε) 426 (188000), 472 (6100), 505 (27200), 531 (4000), 619 (2200), 682 nm (3400); HR-FAB-MS: Calcd for C₁₃H₂₄N₂S₂ (M⁺), 536.1381; Found, 536.1371.

**Scheme E2.** Synthesis of Phosphatripyrranes 3 and 3’

**Synthesis of Phosphatripyrranes 3 and 3’**. To a solution of S3’ (7.0 g, 20 mmol) in 230 mL of hexane was added solution of DIBAH (1.0 M, 84 mL, 84 mmol) at −78 °C. After stirring for 1 h elemental sulfur (670 mg, 21 mmol) was added, and the resulting mixture was allowed to warm slowly to room temperature. A saturated NH₄Cl solution (50 mL) and EtOAc (200 mL) was then added, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with EtOAc (50 mL × 3). The combined organic extracts were washed with brine (150 mL), dried over Na₂SO₄, and evaporated. The crude product S4’ was dissolved in pyrrole (45 mL, 650
mmol), and BF₃•OEt₂ (5.1 mL, 40 mmol) was added to the solution at 80 ºC. After stirring for 1.5 h at the same temperature, the second portion of BF₃•OEt₂ (6.1 mL, 47 mmol) was added, and the mixture was stirred for an additional 1 h. After cooling to room temperature, a saturated NaHCO₃ solution (20 mL) and CH₂Cl₂ (50 mL) were added. The organic phase was separated, dried over Na₂SO₄, and evaporated. The products were dissolved by CH₂Cl₂, and filtered through a pad of silica gel. Further purification of the crude products by silica gel column chromatography (hexane/CH₂Cl₂ = 1/1, Rf = 0.3), followed by MeOH wash, afforded 3′ as a colorless solid (670 mg, 8.3%); Similarly, 3 was prepared from S3 as a colorless solid (CH₂Cl₂, Rf = 0.3; 750 mg, 9.7%).

3: Mp 141–143 ºC; ¹H NMR (CDCl₃, 400 MHz) δ 1.98–2.05 (m, 2H), 2.25–2.40 (m, 4H), 3.48–3.53 (m, 4H), 5.85–5.87 (m, 2H), 5.96–5.98 (m, 2H), 6.57–6.58 (m, 2H), 7.39–7.43 (m, 2H), 7.48–7.50 (m, 1H), 7.71–7.75 (m, 2H), 8.77 (br-s, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 23.7 (d, J = 15.6 Hz), 26.7 (d, J = 1.9 Hz), 26.8 (d, J = 11.8 Hz), 106.3 (s), 107.7 (s), 117.3 (s), 127.1 (d, J = 69.0 Hz), 127.2 (d, J = 79.0 Hz), 127.2 (d, J = 3.7 Hz), 128.8 (d, J = 12.5 Hz), 130.3 (d, J = 11.9 Hz), 132.0 (d, J = 2.5 Hz), 157.8 (d, J = 25.5 Hz); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 72.2; HR-FAB-MS: Calcd for C₂₅H₂₄N₂PS (M+H⁺), 391.1398; Found, 391.1398.

3′: Mp 141–142 ºC; ¹H NMR (CDCl₃, 400 MHz) δ 1.60–1.64 (m, 4H), 2.38–2.47 (m, 2H), 2.49–2.58 (m, 2H), 3.39–3.46 (m, 2H), 3.52–3.60 (m, 2H), 5.85–5.87 (m, 2H), 5.96–5.98 (m, 2H), 6.59–6.61 (m, 2H), 7.39–7.44 (m, 2H), 7.49–7.52 (m, 1H), 7.68–7.74 (m, 2H), 9.08 (br-s, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 22.1 (s), 22.9 (d, J = 13.2 Hz), 26.1 (d, J = 14.8 Hz), 106.2 (s), 107.4 (s), 117.3 (s), 126.4 (d, J = 71.6 Hz), 126.8 (s), 128.9 (d, J = 12.3 Hz), 130.3 (d, J = 79.9 Hz), 130.6 (d, J = 11.5 Hz), 132.1 (d, J = 2.5 Hz), 149.7 (d, J = 23.9 Hz); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 51.6; HR-FAB-MS: Calcd for C₂₄H₂₃N₂PS (M⁺), 404.1476; Found, 404.1464.

Synthesis of P₃N₃-Porphyrinogen-P-sulfides 5N–S and 5N’–S. NaBH₄ (720 mg, 18.9 mmol) was added to a solution of 2,5-dibenzoylpyrrole (110 mg, 0.39 mmol) in THF/MeOH (total 24 mL; v/v = 3/1), which was then stirred for 30 min at room temperature. After adding a mixture of water (10 mL) and CH₂Cl₂ (30 mL), the organic phase was separated, dried over K₂CO₃, and evaporated. The crude product 4N was dissolved in CH₂Cl₂ solution (120 mL) containing 3 (120 mg, 0.30 mmol), followed by addition of BF₃•OEt₂ (39 µL, 0.30 mmol). After stirring for 5 min at room temperature, Et₃N (75 µL, 0.54 mmol) was added and the resulting mixture was washed with distilled water (50 mL), dried over Na₂SO₄, and evaporated. The crude product was subjected to silica gel column chromatography (CH₂Cl₂/hexane = 1/1) to give 5N–S as a mixture of three diastereomers (Rf = 0.5–0.6; 82 mg,
43%). The $^1$H and $^{31}$P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 10:5:4; A similar treatment of 3’ with 4N afforded 5N’–S as a mixture of two diastereomers ($R_t = 0.5–0.6$; 220 mg, 22%). The $^1$H and $^{31}$P NMR spectra indicated that two major diastereomers (A, B) were included in a ratio of 3:1.

5N–S: $^1$H NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 1.92–2.00 (m, 1H), 2.06–2.14 (m, 1H), 2.31–2.43 (m, 4H), 3.42–3.50 (m, 4H), 5.25 (s, 1H), 5.40 (s, 1H), 5.47–5.48 (m, 1H), 5.53–5.54 (m, 1H), 5.72–5.73 (m, 1H), 5.81–5.82 (m, 1H), 5.87–5.88 (m, 1H), 6.09 (dd, $J = 2.9$ Hz, $J = 2.9$ Hz, 1H), 7.11–7.37 (m, 10H), 7.47–7.54 (m, 3H), 7.67 (br-s, 1H), 7.83–7.89 (m, 2H), 9.64 (br-s, 1H), 10.10 (br-s, 1H); Diastereomer B: $\delta$ 1.86–1.93 (m, 1H), 2.06–2.14 (m, 1H), 2.31–2.39 (m, 4H), 3.42–3.50 (m, 4H), 5.41–5.42 (m, 4H), 5.82–5.83 (m, 2H), 6.16 (d, $J = 2.4$ Hz, 2H), 7.12–7.40 (m, 10H), 7.45–7.54 (m, 3H), 7.67 (br-s, 1H), 7.82–7.87 (m, 2H), 9.64 (br-s, 2H); Diastereomer C: $\delta$ 2.02–2.09 (m, 2H), 2.30–2.46 (m, 4H), 3.43–3.47 (m, 4H), 5.36 (s, 2H), 5.51 (d, $J = 2.4$ Hz, 2H), 5.75–5.76 (m, 2H), 5.83–5.84 (m, 2H), 7.13–7.30 (m, 10H), 7.44–7.55 (m, 3H), 7.83–7.87 (m, 2H), 8.05 (br-s, 1H), 9.99 (br-s, 2H); $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz) $\delta$ 70.4, 71.2, 72.0; MS (MALDI-TOF): m/z 633 (M$^+$; C$_{41}$H$_{36}$N$_{3}$PS).

5N’–S: $^1$H NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 1.50–1.72 (m, 4H), 2.28–2.60 (m, 4H), 3.40–3.59 (m, 4H), 5.26 (s, 1H), 5.42 (s, 1H), 5.48–5.52 (m, 1H), 5.53–5.57 (m, 1H), 5.72–5.76 (m, 1H), 5.81–5.85 (m, 1H), 5.86–5.90 (m, 1H), 6.07–6.11 (m, 1H), 7.08–7.40 (m, 10H), 7.44–7.50 (m, 2H), 7.51–7.54 (m, 1H), 7.64 (br-s, 1H), 7.79–7.84 (m, 2H), 9.67 (br-s, 1H), 10.19 (br-s, 1H); Diastereomer B: $\delta$ 1.48–1.72 (m, 4H), 2.28–2.60 (m, 4H), 3.40–3.56 (m, 4H), 5.42–5.47 (m, 4H), 5.82–5.86 (m, 2H), 6.14–6.18 (m, 2H), 7.00–7.40 (m, 11H), 7.42–7.48 (m, 2H), 7.50–7.54 (m, 1H), 7.78–7.83 (m, 2H), 9.70 (br-s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz) $\delta$ 21.8, 22.0, 22.1, 22.7, 22.8, 22.9, 23.0, 23.1, 25.6, 25.70, 25.73, 25.88, 25.92, 26.1, 44.0, 44.3, 44.7, 104.5, 105.0, 105.2, 106.29, 106.33, 106.4, 108.4, 108.6, 109.6, 125.7, 125.9, 126.0, 126.2, 126.5, 126.7, 126.8, 127.6, 128.1, 128.26, 128.29, 128.5, 128.8, 128.9, 129.0, 130.46, 130.58, 130.60, 131.37, 131.43, 131.5, 131.6, 132.07, 132.10, 133.2, 133.4, 133.5, 133.7, 142.4, 142.5, 143.5, 149.7, 149.85, 149.97, 150.04, 150.1, 150.3; $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz) $\delta$ 50.5, 51.2; HR-FAB-MS: Calcd for C$_{42}$H$_{38}$N$_{3}$PS (M$^+$), 647.2526; Found, 647.2524.

**Synthesis of P$_3$N$_3$-Porphyrinogens 5N and 5N’**. To a toluene solution (10 mL) of 5N–S (135 mg, 0.21 mmol) was added P(NMe$_3$)$_3$ (0.25 mL, 1.4 mmol), and the mixture was then stirred under reflux for 40 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 1/1) to give 5N as a mixture of three diastereomers ($R_t = 0.4–0.5$; 120 mg, 95%). The $^1$H and $^{31}$P NMR spectra
indicated that three major diastereomers (A, B, C) were included in a ratio of 10:4:4; A similar treatment of 5N'–S with P(NMe₂)₃ afforded 5N' as a mixture of two diastereomers ($R_f = 0.7–0.8$; 140 mg, 79%). The $^1$H and $^{31}$P NMR spectra indicated that two major diastereomers (A, B) were included in a ratio of 5:1.

5N: $^1$H NMR (CDCl₃, 400 MHz): Diastereomer A: $\delta$ 2.12–2.16 (m, 2H), 2.22–2.34 (m, 2H), 2.51–2.59 (m, 2H), 3.34–3.42 (m, 2H), 3.62–3.75 (m, 2H), 5.33 (s, 1H), 5.41 (s, 1H), 5.65–5.66 (m, 1H), 5.68–5.69 (m, 1H), 5.79–5.80 (m, 1H), 5.84–5.85 (m, 2H), 5.99–6.00 (m, 1H), 7.14–7.33 (m, 15H), 7.79 (br-s, 1H), 8.23 (br-s, 1H), 8.35 (br-s, 1H); Diastereomer B: $\delta$ 2.19–2.28 (m, 2H), 2.35–2.39 (m, 2H), 2.57–2.62 (m, 2H), 3.39–3.43 (m, 2H), 3.68–3.77 (m, 2H), 5.40 (s, 2H), 5.73–5.74 (m, 2H), 5.78–5.80 (m, 4H), 7.14–7.32 (m, 15H), 7.81 (br-s, 1H), 7.98 (br-s, 2H); Diastereomer C: $\delta$ 2.22 (m, 4H), 2.54 (m, 2H), 3.35–3.42 (m, 2H), 3.62–3.75 (m, 2H), 5.39 (s, 2H), 5.67–5.69 (m, 2H), 5.79–5.80 (m, 2H), 5.83–5.84 (m, 2H), 7.14–7.33 (m, 15H), 7.94 (br-s, 1H), 8.32 (br-s, 2H); $^{31}$P($^1$H) NMR (CDCl₃, 162 MHz) $\delta$ 30.4, 32.5, 32.7; MS (MALDI-TOF): m/z 601 (M⁺); C₄₁H₃₈N₃P.

5N': $^1$H NMR (CDCl₃, 400 MHz): Diastereomer A: $\delta$ 1.62–1.74 (m, 4H), 2.38–2.71 (m, 4H), 3.28–3.39 (m, 2H), 3.68–3.83 (m, 2H), 5.32 (s, 1H), 5.41 (s, 1H), 5.63–5.66 (m, 1H), 5.70–5.72 (m, 1H), 5.79–5.83 (m, 2H), 5.85–5.88 (m, 1H), 6.01–6.04 (m, 1H), 7.12–7.32 (m, 15H), 7.80 (br-s, 1H), 8.18 (br-s, 1H), 8.32 (br-s, 1H); Diastereomer B: $\delta$ 1.62–1.74 (m, 4H), 2.38–2.71 (m, 4H), 3.28–3.39 (m, 2H), 3.68–3.83 (m, 2H), 5.39 (s, 2H), 5.68–5.71 (m, 2H), 5.81–5.84 (m, 2H), 5.82–5.84 (m, 2H), 7.12–7.32 (m, 15H), 7.87 (br-s, 3H); $^{13}$C($^1$H) NMR (CDCl₃, 100 MHz) $\delta$ 22.8, 22.9, 23.2, 25.1, 25.18, 25.23, 25.4, 25.89, 25.92, 25.97, 26.01, 26.20, 26.21, 43.9, 44.0, 44.3, 44.8, 45.1, 105.41, 105.48, 105.54, 105.72, 105.75, 106.1, 107.9, 108.05, 108.08, 126.5, 126.9, 128.15, 128.23, 128.26, 128.30, 128.5, 128.74, 128.78, 128.83, 129.5, 130.75, 130.86, 131.58, 131.62, 131.67, 132.4, 132.6, 133.3, 133.48, 133.53, 133.7, 134.0, 136.61, 136.65, 137.19, 137.22, 141.9, 142.4, 143.1, 144.6, 144.7, 144.95, 144.98, 145.04; $^{31}$P($^1$H) NMR (CDCl₃, 162 MHz) $\delta$ 2.6, 4.1; HR-FAB-MS: Calcd for C₄₁H₃₈N₃P(M⁺) 615.2806; Found, 615.2803.

**Synthesis of P₅S₅N₅ and P₅O₅N₅-Porphyrinogen-P-sulfides 5S–S and 5O–S.** A CH₂Cl₂ solution (530 mL) containing 3 (370 mg, 0.95 mmol) and 4S (280 mg, 0.95 mmol) was bubbled with N₂ for 30 min. BF₃•OEt₂ (0.12 mL, 0.95 mmol) was added to the solution, and the mixture was then stirred for 30 min at room temperature. The resulting mixture was washed with distilled water (2 × 500 mL), dried over Na₂SO₄, and evaporated. The crude product was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 1/1) to give 5S–S as a mixture of three diastereomers ($R_f = 0.5–0.6$; 220 mg, 36%). The $^1$H and $^{31}$P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 6:5:3; A
similar treatment of 3 with 4O afforded 5O–S as a mixture of two diastereomers ($R_e = 0.4–0.5; 110 \text{ mg}, 9\%$). The $^1\text{H}$ and $^{31}\text{P}$ NMR spectra indicated that two major diastereomers (A, B) were included in a ratio of $8:3$.

5S–S: $^1\text{H}$ NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.37–5.39 (m, 1H), 5.46 (s, 1H), 5.54 (d, $^4J = 1.6$ Hz, 1H), 5.75–5.78 (m, 1H), 5.82–5.83 (m, 1H), 5.87–5.89 (m, 1H), 6.19 (dd, $J = 3.6$ Hz, $^4J = 1.6$ Hz, 1H), 6.82 (d, $J = 3.6$ Hz, 1H), 7.18–7.39 (m, 10H), 7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.38 (br-s, 1H), 9.74 (br-s, 1H); Diastereomer B: $\delta$ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.54 (s, 2H), 5.77–5.78 (m, 2H), 5.87–5.88 (m, 2H), 6.14 (s, 2H), 7.18–7.39 (m, 10H), 7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.61 (br-s, 2H); Diastereomer C: $\delta$ 1.76–1.90 (m, 1H), 2.00–2.19 (m, 1H), 2.20–2.46 (m, 4H), 3.42–3.49 (m, 4H), 5.29–5.32 (m, 2H), 5.59 (s, 2H), 5.79–5.81 (m, 2H), 6.90 (s, 2H), 7.18–7.39 (m, 10H), 7.47–7.49 (m, 2H), 7.52–7.56 (m, 1H), 7.82–7.87 (m, 2H), 9.51 (br-s, 2H); $^{31}\text{P}$($^1\text{H}$) NMR (CDCl$_3$, 162 MHz) $\delta$ 72.6, 72.7, 72.8; MS (MALDI-TOF) m/z 650 (M$^+$; C$_{41}$H$_{35}$N$_2$PS$_2$).

5O–S: $^1\text{H}$ NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 1.94–2.15 (m, 2H), 2.25–2.48 (m, 4H), 3.39–3.49 (m, 4H), 5.23–5.26 (m, 1H), 5.27 (s, 1H), 5.42 (s, 1H), 5.67–5.71 (m, 1H), 5.73–5.76 (m, 1H), 5.78 (d, $J = 3.4$ Hz, 1H), 5.89–5.91 (m, 1H), 6.31 (d, $J = 3.4$ Hz, 1H), 7.10–7.36 (m, 8H), 7.45–7.59 (m, 5H), 7.84–7.90 (m, 2H), 9.88 (br-s, 1H), 9.90 (br-s, 1H); Diastereomer B: $\delta$ 1.94–2.15 (m, 2H), 2.25–2.48 (m, 4H), 3.39–3.49 (m, 4H), 5.46 (s, 2H), 5.72–5.74 (m, 2H), 5.78 (s, 2H), 5.86–5.88 (m, 2H), 7.10–7.36 (m, 8H), 7.45–7.59 (m, 5H), 7.84–7.90 (m, 2H), 9.90 (br-s, 2H); $^{31}\text{P}$($^1\text{H}$) NMR (CDCl$_3$, 162 MHz) $\delta$ 70.7, 71.0; MS (MALDI-TOF) m/z 635 (M$^+$; C$_{41}$H$_{35}$N$_2$OPS).

Synthesis of PS$_3$N$_2$- and P$_2$O$_5$N$_2$-Porphyrinogens 5S and 5O. To a toluene solution (40 mL) of 5S–S (370 mg, 0.57 mmol) was added P(NMe$_2$)$_3$ (0.66 mL, 3.6 mmol), and the mixture was then stirred under reflux for 23 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1) to give 5S as a mixture of three diastereomers ($R_e = 0.3–0.4; 330 \text{ mg}, 93\%$): The $^1\text{H}$ and $^{31}\text{P}$ NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 8:5:4; A similar treatment of 5O–S with P(NMe$_2$)$_3$ afforded 5O as a mixture of two diastereomers ($R_e = 0.3–0.4; 82 \text{ mg}, 71\%$). The $^1\text{H}$ and $^{31}\text{P}$ NMR spectra indicated that two major diastereomers (A, B) were included in a ratio of 7:3.

5S: $^1\text{H}$ NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.55 (s, 1H), 5.60 (s, 1H), 5.72–5.76 (m, 2H), 5.77–5.81 (m, 1H), 5.82–5.86 (m, 1H), 6.55 (d, $J = 3.6$ Hz, 1H), 6.67 (d, $J = 3.6$ Hz, 1H), 104
7.22–7.30 (m, 15H), 8.20 (br-s, 1H), 8.35 (br-s, 1H); Diastereomer B: δ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.60 (s, 2H), 5.65–5.69 (m, 2H), 5.78–5.82 (m, 2H), 6.67 (s, 2H), 7.22–7.30 (m, 15H), 8.27 (br-s, 2H); Diastereomer C: δ 2.10–2.35 (m, 4H), 2.50–2.63 (m, 2H), 3.40–3.45 (m, 2H), 3.68–3.78 (m, 2H), 5.60–5.62 (m, 4H), 5.78–5.81 (m, 2H), 6.76 (s, 2H), 7.22–7.30 (m, 15H), 8.21 (br-s, 2H); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz) δ 32.7, 33.3, 33.5; MS (MALDI-TOF) m/z 618 (M$^+$; C$_{44}$H$_{36}$N$_2$PS).

5O: $^1$H NMR (400 MHz): Diastereomer A: δ 2.13–2.30 (m, 4H), 2.49–2.57 (m, 2H), 3.35–3.43 (m, 2H), 3.62–3.75 (m, 2H), 5.36 (s, 1H), 5.40 (s, 1H), 5.48–5.51 (m, 1H), 5.62–5.65 (m, 1H), 5.76–5.79 (m, 1H), 5.84–5.87 (m, 1H), 6.04 (d, J = 2.9 Hz, 1H), 6.21 (d, J = 2.9 Hz, 1H), 7.19–7.44 (m, 15H), 8.20 (br-s, 1H), 8.29 (br-s, 1H); Diastereomer B: δ 2.13–2.30 (m, 4H), 2.49–2.57 (m, 2H), 3.35–3.43 (m, 2H), 3.62–3.75 (m, 2H), 5.47 (s, 2H), 5.71–5.74 (m, 2H), 5.84–5.87 (m, 2H), 6.03 (s, 2H), 7.19–7.44 (m, 15H), 8.42 (br-s, 2H); $^{13}$C($^1$H) NMR (CDCl$_3$, 100 MHz) δ 26.3, 26.4, 26.6, 26.7, 28.5, 28.7, 44.5, 44.7, 45.1, 105.5, 105.6, 105.7, 105.9, 106.0, 106.1, 109.0, 109.2, 109.3, 126.68, 126.73, 126.9, 128.2, 128.3, 128.5, 128.76, 128.83, 128.9, 129.17, 129.25, 129.5, 129.6, 130.6, 130.9, 131.2, 131.3, 131.5, 131.6, 132.1, 132.7, 133.0, 133.1, 133.2, 133.3, 140.2, 141.7, 141.9, 154.4, 154.8, 154.9, 155.1, 155.2, 155.4, 155.5, 155.6, 156.0; $^{31}$P($^1$H) NMR δ 32.4, 33.6; MS (MALDI-TOF) m/z 603 (M$^+$; C$_{44}$H$_{35}$N$_2$OP).

**Synthesis of P$_3$N$_3$- and P$_3$S$_3$N$_2$-Porphyrinogen-P-oxides 5N–O and 5S–O.** Hydrogen peroxide (4.3 mg, 0.038 mmol, 30% solution in H$_2$O) was added to a solution of 5N (20 mg, 0.032 mmol) in THF (1 mL) at room temperature. After stirring for 16 h at the same temperature, the reaction mixture was dried in vacuo. The crude product was washed with cold (~78 °C) hexane to give 5N–O as a mixture of three diastereomers (20 mg, 97%). The $^1$H and $^{31}$P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 10:4:4; A similar treatment of 5S with hydrogen peroxide gave 5S–O as a mixture of three diastereomers (21 mg, 90%). The $^1$H and $^{31}$P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 10:7:5.

5N–O: $^1$H NMR (CDCl$_3$, 400 MHz): Diastereomer A: δ 1.92–2.00 (m, 1H), 2.02–2.11 (m, 1H), 2.43–2.54 (m, 4H), 3.35–3.63 (m, 4H), 5.32 (s, 1H), 5.42 (s, 1H), 5.49–5.51 (m, 1H), 5.56–5.58 (m, 1H), 5.75–5.77 (m, 1H), 5.78–5.80 (m, 1H), 5.89–5.91 (m, 1H), 6.12–6.14 (m, 1H), 7.10–7.34 (m, 8H), 7.43–7.56 (m, 5H), 7.76–7.81 (m, 2H), 7.89 (br-s, 1H), 10.05 (br-s, 1H), 10.40 (br-s, 1H); Diastereomer B: δ 1.92–2.00 (m, 1H), 2.02–2.11 (m, 1H), 2.38–2.58 (m, 4H), 3.38–3.62 (m, 4H), 5.42 (s, 2H), 5.69 (d, J = 2.4 Hz, 2H), 5.81–5.83 (m, 4H), 7.13–7.26 (m, 10H), 7.46–7.56 (m, 3H), 7.71–7.79 (m, 2H), 8.24 (br-s, 1H), 10.23 (br-s, 2H); Diastereomer C: δ 1.90–2.16 (m, 2H), 2.35–2.46 (m, 2H), 2.53–2.62 (m, 2H), 3.41–3.66 (m,
2H), 5.44 (s, 2H), 5.46–5.47 (m, 2H), 5.81–5.82 (m, 2H), 6.19 (d, J = 2.4 Hz, 2H), 7.16–7.30 (m, 10H), 7.46–7.54 (m, 3H), 7.71–7.80 (m, 2H), 8.22 (br-s, 1H), 10.21 (br-s, 2H); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz) $\delta$ 59.2, 59.5, 59.6; MS (MALDI-TOF) $m/z$ 617 (M$^+$; C$_9$H$_{36}$N$_3$OP).

5S–O: $^1$H NMR (CDCl$_3$, 400 MHz): Diastereomer A: $\delta$ 1.95–2.08 (m, 2H), 2.19–2.30 (m, 4H), 3.29–3.64 (m, 4 H), 5.40–5.44 (m, 1H) 5.55 (s, 1H), 5.58 (s, 1H), 5.75–5.81 (m, 2H), 5.85–5.89 (m, 1H), 6.27 (d, J = 3.9 Hz, 1H), 6.91 (d, J = 3.9 Hz, 1H), 7.18–7.34 (m, 8H), 7.44–7.51 (m, 4H), 7.53–7.58 (m, 1H), 7.72–7.77 (m, 2H), 10.12 (br-s, 1H), 10.15 (br-s, 1H); Diastereomer B: $\delta$ 1.92–2.18 (m, 2H), 2.38–2.64 (m, 4H), 3.37–3.61 (m, 4H), 5.62 (s, 2H), 5.78–5.82 (m, 2H), 5.83–5.87 (m, 2H), 6.26 (s, 2H), 7.15–7.28 (m, 10H), 7.45–7.63 (m, 3H), 7.72–7.79 (m, 2H), 10.11 (br-s, 2H); Diastereomer C: $\delta$ 1.94–2.18 (m, 2H), 2.36–2.65 (m, 4H), 3.34–3.61 (m, 4H), 5.34–5.38 (m, 2H), 5.60 (s, 2H), 5.75–5.79 (m, 2H), 6.98 (s, 2H), 7.15–7.28 (m, 6H), 7.36–7.42 (m, 4H), 7.44–7.50 (m, 2H), 7.52–7.55 (m, 1H), 7.72–7.78 (m, 2H), 10.12 (br-s, 2H): $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz) $\delta$ 58.5, 58.6. (two of the three diastereomers show an identical chemical shift); MS (MALDI-TOF) $m/z$ 635 (M$^+$; C$_{41}$H$_{35}$N$_2$OPS).

**Synthesis of P$_2$N$_3$-Porphyrins 1N and 6–O.** To a solution of 5N (30 mg, 0.050 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (CH$_2$Cl$_2$). Further purification of the crude products by alumina column chromatography (CH$_2$Cl$_2$/hexane = 1/1), followed by recrystallization from CH$_2$Cl$_2$/MeOH, afforded 1N ($R_t = 0.9$) as a reddish purple solid (5.1 mg, 17%) and 6–O ($R_t = 0.5$) as a dark-purple solid (2.4 mg, 8%).

**1N:** Mp ca. 250 °C (decomp); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ –0.59 (br-s, 1H), 2.43 (dd, J = 7.3 Hz, $^3J_{pH} = 4.4$ Hz, 2H), 3.04–3.08 (m, 1H), 3.31–3.35 (m, 1H), 3.80–3.86 (m, 2H), 4.50–4.56 (m, 2H), 5.23 (dd, J = 7.3 Hz, J = 7.3 Hz, 2H), 5.68 (t, J = 7.3 Hz, 1H), 7.62–7.76 (m, 6H), 7.97 (d, J = 7.3 Hz, 2H), 8.23–8.26 (m, 2H), 8.35 (d, J = 4.4 Hz, 2H), 8.62 (d, $^3J = 2.0$ Hz, 2H), 8.67 (d, J = 4.4 Hz, 2H) 10.18 (d, $^3J_{pH} = 16.1$ Hz, 2H); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz) $\delta$ –5.2; UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$): 431 (177000), 486 (9500), 522 (10100), 555 (7200), 636 (2300), 698 nm (3100); HR-FAB-MS: Calcd for C$_{41}$H$_{35}$N$_3$P (M$^+$), 595.2177; Found, 595.2182.

**6–O:** Mp ca. 230 °C (decomp); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.40 (br-s, 2H), 5.60 (dd, J = 7.3 Hz, $^3J_{pH} = 12.2$ Hz, 2H), 6.58–6.62 (m, 2H), 6.92 (t, J = 7.6 Hz, 1H), 7.58–7.85 (m, 8H), 7.94 (s, 2H), 8.02 (d, J = 4.4 Hz, 2H), 8.16 (d, J = 3.9 Hz, 2H), 8.19 (d, J = 4.4 Hz, 2H), 8.25 (d, J = 7.3 Hz, 2H), 9.06 (dt, J = 3.9 Hz, $^5J_{pH} = 5.4$ Hz, 1H), 9.21 (d, $^3J_{pH} = 35.6$ Hz, 2H); $^{31}$P($^1$H) NMR (CDCl$_3$, 162 MHz) $\delta$ 28.6; UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$): 422 (42100), 494 (77200),
Synthesis of P,N-2-Porphyrin 1N’. To a solution of 5N’ (30 mg, 0.049 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (CH₂Cl₂). The crude product was recrystallized from CH₂Cl₂/MeOH to give 5N’ as a reddish purple solid (10 mg, 33%): Mp ca. 250 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ −0.05 (br-s, 1H), 2.22–2.32 (m, 2H), 2.52–2.62 (m, 4H), 3.85–3.98 (m, 2H), 4.41–4.51 (m, 2H), 5.22 (dd, J = 7.3 Hz, J = 7.3 Hz, ¹Jₚ,Η = 2.0 Hz, 2H), 5.66 (dt, J = 7.3 Hz, ³Jₚ,Η = 1.0 Hz, 1H), 7.55–7.60 (m, 2H), 7.63–7.66 (m, 4H), 7.86–7.95 (m, 2H), 8.13–8.17 (m, 2H), 8.21 (d, J = 4.4 Hz, 2H), 8.45 (d, ³J = 2.0 Hz, 2H), 8.52 (d, J = 4.4 Hz, 2H) 10.03 (d, ³Jₚ,Η = 16.1 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 23.5 (s), 27.2 (s), 119.1 (d, J = 4.9 Hz), 124.8 (d, J = 4.9 Hz), 125.1 (s), 126.4 (d, J = 3.3 Hz), 126.5 (d, J = 2.5 Hz), 127.3 (s), 127.8 (s), 128.4 (d, J = 9.1 Hz), 133.3 (s), 134.0 (s), 134.4 (s), 135.9 (d, J = 3.3 Hz), 137.5 (s), 142.4 (s), 149.1 (s), 153.1 (s), 153.8 (d, J = 14.0 Hz), 159.7 (s); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ −32.6; UV-vis (CH₂Cl₂) λ_max (є): 431 (172000), 488 (107000), 525 (101000), 561 (9100), 626 (2900), 692 nm (3200); HR-FAB-MS: Calcd for C₄₅H₃₂N₃P (M''), Found, 609.2334; Found, 609.1975.

Synthesis of P,S,N₂-Porphyrins 1S and 7–O. To a solution of 5S (30 mg, 0.050 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (CH₂Cl₂). Further purification of the crude products by alumina column chromatography (CH₂Cl₂/hexane = 1/1), followed by recrystallization from CH₂Cl₂/MeOH, afforded 1S (R_f = 0.7) as a reddish purple solid (1.5 mg, 5%) and 7–O (R_f = 0.9) as a dark-green solid (ca. 0.3 mg, ca. 1%). Although the yields are low, the syntheses of 1S and 7–O are quite reproducible.

1S: Mp ca. 250 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ 2.29 (dd, J = 7.6 Hz, ³Jₚ,Η = 4.5 Hz, 2H), 2.90–3.00 (m, 1H), 3.20–3.31 (m, 1H), 3.53–3.59 (m, 2H), 4.40–4.51 (m, 2H), 5.27 (dd, J = 7.6 Hz, J = 7.2 Hz, 2H), 5.66 (t, J = 7.2 Hz, 1H), 7.67–7.82 (m, 6H), 7.82–8.01 (m, 2H), 8.26–8.45 (m, 2H), 8.67 (d, J = 4.4 Hz, 2H), 8.93 (d, J = 4.4 Hz, 2H), 9.22 (s, 2H), 10.44 (d, ³Jₚ,Η = 18.8 Hz, 2H); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 18.6; UV-vis (CH₂Cl₂) λ_max (є): 440 (164000), 492 (12800), 518 (10800), 547 (7000), 647 (1700), 718 nm (3100); HR-FAB-MS: Calcd for C₄₅H₃₂N₃P (M'''), 612.1789; Found, 612.1788.

7–O: Mp ca. 140 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ 1.67–1.73 (m, 3H), 1.82–1.90 (m, 1H), 2.22–2.30 (m, 2H), 4.99–5.02 (m, 2H), 5.20 (d, ³Jₚ,Η = 37.8 Hz, 2H), 5.66–5.68 (m,
2H), 5.75 (s, 2H), 7.05–7.07 (m, 4H), 7.16–7.17 (m, 6H), 7.75–7.77 (m, 3H), 8.60–8.64 (m, 2H), 18.0 (s, 2H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\), 75 MHz) \(\delta\) 22.6, 29.7, 127.8, 128.0, 129.0, 129.2, 129.8, 130.4, 130.6, 132.2, 132.3, 133.9; \(^{31}\)P\{\(^1\)H\} NMR (CDCl\(_3\), 162 MHz) \(\delta\) 45.3; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (\(\epsilon\)): 394 (66100), 650 (1800), 1130 nm (800); HR-FAB-MS: Calcd for C\(_{41}\)H\(_{31}\)N\(_2\)OPS (M\(^+\)), 630.1895; Found, 630.1895.

In the \(^{13}\)C\{\(^1\)H\} NMR spectrum, we could detect only partial peaks owing to low solubility of 7–O.

**Attempt to Synthesize 1O from 5O.** To a solution of 5O (30 mg, 0.050 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (CH\(_2\)Cl\(_2\)), affording a complex mixture, and 1O was not obtained (checked by \(^1\)H NMR).

**Synthesis of 6–O and 6–S from 5N–O and 5N–S.** To a solution of 5N–O (30 mg, 0.049 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (34 mg, 0.15 mmol) over 15 min at room temperature. After stirred for 1 h, the reaction mixture was filtered through a pad of alumina (CH\(_2\)Cl\(_2\)). Further purification of the crude product by alumina column chromatography (CH\(_2\)Cl\(_2\)/hexane = 1/1), followed by recrystallization from CH\(_2\)Cl\(_2\)/MeOH, afforded 6–O (\(R_f = 0.5\)) as a dark-purple solid (7.8 mg, 26%); A similar treatment of 5N–S with DDQ gave 6–S (silica gel column, CH\(_2\)Cl\(_2\)/hexane = 1/1, \(R_f = 0.2\)) as a dark-brown solid (5.0 mg, 17%).

6–S: Mp ca. 220 °C (decomp); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.80 (d, \(J = 3.4\) Hz, 2H), 4.35 (br-s, 2H), 5.70 (dt, \(J = 3.4\) Hz, \(J_{PH} = 5.4\) Hz, 1H), 7.38 (s, 2H), 7.5–7.7 (m, 9H), 7.51 (d, \(J = 4.9\) Hz, 2H), 7.53 (d, \(J = 4.9\) Hz, 2H), 7.56 (d, \(J_{PH} = 11.2\) Hz, 2H), 7.7–7.8 (m, 2H), 7.8–7.9 (m, 2H), 8.16–8.23 (m, 2H). \(^{31}\)P\{\(^1\)H\} NMR (CDCl\(_3\), 162 MHz) \(\delta\) 79.6; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (\(\epsilon\)): 318 (24000), 352 (22300), 405 (25100), 424 (25700), 485 (29400), 533 (4100), 635 (5800), 707 (5700), 750–1200 nm (sh); HR-FAB-MS: Calcd for C\(_{41}\)H\(_{28}\)N\(_3\)PS (M\(^+\)), 625.1742; Found, 625.1738.

**Attempt to Synthesize 7–O and 7–S from 5S–O and 5S–S.** To a solution of 5S–O (32 mg, 0.050 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (CH\(_2\)Cl\(_2\)), affording a complex mixture, and 7–O was not obtained (checked by \(^1\)H NMR); A similar treatment of 5S–S with DDQ also gave a complex mixture.

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**DDQ Oxidation of 5O–S.** To a solution of 5O–S (10 mg, 0.016 mmol) in degassed toluene (1 mL), was added a toluene (1 mL) solution of DDQ (11 mg, 0.048 mmol) over 15 min at room temperature. After stirred for 1 h, a saturated Na₂CO₃ solution (5 mL) and CH₂Cl₂ (5 mL) were added. The organic phase was separated, dried over Na₂SO₄, and evaporated. The crude products were subjected to silica gel column chromatography (CH₂Cl₂/hexane = 1/1), affording S5 (Rᵣ = 0.2) as a dark-yellow solid (1.5 mg, 15%): Mp ca. 170 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ 2.00–2.07 (m, 1H), 2.37–2.51 (m, 1H), 3.08–3.14 (m, 2H), 3.70–3.80 (m, 2H), 5.72 (d, J = 5.4 Hz, 2H), 6.11 (s, 2H), 6.38 (d, J = 5.4 Hz, 2H), 6.89 (d, JₚH = 6.9 Hz, 2H), 7.13–7.17 (m, 2H), 7.26–7.39 (m, 8H), 7.49–7.54 (m, 3H), 7.91–7.99 (m, 2H). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 26.7; HR-FAB-MS: Calcd for C₄₁H₂₉N₂O₆P (M⁺), 628.1738; Found, 628.1741. The crystal structure and UV-vis absorption spectrum (CH₂Cl₂) of S5 are shown in Figures A8 and A9 in Appendix, respectively.

**Reactions of 1N, 1N’, and 1S with H₂O₂.** To a NMR tube containing CDCl₃ (0.60 mL) solution of 1N (2.0 mg, 3.3 µmol) and 1,1,2,2-Tetrachloroethane (internal standard: ca. 3–5 µmol), was added a THF-d₈ (40 µL) solution of H₂O₂ (30 wt%, 3.6 µmol). After shaking the tube for about 10 seconds, the reaction was monitored in the dark by ¹H and ³¹P NMR. After 3 h, the reaction mixture was subjected to alumina column chromatography followed by washing with MeOH, and the 22π porphyrin 6–O was obtained in 77% yield (1.5 mg, 2.5 µmol). Similarly, the reactions of 1N’ and 1S with H₂O₂ were monitored to afford the compound 12’ (1 h) and the 20π porphyrin 7–O (48 h), respectively. The 20π porphyrin 7–O was purified by silica gel column (CH₂Cl₂), and was isolated in 16% yield (0.20 mg, 0.52 µmol: As the amount of 7–O was too small to be accurately weighed, we determined the isolated yield based on the absorbance at 394 nm in CH₂Cl₂). The compound 12’ was gradually decomposed in the reaction mixture, and no isolable product was obtained in the reaction of 1N’. In some cases, 1,4-benzoquinone (3.3 µmol, in 30 µL of CDCl₃) or an additional 1S (1.6 µmol, in 0.32 mL of CDCl₃/THF-d₈ = 14/1) were added to the reaction mixture (see text).

**X-ray Crystallography.** Single crystals suitable for X-ray analysis were grown from CH₂Cl₂–MeOH (for 1N, 6–O, and S5) or from CH₂Cl₂ (for 7–O). X-ray crystallographic measurements were made on a Rigaku Saturn CCD area detector with graphite
monochromated Mo-Kα radiation (0.71070 Å) at –150 °C. The data were corrected for Lorentz and polarization effects. The structures were solved by using direct methods\textsuperscript{47} and refined by full-matrix least squares techniques against $F^2$ using SHELXL-97.\textsuperscript{48} The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model.

**Density Functional Theory (DFT) Calculations on Model Compounds.** The structures of model compounds were optimized using density functional theory (DFT). The basis set used was 6-311G(d,p).\textsuperscript{49} The functionals of DFT was the Becke 1988 exchange and Lee-Yang-Parr correlation functionals (B3LYP).\textsuperscript{50} The nucleus independent chemical shift (NICS) values\textsuperscript{51} were calculated at the Hartree-Fock level with gauge-including atomic orbitals (GIAOs) at the DFT optimized structures. The basis set used in the NICS value computations was 6-31+G(d).\textsuperscript{52} All the calculations were carried out using the Gaussian 03 suite of programs.\textsuperscript{53} In the optimized structures of model compounds except for 1S-m, the P-phenyl group is parallel to the P–X axis (X = NH, S). In the optimized structure of 1S-m, the P-phenyl ring is found to be vertical to the P–S axis.\textsuperscript{23a} However, the difference in energy between the optimized structure and the structure in which the P-phenyl ring is rotated by 90 degrees (i.e. the P-phenyl ring is parallel to the P–S axis) is very small (1.87 kcal mol$^{-1}$). Thus, the binding for the P-phenyl ring rotation is considered to be very weak. In this paper, the parallel structure was used for discussion.
Appendix

A: NMR Data for Intermediates

Figure A1. \(^1\)H NMR peak assignments for the intermediates in the reactions of 1N, 1N' and 1S with \(\text{H}_2\text{O}_2\). a) 1N–O, b) 1N'O, and c) 1S–O.

Table A1. \(^1\)H and \(^{31}\)P Chemical Shifts of Intermediate 18\(\pi\) P-oxo Porphyrins 1X–O (X = N, N', S)

<table>
<thead>
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<th>Porphyrins</th>
<th>(\delta_{\text{t}}/\text{ppm})</th>
<th>(\delta_{\text{p}}/\text{ppm})</th>
<th>(\Delta\delta_{\text{t}}/\text{ppm})</th>
<th>(\Delta\delta_{\text{p}}/\text{ppm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N–O</td>
<td>7.90–8.11, 5.74, 2.47–5.76</td>
<td>36.4</td>
<td>0.45–0.64, 6.33(^b), 0.04–0.08</td>
<td>+38.9</td>
</tr>
<tr>
<td>1N'O–O</td>
<td>7.79–7.98, 6.74, 2.85–5.88</td>
<td>21.8</td>
<td>0.42–0.64, 6.79(^b), 0.13–0.33</td>
<td>+54.4</td>
</tr>
<tr>
<td>1S–O</td>
<td>6.33–6.74, - , 7.45–7.94</td>
<td>43.8</td>
<td>1.93–2.60, - , 1.8 –5.6</td>
<td>+25.2</td>
</tr>
</tbody>
</table>

\(^a\) Sifts from the corresponding \(\sigma^3\)-P porphyrins 1X (X = N, N', S): upfield shifts for the outer (i.e. pyrrole-\(\beta\)) protons, and downfield shifts for the inner (i.e. NH and P-Ph) protons. \(^b\) The considerably upfield shifts for the NH protons of 1X–O (X = N, N') as compared with those of 1X are explained not only by diminished ring current effect but also hydrogen bonding effect with the P-oxo moiety.
Figure A2. $^1$H NMR peak assignments for the intermediates in the reactions of 1N, 1N' and 1S with H$_2$O$_2$. a) 12, b) 12', and c) IM: As shown in the lower spectrum, the signals of the NH protons at $\delta$ 10.1 and 4.28 ppm disappeared when a few drops of D$_2$O were added to the reaction mixture.
B: Detailed Discussion on the Reactions of 1X (X = N, N', S) with H₂O₂

Scheme A1. Plausible Mechanism for the Reaction of 1N with H₂O₂

Based on the results of the NMR monitoring (Figures A3a and A4), we would like to propose the following reaction mechanism for the reaction of 1N with H₂O₂ (Scheme A1). First, the P-oxygenation of 1N proceeds rapidly (within 5 min) to give the initial product 1N-O, a part of which tautomerizes to produce compound 12 to relieve an electrostatic repulsion between the P=O moiety and two N-lone pairs at the core. Subsequently, disproportionation reaction, namely a coupled 2e-oxidation/2e-reduction, takes place from an...

Figure A3. Time course of the reaction of P,X,N₂-porphyrins with H₂O₂. (a) 1N, (b) 1N: 1,4-benzoquinone was added at 2 min, (c) 1N', (d) 1S, and (e) 1S: additional 1S (50 mol % of initial amount) was added at 50 min.
**Figure A4.** $^1$H NMR monitoring experiments of the reactions between P,N$_3$-porphyrin 1N (3.3 mmol) and H$_2$O$_2$ (30 wt%, 3.6 mmol) in CDCl$_3$/THF-d$_8$ (total 0.64 mL; v/v = 14/1) with 1,1,2,2-tetrachloroethane as an internal standard; 1N (open red circle), 1N–O (pink circle), 12 (brown circle), IM (light blue circle), and 6–O (purple circle); Asterisk (*) indicates the peaks of residual solvents.

**Figure A5.** $^1$H NMR monitoring experiments of the reactions between P,N$_3$-porphyrins 1N (3.3 mmol) and H$_2$O$_2$ (30 wt%, 3.6 mmol) in CDCl$_3$/THF-d$_8$ (total 0.64 mL; v/v = 14/1) with 1,1,2,2-tetrachloroethane as an internal standard. After 2 min, 1,4-benzoquinone (3.3 mmol) was added to the reaction mixture; 1N (open red circle), 1N–O (pink circle), 12 (brown circle), and 6–O (purple circle); Asterisk (*) indicates the peaks of residual solvents.
equilibrium mixture of 1N−O and 12 to produce a pair of the 22π P-oxo porphyrin 6−O (oxidized form) and intermediate IM (reduced form).\textsuperscript{55,56} Compound IM is slowly oxidized under the reaction conditions to afford 6−O as the final product. This mechanism is supported by the fact that the 2e-reduced intermediate IM was not detected when 1,4-benzoquinone (ca. 1.0 eq for 1N−O) was added as an external oxidant immediately after the consumption of 1N (2 min after the addition of H$_2$O$_2$). In this case, all of 1N−O and 12 were converted to 7−O within 30 min (Figures A3b and Figure A5).

\textit{Scheme A2.} Plausible Mechanism for the Reaction of 1S with H$_2$O$_2$

Based on the results of the NMR monitoring (Figures A3d and A6), the author would like to propose the following reaction mechanism for the reaction of 1S with H$_2$O$_2$ (Scheme A2). The P-oxygenation of 1S gives 1S−O as the initial product. In this case, the formation of a tautomer like 13 is inhibited probably because such an intermediate is not stabilized sufficiently by one hydrogen-bond at the core. Instead, the 2e-reduction of 1S−O proceeds to afford the final product 7−O accompanied by the gradual decomposition of 1S−O.\textsuperscript{40} The author assume sthat the 1S, which is remained in the early period (0−10 min), might work as the 2e-reductant for 1S−O. In fact, the formation of 7−O was stopped after 1S was consumed (Figure A3d). To verify this hypothesis, an additional 1S (50% of the initial amount) was added to the reaction mixture after 50 min from the addition of H$_2$O$_2$ (Figures A3e and A7). As 1S was gradually consumed, the amount of 7−O was increased with the amount of 1S−O almost kept stand. This result strongly suggests that 1S reduces 1S−O to afford 7−O with 1S itself oxidized to 1S−O (Scheme A2).
Figure A6. $^1$H NMR monitoring experiments of the reactions between P,S,N$_2$-porphyrin 1S (3.3 mmol) and H$_2$O$_2$ (30 wt%, 3.6 mmol) in CDCl$_3$/THF-$d_8$ (total 0.64 mL; v/v = 14/1) with 1,1,2,2-tetrachloroethane as an internal standard; 1S (open red circle), 1S−O (pink circle) and 7−O (green circle); Asterisk (*) indicates the peaks of residual solvents.

Figure A7. $^1$H NMR monitoring experiments of the reactions between P,S,N$_2$-porphyrin 1S (3.3 mmol) and H$_2$O$_2$ (30 wt%, 3.6 mmol) in CDCl$_3$/THF-$d_8$ (total 0.64 mL; v/v = 14/1) with 1,1,2,2-tetrachloroethane as an internal standard. After 50 min, an additional 1S (1.0 mg, 1.7 mmol) was added to the reaction mixture; 1S (open red circle), 1S−O (pink circle), and 7−O (green circle); Asterisk (*) indicates the peaks of residual solvents.
C: X-Ray Structure and UV-Vis Absorption Spectrum of S5

**Figure A8.** Top and side views of S5. (30% probability ellipsoids). Hydrogen atoms are omitted for clarity: gray (C), blue (N), red (O), orange (P), yellow (S).

**Figure A9.** UV-vis absorption spectrum of S5 in CH$_2$Cl$_2$. 
References and Footnotes


(27) After the preliminary results were published (ref. 23a), the author noticed that a small amount of $^{17}$O was also isolable beside $^{13}$S.


(29) Phosphorus-31 chemical shifts of phospholes are sensitive to the substituents on the phosphorus atom and $\beta$-carbons. Since the author has no data about $^{31}$P chemical shifts of P-oxo calixphyrins and the $C_4$-bridge type calixphyrins, the $^{31}$P chemical shifts of the $C_n$-bridge type P($E$),$X,N_2$-porphyrins ($n = 3, 4$; $E =$ lone pair, O, S; $X = N, S$) are compared with those of the corresponding porphyrinogens.

(30) In the previous reports (ref. 23), the author underestimated the molar absorbance coefficients ($\varepsilon$) for $^{13}$N and $^{13}$S owing to their gradual decomposition during sample preparation. Therefore, the samples for the UV-vis measurement of $^{13}X$ were prepared quickly under very weak light and re-measured. We checked that the spectra did not change under the measurement conditions.

(31) Delaere and Nguyen performed TD-DFT calculations on P,N$_3$-porphyrin $^{13}$N(H)-m at the B3LYP/SV(P) level, and predicted the red-shifts of the Soret and Q bands by 18–23 nm and 16–26 nm, respectively, as compared to those of N$_4$-porphyrin $^{10}$-m (see ref. 18).

(32) In ref. 18, Delaere and Nguyen calculated the optimized structure and orbital energies of $^{13}$N(H)-m at the B3LYP/6-31G* and B3LYP/SV(P) levels, respectively. The orbital energies reported by these authors are as follows: $-5.88$ (HOMO–2), $-5.50$ (HOMO–1), $-5.47$ (HOMO), $-2.69$ (LUMO), and $-2.44$ eV (LUMO+1).


(35) The peripheral and P-phenyl protons of $1X-O$ ($X = N, N', S$) are upfield-shifted and downfield-shifted, respectively, as compared with those of $1X$ ($X = N, N', S$), suggesting that $1X-O$ form more deviated structures than $1X$. See, Table A1 in Appendix.

(36) This type of tautomerization from $\sigma^4$-phospholes to $\sigma^4$-phospholenes was reported for the C$_4$-bridge type 2,5-diaarylphosphole-P-sulfides. Nyulászi, L.; Hollóczki, O.; Lescop, C.; Hisler, M.; Réau, R. Org. Biomol. Chem. 2006, 4, 996–998.

(37) DDQ oxidation of the P,O,N$_2$-type porphyrinogen-P-sulfide $5O-S$ gave an unexpected N–C fused macrocyclic product ($S5$). For details, see Experimental Section.

(38) Isophlorins have an intrinsic nature to undergo 2e-oxidation (aromatization to 18π structure) under ambient conditions. See, ref. 6.

(39) On the basis of the time course of the reaction (Figures A3a and A4 in Appendix) and the result of an independent experiment (Figures A3b and A5 in Appendix), the author presumes that a coupled 2e-oxidation/2e-reduction between $12$ and $1N-O$ takes place to produce equimolar amounts of $6-O$ (oxidized form) and an unidentified intermediate (reduced form; denoted as $1M$ in Figures A3 and A4). Compound $1M$ (not shown in Figure 7b) was slowly oxidized in situ to afford $6-O$ (Scheme A1 in Appendix). For details, see Appendix B.

(40) Deducing from the reduction potentials of $1S$ ($E_{\text{red,1}} = -1.36$ V, $E_{\text{red,2}} = -1.56$ V), $1N$ ($-1.51$ V, $-1.74$ V) and $1N'$ ($-1.52$ V, $-1.72$ V), $1S-O$ should have higher electron affinity than $1N-O$ and $1N'-O$.

(41) On the basis of the time course of the reaction (Figures A3d and A6 in Appendix) and the result of an independent experiment (Figures A3e and A7 in Appendix), the author presumes that unreacted $1S$ reduces $1S-O$ to $7-O$ and is transformed to $1S-O$ (Scheme A2 in Appendix). Indeed, the addition of $1S$ to a solution containing $1S-O$ produces $7-O$ quantitatively. For details, see Appendix.

(42) The reference S,N$_3$-porphyrin $2N$ does not react with H$_2$O$_2$ even under more harsh conditions (ca. 100 equiv of H$_2$O$_2$, 24 h).


(44) The phosphorus atom deviates from the respective mean π planes by 0.30 Å (for $1N$-m), 1.16 Å (for $6-O$-m), 1.35 Å (for $6-S$-m), and 1.24 Å (for $7-O$-m), and the P–C(Ph) bond axis slants against the plane by 84.7° (for $1N$-m), 116.4° (for $6-O$-m), 135.2° (for $6-S$-m), and 113.9° (for $7-O$-m).


(55) **IM**: δ\textsubscript{p} 44.5 ppm

(56) Owing to the instability together with the inevitable coexistence of **6−O**, the author could not thoroughly characterize the intermediate **IM**. On the basis of the time courses of the reaction shown in Figures A3a and A3b, it is plausible that the intermediate **IM** has a reduced structure (i.e. +2e as compared to **1N−O/12**).
Chapter 5

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

Abstract: Core-modified isophlorin–metal complexes were successfully prepared by redox-coupled complexation of P,S,N$_2$-hybrid porphyrin with zerovalent palladium, nickel, and platinum. In this transformation, 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. The isolated Pd and Pt complexes are chemically stable under ambient conditions. The Pd–P,S,N$_2$ isophlorin complex was structurally characterized by X-ray crystallography, which revealed a distorted 20π plane with a square planar palladium(II) center. Experimental ('H NMR, UV-vis, and X-ray) and theoretical (DFT calculations) results suggest that the P,S,N$_2$-isophlorin–metal complexes possess nonaromaticity in terms of both magnetic and geometrical criteria.
1. Introduction

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. 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] and a diboranyl isophlorin complex [B_2(TTP); TPP: tetraanion of tetra-p-tolylporphyrin], respectively, by 2e-reduction of the corresponding metalloporphyrins and disclosed their antiaromatic character on the basis of experimental and theoretical results. 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. We anticipated that replacement of pyrrole nitrogens with other heteroatoms, namely core-modification, would bring chemical stability to isophlorin complexes by alternating the coordinating abilities, charges, and redox properties of their 20π macrocyclic platforms. This Chapter describes 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. The structure and the aromaticity of P,S,N_2-isophlorin–Pd and –Pt complexes are also examined.

2. Results and Discussion

Scheme 1. Synthesis of P,S,N_2-Isophlorin–Metal Complexes 3M

In this study, the author used P,S,N_2-hybrid 1 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. When treated with 1 equiv of Pd(dba)_2 (dba = dibenzalacetone) in CH_2Cl_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,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) (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 (J_P,H = 37.6 Hz), 5.58–6.13, and 7.65–8.37 ppm, respectively, and they are upfield-shifted (Δδ = −4.4 to −2.5 ppm for meso, β) or downfield-shifted (Δδ = +6.1 to +2.4 ppm for P-phenyl) as compared to the corresponding protons of 1 (Figure 1b). The slight differences

![Figure 1](image-url)

Figure 1. ¹H NMR spectra (δ 5.4–8.7 ppm) of (a) 3Ni in CD₂Cl₂, (b) 3Pd in CDCl₃, and (c) 3Pt in CDCl₃ (400 MHz). Asterisk (*) indicates the peak of CHCl₃. Values in blue and red are differences in chemical shifts (ppm) from the respective peaks of 1.
in chemical shifts among 3Ni, 3Pd, and 3Pt imply that the central metal does not perturb the ring current effect in 3M dramatically (Figure 1).\textsuperscript{13} In the 31P{1H} NMR spectra, a singlet (3Ni and 3Pd) or doublet (3Pt, \textit{J}_{P,P} = 3190 Hz) peak appears at \( \delta 35.1-61.9 \) ppm, and it is deshielded relative to the \( ^{31}\text{P} \) peak of 1 (\( \delta 18.6 \) ppm). These data show that 3M essentially possesses nonaromatic character.

The crystal structure of 3Pd was unambiguously elucidated by X-ray diffraction analysis.\textsuperscript{14} As shown in Figure 2a, 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 Å and 0.93 Å, respectively, from the mean \( \pi \) plane composed of the peripheral 20 carbon atoms (Figure 2b). The Pd–X (X = N, S) bond lengths are very close to those observed for a square planar Pd(II)–P,S,N\textsubscript{2}-hybrid calixphyrin complex,\textsuperscript{15} and the peripheral C–C bond alternation well explains the 20\( \pi \) valence-bond structure for the P,S,N\textsubscript{2}-hybrid ligand (Figure 2c). These data suggest that oxidation states of the metal center and the hybrid \( \pi \) ligand in 3Pd are +2 and −2, respectively. The whole structure of 3Pd differs considerably from the structures of ruffled Si(TPP)(THF)\textsubscript{2}\textsuperscript{5a} and Ge(TPP)(py)\textsubscript{2}\textsuperscript{7} and planar \textit{meso}-pentafluorophenyl core-modified O\textsubscript{2} and O\textsubscript{2},S\textsubscript{2}-isophlorins,\textsuperscript{4} all of which were reported to be antiaromatic. Variable-temperature \( ^{1}\text{H} \) NMR measurement of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Top and (b) side views of 3Pd. Hydrogen atoms and \textit{meso}-phenyl groups 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).}
\end{figure}
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 $\lambda_{\text{max}}$ 375–414 nm and no detectable Q bands (Figure 3a), which is characteristic of highly ruffled, nonaromatic 4nπ porphyrinoids. The electrochemical oxidation processes of 3Pd occurred reversibly at −0.26 V and +0.06 V vs Fc/Fc⁺ (Figure 4a). 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. As shown in Figures 3b and 4b, the Pt complex 3Pt exhibited similar optical and electrochemical properties ($\lambda_{\text{max}}$ 312–407 nm; $E_{\text{ox}}$ = −0.24 V and +0.07 V).

To gain a deeper insight into the aromaticity of the P,S,N₂-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 Experimental Section). As indicated in Figures 5 and 6, 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 1). 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 (18.9–19.7) and close to zero, suggesting that the 20π P,S,N,colorful-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, 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,N, and Mg–P,S,N complexes (Pd–S,N-m and Mg–P,S,N-m) as references (Figures 7 and 8). At the optimized structures, Pd–S,N-m shows a NICS value of −0.12, whereas Mg–P,S,N-m displays positive NICS values of +2.66 and +3.03. These results imply that the lack of paratropic ring currents in the NI–, Pd–, and Pt–P,S,N complexes is due in a part to the central group 10 metals.

<table>
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<sup>a</sup> For directions of x, y, z axes, see Figures 5 and 6. <sup>b</sup> Data from ref. 31.

**Table 1. Natural Atomic Orbital Occupancies of d Orbitals for 3M-m and a Pd(II) Reference**

**Figure 5.** The results of DFT calculations for 3Pd-m. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, P, S, and Pd atoms are indicated as gray, light blue, blue, orange, yellow, and indigo balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg). (c) NICS values at the center of two adjacent heterole rings.
Figure 6. The results of DFT calculations for 3Pt-m. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, P, S, and Pt atoms are indicated as gray, light blue, blue, orange, yellow, and indigo balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg). (c) NICS values at the center of two adjacent heterole rings.

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<th>Bond Description</th>
<th>Value (Å)</th>
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<td>S–Pt–N²</td>
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Figure 7. The results of DFT calculations for Pd–S₂,N₂-m. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, S, and Pd atoms are indicated as gray, light blue, blue, yellow, and indigo balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg).

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Figure 8. The results of DFT calculations for 3Mg-m. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, P, S, and Mg atoms are indicated as gray, light blue, blue, orange, yellow, and gold balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg). (c) NICS values at the center of two adjacent heterole rings.

<table>
<thead>
<tr>
<th>Bond Description</th>
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<td>Mg–N</td>
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To evaluate the coordinating ability of 1, we next calculated heat of formation of 3Pd-m by the DFT method. As shown in Scheme 2, 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 S₂N₂-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 18$\pi$ porphyrin ring and stabilizing the 20$\pi$ 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 20$\pi$ system from −4 to −2. Thus, 3M are regarded as neutral M(II) complexes.

**Scheme 2. Heat of Formation of 3Pd-m and Pd–S₂N₂-m Calculated by DFT Method**

3. Conclusion

In conclusion, it have been revealed that isophlorin–metal complexes are readily accessible by redox-coupled complexation of P,S,N₂-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 18$\pi$ porphyrin ring efficiently. The experimental and theoretical results represent that the P,S,N₂-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$n\pi$ porphyrids.
Experimental Section

General. $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra were measured in CDCl$_3$ or CD$_2$Cl$_2$. Chemical shifts are reported as the relative value vs. tetramethylsilane ($^1$H, $^{13}$C) and H$_3$PO$_4$ ($^{31}$P), respectively. MALDI-TOF and HR-FAB-MS mass spectra were measured using CHCA and 3-nitrobenzyl alcohol as matrices, respectively. Electrochemical measurements were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ [0.01 M AgNO$_3$, 0.1 M nBu$_4$NPF$_6$ (MeCN)] reference electrode. The potentials were calibrated with ferrocenium/ferrocene [$E_{\text{mid}}$ = +0.20 V vs Ag/AgNO$_3$]. Dichloromethane, 1,2-dichlorobenzene, and hexane were distilled from CaH$_2$ before use. The P,S,N$_2$-hybrid porphyrin 1 was prepared according to the reported procedure.$^{11}$ The S$_2$N$_2$-hybrid porphyrin 2 was prepared starting from 2,5-difunctionalized thiophene 4$^{21}$ (Scheme E1: for details, see below). Other chemicals and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F$_{254}$ (Merck). Gravity column chromatography was carried out using Silica gel or Alumina in open air.

Scheme E1. Synthesis of S$_2$N$_2$-Porphyryn 2

Synthesis of Diol 5. To a solution of 4 (1.0 g, 3.7 mmol) in 40 mL of hexane was added a hexane solution of DIBAH (1.0 M, 16 mL, 16 mmol) at –78 °C, and the reaction mixture was allowed to warm slowly to room temperature. A saturated NH$_4$Cl solution (10 mL) was then added at 0 °C, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic extracts were treated with brine (50 mL), dried over Na$_2$SO$_4$, and evaporated to give a crude product, which was recrystallized from CH$_2$Cl$_2$ to afford 5 (470 mg, 69%) as a colorless solid. Mp 108–110 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.59 (t, $J$ = 5.4 Hz, 133
2H), 2.37 (quin, J = 6.8 Hz, 2H), 2.63 (t, J = 6.8 Hz, 4H), 4.67 (d, J = 5.4 Hz, 4H); 13C{1H} NMR (CDCl3, 100 MHz) δ 26.3, 31.1, 58.7, 131.2, 146.9; HR-FAB-MS: Calcd for C9H12O2S [M’], 184.0558; Found, 184.0556. Anal. Calcd for C9H12O2S: C, 58.67; H, 6.56. Found: C, 58.57; H, 6.54.

Synthesis of S2N2-Porphyrin 2. A solution of 5 (430 mg, 2.3 mmol) and 622 (910 mg, 2.3 mmol) in CH2Cl2 (700 mL) was bubbled with N2 for 15 min, and BF3•OEt2 (0.12 mL, 0.92 mmol) was added to the mixture. After stirring for 10 min, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (1.57 g, 6.9 mmol) was added to the mixture. After stirring for an additional 20 min, the reaction mixture was condensed, and subjected to alumina column chromatography (CH2Cl2). A greenish yellow band was collected, evaporated, and recrystallized from CH2Cl2/MeOH to give 2 as a purple solid (54 mg, 4.4%). Mp > 300 °C; 1H NMR (CDCl3, 400 MHz) δ 3.34 (quin, J = 7.3 Hz, 2H), 4.32 (t, J = 7.3 Hz, 4H), 7.80–7.81 (m, 6H), 8.24–8.25 (m, 4H), 8.80 (d, J = 4.4 Hz, 2H), 9.05 (d, J = 4.4 Hz, 2H), 9.71 (s, 2H), 10.54 (s, 2H); 13C{1H} NMR (CDCl3, 75 MHz) δ 29.3, 30.2, 115.9, 127.4, 128.0, 133.99, 134.04, 134.2, 135.01, 135.04, 141.3, 141.4, 147.6, 155.5, 155.8, 156.2; UV/Vis (CH2Cl2) λmax (ε): 426 (188000), 472 (6100), 505 (27200), 531 (4000), 619 (2200), 682 (3400); HR-FAB-MS: Calcd for C9H12N2S2 [M’], 536.1381; Found, 536.1371.

Synthesis of 3Pd. To a Schlenk tube containing 1 (10 mg, 0.016 mmol) and Pd(dbach)2 (9.2 mg, 0.016 mmol) was added 1 mL of CH2Cl2. After stirring for 5 min, the resulting mixture was dried in vacuo and subjected to short alumina column chromatography (CH2Cl2). The fraction of Rf = ~1 (pale green band) was collected and washed with MeOH to give 3Pd as a dark green solid (11 mg, 95%). Mp > 300 °C; 1H NMR (CDCl3, 400 MHz) δ 2.02–2.26 (m, 6H), 5.58 (s, 2H), 5.72 (d, J = 3.7 Hz, 2H), 6.01 (d, 3JpH = 37.6 Hz, 2H), 6.13 (d, J = 3.7 Hz, 2H), 7.15–7.30 (m, 10H), 7.62–7.70 (m, 3H), 8.32–8.37 (m, 2H); 31P{1H} NMR (CDCl3, 162 MHz) δ 61.9; UV-vis (CH2Cl2) λmax (ε): 375 (39400), 394 (40000), 414 (45600); HR-FAB-MS: Calcd for C41H26N2Pd [M’], 718.0824; Found, 718.0823.

Synthesis of 3Ni. To a Schlenk tube containing 1 (5.0 mg, 8.2 μmol) and Ni(cod)2 (6.9 mg, 0.025 mmol) was added 1 mL of CH2Cl2. After stirring for 10 min, the resulting mixture was dried in vacuo. The crude product was extracted with CH2Cl2 and filtered, followed by reprecipitation from hexane to give 3Ni as a dark yellow solid (ca. 4 mg, ca. 80%). As 3Ni gradually decomposed in solution, we could not isolate it in a pure form. 1H NMR (CD2Cl2, 400 MHz) δ 2.10–2.29 (m, 6H), 5.77 (s, 2H), 5.79 (d, J = 3.4 Hz, 2H), 6.19 (d, 3JpH = 36.2 Hz, 2H), 6.19 (d, J = 3.4 Hz, 2H), 7.18–7.25 (m, 4H), 7.26–7.36 (m, 6H), 7.57–7.62 (m, 2H), 7.63–7.68 (m, 1H), 8.09–8.15 (m, 2H); 31P{1H} NMR (CD2Cl2, 162 MHz) δ 61.8; HR-FAB-MS: Calcd for C41H26Ni2PS [M’], 670.1143; Found, 670.1142.
Synthesis of 3Pt. To a Schlenk tube containing 1 (4.9 mg, 8.0 \( \mu \)mol) and Pt(dba)\(_2\) (53 mg, 0.080 mmol) was added 2 mL of 1,2-dichlorobenzene. After stirring for 2 h at 60 °C, the resulting mixture was dried in vacuo at 60 °C and subjected to silica gel column chromatography (CH\(_2\)Cl\(_2\)). The fraction of \( R_t = 0.9 \) (green band) was collected and washed with MeOH to give 3Pt as a dark green solid (2.5 mg, 39%). \( \text{Mp} > 300 ^\circ\text{C} \); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta 2.00–2.28 \) (m, 6H), 5.58 (s, 2H), 5.65 (d, \( J = 3.7 \) Hz, 2H), 5.80 (d, \( J_{\text{P, H}} = 37.1 \) Hz, 2H), 6.03 (d, \( J = 3.7 \) Hz, 2H), 7.15–7.30 (m, 10H), 7.68–7.73 (m, 3H), 8.38–8.42 (m, 2H); \(^{31}\)P\(^{1}\)H) NMR (CDCl\(_3\), 162 MHz) \( \delta 35.1 \) (\( J_{\text{P, P}} = 3190 \) Hz); UV-vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}} (\epsilon) \): 312 (29300), 407 (44800); HR-FAB-MS: Calcd for C\(_{41}\)H\(_{29}\)N\(_2\)PSPt [\( M^+ \)], 807.1437; Found, 807.1432.

Attempts to Synthesize Pd–S\(_2\)N\(_2\) Complex. We attempted to prepare Pd–S\(_2\)N\(_2\) complex by the following two procedures: (A) To a Schlenk tube containing 2 (2.1 mg, 0.0039 mmol) and Pd(dba)\(_2\) (2.2 mg, 0.0039 mmol) was added 1 mL of CH\(_2\)Cl\(_2\). After stirring for 1 h, the resulting mixture was dried in vacuo. (B) To a Schlenk tube containing 2 (1.7 mg, 0.0032 mmol) and Pd(dba)\(_2\) (5.5 mg, 0.0096 mmol) was added 1 mL of 1,2-dichlorobenzene. After stirring for 5 h at 180 °C, the resulting mixture was dried in vacuo. In both cases, however, Pd–S\(_2\)N\(_2\) complex was not obtained at all, and free base 2 was recovered (>90%) after alumina column chromatography (CH\(_2\)Cl\(_2\)).

X-ray Crystallographic Analysis of 3Pd. Single crystals were grown from CH\(_2\)Cl\(_2\)–MeOH at room temperature. The X-ray crystallographic measurement was made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K\(\alpha\) radiation (0.71070 Å) at –150 °C. The data were corrected for Lorentz and polarization effects. The structures were solved by using direct methods\(^{23}\) and refined by full-matrix least squares techniques against \( F^2 \) using SHELXL-97.\(^{24}\) The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model.

Density Functional Theory (DFT) Calculations on Model Compounds. The structures of 3Pd-m, 3Pt-m, 1-m,\(^{11}\) and 2-m (not shown), as models for 3Pd, 3Pt, 1, and 2, respectively, were optimized using DFT. The structure of an imaginary Pd–S\(_2\)N\(_2\) and Mg–P,S,N\(_2\) isophlorin complexes (Pd–S\(_2\)N\(_2\)-m and 3Mg-m) were also calculated. The basis sets used were 6-31G(d,p)\(^{25}\) for H, C, N, Mg, P, and S atoms and LANL2DZ\(^{26}\) for Pd and Pt atoms. The functionals of DFT was the Becke 1988 exchange and Lee-Yang-Parr correlation functionals (B3LYP).\(^{27}\) The nucleus independent chemical shift (NICS) values\(^{28}\) were calculated at the Hartree-Fock level with gauge-including atomic orbitals (GIAOs) at the DFT optimized structures. The basis set used in the NICS value computations was 6-31+G(d).\(^{25,29}\) The optimized structures of 3Pd-m, 3Pt-m, Pd–S\(_2\)N\(_2\)-m, and 3Mg-m are depicted in Figures
5(a), 6(a), 7(a), and 8(a), respectively, and their bond lengths and angles are shown in Figures 5(b)–8(b). The NICS values at the center of two adjacent heterole rings are depicted in Figures 5(c)–8(c). The natural atomic orbital (NAO) occupancies\(^\text{30}\) for \(d\) orbitals of \(\text{3Pd-m}\) and \(\text{3Pt-m}\) are listed in Table 1 together with those of a Pd(II) reference.\(^\text{31}\) In the estimation of the heat of formation of \(\text{3Pd-m}\) and \(\text{Pd-S\textsubscript{2}N\textsubscript{2}-m}\), the energies of Pd(dba)\(_2\) and dba were calculated at the same level of the functional and basis sets used for \(\text{3Pd-m}\) and \(\text{Pd-S\textsubscript{2}N\textsubscript{2}-m}\). All the calculations were carried out using the Gaussian 03 suite of programs.\(^\text{32}\)
References and Footnotes


(8) For 20π Si(IV) and Ge(IV) phthalocyanines, see: Cissell, J. A.; Vaid, T. P.; DiPasquale, A. G.; Rheingold, A. L. Inorg. Chem. 2007, 46, 7713.


(13) As descended from Ni to Pd to Pt, the peripheral protons of 3M slightly shift to upfield ($\Delta \delta = 0.08$–$0.43$ ppm), and the P-phenyl-ortho protons slightly shift to downfield ($\Delta \delta =
138

0.34 ppm).

(14) C_{41}H_{29}N_2PPdS, MW = 719.09, monoclinic, P2_1/n, a = 9.352(3) Å, b = 17.763(5) Å, c = 18.934(6) Å, β = 102.440(5)°, V = 3071.4(17) Å³, Z = 4, D_c = 1.555 g cm⁻³, 6950 observed, 416 variables, R_w = 0.1061, R = 0.0528 (I > 2.00σ(I)), GOF = 1.010.


(17) Redox potentials were measured in CH₂Cl₂ with 0.1 M nBu₄N⁺PF₆⁻; Ag/Ag⁺ [0.01 M AgNO₃ (MeCN)].

(18) Conformation-induced loss of paratropicity was observed for a highly ruffled β-trifluoromethyl-substituted N₄-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 attributed to difference in their oxidizing abilities: the first and second reduction potentials of 1 (−1.35 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⁺).


Remarkable Effects of P-Perfluorophenyl Group on the Synthesis of Core-Modified Phosphaporphyrinoids and Phosphadithiasapphyrin

Abstract: P,X,N₂-type phosphaporphyrins and phosphacalixphyrins (X = N, S) bearing a perfluorophenyl (C₆F₅) group at the core phosphorus atom were prepared in high overall yield from 1-perfluorophenyl-2,5-di(ethoxycarbonyl)phosphole as a common starting material. In addition, P–C₆F₅ P,S₂,N₂-type sapphyrin was successfully prepared as the first example of ring-expanded phosphorus-containing porphyrin.
1. Introduction

Core modification of porphyrins, namely, replacement of the core pyrrolic nitrogen atom by another heteroatom or carbon, has been known as a powerful tool to alter their optical/electrochemical properties and coordinating ability drastically. Recently, we prepared the first examples of phosphorus-containing core-modified porphyrins $1X$ and calixphyrins $2X$ (Figure 1) and disclosed their characteristic optical and electrochemical properties, coordinating behavior, and reactivity. For instance, $P,X,N_2$-porphyrins $1X$ were found to possess considerably small HOMO–LUMO gaps as compared with $N_4$- and $S,X,N_2$-porphyrins ($X = N, S$), and the $18\pi$-systems of $1X$ were easily reconstructed by complexation with zerovalent group 10 metals and $P$-oxidation with $H_2O_2$, affording unique $20\pi$ and/or $22\pi$ systems. While these properties and reactivities of phosphaporphyrins are of interest, there were distinct drawbacks for the synthesis due to the high reactivity of a $\sigma^3$-phosphorus atom. First, $P$-masking/demasking steps are necessary in the synthesis of $1X$ and $2X$, which increases the number of reaction steps. Second, $P$-oxidation inevitably occurs in the ring oxidation of $\sigma^3$-$P$ porphyrinogens to give significant amounts of $P$–oxo side products, which severely reduces the yield of target porphyrins $1X$. A possible solution to these drawbacks is to improve the durability of the $\sigma^3$-phosphorus center under acidic and oxidizing conditions. In this regard, attachment of an electron-withdrawing group onto the phosphorus atom is a highly promising approach.

This Chapter describes the synthesis of $P,X,N_2$-porphyrins $1XF$ and $P,X,N_2$-calixphyrins $2XF$ ($X = N, S$) bearing a perfluorophenyl ($C_6F_5$) group at the core phosphorus atom. Notably, the introduction of $C_6F_5$ group improves the chemical stability of the $\sigma^3$-phosphorus center dramatically, and both $1XF$ and $2XF$ are readily available in high overall yield from a common starting material. Moreover, $P,S_2,N_2$-sapphyrin, the first example of $P$-containing expanded porphyrin, was successfully prepared by taking advantage of the electron-withdrawing nature of the $C_6F_5$ group.

![Figure 1. $P,X,N_2$-Porphyrins $1X$, $1XF$ and $P,X,N_2$-calixphyrins $2X$, $2XF$ ($X = N, S$).](image-url)
2. Results and Discussion

The P–C₆F₅-type P,X,N₂-porphyrins 1Xᵣ (X = N, S) were prepared starting from 1-perfluorophenyl-2,5-di(ethoxycarbonyl)phosphole 3² by a similar method used for the synthesis of 1X²ᵃᵇᵈ (Scheme 1). Reaction of 3 with diisobutylaluminium hydride (DIBAH) in hexane gave 2,5-di(hydroxymethyl)phosphole 4, which was then treated with excess pyrrole in the presence of BF₃•OEt₂ to afford phosphatripyrrane 5 in 45% yield based on 3.² The BF₃-promoted dehydrative condensation of 5 with 2,5-di[hydroxy(phenyl)methyl]pyrrole 6N⁹ gave σ³-P,N₃-porphyrinogen 7 in 35% yield as a mixture of three diastereomers. In sharp contrast to the corresponding P–Ph analogues, diol 4 and phosphatripyrrane 5 are sufficiently stable against air and acids. Therefore, it is not necessary to protect the σ³-phosphorus center throughout the sequential BF₃-promoted dehydrative condensation reactions from 4 to 7. Finally, the ring oxidation of the porphyrinogen 7 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded target porphyrin 1Nᵣ. In the present synthesis, only trace amounts of P-oxo byproducts were found in the crude reaction mixture, and the yield of 1Nᵣ from 7 (50%) was almost three times larger than that of 1N from the P–Ph-type porphyrinogen (17%).²ᵇᵈ Alternatively, 1Nᵣ can be prepared in a one-pot procedure from 5 and 6N in 15% yield (18% yield for stepwise synthesis). According to a similar procedure,

Scheme 1. Synthesis of C₆F₅-Type P,X,N₂-Porphyrins 1Xᵣ
P,S,N$_2$-porphyrin 1S$_F$ was prepared from 5 and 2,5-di[hydroxy(phenyl)methyl]thiophene 6S$^{10}$ in 8% yield (based on 5).

The P–C$_6$F$_5$-type P,X,N$_2$-calixphyrins 2X$_F$ (X = N, S) were also prepared starting from 3 without P-masking (Scheme 2). Treatment of 3 with excess MeMgBr gave tertiary diol 8 in 29% yield. Dehydrative condensation of 8 with excess pyrrole afforded phosphatripyrrane 9 in 83% yield. The BF$_3$-promoted dehydrative condensation of 9 with 6X (X = N, S) followed by DDQ oxidation afforded P,X,N$_2$-calixphyrins 2N$_F$ and 2S$_F$ in 43% and 17% yields, respectively.

Notably, the overall yields of P–C$_6$F$_5$-type P,X,N$_2$-porphyrins 1X$_F$ and P,X,N$_2$-calixphyrins 2X$_F$ from 3 are increased by 1.5–10 times as compared with those of P–Ph analogues 1X and 2X. In addition, the number of reaction processes is reduced by 1–2 steps.

**Scheme 2.** Synthesis of C$_6$F$_5$-Type P,X,N$_2$-Calixphyrins 2X$_F$

![Diagram of Scheme 2]

Compounds 1X$_F$ and 2X$_F$ were isolated as purple and red solids, respectively, and fully characterized by standard spectroscopic techniques. In the $^{19}$F NMR spectra of 1X$_F$ and 2X$_F$, the ortho, meta, and para $^{19}$F signals of the P–C$_6$F$_5$ group were observed at $\delta_F$ –165.9 to –163.0, –132.7 to –126.4, and –156.8 to –154.3, respectively. The $^1$H NMR spectra of 1X$_F$ and 2X$_F$ essentially resemble those of P–Ph counterparts 1X and 2X. For instance, the pyrrole-β protons of 1N$_F$ appeared at the downfield region ($\delta$ 8.38–8.69) relative to the corresponding protons of 2N$_F$ ($\delta$ 5.93–6.60). Figure 2 summarizes differences in chemical shifts ($\Delta\delta$) of the peripheral (heterole-β) protons between 1X$_F$ and 2X$_F$. Significant diatropic ring current effects ($\Delta\delta = 1.82–2.75$) stemming from the 18π annulene circuit are clearly observed for 1X$_F$. The ring current effects in 1X$_F$ also emerged as upfield resonances of $^{31}$P nucleus (1N$_F$, $\delta_p$ –30.7 vs. 2N$_F$, $\delta_p$ –15.9; 1S$_F$, $\delta_p$ –22.5 vs. 2S$_F$, $\delta_p$ –15.8). It seems that
introduction of the electron-withdrawing C₆F₅ group at the core phosphorus atom perturbs the aromaticity of P,X,N₂-porphyrin π-circuits only slightly.

![Diagram](image)

**Figure 2.** Downfield shifts ($\Delta \delta$) of the $\beta$ protons of 1NF (black) and 1SF (gray) from those of 2NF and 2SF.

The UV-vis absorption spectrum of P,N₂-porphyrin 1NF is similar to that of the P-Ph counterpart 1N (Tables 1 and 2, and Figures 3a,c), whereas both Soret and Q bands of P,S,N₂-porphyrin 1SF were broadened and the Q₀₀ band was red-shifted by ca 60 nm as compared to that of 1S (Table 1 and Figure 3b). The electrochemical properties of 1XF were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Figure 4). The first oxidation potential ($E_{ox,1}$) and the first and second reduction potentials ($E_{red,1}$ and $E_{red,2}$) of 1NF and 1SF determined by DPV are shifted to the negative side compared to the respective potentials of the P-Ph analogues 1X ($\Delta E_{ox,1} = 0.05–0.15 \text{ V}; \Delta E_{red,1} = 0.01–0.06 \text{ V}; \Delta E_{red,2} = 0.08–0.10 \text{ V}$). The replacement of the P-phenyl group with the P-perfluorophenyl group has proven to enhance the electron-accepting ability of the phosphaporphyrin π-systems slightly.

![Graph](image)

**Figure 3.** UV-vis absorption spectra in CH₂Cl₂. (a) 1N (black), 1NF (purple), (b) 1S (black), 1SF (purple), 11 (green), (c) 2NF (red), 2SF (orange).
Table 1. UV-vis Absorption Maxima and Redox Potentials (vs Fc/Fc\(^+\))\(^a,b\) of 1X, 1XF, and 11 in CH\(_2\)Cl\(_2\)

<table>
<thead>
<tr>
<th>Compd</th>
<th>(\lambda_{\text{max}}) (Soret; Q), nm</th>
<th>(E_{\text{ox,1}}, \text{V})</th>
<th>(E_{\text{red,1}}; E_{\text{red,2}}, \text{V})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N(^c)</td>
<td>431; 486, 522, 555, 636, 698</td>
<td>+0.38 (ir)</td>
<td>+0.38 (ir); −1.74 (q-r)</td>
</tr>
<tr>
<td>1S(^c)</td>
<td>440; 492, 518, 547, 647, 718</td>
<td>+0.45 (ir)</td>
<td>+0.45 (ir); −1.56 (q-r)</td>
</tr>
<tr>
<td>1N(_F)</td>
<td>433; 528, 560, 640, 704</td>
<td>+0.53 (ir)</td>
<td>+0.53 (ir); −1.66 (ir)</td>
</tr>
<tr>
<td>1S(_F)</td>
<td>441; 544, 780</td>
<td>+0.50 (ir)</td>
<td>+0.50 (ir); −1.46 (ir)</td>
</tr>
<tr>
<td>11</td>
<td>500; 599, 740, 835</td>
<td>+0.43 (ir)</td>
<td>+0.43 (ir); −1.59 (ir)</td>
</tr>
</tbody>
</table>

\(^a\) Reference electrode: Ag/Ag\(^+\) [0.01 M AgNO\(_3\), 0.1 M \(n\-Bu_4\)NPF\(_6\) (MeCN)]. \(^b\) “r”, “q-r”, and “ir” in parentheses indicate that the processes occur reversibly, quasi-reversibly, and irreversibly. \(^c\) Data from ref 2d.

Table 2. UV-vis Absorption Maxima of 2X\(^a\) and 2XF (X = N, S) in CH\(_2\)Cl\(_2\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{ab}/\text{nm (}\varepsilon/10^3 \text{M}^{-1}\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N</td>
<td>324 (34.4), 503 (23.4), 533 (24.0)</td>
</tr>
<tr>
<td>2S</td>
<td>326 (42.6), 493 (21.2)</td>
</tr>
<tr>
<td>2N(_F)</td>
<td>323 (32.8), 503 (23.2), 536 (25.4)</td>
</tr>
<tr>
<td>2S(_F)</td>
<td>328 (38.6), 493 (19.9)</td>
</tr>
</tbody>
</table>

\(^a\) Data from ref 5b.

Considering rich coordination chemistry of expanded porphyrins,\(^{12}\) the synthesis of phosphorus-containing expanded porphyrins is a challenging subject.\(^{13}\) However, all attempts to prepare expanded phosphaporphyrins from the P–Ph-type phosphatripyrrane have been unsuccessful so far. In this context, the successful result on the synthesis of 1XF was quite encouraging, and the author decided to use P–C\(_5\)F\(_5\)-type phosphatripyrrane 5 as a key precursor for the synthesis of expanded phosphaporphyrins. The first target, P–C\(_5\)F\(_5\)-type phosphadithiasapphyrin 11,\(^{14,15}\) was successfully prepared by the BF\(_3\)-promoted [3+2] dehydrative condensation between 5 and 5,5′- bis[hydroxy(phenyl)methyl]bithiophene 10\(^{16}\) followed by in situ DDQ oxidation (eq 1). It should be emphasized again that P-masking is not involved in the condensation/oxidation steps. The sapphyrin 11 was isolated as an
Figure 4. Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of (a) 1N$_F$, (b) 1S$_F$, and (c) 11. Measured in CH$_2$Cl$_2$; 0.1 M nBu$_4$NPF$_6$, Ag$^+$/Ag (0.01 M AgNO$_3$). Scan rate 20 mV s$^{-1}$. Asterisk (*) indicates ferrocene/ferrocenium couple.

air-stable shiny green solid. The diagnostic spectral features of 11 are as follows. In the $^{19}$F and $^{31}$P NMR spectra, 11 showed three $^{19}$F signals at $\delta_F$ $-165.2$ (ortho), $-128.5$ (meta), and $-155.2$ (para), and one $^{31}$P signal at $\delta_P$ $-28.4$. In the $^1$H NMR spectrum of 11, peripheral (meso, pyrrole-$\beta$, and thiophene-$\beta$) protons resonate significantly downfield ($\delta$ 8.49–10.11), which corroborates the 22$\pi$ aromaticity of 11 (Figure 5). The relatively downfield appearance ($\delta$ 2.90–4.58) of the peripherally fused trimethylene protons of 11 originates from the 22$\pi$ diatropic ring current effect. It is therefore likely that the phosphole ring in 11 takes on a non-inverted conformation as represented schematically in eq 1. This structural feature is in marked contrast to that of previously reported X,S$_2$N$_2$-sapphyrins (X = N, O, S, Se), where the heterocyclic rings opposite to the bithiophene unit take an inverted conformation.$^{15a,b}$ Presumably, in P,S$_2$N$_2$-sapphyrin 11, the trimethylene substituents at the phosphole ring disturb its inversion sterically.$^{17,18}$ The UV-vis absorption spectrum of 11 shows an intense Soret band at $\lambda_{\text{max}}$ 500 nm and weak Q bands at $\lambda_{\text{max}}$ 599–835 nm (Figure 3b), both

Figure 5. $^1$H NMR spectrum of 11 in CDCl$_3$. Asterisks (*) indicate residual solvents.
of which are close to the values reported for the inverted X,S\textsubscript{2},N\textsubscript{2}-sapphryins (Soret: \(\lambda_{\text{max}}\) 490–510 nm, Q: \(\lambda_{\text{max}}\) 600–880 nm).\textsuperscript{15a,b} The redox potentials of 11 determined by DPV were more cathodic in comparision with the respective values of 1S\textsubscript{P} (Table 1 and Figures 4c).

3. Conclusion

In conclusion, it has been revealed that the P–C\textsubscript{6}F\textsubscript{5}-type P,X,N\textsubscript{2}-porphyrins and P,X,N\textsubscript{2}-calixphyrins (X = N, S) can be prepared more easily than their P–Ph analogues. In addition, the first example of phosphorus-containing core-modified sapphyrin was successfully prepared from P–C\textsubscript{6}F\textsubscript{5} phosphatripyrrane as the key precursor. The present results exemplify that the functionalization at the phosphorus atom is a highly promising strategy to bring chemical stability to the phosphaporphyrin skeleton. Studies on the coordination chemistry of this new series of core-modified porphyrin ligands are now in progress.
Experimental Section

General. $^{1}$H, $^{13}$C($^{1}$H), $^{19}$F($^{1}$H), and $^{31}$P($^{1}$H) NMR spectra were measured in CDCl$_3$. Chemical shifts are reported as the relative value vs. tetramethylsilane ($^{1}$H, $^{13}$C), CFCl$_3$ ($^{19}$F), and H$_2$PO$_4$ ($^{31}$P), respectively. MALDI-TOF and HR-FAB-MS mass spectra were measured using CHCA and 3-nitrobenzyl alcohol as matrices, respectively. Electrochemical measurements were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^{+}$ [0.01 M AgNO$_3$, 0.1 M nBu$_4$NPF$_6$ (MeCN)] reference electrode. The potentials were calibrated with ferrocenium/ferrocene [$E_{\text{mid}} = +0.20 \text{ V vs Ag/AgNO}_3$]. Dichloromethane (CH$_2$Cl$_2$), diethyl ether (Et$_2$O), THF, and toluene were distilled from CaH$_2$ (CH$_2$Cl$_2$), toluene) or sodium benzophenone ketyl (Et$_2$O, THF) before use. Other chemicals and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F$_{254}$ (Merck). Gravity column chromatography was carried out using Silica gel or Alumina (neutral or basic) in open air. Starting materials C$_6$F$_5$PCl$_2$, $^{19}$6N, $^{9}$6S, $^{10}$10, and S1$^{20}$ were prepared according to the reported procedures.

Scheme E1. Synthesis of Diester 3

Synthesis of Diester 3. To a mixture of diyne S1 (8.3 g, 35 mmol), Ti(O-i-Pr)$_4$ (10 mL, 35 mmol), and Et$_2$O (350 mL) was slowly added an ether solution of i-PrMgCl (2.0 M × 35 mL, 70 mmol) at −78 °C, and the resulting mixture was stirred for 2 h at −50 °C. Then an ether solution (70 mL) of crude C$_6$F$_5$PCl$_2$ ($< 50 \text{ mmol}) prepared from PCl$_3$ (50 mmol) and C$_6$F$_5$MgBr (ca. 50 mmol) was added to the mixture at this temperature, and the resulting suspension was allowed to warm to room temperature. After stirring for an additional 2 h at room temperature, a saturated NH$_4$Cl solution (100 mL) was poured into the reaction mixture, and insoluble substances were filtered off through a Celite bed. The filtrate was separated, and the aqueous phase was extracted with Et$_2$O (100 mL × 2). The combined organic extracts was washed with brine (200 mL), dried over MgSO$_4$, and concentrated in vacuo to give an oily residue, which was crystallized from cold MeOH at −78 °C to afford 3 (3.5 g, 23%) as a pale yellow solid: Mp 123−124 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.22 (t, $J = 7.3 \text{ Hz}, 6$H),
2.24–2.41 (m, 2H), 2.77–2.85 (m, 2H), 3.12–3.19 (m, 2H), 4.14–4.21 (m, 4H); \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\), 75 MHz) \(\delta\) 14.1 (s), 28.1 (d, \(J = 1.9\) Hz), 30.4 (d, \(J = 1.2\) Hz), 60.8 (s), 130.3 (m), 163.8 (d, \(J = 21.1\) Hz), 168.6 (d, \(J = 13.7\) Hz); \(^{19}\)F\(^{1}\)H NMR (CDCl\(_3\), 376 MHz) \(\delta\) −164.7 (m, 2F), −151.1 (m, 1F), −130.7 (m, 2F); \(^{31}\)P\(^{1}\)H NMR (CDCl\(_3\), 162 MHz) \(\delta\) −8.8 (t, \(3\)\(^{1}\)J\(_{PF}\) = 24.4 Hz); HR-FAB-MS: Calcd for C\(_{15}\)H\(_{14}\)F\(_3\)O\(_2\)P (M\(^{+}\)), 434.0701; Found, 434.0706; Anal. Calcd for C\(_{15}\)H\(_{16}\)F\(_5\)O\(_4\)P, C, 52.55; H, 3.71. Found, C, 52.39; H, 3.80.

**Synthesis of Diol 4.** To a solution of 3 (700 mg, 1.6 mmol) in 20 mL of hexane was added a solution of DIBAH (1.0 M, 6.8 mL, 6.8 mmol) at −78 °C. After stirring for 30 min, the resulting mixture was allowed to warm slowly to room temperature. A saturated NaHCO\(_3\) solution (10 mL) and EtOAc (50 mL) were then added, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with CH\(_2\)Cl\(_2\) (10 mL × 3). The combined organic extracts was washed with brine (30 mL), dried over Na\(_2\)SO\(_4\), and evaporated. The crude products were recrystallized from cold hexane/CH\(_2\)Cl\(_2\) = 1/1 at −78 °C to afford 4 as a colorless solid (340 mg, 61%): Mp 95–96 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.09–2.14 (m, 1H), 2.27–2.32 (m, 1H), 2.40–2.48 (m, 2H), 2.61–2.69 (m, 2H), 4.44–4.50 (m, 2H), 4.57–4.62 (m, 2H); \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\), 75 MHz) \(\delta\) 27.4 (d, \(J = 1.2\) Hz), 28.5 (d, \(J = 1.2\) Hz), 59.9 (d, \(J = 19.2\) Hz), 134.0 (s), 155.6 (d, \(J = 13.7\) Hz); \(^{19}\)F\(^{1}\)H NMR (CDCl\(_3\), 376 MHz) \(\delta\) −162.7 (m, 2F), −152.5 (t, \(3\)\(^{1}\)J\(_{PF}\) = 22.0 Hz, 1F), −131.3 (m, 2F); \(^{31}\)P\(^{1}\)H NMR (CDCl\(_3\), 162 MHz) \(\delta\) −9.9 (t, \(3\)\(^{1}\)J\(_{PF}\) = 24.4 Hz); HR-FAB-MS: Calcd for C\(_{15}\)H\(_{16}\)F\(_5\)O\(_2\)P (M\(^{+}\)), 350.0495; Found, 350.0497. In the \(^1\)H NMR spectrum, the hydroxy protons could not be observed clearly.

**Synthesis of Phosphatripyrrane 5.** To a mixture of 4 (220 mg, 0.63 mmol) and pyrrole (8.0 mL, 120 mmol) was added BF\(_3\)•OEt\(_2\) (80 µL, 0.63 mmol). After stirring for 10 min at room temperature, a saturated NaHCO\(_3\) solution (10 mL) and CH\(_2\)Cl\(_2\) (40 mL) were added. The organic phase was separated, dried over Na\(_2\)SO\(_4\), and evaporated. The crude mixture was filtered through a pad of silica gel (CH\(_2\)Cl\(_2\)), and recrystallized from hexane to afford 5 (180 mg, 65%) as a colorless solid: Mp 156–158 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.04–2.11 (m, 1H), 2.23–2.38 (m, 3H), 2.52–2.61 (m, 2H), 3.59–3.74 (m, 4H), 5.75–5.77 (m, 2H), 5.85–5.87 (m, 2H), 6.43–6.45 (m, 2H), 7.77 (br-s, 2H); \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\), 75 MHz) \(\delta\) 27.0 (d, \(J = 19.9\) Hz), 27.4 (d, \(J = 1.9\) Hz), 28.4 (d, \(J = 1.2\) Hz), 106.2 (s), 108.2 (s), 116.5 (s), 129.3 (d, \(J = 1.9\) Hz), 131.7 (m), 154.4 (d, \(J = 14.9\) Hz); \(^{19}\)F\(^{1}\)H NMR (CDCl\(_3\), 376 MHz) \(\delta\) −164.1 (m, 2F), −153.8 (t, \(3\)\(^{1}\)J\(_{PF}\) = 20.7 Hz, 1F), −132.3 (m, 2F); \(^{31}\)P\(^{1}\)H NMR (CDCl\(_3\), 162 MHz) \(\delta\) −5.7 (t, \(3\)\(^{1}\)J\(_{PF}\) = 24.4 Hz); HR-FAB-MS: Calcd for C\(_{23}\)H\(_{18}\)F\(_5\)N\(_2\)P (M\(^{+}\)), 448.1128; Found, 448.1134; Anal. Calcd for C\(_{23}\)H\(_{16}\)F\(_5\)N\(_2\)P, C, 61.61; H, 4.05; N, 6.25; Found, C, 61.33; H, 4.11; N, 6.28.
Direct synthesis of Phosphatripyrrane 5 from 3. To a solution of 3 (5.0 g, 12 mmol) in 150 mL of hexane was added a solution of DIBAH (1.0 M, 50 mL, 50 mmol) at −78 °C. After stirring for 30 min, the resulting mixture was allowed to warm slowly to room temperature. A saturated NH₄Cl solution (50 mL) and EtOAc (150 mL) were then added, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with CH₂Cl₂ (50 mL × 3). The combined organic extracts was washed with brine (150 mL), dried over Na₂SO₄, and evaporated. The crude product 4 was dissolved in pyrrole (150 mL, 2.2 mol), and BF₃•OEt₂ (1.3 mL, 10 mmol) was added to the solution at room temperature. After stirring for 10 min at room temperature, a saturated NaHCO₃ solution (100 mL) and CH₂Cl₂ (300 mL) were added. The organic phase was separated, dried over Na₂SO₄, and evaporated. The crude mixture was filtered through a pad of silica gel (CH₂Cl₂), and recrystallized from hexane to afford 5 (2.4 g, 45%) as a colorless solid.

Synthesis of P,N₃-Porphyrinogen 7. NaBH₄ (2.4 g, 63 mmol) was added to a solution of 2,5-dibenzoylpyrrole (340 mg, 1.2 mmol) in THF/MeOH (total 80 mL; v/v = 3/1), which was then stirred for 30 min at room temperature. After adding a mixture of water (30 mL) and CH₂Cl₂ (150 mL), the organic phase was separated, dried over K₂CO₃, and evaporated. The crude product 6N was dissolved in CH₂Cl₂ solution (380 mL) containing 5 (420 mg, 0.94 mmol), followed by addition of BF₃•OEt₂ (120 µL, 0.94 mmol). After stirring for 10 min at room temperature, Et₃N (140 µL, 1.0 mmol) was added and the resulting mixture was washed with water (100 mL), dried over Na₂SO₄, and evaporated. The crude product was subjected to silica gel column chromatography (CH₂Cl₂/hexane = 1/1) to give 7 as a mixture of three diastereomers (R_f = 0.4–0.5; 230 mg, 35%). The ¹H, ¹³C{¹H} NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 5:2:2. ¹H NMR (CDCl₃, 400 MHz): Diastereomer A: δ 2.13–2.43 (m, 4H), 2.58–2.67 (m, 2H), 3.43–3.48 (m, 2H), 3.70–3.83 (m, 1H), 5.38 (s, 1H), 5.44 (s, 1H), 5.69–5.72 (m, 2H), 5.77–5.79 (m, 1H), 5.84–5.85 (m, 1H), 5.88–5.89 (m, 1H), 5.95–5.96 (m, 1H), 7.19–7.40 (m, 10H), 7.90 (br-s, 1H), 8.08 (br-s, 1H), 8.24 (br-s, 1H); Diastereomer B: δ 2.08–2.43 (m, 4H), 2.50–2.63 (m, 2H), 3.38–3.45 (m, 2H), 3.62–3.79 (m, 2H), 5.38 (s, 2H), 5.68–5.69 (m, 2H), 5.71–5.74 (m, 4H), 7.12–7.27 (m, 10H), 7.76 (br-s, 1H), 8.06 (br-s, 2H); Diastereomer C: δ 2.08–2.43 (m, 4H), 2.50–2.63 (m, 2H), 3.38–3.45 (m, 2H), 3.62–3.79 (m, 2H), 5.38 (s, 2H), 5.63–5.64 (m, 2H), 5.75–5.76 (m, 2H), 5.84–5.85 (m, 2H), 7.12–7.27 (m, 10H), 7.76 (br-s, 1H), 8.15 (br-s, 2H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 26.50, 26.53, 26.75, 26.77, 26.8, 27.0, 27.09, 27.12, 27.2, 27.35, 27.37, 28.4, 28.5, 28.8, 29.7, 44.0, 44.1, 44.3, 105.6, 105.8, 105.9, 106.02, 106.08, 106.12, 106.18, 106.26, 106.29, 107.7, 107.8, 108.17, 108.19, 116.5, 126.5, 126.6, 126.9, 151
After stirring for 10 min at room temperature, DDQ (750 mg, 3.3 mmol) was added, and the (420 mg, 0.94 mmol) and crude 685 (CDCl3, 376 MHz): Diastereomer A: δ = −162.3 (m, 2F), −152.4 (m, 1F), −130.6 (m, 2F); Diastereomer B and C: δ = −164.1 (m, 2F), −162.7 (m, 2F), −153.9 (m, 1F), −152.8 (m, 1F), −132.3 (m, 2F), −130.6 (m, 2F); 31P{1H} NMR (CDCl3, 162 MHz) δ = −6.9 (t, 3JPF = 24.4 Hz), −5.7 (t, 3JPF = 24.4 Hz), −5.6 (t, 3JPF = 24.4 Hz); MS (MALDI-TOF): m/z 692 (M+, C4,H3,F3,N3,P).

Synthesis of P,N2-Porphyrin 1NF. To a solution of 7 (35 mg, 0.050 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (37 mg, 0.16 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was quickly filtered through a pad of neutral alumina (CH2Cl2). The crude product was recrystallized from hexane at −78 °C to give 1NF as a reddish purple solid (17 mg, 50%): Mp ca. 250 °C (decomp); 1H NMR (CDCl3, 400 MHz) δ = 0.80 (br-s, 1H), 2.82−2.91 (m, 1H), 3.31−3.40 (m, 1H), 3.55−3.66 (m, 2H), 4.50−4.61 (m, 2H), 7.63−7.68 (m, 2H), 7.74−7.78 (m, 4H), 7.94−7.97 (m, 2H), 8.31−8.35 (m, 2H), 8.38 (d, J = 4.4 Hz, 2H), 8.68 (s, 2H), 8.69 (d, J = 4.4 Hz, 2H) 10.19 (d, 3JPF = 17.6 Hz, 2H); 13C{1H} NMR (CDCl3, 100 MHz) δ 28.9, 30.1, 121.5, 121.6, 126.1, 126.49, 126.54, 127.8, 128.1, 131.6, 134.4, 134.7, 136.0, 137.7, 142.7, 143.0, 143.1, 154.3, 154.5, 159.2; 19F{1H} NMR (CDCl3, 376 MHz): δ = −165.9 (dd, 3JFF = 22.0 Hz, 3JPF = 20.7 Hz, 2F), −156.6 (t, 3JPF = 20.7 Hz, 1F), −129.0 (dd, 3JFF = 24.4 Hz, 3JPF = 22.0 Hz, 2F); 31P{1H} NMR (CDCl3, 162 MHz) δ = −30.7 (t, 3JPF = 24.4 Hz); UV-vis (CH2Cl2) λmax (ε): 433 (184000), 528 (14600), 560 (9300), 640 (3100), 704 nm (4600); HR-FAB-MS: Calcd for C41H25F7N3P (M+), 685.1706; Found, 685.1693.

One-Pot Synthesis of P,X,N2-Porphyrins 1Xf (X = N, S) from 5. Phosphatripyrrane 5 (420 mg, 0.94 mmol) and crude 6N (ca. 1.2 mmol), prepared as described above, were dissolved in 380 mL of CH2Cl2, and BF3•OEt2 (120 µL, 0.94 mmol) was added to the solution. After stirring for 10 min at room temperature, DDQ (750 mg, 3.3 mmol) was added, and the resulting mixture was stirred for an additional 40 min, then quickly filtered through a pad of neutral alumina (CH2Cl2). The crude product was recrystallized from hexane to give 1NF as a reddish purple solid (97 mg, 15%); Similarly, 1SF was prepared from 5 (500 mg, 1.1 mmol) and 6S (500 mg, 1.1 mmol) in 8% yield (62 mg) after recrystallization from MeOH. 1SF: Mp ca. 250 °C (decomp); 1H NMR (CDCl3, 400 MHz) δ 2.82−2.90 (m, 1H), 3.37−3.49 (m, 3H), 4.42−4.52 (m, 2H), 7.72−7.82 (m, 6H), 7.98−8.16 (m, 2H), 8.22−8.40 (m, 2H), 8.49 (d, J = 4.4 Hz, 2H), 8.72 (d, J = 4.4 Hz, 2H), 9.29 (s, 2H), 10.19 (d, 3JPF = 18.5 Hz, 2H); 13C{1H} NMR (CDCl3, 100 MHz) δ 29.1, 29.88, 29.89, 123.7, 123.8, 127.3, 128.1, 133.8,
134.4, 134.50, 134.51, 135.02, 135.04, 135.72, 135.74, 141.2, 145.9, 146.1, 147.1, 147.2, 157.3, 160.0, 161.7; $\text{^{19}F}\{\text{^1H}\}$ NMR (CDCl$_3$, 376 MHz): $\delta$ −165.4 (dd, $^3J_{FP} = 22.0$ Hz, $^3J_{FF} = 20.7$ Hz, 2F), −156.8 (t, $^3J_{FP} = 20.7$ Hz, 1F), −126.4 (dd, $^3J_{FP} = 24.4$ Hz, $^3J_{FF} = 22.0$ Hz, 2F); $^3\text{P}\{\text{^1H}\}$ NMR (CDCl$_3$, 162 MHz) $\delta$ −22.5 (t, $^3J_{FP} = 24.4$ Hz); UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$): 441 (72600), 544 (7500), 780 nm (2900); HR-FAB-MS: Calcd for C$_4$H$_{25}$N$_2$F$_3$PS (M$^+$H$^+$), 703.1391; Found, 703.1408.

**Synthesis of Diol 8.** To a solution of 3 (2.0 g, 4.6 mmol) in 20 mL of THF was added MeMgBr (21 mL, 0.93 M in THF, 20 mmol) at −78 °C. The mixture was gradually warmed to room temperature during 30 min, and stirred for an additional 3 h. The mixture was acidified by saturated NH$_4$Cl solution at 0 °C, and the aqueous phase was extracted with CH$_2$Cl$_2$ (20 mL × 3). The combined organic extracts was dried over Na$_2$SO$_4$, and evaporated. The crude products were subjected to silica gel column chromatography (CH$_2$Cl$_2$/acetone = 100:1; $R_f = 0.2$), and washed with hexane to afford 8 as a colorless solid (540 mg, 29%): Mp 105–107 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.39 (s, 6H), 1.43 (s, 6H), 1.64 (s, 2H), 2.07–2.14 (m, 1H), 2.20–2.28 (m, 1H), 2.42–2.51 (m, 2H), 2.67–2.75 (m, 2H); $^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz): $\delta$ −163.7 (m, 1F), −162.6 (m, 1F), −153.3 (m, 1F), −134.0 (ddm, $^3J_{FP} = 24.4$ Hz, $^3J_{FF} = 20.7$ Hz, 1F), −130.7 (dd, $^3J_{FP} = 79.4$ Hz, $^3J_{FF} = 24.4$ Hz, $^3J_{FF} = 7.3$ Hz, 1F); $^3\text{P}\{\text{^1H}\}$ NMR (CDCl$_3$, 162 MHz) $\delta$ −12.8 (dd, $^3J_{FP} = 79.4$ Hz, $^3J_{FP} = 24.4$ Hz); HR-FAB-MS: Calcd for C$_{19}$H$_{29}$O$_2$F$_3$P (M$^+$), 406.1121; Found, 406.1110. We were not successful in obtaining satisfactory $^{13}$C NMR spectrum of 8 because it gradually decomposed in CDCl$_3$ solution during the prolonged measurement time.

**Synthesis of Phosphatryptipyrrene 9.** To a mixture of 8 (540 mg, 1.2 mmol) and pyrrole (10 mL, 150 mmol) was added BF$_3$•OEt$_2$ (160 µL, 1.2 mmol). After stirring for 1 h at room temperature, a saturated NaHCO$_3$ solution (10 mL) and CH$_2$Cl$_2$ (150 mL) were added. The organic phase was separated, dried over Na$_2$SO$_4$, and evaporated. The crude mixture was filtered through a pad of silica gel (CH$_2$Cl$_2$), and recrystallized from hexane to afford 9 (500 mg, 83%) as a colorless solid: Mp 71–72 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.42 (s, 6H), 1.53 (s, 6H), 1.89–1.96 (m, 1H), 2.00–2.15 (m, 3H), 2.20–2.28 (m, 2H), 5.81–5.84 (m, 2H), 5.89–5.93 (m, 2H), 6.49–6.53 (m, 2H), 7.82 (br s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) $\delta$ 28.2 (s), 28.7 (s), 29.5 (d, $J = 5.6$ Hz), 30.4 (d, $J = 6.2$ Hz), 37.9 (d, $J = 16.8$ Hz), 103.6 (s), 107.4 (s), 116.3 (s), 139.7 (d, $J = 2.5$ Hz), 141.3 (m), 154.3 (d, $J = 15.5$ Hz); $^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz): $\delta$ −163.8 (m, 1F), −162.8 (m, 1F), −153.7 (t, $^3J_{FP} = 19.5$ Hz, 1F), −134.9 (ddm, $^3J_{FP} = 25.6$ Hz, $^3J_{FF} = 24.4$ Hz, 1F), −130.3 (dd, $^3J_{FP} = 76.4$ Hz, $^3J_{FP} = 24.4$ Hz, $^3J_{FF} = 7.3$ Hz, 1F); $^3\text{P}\{\text{^1H}\}$ NMR (CDCl$_3$, 162 MHz) $\delta$ −12.7 (t, $^3J_{FP} = 76.4$ Hz, $^3J_{FP} = 24.4$ Hz); HR-FAB-MS: Calcd for C$_{27}$H$_{29}$F$_3$N$_2$P (M$^+$), 504.1754; Found, 504.1738; Anal. Calcd for
C₂₇H₂₆F₅N₂P, C, 64.28; H, 5.19; N, 5.55; Found, C, 64.33; H, 5.08; N, 5.53.

**Synthesis of P,X,N₂-Calixphyrins 2Xₚ (X = N, S).** Phosphatripyrane 9 (160 mg, 0.32 mmol) and 6S (94 mg, 0.32 mmol) were dissolved in 160 mL of CH₂Cl₂, and BF₃•OEt₂ (40 µL, 0.32 mmol) was added to the solution. After stirring for 30 min at room temperature, DDQ (160 mg, 0.70 mmol) was added, and the resulting mixture was stirred for an additional 1 h, then filtered through a pad of basic alumina (CH₂Cl₂). The crude product was recrystallized from MeOH at −78 °C to give 2Sₚ as a red solid (40 mg, 17%). Similarly, 1Nₚ was prepared from 9 (150 mg, 0.30 mmol) and 6N (ca. 0.30 mmol) in 43% yield (96 mg).

2Nₚ: Mp ca. 150 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ 1.38 (s, 6H), 1.63 (s, 6H), 2.05–2.13 (m, 2H), 2.22–2.30 (m, 2H), 2.52–2.60 (m, 2H), 5.93 (s, 2H), 6.56 (d, J = 4.4 Hz, 2H), 6.60 (d, J = 4.4 Hz, 2H), 7.30–7.44 (m, 10H), 11.28 (br s, 2H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 26.77, 26.81, 28.77, 28.9, 29.4, 29.60, 29.64, 41.3, 41.6, 123.1, 124.0, 127.3, 128.0, 130.9, 135.79, 135.83, 136.9, 137.4, 139.3, 139.6, 151.2, 157.4, 157.5, 182.9; ¹⁹F{¹H} NMR (CDCl₃, 376 MHz): δ −136.5 (m, 1F), −136.1 (ddd, ³JₚF = 22.0 Hz, ³JₑF = 20.7 Hz, ⁴JₑF = 9.8 Hz, 1F), −154.3 (t, ²JₑF = 20.7 Hz, 1F), −132.4 (ddm, ³JₑF = 30.4 Hz, ⁴JₑF = 22.0 Hz, 1F), −129.9 (ddd, ³JₑF = 73.4 Hz, ⁴JₑF = 24.0 Hz, ⁴JₑF = 7.3 Hz, 1F); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ −15.9 (dd, ³JₑF = 73.4 Hz, ⁴JₑF = 30.5 Hz); UV-vis (CH₂Cl₂) λᵥmax (ε): 323 (32800), 503 (23200), 536 nm (25400); HR-FAB-MS: Calcd for C₅₄H₄₆F₅N₆P (M+H⁺), 744.2567; Found, 744.2581.

2Sₚ: Mp ca. 170 °C (decomp); ¹H NMR (CDCl₃, 400 MHz) δ 1.39 (s, 6H), 1.58 (s, 6H), 2.02–2.08 (m, 2H), 2.20–2.32 (m, 3H), 2.47–2.55 (m, 2H), 6.61 (s, 2H), 6.61 (d, J = 4.4 Hz, 2H), 6.65 (d, J = 4.4 Hz, 2H), 7.33–7.47 (m, 10H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 26.26, 26.29, 28.6, 28.7, 29.4, 29.97, 30.01, 31.4, 31.6, 125.9, 127.6, 128.3, 130.6, 134.0, 135.8, 136.5, 138.1, 141.5, 152.3, 152.7, 157.9, 158.1, 182.0; ¹⁹F{¹H} NMR (CDCl₃, 376 MHz): δ −163.5 (m, 1F), −163.0 (ddd, ³JₑF = 22.0 Hz, ³JₑF = 20.7 Hz, ⁴JₑF = 9.8 Hz, 1F), −154.3 (t, ³JₑF = 20.7 Hz, 1F), −132.7 (ddd, ³JₑF = 24.4 Hz, ³JₑF = 22.0 Hz, ⁴JₑF = 9.8 Hz, 1F), −129.7 (ddd, ³JₑF = 70.3 Hz, ³JₑF = 24.0 Hz, ⁴JₑF = 9.8 Hz, 1F); ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ −15.8 (dd, ³JₑF = 70.3 Hz, ⁴JₑF = 24.4 Hz); UV-vis (CH₂Cl₂) λᵥmax (ε): 328 (38600), 493 nm (19900); HR-FAB-MS: Calcd for C₅₄H₄₆F₅N₆PS (M+H⁺), 761.2179; Found, 761.2189.

**Synthesis of P,S₂,N₂-Sapphyrin 11.** Phosphatripyrane 5 (250 mg, 0.55 mmol) and 10 (210 mg, 0.55 mmol) were dissolved in 330 mL of CH₂Cl₂, and BF₃•OEt₂ (90 µL, 0.71 mmol) was added to the solution. After stirring for 10 min at room temperature, DDQ (380 mg, 1.7 mmol) was added, and the resulting mixture was stirred for an additional 30 min, then filtered through a pad of basic alumina (CH₂Cl₂). The crude product was subjected to short alumina column chromatography (basic alumina, hexane/CH₂Cl₂ = 1/1), and recrystallized from
hexane to give 11 as a shiny green solid (27 mg, 6%): Mp ca. 190 °C (decomp); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.90–2.98 (m, 1H), 3.35–3.43 (m, 1H), 3.65–3.73 (m, 2H), 4.50–4.58 (m, 2H), 7.76–7.84 (m, 6H), 8.17–8.21 (m, 2H), 8.22–8.26 (m, 2H), 8.49 (d, $J = 4.4$ Hz, 2H), 8.60 (d, $J = 4.4$ Hz, 2H), 9.37 (d, $J = 4.4$ Hz, 2H), 9.82 (d, $J = 4.4$ Hz, 2H), 10.11 (d, $^3J_{PH} = 19.5$ Hz, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz) $\delta$ 28.2, 29.7, 30.7, 122.0, 122.1, 124.2, 127.6, 128.4, 133.6, 133.9, 134.1, 135.77, 135.85, 137.1, 139.0, 140.3, 147.7, 153.7, 158.9, 161.8; $^{19}$F{$^1$H} NMR (CDCl$_3$, 376 MHz): $\delta$ −165.2 (dd, $^3J_{FF} = 22.0$ Hz, $^3J_{FF} = 19.5$ Hz, 2F), −155.2 (t, $^3J_{FF} = 19.5$ Hz, 1F), −128.5 (dd, $^3J_{FF} = 22.0$ Hz, $^3J_{FF} = 4.9$ Hz, 2F); $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz) $\delta$ −28.4 (pseudo s); UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ ($\varepsilon$): 500 (180000), 599 (182000), 740 (600), 835 nm (1000); HR-FAB-MS: Calcd for C$_{45}$H$_{27}$F$_5$N$_2$PS$_2$ (M+H$^+$), 785.1268; Found, 785.1286.
References and Footnotes


(6) Ring oxidation of P-masked P,X,N2-porphyrinogens (X = N, S, O) did not afford 18π P,X,N2-porphyrins. See, ref 2b,d.

(7) Compound 3 was prepared via TiIII-mediated cyclization of 1,7-bis(ethoxycarbonyl)hepta-1,6-diyne followed by treatment with CF5PCl2 according to the reported procedure for the synthesis of 1-phenyl-2,5-di(ethoxycarbonyl)phosphole. Matano, Y.; Miyajima, T.; Nakabuchi, T.; Matsutani, Y.; Imahori, H. J. Org. Chem. 2006, 71, 5792.

(8) It was convenient to use 4 in a semi-purified state for the subsequent reaction with pyrrole, although 4 is isolable as a colorless solid in 61% yield. For details, see Experimental Section.


(11) The broadening and bathochromic shift of $1S_F$ may be due to electronic repulsion between the core sulfur atom and the P-$C_6F_5$ fluorine atoms in $1S_F$.


(17) In the variable temperature $^1H$ NMR spectra of $11$ (−100 °C to +80 °C: CD$_2$Cl$_2$ or CDCl$_2$CDCl$_2$), the signals due to the peripheral (meso, pyrrole-$\beta$, thiophene-$\beta$, and trimethylene) protons show negligible changes ($\Delta\delta < 0.5$ ppm). This implies that the structure of $\pi$-system in $11$ is not flexible in solution.


Concluding Remarks

This thesis has described the synthesis, structures, aromaticities, and optical and electrochemical properties of the phosphole-containing porphyrins and calixpyrroles. The characteristic metalation chemistry and reactivity of these phosphaporphyrinoids have also been disclosed. The results and findings in this work are summarized as follows.

In Chapters 1 and 2, the synthesis, structures, and coordination abilities of phosphole-containing calixpyrroles have been described. The symmetric and asymmetric hybrid calixpyrroles containing a phosphole or 2,3-dihydrophosphole unit (symmetric and asymmetric P,X,N₂-calixpyrroles: X = S, O) were prepared by using acid-promoted condensation reactions of the corresponding σ⁴-phosphatripyrranes with 2,5-bis(1-hydroxy-1-methylethyl)heteroles. It was revealed that the symmetric and asymmetric P,S,N₂-calixpyrroles behave as macrocyclic monophosphine ligands toward Au(I), Pt(II), and Pd(II) ions. Interestingly, these P,S,N₂-calixpyrroles bind the M–Cl fragments through the P–M coordination and the cooperative NH–Cl hydrogen-bonding interactions.

In Chapters 3 and 4, the synthesis, structures, optical and redox properties of phosphole-containing porphyrins have been described. The P,N₃-porphyrin and P,S,N₂-porphyrin were prepared via acid-promoted dehydrative condensation between a σ⁴-phosphatripyrrane and the corresponding 2,5-bis[hydroxy(phenyl)methyl]heteroles followed by DDQ oxidation. Both experimental (NMR, UV-vis, and X-ray) and theoretical (DFT calculations) results suggest that the 18π aromatic character inherent in regular N₄-porphyrins is maintained in these phosphaporphyrins. DFT calculations on model compounds showed that the P,X,N₂-porphyrins (X = N, S) possess considerably small HOMO–LUMO gaps as compared with N₄- and S,N₃-porphyrins, which is reflected in the red-shifted absorptions, low oxidation potentials, and high reduction potentials of the phosphaporphyrins.

Chapter 4 also has dealt with the unique π-reconstruction reactions triggered by P-oxygenation of the phosphole-containing porphyrins. The P-oxygenation of the P,X,N₂-porphyrins with H₂O₂ has been found to lead to the formation of different types of products. The 18π P,N₃-porphyrin was transformed into the 22π aromatic P(O),N₃-porphyrin.
accompanied by the oxidative π extension at the peripheral C₃ bridge, whereas the 18π P,S,N₂-porphyrin was reduced to the isophlorin-type 20π antiaromatic P(O),S,N₂-porphyrin. In both of the reactions, simple P-oxygenated 18π P(O).X,N₂-porphyrins were formed as the initial products, which were subsequently transformed into the 22π or 20π porphyrins. The two reaction courses from 18π to 20π/22π are apparently determined by the combination of the core heteroatoms (i.e. P,N₃ or P,S,N₂) and the structure of the peripherally fused carbocycles. These results demonstrate that the incorporation of a phosphorus atom into the core is not only a highly promising way to modify the fundamental properties of the porphyrin 18π system but also a reliable tool to stabilize uncommon 22π and 20π systems through the chemical modifications at the core-phosphorus atom.

In Chapter 5, unique complexation reactions of the P,S,N₂-porphyrin with zerovalent group 10 metals have been described. These reaction underwent accompanied by a redox (2e) between the P,S,N₂-porphyrin and M(0) (M = Ni, Pd, Pt) to afford the P,S,N₂-isophlorin–M(II) complexes. In marked contrast, no complexation took place between the S₂,N₂-porphyrin and Pd(0). These results indicate that, core-phosphorus atom of the P,S,N₂-porphyrin plays crucial roles in the redox-coupled complexation: The core-phosphorus atom i) enhances the electron-accepting ability of the 18π porphyrin ring, and ii) stabilizes the atypical 20π isophlorin ring due to high P–M affinity.

In Chapter 6, remarkable effects of P-perfluorophenyl group on the synthesis of phosphole-containing porphyrinoids have been described. It has been revealed that, thanks to the increased stability of the C₆F₅-substituted σ³-phosphorus atom under the synthetic condition, P-C₆F₅ type P,X,N₂-porphyrins (X = N, S) can be prepared more easily in better yield than their P-Ph counterparts. Notably, a P,S₄,N₂-hybrid expanded porphyrin (sapphyrin type) was successfully prepared by taking advantage of the electron-withdrawing nature of the C₆F₅ group.

The author believes that these studies not only highlight the characteristics of phosphorus in porphyrin chemistry and heteroatom chemistry, but also offer fruitful insight into the aromaticity, optical, electrochemical, and coordinating properties of porphyrinoids.
List of Publications

Chapter 1
Phosphole-Containing Hybrid Calixpyrroles: New Multifunctional Macrocyclic Ligands for Platinum(II) Ions

Chapter 2
Synthesis, Structures, and Coordinating Properties of Phosphole-Containing Hybrid Calixpyrroles

Chapter 3
Synthesis of a Phosphorus-Containing Hybrid Porphyrin

Chapter 4
Synthesis and Reactions of Phosphaporphyrins: Reconstruction of π-Skeleton Triggered by Oxygenation of a Core Phosphorus Atom

Chapter 5
Redox-Coupled Complexation of 23-Phospha-21-thiaporphyrin with Group 10 Metals: A Convenient Access to Stable Core-Modified Isophlorin–Metal Complexes

Chapter 6
Remarkable Effects of P-Perfluorophenyl Group on the Synthesis of Core-Modified Phosphaporphyrinoids and Phosphadithiasapphyrin
Other Publications

A Convenient Method For the Synthesis of 2,5-Difunctionalized Phospholes Bearing Ester Groups

Phosphorus-Containing Hybrid Calixphyrins: Promising Mixed-Donor Ligands for Visible and Efficient Palladium Catalysts

Syntheses, Structures, and Coordination Chemistry of Phosphole-Containing Hybrid Calixphyrins: Promising Macrocyclic P,N₂,X-Mixed Donor Ligands for Designing Reactive Transition-Metal Complexes

Monophosphaporphyrins: Oxidative π-Extension at the Peripherally Fused Carbocycle of the Phosphaporphyrin Ring

Review

Synthesis, Structures and Aromaticity of Phosphole-Containing Porphyrins and Their Metal Complexes
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Takashi Nakabuchi

Department of Molecular Engineering
Graduate School of Engineering
Kyoto University
Kyoto, Japan
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