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Review

Metal Complexes of Porphyrinoids Containing Nonpyrrolic Heterocycles

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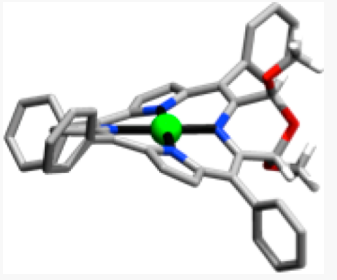
ABSTRACT: The replacement of one or more pyrrolic building block(s) of a porphyrin by a nonpyrrolic heterocycle leads to the formation of so-called pyrrole-modified porphyrins (PMPs), porphyrinoids of broad structural variability. The wide range of coordination environments (type, number, charge, and architecture of the donor atoms) that the pyrrole-modified frameworks provide to the central metal ions, the frequent presence of donor atoms at their periphery, and their often observed nonplanarity or conformational flexibility distinguish the complexes of the PMPs clearly from those of the traditional square-planar, dianionic, N_4-coordinating (hydro)-porphyrins. Their different coordination properties suggest their utilization in areas beyond which regular metalloporphyrins are suitable. Following a general introduction to the synthetic methodologies available to generate pyrrole-modified porphyrins, their general structure, history, coordination chemistry, and optical properties, this Review highlights the chemical, electronic (optical), and structural differences of specific classes of metalloporphyrinoids containing nonpyrrolic heterocycles. The focus is on macrocycles with similar "tetrapyrrolic" architectures as porphyrins, thusly excluding the majority of expanded porphyrins. We highlight the relevance and application of these metal complexes in biological and technical fields as chemosensors, catalysts, photochemotherapeutics, or imaging agents. This Review provides an introduction to the field of metallo-PMPs as well as a comprehensive snapshot of the current state of the art of their synthesis, structures, and properties. It also aims to provide encouragement for the further study of these intriguing and structurally versatile metalloporphyrinoids.



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1. INTRODUCTION

1.1. Porphyrins, Hydroporphyrins, and Pyrrole-Modified Porphyrins (PMPs)

Porphyrins and hydroporphyrins are tetrapyrrolic macrocycles with an 18 π-electron aromatic system and two, one, or no cross-conjugated double bonds, respectively (Figure 1).[1] The vast majority of (hydro)porphyrins occurring in nature and a large fraction of the porphyrins found in biological and technical applications are coordinated to a metal ion in their center, where the porphyrinic ligands provide idealized square-planar, dianionic, N_4-coordination environments.[2] Variations of out-of-plane coordinating double- and triple-decker complexes involving synthetic porphyrins are known, but they also rely on the N_4-coordination environment of the constituent porphyrins.[3,4]

Next to classic (hydro)porphyrins, contemporary porphyrin chemistry also generated families of pyrrole-based macrocycles with porphyrin-like structures and π-systems, including porphyrin isomers or analogues that contain a different number of pyrrolic building blocks: three in the so-called contracted porphyrins and five, or more, in the so-called expanded porphyrins (Figure 1).[5,6] Framework contraction may also be accomplished by a reduction of the number of carbon atoms between the pyrrolic moieties, as present in corroles.[7,8]

The metalloporphyrinoids subject to this Review are the metal complexes of those (hydro)porphyrin-analogues that contain one, or more, nonpyrrolic building blocks in their macrocycle framework in place of one, or more, pyrroles. These building blocks may be, for example, carbacycles[9−11] or 4- to 6-membered (or larger) heterocycles (such as azetes, oxazoles, imidazoles, triazoles, benzenes, pyridines, or morpholines, etc.; Figure 2).[12−14]

We also included here select porphyrin isomers and contracted or expanded porphyrins that contain nonpyrrolic carba- or heterocycles. For simplicity, we will refer to all of these macrocycles as pyrrole-modified porphyrins (PMPs).[13] Others have referred to a select group among them as heteroporphyrins (or their expanded analogues)[15] or as core-modified porphyrins.[16,17] Irrespective of their naming, the group of PMPs is inherently different from heterocycle-appended porphyrins (that are not subject of this Review).[18,19]

A number of general reviews on the syntheses and properties of PMPs are available.[12−14] Likewise, timely and comprehensive reviews of hydroporphyrins,[20] flexible porphyrinoids,[21] or core-modified expanded porphyrins[16,22−25] that also include some pyrrole-modified hydroporphyrin-analogues, as well as dedicated reviews on specific PMP classes, such as carbaporphyrins[9−11,26,27] or heteroporphyrins,[16,28−31] are available. In contrast to the existing reviews, however, we focus here exclusively on the metal complexes of the PMPs, with a particular aim on the structural, electronic (optical), and chemical differences between complexes of the corresponding regular porphyrins and hydroporphyrins. Our focus is on macrocycles of similar "tetrapyrrolic" architectures as porphyrins.

Thusly, we will not include pyrrole-modified derivatives for which no metal complexes were reported, the metal complexes of nonconjugated macrocycles, such as the calixpyrroles (and derivatives),[32−36] phlorins,[37] isophlorinoids,[38] porphodimethenes,[39] corroles,[22] heterocorroles,[40,41] or PMP-type analogues of the macrocycles with *meso*-nitrogen atoms,[42−50] such as phthalocyanine or porphyrazines.[51] Inner *N*-substituted por-

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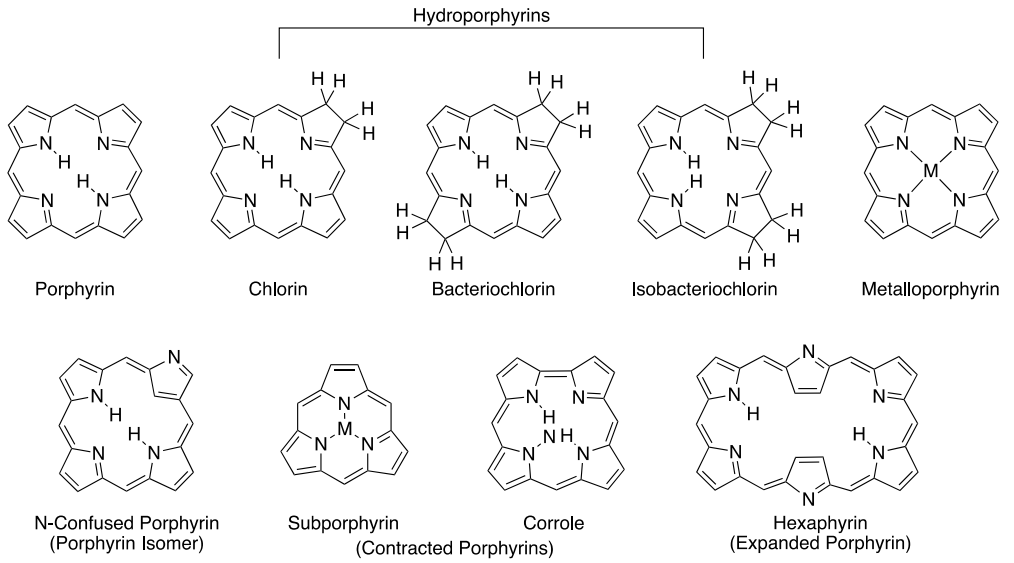

Figure 1. Structures of the classic porphyrins, hydroporphyrins, and metalloporphyrins and examples of porphyrin isomers and contracted and expanded porphyrins.

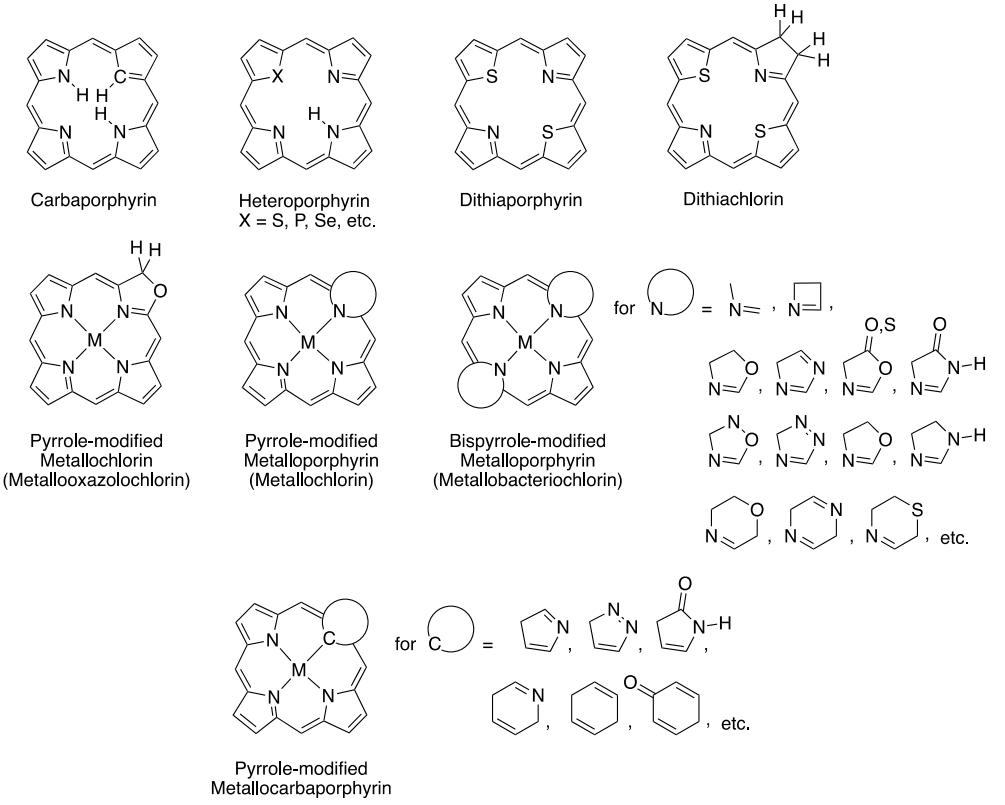

Figure 2. Structures of general examples of the metalloporphyrinoids containing nonpyrrolic heterocycles discussed here.

phyrinoids may also be regarded as "pyrrole-modified" porphyrins. Indeed, they are an important class of porphyrinoids of biological relevance and of emerging technical importance.[52−54] *N*-Alkylation or *N*-arylation affects their conformation, metal complexing abilities, and electronic structures;[52,54−56] porphyrin *N*-alkylation may even elicit the rearrangement of the porphyrin to a PMP.[57] Nonetheless, they are not specifically reviewed here, but *N*-alkylated derivatives of the PMPs are discussed together with their parent macrocycles.

Select examples of carbaporphyrins and heteroporphyrins have been known longer and were studied more intensely than most other examples, including their coordination chemistry. Examples include N-confused and N-fused porphyrins,[58−62] benzocarbaporphyrins,[63] and their heteroanalogues.[10,64,65] They have been thoroughly reviewed in the ~~contemporaneous~~ literature; consequently, we provide only an abbreviated overview, with reference to the detailed accounts.

When compared to the square-planar, dianionic, N_4-donor environment of the regular metalloporphyrins, the metal

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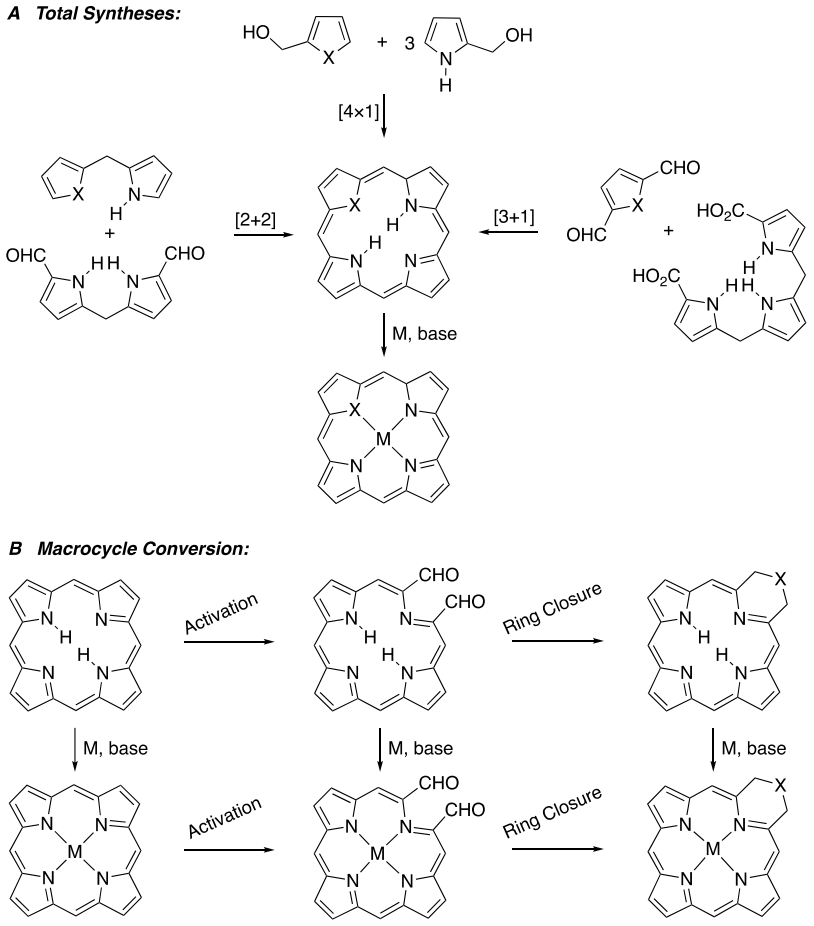
Scheme 1. Principal Pathways toward Metallo-PMPs



complexes of PMPs may exhibit a range of different donor environments in terms of donor atom types, charges, numbers, and geometries. Thus, following the introductory sections, this Review is organized according to the coordination environments that the PMPs provide to the central metal. The metal ions are also frequently crucial in the formation of the macrocycles, as are the expression of their conformations, electronic properties, or function. We highlight the roles of the metals in their formation or properties that inspire their recommendation for a number of applications.

1.2. General Synthetic Methods toward PMP Macrocycles

We can distinguish two principally different methods toward the synthesis of PMPs: total syntheses and modifications of a preformed macrocycle (Scheme 1A).[13]

Most frequently pursued are total syntheses, many of which were adopted from methodologies toward the synthesis of regular porphyrins. These total syntheses may be classified according to the number of "pyrrolic" units—we also include here the nonpyrrolic stand-ins for pyrroles—present in the building blocks used for the macrocycle formation step; thus, [4 × 1] (also known as Rothemund condensations), [2 + 2], [3 + 1],[66] [3 + 2], etc. syntheses can be distinguished. The [4 × 1]-type syntheses are the condensation of pyrrole and a suitable aldehyde (or equivalent) or the self-condensation of a suitably substituted pyrrole. While these reactions are very popular for the synthesis of symmetric porphyrins,[67−70] only few PMPs are formed in this way and generally only because of a productive side reaction to the regular, expected porphyrin formation, as is the case for the so-called N-confused porphyrins (see also Section 2.4.1).[71−73] Those [2 + 2] syntheses comprising the acid-catalyzed condensation of a dipyrromethane (also known as dipyrrylmethanes) and a dipyrromethane bisaldehyde (or their analogues) are referred to as MacDonald condensations.[74,75] The condensation reactions are often acid-induced, followed by an oxidative step to convert the initially formed nonconjugated macrocycle to the final conjugated (or even aromatized) product. In select cases, the fully conjugated systems are formed upon metalation.[76−78] As the examples below will demonstrate, these methods have consistently and efficiently been utilized to make a range of porphyrinoids containing 5-, 6-, and 7-membered carba- and heterocycles (see, e.g., most examples in Sections 2.3−2.8).[13] Total syntheses were also suitable for the insertion of more than one nonpyrrolic building block. However, few of the reactions lend themselves naturally to upscaling, an important aspect when considering practical applications for the products. Generally, the metal ion is inserted once the free-base porphyrinoid is formed, though exceptions are known (see below for a discussion of the metalation reaction step).

Less frequently applied, but nonetheless standing out as a versatile approach, the synthesis of metallo-PMPs can also be achieved via the conversion of a preformed porphyrin, chlorin, or subporphyrin (see, e.g., many examples in Sections 2.1 and 2.2).[12−14,79] Often, several distinct steps in these processes can be distinguished (Scheme 1B): The porphyrin is functionalized at its pyrrolic β-positions. This functionalization is the synthetic handle for an oxidative pyrrole ring-opening/activation step,

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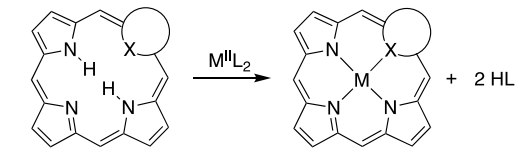
followed by a (ring-closing) step that generates the nonpyrrolic heterocycle of the same or different ring size as the 5-membered pyrrole from which it is derived. At times, multiple elementary steps may take place in a single reaction. Also, the reaction sequence can be performed twice on the same molecule, either in parallel or in succession, to generate dimodified systems. PMPs of one class are susceptible to conversion into other classes of PMPs using functional group interconversion strategies.[12−14,79] PMP syntheses and modifications may also not involve the β-positions altogether (see, for example, the vacataporphyrins, Section 2.1.2). The metal ion may be inserted once the free-base PMP is formed, or at any other stage. In some instances, the metal plays an important role in stabilizing the intermediates of the ring-opening step, a point highlighted below with specific examples.

1.3. Metal Insertion Reactions

The formation of metalloporphyrinoids is key for their broad utilization in, for example, catalysis,[80] biomedicine,[81] molecular electronics,[82] or artificial light-harvesting.[83] The formation of metalloporphyrinoids from their free-base compounds is a classic metathesis reaction.[2] In its simplest form, the reaction of a divalent metal salt (ML_2) with a dibasic porphyrinoid forms the metalloporphyrinoid [and the corresponding acid of the metal salt anion (HL); Scheme 2].[2,84]

Scheme 2. Generalized Metathesis-Type Metal Insertion Reaction into a PMP-Type Porphyrinoid



Many variations of this reaction are known, such as involving metals of oxidation states lower than the final oxidation state of the metal found in the PMP, implying the involvement of redox reactions during the metal insertion.[2,84,85] Furthermore, a varied selection of mono- and multidentate axial ligands to the metalloporphyrinoid may be present, or double-decker or multinuclear complex assemblies may form.[2,4,86,87]

Regular (hydro)porphyrins generally provide dianionic idealized square-planar N_4-coordination environments to metals located in their central cavity. (Hydro)porphyrins are also typical noninnocent ligands, able to partake in redox events at the metal.[88,89] Many PMPs also provide porphyrin-like N_4-donor sets (see Section 2.2). Those that are planar and of similar basicity are expected to also possess coordination chemistry properties that are similar to those of metalloporphyrins. Others that are nonplanar or have much altered donor atoms show the corresponding variations in their coordination behavior. In addition, PMPs may provide neutral, monoanionic, dianionic, or trianionic coordination environments with S_4, N_3C, N_2C_2, N_3S, NCNS, N_4−N_4,[90] etc., donor sets in a conformationally malleable framework,[21] as the examples below will illustrate. This changes their coordination chemistry in fundamental ways compared to those of the N_4-porphyrins and N_4-porphyrinoids (such as corroles[22] or porphyrin isomers such as porphycenes,[91−95] etc.). To which degree some PMPs (or porphyrin-like macrocycles likes corroles)[96] are noninnocent only began to be studied more recently.[90]

Upon the insertion of a metal ion into all carbaporphyrin-type PMPs, i.e., PMPs containing one (Section 2.4) or two (Section 2.5) inner carbon atom(s) in place of a (pyrrolic) nitrogen atom of the regular (hydro)porphyrins,[10,97] the potential for the formation of a metal−C bond is given (see, e.g., N-confused porphyrins,[98] azuliporphyrins,[99,100] or benziporphyrins[101]).[9,28] By definition, these M−C bond-containing entities are organometallic species. To some extent, the potential for the formation of an organometallic complex is also given for some metallocethyneporphyrins (e.g., Section 2.3.5) or PMPs containing inverted building blocks (e.g., Sections 2.4.3, 2.4.4, or 2.4.7), allowing in the latter case pyrrolic β-carbon atoms to coordinate to the central metal ion.

Generally, the rate-limiting steps in the metal insertion reaction into a porphyrin are determined by the considerable kinetic barrier of the initial metal insertion step into the planar and relatively rigid macrocycle.[84] The porphyrin points its (protonated) donor atoms of low basicity toward the center of its (small) central cavity; the nitrogen atoms are thusly shielded from facile deprotonation and/or coordination to metal ions. Nature overcomes these barriers with the help of metal (iron, magnesium, or cobalt) insertion enzymes that induce a deformation of the porphyrin (or related tetrapyrroles) from planarity upon binding to the enzyme, thereby exposing the inner NH/N atoms; these deformation enzymes therefore catalyze the formation of the complexes.[102−104] Since some PMPs are intrinsically nonplanar or conformationally more flexible than a native porphyrin,[21] it is not surprising that many traditionally slow metal insertion reactions take place more readily,[105] though detailed kinetic analyses are not available. Above and beyond the conformational effects, there are also the intrinsic kinetic barriers inherent to any specific metal ion that need to be overcome.[106]

Therefore, traditional approaches toward the formation of metalloporphyrins frequently employ the reaction of the porphyrin and a metal salt in a (relatively) kinetically labile (often low) oxidation state in a high-boiling donor solvent (pyridine, bp 115 °C; DMF, bp 153 °C; PhCN, bp 191 °C) under reflux conditions over extended periods of time.[2,107] Microwave-assisted heating methods and mechanochemical approaches are also available.[108−110] The use of M(0) sources at low temperatures may also offer milder insertion conditions for sensitive porphyrinoids,[85,110] but we are not aware of the utilization of these methods for the formation of metal complexes of pyrrole-modified derivatives. The stable oxidation state of the metal in the metalloporphyrin is then frequently reached by a subsequent (air) oxidation step.[2,4,111]

1.4. Role of the Coordinated Metal Ions

The coordination chemistry of porphyrins is exceedingly rich, with nearly all metals (and many metalloids—largely ignored here) shown to coordinate to the porphyrin nitrogen atoms, forming a large variety of metal−ligand architectures.[2−4,86,87] Also, the electrochemistry of the metalloporphyrins is well-studied and serves as a benchmarks for PMP metal complex electrochemical studies.[112,113] In comparison, much fewer metal complexes of the PMPs have been studied.[12−14] Among those, a small number of metal ions have been used frequently, mostly for practical reasons: When metal ions are needed as protection groups to prevent either the protonation of the inner imine nitrogen atoms or the formation of deprotonated forms of the free-base ligand, the use of the diamagnetic metal ion Zn^{2+} (74 pm, d^{10}, square-planar, square-pyramidal, or octahedral)[114] is

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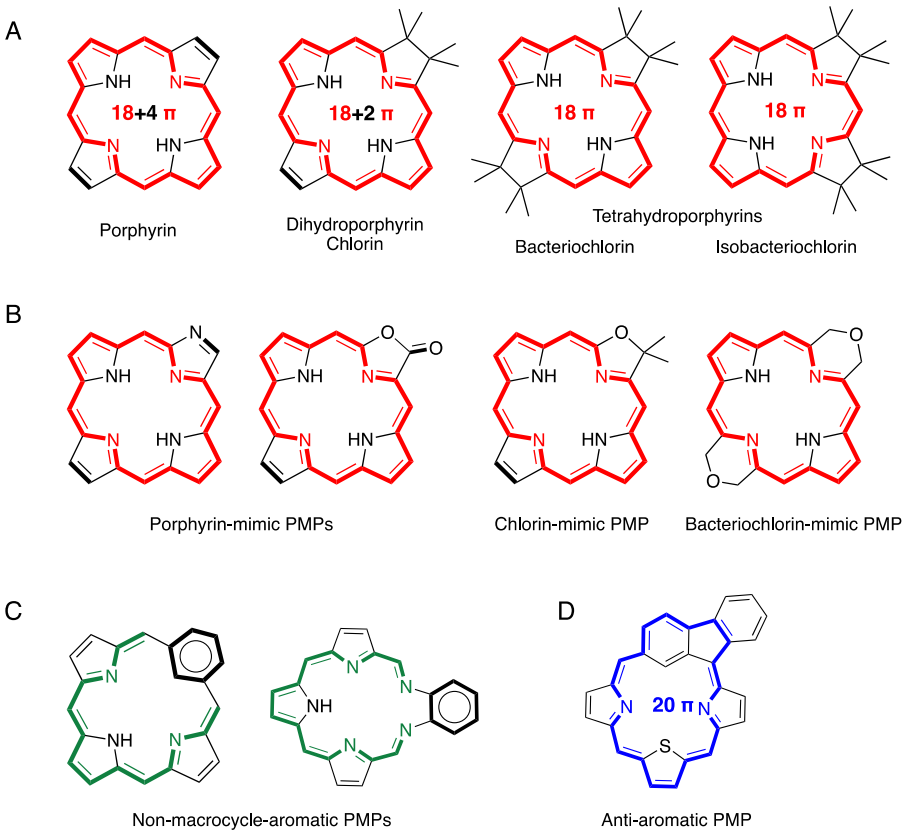

Figure 3. Graphical representation of the macrocycle-aromatic π-systems (in bold red); conjugated, but nonmacrocyclic-aromatic π-systems (in bold green); and macrocyclic antiaromatic π-systems (in bold blue) within the porphyrinoids shown.

advantageous as this complex generally forms readily, but the metal ions can also be removed readily (using acid).[2,107] Other practical considerations like availability, cost, (low) toxicity, solubility of the salts in the solvents suitable for porphyrins, etc., also play into zinc's favor. The choice of diamagnetic metal ions retains the option to obtain regular NMR spectra. More robust than Zn^{2+} toward adventitious (acid-induced) removal is Ni^{2+} (63 pm, d^8, l.s.)[114] or the larger Pd^{2+} (78 pm, d^8);[114] both form diamagnetic, square-planar complexes that are overall neutral (with dianionic ligands, like porphyrins),[2,86] also making them the metals of choice for many porphyrinoids.[12,13] Alas, Ni^{2+} and Pd^{2+} generally cannot be removed from the ligand without ligand destruction. Also, in the presence of high concentrations of other N-donor ligands (like when dissolved in pyridine), Ni^{2+} complexes frequently lead to the formation of octahedral paramagnetic high-spin complexes. The Ni^{2+} ion is typically a little bit too small to fit perfectly into a porphyrin-sized cavity and thus introduces some strain that generally leads to nonplanar (ruffled) conformation modes of the porphyrinic macrocycle.[115−118] Nonetheless, the presence of Ni^{2+} was often observed to lead to a great stabilization of the porphyrinoids,[79] and thus, their Ni^{2+} complexes are routinely prepared; their redox chemistry is well-studied.[119−121] Nickel complexes of PMPs were also used in electrocatalytic proton reduction reactions.[122,123] The copper ion Cu^{2+} (71 pm, d^9, l.s.)[114] also inserts readily into many porphyrinoids and may have similarly stabilizing effects without introducing as many (or any) distortions as nickel, but it renders the complexes paramagnetic. This makes this metal ion a less preferred choice for the synthetic chemist reliant on diamagnetic NMR spectroscopy, albeit the NMR spectroscopic investigation of paramagnetic Ni(II), Ni(III), and Cu(II) complexes of carbaporphyrin-based PMPs is practiced.[124] As many examples presented below will show, many copper PMP complexes contain the metal in the +III oxidation state; the copper(III) d^8 ion is diamagnetic. Though more costly, the use of Pt^{2+} (74 pm, d^8)[114] is also popular; the complexes are similar to the corresponding Pd^{2+} complexes, but this nonlabile metal ion is much harder to insert into any ligand, including porphyrins.[86] The 4d and 5d group 10 metal ions also readily form organometallic complexes with the inner carbon atoms of the carbaporphyrinoids and are therefore advantageous to be used if a carbon atom is part of the PMP donor set.[10,11] The strong spin−orbit coupling (heavy atom effect) between the porphyrinic chromophore and the luminescence and long-lived triplet states of the Pd^{2+} and Pt^{2+} ions is the basis for several applications of the Pd/Pt-porphyrinoids.[125−127] Regular N_4-dianionic porphyrin and porphyrinoids form freely paramagnetic complexes with Ag^{2+} (d^9, 93 pm).[114] On the other hand, many porphyrinoids—particularly from the family of carbaporphyrins with "regular tetrapyrrole-like" architectures and N_3C donor sets—are trianionic ligands. Because of the higher charge density of these carbaporphyrins, they were shown to form neutral, diamagnetic, and fairly stable complexes with Ag^{3+} (d^8, 81 pm).[114] Hence, this otherwise unusual oxidation state of silver is frequently found in the metallocarbaporphyrinoid literature.[10,11] Most other metals used were chosen as synthons to saturate bi- or tridentate coordination sites ($Rh^{I}(CO)_2$, $Re^{I}(CO)_3$, respectively) or for their specific catalytic ($Fe^{2+/3+}$, Mn^{2+}, $Co^{2+/3+}$) or optical (Ln^{2+} like Yb^{2+}, Eu^{2+}, Nd^{2+})[128−133] properties. Examples presented below will illustrate the use of these metal ions.

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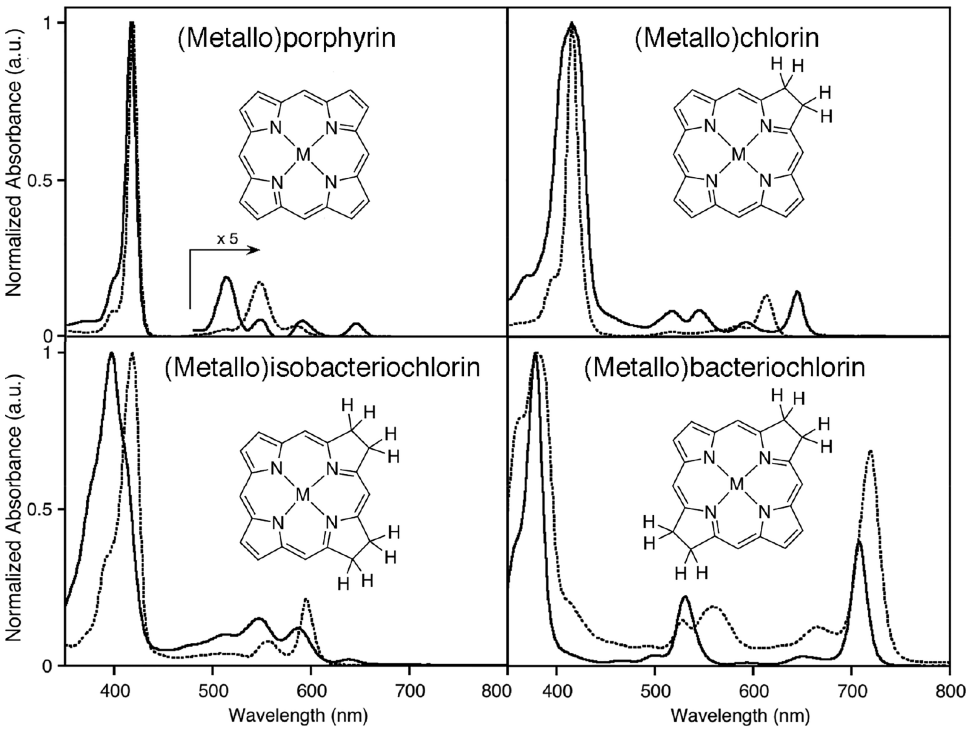

Figure 4. Normalized UV−vis spectra (CH_2Cl_2) of the four archetype classes of free-base porphyrin and hydroporphyrins (solid trace) and their zinc complexes (broken trace). Spectra are of the *meso*-tetraphenyl-di/tetrahydroxy-chlorin/isobacterio/bacteriochlorin series,[169−171] respectively, illustrating the relative appearance of the archetype spectra of the free-bases and metal complexes; the absolute peak positions vary with different *meso*- or *β*-substituents and particularly with the specific metal inserted.

Lastly, many of the PMPs are more chemically reactive than regular porphyrins or N_4-porphyrinoids. Thus, insertion of the metal ions may also induce framework modifications. These reactions—not all of which were metal-induced—have been reviewed.[17] We will point out only those reactions that can be directly linked to the presence of a metal.

1.5. π-System of Porphyrinoids and PMPs

Regular (tetrapyrrolic) porphyrins are characterized by the presence of a Hückel-aromatic 18 π-electron system, cross-conjugated with two additional double bonds, resulting in what is typically described as an 18 + 4 π-system. Figure 3 shows a graphical representation of the macrocycle-aromatic π-systems (in bold red) and conjugated, but non-macrocyclic-aromatic π-systems (in bold green), and macrocyclic antiaromatic π-systems (in bold blue) within the porphyrinoids.[134] Sequential reactions that convert one or both cross-conjugated *β*,*β*′-double bonds to single bonds—i.e., that convert the pyrrole building blocks to pyrrolines—generate chlorins, bacteriochlorins, or isobacteriochlorins, respectively.[20,135,136] In all cases, their resonance structures preferably take the so-called "inner−outer−inner−outer" pathways indicated.[134] The aromatic 18 + 4, 18 + 2, or 18 π-electron systems of the (hydro)porphyrins are primarily responsible for their characteristic electronic properties, discussed in more detail below.[137]

The replacement of one or more pyrroles by nonaromatic building blocks can have many different outcomes on the π-system of the resulting PMP (Figure 3B): In the simplest case, the nonpyrrolic building block electronically mimics the presence of a pyrrole—and the resulting PMP has a porphyrin-like 18 + 4 π-system and expresses a porphyrin-like optical spectrum. This is the case with, e.g., the imidazoloporphyrins (Section 2.2.7)[138−140] or porpholactones (Section 2.2.4).[141] If the nonpyrrolic building block is an electronic stand-in for a pyrroline, then a chlorin-like π-system with a chlorin-like optical spectrum is expressed; two pyrroline stand-ins form bacterio- or isobacteriochlorins (Section 2.2.5).[142−145] The interaction of multiple substituents in conjugation with the macrocycle-aromatic system may lead to strong interactions and distortions of these ideal cases (cf., e.g., Sections 2.2.4 and 2.4.1).[98,146−148]

In other cases, a nonpyrrolic building block may not be able to carry a macrocycle-aromatic π-system, even though (or because) these building blocks carry themselves local aromatic π-systems (Figure 3C). In these cases, no macrocycle-aromatic π-system is expressed, and the optical properties of these PMPs resemble linear, conjugated, but nonaromatic oligopyrroles. The benzi- and pyriporphyrins are an archetypical example (Sections 2.4.6 and 2.2.10).[149,150] However, substituents on the nonpyrrolic moieties may break the local aromaticity to enable a (partial) ring-current (see, e.g., Sections 2.4.6 and 2.2.10).[150]

Nonpyrrolic building blocks that enforce a macrocycle conjugation pathway involving 4n π-electrons are antiaromatic (Figure 3D). Albeit rare, they have been formed and are surprisingly stable (see Section 2.4.6).[151]

Importantly, the removal of a third cross-conjugated double bond from the tetrahydroporphyrins results in the interruption of the classic Hückel-aromatic 18 π-electron system. Thus, the reduction of (hydro)porphyrins may lead to the formation of their *leuco*-form, the porphyrinogens.[152,153] While their free-bases are preferentially in the porphyrinogen tautomeric form (5,10,15,20,22,24-hexahydroporphyrin), their nickel(II) complexes are in the pyrrocorphin form (2,3,7,8,12,13-hexahydroporphyrin).[152] Tris-modified (or even tetrakis-modified)[154−161] PMPs are rare (even including PMPs with pyrrolines as well as

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nonpyrrolic moieties), and only comparatively little is known about their metal complexes and electronic structures.[65,162]

In all cases, functionalizations/substitutions, metalation, and/or protonation of the macrocycles may alter their conjugation pathways and, thus, their electronic structures.[9,163,164]

1.6. Optical Properties

The aromatic 18 π-electron systems of porphyrins and hydroporphyrins are reflected in their characteristic UV−vis spectra (Figure 4).[137] Insertion of a central metal also results in diagnostic changes to the spectra that generally simplify (in some cases because of increased symmetry), often sharpen (because of increased rigidity of the macrocycle), and usually (metallobacteriochlorins represent an important and systematic exception[165−167]) blue-shift (because of the higher electronegativity of the metal cation that displaced two protons). Metal-based d−d transitions are generally not visible in the UV−vis spectra of any porphyrinoid as their intensities are several orders of magnitude smaller than the intense $\pi-\pi^*$ transitions of the ligand that dominate the spectra.[2,137] The nonlinear optical properties of porphyrins, including some porphyrin-analogues and their metal complexes, have been reviewed.[168]

The metal ion is tightly interacting with the π-system: Porphyrinoids are archetypical noninnocent ligands—as seen through strong spin−orbit couplings, the strong optical and bond length changes upon changes of the metal oxidation states,[88] changes in their electrochemical behavior,[113] or the electronic changes in the number or type of axial ligands on the metal, etc.[2] These effects are harnessed in the utilization of the metalloporphyrinoids as chemosensors, for example.[127,172]

All PMPs possess strong $\pi-\pi^*$ transition-based optical spectra. The optical spectra of non-macrocycle-aromatic PMPs frequently resemble those of linear, conjugated oligopyrroles.[173] Those that are macrocycle-aromatic sometimes resemble those of the (hydro)porphyrins, but as in the examples presented below, they often also vary significantly from those of the (hydro)porphyrin archetypes.

Metal insertion into PMPs has often diagnostic consequences for their optical properties, but again, the optical changes observed upon metalation vary vastly and are frequently also not along the lines of their regular (hydro)porphyrin congeners. The differences to the standard hydroporphyrin spectra—such as the frequently much red-shifted optical spectra—are one of the attractions of the metallo-PMPs.

The emission spectra of most metalloporphyrinoids are generally ligand-based.[137] However, as examples presented below will demonstrate, some porphyrinoids are good lanthanide sensitizers, and their emission spectra are therefore dominated by lanthanide f−f transitions.

1.7. Historical Perspective

Heteroporphyrins have been known for longer than most other PMP classes.[29,174] Pioneers in the total synthesis of heteroporphyrins (and porphyrin isomers) included the groups of Vogel.[155,157,175,176] Their coordination chemistry was studied early on by the groups of Balch and Latos-Grażyński.[28] Most other PMP classes were developed after the mid-1990s, with an exemption of the forays of the group of Flitch into the total synthesis of annulenes to represent the basic frameworks of isobacteriochlorins.[177−179] The important porphyrin isomer N-confused porphyrin was first reported contemporaneously by the groups of Latos-Grażyński[72] and Furuta[71] in 1994. Their discovery was the start of an unprecedented interest in the synthesis, modification, and coordination chemistry of carbaporphyrins and other PMP-type molecules derived from them.[9−11,27,58−61,100,180] It is surprising that it took as long as it did, as Aronoff and Calvin considered such isomers as early as 1943 as possible products from the Rothemund reaction (condensation of pyrrole and benzaldehyde)[181] as well as Pauling in 1944 (though his studies remained unpublished, as Senge noticed, in 2011).[182] The rapid development of expanded porphyrins by the groups of Sessler and Osuka (some of which could be defined as PMPs) intersected with the synthetic work by Maeda and Furuta on (fused and confused) PMPs[58−61] and some of their heteroanalogues, particularly as many of these conformational systems allowed the probing of fundamental concepts of aromaticity (as frequently probed by the group of Kim).[134,183−186] The groups of Chandrashekar and (later independently) Ravikanth explored a large number of so-called core-modified expanded porphyrins, the PMP-analogues of the expanded porphyrins, and their coordination chemistry.[15,16,25,31,187,188] Other key events that enabled the field of total synthesis of PMPs were the [3 + 1]-type synthetic methodologies[66,189] (and later [2 + 2] methods) that were perfected by the group of Lash for their application in the preparation of a structurally wide variety of (mostly carbaporphyrin-type) PMPs.[9,10,27,100,180] More generally, an early book on expanded porphyrins by Sessler[190] certainly inspired the field, as was the scientific success and general resonance that his work on the Texas-sized texaphyrin-class of PMPs generated.[76−78,191,192] Even though the group of Lindsey was not engaged in the total synthesis of PMPs, many of the strategies and building blocks developed have also undoubtedly influenced the field of PMP synthesis.[20,193−197] The field continues to be very dynamic.

The preparations of the first PMPs (considering free-base as well as their metal complexes) by conversions of porphyrins (and other porphyrinic compounds) were accidental. It took decades (until 1977) until the earliest (1933) porphyrin-to-PMP conversions described by the group of Fischer[198] were interpreted correctly.[199,200] The group of Callot reported the first pyrrole expansion reaction by a carbon atom—named at the time as a porphyrin homologation reaction—in 1978.[201,202] Even after further fortuitous discoveries of examples by the groups of Crossley (in 1984),[203] Gouterman (in 1989), and Chang (in 1992)[204] that converted (hydro)porphyrins into PMPs, it took until 1993 for the group of Bonnett to describe the first targeted preparation of a β,β'-ring-opened PMP (a chlorophin) and its ring-closure to a PMP containing a pyridinone moiety.[205] A forward-thinking review by Latos-Grażyński, in 1999, provided some early guidance in the insertion of atoms into a (metalloporphyrin) framework and reactions that would rearrange the framework.[206] After a gestation period during the early aughts, porphyrin-to-PMP conversion papers became more common, with the majority of the papers published in the recent decade.[12−14] A variety of groups have defined the field since, ranging from the expansion of the synthetic methodologies by the groups of Brückner[79] to the creativity of the group of Latos-Grażyński that presented new classes of PMPs and unprecedented PMP interconversion strategies[17,21] and to the group of Zhang[128] that can be credited for their recognition—and subsequent imaginative exploitation—of the utility of some PMPs in a wide range of fundamental and applied fields. This field of porphyrin conversions, complementary to the PMP total synthesis field, is likewise very dynamic, and new chromophores and applications emerge regularly.

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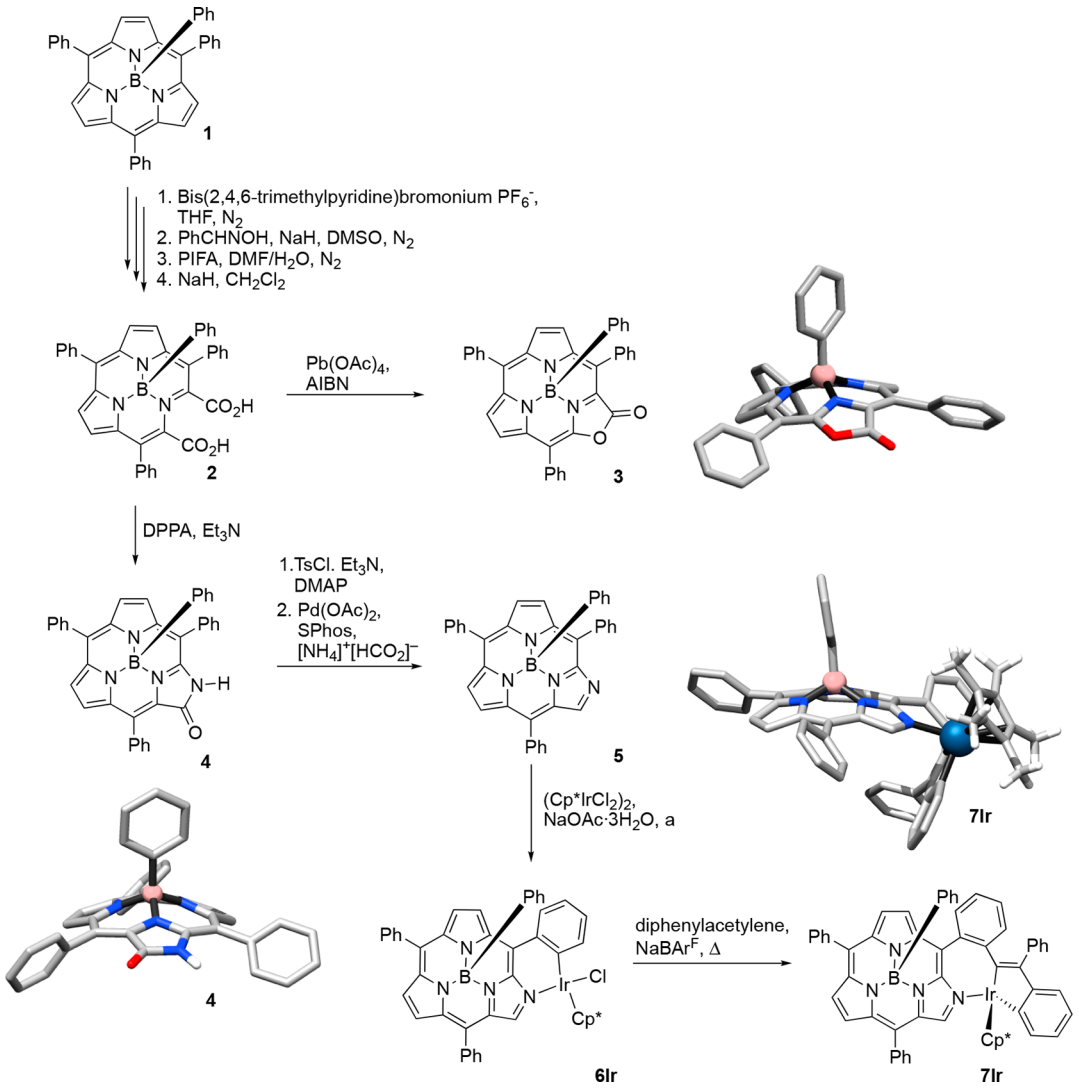
Scheme 3. Synthesis[a] of Pyrrole-Modified Subporphyrins[256,257]



[a]Stick representations of the X-ray structures of **3**, **4**, and **7Ir** adapted with permission from ref 256. Copyright 2018 Wiley-VCH.

Naturally, this overview is not comprehensive. Likewise, all of the research groups mentioned stood on the shoulders of early giants in the field of (hydro)porphyrins who provided important touch points that guided the thinking and synthetic methodology in the PMP field. These include Fischer,[207−209] the father of all synthetic tetrapyrrole chemistry; Johnson,[210−212] who introduced heteroporphyrins, expanded heteroporphyrins, and presented early examples of expanded porphyrins; and Vogel,[155,175,176,213] whose work included the presentation of porphyrin isomers and heteroporphyrins. Inhoffen,[214−216] Woodward,[217−220] Eschenmoser,[221−225] Smith,[226−232] and Dolphin[219,233−238] must be credited, *inter alia*, for their extensive pioneering work on synthetic methodologies in tetrapyrrole chemistry as well as on early expanded and ring-modified systems. Buchler[2,3,86,111] systematized the understanding of porphyrinoid coordination chemistry. A pioneer in the systematic study of the coordination chemistry of the heteroporphyrins was Balch,[239−244] including their paramagnetic NMR spectroscopic studies of a range of porphyrin metal complexes. Gouterman[245−248] must be credited for the rationalization of the porphyrin optical spectra but also for the discovery of the direct conversion of porphyrins to porpholactones. Montforts[135,249−253] (and others) contributed extensive work on the conversion of porphyrins to hydroporphyrins. The study of, and appreciation for, the conformational malleability of porphyrin conformations was formalized, for example, by Shelnutt[117,254] and, more recently, by Senge.[118] Their work remains most relevant also for the description of PMP conformations. Treatises on the aromaticity of porphyrinoids by the groups of Latos-Grażyński, Osuka, and Lash are also landmarks.[27,134,183,186]

2. METALLOPORPHYRINOIDS CONTAINING NONPYRROLIC BUILDING BLOCKS

2.1. Metalloporphyrinoids with N_3-Coordination Spheres

2.1.1. Boron Subporphyrin-Based PMPs and Their Iridium Complexes. Subporphyrins are a class of tripyrrolic ring-contracted macrocycles with 14π-electron systems that were assembled around a central boron(III) atom. These aromatic compounds possess strained, bowl-shaped conformations and are characterized by high-intensity fluorescence emissions.[24,50,255] In subporphyrin-based PMPs, one of the

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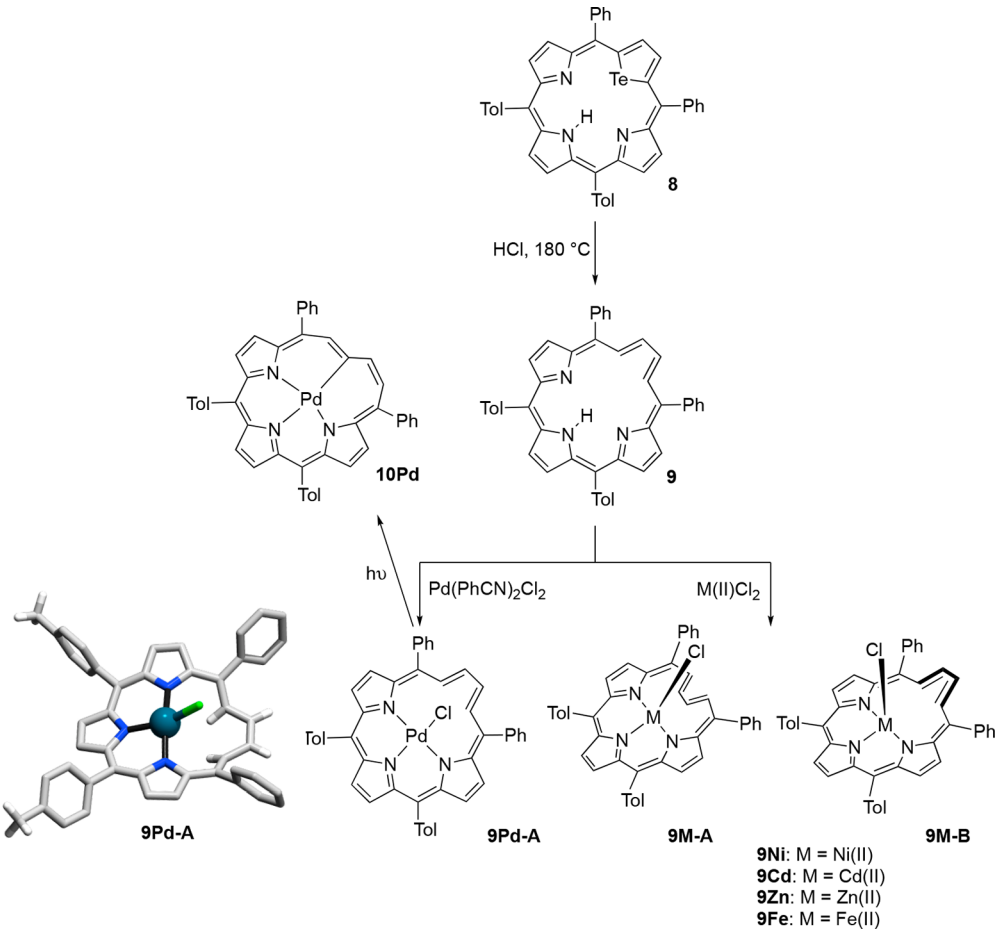
Scheme 4. Synthesis and Coordination Chemistry of Vacataporphyrin[a]



[a]Stick representation of the X-ray structure of **9Pd-A** adapted with permission from ref 261. Copyright 2008 American Chemical Society.

three pyrroles of a subporphyrin has been replaced by a nonpyrrolic building block.

Osuka and co-workers detailed the degradation of a pyrrole moiety in subporphyrin **1** to an imine functionality, generating subchlorophin **2** (Scheme 3).[256,257] This group also accomplished the formal replacements of a pyrrole by an oxazolone or imidazolone moiety, generating subporpholactone **3** or subporpholactam **4**, respectively, by functionalization and conversion of subporphyrin.[256] Subporpholactam **4** can be further converted to imidazolosubporphyrin **5**. The stepwise oxidative and functional group transformation approaches used are comparable to the pathways applied to regular porphyrins toward their conversion to PMPs (cf. multiple examples in Section 2.2).[139−141,258] Parallel to the porphyrin-based congeners, the optical spectra of the subporpholactone **3**, subporpholactam **4**, and imidazolosubporphyrins **5** are similar to those of the parent chromophore.[24,256] Also, the crystal structures of all three pyrrole-modified subporphyrins **3**−**5** show the retention of the pseudo-C_3-symmetric bowl shape of the parent subporphyrin **1**.[256]

Subimidazolosubporphyrin **5** carries an outer imine nitrogen, capable of metal coordination at the macrocycle periphery, as demonstrated with the formation of iridium complexes **6Ir** and **7Ir**.[256] Further transformation of this complex was shown to be possible, extending the annulated metalla-carbon framework. These subporphyrinoids have yet to show any applications but, like their parent subporphyrins,[50] were suggested to have promise in photovoltaics, light-emitting diodes, and nonlinear optics.[256]

2.1.2. Vacataporphyrin Metal Complexes. Vacataporphyrins are a class of aza-deficient porphyrins that possess the connectivity and aromatic macrocycle of a porphyrin but lack one inner nitrogen atom; this vacancy is filled by two hydrogen atoms, forming an annulene bridge.[259−261] The removal of one nitrogen from a porphyrin was initially accomplished by the conversion of a heteroporphyrin, namely, the acid-induced removal of tellurium from *meso*-tetraaryl-21-telluraporphyrin **8** (Scheme 4).[259]

meso-Tetraarylvacataporphyrin **8** can coordinate as a monoanionic N_3-ligand to a variety of metal ions, affording diamagnetic complexes **9Cd**, **9Zn**, and **9Pd** and the paramagnetic nickel(II) complexes **9Ni** and **9Fe**.[260−262] The metal ion coordination spheres are saturated through pseudoaxial ligands, as shown in the crystal structure of **9Pd-A**.[261] This may lead to the formation of stereoisomers, distinguished by the downward (inward) or upward (outward) orientation of the axial ligand. The macrocycle ligand is nonplanar, with the butadiene fragment bent away from the chloride bound to the coordinated central metal. Ligand exchange reactions of the axial chloride and ligand addition reactions forming five-coordinated metal species were reported.[260] Palladium vacataporphyrin **9Pd** reveals conformational rearrangements involving Hückel and Möbius macrocyclic topologies; light converts this complex to the organometallic species **10Pd**, containing now a dianionic

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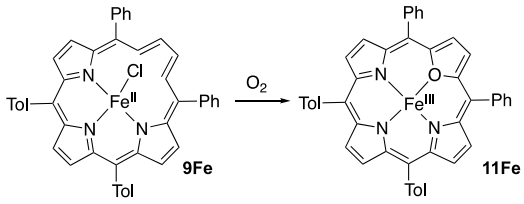
N_3C donor set (cf. the class of carbaporphyrins featuring a similar donor set, Section 2.4).[261] Protonation and methylation reactions of **9Pd** resulted in changes of the macrocycle conformation and palladium coordination modes.[261] Thermally induced conformational rearrangements of the iron complex ~~**11**~~**Fe** were also studied using paramagnetic ^{1}H NMR spectroscopy.[262]

One intriguing reaction is the activation of O_2 by [vacataporphyrinato]iron(II) chloro complex **9Fe** to form the [monooxaporphyrinato]iron(III) chloro complex **11Fe** (Scheme 5).[262] This reaction is principally the reversal of the

Scheme 5. Oxidation/Oxygen Insertion Reaction of Vacataporphyrin Iron(III) Complex 9Fe to Form Oxaporphyrin Iron Complex 11Fe



formation reaction of vacataporphyrins by extrusion of the heteroatom from monotelluraporphyrins.[259] It is also a unique way of forming furan-based heteroporphyrins (cf. Section 2.3.3).

The vacataporphyrin modification has led to altered optical spectra compared to those of the corresponding porphyrin though, except for the reduced number of Q-bands and their general blue-shift, the optical spectrum of **9** is aromatic porphyrin-like (Figure 5).[259] The two spectra for the palladium

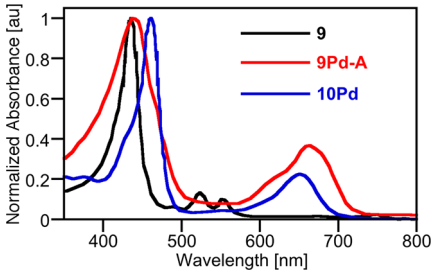


Figure 5. Normalized UV−vis spectra (toluene) of **9**, **9Pd-A**, and **10Pd**. Spectra of **9Pd-A** and **10Pd** adapted from ref 261. Copyright 2008 American Chemical Society. Spectrum of **9** adapted from ref 262. Copyright 2011 American Chemical Society.

complexes **9Pd−Cl** and **10Pd** are significantly red-shifted and broadened metalloporphyrin-like spectra, with only some differences in the position of the Soret band as a result of the changes of the conformation of the ligand and the bonding mode of the metal.[261,262]

2.2. Metalloporphyrinoids with N_4-Coordination Spheres

2.2.1. Chlorophin and Secochlorin Metal Complexes.

Both chlorophins and secochlorins are derived from regular porphyrins by β,β'-cleavage of the pyrrolic moiety.[13] While secochlorins retain a $C_\alpha-C_\beta$ bond, this bond is reduced in chlorophins to a $C_\alpha-H$ bond. While the first discovery of a metallosecoporphyrin was by fortuity,[204] a number of rational oxidative β,β'-bond cleavage reaction sequences have since been developed to prepare metallosecochlorins from adequately derivatized β-octaalkylchlorins as well as *meso*-tetraarylporphyrin/chlorin metal complexes (Scheme 6). For instance, classic diol cleavage reactions of diols of **13Ni** and **16M**, made by OsO_4-mediated dihydroxylation of the corresponding porphyrins, followed my metal insertion reactions, generated the diketone[263] and dialdehyde[170,258] secochlorins **14Ni** and **17M**, respectively. Metal insertion reactions into free-base secochlorins are not known. *meso*-Tetraarylsecochlorin diketone **19Ni** can be prepared in several steps from the corresponding β,β'-dione **18Ni**, itself accessible by oxidation of diol **16Ni** using either 2-iodoxybenzoic acid (IBX)[264,265] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[266] Dinitrile-substituted metallosecochlorins **21M**,[267] prepared by diacetoxyiodobenzene (DIB)-mediated oxidation of the β,β'-diamine **20M**, are, like the other secochlorins, fairly reactive and stabilized in the presence of a metal ion. Many metallosecochlorins have shown their utility for the preparation of other PMP classes (see, e.g., Sections 2.2.2−2.2.4 and 2.2.8−2.2.12).

Historically, the first synthesis of chlorophins, including metalloisobacteriochlorophin **24Cu**, was a total synthesis approach that formed a nonaromatic precursor macrocycle **23** that was then subjected to a rare flash pyrolysis step (Scheme 7).[177] Though some of the pioneering experiments failed to produce enough free-base material for reliable characterization, the preparation of copper complex **24Cu** suggested that this metal complex is much more stable and can be made in higher yields compared to the corresponding free-bases.[177] This prediction proved to be prescient.

All other metallochlorophin and metallosecochlorin syntheses known to date convert a (hydro)porphyrin (or subporphyrin, see Scheme 3), whereby a number of strategies have been pursued: Either the β-carbons of a β-brominated metalloporphyrin **25Ni** are removed in a single step (Scheme 8A),[268] or a secochlorin metal complex is first prepared and subsequently decarbonylated (Scheme 8B).[258,269] The square-planar copper(II) or nickel(II) complexes significantly stabilize these chromophores. In fact, these reaction sequences were reported to be only feasible for these metal complexes. The crystal structures of the nickel(II) complexes show them to be much more ruffled than the corresponding nickel(II) porphyrin or hydroporphyrins, as expected for an analogue of broken structural integrity. The removal of a β,β'-bond from a (hydro)porphyrin creates a conformationally more flexible analogue to the metalloporphyrin or metallochlorin from which it was derived.[268,269]

2.2.2. Indaphyrin Metal Complexes.

Indaphyrins are a class of secochlorin-like pyrrole-modified *meso*-arylporphyrins in which one pyrrole moiety was cleaved and (one or two) of the former β-carbons were linked to the *o*-positions of the neighboring *meso*-phenyl groups (Scheme 9).[105,270,271] Indaphyrins **31M** were synthesized in a one-pot, two-step process by oxidative cleavage of a chlorin diol (cf. Scheme 6) and subsequent intramolecular ring-formation reaction of the secochlorin **17**. Metal insertion into the conformationally flexible macrocycle is, likely because of their nonplanarity and increased flexibility, facile, and indaphyrin nickel(II), copper(II), zinc(II), and platinum(II) complexes were described,[105,270] including a crystal structure of the platinum(II) complex.[105] Their persistent chiral helimeric conformations allow their separation by chiral HPLC.[271] This suggests that the racemization barrier is larger than can be overcome at ambient temperature; the metal-dependent racemization barrier was computed.[271]

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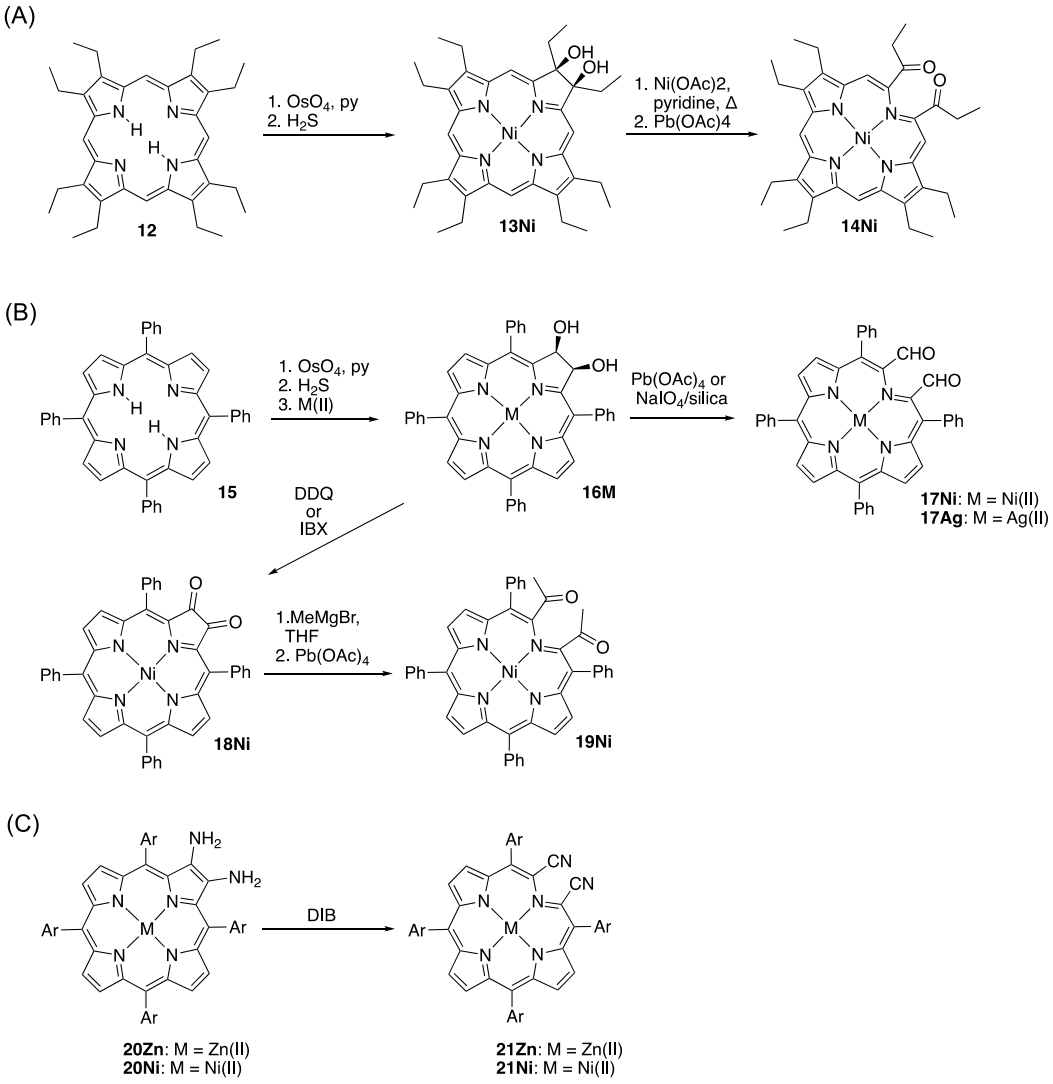
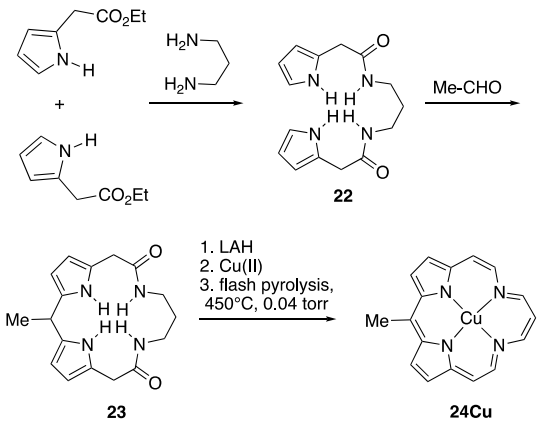
Scheme 6. Examples of the Synthesis of Metallosecochlorins



Scheme 7. Total Synthesis Approach toward Metalloisobacteriochlorophin 24Cu



The indanone moieties thusly fused to the chlorin-type chromophore extend the conjugated π-system, altering it substantially from that of regular (hydro)porphyrins, and force the macrocycle into a ruffled conformation, even in its free-base form.

As a direct consequence of the altered electronics and conformation, the UV−vis spectra of the free-base and metalloindaphyrins are very much distorted from any of the standard porphyrinoid spectra (Figure 6; cf. Figure 4). The indaphyrin platinum(II) complexes **31Pt** and its *meso*-thiophene-analogue show emissions well beyond 1100 nm, albeit at low emission yields and at cryogenic temperatures.[105]

An analogue to nickel complex **31Ni** lacking the ketone groups could also be prepared by a desulfurization reaction of a thiomorpholinochlorin (see Section 2.2.9).[272] Because of the absence of the ketone functionalities that are in conjugation with the porphyrinic π-system, the optical properties of the two compounds are clearly distinct from each other.[272]

2.2.3. Azeteoporphyrin and Azeteochlorin Metal Complexes. Azeteoporphyrins are compounds derived from the contraction of a pyrrolic building block in a porphyrin to a 4-membered azete ring. This β-atom ring loss allows the retention of the porphyrinic 18 π-aromatic system without inducing undue strain to the macrocycle; it also retains the porphyrin-like N_4-coordination environment. If the retained β-carbon atom in the modified moiety is sp^2-hybridized, we refer to these systems as azeteoporphyrins; in azeteochlorins, it is sp^3-hybridized. The nomenclature also correctly reflects the principal characteristics

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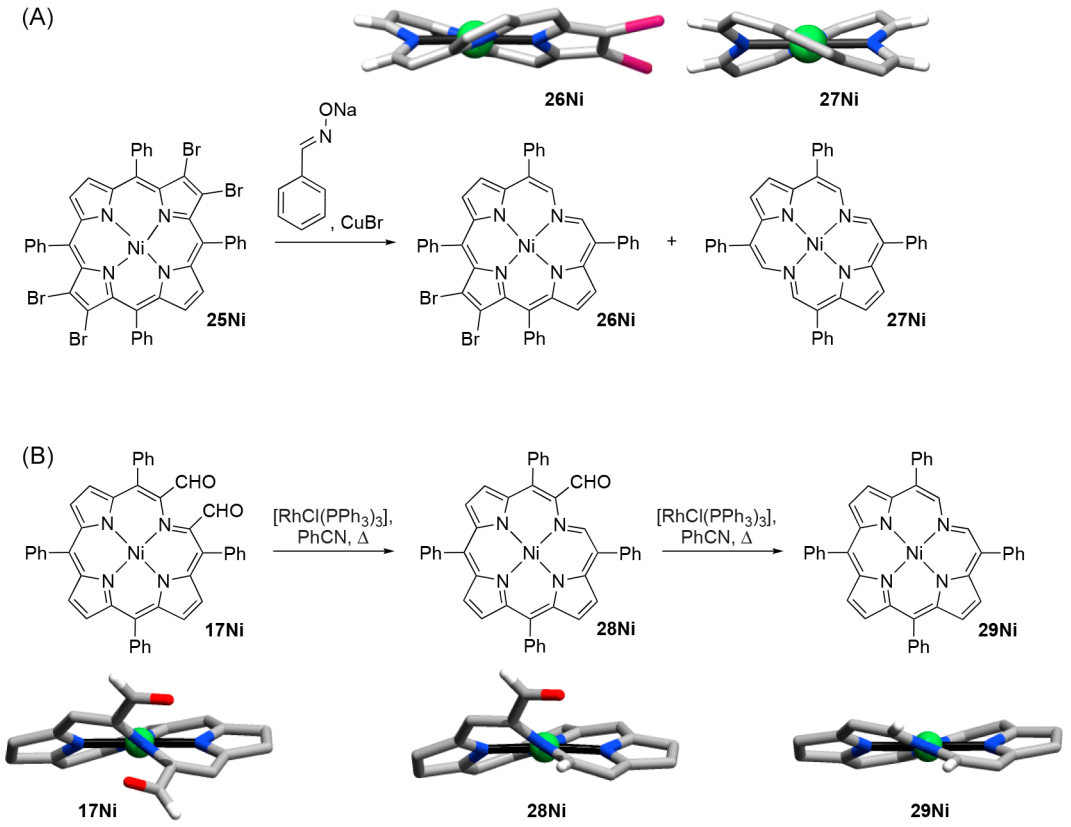
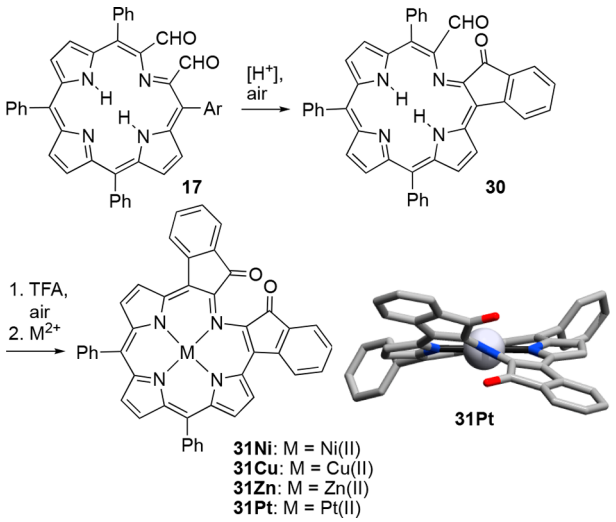
Scheme 8. Synthesis of Metallochlorophins by Degradation of a Pyrrolic Moiety[a]



[a]Stick representations of the X-ray structures of **17Ni** and **29Ni** adapted with permission from ref 258. Copyright 1999 American Chemical Society. Stick representations of the X-ray structures of **26Ni** and **27Ni** adapted with permission from ref 268. Copyright 2009 American Chemical Society. Stick representations of the X-ray structure of **28Ni** adapted with permission from ref 269. Copyright 2005 Elsevier. *meso*-Phenyl groups on all crystal structures removed for clarity.

Scheme 9. Synthesis of Metalloindaphyrins 31M by Intramolecular Ring-Closure of Secochlorin Bisaldehyde 17[a]



[a]Stick representation of the X-ray structure of **31Pt** adapted with permission from ref 105. Copyright 2009 American Chemical Society.

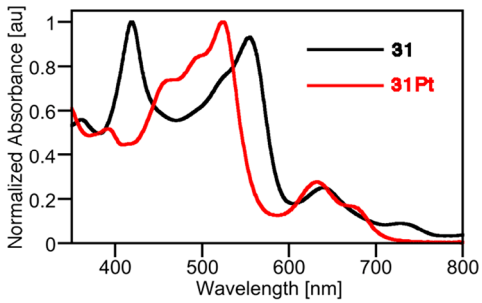


Figure 6. Normalized UV−vis spectra (CH_2Cl_2) of indaphyrin **31** and its platinum complex **31Pt**. Spectrum of **31** adapted with permission from ref 270. Copyright 2004 Royal Society of Chemistry. Spectrum of **31Pt** adapted with permission from ref 105. Copyright 2009 American Chemical Society.

of the optical properties of these azeteo-derived porphyrinoids.[203,273]

The first discovery of an azeteoporphyrin was a fortuitous (formal) CO extrusion from porphyrin β,β'-diones.[203] Later preparations were more directed. For example, the oxidative cleavage of dione **18M** generated the 4-membered ketone **32M**.[273] The photochemical activation of the copper(II) and nickel(II) complexes of an α-diazoketone **33M** yielded the corresponding metalloazeteochlorins **34M** via a Wolff rearrangement pathway (Scheme 10A).[274,275] The authors deduced this azeteoporphyrin to be an intermediate in the formation of porpholactone **37** (Section 2.2.4).

Metalloazeteoporphyrins show a remarkable degree of planarity. This planarity is especially surprising in the nickel(II) complex **32Ni** as it could have been expected to be, analogous to the conformation of nickel porphyrins,[118,276,277] ruffled (cf. also

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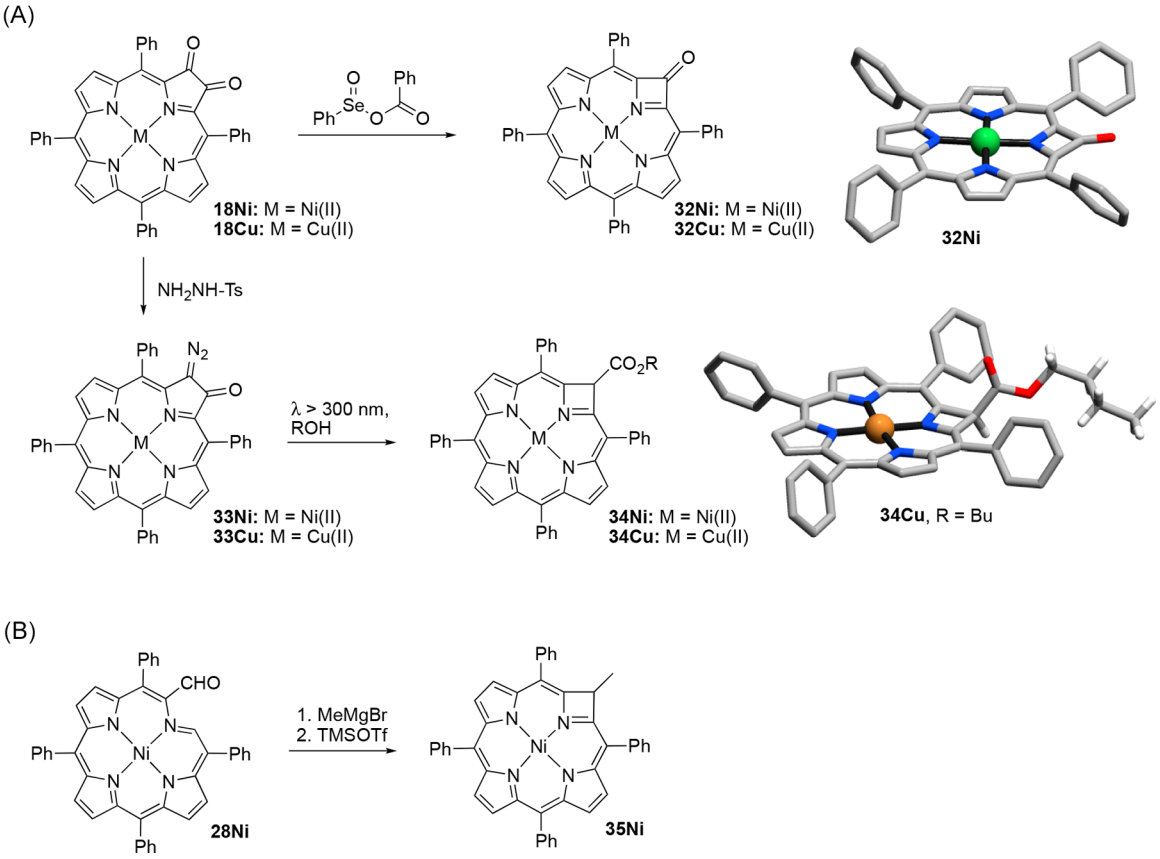
Scheme 10. Metalloazeteoporphyrin and Metalloazeteochlorin Syntheses[a]



[a]Stick representations of the X-ray structures of **32Ni** and **34Cu** adapted with permission from ref 274. Copyright 2006 Royal Society of Chemistry.

the nickel(II) secochlorin conformations, Scheme 8). However, the Ni−N bond lengths observed in the smaller-ring-size macrocycle **32Ni** are already in the regime of those of the strongly ruffled porphyrins and close to those of unrestricted Ni−N_{sp^2} bonds, alleviating all driving forces for the macrocycle to ruffle to further reduce the lengths of the Ni−N bonds.

Secochlorin monoaldehyde **28Ni**[269] could also be converted to a secondary alcohol by a reaction with a methyl Grignard reagent; the intermediate alcohol was not isolated but instead underwent an acid-induced intramolecular electrophilic aromatic substitution reaction to ring-close to form azeteochlorin **33Ni** (Scheme 10B).[269] The free-base analogues of these metalloazeteochlorins were not reported, and it is believed that only the nickel(II) ion sufficiently stabilized the intermediates to allow the reactions to proceed.

2.2.4. Porpholactone Metal Complexes. Porpholactones are a class of PMPs incorporating an oxazolone moiety.[128,203,247] Porpholactones were surmised to be a thermodynamic sink in *β,β′*-centered (hydro)porphyrin degradation reactions.[141] Thus, they have been efficiently prepared by oxidative conversion of porphyrins and hydroporphyrins, whereby numerous substrates and methods are suitable to affect this conversion (Scheme 11).[141,247,278−280] If the metalloporpholactones are desired, the metal ions can already be present in a metalloporphyrin/chlorin to be oxidized. Alternatively, metal insertion reactions into free-base porpholactones using standard methodologies for porphyrins are adequate to prepare a range of metal complexes.[141,281]

meso-Tetrakis(pentafluorophenyl)porphyrin **15^F** is a particularly suitable porphyrin for its direct conversion to the corresponding porpholactone, as well as every isomer of the dilactones using a number of oxidants (Scheme 12).[147,247,279] Stepwise, controlled methods toward the synthesis of all five isomers of the dilactones (three with an isobacteriochlorin-type and two with a bacteriochlorin-type substituent pattern) have also been reported.[147] The zinc(II) and palladium(II) complexes also became available by oxidation of the corresponding metallochlorins.[147] Each methodology has its unique product profile, making the methods highly complementary. Metal insertions into the dilactones is possible.[128,147,283]

Select metalloporpholactones (**37Fe** and **37Mn**) have shown their efficacy to catalyze aziridation reactions of alkenes as well as sulfoxidation reactions.[284,285] In both cases, their activity was higher than those of the corresponding metalloporphyrin. This was attributed to the lower HOMO energy of the metalloporpholactones, resulting in higher stabilities toward oxidative degradations. Metalloporpholactones, such as **37^{F}Pt**, **37^{F}Ga**, and **37^{F}Yb**, have also found use as photosensitizers and oxygen and halochromic (base) sensors in technical and biological applications.[128,132]

Surprisingly, the optical properties of the free-base porpholactones resemble those of the corresponding free-base porphyrins, while those of the metalloporpholactones resemble more metallochlorins (Figure 7A).[141] Neither the isobacteriochlorindilactones nor the bacteriochlorindilactones show typical isobacteriochlorin (Figure 7B) or bacteriochlorin spectra

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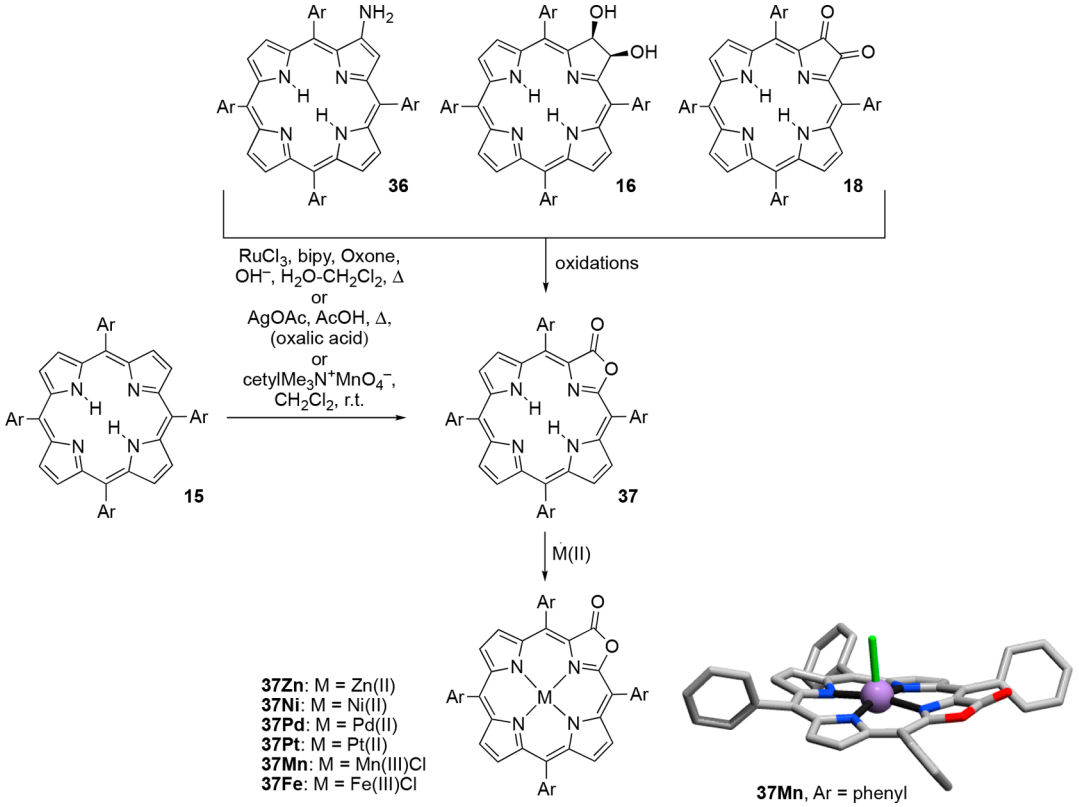
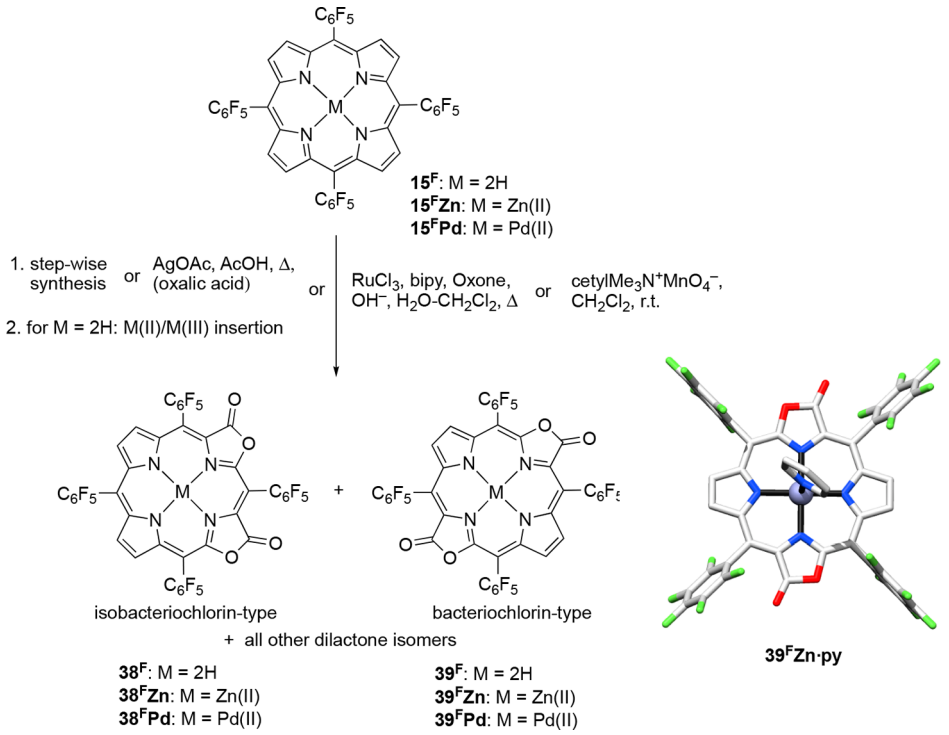
Scheme 11. Synthesis of Metalloporpholactones Using Direct Porphyrin Oxidations or the "Breaking and Mending Approach", Followed by Metal Insertion[a]



[a]Stick representation of the X-ray structure of **37Mn** adapted with permission from ref 282. Copyright 2005 Royal Society of Chemistry.

Scheme 12. Synthesis of Dilactone Metal Complexes[a]



[a]Stick representation of the X-ray structure of **39^{F}Zn·py** adapted with permission from ref 283. Copyright 2014 American Chemical Society.

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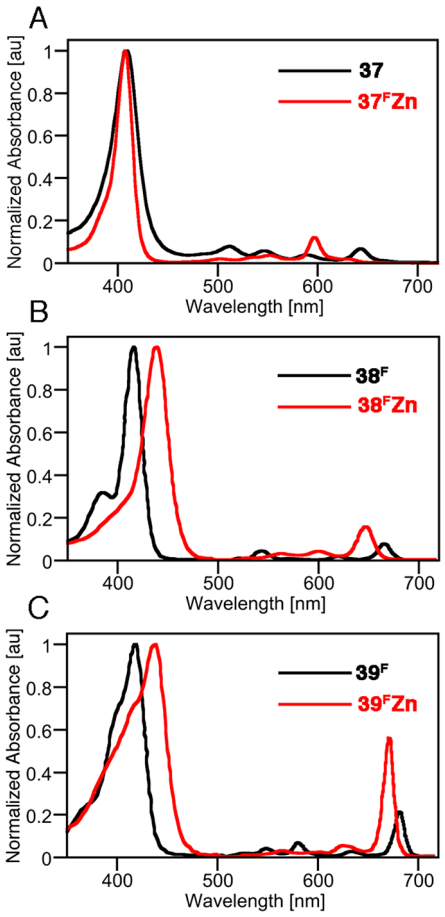

Figure 7. Normalized UV−vis spectra (CH_2Cl_2) of (A) porpholactones **37** and **37Zn**, (B) *cis*-dilactones **38**^{F} and **38**^{F}**Zn**, and (C) of *trans*-dilactones **39**^{F} and **39**^{F}**Zn**. Spectra of **37** and **37Zn** adapted from refs 141. Copyright 2012 American Chemical Society. Spectra of **38**^{F}, **38**^{F}**Zn**, **39**^{F}, and **39**^{F}**Zn** adapted from ref 283. Copyright 2014 American Chemical Society.

(Figure 7C), respectively. Thus, their naming describes only the regiochemistry of the site of the lactone modifications, not their electronic structures. The intriguing electronic influences of the lactone moieties, including their distinct regioisomeric optical differences and the remarkably differentiated ability of the regioisomers to sensitize lanthanides, were studied.[128,132,283,286]

The platinum(II) complexes of the *meso*-tetrakis-(pentafluorophenyl)-substituted porpholactones (**37**^{F}**Pt**) show, because of a strong spin−orbit coupling, intense phosphorescence; other metal complexes were also photophysically characterized.[281] Their triplet states and associated luminescence can be quenched with triplet oxygen (Stern−Volmer quenching), giving rise to their use as optical oxygen pressure sensors.[287,288] Thus, polymer formulations of these oxygen sensors have become known as pressure-sensitive paints.[248,289,290] The platinum(II) complexes were also utilized as optical cyanide or optical ratiometric high-pH sensors, relying on the optical changes induced by nucleophilic attack on the lactone carbonyl group.[291−293]

Lanthanides such as ytterbium(III) are attractive because they possess NIR luminescence properties of potential value for biological imaging applications. However, the direct excitation of the lanthanides is quantum-forbidden, necessitating a sensitizer. Porphyrins prove to be suitable sensitizers for lanthanides, whereby the sensitization efficiency of porpholactones exceeds those of the corresponding porphyrins (Figure 8).[113,132] Again, this highlights the electronic influence of the nonpyrrolic moiety and the opportunities presented by the alteration of the porphyrinic framework.

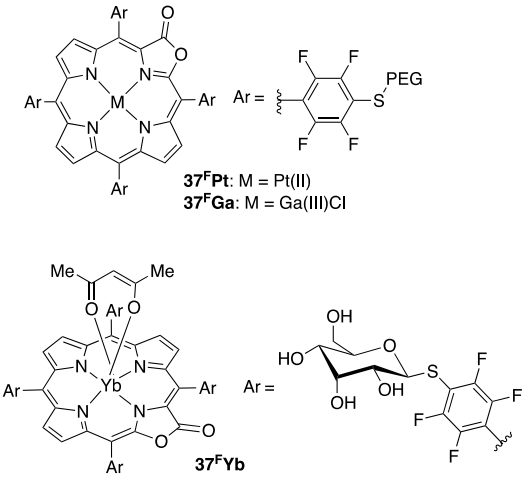

Figure 8. Metalloporpholactone derivatives with technical and biological applications.

2.2.5. Oxazolochlorin and Oxazoloisobacteriochlorin Metal Complexes. Oxazolochlorins, generally as their zinc complexes **40Zn**, were generated by reduction of the corresponding porpholactones, such as **37Zn** (Scheme 13).[123,141,142,162] In some processes, they form directly from metalated (silver(II))[294] or free-base nonporpholactone precursors.[295] The hemiacetal hydroxy moiety on lactol **40Zn** can be readily exchanged for alkoxides, amines, or thiolates,[141] creating a large variety of conjugates, some of which were shown to be biologically active and suitable as MRI imaging agents.[296]

The reduction leads to a large red-shift of their optical spectra compared to those of the parent porpholactones and the establishment of a typical (metallo)chlorin spectrum (Figure 9). The two pyrroline stereoisomers of an ytterbium(III) chlorolactol complex **40**^{F}**Yb** with a large axial ligand (the Kläui ligand) showed differentiated optical responses to temperature (when embedded in a polymer matrix); they were also utilized as optical viscosity sensors.[133]

The reduction of pyrrolic moieties in the porpholactones is also possible using a variety of reagents; the reaction is regioselective (one example is shown in Scheme 14).[133,139,162] The porpholactol zinc complex **40Zn** shows distinctly different biological and photophysical properties compared to the corresponding porpholactone or isobacteriochlorin zinc complexes.[128,162] The nickel(II) complex **41**^{F}**Ni** was shown to be a much more effective catalyst for the hydrogen evolution reaction (proton reduction) than the corresponding nickel porpholactone or nickel chlorin complexes (Scheme 14).[122] In addition, the influence of the hemiacetal hydroxy group—generated through reduction of the corresponding porpholactone (Scheme 13)—on hydrogen evolution catalysis was also demonstrated.[123]

2.2.6. Octaalkyloxazolochlorin Metal Complexes. The conversion of β-alkylporphyrins into chlorin-like chromophores using ozone was already reported in 1933 by Fischer and Deželić, but the products were misidentified.[198] The surprising finding that oxidations of porphyrins lead to hydroporphyrin-type chromophores was later investigated using octaethylpor-

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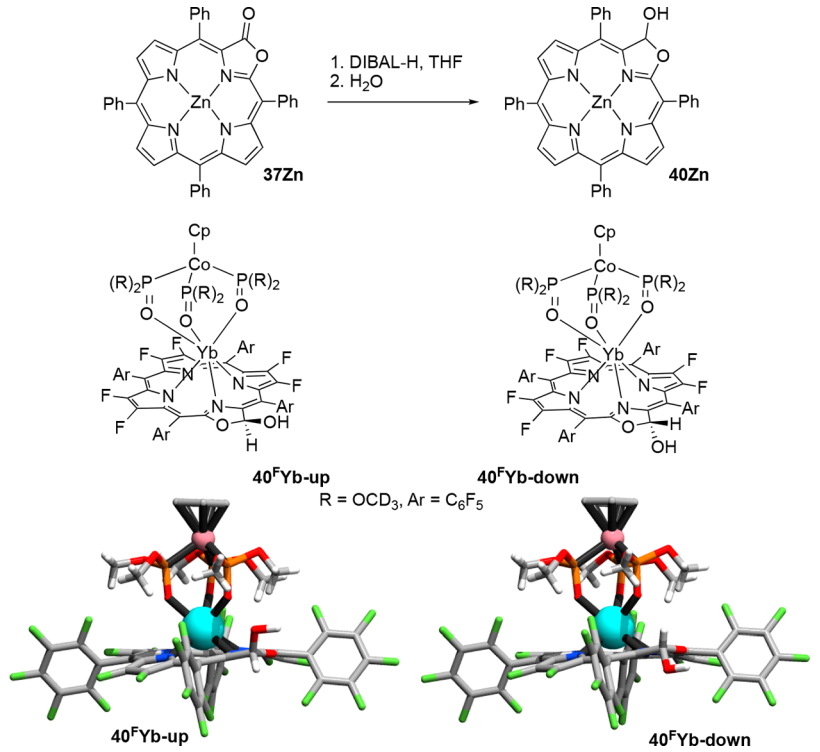
Scheme 13. Synthesis of the Metallooxazolochlorins by Reduction of a Metalloporpholactone and Structures of the Viscosity Sensors 40^{F}Yb[a]



[a]Stick representations of the X-ray structures of **40^{F}Yb-up** and **40^{F}Yb-down** adapted with permission from ref 133. Copyright 2018 American Chemical Society.

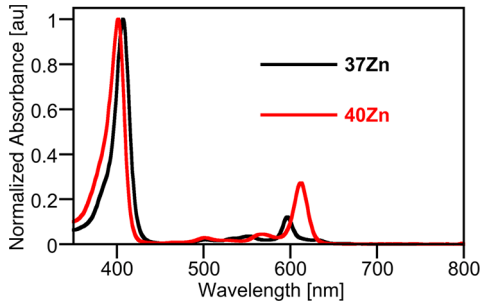
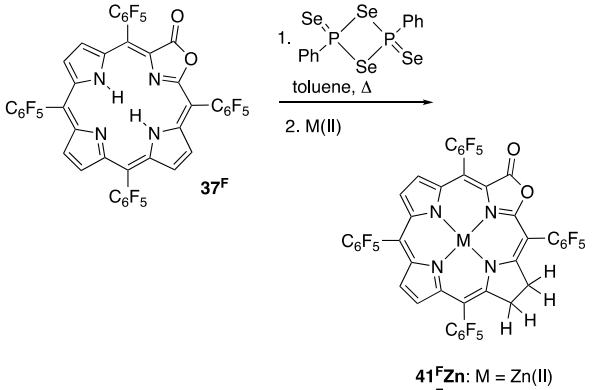


Figure 9. Normalized UV−vis spectra (CH_2Cl_2) of **37Zn** and **40Zn**. Spectra adapted with permission from ref 141. Copyright 2012 American Chemical Society.

Scheme 14. Synthesis of Metalloisobacteriolactone Derivatives 41^{F}M

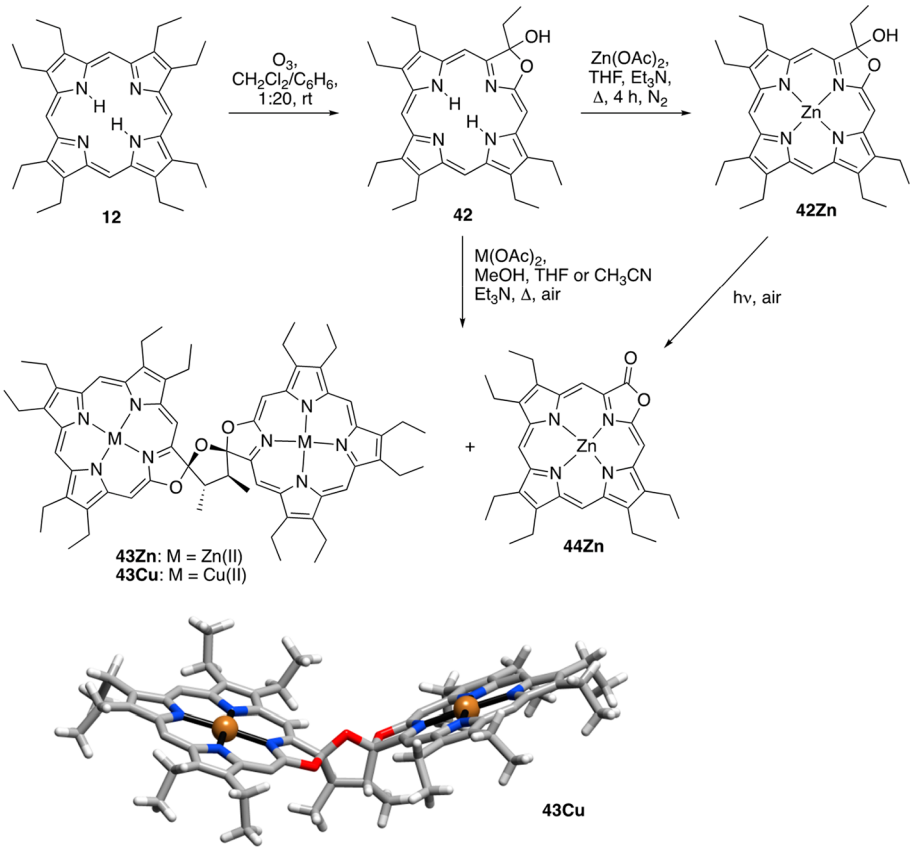


phyrin **12** (Scheme 15).[199,200] Indeed, a reaction of **12** with ozone generated the corresponding heptaethyloxazolochlorin hemiacetal **42**. Thus, a pyrrolic β-carbon with its alkyl substituent was excised and replaced by an oxygen atom, and the neighboring β-carbon was hydroxylated; the reaction presumably proceeded via classic ozone-addition, rearrangement, and oxidative cleavage steps.[199,200]

In a most surprising and as yet not fully rationalized reaction, metal insertion under aerobic conditions generated furan-linked bis([oxazolochlorinato]metal) dimer **43M** and heptaethyl-2-oxa-3-oxoporphyrinato]zinc(II) **44Zn**.[200] The X-ray crystal of the furan-linked **43Cu** shows the symmetric dimer structure of two essentially planar [oxazolochlorinato]copper(II) moieties linked through an acetal oxygen and a direct carbon−carbon linkage between two ethyl groups, forming a tetrahydrofuran. The two oxazolochlorins are arranged *trans* to each other and are connected by spiro-linkages to the 2- and 5-positions of the tetrahydrofuran.[200] Thus, metal insertion evidently led to a C−C coupling reaction involving an otherwise not activated alkane side chain.

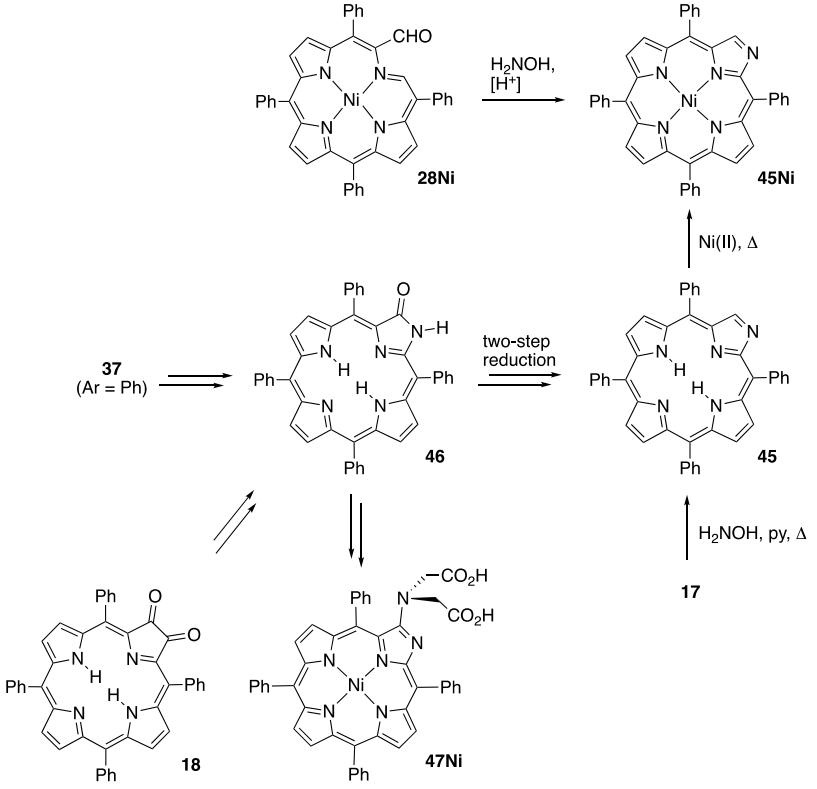
2.2.7. Imidazoloporphyrin (Including Porpholactams) and Triazoloporphyrin Metal Complexes. *meso*-Arylimidazoloporphyrins are derived from a regular *meso*-arylporphyrin by replacement of a β-carbon by an sp^2-hybridized nitrogen atom. No one-step method to accomplish this transformation from a porphyrin or chlorin is known, but three stepwise approaches have been reported (Scheme 16): reduction of porpholactam **46**;[140] a complex reaction mechanism involving the collapse of an intermediate presumed 7-membered nonpyrrolic building block arising from the reaction of secochlorin dialdehyde **17**

Scheme 15. Synthesis and Reaction of β-Alkyloxazolometallochlorins 43Zn and 43Cu[a]



[a]Stick representations of the X-ray structure of **43Cu** adapted with permission from ref 200. Copyright 2016 Wiley-VCH.

Scheme 16. Alternate Syntheses of Metalloimidazoloporphyrin 45N



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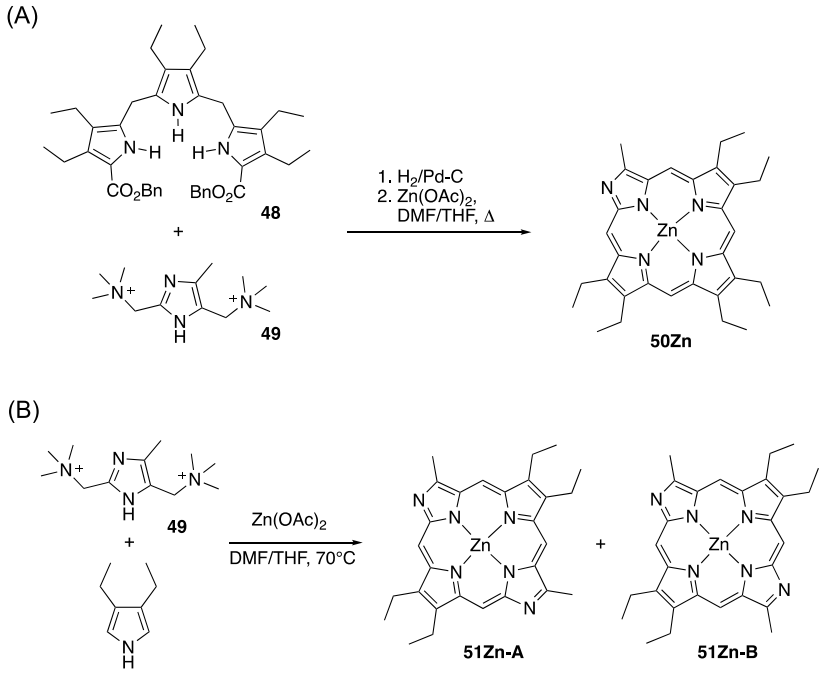
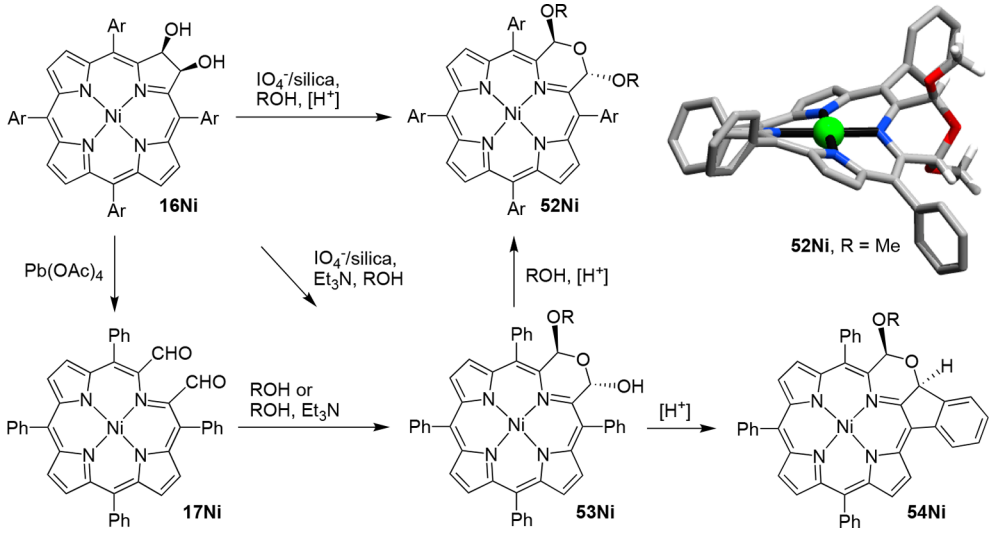
Scheme 17. Total Syntheses of Metallomono- and Metallobisimidazoloporphyrins



Scheme 18. Syntheses and Modification of Metallomorpholinochlorin Derivatives[a]



[a]Stick representation of the X-ray structure of **52Ni** adapted with permission from ref 298. Copyright 2011 American Chemical Society.

with hydroxylamine;[139] or the reaction of a secochlorin monoaldehyde **28Ni** with hydroxylamine.[138]

A reaction of the secochlorin aldehyde **28Ni** with hydroxylamine under acidic conditions leads to a dehydration with concomitant oxidative ring-closure to form imidazoloporphyrin **45Ni** without the observation of an intermediate.[138] Only the latter path was shown to directly deliver the metal complex **45Ni**. The other pathways generate the free-base imidazoloporphyrin and therefore require subsequent metal insertion reactions. This reaction highlights the high driving force toward the formation of products with porphyrin-like framework architectures. The outside nitrogen atom can be protonated and was proposed to be utilized for metal recognition.[138,140] Imidazoloporphyrins possess porphyrin-like optical properties.

The preparation of the subporphyrin-analogue to the imidazoloporphyrins by reduction of the corresponding subporphyrin lactone moiety is shown in Scheme 3.[256]

By virtue of the presence of the basic imine nitrogen atom at the periphery of the porphyrin ring, imidazoloporphyrin **45Ni** shows, unlike the corresponding nickel porphyrin complex **15Ni**, a halochromic response upon protonation.[138] In an attempt to utilize the potential coordination of this peripheral nitrogen atom to metal ions, porpholactam **46** was converted to the aminodiacetate derivative **47Ni** (Scheme 16).[140] However, it proved to be unsuitable as a chemosensor for metals, presumably because of the small bite angle between the outer ring nitrogen and the chelating group attached.[140]

Porpholactam **46** is accessible either through conversion of porpholactone **37** over several steps or along an unusual (but

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efficient) reaction path starting from dioxo-compound **18**.[139,140,145]

Only total synthesis approaches toward β-hexaalkylimidazoloporphyrins containing one or two imidazole moieties are known (Scheme 17A).[297] One approach is that, along a [3 + 1] pathway, a tripyrrane **48** is reacted with imidazole **49** derivatized with two good leaving groups in the presence of zinc(II), providing imidazoloporphyrin **50Zn**. Alternatively, the condensation of imidazole derivative **49** and diethylpyrrole in the presence of zinc acetate (that may act as a template and Lewis acid catalyst) generated a bisimidazoloporphyrin zinc(II) complex **51Zn**, in two regioisomeric forms **51Zn-A** and **51Zn-B** (Scheme 17B). Note that the number of pyrrole replacements does not change the central N_4-coordination sphere of the ligand. The optical properties of these complexes are surprisingly similar to those of the corresponding octaethylporphyrin zinc complex.[297]

2.2.8. Morpholinochlorin Metal Complexes. Morpholinochlorins incorporate a 6-membered morpholine ring in place of a pyrrole. They were synthesized by ring-closure of a secochlorin dialdehyde (such as **17Ni**, cf. Scheme 6) with an oxygen nucleophile (Scheme 18).[170,298] Thus, the nickel(II)-templated, acid-catalyzed, and primary alcohol-induced ring-closure of the stable secochlorin dialdehyde nickel(II) complex **17Ni** (isolated or generated *in situ*) generated [*meso*-tetraphenylmorpholinochlorinato]Ni(II) double-acetal complexes **52Ni**.[170,298] A range of alcohols proved suitable to affect this reaction. The first formed acetal−hemiacetal compound **53Ni** can undergo an acid-catalyzed Friedel−Crafts-type reaction with the *o*-position of an adjacent *meso*-aryl group, leading to the polycyclic system **54Ni**.[170,298]

The strongly nonplanar, ruffled conformation of the dialdehyde nickel complex **17Ni** is preserved and leads to a steric stereocontrol (in cooperation with an electronic, anomeric effect-type of control) of the relative position of the alkoxy-substituents to be *trans* to each other. The helimeric enantiomers of the morpholinochlorins are persistent (i.e., they do not racemize) and thus can be resolved.[298,299] The nonplanar, ruffled conformation of **53Ni** leads to an ideal accommodation of the small nickel(II) ion. This, in turn, leads to an unusual electrochemical behavior of **53Ni** compared to the corresponding porphyrin or chlorin in that cathodic reduction does not lead to the formation of a nickel(I) complex (like observed for regular porphyrin or chlorin nickel(II) complexes) but to a ligand anion radical nickel(II) species.[300] Irrespective of the involvement of the nickel ion, the synthesis of free-base morpholinochlorins using *in situ* generated secochlorin dialdehyde **17** is also feasible.[298,301]

The optical properties of free-base morpholinochlorins correspond to those of a bathochromically shifted (compared to the corresponding free-based diolchlorin) chlorin-type spectrum.[170,298] The spectrum of the nickel(II) complex mirrors these characteristics; it is a red-shifted (compared to the spectrum of **16Ni**) metallochlorin spectrum (Figure 10).[170,298] These shifts can be attributed to conformational effects, particularly the dihedral angle between the two $C_\alpha-C_\beta$ bonds within the morpholine moiety.[144]

2.2.9. Thiomorpholinochlorin Nickel Complexes. Secochlorin **19Ni** can also be ring-closed with a sulfur nucleophile, such as by treatment with Lawesson's reagent to form thiomorpholinochlorin **55Ni**, the thioanalogue to the morpholinochlorins (Scheme 19).[302] Since only the nickel(II) secochlorin complex **19Ni** was found to be stable under the reaction conditions, the preparation of free-base thiomorpholinochlorin has not yet been accomplished. The thiomorpholino framework could be altered by an acid-induced double intramolecular cyclization reaction to form the annulated polycyclic system **56Ni**. Despite this framework alteration, the optical properties of the two compounds **55Ni** and **56Ni** proved to be very similar to each other and metallochlorin-like, as are their conformations.[272] Again, this serves as an example for a central metal-induced conformational (and thus also largely electronic) control of the macrocycle.

The thiomorpholine framework can be hydro-desulfurized, generating compound **57Ni**, a ketone-free, sp^3-analogue to indaphyrin **31Ni** (cf. Scheme 9).[272] The electronic properties of

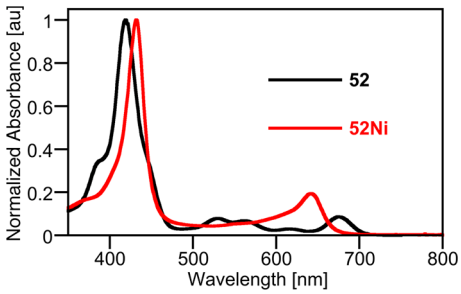
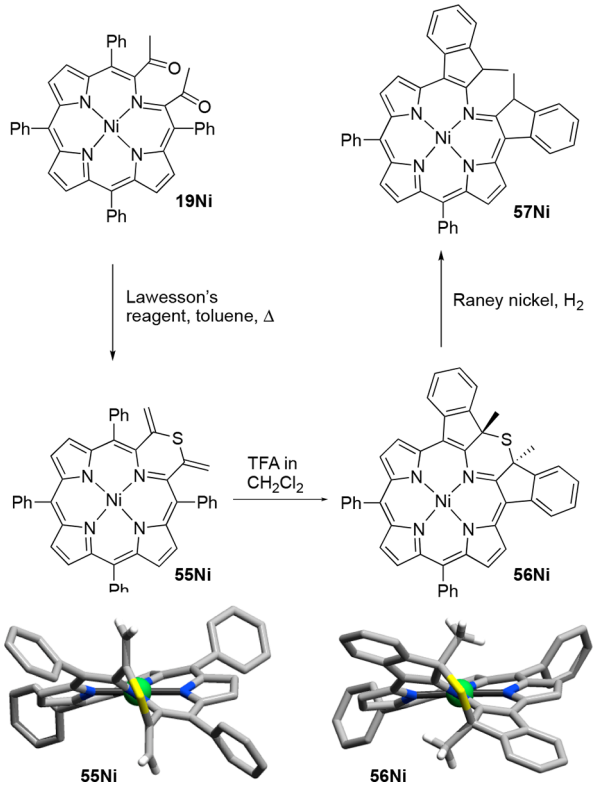


Figure 10. Normalized UV−vis spectra (CH_2Cl_2) of morpholinochlorins **52** and **52Ni**. Spectrum of **52** adapted with permission from ref 301. Copyright 2003 American Chemical Society. Spectrum of **52Ni** adapted with permission from ref 298. Copyright 2011 American Chemical Society.

Scheme 19. Syntheses and Modification of Metallothiomorpholinochlorin Derivatives[a]



[a]Stick representations of the X-ray structures of **55Ni** and **56Ni** adapted with permission from ref 272. Copyright 2016 American Chemical Society.

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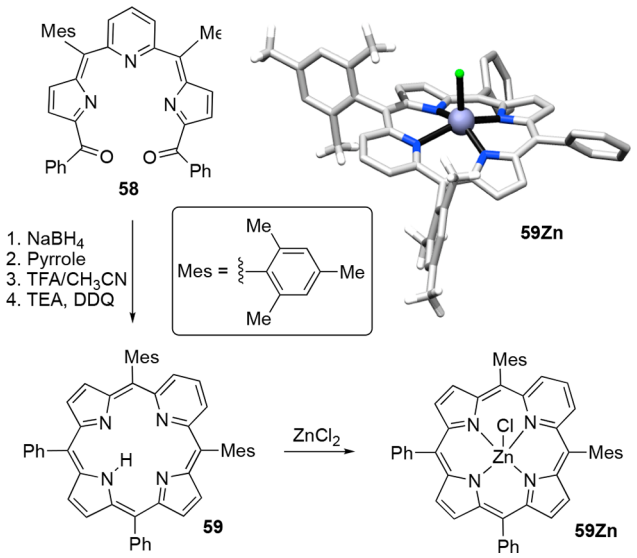
57Ni are altered compared to those of the regular indaphyrins, showing the electronic influences of the π-conjugated ketone functionality.

2.2.10. Pyri- and Oxypyriporphyrin Metal Complexes. In pyri- and oxypyriporphyrins, a pyrrole is replaced by a pyridine or pyridinone moiety, respectively, with the nitrogen of the heterocycle at the regular inner macrocycle position. The pyriporphyrins are the N_4-analogues of the N_3C-coordinating *m*-benziporphyrins (see Section 2.4.6). An example of a N-confused pyriporphyrin exhibiting the N_3C-coordinating typical of a carbaporphyrin is also known and is discussed with the carbaporphyrins (see Section 2.4.7). Pyriporphyrins share with the benziporphyrins the disadvantage that macrocycle aromaticity is only possible upon interruption of the local aromaticity of the pyridine group. However, the introduction of ketone groups into the pyridine moiety, forming oxypyriporphyrins, perturbs the local nonpyrrolic π-system sufficiently to enable the expression of a macrocycle-aromatic system.[303,304]

Synthetic approaches toward pyriporphyrins and oxypyriporphyrins include established [3 + 1] routes for PMPs (Scheme 20).[305,306] Unlike benziporphyrin, pyriporphyrins possess an inner nitrogen atom that readily engages in a coordination interaction with a central metal. Because of this, the resulting complexes of the monoanionic N_4-ligand are much more planarized compared to the corresponding benziporphyrin complexes; in this respect, they generally behave more like regular porphyrins. A comparison of the crystal structure of pyriporphyrin **59Zn** with that of the corresponding benziporphyrin metal complex **112M** (Section 2.4.6) illustrates this point.[306,307]

The electronic spectrum of free-base pyriporphyrin **59** resembles that of the structurally related benziporphyrin (Figure 11; cf to Figure 17).[306] The UV−vis spectrum of the zinc(II) complex **59Zn** is much red-shifted compared to its free-base spectrum, but the broad, featureless bands and the small intensity ratio of the Soret band to the Q-band region highlight the nonaromatic nature of this metal complex.

Scheme 20. Synthesis of Pyriporphyrins and Metal Complexes[a]



[a]Stick representation of the X-ray structure of **59Zn** adapted with permission from ref 308. Copyright 2006 Wiley-VCH.

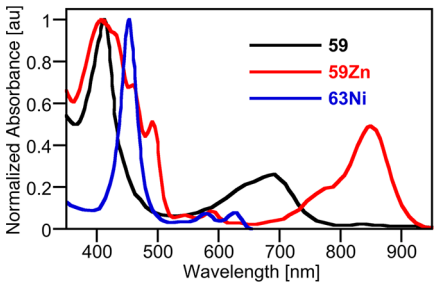


Figure 11. Normalized UV−vis spectra (CH_2Cl_2) of free-base pyriporphyrin **59**, of its Zn(II) complex **59Zn**, and of oxypyriporphyrin Ni(II) complex **63Ni** (2% TFA/CH_2Cl_2). Spectra of **59** and **59Zn** adapted with permission from ref 307. Copyright 2006 Wiley-VCH. Spectrum of **63Ni** adapted with permission from ref 302. Copyright 2012 World Scientific.

Reactions that convert porphyrins into oxypyriporphyrins (and related macrocycles) are available (Scheme 21A−C); this distinguishes them from the structurally similar benziporphyrins for which such conversions are not known (see Section 2.4.6). In fact, oxypyriporphyrins are a rare group of PMPs for which both types of syntheses are available.

These syntheses include the fortuitous migration of the *N*-alkyl group of *N*-alkylated porphyrin **60** into a pyrrole upon its metalation with nickel(II), forming PMP complex **61Ni**.[57,202,309] A more rational synthesis of oxypyriporphyrins is the aldol condensation of the octaalkylsecochlorin nickel complex **14Ni** (for its formation, see Scheme 6) to form oxypyriporphyrin **62Ni** (the latter two reactions represent some of the earliest PMP syntheses, cf. Section 1.7).[205,263] This reaction was expanded to the free-base systems and the synthesis of dioxypyribacteriochlorins.[310] Similarly, the *meso*-aryl-porphyrin series can also be converted, via secochlorin **19Ni**, to oxypyriporphyrin nickel complex **63Ni**. The nonpyrrolic moiety of oxypyriporphyrin **63Ni** can be reduced, generating metallochlorin-analogue **64Ni**.[302]

The metalloporphyrin-type UV−vis spectrum of oxypyriporphyrin **63Ni** is, on account of its aromaticity, metalloporphyrin-like, with much sharpened bands, including two well-defined Q-bands compared to, for instance, the spectrum of the broad and featureless spectrum of benziporphyrin complex **114Ru^{II}** (Section 2.4.6).[302]

2.2.11. Pyrazinoporphyrin Metal Complexes. Pyrazinoporphyrins are PMPs in which one pyrrole unit of a porphyrin has been replaced by a (dihydro)pyrazine moiety. Similarly to the morpholinochlorins, all pyrazinoporphyrins and pyrazinochlorins were made by conversion of porphyrins (Scheme 24A).[300,311]

A reaction of nickel secochlorin dialdehyde **17Ni** with ammonia induced an amine-nitrogen-induced intramolecular ring-closing reaction, generating a hydroxy-substituted pyrazinoporphyrin framework; this intermediate could be (formally) alkylated using a substitution reaction with ethanol to generate alkoxy derivative **65Ni**.[300,311] This ~~reasonably chemically stable~~ metallo-PMP possesses metalloporphyrin-like optical spectra. Free-base pyrazinochlorins are accessible along equivalent pathways from free-base secochlorin dialdehyde **17** but are characterized by low chemical stability, but the nickel complexes are reasonably stable.[300,311] The ligand-centered electrochemical reduction of nickel(II) complex **65Ni** was studied.[300]

A second reaction that expands the pyrrole of a porphyrin by a nitrogen atom is a Beckmann-like ring expansion of oxime **66M**,

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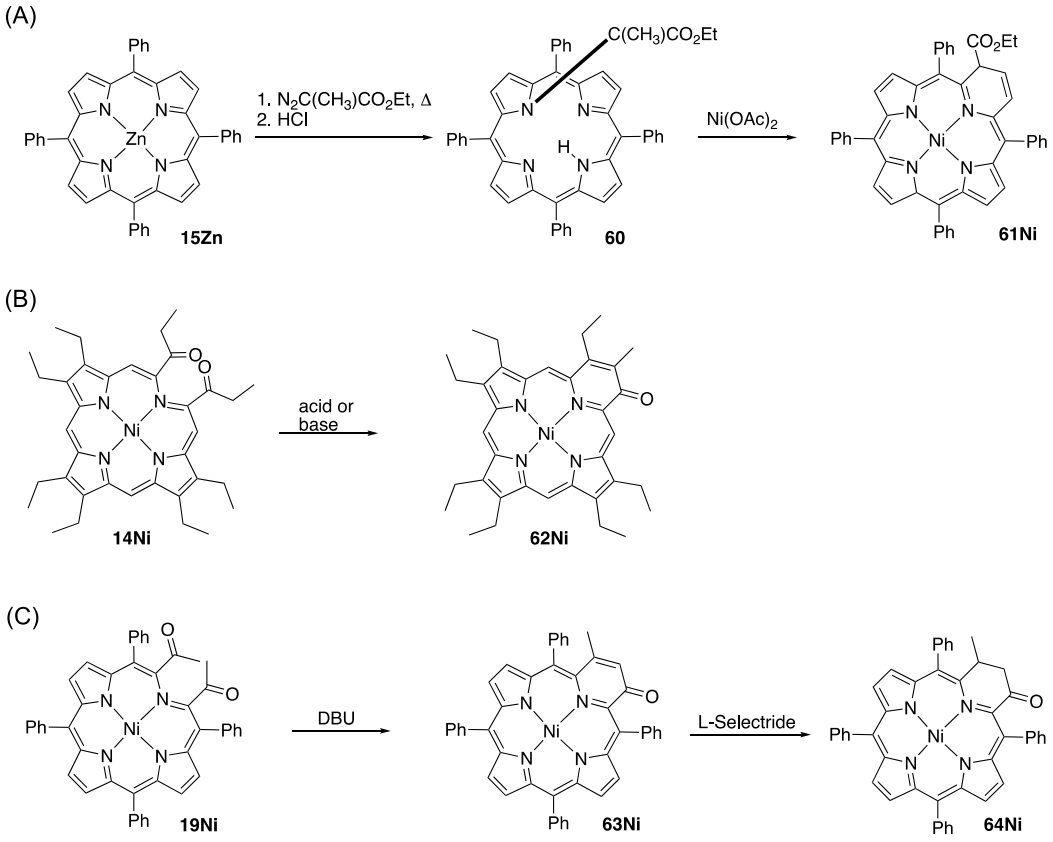
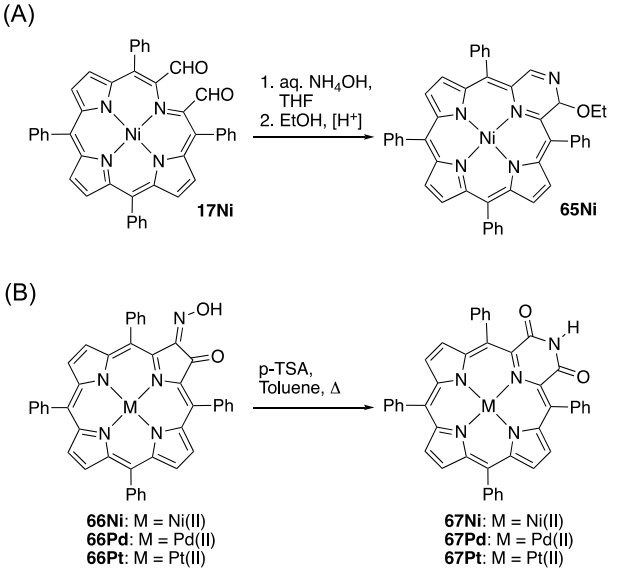
Scheme 21. Synthesis of Oxy- and Hydropyriporphyrin Metal Complexes



itself made by stepwise modification of the corresponding *meso*-tetraphenylporphyrin (OsO_4-mediated dihydroxylation, oxidation, oximation).[312] This ring expansion resulted in the formation of the pyrazine imide-type PMP **67M** (Scheme 22B). The metal plays a very important role guiding this reaction pathway: An application of the same reaction conditions to the free-base oxime fails to induce a ring expansion. Instead, it results in the reaction with a flanking *meso*-aryl group and the formation of a quinoline-annulated porphyrin,[313,314] a π-expanded porphyrin of utility,[315,316] but not belonging to the class of PMPs. What, other than metalation in general, controls the reaction, from a mechanistic point of view, to proceed along one path or the other is unknown. However, since small (nickel(II)) as well as large (platinum(II)) ions induced the formation of the pyrazine imide-type PMP **67M**, simple conformational effects are unlikely controlling the reaction.

Scheme 22. Ring Expansion Reactions to Generate Metallopyrazinoporphyrins



2.2.12. Nickel(II) Complexes of PMPs Incorporating an 8-Membered Ring. Several "breaking and mending" approaches toward PMPs planned to contain 7-membered rings failed because the large ring collapsed to form porphyrin-like architectures before they could be isolated and characterized (cf. Scheme 16).[138,317] In a quest to prepare PMPs with larger than 6-membered rings from a porphyrin, the "breaking and mending" steps (cf. Scheme 1) were inverted, and inspired by work on porphyrazines,[46] the "mending and breaking" approach was developed (Scheme 23): A *cis-vic*-chlorin diol **68Ni** was formed by an addition of *N,N′*-dimethylated urea to known *β,β′*-porphyrin dione (available along multiple pathways, including the oxidation of diol **16Ni**).[266,318] The diol functionality on the annulated species **68Ni** thus formed was oxidatively cleaved, resulting in the fusion of the 5-membered pyrroline with the three annulated atoms to form an 8-membered 1,3,6-triazocine-2,4,8-trione ring.[145,319] Using a nonmethylated urea, the 8-membered ring collapses to form a porpholactam (such as **46Ni** from **18**, cf. Scheme 16).[140,145,319]

The crystal structure of **69Ni** shows it to be severely ruffled,[145] as expected for a (flexible) nickel(II) porphyrinoid.[118] However, the structure of free-base analogue **69** (not shown) is similarly ruffled.[319,145] This presents another example in which the ruffled conformation of the PMP is intrinsic to the framework (cf. also

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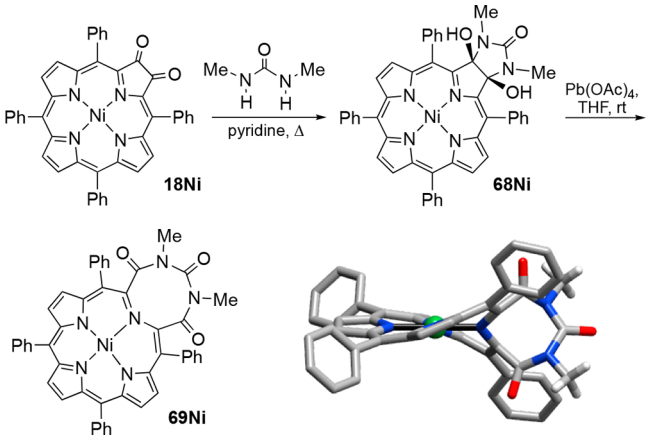
Scheme 23. "Mending and Breaking" Approach toward the Generation of PMPs Containing an 8-Membered Ring[a]



[a]Stick representation of the X-ray structure of **69Ni** adapted with permission from ref 145. Copyright 2020 American Chemical Society.

to the indaphyrins, Scheme 9, or the indachlorins[320]) and not determined by coordination to, for example, nickel(II).

The optical properties of the 8-membered PMPs **69** and **69Ni** resemble red-shifted chlorins and metallochlorins, respectively (Figure 12).[145]

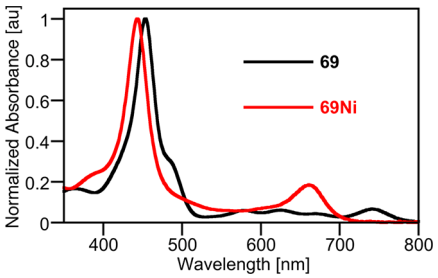


Figure 12. Normalized UV−vis spectra (CH_2Cl_2) of 8-membered PMP **69** and its nickel(II) complex **69Ni**. Spectra adapted with permission from ref 145. Copyright 2020 American Chemical Society.

2.2.13. *N*-Heterocycle-Fused Nickel Pyrrole-Modified Porphyrin Dimers. Interesting cases from structural as well as mechanistic points of view are the *N*-heterocycle-fused PMP dimer nickel(II) complexes **73Ni$_2$** through **75Ni$_2$** (Scheme 24).[321] A palladium-catalyzed Suzuki−Miyaura coupling reaction of *meso*-triaryl, *meso*-bromo nickel(II) porphyrin **70Ni** with *β*-borylated *meso*-triaryl nickel(II) porphyrin **71Ni** afforded a *meso*-to-*β*-linked porphyrin dimer. This could be nitrated and then reduced to form the *meso*-amino porphyrin dimer **72Ni$_2$**, the key precursor. Oxidation of this dimer with MnO_2 at room temperature formed dimers **73Ni$_2$**, **74Ni$_2$**, and **75Ni$_2$**; a PbO_2-mediated oxidation only formed **74Ni$_2$** and **75Ni$_2$**. The formation of the 3-keto-4-imidopyrrole-based dimer **73Ni$_2$** is the result of an oxidative coupling/framework oxidation, without alteration of the porphyrin frameworks. However, the formation of the pyrrole-modified 6-membered dihydropyridine **74Ni$_2$** and imidazolinone **75Ni$_2$** involved the insertion of the (former) amine nitrogen into the fused pyrrole or the formal replacement of a *β*-carbon atom by the amine nitrogen atom, respectively.[321] While the former reaction is unprecedented among the reactions converting porphyrins to their pyrrole-modified analogues, the latter reaction resembles the formation of porpholactams[139,322] by means of the collapse of a larger ring (see Section 2.2.12).[140]

All derivatives possess strong NIR absorbances, with the non-pyrrole-modified dimer possessing absorbances well past 1000 nm. Conformational as well as electronic effects are responsible for their electronic structure, with the linking heterocycles determining the relative positions of the two nonplanar nickel(II) porphyrinoid moieties.

2.3. Metalloheteroporphyrinoids with N_3X and N_2X_2 (X = O, S, Se, N_2S, N_2CS, etc.) Coordination Spheres

2.3.1. Heteroporphyrins. Heteroporphyrins are porphyrinoids where one or more pyrrole nitrogen atoms have been replaced by other heteroatoms, such as O, S, Se, Te, Si, or P (C-based heteroporphyrins are discussed separately as carbaporphyrins; see below). Different synthetic strategies were employed toward their formation, but the vast majority are total syntheses. The most common method used for the synthesis of monothia-, monooxa-, monoselena-, and monotelluraporphyrins is the condensation of a 2,5-bis(arylhydroxymethyl)heterocyclopentadiene with benzaldehyde and pyrrole under mildly acidic conditions (Scheme 25).[323] Functionalization of the heteroporphyrin at the *meso*-position is also possible by using an appropriate functionalized (non-symmetric) dicarbinol or aldehydes other than benzaldehyde.[323]

The replacement on an NH functionality of porphyrins (or porphyrin isomers)[91] by an O, S, Se, etc., atom results in different physicochemical properties compared to regular N_4-porphyrins, often expressed in bathochromically shifted optical spectra. Most importantly, the heteroporphyrins possess much differing coordination properties because the coordination environment is of lower charge, and the cavity is smaller (particularly in the case of the incorporation of relatively large atoms such as Te, Se, or even S). The increase in the number of heteroatoms induces nonplanarity, further eroding the metal binding properties of the oligoheteroporphyrins.[16] Nonetheless, many metal complexes of the heteroporphyrins are known and have been reviewed.[16,30] We will discuss only a few representative examples.

2.3.2. Thiaporphyrin Metal Complexes. A thiaporphyrin is a monoheteroporphyrin where one pyrrole has been replaced by a thiophene. The monoanionic N_3S-coordination environment of 21-thiaporphyrins is suited to stabilize copper and nickel in the +I oxidation state (Scheme 25),[30] in contrast to the stabilization of the +II oxidation states of these metals by N_4-porphyrins. Also, axial ligands are needed in the thiaporphyrin complexes for the charge neutralization of metal ions in +II and +III oxidation states. A wide range of metallothiaporphyrins such as **77Li**,[324] **77Fe**,[325] **77Ni**,[325] **77Cu**,[325] **77Rh**,[326] and **77Pd**[327] have been synthesized and structurally characterized.[16] The X-ray structures of multiple metal complexes have been reported. For instance, the metal complexes of copper(II), iron(II), nickel(II), and mercury(II) are five-coordinated complexes carrying axial ligands and adopting a square-pyramidal or distorted trigonal bipyramidal geometry.[16,325] The nickel(I)[328] and palladium(I)[327] ions are tetracoordinated and located at the center of idealized square-planar coordination geometries. The lithium(I) complex formed five-coordinated square-pyramidal complexes with tetrahydrofuran as the axial ligand,[324] while the **77Ru**,[329] **77Rh**,[326] and **77Re**[330] complexes are hexacoordinated.

The absorption spectrum of free-base thiaporphyrin **77** is porphyrin-like with four well-defined Q-bands and one strong,

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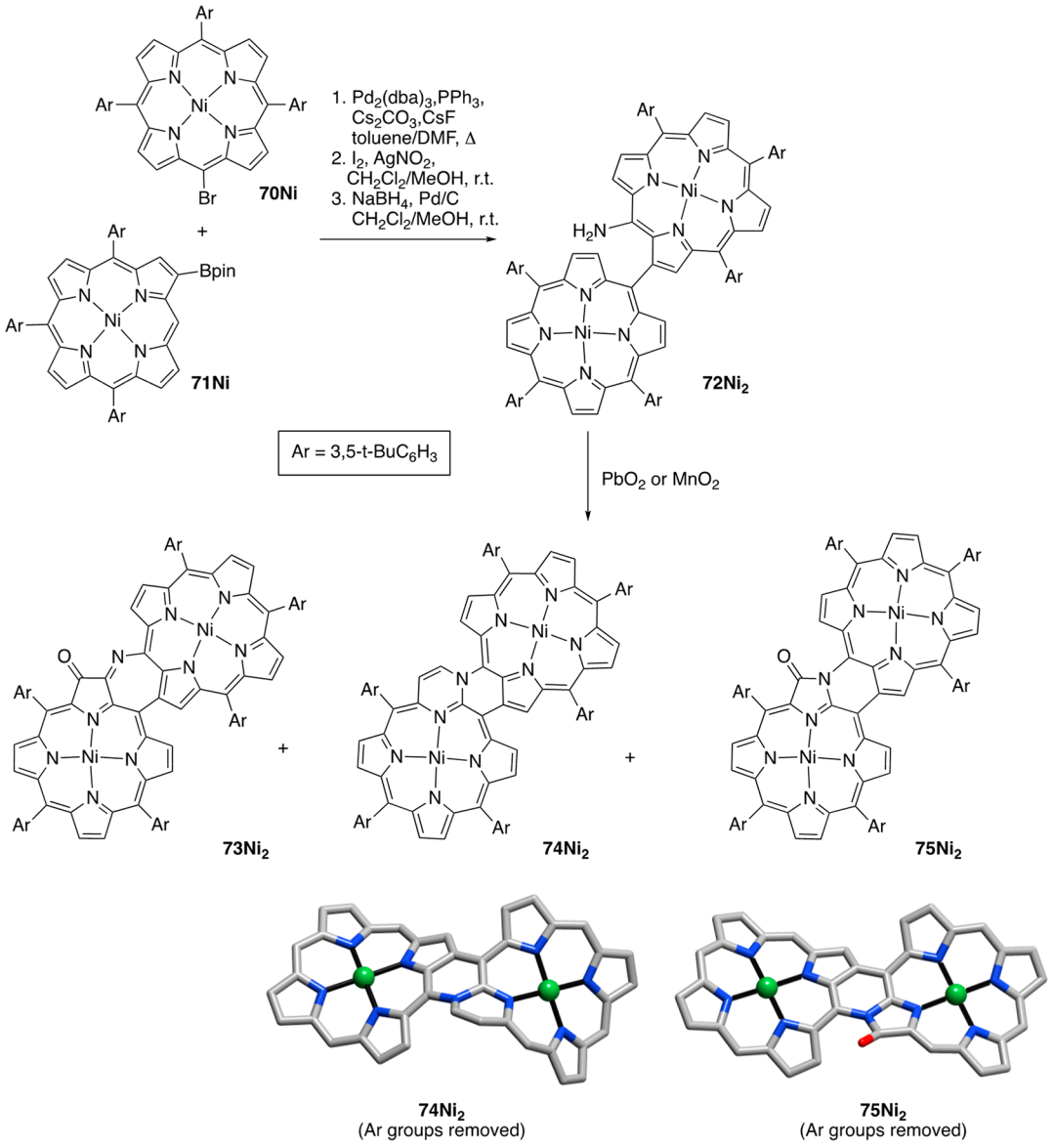
Scheme 24. Syntheses of Nickel(II) Pyrrole-Modified Porphyrin Dimers $73Ni_2$, $74Ni_2$, and $75Ni_2$[a]



[a]Stick representations of the X-ray structures of $74Ni_2$ and $75Ni_2$ adapted with permission from ref 321. Copyright 2020 American Chemical Society.

albeit red-shifted, Soret band. The electronic absorption spectrum of the in-plane bound **77Pd·Cl** shows a spectrum not unlike that of a metalloporphyrin but with a much broadened and split Soret-like band (Figure 13); the absence of any solvochromic effects was interpreted as an indication that the anion is not coordinated to the metal in solution.[327] The spectrum of the out-of-plane-bound rhenium(I) complex of thiaporphyrin **77Re** (not shown) is also broadened and vaguely metalloporphyrin-like[330] and differs from that of **77Pd·Cl**.[327] Thus, metal type and coordination modes affect the optical spectra of the metallothiaporphyrins.

The coordination chemistry of the heavier analogues to the thiaporphyrins, the selena- and telluraporphyrins, has also been described and follows similar principles as shown by the thiaporphyrins, with changes induced by the significantly larger size of the heavier chalcogen atoms.[242,331−333] Telluraporphyrins also take on a special role for their transformation into other PMPs, such as vacataporphyrins (Section 2.1.2) or pallada- and platinacyclopendadiene-modified porphyrins (Section 2.3.6).[17,259,334,335]

2.3.3. Oxaporphyrin Metal Complexes. 21-Oxaporphyrins are heteroporphyrins in which one pyrrole has been replaced by a furan moiety. Their syntheses may follow the general heteroporphyrin synthesis principles, but important unique pathways, like the oxygen insertion reaction into vacataporphyrin **9Fe**, are also known (Scheme 4).[262] Metal insertion into the free-base oxaporphyrins forms the metal complexes (Scheme 26). Similarly to the thiaporphyrins, the complexes of zinc(II),[336] nickel(II),[337] iron(II),[338] manganese(II),[339] cobalt(II),[339] and copper(II)[339] possess an axial ligand and adopt a square-pyramidal geometry. The nickel(I)[337] complex is a paramagnetic tetracoordinated species while the iron(III)[340] and rhenium(III)[330] complexes are hexacoordinated octahedral complexes with two axial ligands. The ligand framework in the metallo-21-oxaporphyrins tends to adopt a more planar conformation in comparison to the sterically more encumbered

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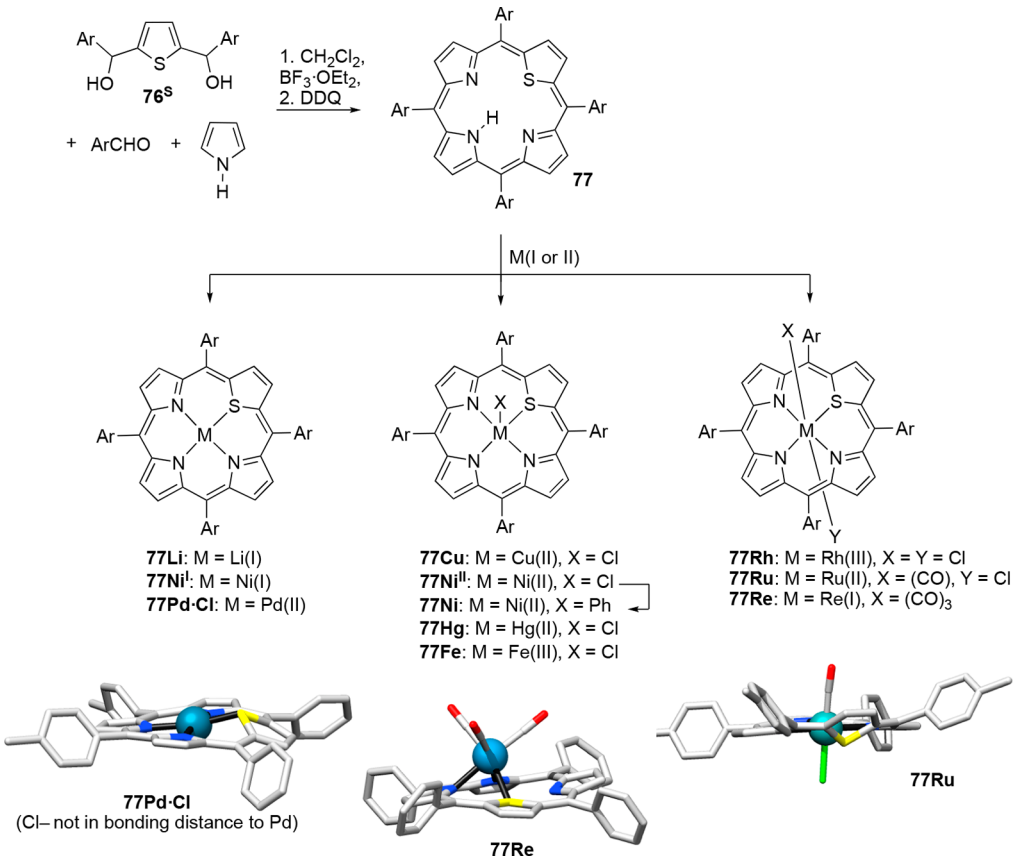
Scheme 25. Syntheses of Metallothiaporphyrins[a]



[a]Stick representation of the X-ray structure of **77Ru** adapted with permission from ref 329. Copyright 2011 American Chemical Society. Stick representation of the X-ray structure of **77Pd·Cl** adapted with permission from ref 327. Copyright 1994 American Chemical Society. Stick representation of the X-ray structure of **77Re** adapted with permission from ref 330. Copyright 2012 American Chemical Society.

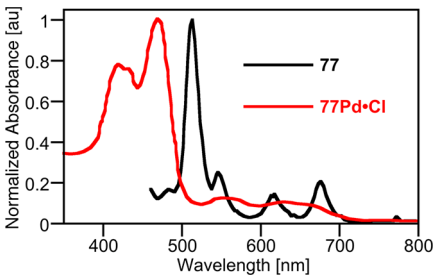


Figure 13. Normalized UV−vis spectra of 77 (CH_2Cl_2) and **77Pd·Cl** ($CHCl_3$). Spectrum of 77 adapted with permission from ref 330. Copyright 2012 American Chemical Society. Spectrum of **77Pd·Cl** adapted with permission from ref 327. Copyright 1994 American Chemical Society.

metallo-21-thiaporphyrin complexes. A description of the rare metal complexes of oxaporphyrins containing more than one furan ring is presented below.

2.3.4. Diheteroporphyrin Metal Complexes. Diheteroporphyrins are porphyrinoids where two pyrrole nitrogens have been replaced with either two of the same heteroatoms (N_2X_2-type) or different heteroatoms (N_2XY-type), whereby the two heteroatoms can be located at opposite positions (21,23-diheteroporphyrins) or adjacent positions (21,22-diheteroporphyrins). The syntheses of the N_2X_2 porphyrinoids most frequently entailed the condensation of a larger stoichiometric ratio of 2,5-bis(aryl-α-hydroxymethyl)-heterocycle with pyrrole under mildly acidic conditions while the N_2XY-type were prepared via condensation of heterocyclopentadiene diols with modified heterotripyrranes ([3 + 1]-type syntheses), some in a two-step, one-flask process (Scheme 27).[16,341] The diheteroporphyrins are neutral ligands, and thus, coordinated metal ions require a larger number of axial ligands (or noncoordinated counteranions) for charge neutralization than do their monoheteroporphyrin congeners (or especially the dianionic porphyrinoids). Dioxoporphyrin **79** is already "soft" enough to stabilize nickel(I), thus allowing the octahedral nickel(II) complex to be reduced to the nickel(I) complex (Scheme 27A).[337] Alas, it was not isolated and reverted back to the nickel(II) on addition of an oxidant.

The ruthenium(II)[342] and rhenium(I)[343] complexes of 21,23-dithiaporphyrin show that **80Ru** exhibits a near-perfect octahedral geometry (Scheme 27B). In order to accommodate the large ruthenium(II) ion in the small (relative to regular porphyrins containing the smaller nitrogen donors) dithiaporphyrin core, the thiophene rings are tilted out of plane into opposite directions. On the other hand, in the rhenium(I) metal complex **80Re**, the metal ion resides on top of the macrocycle plane, and the thiophene rings are tilted to the same side, forming an overall domed macrocycle. A metric comparison of the cationic dithiaporphyrin rhenium(I) triscarbonyl complex **80Re** with its diselenaporphyrin-analogue was reported, highlighting the effects of the larger size of the selenium atoms.[344]

21,23-Ditelluraporphyrin was prepared.[345] As a response to the steric repulsion of the two inner tellurium atoms, one of the

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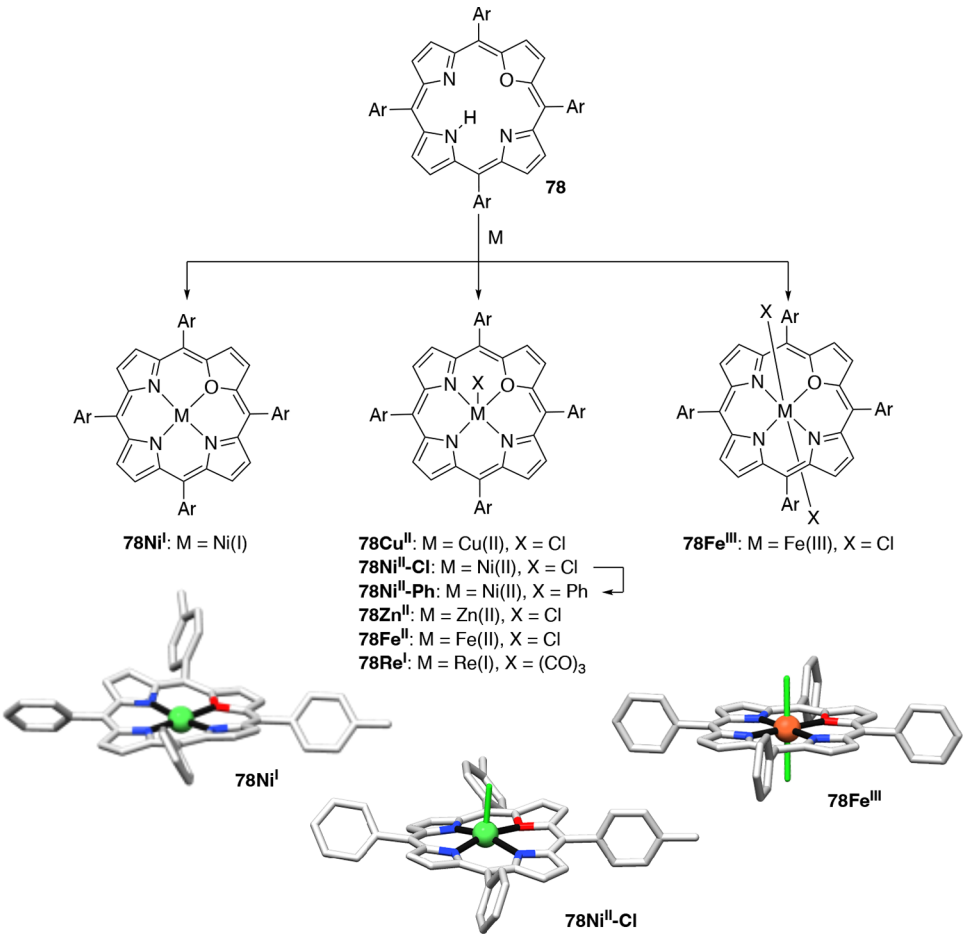
Scheme 26. Syntheses of Metallooxaporphyrins[a]



[a]Stick representations of the X-ray structures of **78Ni^{I}** and **78Ni^{II}** adapted with permission from ref 337. Copyright 1997 Wiley-VCH. Stick representation of the X-ray structure of **78Fe^{III}** adapted with permission from ref 330. Copyright 2012 American Chemical Society.

tellurophene moieties is almost completely flipped (the inverted tellurophene plane in the solid state possesses a 123.0(2)° dihedral angle with respect to the mean plane of the remainder of the macrocycle). In solution, this diheteroporphyrin is dynamic and interchanges between two energetically identical flipped forms. One aspect of the coordination chemistry of the 21,23-ditelluraporphyrin is delineated in Section 2.3.6.

2.3.5. Metallothiaethyneporphyrin Metal Complexes. The formal replacement of a pyrrolic building block within a *meso*-tetrarylthioporphyrin by an acetylene moiety is also possible, giving rise to the triphyrin(4.1.1) frame of thiaethyneporphyrin **82**, an atypical arrangement for a contracted, but still 18 π-electron aromatic, porphyrin.[346] 20-Thiaethyneporphyrin is formed by a simple modification of the [3 + 1] approach using the ethyne-analogue of tripyrrane **81** and 2,5-bis(tolylhydroxymethyl)thiophene **76^{S}** (Scheme 28).

The nickel **82Ni**, palladium **82Pd**, and copper **82Cu** complexes of free-base **82** have been reported.[347] In these complexes, thiaethyneporphyrin **82** acts as a dianionic ligand coordinating through the two nitrogen and the sulfur atom (Scheme 28A). An interaction of the metal with the ethyne moiety is weak, but the bond distance is shorter than the sum of van der Waals radii.[347] The X-ray crystal structure reveals that coordination to nickel(II) and palladium(II) by a N_2S-η^2-C_2-donor set provides distorted pseudo-square-planar, low-spin diamagnetic nickel(II) and palladium(II) complexes **82Ni** and **82Pd**, respectively. Axial coordination to **82Ni** forms a high-spin, paramagnetic nickel(II) complex. Complex **82Pd** reacts with sodium borohydride to form an aromatic palladium(II) thiaetheneporphyrin **83Pd** in which the metal is coordinated by an idealized square-planar N_2SC-donor set.[347]

Dithiaethyneporphyrin **85** has also been prepared by a [3 + 1] strategy (Scheme 28B).[348] The potential monoanionic NS_2 ligand (with or without the involvement of the carbon atoms of the ethyne moiety) acts as a monoanionic, monodentate N-donor ligand when coordinated to ruthenium(II). Dithiaethyneazuliporphyrin and its ruthenium complexes have also been reported; here, the ligand acts as a monodentate, anionic C-donor ligand.[349]

2.3.6. Pallada- and Platinacyclopentadiene-Modified Telluraporphyrin and Tellurachlorin. The reaction of 21,23-ditelluraporphyrin **86** with platinum(II) led, at low temperatures, to an out-of-plane binding of the metal to form **86PtCl$_2$** (Scheme 29).[335] At higher temperatures, or assisted by silver(I), platinum replaced one tellurium atom in the ditellurophene forming a platinacyclopentadiene ring; concomitantly, the remaining tellurophene inverts and presents the tellurium atom to the inside and within bonding distance to the neighboring nitrogen atom, forming in **87Pt** a C_2NTe distorted square-planar coordination sphere for the platinum ion.[335] The aromatic metallaporphyrin **87Pt** can be subjected to the (reversible) reduction of the β,β'-bonds of one pyrrole, forming

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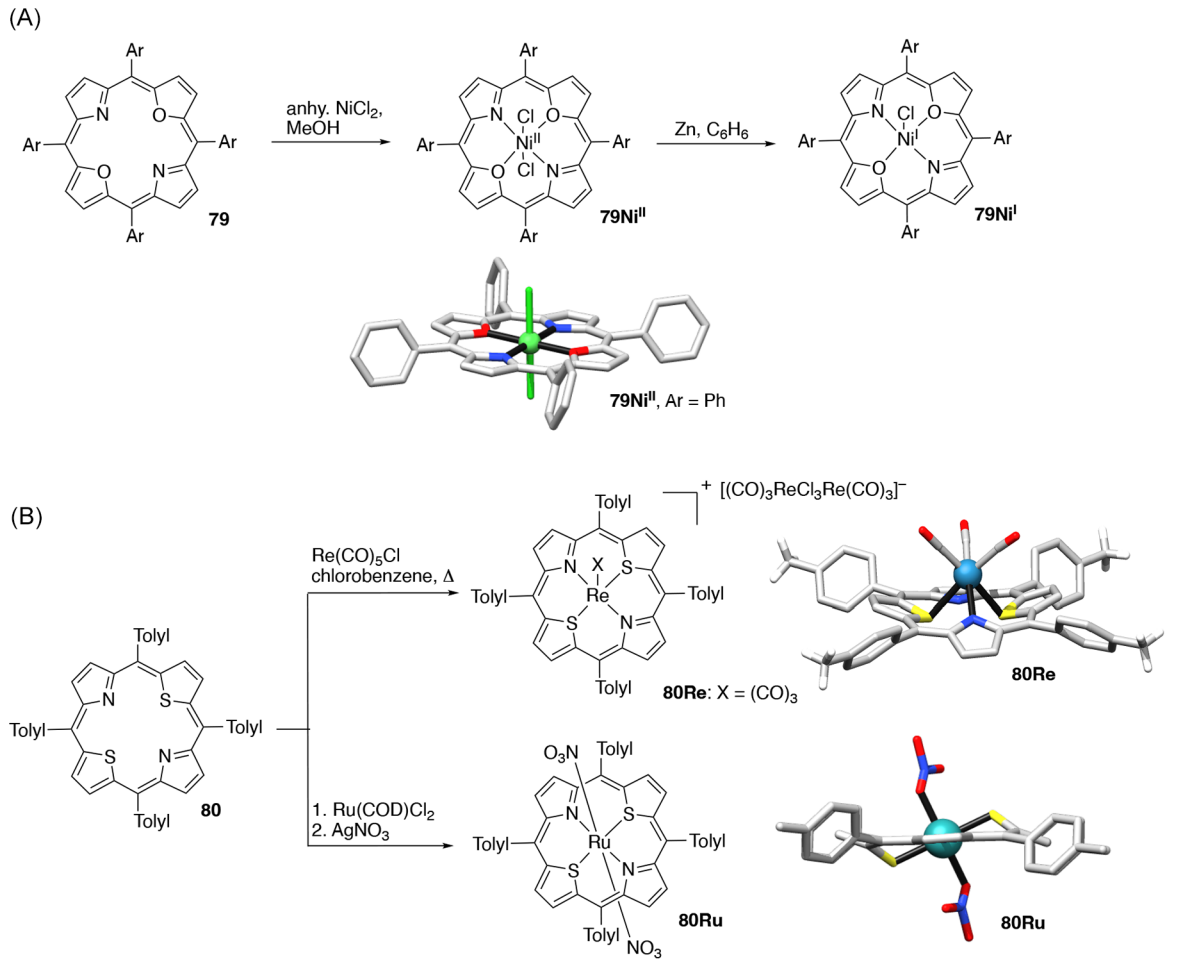
Scheme 27. Examples of Diheteroporphyrins[a]



[a]Stick representations of the X-ray structures of **79Ni^{II}** adapted with permission from Ref 337. Copyright 1997 Wiley-VCH. Stick representations of the X-ray structure of **80Ru** adapted with permission from ref 342. Copyright 2001 American Chemical Society. Stick representations of the X-ray structure of **80Re** adapted with permission from ref 343. Copyright 2014 American Chemical Society.

the chlorin-analogue **88Pt**. This can be subjected to (reversible) oxidative additions of XY to the platinum, forming the corresponding platinum(IV) complexes **87PtXY** containing (idealized) octahedrally coordinated platinum centers. The deformations present in the structures of the platinatellurophyrins are largely a result of the sizes and of the tellurium platinum atoms within the steric constraints of the porphyrinoid macrocycle.[335] While the DDQ-mediated oxidation of a chlorin (or other hydroporphyrins) to the corresponding porphyrin is also a standard reaction in porphyrinoid chemistry,[350] the reduction of metallaporphyrin **87Pt** or **87PtXY** using aqueous dithionite ($Na_2S_2SO_4$) is unusual. This likely nongeneral method might only be applicable to platinatelluraporphyrins that appear to be particularly sensitive toward reduction.

An equivalent palladacyclopentadiene incorporated into the porphyrinoid frame was formed by a transformation of 21,23-ditelluraporphyrin triggered by coordination to palladium(II).[351] This resulted in the replacement of a tellurium atom by a palladium atom to form an aromatic 21-pallada-23-telluraporphyrin. The nonplanar molecule is in equilibrium between two forms.

2.4. Metalloporphyrinoids with N_3C-Coordination Spheres

2.4.1. N-Confused Porphyrin Metal Complexes. 2-Aza-21-carbaporphyrins, also known as N-confused porphyrins, are porphyrin isomers in which one of the pyrrole subunits was inverted in place, resulting in a switch between an inner nitrogen atom with a β-carbon atom.[60] Curiously, these porphyrin isomers were theoretically considered[181,182] decades before the *meso*-tetraaryl derivatives were first realized by means of [4 × 1] condensation reactions under conditions that are similar to those for syntheses of regular tetraarylporphyrins.[71,72] Over time, a number of alternative [4 × 1]-,[352,353] [2 + 2]-,[354] and [3 + 1]-type[355] syntheses of the *meso*-aryl-, as well as β-alkyl-, N-confused porphyrin series were introduced and now dominate their generation (Scheme 30). Since their discovery,[71,72] the chemistry of N-confused porphyrins flourished and greatly expanded in breadth and depth like no other PMP. Many aspects of this field have been amply reviewed,[10,28,58,60,98,356−358] including their coordination chemistry.[359]

The optical properties of tetraphenyl N-confused porphyrin are porphyrin-like but significantly red-shifted compared to a regular tetraphenylporphyrin. As a result of the existence of different tautomers and the interaction of the solvent with the outer nitrogen atom, their optical spectra are strongly tautomer-

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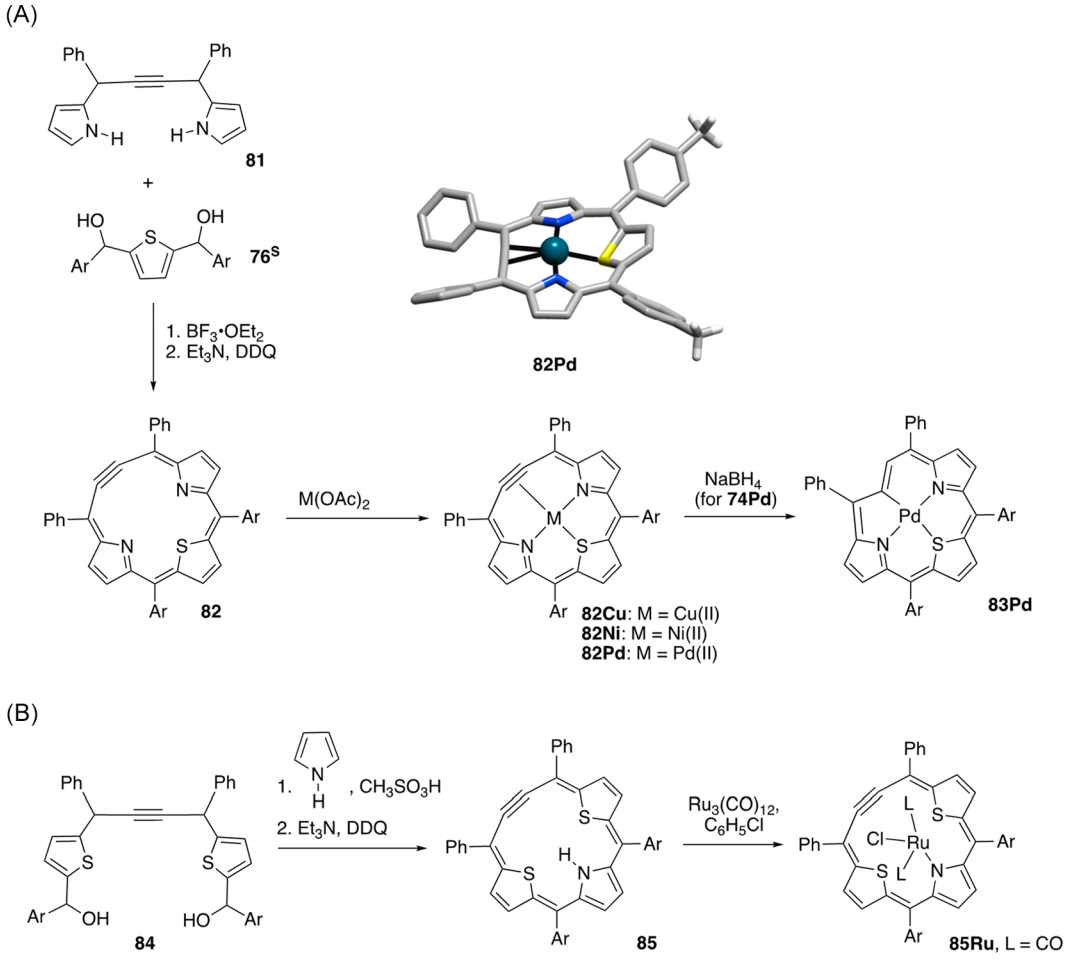
Scheme 28. Syntheses and Reactions of Metallothiaethyneporphyrins[a]



[a]Stick representations of the X-ray structure of **82Pd** adapted with permission from ref 346. Copyright 2012 American Chemical Society.

dependent, controlled by *N*-alkylation, and solvatochromic.[358,360−363]

With respect to their coordination chemistry, N-confused porphyrins are an interesting class of PMPs as they are able to bind to a metal inside and outside of the macrocycle,[364] leading to the formation of a multitude of homo- and heterobimetallic di-, oligo-, and polymeric supramolecular assemblies with metal ions such as palladium(II), platinum(II), zinc(II), cadmium(II), mercury(II), and iron(II).[60,61,98,356,359,364−367] Participation of the outer nitrogen atom in atom transfer catalysis by a metallo-N-confused porphyrin was shown.[368] The metal coordination chemistry at the center of N-confused porphyrins shows differences from that of carbaporphyrins (inner C− but no *β*-N atom; discussed below) since the macrocycle may, dependent on solvents and pH, adopt two different tautomeric forms, both maintaining the aromatic 18 *π*-system (Scheme 31). However, both tautomeric forms vary in the number of inner hydrogens (two or three), thus switching the ligand properties from a dianionic N_3C ligand (form A) to trianionic N_3C ligand (form B).[360,369,370]

In cases of the square-planar copper(II), palladium(II), and platinum(II) complexes, the ligand acts as a dianionic N_3C ligand.[61,359] The macrocycle flattens upon metal coordination. These types of complexes bear a proton on the 2-aza atom of the ligand that can be deprotonated. Deprotonation of a neutral M(II) complex results in an anionic complex of the metal in the same oxidation state as the neutral complex, as illustrated with, e.g., the platinum(II) complexes (Scheme 32A).[371] Alkylation of the external nitrogen fixes the ligand to be a dianionic N_3C donor ligand.[372]

The electronic states of isostructural porphyrin and N-confused porphyrin molybdenum(II) and manganese(III) complexes have been compared.[373,374] The functional connection of the coordinating inner carbon to nucleophilic carbenes[368] was illuminated.[370,375] In fact, all PMP carbaporphyrins variants that contain inverted or N-confused porphyrins are of particular interest since they form metal complexes with stable metal−carbon bonds under mild conditions. Theoretical studies have been carried out to understand the carbon acidity and metal-complexing ability of inverted porphyrins.[370,376] Key factors underlying the ease of formation of, for example, the organometallic nickel(II) complexes are the highly favorable covalent interaction between the empty d_s orbital of the d^8 Ni^{2+} ion in a square-planar ligand field and the central carbon of the nonpyrrolic (or inverted pyrrolic) building block. Density functional calculations on various tautomers of inverted porphyrins, carba-, oxacarba-, and thiacarbaporphyrins, correlated the stabilities of their carbenic tautomers to their ability to form metal complexes with metal−carbon bonds; these studies also identified the central carbon atom as the most nucleophilic carbon in the macrocycle.[370] These factors are the basis for the

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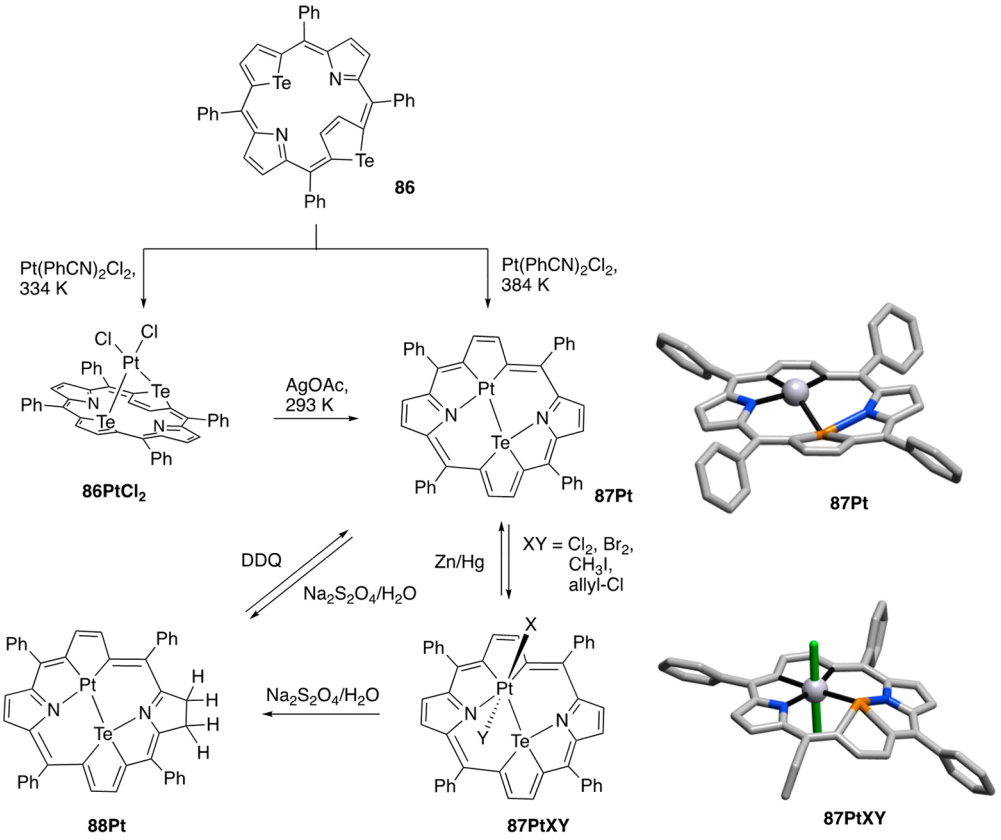
Scheme 29. Formation and Interconversions of Platinatelluraporphyrins 87Pt and 87PtCl$_2$ and Platinatellurachlorin 88Pt[a]



[a]Stick representations of the X-ray structures of **87Pt** and **87PtCl$_2$** adapted with permission from ref 335. Copyright 2020 Wiley-VCH.

organometallic chemistry of the carbaporphyrins; this topic has been reviewed.[9,10,28,100]

The copper(II) *meso*-C_6F_5-derivative **91^{F}Cu** can be (reversibly) converted into the square-planar copper(III)-analogue **83^{F}Cu** via chemical oxidation (Scheme 32B).[365] The silver(III) complex of **83Ag** is an example in which the macrocycle acts as a trianionic N_3C ligand,[367,377,378] distinguishing it from the stable silver(II) complexes of the porphyrins (Scheme 32A).[379] The stabilization of the silver(III) oxidation state is a characteristic of trianionic carbaporphyrins[10,380] and corroles.[381]

Comparing the UV−vis absorption spectra of the copper(II) complex **91^{F}Cu** and the corresponding copper(III) complex **99^{F}Cu**, the change in the oxidation state of the central metal is primarily reflected in a change in the Q-band region of the spectrum, with much longer wavelength absorbances for the copper(III) complex (Figure 14A).[385]

Some metals coordinated to N-confused porphyrins do not form a M−C bond. Instead, a N_3-donor set is observed, and the inverted pyrrole unit is slanted out of planarity, thus positioning the C−H bond away from the coordinated metal. One example is the distorted tetrahedral and air-sensitive manganese(II) complex **91Mn^{II}**, also carrying an additional monodentate ligand; this complex can also dimerize in a self-complementary fashion, forming **(91)$_2$Mn** (Scheme 33):[382,386] The outer nitrogen atom of one complex forms the axial ligand of another, and *vice versa*. The coordination geometry observed in complex **91Mn^{II}** resembles those of other first row transition metals[359] as well as those of vacataporphyrins or benziporphyrins (see Sections 2.1.2 and 2.4.6, respectively). Oxidation of **91Mn^{II}** formed the planarized manganese(III) complex **91Mn^{III}** in which the N-confused porphyrin is forced to coordinate as a trianionic N_3C ligand. Deprotonation of the inner CH moiety removes all steric interactions with the central metal, and a nearly perfectly planar macrocycle is obtained.[374]

The N-confused porphyrin in iron(II) complex **99Fe^{II}** also acts as a N_3-donor ligand.[387] However, oxidation of this ferrous complex by oxygen, iodine, or bromine leads to the formation of the corresponding ferric complex **99Fe^{III}** containing an Fe−C bond (Scheme 33).[389] Further oxidation leads to the insertion of an oxygen into the Fe−C bond, forming complex **100Fe**.[388] A number of carbaporphyrins, such as O-confused oxaporphyrins or azuliporphyrins, have also shown similar metal-activated inner carbon atom oxidations (cf. Sections 2.4.3 and 2.4.2, respectively). In some circumstances, oxidations may lead to a complete degradation of the confused pyrrole.[390]

The manganese complex **(91)$_2$Mn** has a distinctly different optical spectrum compared to that of the free-base precursor: Both the Soret and Q-band regions are very broad and nearly featureless (Figure 14B). The Soret band also has a lower extinction coefficient, shifting the relative intensity ratios of the Soret and Q-bands from those typically observed in metalloporphyrins. As a result of the axial coordination and the split of the dimer structure, the spectrum of monomer **99Mn^{II}** is much different, exhibiting a sharp and much red-shifted Soret band that is, relative to the Q-band, much more intense. Nonetheless, the Q bands are still unusually broad (for a metalloporphyrin).[382]

The ability of the N-confused porphyrins for coordination using both the inner and outer nitrogen atoms is illustrated with the bis[rhodium-(I)] complex **91Rh$_2$** (Scheme 34) in which one

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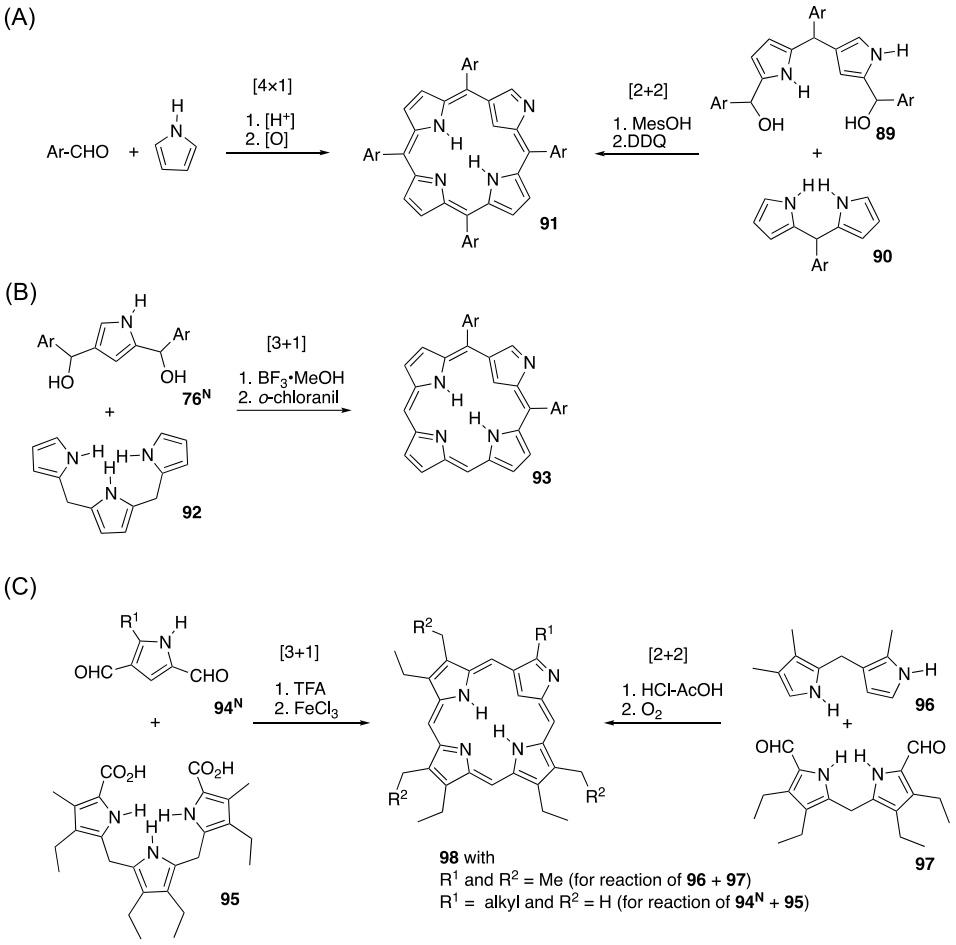
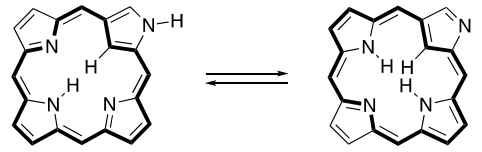
Scheme 30. Total Synthesis Approaches toward N-Confused Porphyrins



Scheme 31. Tautomeric Forms of N-Confused Porphyrins



of the rhodium atoms has been placed at the peripheral position, and a second one is located in the cavity.[391] Additionally, the use of the inner and outer nitrogen atoms was investigated for neutral molecule and anion binding/anion recognition.[60,61,371,392,393]

The conformational flexibility of NCPs extends to the relative orientation of the confused pyrrole—it can invert, bringing the N-confused ~~carbon~~ nitrogen back into the central cavity.[395] Large substituents on the inner carbon or coordination interactions can induce this inversion. Iridium dicarbonyl exhibits such a mode when coordinated to **91**, exemplified in the structure of **91Ir$_2$** (Scheme 34).[394]

2-Aryl- and 2-alky-substituted N-confused porphyrins were also prepared either by [3 + 1] approaches involving *N*-alkylated building blocks or by alkylation/arylation of the "confused" nitrogen atom.[396,397] Their nickel(II), cobalt(II), silver(II), palladium(II), mercury(II), and manganese(III) complexes have been reported.[396−402]

Internal N−C bond formations within (suitably derivatized) N-confused porphyrins led to the formation of N-fused porphyrins. Their formation and rich and often unusual coordination chemistry (*inter alia*, the N-fused porphyrins form inner ruthenium complexes[403] as well as a remarkable ruthenocene-like complex in which the N-fused porphyrin and cyclopentadiene sandwich a ruthenium(II) ion),[404] have been well-reviewed.[60,62,405−410]

2.4.2. Azuliporphyrin Metal Complexes. Azuliporphyrins are azulene-based carbaporphyrins; i.e., one of the pyrrole rings of a porphyrin has been replaced with a cyclopentadiene moiety that is annulated to a 7-membered carbacycle. They are best synthesized along [3 + 1]-type pathways (Scheme 35A).[411] The azulene subunit interrupts the macrocycle aromaticity significantly (cf. the benzi- and pyriporphyrins, Sections 2.4.6 and 2.2.10, respectively). Evidently, a resonance structure forming an aromatic tropylium and a macrocyclic aromatic π-system does not dominate within the ensemble of canonical forms at ambient temperature. As a result, the UV−vis spectra of both the free-base chromophore and its metal complexes are not porphyrin-like.

Syntheses of the nickel(II), palladium(II), and platinum(II) complexes of azuliporphyrins were accomplished via metal insertion into the free-base. In these complexes, the central metal ions are all coordinated by an idealized square-planar N_3C donor set (Scheme 35).[99] The conformation of **103Ni** is, like many of the nickel porphyrinoids, significantly distorted from planarity and takes up a ruffled deformation mode.[99] Complex

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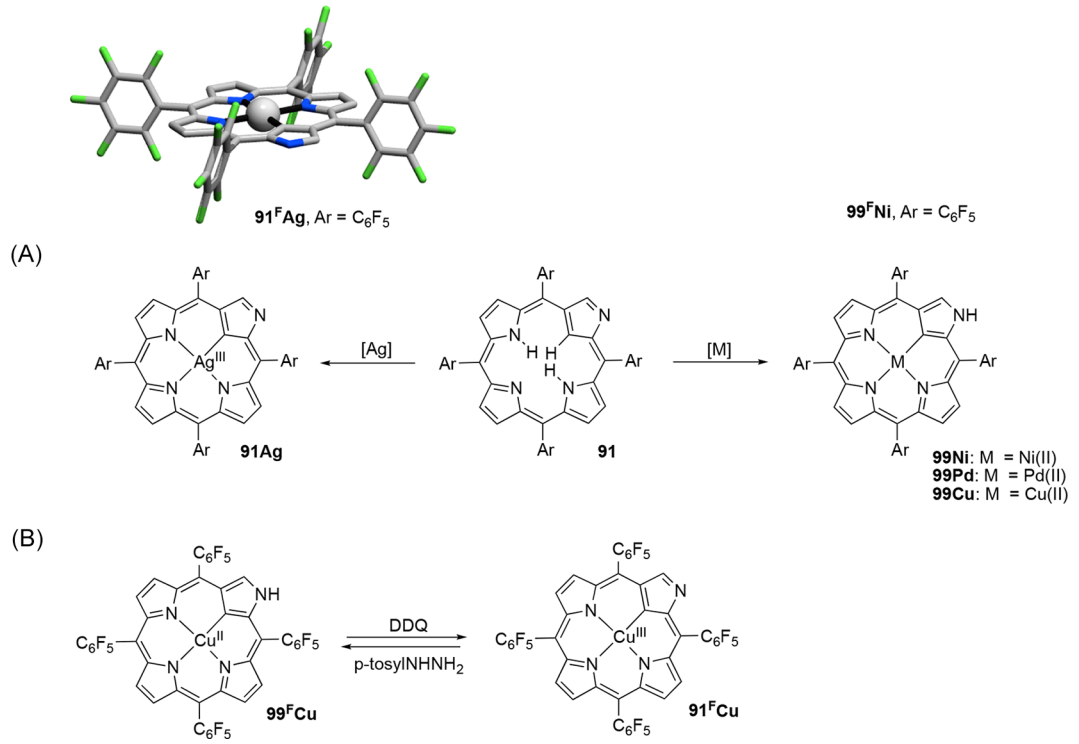
Scheme 3. Coordination Chemistry of N-Confused Porphyrin 91 and 99 Highlighting the Relationship between the Tautomeric Forms and the Metal Oxidation State[a]



[a]Stick representation of the X-ray structure of **99^{F}Ag** adapted with permission from ref 377. Copyright 1999 American Chemical Society.

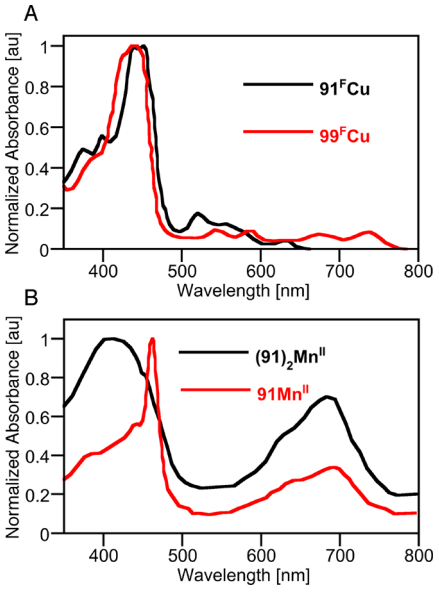


Figure 14. Normalized UV−vis spectra (CH_2Cl_2) of (A) **91^{F}Cu** and **99^{F}Cu** and (b) **91Mn^{II}** and **(91)$_2$Mn**. Spectra of **91Mn^{II}** and **(91)$_2$Mn** adapted with permission from ref 382. Copyright 2002 Royal Society of Chemistry. Spectrum of **91^F** adapted with permission from ref 383. Copyright 2014 American Chemical Society. Spectrum of **99^{F}Cu** adapted with permission from ref 384. Copyright 2003 American Chemical Society.

101Pd containing the larger palladium(II) ion is much more planar, albeit slightly saddled. The conformation and Pd−N bond distances are identical to those found in regular [porphyrinato]palladium(II) complexes.[412]

The electronic structure of azuliporphyrins is significantly different from that of porphyrins or most other carbaporphyrins. The UV−vis spectrum for free-base azuliporphyrin **101** is characterized by a distinct split Soret band region and one broad, little-structured absorption band in the Q-band region of the spectrum (Figure 15).[100,411,414] Both the nickel(II) and palladium(II) complexes of azuliporphyrin **101** maintain the azuliporphyrin characteristics.

The metalation reaction of **101** with copper(II) resulted in an oxidation of the inner carbon and the formation of a N_3O-coordinated copper complex **102CuO** containing an oxygen atom bridging the copper and inner carbon atoms (Scheme 35).[413] These types of metal-induced inner carbon oxidations are also observed for other carbaporphyrins, such as O-confused oxaporphyrins (Scheme 36) and N-confused porphyrins (Scheme 32). The crystal structure of **102CuO** highlights the dramatic distortion from planarity of the macrocycle caused by the presence of the oxygen atom.[413] The steric imposition of the oxo-group forces the azulene moiety to be canted with respect to the mean plane of the remainder of the macrocycle.[413]

The iridium(III) complex **103Ir** of β-alkylazuliporphyrins was formed utilizing bis(cycloocta-1,5-diene) diiridium(I) dichloride $[Ir(COD)Cl]_2$ in xylene as the metal source (Scheme 35B).[9,415] Thus, metal insertion was accompanied by a metal ion oxidation step. A rhodium(III) complex **103Rh** that shows structural similarities to the iridium complex has also been explored.[416]

2.4.3. O-Confused Oxacarbaporphyrin Metal Complexes. 2-Oxa-21-carbaporphyrins, such as (variously substituted) compounds **104**, are furan-analogues of the N-confused porphyrins; i.e., the inverted pyrrole has been replaced by an inverted furan subunit (Scheme 36). Synthesized by mixed

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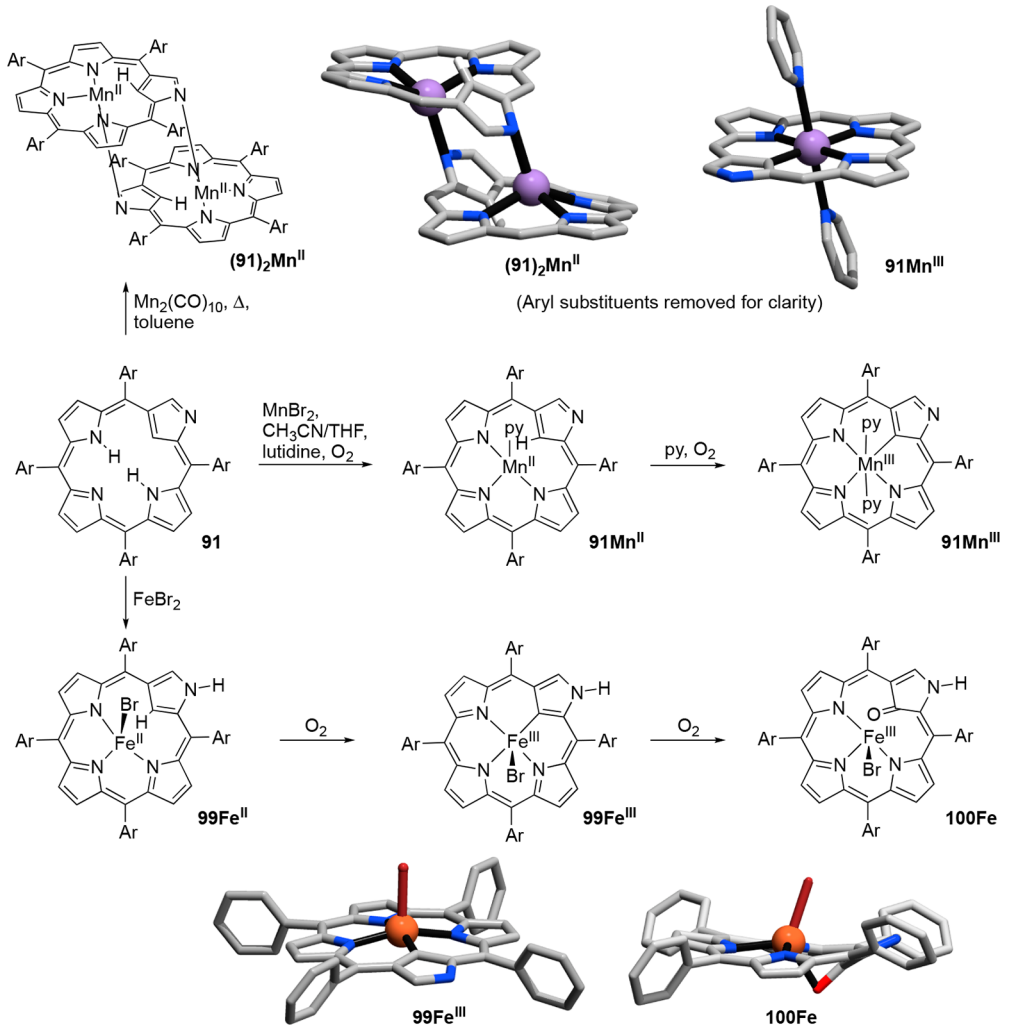
Scheme 33. Coordination Chemistry of N-Confused Porphyrin with Iron and Manganese[a]



[a]Stick representation of the X-ray structure of $(\mathbf{91})_2\mathbf{Mn}^{\mathbf{II}}$ adapted with permission from ref 382. Copyright 2006 Royal Society of Chemistry. Stick representation of the X-ray structure of $\mathbf{99Fe}^{\mathbf{III}}$ adapted with permission from ref 387. Copyright 2001 American Chemical Society. Stick representation of the X-ray structure of $\mathbf{91Mn}^{\mathbf{III}}$ adapted with permission from ref 374. Copyright 2005 American Chemical Society. Stick representation of the X-ray structure of **100Fe** adapted with permission from ref 388. Copyright 2004 American Chemical Society.

condensation, these carbaporphyrins are attractive analogues to their all-aza-analogues as they permit a fine delineation of the subtle interplay between structural flexibility, perimeter substitution, and aromaticity on the coordination chemistry of these carbaporphyrins.[417]

Oxacarbaporphyrin $\mathbf{104}^{\mathbf{pyr}}$ readily forms nickel(II) ($\mathbf{105}^{\mathbf{pyr}}\mathbf{Ni}$) and palladium(II) ($\mathbf{105}^{\mathbf{pyr}}\mathbf{Pd}$) complexes.[9,418] The crystal structure of $\mathbf{105}^{\mathbf{pyr}}\mathbf{Ni}$ shows only a slight macrocycle distortion from planarity; the dihedral angles between the macrocyclic and substituted pyrrole ring planes reflect their biphenyl-like arrangement. The inverted furan moiety is reactive toward nucleophilic attack at the peripheral position, a result of the redirection of the macrocyclic π-delocalization.[418,419] The insertion of silver into $\mathbf{104}^{\mathbf{OEt}}$ results in, similarly to other carbaporphyrins, the formation of the d^8 silver(III) complex $\mathbf{104}^{\mathbf{OEt}}\mathbf{Ag}$.[418] Treatment of $\mathbf{104}^{\mathbf{OEt}}\mathbf{Ag}$ with acid eliminates the alkoxy group to generate the stable carbacationic species $\mathbf{104}^{+}\mathbf{Ag}$. This reactivity controlled by the presence of the ring oxa group is reminiscent of the facile modification of the oxazolochlorins (cf. Scheme 13).

The insertion of copper into $\mathbf{104}^{\mathbf{pyr}}$ resulted in the quantitative formation of the copper(III) complex $\mathbf{104}^{\mathbf{pyr}}\mathbf{Cu}$. This complex is unstable; prolonged exposure to aerobic conditions resulted in the formation of the paramagnetic complex **105Cu** where the metal, now formally in a +II oxidation state, is still bonded to the three nitrogen atoms and the carbon atom on the inverted furan (Scheme 36).[420] Further exposure to oxygen resulted in the formation of two stable compounds: the furan-oxidized complex **106Cu** and a ring-opened degradation product, oxotriphyrin complex **107Cu**.[420] Alternatively, the reaction of **105Cu** with hydrogen peroxide/potassium hydroxide also led to the formation of **106Cu** in a reaction that parallels oxygen insertion reactions between the metal and the inner, coordinated carbon atom in other copper(III) carbaporphyrins (cf. Scheme 35).[420] The X-ray crystal structure of **106Cu** (not shown) features a macrocycle that is, as expected, slightly distorted from planarity.[420]

2.4.4. N-Confused Pyrazoloporphyrin Metal Complexes. Pyrazoloporphyrins are a class of PMPs in which a pyrrole subunit has been replaced by an inverted pyrazole moiety.[422,423] Pyrazoloporphyrins, such as free-base compound

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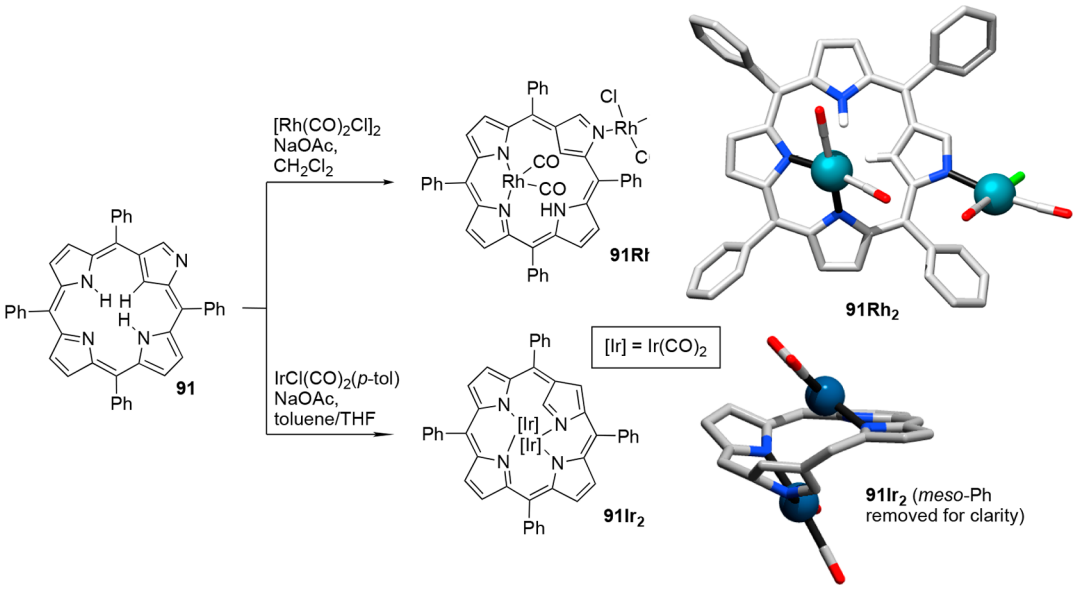
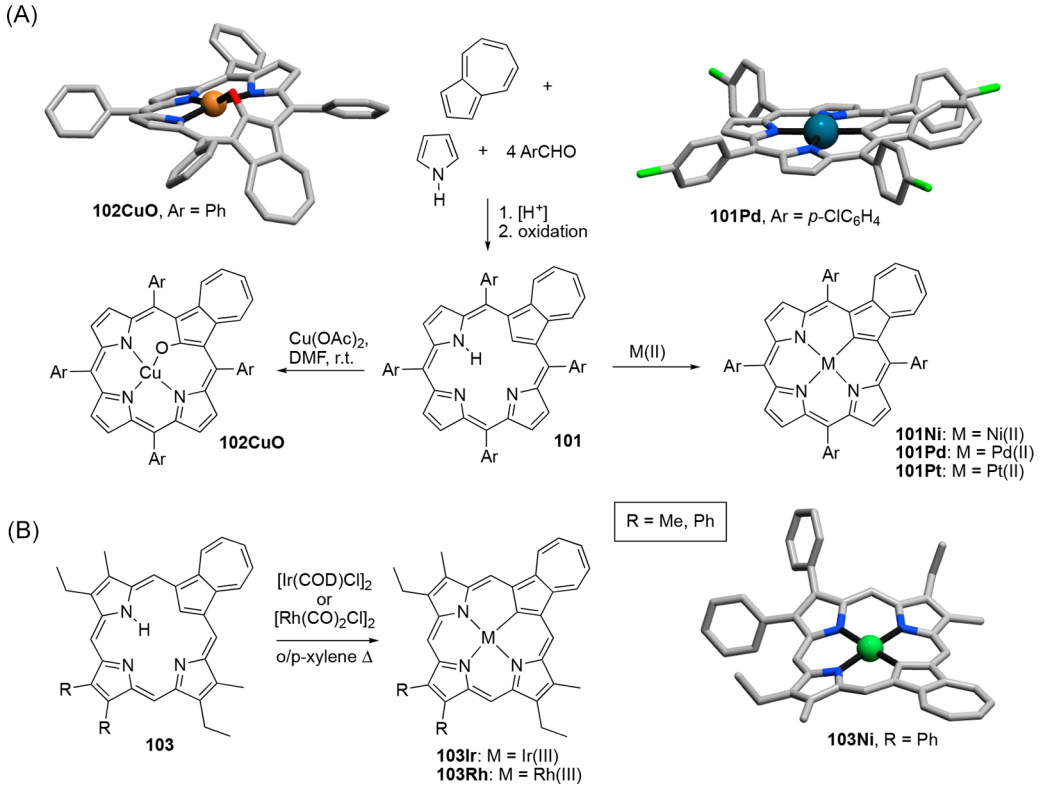
Scheme 34. Coordination Chemistry of N-Confused Porphyrin 91 Highlighting the Involvement of the Outer Nitrogen Atom[a]



[a]Stick representation of the X-ray structure of **91Ir$_2$** adapted with permission from ref 394. Copyright 2006 American Chemical Society. Stick representation of the X-ray structure of **91Rh$_2$** adapted with permission from ref 391. Copyright 2001 Royal Society of Chemistry.

Scheme 35. Single-Crystal X-ray Structure of Azuliporphyrinato Ni(II)[a]



[a]Stick representation of the X-ray structure of **102CuO** adapted with permission from ref 413. Copyright 2004 Wiley-VCH. Stick representation of the X-ray structure of **103Ni** and **101Pd** adapted with permission from ref 99. Copyright 2003 American Chemical Society.

108, are available only via a [3 + 1]-type total synthesis pathway between pyrazole dialdehyde **94**$^{N-N}$ and tripyrrane **95**, and only *β*-alkyl derivatives have been prepared to date (Scheme 37).[422] They are considered borderline aromatic carbaporphyrins. As a consequence, these PMPs possess optical and chemical properties that are distinctly different from those of porphyrins, N-confused porphyrins, or imidazoloporphyrins.

This member of the carbaporphyrins forms metal complexes with nickel(II) and palladium(II) in which the pyrazoloporphyrin acts as dianionic N_3C ligands. The crystal structure of the neutral palladium(II) complex **108Pd** shows it to be nearly

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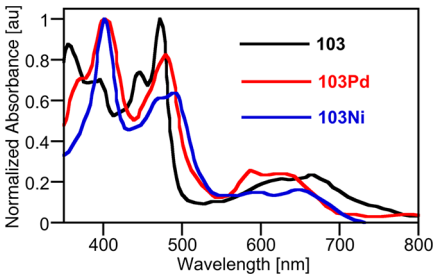
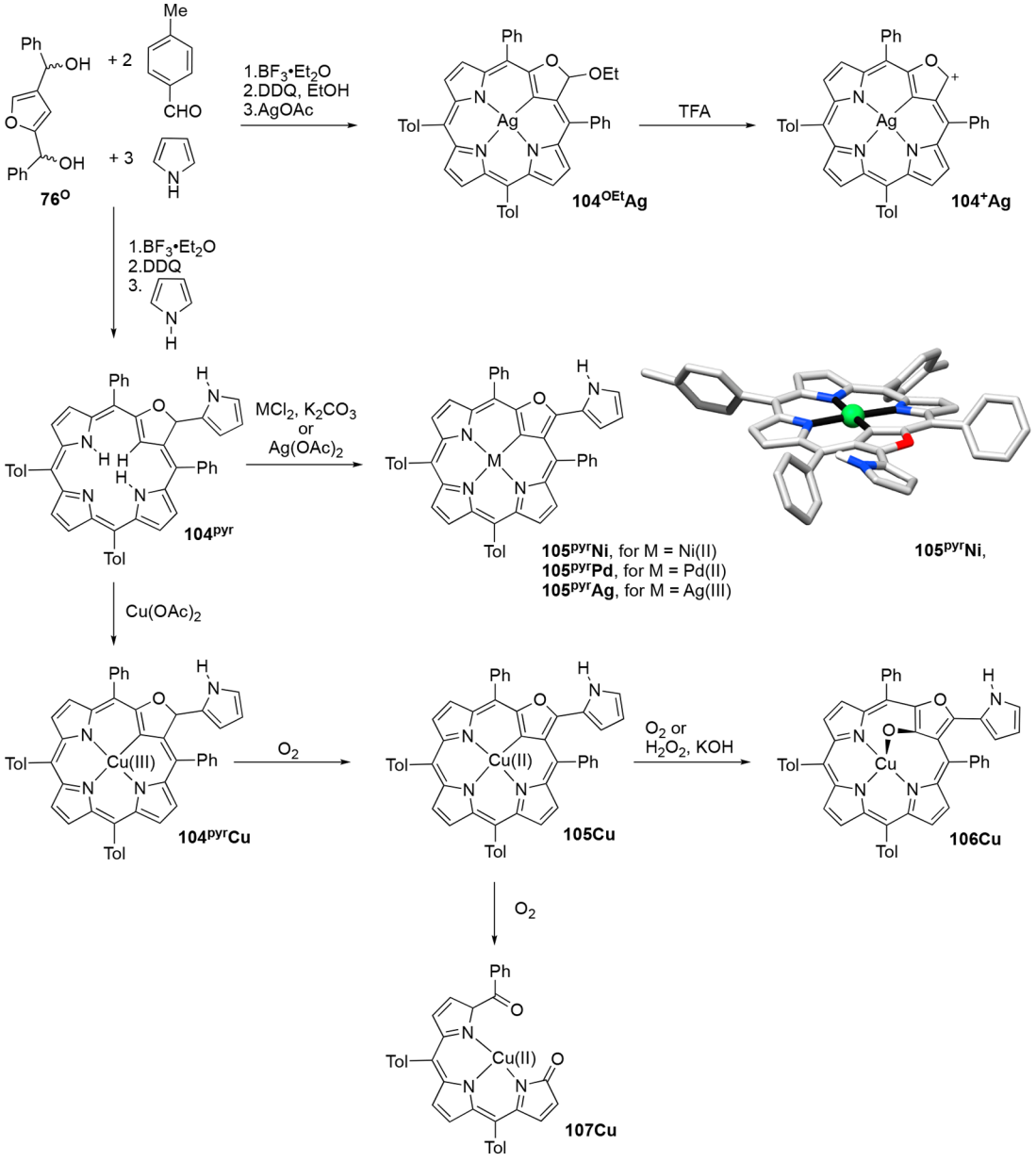


Figure 15. Normalized UV−vis spectra of **101** (1% $Et_3N/CHCl_3$) and **101Pd** and **101Ni** ($CHCl_3$) and spectra adapted from refs 99 and 100. Spectrum of **102CuO** adapted with permission from ref 99. Copyright 2003 American Chemical Society. Spectra of **103Ni** and **101Pd** adapted with permission from ref 100. Copyright 2016 American Chemical Society.

perfectly planar with regular Pd−N and Pd−C bond distances, comparable to the palladium(II) complexes of other carbaporphyrins, such as metalloazuliporphyrins (Scheme 35).[9,422] Metal coordination to the outer nitrogen atoms was not (yet) demonstrated.

2.4.5. Neo-Confused Porphyrin Metal Complexes. Neo-confused porphyrins are tetrapyrrolic carbaporphyrinoids resulting from the formal in-place turning of one pyrrole moiety such that the pyrrole nitrogen is located on an α-position.[424] Thus, this nitrogen atom participates in macrocyclic conjugation. Like the N-confused porphyrins, they are strictly speaking not PMPs (after all, a rotated pyrrole is still a pyrrole), but because of their close relationship to other PMP-type carbaporphyrins, they are included here. Neo-confused porphyrins **110** were prepared via [2 + 2] condensation of an 1,2′-dipyrrylmethane dialdehyde with a 2,2′-dipyrrylmethane

Scheme 36. Synthesis and Manipulation of O-Confused Furanoporphyrins[a]



[a]Stick representation of the X-ray structure **105pyrNi** adapted with permission from ref 421. Copyright 2003 Wiley-VCH.

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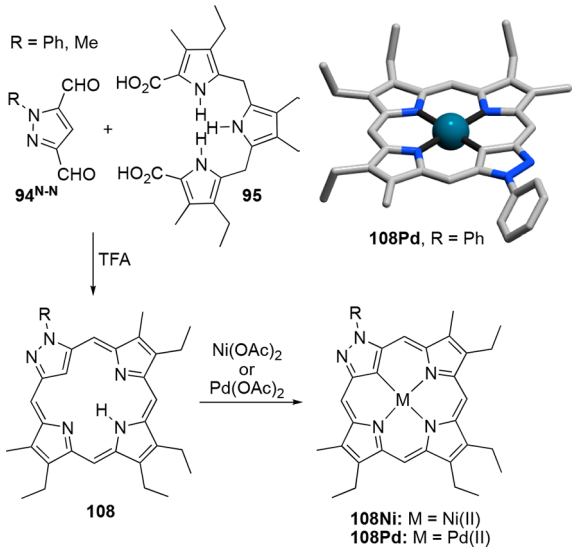
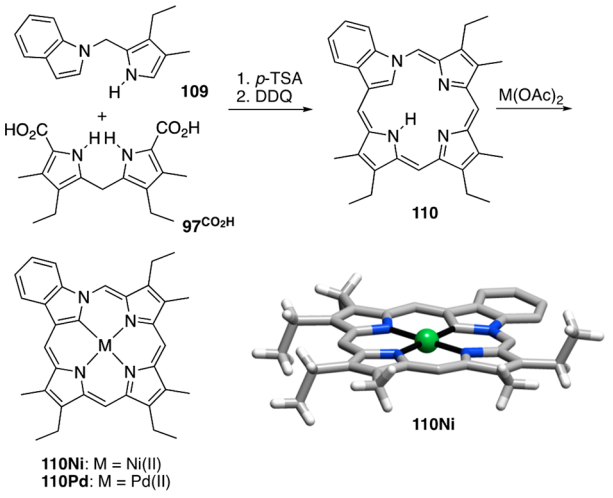
Scheme 37. Total Synthesis of Metallopyrazoloporphyrins[a]



[a]Stick representation of the X-ray structure of **108Pd** adapted with permission from ref 423. Copyright 2008 Royal Society of Chemistry.

(Scheme 38).[424] This carbaporphyrinoid possesses a high degree of aromatic character.

Scheme 38. Examples of Synthetic Pathways and Metalation of Neo-Confused Porphyrin 102[a]



[a]Stick representation of the X-ray structure of **110Ni** adapted with permission from ref 424. Copyright 2011 Wiley-VCH.

The nickel and palladium complexes of neo-confused porphyrin have been reported.[424] While the nickel(II) complex **110Ni** formed smoothly, and its crystal structure confirmed the macrocycle to act—like in other N_3C-donor PMPs—as a square-planar, trianionic ligand, the formation of the palladium(II) complex **110Pd** proved challenging and could initially be accomplished only in low yields.[424] However, this problem was later overcome.[425] The nickel(II) and palladium(II) complexes are essentially isostructural. The planarity and coordination sphere metrics of the palladium complex are very similar to the related palladium(II) complexes of two *N*-substituted N-confused tetraphenylporphyrins[398,399] as well as a palladium(II) azuliporphyrin **101Pd**[99] (Scheme 35A) and palladium(II) pyrazoloporphyrin **108Pd**[423] (Scheme 37).

In the decade since their discovery, regular, contracted, and expanded neoporphyrinoids have been reported, including their spectral, structural, aromatic, and coordination properties. These structurally variable systems have been reviewed.[426]

2.4.6. Benzi- and Oxybenziporphyrin Metal Complexes. In benziporphyrins, a pyrrole of a porphyrin has been replaced by a benzene (phenylene) ring, linked in a 1,3- or 1,4-fashion, forming *m*- and *p*-benziporphyrins, respectively. The *m*-isomers are accessible along a number of routes (Scheme 39A,B) while the *p*-isomer has been prepared exclusively along [3 + 1] routes (Scheme 39C). Benziporphyrins do not possess macrocycle aromaticity since this is possible only at the expense of the 6 π-aromatic system of the benzene moiety, a process that is evidently energetically more costly than the gain in macrocycle aromaticity would offset (in contrast to the oxybenziporphyrins described below).[149,427] Thus, the π-resonance of the benzene moiety exists within the macrocycle essentially isolated from the conjugated π-system of the tripyrrin fragment. This situation is also reflected in their non-porphyrin-like, linear oligopyrrole-type UV−vis spectra. Nonetheless, the absence of aromaticity is not necessarily an indication of chemical instability, as the many examples of benziporphyrins (and related macrocycles) amply demonstrate.[428]

Metalation of *m*-benziporphyrin **112** with, for example, nickel(II) or iron(II) generates the metal complexes of the connectivity shown for **112NiCl** and **112FeBr**, respectively, in which the metal is (distorted) tetrahedrally coordinated by the three nitrogens of the tripyrrin fragment and an additional axial ligand (Scheme 40).[429,430] Thus, *m*-benziporphyrins act here as monoanionic N_3-ligands. The benzene moiety is not strongly bound to the metal; the Fe−C atom distance, for example, is longer than in the corresponding N-confused porphyrin iron(II) complexes **108Fe** or **99Fe^{II}** but shorter than the van der Waals contact distance. Other metal ions that show this type of agostic interactions with the macrocycle includes zinc(II), cadmium(II), and mercury(II).[10,429] The conformational flexibility of this arrangement with respect to the relative position of the phenylene moiety has been investigated for the paramagnetic nickel(II) complex using NMR spectroscopy and DFT calculations.[430] Heating of **112NiCl** in solution transforms it to the square-planar complex **112Ni**.[431] In the case of coordination to copper(II), the formation of a tetranuclear, mixed valence copper complex **115Cu** is observed.[429] The benzene ring in this complex was also chlorinated during the metalation reaction, but the benzene moiety shows no further involvement in the coordination to the metal. The reaction of free-base **112** with silver(I) acetate affords an oxidative acetoxylation but otherwise delivers only a free-base product.[101]

On the other hand, coordination to palladium(II) or platinum(II) forms the (idealized) square-planar complexes **112Pd** and **112Pt** containing formal metal−carbon bonds.[101] Here, the *m*-benziporphyrin acts as a dianionic N_3C-ligand.

β-Alkyloxybenziporphyrin **116** was also generated along a classic [3 + 1] pathway (Scheme 41A).[164,304,432] Importantly, the oxybenziporphyrins incorporate a ketone functionality on the benzene ring that breaks the local 6 π-electron aromaticity of the nonpyrrolic building block, thereby facilitating the expression of a macrocyclic aromatic resonance form in which the oxybenzi moiety takes up a quinoidal resonance form.[164] The large effects of the oxy-modification on the electronic properties of the oxybenziporphyrin chromophore are reflected

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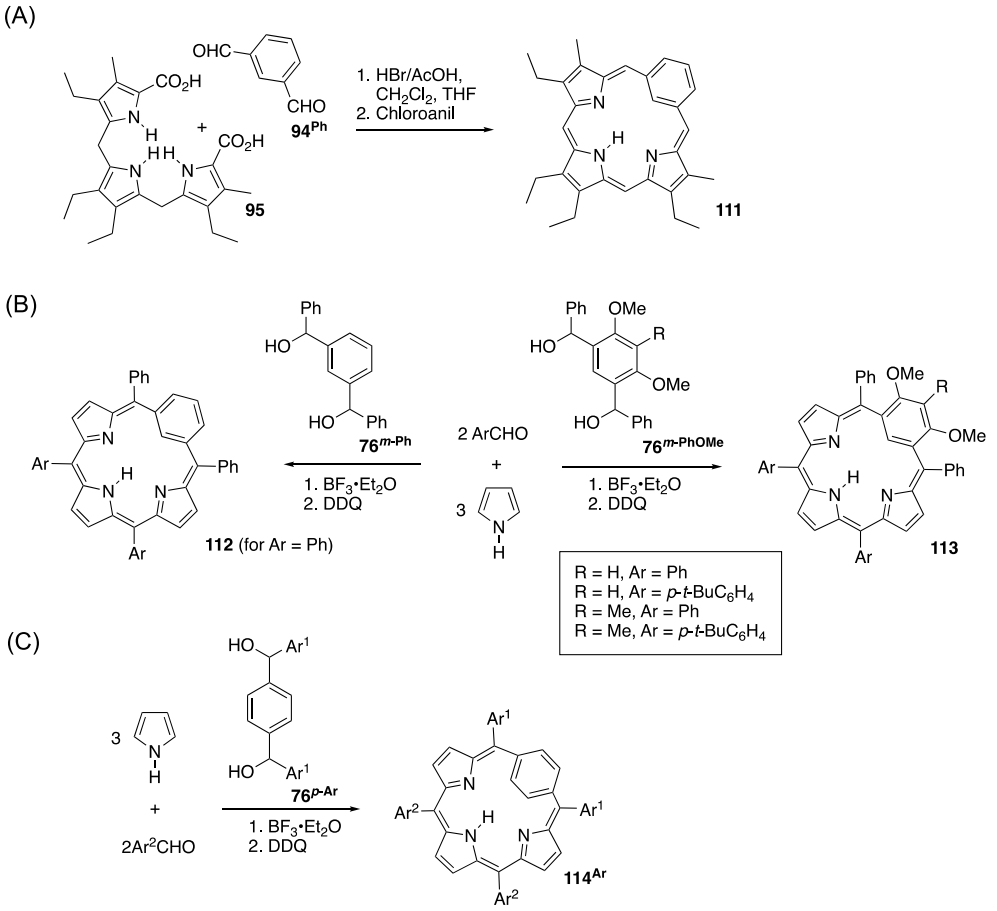
Scheme 39. Examples of Synthetic Pathways Used for the Formation of *meta*- and *para*-Benziporphyrins



in the large differences in the optical spectra of the two macrocycles (see below).

MacDonald-type [3 + 1] condensations of an *N*-methyltripyrrane **95**^{Me} with dialdehyde **94**$^{Ph-OH}$ afforded *N*-methyloxybenziporphyrin **116**^{Me} (Scheme 41B); the presence of the internal alkyl substituents affected the UV−vis spectrum of the chromophore greatly but had little effect on the global aromatic characteristics.[433]

Like the benziporphyrins, the oxybenziporphyrins form a range of metal complexes, including palladium(II) complex **116Pd** in which the ligands act as trianionic N_3C donors, forming an anionic complex (Scheme 41A).[434] Remarkably, the inner carbon of the complex **116Pd** is sufficiently nucleophilic to be alkylated, forming the neutral *N*-methyloxybenziporphyrin palladium complex **116**$^{Me\text{-}I}$**Pd**. While conventional metal insertion conditions failed to result in the formation of the targeted platinum(II) complex of oxybenziporphyrins, moderate yields were obtained when oxypyriporphyrin was reacted with platinum(II) chloride in refluxing mixtures of DMF and acetic acid containing potassium acetate.[435]

Core-modified oxybenziporphyrins are oxybenziporphyrins in which at least one pyrrolic nitrogen has been replaced by an O, S, or Se atom (cf. the heteroporphyrins described in Section 2.3). Even with this change of donor sets, they are competent to form metal complexes.[427,437]

Dimethoxybenziporphyrin **113** is a special benziporphyrin case (Scheme 41C). PMP **113** proved to be nonaromatic in the neutral state, but modest 18 π-aromaticity was achieved in its monocation (inner nitrogen protonated) and dication (oxo-group and inner nitrogen atom protonated) on addition of acid.[164,436] It thus forms an intermediate between the benziporphyrins and the oxybenziporphyrins. Metalation of the diprotic dimethoxybenziporphyrins with nickel(II) and palladium(II) resulted in the formation of **113Ni** and **113Pd**, respectively.[436] The X-ray structure of **113Ni** shows that the macrocycle adopts a saddled geometry with the dimethoxybenzene bent out of plane, generating a distorted square-planar N_3C-coordination geometry.[435,438]

The UV−vis spectrum of dimethoxybenziporphyrins shows two broad bands that are frequently observed in non-macrocycle-aromatic porphyrinoids (Figure 16; cf. also Figure 17). The UV−vis spectrum for palladium complex **113Pd** sharpened all features of the spectrum, likely a reflection of the modulation of the macrocycle aromaticity.[439]

Free-base *p*-benziporphyrin **114** is nonplanar and nonaromatic. It can coordinate metal ions, but the complexed metal ions show either no or only weak interactions with the *p*-phenylene moiety (Scheme 42). In these cases, *p*-benziporphyrin acts as a monoanionic N_3-ligand. For example, the crystal structure of palladium(II) complex **114Pd** highlights the degree to which the *p*-phenylene unit is slanted away from the mean macrocycle plane. However, the palladium ion in complex **114Pd** is close enough to activate the neighboring carbon positions to undergo, upon thermal activation in the presence of base in polar solvents, a ring-contraction reaction to form the aromatic carbaporphyrinoid complexes **117Pd**^{CHO} and **117Pd**^{H}.[440] This reaction shows the large driving forces toward the achievement of the planar macrocycle-conjugated porphyr-

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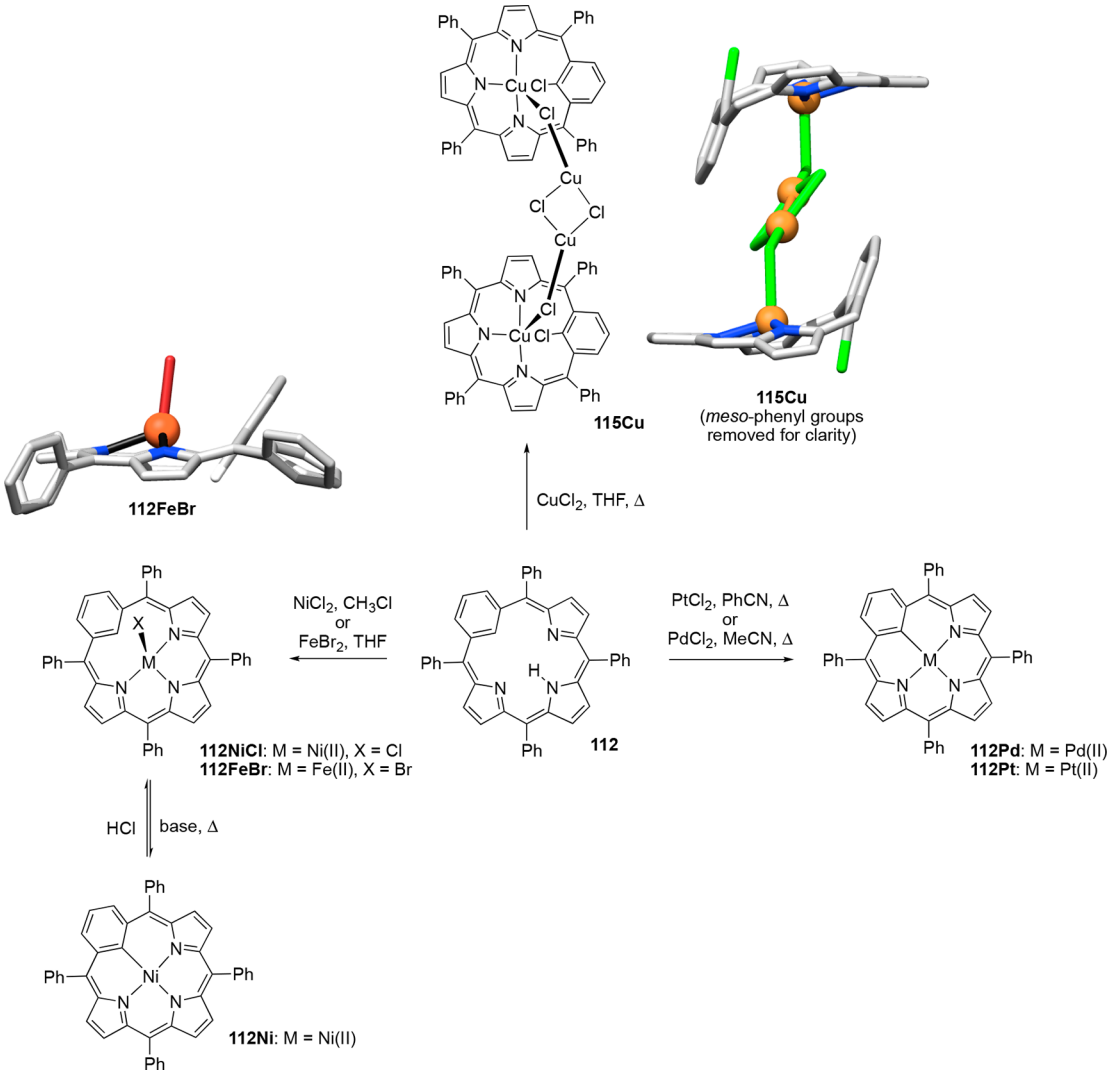
Scheme 40. Syntheses of Metallo-1,3-benziporphyrins[a]



[a]Stick representations of the X-ray structures of **112FeBr** and **115Cu** adapted with permission from ref 429. Copyright 2004 American Chemical Society.

in-like arrangement of four 5-membered rings linked by single carbon atoms. Alternatively, the relative orientation of the *p*-phenylene unit facilitates an η^2-interaction in the diamagnetic ruthenium(II) complex **114Ru^{II}**, as well as in the paramagnetic ruthenium(III) complex **114Ru^{III}**.[441]

The UV−vis spectrum of *p*-benziporphyrins **114** reflects their nonmacrocycle aromaticity (Figure 17).[101] Coordination of ruthenium(II) to form complex **114Ru^{II}** changes the character of the free-base spectrum and introduces complexity and a significant red-shift, testament to the much different electronic structure of the metal complex compared to the free-base chromophore.[442]

p-Benziporphyrin derivatives, such as naphthiporphyrin and anthriporphyrin **118**, have also been synthesized along [3 + 1]-pathways and exhibiting parallels in their structure and metalation characteristics (Scheme 43), while exhibiting the expected changes in their electronic properties that come with the presence of expanded π-systems.[252−444]

Using a fluorene building block fused into a heteroporphyrinic macrocycle, the antiaromatic *meso*-fused heterobenziporphyrins **120** were synthesized (Scheme 44).[151] Their formation followed [3 + 1] routes involving a fluorene-analogue to a tripyrrane with a heterocyclic diol. The antiaromaticity decreases in sequence from the thiophene-based system to the selenophene-based system to the tellurophene-based system. All macrocycles form stable palladium(II) complexes **120^{S}Pd**, **120^{Se}Pd**, and **120TePd**.

2.4.7. N-Confused Pyriporphyrin. An interesting twist on the pyriporphyrins is presented by the N-confused derivative **123** (Scheme 45). Here, the pyridine moiety is oriented such that the pyridine nitrogen is located on either one of the peripheral positions, and conversely, a pyridine carbon is pointed inward. The macrocycle is synthesized along a classic [3 + 1] route. In its neutral state, it is non-macrocycle-aromatic, but in a remarkable reaction, when protonated, it shows macrocycle aromaticity. Likewise, its palladium(II) complex **123Pd** is nonaromatic but can be monoprotonated with TFA on the external nitrogen to give an aromatic monocation.

2.4.8. Tropiporphyrin Metal Complexes. Tropiporphyrins are PMPs in which a pyrrole of a porphyrin has been replaced by a 7-membered carbacycle and are the only isolated PMPs containing 7-membered rings. They were synthesized along [3 + 1] total synthesis routes typical for many carbaporphyrins (see,

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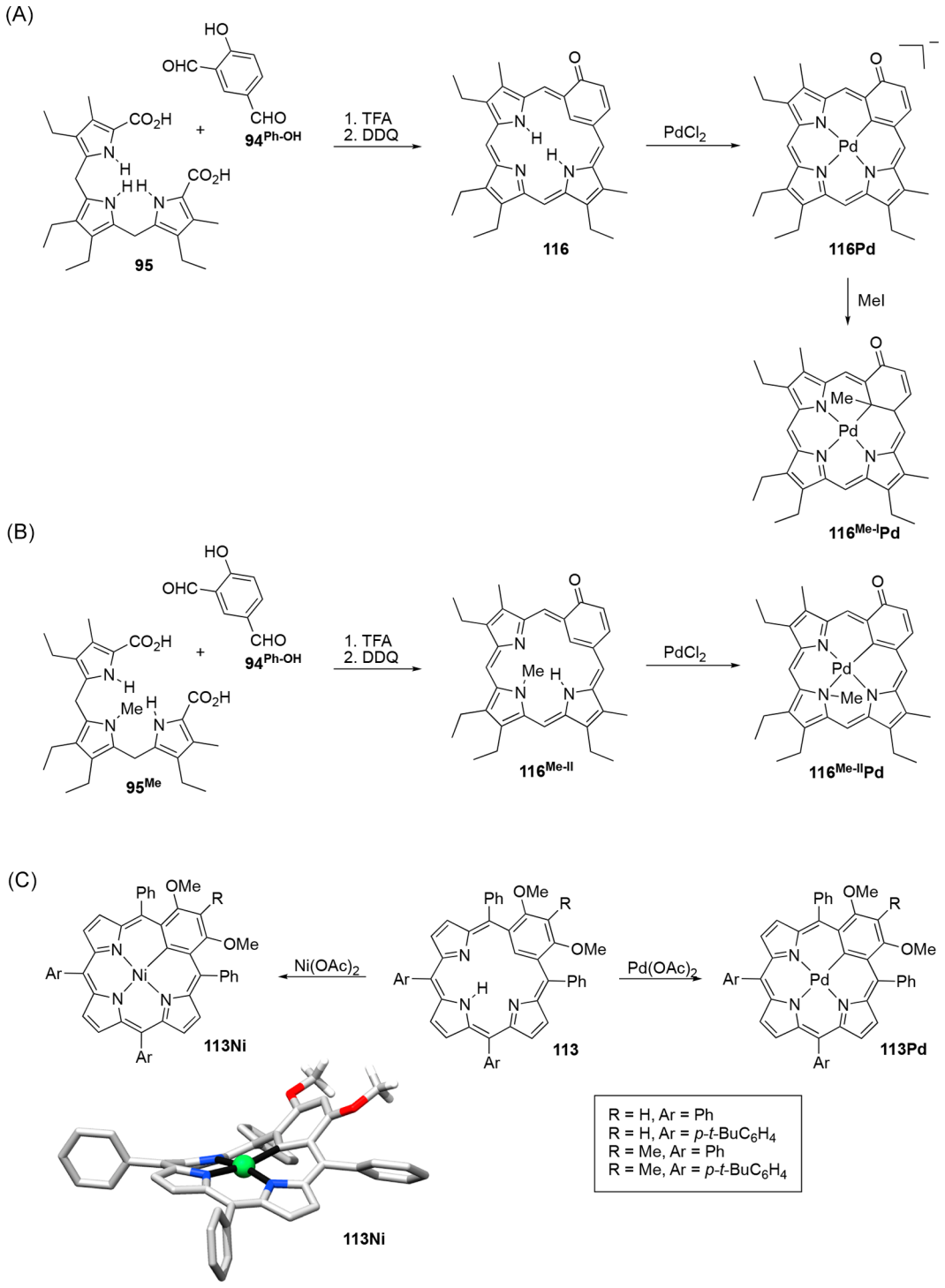
Scheme 41. Examples of Metallo-oxy- and Dimethoxybenziporphyrins[a]



[a]Stick representation of the X-ray structure of **113Ni** adapted with permission from ref 436. Copyright 2007 American Chemical Society.

e.g., Scheme 28 or 37).[445] The optical properties of tropiporphyrins are considerably different from those of other aromatic carbaporphyrins and are characterized by very broad and red-shifted Q-bands.[445]

The coordination chemistry of the tropiporphyrins is also not fundamentally different from that of any typical carbaporphyrin (cf., e.g., Scheme 32 or 40). The structure of the silver(III) complex **124Ag** (Scheme 46) shows that the fully conjugated 7-membered ring is too large to adopt a planar conformation within the steric constraints imposed by the porphyrinic macrocycle. As a result of the resulting strain, the macrocycle assumes a slightly twisted conformation.[380] Nonetheless, the N_3C donor set of this carbaporphyrin coordinates to the silver(III) ion in a square-planar fashion. This is also the case for the palladium(II) complex of tropiporphyrin **124**.[446]

A reaction of tropiporphyrin **124** with palladium(II) acetate led to ring-contraction of its 7-membered ring to form two benziporphyrin palladium(II) complexes, one of which carries a

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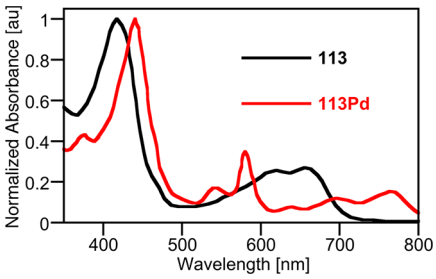


Figure 16. Normalized UV−vis spectra of free-base dimethoxybenziporphyrin **113** (1% $Et_3N/CHCl_3$) and its palladium(II) complex **113Pd** ($CHCl_3$). Spectrum of **113** adapted with permission from ref 436. Copyright 2007 American Chemical Society. Spectrum of **113Pd** adapted with permission from ref 439. Copyright 2014 American Chemical Society.

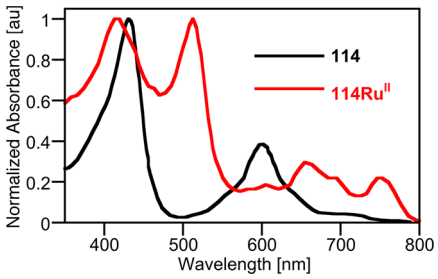


Figure 17. Normalized UV−vis spectra (CH_2Cl_2) of *p*-benziporphyrin **114** and its Ru(II) complex **114Ru^{II}**. Spectra adapted with permission from ref 442. Copyright 2017 American Chemical Society.

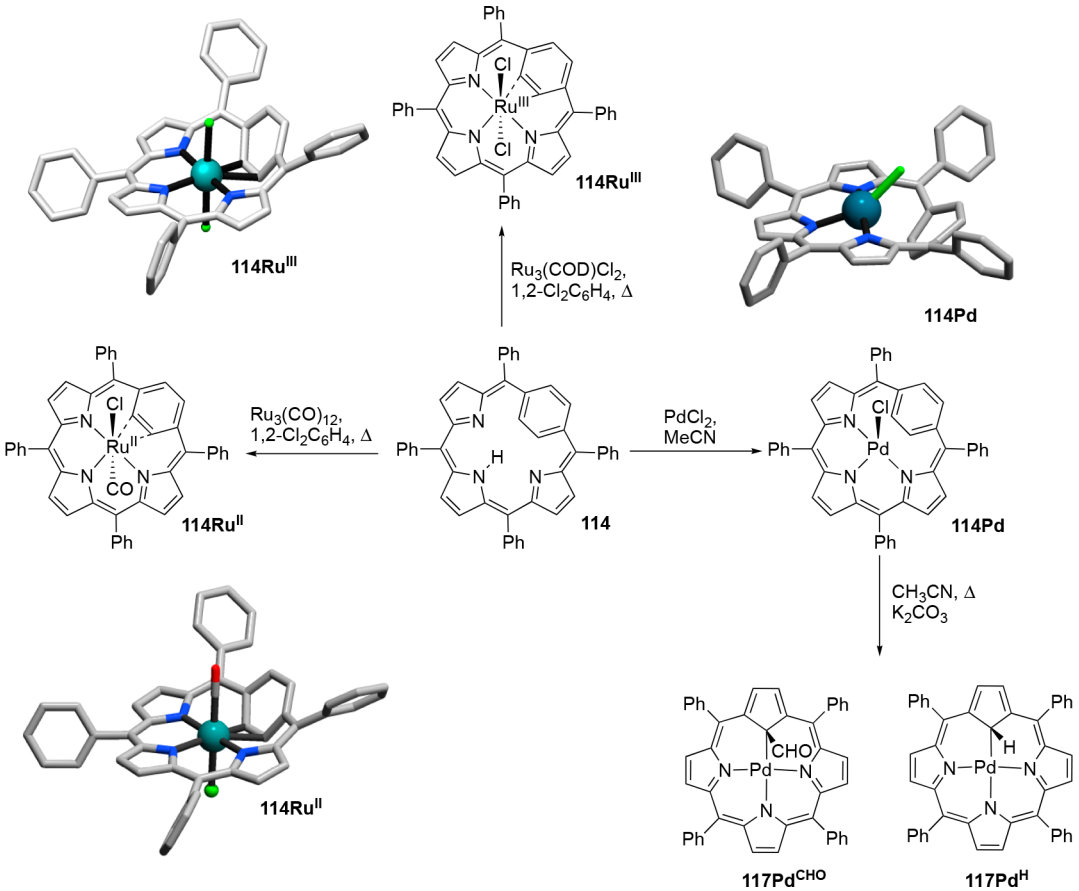
formyl substituent.[447] Tropiporphyrin reacted with excess methyl iodide and base to form the internally *N*-methylated derivative (regioselectively at the 24-position). In an interesting twist, a reaction of the *N*-methyl derivative with palladium(II) acetate afforded a palladium complex that retained the *N*-methyl substituent (cf. also the chemistry of the oxybenziporphyrin palladium(II) complex, Scheme 41).[447]

Compared to other aromatic carbaporphyrinoids, however, the UV−vis spectrum of tropiporphyrins (Figure 18) shows a more broadened and weakened Soret band with broad, indistinct Q-bands. On the other hand, the silver(III) tropiporphyrin **124Ag** demonstrated two broad Soret bands and three additional and well-defined absorption bands throughout the visible region.[445]

2.5. Metalloporphyrinoids with N_2C_2-Coordination Spheres

Examples of the metal complexes of the PMPs containing a N_2C_2-donor set are direct extensions of the metallocarbaporphyrins, except that two N-confused pyrroles, azulenes, etc., building blocks are incorporated. These PMPs are generally synthesized via [2 + 2]-type total synthesis approaches. Many of the traits of the monocarbaporphyrins, like the ability to stabilize higher-oxidation-state complexes (such as silver(III) complexes),[448] are retained.

Scheme 42. Syntheses of Metallo-1,4-benziporphyrins[a]



[a]Stick representations of the X-ray structures of **114Pd** adapted with permission from ref 440. Copyright 2011 American Chemical Society. Stick representations of the X-ray structures of **114Ru^{II}** and **114Ru^{III}** adapted with permission from ref 442. Copyright 2017 Wiley-VCH.

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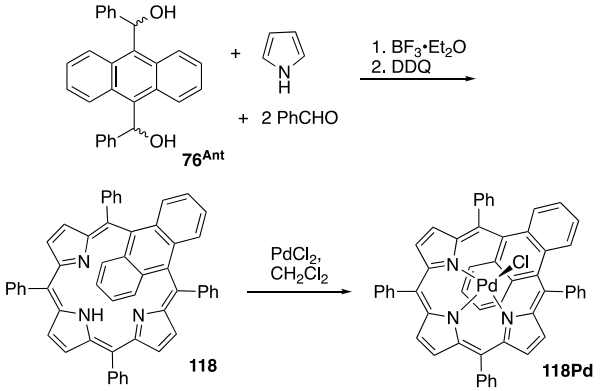
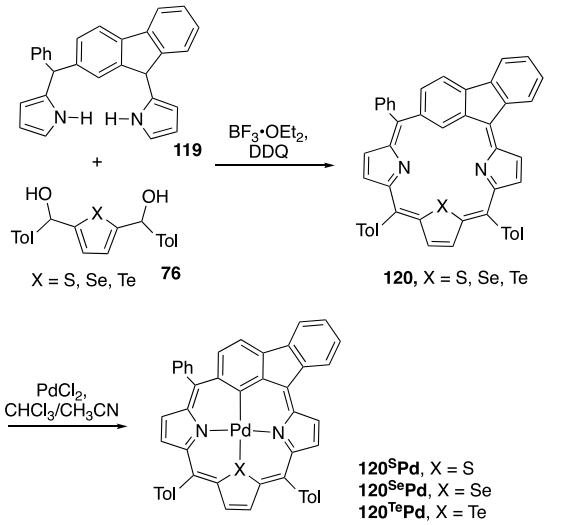
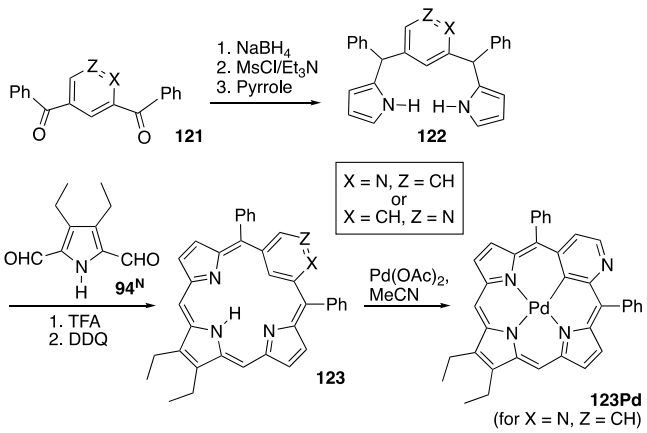
Scheme 43. Total Synthesis of Metalloanthriporphyrin 118Pd



Scheme 44. Synthesis of Antiaromatic Heterobenziporphyrins and Their Palladium Complexes[151]

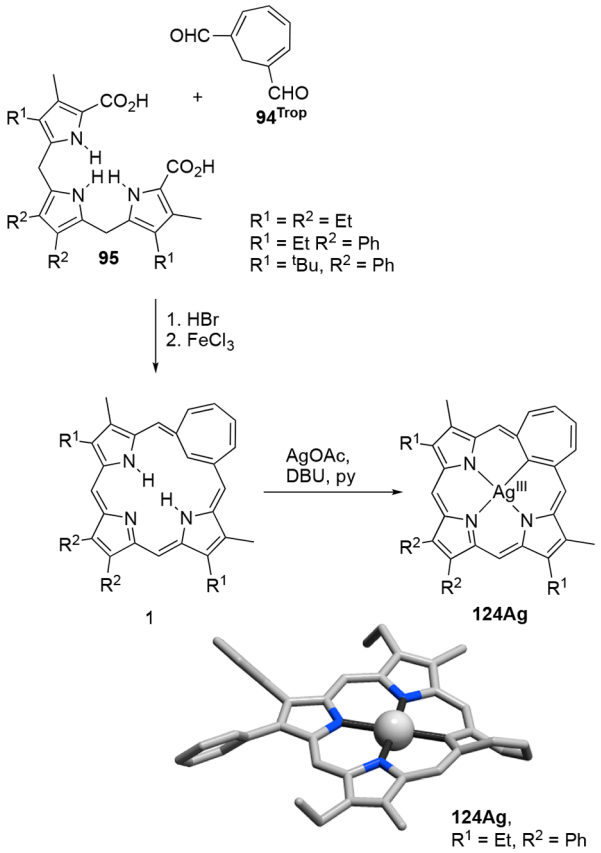


Scheme 45. Synthesis of N-Confused Pyriporphyrins and One of Its Palladium Complexes[151]



2.5.1. Di-N-Confused Porphyrin Metal Complexes. The structure, stability, and aromaticity of multiply N-confused porphyrins were discussed.[449] Five regioisomers of the doubly N-confused porphyrins (N_2CPs) theoretically exist, but only two isomers have been realized to date; they are labeled as the *adj*- and *opp*-isomers, indicating the relative position of the two

Scheme 46. [3 + 1] Synthesis and Metalation of Tropiporphyrin[a]



[a]Stick representation of the X-ray structure of **124Ag** adapted with permission from ref 380. Copyright 2004 American Chemical Society.

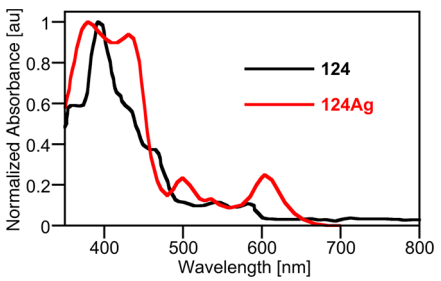


Figure 18. Normalized UV−vis spectra of free-base tropiporphyrin **124** (1% $Et_3N/CHCl_3$) and its Ag(III) complex **124Ag** ($CHCl_3$). Spectra adapted with permission from ref 445. Copyright 2004 American Chemical Society.

peripheral nitrogen atoms on adjacent or opposite pyrrolic building blocks (the *cis/trans*-nomenclature used in the original literature for these regioisomers has been replaced with the *adj/opp* terms throughout this Review).[450] Both examples of N_2CPs were prepared along [2 + 2] strategies generating ligands with either an NCNC or an NNCC coordination sphere (Scheme 47A,B).[449,450] The macrocycles are sensitive toward oxidation and are thus readily derivatized at the peripheral *β*-carbon, during either synthesis or the metal insertion step.

In their metal complexes, the *adj*-N_2CPs act as square-planar, trianionic N_2C_2 ligands, capable of stabilizing higher central metal oxidation states, such as silver(III) and copper(III) (Scheme 47A).[449,450] When metalating *opp*-doubly N-Confused

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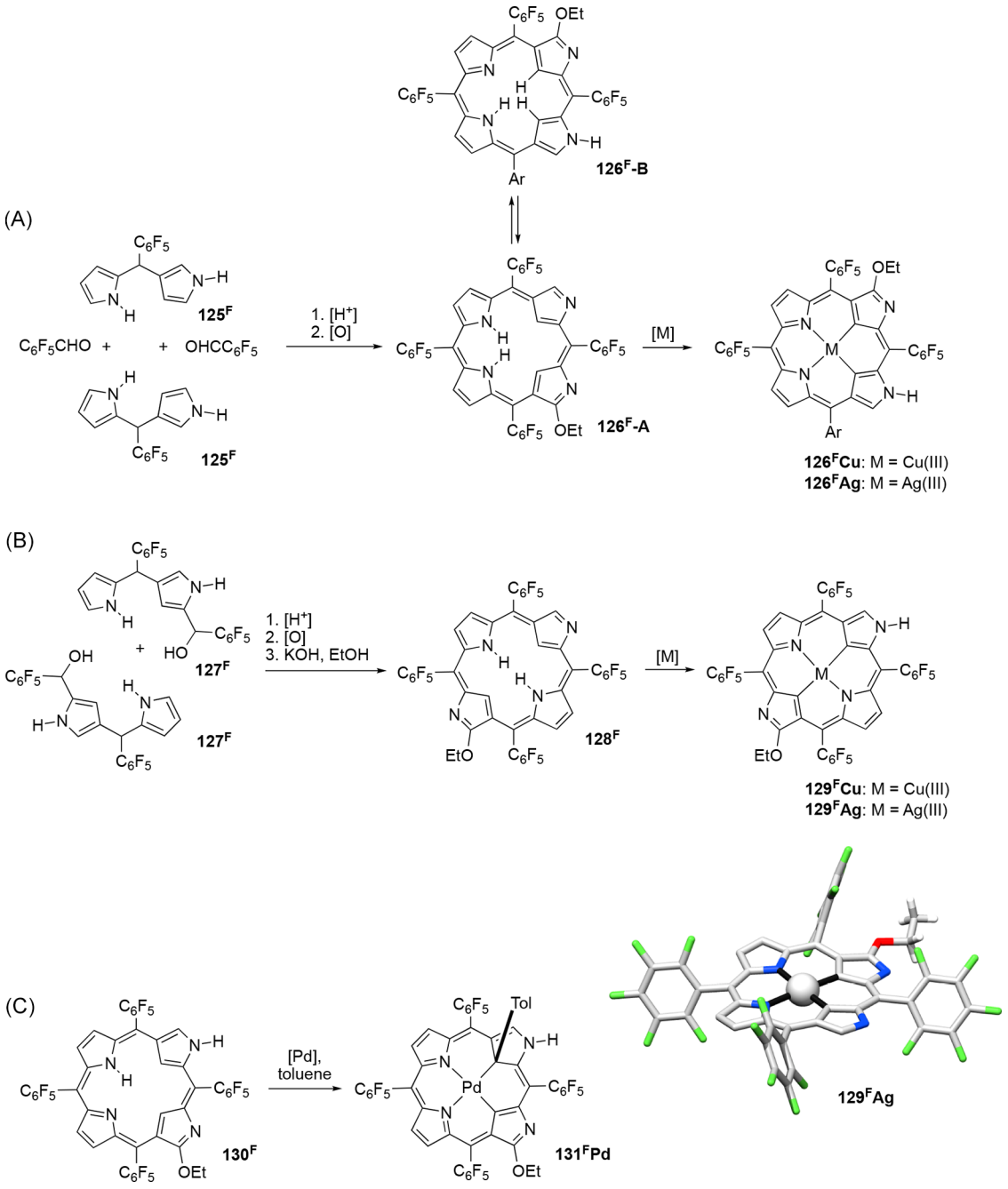
Scheme 47. [2 + 2]-Syntheses and Metalation of Bis-N-Confused Porphyrins[a]



[a]Stick representation of the X-ray structure of **129^{F}Ag** adapted with permission from ref 384. Copyright 2003 American Chemical Society.

128, it similarly serves as a trianionic ligand (Scheme 47B).[383] N_2CPs also express rodlike hydrogen-bonding networks in their crystals that cannot be formed in monofunctionalized PMPs.[365,383] The conformations of the copper(III) complexes **126^{F}Cu** and **128Cu** are both idealized planar.[365,449] Palladium(II) insertion also activates one of the two inner carbons toward a C−C bond formation with the solvent as the conversion of **130^F** to **131^{F}Pd** illustrates (Scheme 47C).[449−451]

The spectro-electrochemical and acid−base properties of N_2CPs and the photochemistry of their copper(III), silver(III), and gold(III) complexes were studied.[452−455] The X-ray crystal structures of the complexes revealed highly planar core geometries along with the presence of peripheral amine and imine nitrogen sites; the central metal affects the amphiprotic character of the complexes.[455] Their syntheses, application as photosensitizers (for the *adj*-isomers)[456] and as anion binders (binding to the peripheral nitrogen atoms),[59,357] and their metal coordination and supramolecular chemistry have been reviewed.[59−61,365]

The UV−vis spectra of the free-base N_2CPs regioisomers **126^F** and **128^F** are much different from each other and very much distorted from those of the porphyrinoid archetypes (Figure 19A,B; cf. Figure 4). They are also much different than those of other dimodified PMPs, such as the dilactones (cf. Figure 7). The corresponding complexes **126^{F}Ag** and **129^{F}Cu** are characterized by relatively sharp bands in their absorption

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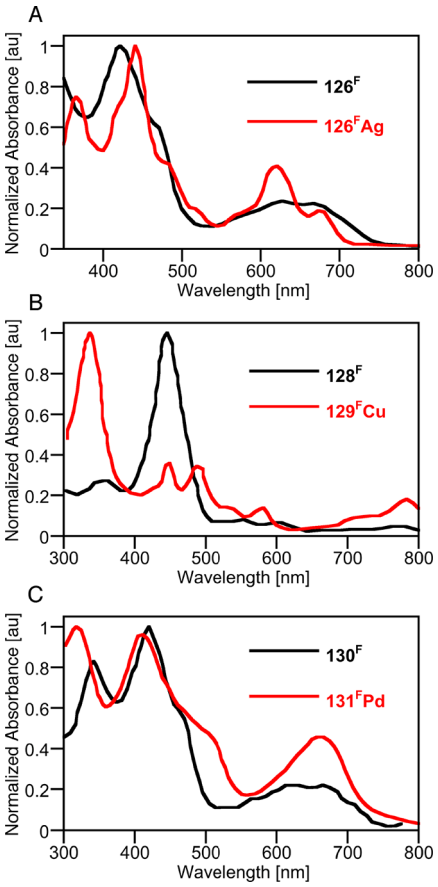


Figure 19. Normalized UV−vis spectra (CH_2Cl_2) of (A) **126^F** and **126^{F}Ag**, (B) **128^F** and **129^{F}Cu**, and (C) **130^F** and **131^{F}Pd**. Spectra of **126^F** and **126^{F}Ag** adapted with permission from ref 383. Copyright 2003 American Chemical Society. Spectra of **128^F**, **129^{F}Cu**, **130^F**, and **131^{F}Pd** adapted with permission from ref 449. Copyright 2000 American Chemical Society.

spectra when compared to their free-bases, whereby the change of the spectrum upon insertion of copper is particularly drastic. The spectra of the *adj*- and *opp*-isomeric copper complexes **126^{F}Cu** (not shown) and **129^{F}Cu** are distinctly different from each other. The spectra of free-base **130** and **131Pd** (Figure 19C) also show distinct solvatochromic behavior, attributed to interactions of the solvent with the peripheral NH-proton.[449]

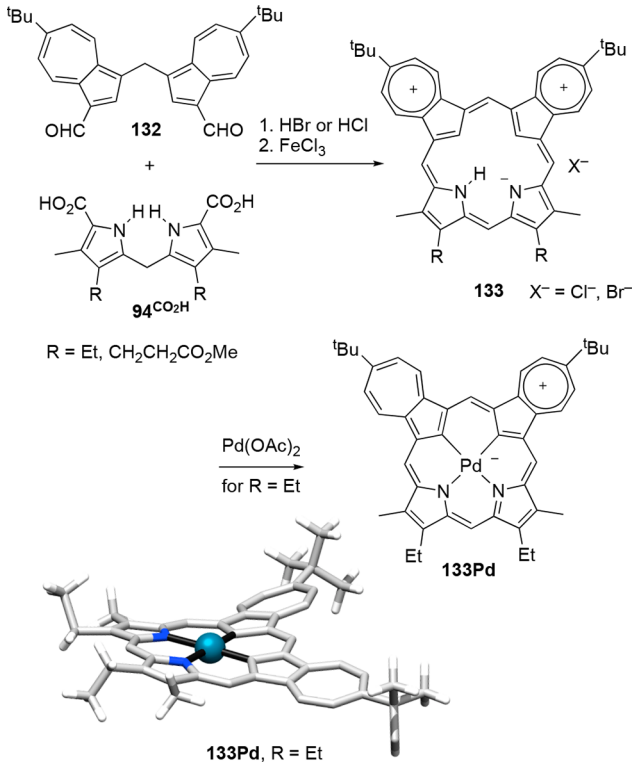
2.5.2. Diazuliporphyrin Palladium Complex. The incorporation of two azulene moieties into a porphyrin-like macrocycle using a [2 + 2] approach generated diazuliporphyrin **133** (Scheme 48). Its palladium(II) complex **133Pd** formed smoothly, and its crystal structure showed the existence of two Pd−C bonds. The loss of a third central hydrogen (from a pyrrolic moiety) and the absence of a counterion in the crystal allowed the formulation of **133Pd** as a non-macrocycle-aromatic but fully conjugated *meso*-ionic palladium(II) complex.[448]

The UV−vis spectra of free-base diazuliporphyrin **133** (in basic conditions) as well as its palladium(II) complex reflect the nonaromatic nature of the macrocycles, with broad bands and small Soret band to Q-band ratios but with absorbances at particularly long wavelengths (Figure 20).[448]

2.5.3. Bisindenyl-Based *adj*-Dicarbaporphyrin Complexes. In this class of dicarbaporphyrinoids, two adjacent pyrroles have been replaced by two indene moieties. Lash and co-workers prepared the aromatic macrocycle **135** via a base-catalyzed [2 + 2] condensation reaction between bis(3-indenyl)methane **134** and a dipyrromethane dialdehyde (Scheme 49). The tautomers of the free-base carbaporphyrins were discussed.[457]

In a metalation reaction of **135** with rhodium(I), the dicarbaporphyrin tautomerizes, and one of the pyrrolic NH protons migrates to the inner indene carbon atom; the other pyrrole NH proton is lost, resulting in a monoanionic ligand that coordinates in a bidentate, out-of-central-cavity fashion to the rhodium(I) fragment $Rh(CO)_2$.[458] Thus, the dicarbaporphyrin ligand in **135Rh** acts not fundamentally different from other PMP macrocycles and even octaethylporphyrin,[459,460] though many porphyrins tend to stabilize rhodium(III) ions in an in-plane coordination mode.[460] Metalation of *adj*-dicarbaporphyrin **135** with palladium(II) resulted in the formation of an unusual tripalladium sandwich complex:[461] Each of the two tetraanionic dicarbaporphyrin units (both NH and inner CH

Scheme 48. [2 + 2]-Synthesis and Metalation of Bisazuliporphyrin[a]



[a]Stick representation of the X-ray structure of **133Pd** adapted with permission from ref 448. Copyright 2009 American Chemical Society.

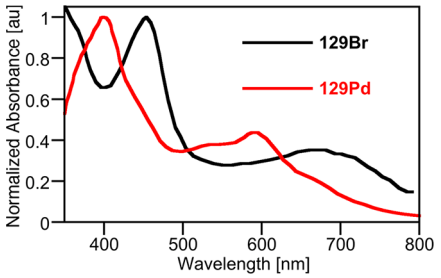


Figure 20. Normalized UV−vis spectra of free-base bisazuliporphyrin **133** (X^- = Br^-) (1% DBU/$CHCl_3$) and its Pd(II) complex **133Pd** ($CHCl_3$). Spectra adapted with permission from ref 448. Copyright 2009 American Chemical Society.

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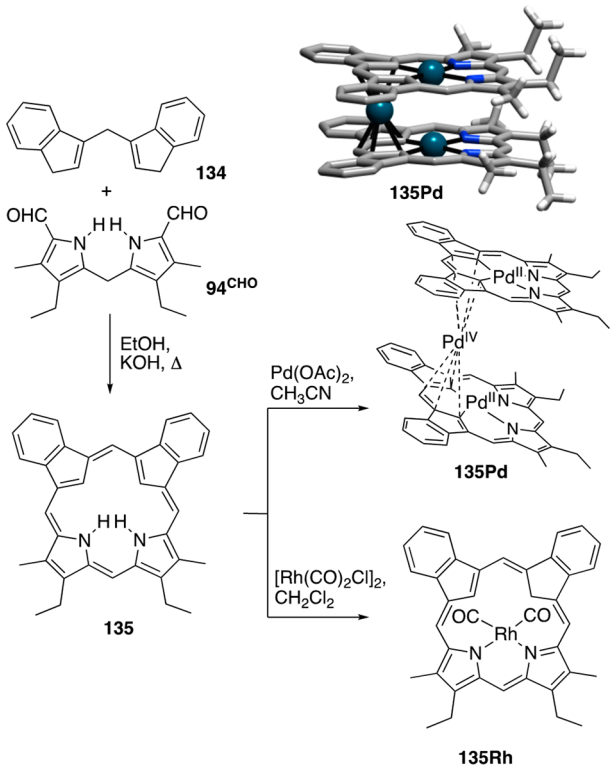
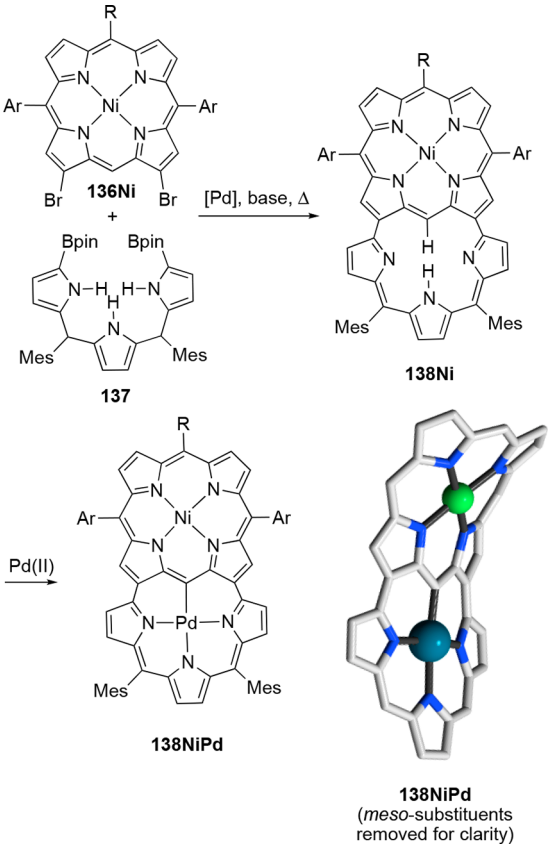
Scheme 49. [2 + 2]-Synthesis and Metalation of Bisdicarbaporphyrin 135[458,461a]



[a]Stick representation of the X-ray structure of **135Pd** adapted with permission from ref 461. Copyright 2014 American Chemical Society.

Scheme 50. Synthesis and Metalation of Earring Porphyrin 138Ni[a]



[a]Stick representation of the X-ray structure of **138NiPd** adapted with permission from ref 462. Copyright 2016 Wiley-VCH.

protons are lost) coordinate the palladium(II) ions as square-planar N_2C_2 donors. The resulting two dianionic metal complexes then form a metallocene-like sandwich, coordinating to a palladium(IV) ion in an η^5-fashion also involving the *meso*-carbon atoms of each macrocycle. Thus, the overall neutral homotrimetallic, mixed oxidation state complex **135Pd** is formed.[461]

2.5.4. Earring Porphyrin Metal Complexes. Earring porphyrins, such as **138Ni** and **138NiPd**, are carbaporphyrin-type PMPs in the sense that one pyrrole of a regular nickel porphyrin has been replaced by an entire porphyrin (Scheme 50). Their [3 + 1]-type synthesis utilized a Suzuki–Miyaura coupling between a functionalized tripyrrane **137** and a suitably derivatized porphyrin **136Ni**. The *meso*-carbon of this annulated porphyrin serves as the carbon atom donor atom of the N_3C donor set of the "ear". Next to the nickel(II) ion in the regular porphyrin portion of the molecule, a second metal ion can be accommodated in the N_3C coordination environment of the carbaporphyrin-type "ear". A subporphyrin variety and heterole-fused earring porphyrins have also become known.[462,463]

The X-ray structure of **138NiPd** shows the assembly to be a smoothly curved plane, whereby the porphyrin half is more displaced from planarity than the Pd-ear. Since the structure of "free-base" ligand **138Ni** is also known,[462] it could be shown that the insertion of Pd(II) caused an increased curvature of the assembly **138NiPd**.

The π-systems of both chromophores are tightly coupled, but the aromatic pathways of these PMPs do not extend over the whole molecule. Instead, the two regions possess distinct aromatic (nickel porphyrin) or antiaromatic (ear) π-systems.[462]

The character of the metalloporphyrin-like absorption spectrum of **138Ni** is not principally changed but red-shifted upon insertion of the second metal ion, palladium(II) (Figure 21). Arising from an effective π-conjugation upon palladium(II) insertion, a weak NIR Q-band of earring **138Ni** extends to 1500 nm in **138NiPd**.[462]

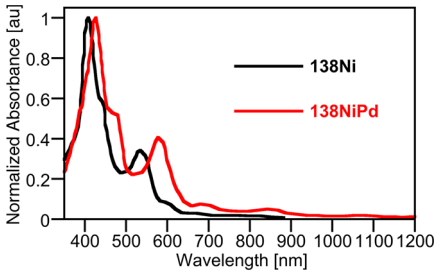


Figure 21. Normalized UV–vis spectra (CH_2Cl_2) of monometallic earring porphyrin **138Ni** and its heterobimetallic complex **138NiPd**. Spectra adapted with permission from ref 462. Copyright 2016 Wiley-VCH.

2.5.5. Phenanthriporphyrin Metal Complexes. Phenanthriporphyrinoids are antiaromatic hybrid macrocycles where a dipyrrin subunit of a regular porphyrin has been replaced with a phenacene moiety (Scheme 51).[163,464] The presence of the N_2C_2 coordination sphere and two adjacent inner carbon atoms classifies phenanthriporphyrin **140** as a *syn*-dicarbaporphyr-

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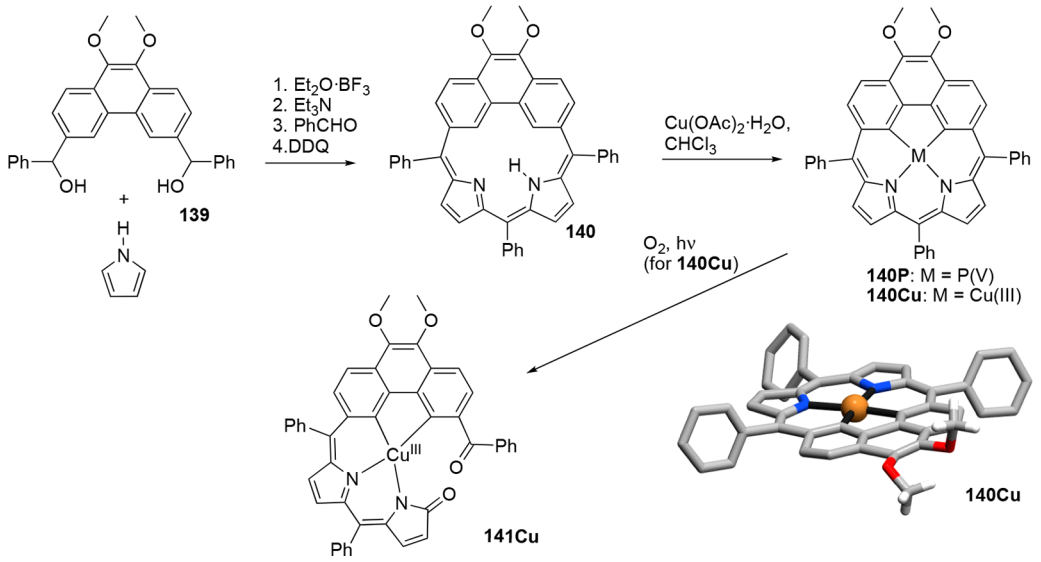
Scheme 51. Synthesis, Metalation, and Oxidative Ring-Opening of Metallophenanthriporphyrin[a]



[a]Stick representation of the X-ray structure of **140Cu** adapted with permission from ref 464. Copyright 2015 Wiley-VCH.

inoid. Made by the condensation of pyrrole, aldehyde, and a phenanthrene precursor, it is suitable to accommodate copper(III) and phosphorus(V) ions. The methoxy groups on the phenanthrene moiety can be converted to oxo-functionalities, switching the nonaromatic macrocycle in a proton-dependent process to become aromatic.[163] The copper(III) complex **140Cu** is sensitive toward light and oxygen. Upon exposure, it oxidatively and regioselectively cleaved at the *meso*-position adjacent to the phenanthrene unit, resulting in the formation of acyclic helical organometallic copper(III) phenanthribilinone complex **140Cu**.[465] This molecule is a pyrrole-modified analogue of the naturally occurring porphyrin degradation products, the biliverdins.

Reflecting their antiaromaticity, the electronic spectra of **140**, **140P**, and **140Cu** are similar to each other and primarily consist of a narrow Soret-like band at a significantly shorter wavelength than a typical porphyrin and very weak and broad absorption bands that extend up to 1000 nm (Figure 22).[464,466]

2.6. Metalloporphyrinoids with NCNX-Coordination Spheres (X = O, S, Se)

Heterocarbaporphyrins possessing NCNX-coordination spheres (X = O, S, Se, Te) combine the features of the trianionic carbaporphyrins with those of the monoanionic chalcogen-based heteroporphyrins and may act as dianionic ligands (examples shown in Scheme 52). Derivatives featuring, for instance, isomeric CONN or tris-modified CNTeO cores have also become known.[65] Synthesized along classic [3 + 1]-type pathways using a heterotripyrrane and a carba-building block,[467,468] the *β*-alkyl-[467,468] as well as the *meso*-aryl-derivatives[427,469] were reported. These compounds are the heteroanalogues of, for example, benziporphyrins (cf. Section 2.4.6),[468,470] oxybenziporphyrins (cf. Section 2.4.6),[468] oxypyriporphyrins (cf. Section 2.2.10),[468] or azuliporphyrins (cf. Section 2.4.2),[471] etc. These oxa- and thia-based ligands form neutral, organometallic complexes with the divalent metal ions nickel(II) and palladium(II).[427,467,468,470,472]

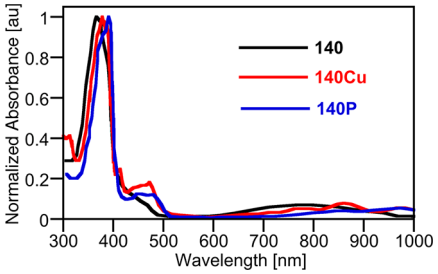


Figure 22. Normalized UV−vis spectra (CH_2Cl_2) of free-base phenanthriporphyrin **136** and its Cu(II) and P(V) complexes **136Cu** and **136P**. Spectra of **140** and **140P** adapted with permission from ref 464. Copyright 2015 Wiley-VCH. Spectrum of **140Cu** adapted with permission from ref 465. Copyright 2019 American Chemical Society.

2.7. Metal Complexes of Selected Expanded Porphyrins

While the classic expanded porphyrins (porphyrins containing more than four pyrroles) could also be defined as PMPs—one pyrrole in a porphyrin has been replaced by a dipyrrin, bipyrrole, tripyrrin, etc.—they do not contain nonpyrrolic building blocks. We do not consider the classic all-pyrrole expanded porphyrins here. Many expanded porphyrins also include thiophene or furan building blocks; they have also become known as core-modified expanded porphyrins.[15] Even though they fit our definition of PMPs and some form metal complexes, we omitted them here for brevity; they have been well-reviewed.[15,31,188,473]

Nonetheless, we highlight here select expanded PMP metal complexes that are noteworthy for their structures, rich coordination chemistry, or close relationship to traditional PMPs.

2.7.1. Texaphyrin Metal Complexes. The Schiff-base oligopyrrolic macrocycle texaphyrin **146** is an expanded pyrrole-modified-porphyrin in which an *o*-phenylene-diamine moiety formally replaced one pyrrole ring (Scheme 53). It is among the oldest, most versatile, and best investigated PMPs.[76,77,192,474] Texaphyrins are synthesized along [3 + 1]-type pathways. This nonaromatic macrocycle offers a N_5-donor set in an idealized planar geometry and is characterized by rich coordination chemistry, including the ability to coordinate to transition metals and notably the larger f-metal ions.[78,475] The texaphyrin ligand containing sp^3-hybridized *meso*-carbons undergoes

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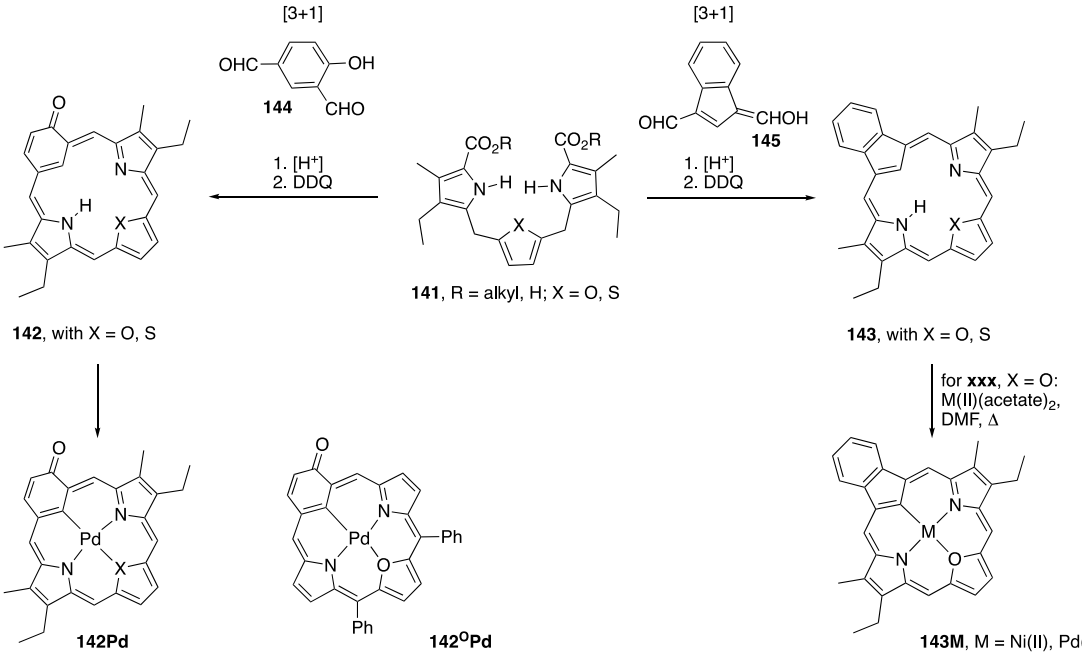
Scheme Synthesis and Metalation of Heterocarbaporphyrins



oxidation to the fully conjugated form upon complexation with a number of metal cations.[78] The coordination chemistry of this expanded macrocycle is in some cases reminiscent of that of a porphyrin. For example, insertion of iron afforded the formation of a μ-oxo dimer **146Fe**.[78] The molecule can spin about the iron−oxygen bond to allow for a number of different relative orientations of the ligands with respect to each other. μ-Oxo dimers, such as **146Fe**, are well-known products formed by iron porphyrins.[87] Iron(II) porphyrins are being readily oxidized to the corresponding iron(III)-oxo dimers upon exposure to air, a reaction with multiple biological implications for the hemes.[476]

However, differences are also noted. For instance, the corresponding manganese(II) and cobalt(II) complexes **146Mn** and **146Co** are stable in their +II oxidation states, whereas the +III oxidation states are stabilized in the corresponding porphyrin complexes. This is due to the increased cavity size and the decreased ligand charge; the six- or seven-coordinate geometries with low-charge donor atoms favor the stabilization of lower oxidation states.[78,475] Also, an acid-induced cleavage of the dimer **146Fe** to generate and isolate the corresponding monomeric iron(III) complexes is, for the acid-sensitivity and concomitant decomposition of the texaphyrin complex, not possible for **146Fe**,[78] though this reaction is commonly possible for regular porphyrin μ-oxo dimers.[476]

The zinc(II) complex **146Zn** was the first example of texaphyrin acting as a tridentate ligand. Its crystal structure indicates that the zinc(II) cation coordinates with the tripyrrane subunit.[475] In the lanthanide complexes of texaphyrins, the central metal sits above the plane of the ligand and coordinates to all five nitrogen atoms (plus additional ligands).[477]

The UV−vis spectra of free-base texaphyrin **146** and metallotexaphyrins **146Ni** and **146Fe** (or even the lanthanide complexes, not shown) are in contrast to those of the corresponding porphyrin complexes that are surprisingly similar to each other and are the ligand-derived two-band spectra typical of nonaromatic PMPs (Figure 23).[78,478]

Clinical studies of lutetium(III) and gadolinium(III) complexes of a water-soluble texaphyrin have shown their potential applications as photosensitizers and radiation enhancers for arteriosclerotic disease and cancer, respectively.[479] The manganese(II) texaphyrin complex **146Mn** was found to act as an *in vitro* catalyst for the decomposition of peroxynitrite,[480] a cytotoxic reactive oxygen species of relevance in diseases such as cancer, amyotrophic lateral sclerosis, or atherosclerosis.

2.7.2. Twin Porphyrin Metal Complexes. A number of expanded porphyrins are large enough to accommodate more than one metal ion in their cavity, whereby metal coordination frequently affects the often severely nonplanar conformation and electronic structure (aromaticity) of the chromophore.[183,475,481,482] A number of examples of pyrrole-modified expanded porphyrins were also prepared that retained this two-metal coordination ability.[183]

Twin porphyrin **148** is formally derived from the expanded porphyrin hexaphyrin by a replacement of two pyrrolic moieties at opposite positions by pyrazole moieties. However, both pyrazoles are in an inverted position, pointing their nitrogen atoms inward. The result is the formation of two porphyrin-like square-planar N_4-coordination sites that are linked through the pyrazole moieties.[483−486]

Twin porphyrin **148** was specifically designed to hold two metals in close proximity either to exploit metal−metal interactions or to interact/activate a small molecule (axial ligand) with two metal centers at once (Scheme 54).[483,484] The twin porphyrin framework was synthesized along a [3 + 3]-type condensation pathway.[483−485] A number of mono- (**148M^1**), and homo- (**148M$_2$**), and heterobimetallic (**148M^{1}M^2**) complexes were formed.[483−486] The near-invariant twisted conformations of the free-base and metalated compounds were structurally characterized.[483−486] Monometalation strongly affects the basicity and tautomeric state of the other, free-base half of the complex.[487] The strong electronic and magnetic interactions of the two metals in mono- and heterobimetallic complexes with each other and the non-innocence of the ligand were described.[90,483,484,486−488] The complexes have yet to demonstrate catalytic abilities.

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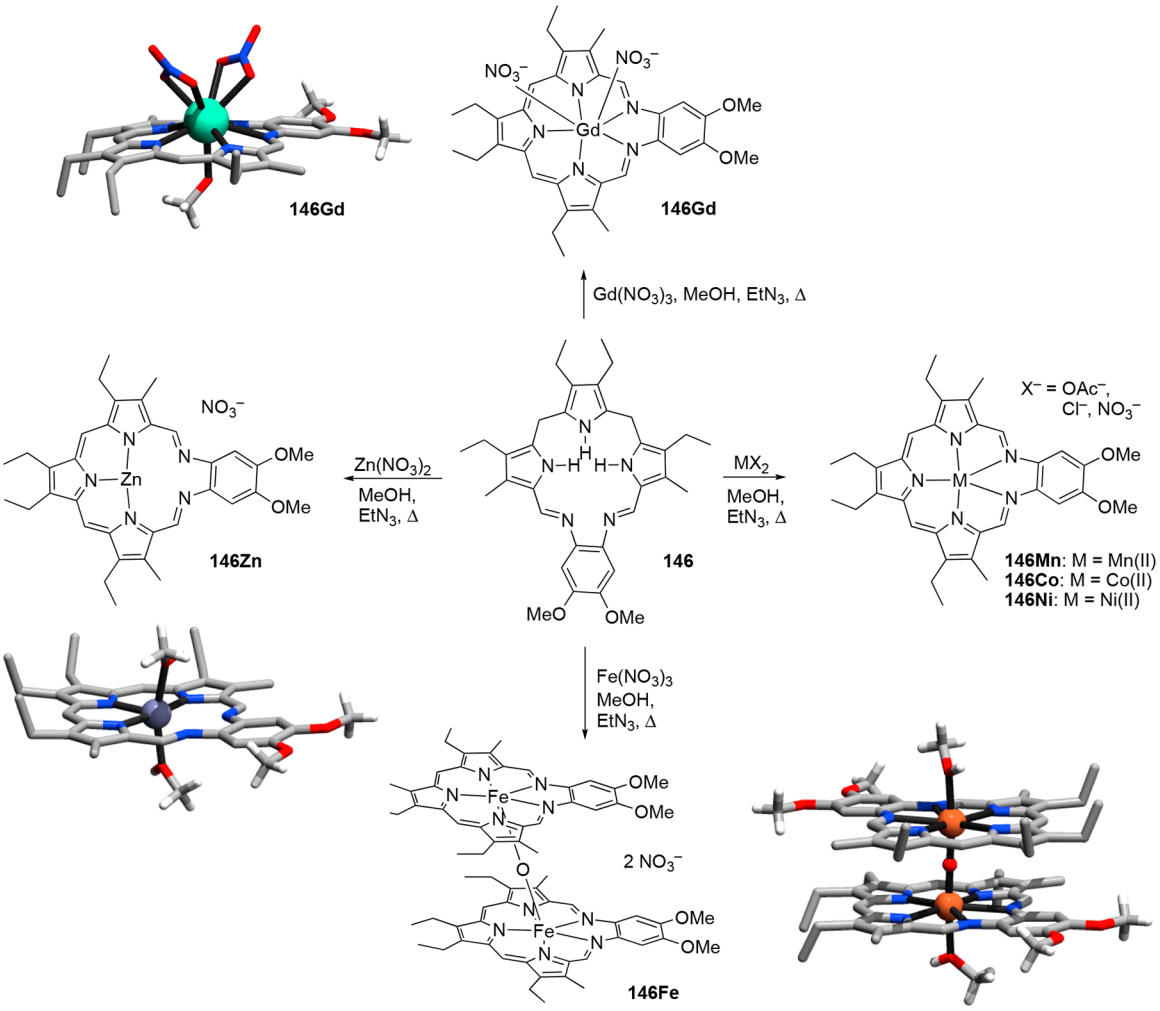
Scheme 53. Complexation of Texaphyrin 146[a]



[a]Stick representations of the X-ray structures of **146Zn·2MeOH** and **146Fe** adapted with permission from ref 78. Copyright 2002 American Chemical Society. Stick representation of the X-ray structure of **146Gd** adapted with permission from ref 477. Copyright 1993 American Chemical Society.

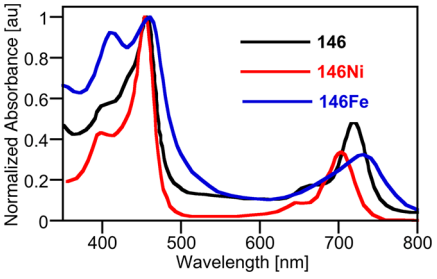


Figure 23. UV−vis spectra of texaphyrin **146** (CH_3CN) and its Ni(II) and Fe(III) complexes **146Ni** and **146Fe** (CH_3OH). Spectra of **146Ni** and **146Fe** adapted with permission from ref 78. Copyright 2002 American Chemical Society. Spectrum of **146** adapted with permission from ref 478. Copyright 2001 American Chemical Society.

The optical spectra of the free-base, mono- and bimetallic complexes are characterized by the presence of the broad bands characteristic for nonaromatic, conjugated oligopyrroles;[173] here, the bands are also much less dependent on, for example, metalation compared to regular porphyrins (Figure 24; cf. Figure 4).

2.7.3. Palladium Complexes of Phenylene- and Pyridylene-Based Octaphyrin Analogues. Octaphyrins (and heterooctaphyrins) are a class of expanded porphyrins composed of eight pyrroles and varying numbers of *meso*-carbon atoms linking them.[490−493] In the 1,3-phenylene- and 2,6-pyridylene-analogues of the octaphyrins **150** and **151**, two pyrroles in opposite positions of an octaphyrin were replaced by phenylene and pyridyl moieties, respectively (Scheme 55).

The syntheses of octaphyrin-analogues **150** and **151** can be described as Pd-catalyzed [3 + 5]-type condensations, followed by oxidation to the fully conjugated macrocycles.[494] Unlike nonplanar all-pyrrole-based octaphyrin (of figure-eight conformation), analogues **150**/**151** are idealized planar. The ligand can accommodate two palladium(II) ions that are each coordinated in a N_3C fashion (and to the same phenylene/pyridylene), causing this ligand to act like a dicarbaporphyrin. The bismetal complexes **150Pd$_2$**/**151Pd$_2$** are overall idealized planar with a slight overall bow.

The two-band UV−vis absorption spectra of free-base **150** (not shown) and **151** are similar and reflect their nonaromatic—but conjugated—nature (Figure 25).[494] Bispalladium insertion leads to a drastic broadening and red-shift of the spectra,

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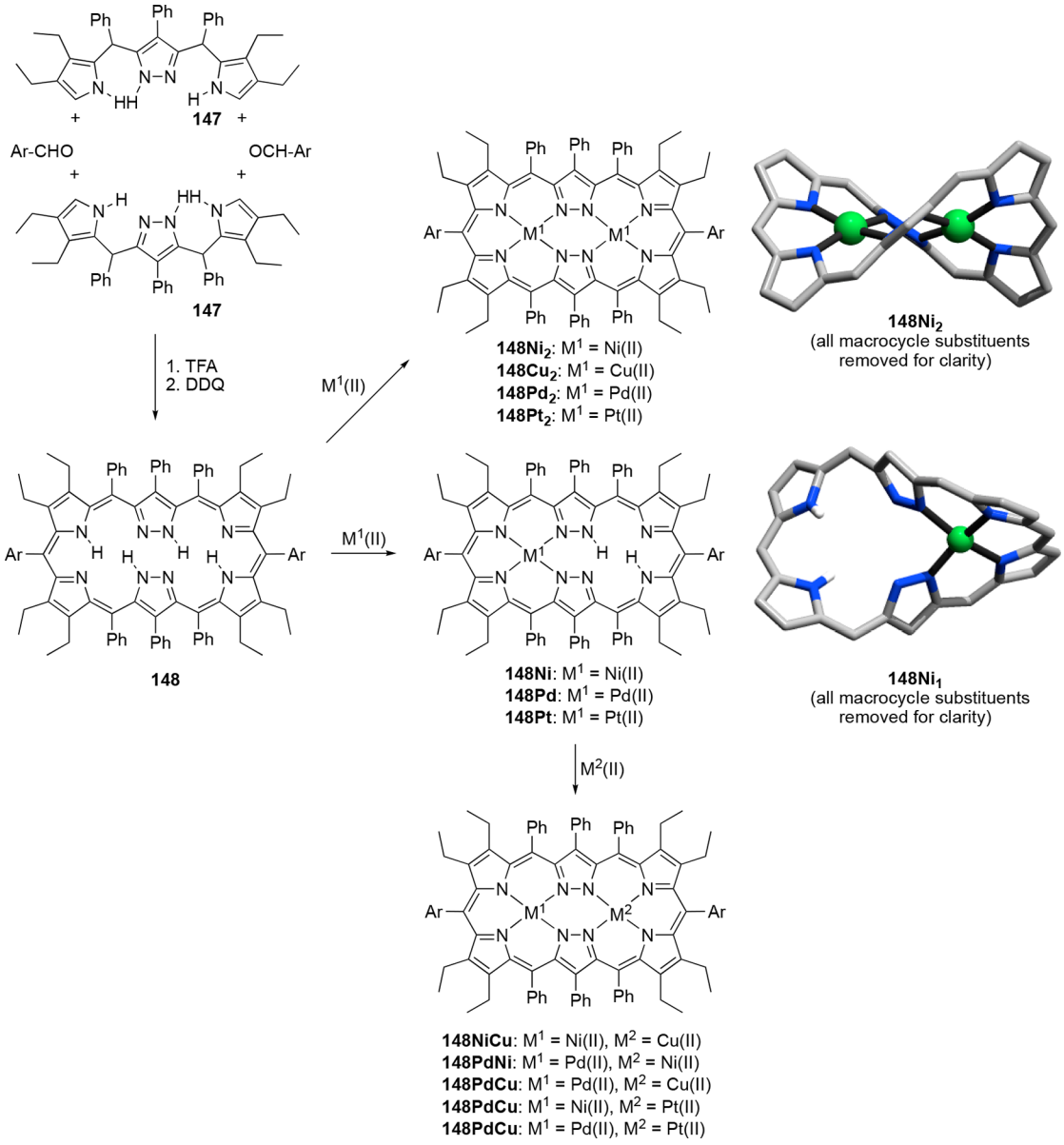
Scheme 54. [3 + 3]-Type Synthesis and Metalation Reactions of Twin-Porphyrin 148[a]



[a]Stick representations of the X-ray structures of **148Ni** and **148Ni$_2$** adapted with permission from ref 484. Copyright 2013 Wiley-VCH.

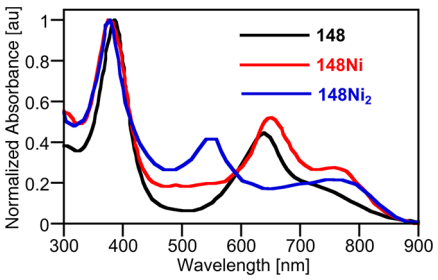


Figure 24. Normalized UV−vis spectra (CH_2Cl_2) of **148**, **148Ni**, and **148Ni$_2$**. Spectrum of **148** adapted with permission from ref 489. Copyright 2016 Wiley-VCH. Spectra of **148Ni** and **148Ni$_2$** adapted with permission from ref 486. Copyright 2020 American Chemical Society.

reflecting the tight interaction of the ligand π-system with the metal.[494]

2.7.4. Ruthenium Complex of a Bisterphenyl-Modified Decaphyrin Analogue. A decaphyrin is an expanded porphyrin-analogue composed of 10 pyrrolic moieties. Decaphyrin-analogue **153** is derived from a porphyrin by formally replacing each of two pyrrole rings with terphenylene units. It could also be seen as a decaphyrin PMP-analogue in which two groups of three adjacent pyrroles were replaced by six phenyl groups.

The bisterphenyl-modified decaphyrin-analogue **153** was synthesized by a [5 + 5] acid-catalyzed condensation of two terphenyl dipyrromethanes **152** linked through aryldehydes, followed by dehydrogenation (Scheme 56).[495] This non-aromatic macrocycle allows for the incorporation of two metal ions in two equivalent sites; its rhodium(I) complex was prepared. The X-ray crystal structure of **153Rh$_2$** demonstrate the (idealized) square-planar coordination of the metals by two carbonyl oxygen atoms and the N_2-chelates of the dipyrrin-like halves of the macrocycle. Complex **153Rh$_2$** retains the

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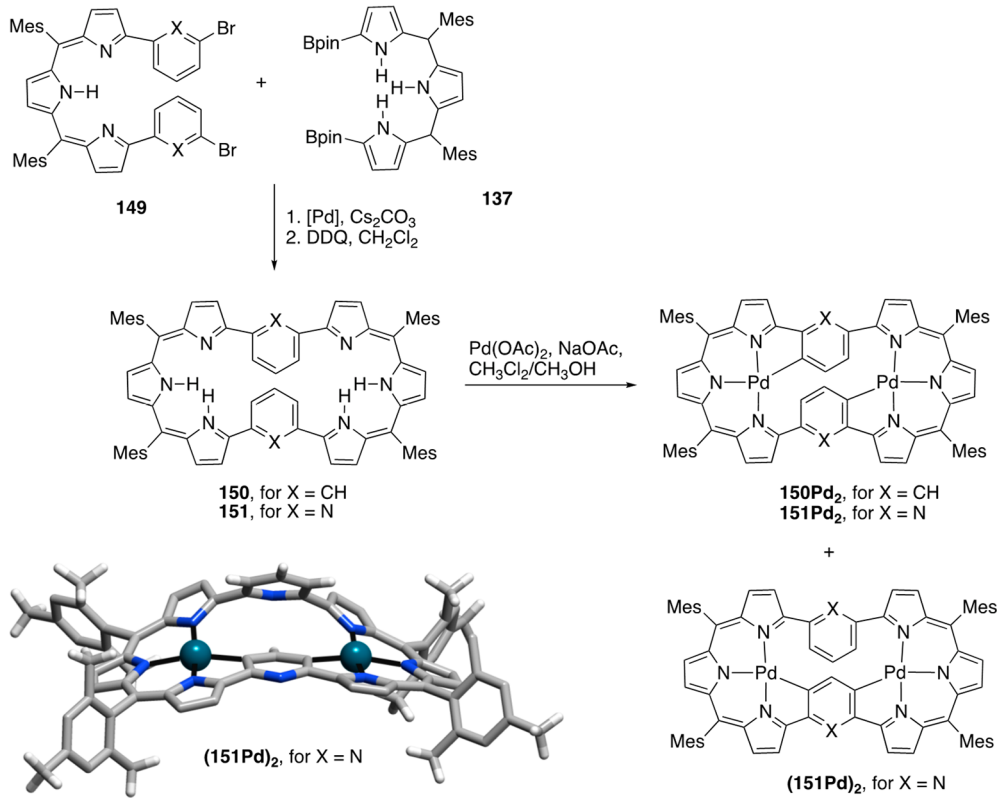
Scheme 55. Synthesis and Metalation of a Pyrrole-Modified Octaphyrin-Analogue[a]



[a]Stick representation of the X-ray structure of **151Pd$_2$** adapted with permission from ref 494. Copyright 2020 Nature-Springer.

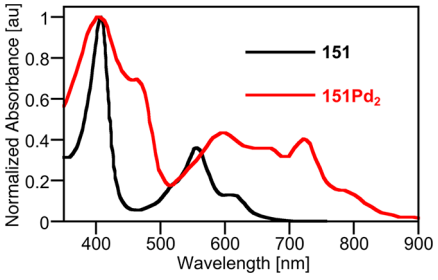


Figure 25. Normalized UV−vis spectra (CH_2Cl_2) of **151** and **151Pd$_2$**. Spectra adapted with permission from ref 494. Copyright 2020 Springer-Nature.

nonaromatic characteristics of its free-base macrocycle. As could be expected based on the coordination of the metal to the distant ends of the macrocycle, no strong electronic coupling of the two halves of the macrocycle is apparent.[495]

2.8. Metallocenoporphyrins

2.8.1. Metallocenoporphyrins and Metallocenoheteroporphyrins. One class of metalloporphyrinoids, metallocenoporphyrins, stands out in the context of the metal complexes of PMPs (and thiaporphyrins) in that a metal complex constitutes the nonpyrrolic moiety.[496−498] Synthesized along [3 + 1] pathways (Scheme 57), they provided the first insight into what extent the transmission of metallamacrocyclic π-electron conjugation can reach across the d-electrons of a metallocene (ferrocene or ruthenocene). Moreover, the hinge-like flexibility of the metallocene sandwich complex allows for a number of compound topologies that affect the porphyrinoid π-system. In contrast to the ferrocenophanes prepared previously, the metallocenoporphyrins possess spectroscopic features suggestive of macrocycle aromaticity. Protonation and redox events modulate the aromaticity of the system.[497]

2.8.2. N-Confused β,β-Fused Ferrocenoporphyrinoids. N-Confused β,β-fused ferrocenoporphyrinoids are weakly aromatic PMPs that combine the structural features of several PMP classes: They feature a 2,4-linked (and oxidized) N-confused pyrrolic moiety (cf. Section 2.4.1). A ferrocene moiety is incorporated in place of a pyrrole, characterizing them as metallocenoporphyrins (cf. Section 2.8.1), and they contain an inverted pyrrole that oxidatively formed a direct β,β-linkage between the N-confused and inverted pyrroles,[499] reminiscent of N-fused porphyrins.[58−62] They are synthesized along a [3 + 1] pathway (Scheme 58) that is similar to the synthesis of regular metallocenoporphyrins (Scheme 57), except a 2,4-modified and *N*-methylated pyrrole is fused into a the metallocene-tripyrrane-analogue, and the oxidative transformations take place concomitantly with the oxidation of the initially formed macrocycle to the final (aromatic) product. The external nitrogen atom of the inverted pyrrolic building block in **157Fe** can coordinate to the rhodium(I) tricarbonyl fragment; the inside of the macrocycle is likely too congested to be able to coordinate to any metal ion. The rigid but helical conformation of the weakly aromatic macrocycle rhodium complex was shown by single-crystal crystallography.[499]

3. RELEVANCE OF METALLO-PMPS

The relevance of metallo-PMPs is derived from fundamental and applied aspects. On the most fundamental level, the alteration of the porphyrin macrocycle and the observation of the resulting perturbation allow one to learn something about the importance

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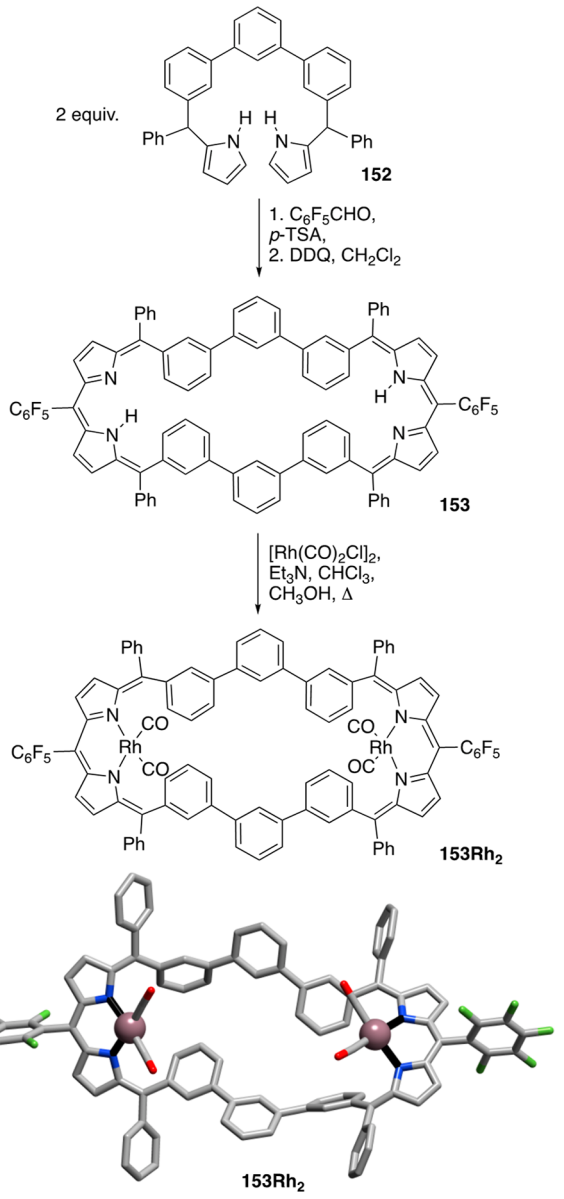
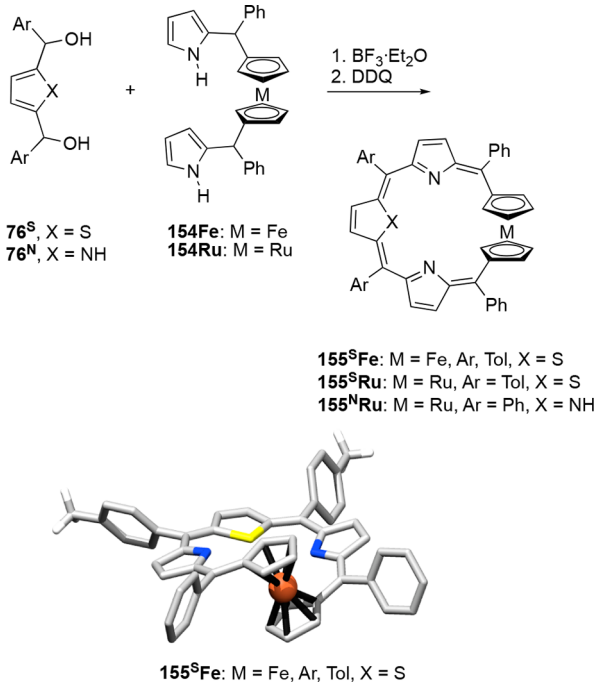
Scheme 56. Synthesis and Metalation of Bisterphenyl-Modified Decaphyrin-Analogue 153 and Its Bisrhodium Complex $153Rh_2$[a]



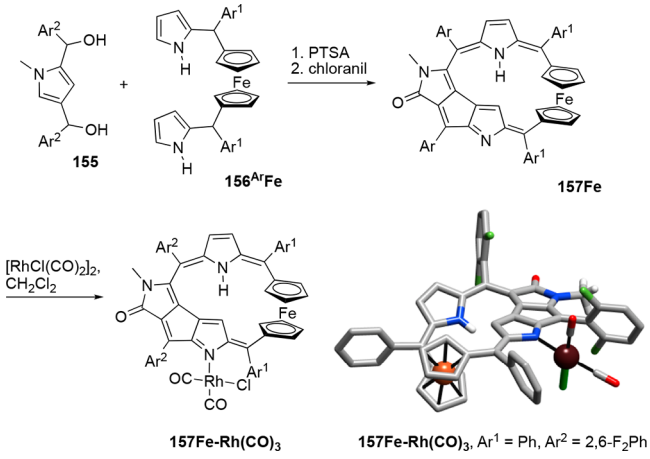
[a]Stick representation of the X-ray structure $153Rh_2$ adapted with permission from ref 495. Copyright 2019 American Chemical Society.

Scheme 57. [3 + 1] Syntheses of Metallocenoporphyrins[a]



[a]Stick representation of the X-ray structure of 155^SFe adapted with permission from ref 497. Copyright 2010 Wiley-VCH.

Scheme 58. [3 + 1] Syntheses of N-Confused β,β-Fused Ferrocenoporphyrinoids[a]



[a]Stick representation of the X-ray structure of $157Fe–Rh(CO)_3$ adapted with permission from ref 499. Copyright 2021 American Chemical Society.

of the specific connectivity of the parent (hydro)porphyrin, one of the pigments of life. On another fundamental level, the PMPs may provide often unique mixed nitrogen, carbon, and chalcogen coordination environments (such as N_3C, N_3O, N_2C_2, N_2S_2, N_2Te_2, N_2CSe, etc.) to a central metal ion in a more or less rigid (planar) arrangement. This allows, for example, the formation of organometallic complexes with great and unprecedented facility or the stabilization of unusual metal ion oxidation states (such as silver(III)).[500] The PMP may even bind in an out-of-plane coordination mode forming half-sandwich or sandwich complexes with larger metal ions.[133,364,461,499] This has led, for example, to the formation of high-valent tungsten(IV) complexes of N-fused porphyrins for which no equivalent is known for porphyrins.[410]

The macrocycle may be aromatic, non-macrocycle-aromatic, or antiaromatic, and the electronics and charge state of the ligand can be modulated by means of protonation and substitutions at the macrocycle periphery; these features help to understand the nature and the fundamental concept of aromaticity and the factors that allow the switching of aromaticity parameters.[134,149,150,428,501,502]

The presence of functional groups and heteroatoms, including the nitrogen atoms of inverted pyrrolic moieties, that are tightly electronically linked to the macrocycle π-system is a common and often characteristic feature of PMPs.[12−14,128] The functionalities at the periphery of many metallo-PMPs

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particularly suggest their utilization as optical chemosensors, with multiple examples already realized (see also 127, 133, 172, 291−293, 371, 393, and 503−506). Moreover, in case the PMPs contain self-complementary functionalities, rodlike networks in their crystals that cannot be formed in monofunctionalized PMPs can be observed, making these chromophores ideal for the study of light-harvesting antennas, etc.[365,383]

Reflecting their different electronic structures, the optical and electrochemical properties of metallo-PMPs can also vary broadly. This broadly influences the reactivity of the coordinated metal ions; thus, the metallo-PMPs are frequently distinctly different from each other and from the corresponding porphyrin or hydroporphyrin metal complexes.[12−14,128] The catalytic properties of the coordinated metals in metallo-PMPs were also explored for a myriad of reactions; comparisons to the reactivities of the corresponding metalloporphyrins are frequently available.[278,284,285,402,507] Some of the applications of PMPs as catalysts in organic transformations reflect this, as is well-documented for metalloporpholactones (see also Section 2.2.4). Generally, the often found superiority of the metallo-PMPs was deduced to lie in their differing electronics or presence of peripheral functionalities.[122,123,402]

The photophysical properties of the metallo-PMPs, like those of regular porphyrins, are the basis for their potential applications as fluorescent sensors in phototheranostic,[130] phototherapeutic,[132,508−513] and technical fields;[503,504] in artificial light-harvesting systems;[18,83,514−516] or in optical switches or logic gates,[517] though it is not always clear to which degree the metallo-PMP carries functional advantages over the corresponding regular metalloporphyrins. The larger coordination sphere of the texaphyrins, for example, has proven to be of tremendous utility: They can readily form stable complexes with lanthanides, and the clinical studies of lutetium(III) and gadolinium(III) complexes of a water-soluble texaphyrin have shown their potential applications as photosensitizers and radiation enhancers for arteriosclerotic disease and cancer, respectively.[479] While manganese(II) texaphyrin complexes were found to act as an *in vitro* catalyst for the decomposition of peroxynitrite, a property not unique to texaphyrin manganese complexes,[480] its *in vivo* utility in the destruction of this cytotoxic reactive oxygen species of relevance to cancer, amyotrophic lateral sclerosis, or atherosclerosis is likely derived from the honed and favorable biodistribution of the texaphyrin.

On the other hand, the finely tunable metalloporpholactone derivatives were again clearly shown to be superior to the corresponding metalloporphyrin in the photosensitization of oxygen and lanthanides or in the ability to function in oxygen-sensing paints.[13,128] PMP metal complexes absorbing or emitting in the NIR,[129] and some even well above 1000 nm, have also been described, a range inaccessible by regular (hydro)porphyrins.[105,133,410]

Porphyrin and PMP metal complexes were incorporated into hybrid metal−organic frameworks (MOFs) with core/shell-like hierarchical structures. The variation of the macrocycle allowed a broader tuning of, for instance, the visible-to-near-infrared (NIR) absorption/emission characteristics, excited-state energy migrations, and photosensitization capabilities of these novel mimics of the photosynthetic pigment system than would be possible using only porphyrins.[518]

Metallo-PMPs may also have (helical) conformations or conformational flexibility that is different than that of the corresponding metallo-(hydro)porphyrins;[271,298,499,519] they clearly occupy a much larger conformational space than porphyrins (that themselves can vary in their conformations broadly).[118] PMPs may also be subject to different steric constraints than porphyrins. For example, the lesser steric congestion around the *meso*-positions in subporphyrins compared to regular *meso*-arylporphyrins[520−522] results in a free rotation of their aryl-substituents and an enhanced electronic influence of the *meso*-aryl substituents on the optical and electrochemical properties of these chromophores;[24] we extend this finding also to the metallo-PMP derivatives of the subporphyrins. This provides PMPs with avenues to adjust their shape and electronic structure not accessible to regular porphyrins.

Beyond their coordination chemistry, many PMPs are nonplanar, exposing the inner NH hydrogen atoms for interactions with their environment. As recently shown for porphyrins, this is the basis for their "molecular engineering" into, for example, organocatalysts or a molecular recognition system.[523,524]

4. CONCLUSION AND OUTLOOK

This Review demonstrates that PMPs are porphyrinoids of large structural variety, conformation and conformational flexibility, chemical stability, and optical and physical properties. Their synthetic pathways either are along total synthesis routes or utilize the conversions of porphyrins, chlorins, or other PMPs; however, only in rare exceptions are complementary routes toward the same class of PMPs available.[310] The extent of the tuning of the electronic properties of the porphyrinic macrocycle that resulted from the replacement of one or two pyrroles by nonpyrrolic heterocycles is readily appreciated by a comparison of the optical properties of PMP-analogues with those of the parent porphyrinoids. The syntheses and structures of aromatic, antiaromatic, and nonaromatic species were shown.

Either the metallo-PMPs are prepared in metalated form, or the metal ions are inserted into the free-base macrocycles via metathesis reactions. The central metals of (sometimes varying) oxidation states play multiple roles or have varying effects on the syntheses, conformation and conformational flexibility, chemical stability, and optical and physical properties of the metalated macrocycles. Despite the structural diversity observed in metallo-PMPs, some general reactivity and (in)stability trends emerged that point toward the highest stability for those systems of architectures and electronics that are similar to those of (hydro)porphyrins. The size of the macrocycle cavity was shown to have a large impact on the type of metals that can bind or the oxidation states of the metal ions they stabilize; inversely, the metal can affect the conformation of the complex. The coordination chemistry of some of the derivatives is rich, while other PMPs have yet to be studied in detail.

It can be safely predicted that the field has yet to reach its full potential and that new discoveries with respect to the formation, reactivity, physical properties, and utility of metallo-PMPs can still be expected. We hope that this overview will guide and inspire further development of one major aspect of modern porphyrinoid chemistry.[525]

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Notes

The authors declare no competing financial interest.

Biographies

Damaris Waiyigo Thuita. Born and raised in Kenya, she earned a BSc. degree from the University of Nairobi with work in the area of industrial chemistry. She then joined the Brückner research group at the University of Connecticut, where she earned a Ph.D., in 2021, with work on the synthesis of free-base and metal complexes of pyrrole-modified porphyrins and their utilization in catalysis or energy-transfer models. She currently applies her synthetic skills in the pharmaceutical industry (and misses her colorful porphyrinic molecules).

Christian Brückner. Born in São Paulo, Brazil, and raised in Mexico and Germany, he studied chemistry and biology at the RWTH Aachen, Germany (*Dipl. Chem.*, 1991) before attending the University of British Columbia, Vancouver, Canada (Ph.D., 1996), where David Dolphin introduced him to porphyrin chemistry. During a postdoctoral appointment at UC Berkeley (with Kenneth N. Raymond), he learned to appreciate metal−ligand interactions. He joined the faculty of the University of Connecticut, where he is currently professor and head of the Department of Chemistry. His research interests lie in the synthesis and evaluation of porphyrinoids, coordination chemistry, and the occurrence of oligopyrroles as dyes in nature. He dreams of becoming a better carpenter.

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