

Phosphole-Containing Calixpyrroles, Calixphyrins, and Porphyrins: Synthesis and Coordination Chemistry

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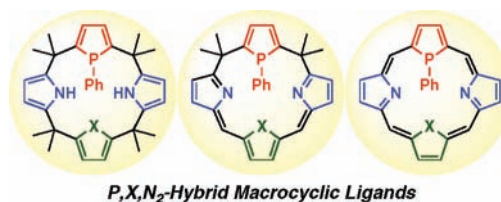
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CON SPECTUS

Porphyrins are large heterocyclic macrocycles that bind metals to form complexes such as heme and chlorophyll. Porphyrinogens are related macrocycles in which the *meso*-carbons, the carbon atoms connecting the pyrroles or the related five-atom heterocycles, are all or partially reduced to methylene, disrupting the π -electron conjugation. Both porphyrins and porphyrinogens are important components of natural and synthetic systems, and they have completely different coordination behavior. Consequently, the coordination chemistry of the entire porphyrin family, including regular porphyrins, porphyrinogens, and their expanded analogs, has been extensively investigated. Core modification, namely, replacing one or more pyrrole rings with other heterocyclic or carbocyclic rings, is a highly promising approach for creating unprecedented coordination properties in the porphyrin family. The size, shape, charge, and binding ability of the core-modified porphyrin platforms are readily tunable by variation of the heterole subunits.

Until recently, however, the only atoms that could be incorporated into the core were carbon and chalcogens (the oxygen family). Phosphole, the phosphorus isologue of pyrrole, is considered a nonaromatic heterole because of insufficient π -conjugation between the *cis*-dienic π -system and the lone electron pair of the phosphorus atom. As a consequence, phospholes behave not only as efficient π -conjugative frameworks but also as ordinary phosphine ligands for transition metals. With this in mind, we started a research project on core-modified porphyrins in which the phosphole subunit plays a crucial role in providing characteristic coordination environments.

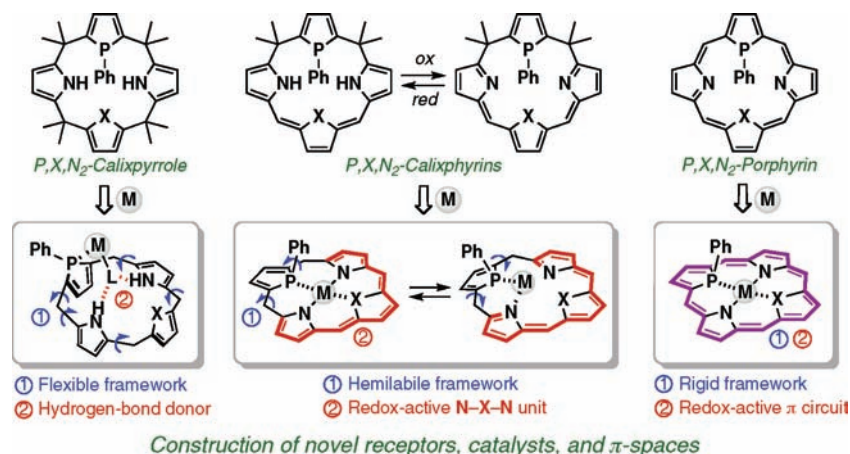
In this Account, we describe our efforts to explore the utility of phosphole-containing porphyrins and porphyrinogens as macrocyclic, mixed-donor ligands. We have established convenient methods for the synthesis of calixpyrroles, calixphyrins, and porphyrins with P and either O or S substitutions, that is, P,X,N₂-hybrids, as well as the phosphatripyrrane precursors. We also have investigated the effects of varying the combination of core heteroatoms (P, N, S, and O) on the coordination properties of the hybrid macrocycles. Our recent investigations have shown that (1) the P,S,N₂-calixpyrroles behave as monophosphine ligands while maintaining the hosting functions that originate from the pyrrole subunits, (2) the P,X,N₂-calixphyrins behave as neutral, monoanionic, or dianionic tetradentate ligands with electronic structures that vary widely depending on the combination of heterole subunits, and (3) the P,S,N₂-porphyrin behaves as a redox-active π -ligand for group 10 (the Ni family) metals, affording a novel class of core-modified isophlorin complexes. As a whole, the incorporation of the phosphole subunit into the macrocyclic framework provides unprecedented coordinating properties for the porphyrin family, affording exceptional synthetic control over the behavior of these important macrocycles.



Introduction

Porphyrins and their *meso*-reduced derivatives (porphyrinogens) play vital roles in both natural

and artificial systems. It is well-known that the oxidative aromatization of porphyrinogens to porphyrins can be suppressed by the introduction of

SCHEME 1. Coordination Chemistry of P,X,N₂-Hybrid Porphyrin Family

suitable substituents onto the sp^3 -hybridized *meso* carbon centers. From a structural point of view, porphyrins and porphyrinogens show completely different coordination behavior. For example, regular porphyrins possess rigid, planar, and redox-active coordination spheres and usually behave as dianionic N₄-ligands for various metals. On the other hand, calix[4]pyrroles, wherein all *meso* carbons are sp^3 -hybridized, provide a flexible cavity for incoming guests and typically behave as tetraanionic N₄-ligands for metals.¹ In this context, the porphyrin family including regular porphyrins, porphyrinogens, and their expanded analogs has been extensively investigated in various areas of coordination chemistry.

Core modification, namely, replacing one or more pyrrole rings with other heterocyclic or carbocyclic rings, is a highly promising approach to add unique coordinating properties into the porphyrin family, because the size, shape, charge, and binding ability of the macrocyclic platforms are readily tunable by altering the combination of core elements.² To date, numerous efforts have been devoted to the chemical modification of the core nitrogen atoms with carbon, silicon, or chalcogen atoms, and the core-modified derivatives thus prepared have proven to exhibit unprecedented coordinating properties. Until recently, however, no attempt had been made to replace the core nitrogen atom with phosphorus.³

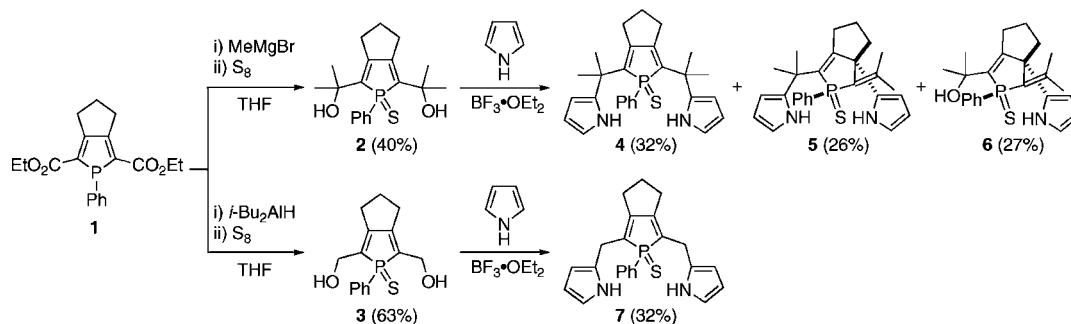
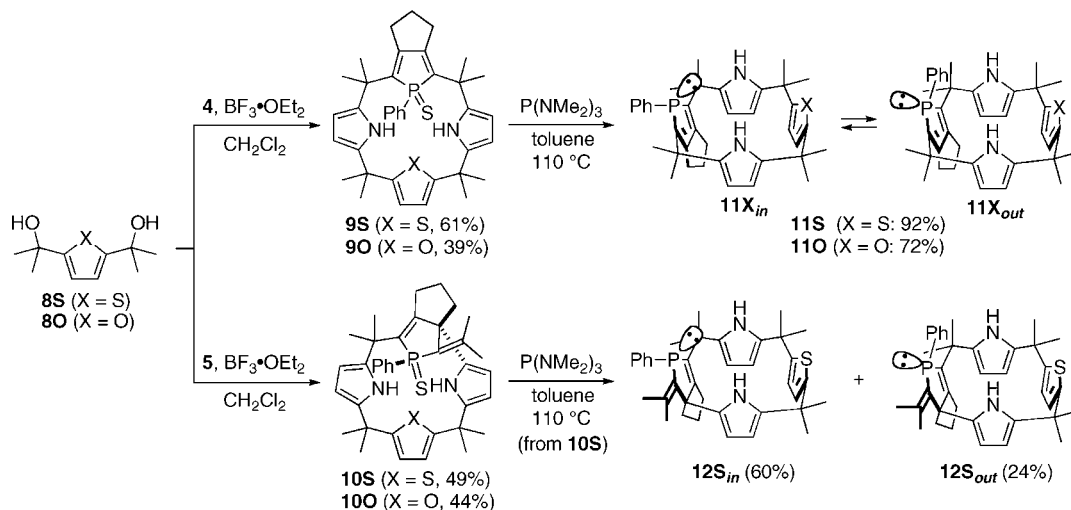
Phosphole, the phosphorus isologue of pyrrole, is known as a basically nonaromatic heterole due to insufficient π -conjugation between the *cis*-dienic π -system and the lone electron pair of the phosphorus atom.⁴ As a consequence, phospholes behave not only as potential building blocks for the π -conjugated materials but also as ordinary phosphine ligands for transition metal catalysts.⁵ Several years ago, we envisioned that replacement of pyrrole rings of the porphyrin family with phosphole and other heteroles would give rise to conceptually new classes of macrocyclic mixed-donor (hybrid) ligands

with their coordinating properties and electronic structures being strongly dependent on the relevant core elements.⁶

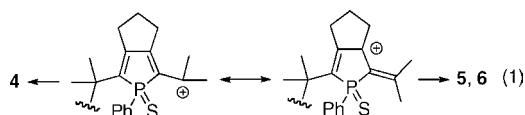
Scheme 1 illustrates our concepts for designing three classes of hybrid macrocycles: (i) In the P,X,N₂-hybrid calixpyrroles, the phosphorus center incorporated in the flexible rim should bind a metal in close vicinity to the cavity without deprotonation of pyrrolic NH groups. This retains the hosting function of the calixpyrrole platform as an anion receptor, which leads to the cooperative, noncovalent interaction at the metal-binding site. (ii) In the P,X,N₂-hybrid calixphyrins, the phosphole subunit is likely to modulate its conformation to provide the most suitable coordination environment for a metal, and the hemilabile nature of the macrocyclic platform is attractive for designing a conceptually new catalytic system. In addition, the redox active π -conjugated tripyrrine unit can control the oxidation state and the reactivity of the metal center. (iii) In the P,X,N₂-hybrid porphyrins, the π -conjugated phosphole ring is expected to alter the optical, electrochemical, and magnetic properties of the rigid 18 π system. Furthermore, the incorporation of phosphorus and other heteroatoms should stabilize the unusual oxidation states for the redox-active π -systems through the mutual electronic communication between the metal center and the macrocyclic ligand. In this Account, we describe our efforts to explore the utility of phosphole-containing porphyrins and porphyrinogens as macrocyclic, mixed-donor ligands.

Synthesis of Phosphatripyrranes

To incorporate a phosphole ring as a component of macrocyclic mixed-donor ligands, it is crucial to establish a facile route to important intermediates, phosphatripyrranes. Scheme 2 illustrates our strategy for the synthesis of phosphatripyrranes starting from 2,5-difunctionalized phosphole **1**. A practical advantage of this protocol is that **1** is readily accessible from

SCHEME 2. Synthesis of Phosphatripyrranes^{8,10,11}SCHEME 3. Synthesis of P,X,N₂-Hybrid Calixpyrroles^{8,11}

commercially available reagents. Alkylation of **1** with MeMgBr, followed by treatment with elemental sulfur, afforded tertiary diol **2**, while reduction of **1** with DIBAL-H produced primary diol **3**. Treatment of **2** with $\text{BF}_3 \cdot \text{OEt}_2$ in pyrrole, followed by column chromatography, gave not only the expected condensation product **4** but also the unexpected condensation products **5** and **6**.⁸ Apparently, the weakly aromatic character of the phosphole ring allows the positive charge of the tertiary carbenium intermediate to delocalize onto the tertiary β -carbon (eq 1). This type of allylic isomerization was also observed by Mathey and co-workers in their synthesis of a P-confused carbaporphyrinoid (*vide infra*).⁹ When **3** was used instead of **2**, *meso*-free phosphatripyrrane **7** was obtained as the major product.¹⁰



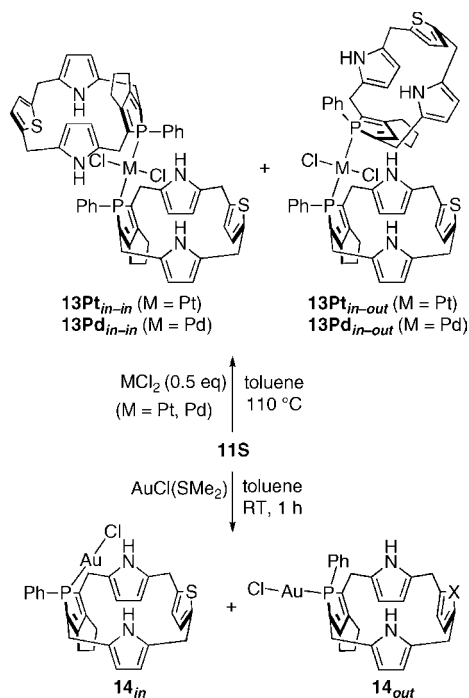
Synthesis of Phosphole-Containing Calixpyrroles

Calixpyrroles are a class of porphyrinoids wherein all *meso*-carbon bridges are sp^3 -hybridized.¹ The most distinctive fea-

ture of calixpyrroles is the hosting function as anion receptors, as have been demonstrated by Sessler and co-workers.^{1a-c} We anticipated that phosphole-containing P,X,N₂-hybrid calixpyrroles would exhibit promising features as the structurally well-defined macrocyclic phosphine ligands while keeping the hydrogen-bonding sites that originate from the parent calixpyrrole platform.

Scheme 3 depicts the synthesis of two kinds of P,S,N₂- and P,O,N₂-hybrid calixpyrroles.^{8,11} The BF_3 -promoted dehydrative condensation of the *gem*-dimethyl-substituted phosphatripyrrane **4** with 2,5-difunctionalized thiophene **8S**¹² or furan **8O**¹² gave symmetric σ^4 -P,X,N₂-hybrids **9S** or **9O**. Similarly, phosphatripyrrane **5** reacted with **8S** and **8O** to afford the respective asymmetric σ^4 -P,X,N₂-hybrids **10S** and **10O**. The spectral and crystallographic data of **10X** indicated that a single diastereomer had been isolated in each reaction. In the solid state, **9X** and **10X** were found to possess a bowl-shaped, trapezoid-like cavity, wherein the P=S moiety is located inside.

Reductive desulfurization of **9X** and **10S** with excess $\text{P}(\text{NMe}_2)_3$ produced symmetric σ^3 -P,X,N₂-hybrids **11X** and asymmetric σ^3 -P,S,N₂-hybrid **12S**, respectively.^{8,11} As the phosphorus center adopts a pyramidal geometry, two conformers

SCHEME 4. Complexations of P,S,N₂-Hybrid Calixpyrrole^{8a}

^a *meso*-Me groups are omitted for clarity.

are conceivable for these σ^3 -P-type macrocycles, where the lone electron pair of phosphorus is located inside or outside the cavity (denoted as $n\mathbf{X}_{in}$ and $n\mathbf{X}_{out}$). The ¹H and ³¹P NMR spectra of **11X** at room temperature indicated the presence of two conformers, but **11X_{in}** and **11X_{out}** could not be separated from each other probably due to a small pyramidal inversion barrier of phosphole (ca. 16 kcal mol⁻¹).¹³ On the other hand, the interconversion between **12S_{in}** and **12S_{out}** was found to be slow on the NMR time scale, and both of them could be isolated by column chromatography. Evidently, the dehydrophosphole ring of **12S** does not allow facile inversion at the pyramidal phosphorus center.

Complexation of Phosphole-Containing Calixpyrroles

With the concept of Scheme 1a in mind, we examined complexation of **11S** with palladium, platinum, and gold salts. Prolonged heating of a toluene solution containing **11S** and PtCl₂ (0.5 equiv) yielded an equilibrium mixture of *trans*-Pt^{II}-bis(phosphine) complexes **13Pt_{in-in}** and **13Pt_{in-out}** in a ratio of 90/10 (Scheme 4).⁸ At the initial stage of this reaction, **13Pt_{out-out}** (not shown in Scheme 4) was also observed. Similarly, the complexation of **11S** with PdCl₂ afforded a mixture of **13Pd_{in-in}** and **13Pd_{in-out}** in a ratio of 92/8. These results show that the thermodynamic stability of **13M** decreases in the order: in–in > in–out >> out–out. At room temperature,

the interconversion among **13M_{in-in}**, **13M_{in-out}**, and **13M_{out-out}** was so slow that these complexes could be separated and characterized by X-ray crystallography. The complexation of **11S** with AuCl(SMe₂) proceeded at room temperature to give a mixture of **14_{in}** and **14_{out}**. The final ratio (93/7) indicates that **14_{in}** is thermodynamically more stable than **14_{out}**. Although detailed results are not presented here, **12S_{in}** also underwent complexation with palladium, platinum, and gold salts, yielding the respective asymmetric complexes.

Structures of Hybrid Calixpyrrole–Metal Complexes

X-ray diffraction analyses of the P,S,N₂-calixpyrrole–metal complexes have revealed that **11S** and **12S** behave as neutral, monodentate P ligands.^{8,11} The structures of **13Pt_{in-in}**, **13Pt_{in-out}**, and **13Pd_{in-in}** are shown in Figure 1, and selected parameters are summarized in Table 1.¹⁴ In all crystal structures depicted in this Account, hydrogen atoms except for NH are omitted for clarity.

Each metal center in **13Pt_{in-in}**, **13Pt_{in-out}**, and **13Pd_{in-in}** has a square-planar geometry with two phosphorus atoms in a *trans* orientation. In the in–in type complexes **13M_{in-in}**, the cone-shaped P,S,N₂-hybrid ligands bind the metal above the cavity. As a result, the phosphole rings lean toward the outside, which is reflected in relatively long P⋯S distances. In **13Pt_{in-out}**, the in-type ligand adopts a cone conformation, whereas the out-type ligand possesses a partial cone conformation. The N⋯N distances are comparable for these bisphosphine complexes.

The most salient feature of the P,S,N₂-hybrid calixpyrrole ligands stems from two facing pyrrole units, which behave as hydrogen-bonding donors. In **13Pt_{in-in}** and **13Pd_{in-in}**, all the pyrrole rings are tilted to direct the NH protons toward the chlorine atom bound to the metal center. The N⋯Cl distances of **13M_{in-in}** (3.23–3.52 Å) are close to those of Sessler's chloride ion complex of *meso*-octamethylcalix[4]pyrrole [3.264(7)–3.331(7) Å],¹⁵ which supports the presence of hydrogen-bonding interaction between the M–Cl fragment and the NH protons. A similar structural feature is observed for the in type ligand of **13Pt_{in-out}**. The ¹H NMR spectra of **13M_{in-in}** in CDCl₃ display the NH peaks at downfield ($\Delta\delta = 1.2$ –2.7 ppm) relative to those of **11S_{in}**, implying that the hydrogen bonds are maintained in solution. Overall, the P,S,N₂-hybrid calixpyrrole has proven to bind the M–Cl fragments through the P–M coordination and the cooperative NH–Cl hydrogen-bonding interaction, as expected.

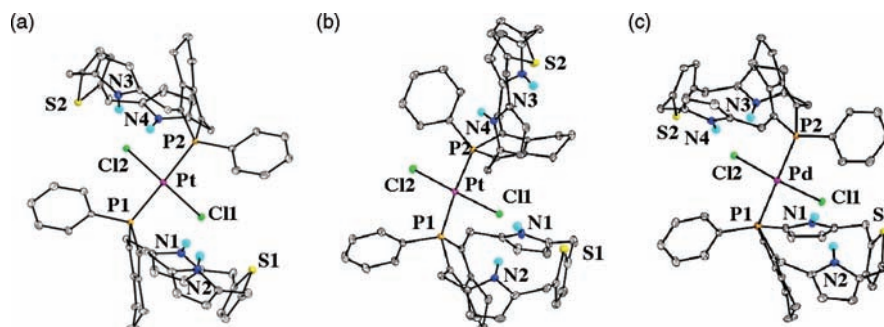
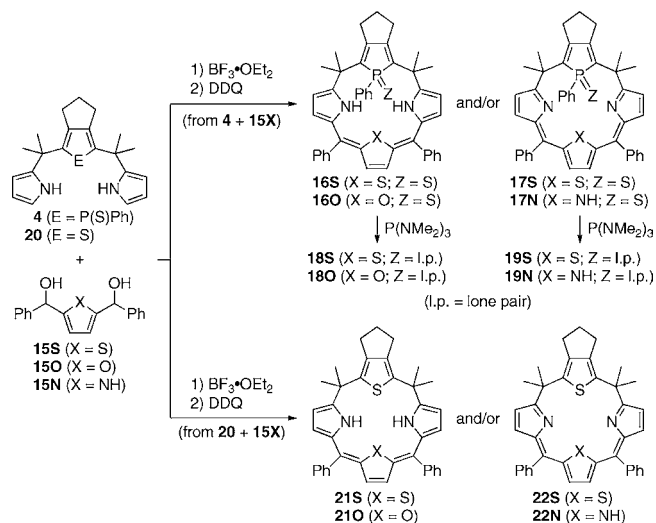


FIGURE 1. Structures of (a) **13Pt_{in-in}**, (b) **13Pt_{in-out}**, and (c) **13Pd_{in-in}**. *meso*-Me groups are omitted for clarity. Reproduced from ref 8. Copyright 2008 American Chemical Society.

TABLE 1. Selected Distances (Å) and Bond Lengths (Å) of **13M**

complex	P...S	N...N	N...Cl	M-P (avg)
13Pt_{in-in} (M = Pt)	5.88, 5.89	5.40, 5.46	3.23–3.52	2.334
13Pt_{in-out} (M = Pt)	5.91 (in)	5.43 (in)	3.40–3.41 (in)	2.335
13Pd_{in-in} (M = Pd)	5.88, 5.88	5.40, 5.44	3.26–3.50	2.352

SCHEME 5. Synthesis of P,X,N₂- and S,X,N₂-Hybrid Calixphyrins^{18–20}



Synthesis of Phosphole-Containing Calixphyrins

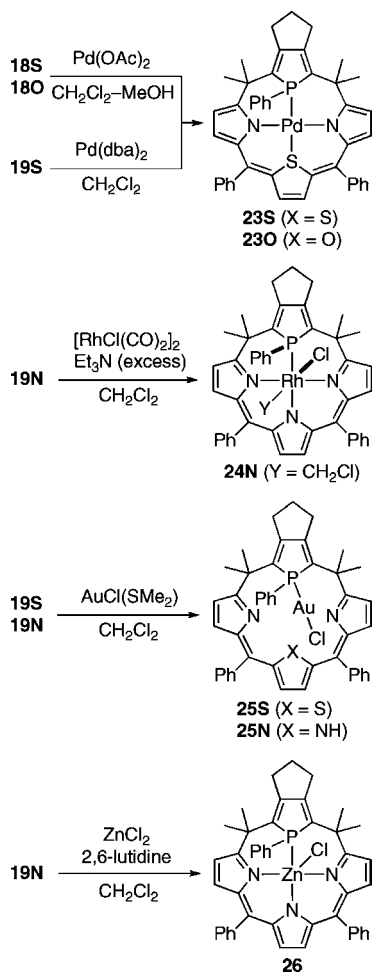
Calixphyrins are a class of porphyrinoids that involve both sp^2 - and sp^3 -hybridized bridging *meso* carbon atoms.¹⁶ Accordingly, calixphyrins possess reasonably flexible frameworks, as well as rather rigid π -conjugated networks, whose characters differ significantly depending on the number and position of the sp^3 -*meso* carbon atoms.¹⁷ To develop a new class of hybrid ligands by taking advantage of the characteristics of the calixphyrin platform, we focused on the chemistry of 5,10-porphodimethene-type phosphole-containing calixphyrins. Scheme 5 summarizes the synthesis of P,X,N₂- and S,X,N₂-hybrid calixphyrins.^{18–20} Treatment of a CH_2Cl_2 solution containing **4** and 2,5-difunctionalized thiophene **15S**²¹ with

$\text{BF}_3 \cdot \text{OEt}_2$ gave a mixture of condensation products, which was then reacted with 2.2 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford two types of σ^4 -P,S,N₂-hybrid calixphyrins **16S** and **17S**. Based on the oxidation state of the π -conjugated moiety, **16S** is classified as a 2e-oxidized product and **17S** as a 4e-oxidized product.

When 2,5-difunctionalized furan **15O**²² or pyrrole **15N**²³ was used in place of **15S**, σ^4 -P,O,N₂-hybrid **16O** (2e-oxidized type) or σ^4 -P,N₃-hybrid **17N** (4e-oxidized type) was isolated as the major product. The reductive desulfurization of the phosphorus center of **16X** and **17X** was accomplished by treatment with excess $\text{P}(\text{NMe}_2)_3$ in refluxing toluene, affording the respective σ^3 -P,X,N₂-hybrids **18X** and **19X**.^{18,19} According to similar procedures, S,X,N₂-hybrid calixphyrins **21X** or **22X** were obtained from the corresponding precursors **20** and **15X**.²⁰ The results summarized in Scheme 5 indicate that the redox properties of the π -conjugated N–X–N units in the 5,10-porphodimethene-type P,X,N₂- and S,X,N₂-hybrid calixphyrins directly reflect the nature of the central heteroles. The difference in thermodynamic stability between the 2e-oxidized and 4e-oxidized forms is reasonably interpreted by considering the attractive hydrogen-bonding interaction of the lone pair (O, N, S) with the pyrrolic NH proton at the core as well as the repulsive electrostatic interaction among the lone pairs or among the multiple NH groups.

Complexation of Phosphole-Containing Calixphyrins

In the complexation with palladium, rhodium, gold, and zinc, the P,X,N₂-hybrid calixphyrins **18X** and **19X** exhibit diverse coordination behavior derived from the flexible phosphole unit and the redox active N–X–N unit (Scheme 6).^{18,19} The 2e-oxidized free base **18S** reacted with $\text{Pd}(\text{OAc})_2$ to afford Pd-P,S,N_2 complex **23S** as an air-stable, purple solid. To our surprise, the reaction of the 4e-oxidized free base **19S** with $\text{Pd}(\text{dba})_2$ (dba = dibenzylideneacetone) produced the same complex, **23S**, as a sole product. The metathesis of **18O** with

SCHEME 6. Complexations of P,X,N₂-Hybrid Calixphyrins^{18,19,24}

Pd(OAc)₂ yielded Pd–P,O,N₂ complex **23O** quantitatively. The electrochemical and structural investigations, as well as DFT calculations, have inevitably shown that the oxidation states of the palladium center and the N–X–N unit in **23X** are +2 and –2, respectively. It is therefore likely that in the complexation between **19S** and Pd(dba)₂, two electrons transfer from palladium(0) to the N–S–N unit.

As shown in Scheme 6, the σ^3 -P,N₃-hybrid **19N** reacted with [RhCl(CO)₂]₂ in the presence of Et₃N to yield Rh^{III}–P,N₃ complex **24N** as a deep blue solid within a few seconds.¹⁹ The DFT calculations on a model reaction suggested that **24N** was formed through the C–Cl bond activation of dichloromethane by an initially formed Rh^I complex, although this intermediate could not be observed due to its high reactivity. Presumably, the monoanion of the P,N₃-hybrid ligand significantly enhances nucleophilicity of the rhodium(I) center enough to oxidatively activate the C–Cl bond.

The coordinating ability observed for the P,X,N₂-calixphyrins stands in marked contrast to what was observed for the S,X,N₂-calixphyrins.²⁰ Thus, the reactions of **21X/22X** with

Pd(OAc)₂, Pd(dba)₂, and [RhCl(CO)₂]₂ resulted in recovery or decomposition of the free bases, and no metal complex was isolated. This demonstrates that the coordinating ability of the 5,10-porphodimethene-type hybrid calixphyrins depends on the intrinsic nature of the sp³-*meso*-carbon-bridged heterole subunits. Obviously, the high coordinating ability of the phosphole subunit in **18X/19X** provides sufficient driving force for promoting the complexation.

The complexation between **19X** and AuCl(SMe₂) proceeded smoothly to give the corresponding Au^I–P,X,N₂ complexes **25X**, in which the P,X,N₂-hybrids behave as neutral monophosphine ligands.¹⁹ In **25X**, the N–X–N units are not involved in the coordination sphere at the gold center. The reaction between **19N** and ZnCl₂ also took place immediately in the presence of 2,6-lutidine to afford Zn^{II}–P,N₃ complex **26**.²⁴ In this complex, the zinc center adopts a distorted square-pyramidal geometry with the chlorine atom at the apical position, and the P,N₃-hybrid occupies the equatorial positions as the monoanionic, tetradentate ligand. A similar type of Zn complexation was observed for the S,N₃-hybrid **22N**, generating highly fluorescent Zn^{II}–S,N₃ complexes.²⁴

Structures of Phosphole-Containing Calixphyrins and Their Metal Complexes

Selected structures of P,X,N₂-hybrid calixphyrins and their metal complexes are depicted in Figures 2 and 3, and selected parameters are listed in Table 2.¹⁹ The 2e-oxidized free base **18O** is largely twisted at the π -conjugated unit, whereas the 4e-oxidized free bases **19S** and **19N** are composed of almost flat N–X–N planes. The difference in the oxidation state of the N–X–N units is clearly seen as the C–C bond length alternation. In all the P,X,N₂-hybrid free bases characterized, the phosphole ring stands perpendicular to a mean plane formed by the four *meso* carbon atoms, and the lone electron pair of phosphorus is oriented inside the macrocycle.

The palladium center in **23S** adopts a square-planar geometry that coordinates the four heteroatoms. To keep this geometry, the hybrid macrocycle is distorted, and the phosphole ring leans toward the inside. The N···N distance of **23S** is shorter by 0.67 Å than that of **19S**, because two covalent bonds are formed between the palladium and two nitrogen atoms in **23S**. The C–C bond length alternation observed for the N–S–N unit of **23S** is indicative of noticeable contribution by the canonical structure illustrated in Scheme 6. The rhodium center in **24N** adopts a distorted octahedral geometry that is characteristic of d₆ rhodium(III) complexes. The macrocyclic P,N₃-platform occupies the four equatorial positions, wherein the N–N–N unit is ruffled to release steric con-

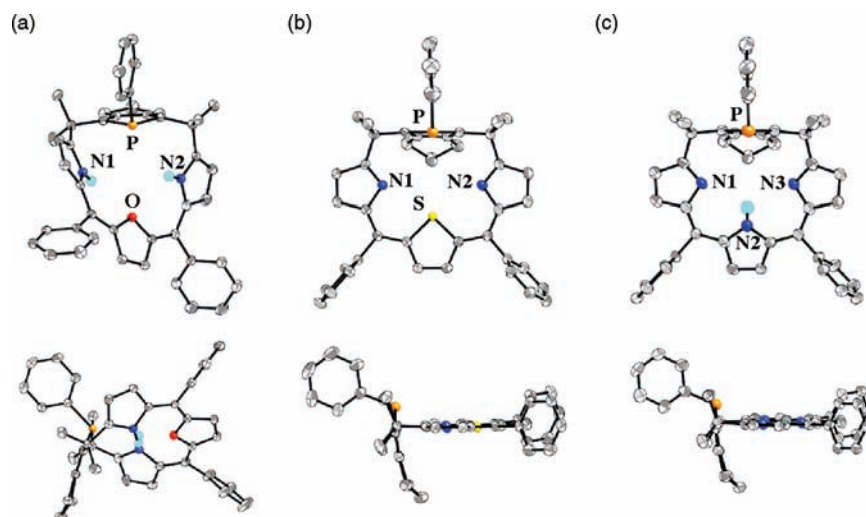


FIGURE 2. Structures (top and side views) of (a) **180**, (b) **19S**, and (c) **19N**. Reproduced from ref 19. Copyright 2008 American Chemical Society.

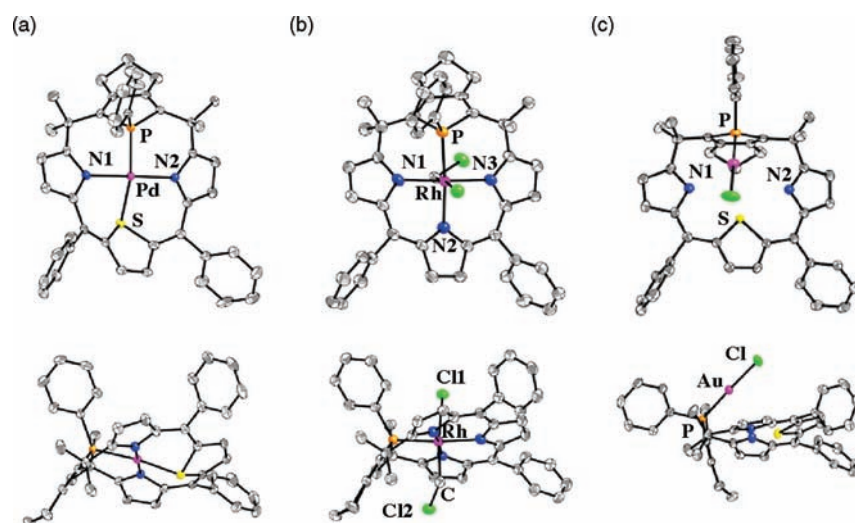


FIGURE 3. Structures (top and side views) of (a) **23S**, (b) **24N**, and (c) **25S**. Reproduced from ref 19. Copyright 2008 American Chemical Society.

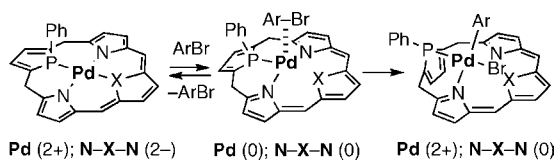
TABLE 2. Selected Distances (Å) and Bond Lengths (Å) of P,X,N₂-Calixphyrins and -Porphyrins

compound	P···X	N···N	M–P	M–X	M–N
Calixphyrins					
190 (X = O)	4.19	4.59			
19S (X = S)	4.23	4.82			
19N (X = N)	4.80	4.53			
23S (M = Pd; X = S)	4.45	4.15	2.2135(8)	2.2667(8)	2.079(2), 2.066(3)
24N (M = Rh; X = N)	4.26	4.16	2.2042(12)	2.062(4)	2.079(3), 2.081(4)
25S (M = Au; X = S)	4.27	4.88	2.2319(9)		
Porphyrins					
28N (X = N)	3.45	4.56			
30Pd (M = Pd; X = S)	4.45	4.13	2.1831(10)	2.2664(9)	2.060(3), 2.070(3)

gestion at the core. Due to the P–Rh coordination, the P···N(23) and N···N distances of **24N** are considerably shortened with respect to those of **19N**. While the N–N–N plane is slightly distorted, the C–C bond length alternation at the N–N–N unit of **24N** is close to that of **19N**. This implies that

the oxidation state of the N–N–N unit is retained through the complexation. The gold center in **25S** possesses a linear geometry, coordinated by the phosphorus and chlorine atoms, and the phosphole ring is perpendicular to a mean plane formed by the four *meso* carbons. The P–Au bond length [2.2319(9) Å] and the P–Au–Cl bond angle [177.52(3)°] of **25S** are close to the respective values of the Au–P,S,N₂-calixphyrrole complex **14** [2.2391(8) Å and 173.20(2)°]. The C–C bond length alternation at the N–X–N unit of **25X** is comparable to that observed for **19X**, reflecting the nonvital role of the π -conjugated unit in the P-coordination to the AuCl moiety.

The observed structural features exemplify that the phosphole-containing calixphyrins behave as neutral, monoanionic, or dianionic ligands, depending on the combination of het-

SCHEME 7. A Proposed Redox-Coupled Oxidative Addition Mechanism for **23X**

erole subunits. Notably, the P,X,N₂-hybrid calixphyrin platform changes its shape, charge, and oxidation state flexibly to provide the most suitable coordination environment for the metal center. We anticipated that the hemilabile nature of the calixphyrin platform could be utilized in a conceptually new metal-assisted C–X bond activation.

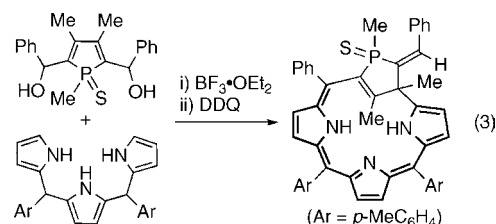
Scheme 7 displays a proposed redox-coupled oxidative addition of an aryl halide by using Pd–P,X,N₂ complex **23X**.¹⁹ Partial dissociation of the heterole rings of **23X** under appropriate conditions generates vacant coordination sites at the metal center. Importantly, two electrons that are necessary to oxidatively cleave the carbon–halogen bond are supplied from the redox active N–X–N unit. Such a bond-activating methodology is of interest, because it highlights the intrinsic properties of the hybrid calixphyrin platform. Although no experimental evidence regarding the aryl–palladium(II)–halide species is in our hand, theoretical calculations on model reactions have supported that this mechanism is worth considering from an energetic viewpoint.²⁵ In fact, Mizoroki–Heck reaction of an activated bromoarene, which probably operates through a commonly admitted catalytic cycle involving the oxidative addition onto Pd(0), is catalyzed by **23X** (eq 2). To verify the above hypothesis, further experimental studies are now ongoing.



Synthesis of Phosphole-Containing Porphyrins

As stated in the Introduction, core modification is now regarded as a highly promising approach to change the electronic structures and coordination environments of the porphyrin ring.² With phosphatripyrrane **7** in hand, we succeeded in preparing the first examples of phosphole-containing P,X,N₂-hybrid porphyrins **28X** (Scheme 8).^{10,26} The BF₃-promoted dehydrative condensation of **7** with **15X** (X = S, N) in CH₂Cl₂, followed by desulfurization with P(NMe₂)₃, afforded the corresponding phosphole-containing porphyrinogens **27X**. Oxidation of **27X** with DDQ produced the target phosphole-

containing porphyrins **28X** as reddish purple solids. In a recent attempt by Mathey and co-workers to synthesize a phosphaporphyrin via a different [3 + 1] approach, a small amount of “P-confused” carbaporphyrinoid was isolated (eq 3).⁹ Therefore, the choice of suitable precursors is important to promote the desired porphyrin-ring formation. To reveal the effect of core-phosphorus atom on the coordination property of hybrid porphyrins, S₂N₂-porphyrin **29** (inset of Scheme 8) was prepared as a reference.²⁷



Complexation of Phosphole-Containing Porphyrin

As the first attempt to make transition metal complexes of phosphole-containing porphyrins, we examined the complexation of **28S** with zero-valent group 10 metals (Scheme 9).²⁷ Treatment of **28S** with 1 equiv of Pd(dba)₂ in CH₂Cl₂ produced Pd–P,S,N₂ complex **30Pd** in quantitative yield within 1 min at room temperature. In marked contrast, no complexation took place between **29** and Pd(dba)₂ even after refluxing in 1,2-dichlorobenzene for 5 h. These results indicate that high coordinating ability of the core-phosphorus atom in **28S** contributes significantly to the facile complexation with palladium. Reactions of **28S** with Ni(cod)₂ and excess Pt(dba)₂ produced **30Ni** and **30Pt**, respectively.

Structures of Phosphole-Containing Porphyrin and Its Metal Complex

As shown in Figure 4a, the porphyrin ring in **28N** is bent to make a slightly distorted 18π-plane, and the P-phenyl group is located above it.²⁶ The C–C bond length alternation in **28N** indicates the significant contribution of the 18π-annulene circuit indicated as a bold line in Scheme 9. It is therefore likely that the lone electron pair at the pyramidal phosphorus center is not involved in the porphyrin 18π system and is directed inside the core. The P⋯N(23) distance of **28N** is considerably shorter than that of P,N₃-calixphyrin **19N**, reflecting the difference in inclination of the phosphole ring between these two hybrid macrocycles (Table 2). On the other hand, the N(22)⋯N(24) distance of **28N** is very close to that of **19N**, exhibiting the similarity of their N–N–N π-conjugated structures.

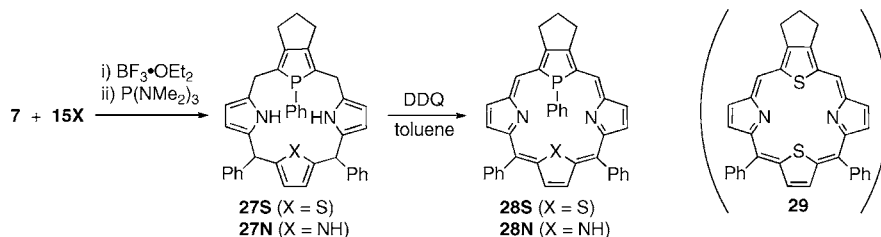
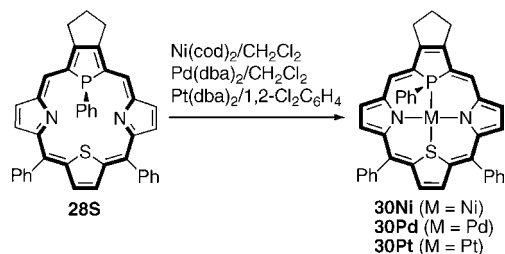
SCHEME 8. Synthesis of P,X,N₂-Hybrid Porphyrins^{10,26}SCHEME 9. Complexations of P,S,N₂-Hybrid Porphyrin²⁷

Figure 4b depicts the structure of **30Pd**, where the palladium center adopts a square-planar geometry.²⁷ Consequently, the phosphorus and sulfur atoms are displaced by 0.93–0.95 Å from the mean π plane comprised of the peripheral 20 carbon atoms. The Pd–S and Pd–N bond lengths of **30Pd** are almost identical to those of Pd–P,S,N₂-calixphyrin complex **23S**, whereas the Pd–P bond length of **30Pd** is somewhat shorter than that of **23S**. These observations reflect the difference in hybridization at the 5,10-*meso* carbon centers between the porphyrin and calixphyrin platforms. The most salient feature of **30Pd** is the peripheral C–C bond length alternation, which indicates the 20 π valence-bond structure (isophlorin character) for the P,S,N₂-hybrid ligand as indicated in Scheme 9.

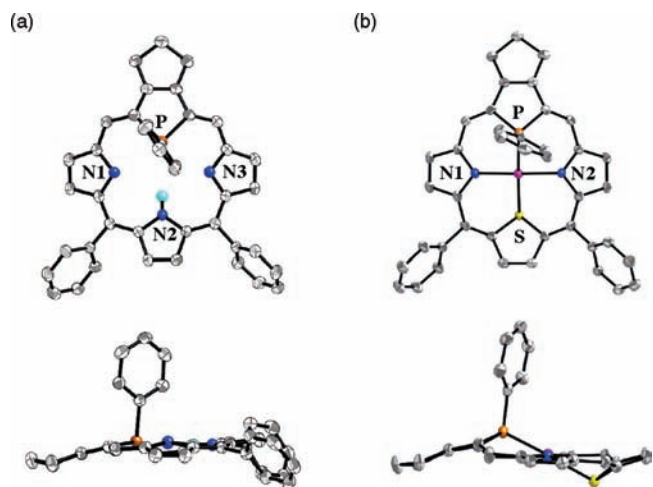


FIGURE 4. Structures (top and side views) of (a) **28N** and (b) **30Pd**. *meso*-Ph groups (b, side view) are omitted for clarity. Reproduced from refs 26 and 27. Copyright 2008 American Chemical Society.

Aromaticity of Hybrid Porphyrins and Their Metal Complexes

As noted above, **28N** possesses a slightly distorted 18 π circuit, whereas **30Pd** contains a highly ruffled 20 π circuit with a bend occurring along the 5,15 axis. In this regard, **28N** possesses aromaticity in terms of a geometrical criterion, whereas **30Pd** does not. Another quantitative index of aromaticity is “ring current effect” of the π circuit. The ring current effects of porphyrin derivatives are experimentally observable as unusual chemical shifts of the inner and outer (peripheral) protons by NMR spectroscopy and are theoretically predictable as nucleus-independent chemical shifts (NICS) by DFT calculations.²⁸

As shown in Figure 5a, both shielding and deshielding effects induced by the 18 π circuit of P,X,N₂-porphyrins **28X** are clearly observed in their ¹H NMR spectra.^{10,26} The pyrrole- β and *meso* protons of **28X** are deshielded compared with the corresponding protons of porphyrinogens **27X**. By contrast, the P-phenyl protons are significantly shielded relative to those of **27X**. An advantage of incorporating a phosphorus atom as the core element is that the ³¹P nuclei is NMR active and reflects the magnetic as well as electronic character of surroundings. In fact, the ring current effect at the core emerged as upfield shifts of the ³¹P peaks of **28N** (δ –5.2) and **28S** (δ 18.6) relative to the respective peaks of **27N** (δ 30.4–32.7) and **27S** (δ 32.7–33.5). The observed spectral features can be explained by considering the diatropic ring current effects induced by the aromatic 18 π circuits. In sharp contrast to **28X**, metal complexes **30M** show negligible diatropic/paratropic ring current effects on the peripheral and P-phenyl protons in the ¹H NMR spectra (Figure 5b), thus indicating the nonaromatic character of the 20 π isophlorin circuit in terms of a magnetic criterion.²⁷ The NICS values calculated for model compounds **28S-m** and **30Pd-m** support the spectral observations (Figure 5c,d).

Recent studies by Vaid²⁹ and by Brothers³⁰ have revealed that silicon, germanium, and diboranyl N₄-isophlorin complexes possess antiaromatic character. Interestingly,

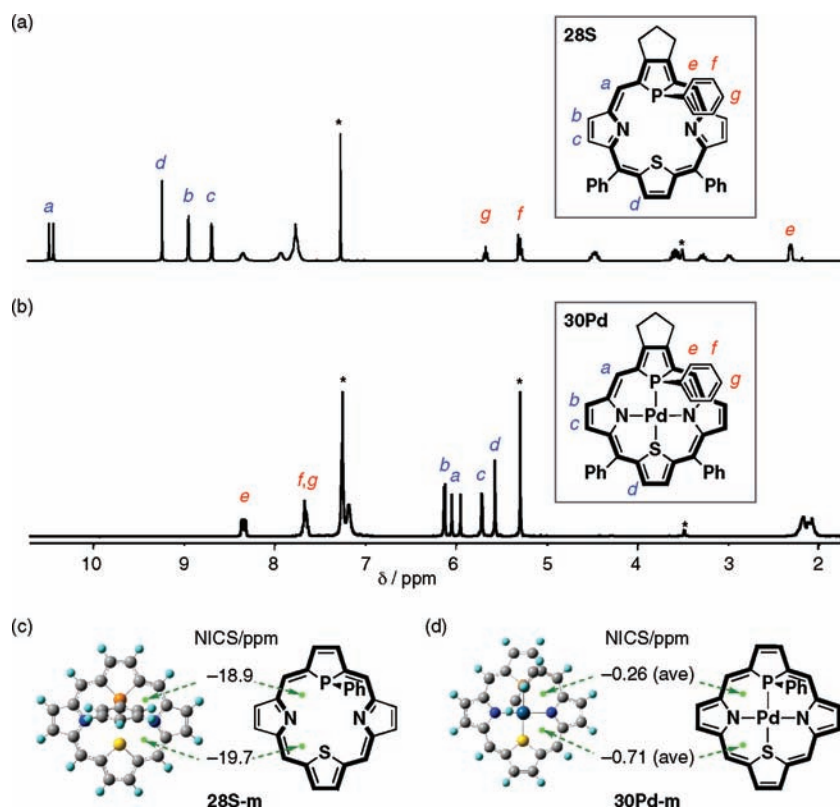


FIGURE 5. ^1H NMR spectra of (a) **28S** and (b) **30Pd** and NICS values of (c) **28-m** and (d) **30Pd-m**.

Vaid's silicon(IV) and germanium(IV) complexes display appreciable paratropic ring current effects despite the extensive ruffling of the TPP-type isophlorin ligand. While not deeply understood at present, the loss of paratropicity in **30M** may be ascribable to the distortion from planarity of the 20π ring system and also to the intrinsic nature of the central group 10 metals.

The optical and redox properties of **28X** and **30M** are also worth mentioning. In the UV–vis absorption spectra, **28N** and **28S** display Soret bands at λ_{max} 431 and 440 nm, respectively, together with low-energy Q bands.^{10,26} Both the Soret and Q bands of **28N** are remarkably red-shifted compared with those of TPP (TPP = 5,10,15,20-tetraphenylporphyrin). The first oxidation and reduction potentials of **28X** are more negative and more positive compared with the respective values reported for TPP.³¹ The difference between the two potentials of **28N** ($\Delta E = 1.89$ V) is considerably smaller than that of TPP ($\Delta E = 2.31$ V). It is now evident that the incorporation of one phosphole subunit into the porphyrin ring significantly narrows the HOMO–LUMO gap of the 18π system.

On the other hand, the UV–vis absorption spectra of **30M** show broad, high-energy Soret-like bands and no detectable Q bands, which is characteristic of highly ruffled, nonaromatic $4n\pi$ porphyrinoids.²⁷ The redox-coupled

complexation with palladium and platinum shifts the oxidation potential of the P,S,N₂-hybrid π system to the negative side by 0.69–0.71 V, certainly reflecting the 20π isophlorin structure of the resulting complexes **30M**. In marked contrast to air-sensitive N₄-isophlorin-metal complexes, the P,S,N₂-isophlorin complexes **30M** are chemically stable, which represents the benefit of core modification with phosphorus.

Concluding Remarks

The establishment of a convenient method for the synthesis of phosphatripyranes enabled us to prepare the first examples of phosphole-containing calixpyrroles, calixphyrins, and porphyrins of the P,X,N₂-type. Our recent investigations on these core-modified derivatives have exemplified that the incorporation of the phosphole subunit into the macrocyclic platform dramatically alters the coordinating, electronic, magnetic, and optical properties of the porphyrin family. It is of utmost interest that the remarkable ability of phosphole to tightly bind metals in neutral form provides unprecedented coordination environments in terms of the size, shape, and charge at the core. Additionally, the redox properties of the calixphyrin and porphyrin platforms are fine-tunable by changing the combination of π -conjugated heterole subunits. Indeed, a variety of metal complexes bearing these new

P,X,N₂-hybrid ligands were prepared and fully characterized. Our next challenge includes the development of new metal-sensing systems, catalytic systems, and well-organized π -spaces by utilizing the phosphole-containing hybrid macrocycles. We believe that the versatile performance of the core-modified porphyrin family will be further explored in these contexts in the future.

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Note Added after ASAP. This paper was published on the web on June 4, 2009 with errors in Figure 5. The revised version was published on June 15, 2009.

BIOGRAPHICAL INFORMATION

Yoshihiro Matano became an Assistant Professor at Faculty of Science, Kyoto University, in 1990 and received his Ph.D. from Kyoto University in 1994. From 1996 to 1997, he joined Prof. James Mayer's group (University of Washington) as a Monbusho visiting scholar. In 2002, he moved to Graduate School of Engineering, Kyoto University, as an Associate Professor. His research interests include elements chemistry and porphyrin chemistry.

Hiroshi Imahori received his Ph.D. in organic chemistry from Kyoto University. He became an Assistant Professor at ISIR, Osaka University, in 1992, an Associate Professor at Graduate School of Engineering, Osaka University, in 1999, and a Professor at Graduate School of Engineering, Kyoto University, in 2002. Since 2007, he has also been a Principal Investigator of iCeMS, Kyoto University. His research interests include novel π -aromatic compounds, carbon nanostructures, self-assembly, photofunctional materials, organic solar cells, and drug delivery systems.

FOOTNOTES

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