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# Core chemistry and skeletal rearrangements of porphyrinoids and metalloporphyrinoids

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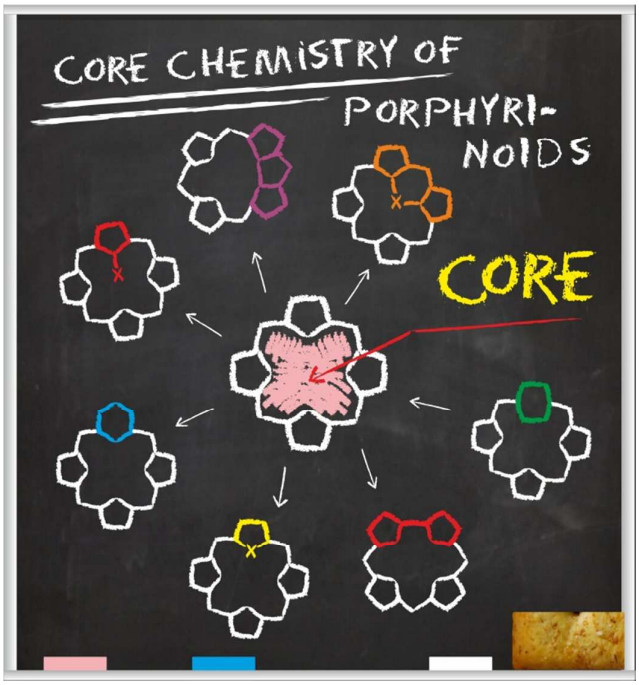



ABSTRACT

Core alteration, affording heteroporphyrinoids and carbaporphyrinoids, allows for the exploration of porphyrin-like or porphyrin-unlike coordination chemistry. Such a strategy has provided a fundamental change in the approach to macrocyclic organometallic chemistry. The specific reactivity of porphyrinoids has offered an insight into reactions inside particularly shaped macrocyclic architecture, including metal-mediated organic transformations. This review focuses on alterations of macrocycles, built of four carbocyclic/heterocyclic subunits which readily resemble the structure of porphyrin or porphyrin isomers, providing, however, remarkable porphyrin-like (XNNN), (CNNN), (CNCN) or ($C_2$NNN) surroundings. To facilitate understanding of the discussed subject matter, all addressed reactions reflecting core reactivity have been formally grouped into nine categories distinguished by the principal type of transformation addressed: (1) alkylation or arylation, (2) core heteroatom replacement, (3) oxidation and oxygenation, (4) substitution, (5) macrocyclic fusion, (6) core bridging, (7) ring contraction, (8) ring expansion, and (9) C-H and C-C bonds activation. The distinctive

macrocyclic environment creates a long-sought opportunity to trap unique organometallic transformations which include instances of benzene ring contraction to cyclopentadiene or the formation of an unprecedented metalloporphyrinoid: 21-pallada-23-telluraporphyrin. The review offers certain challenging perspectives which target the goals of organometallic bond activation.

## 1. Introduction and scope

The concept of porphyrinoids as a class of porphyrin-inspired macrocycles has been dynamically evolving,[1-11] originating from seminal contributions focused on porphyrin isomers[12-17] and heteroporphyrins.[18-22] The discovery of N-confused porphyrin **1**,[16;17] and the subsequent dynamic development of carbaporphyrinoid chemistry has resulted in several lines of research with tremendous implications for general and physical organic and inorganic chemistry.

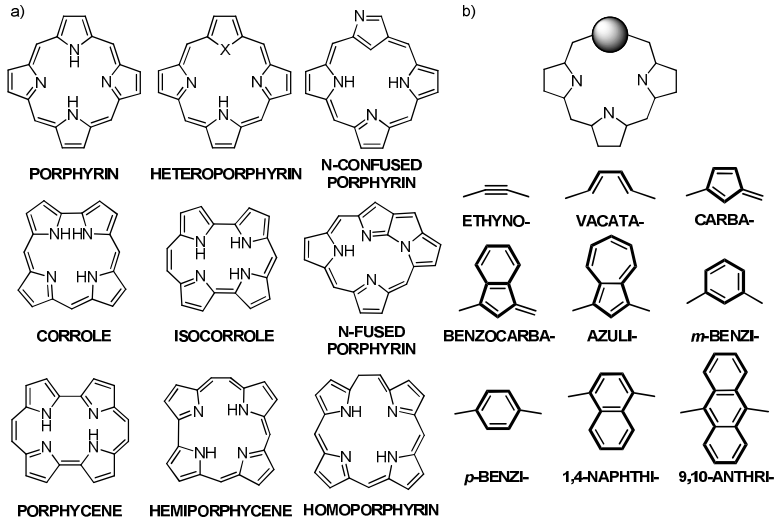
Porphyrinoids may be seen as a special platform for coordination chemistry which creates a unique environment allowing for the observation of unusual oxidation and electronic states of bound metal cations. Consequently, they have created an opportunity to address fundamental issues, investigated in such seemingly distant fields as: (a) the aromaticity of molecules adopting the Möbius topology,[9;23-25] (b) organometallic copper(II) compounds,[26] (c) the contraction of benzene to cyclopentadiene[27;28] or (d) the inclusion of a *d*-electron subunit into a π-electron conjugation.[29;30]

Porphyrinoid chemistry has developed a number of specific synthetic methods and protocols for functionalization.[2;31-39] In the traditional approach, the synthetic strategy – leading to a specifically designed macrocyclic skeleton – is subordinated to the availability and chemical properties of precursors, i.e. building blocks which allow for the intentional incorporation of appropriate motifs into a targeted macrocycle. The alternative scenario, namely post-synthetic functionalization of macrocyclic skeletons, although dynamically

developed by some groups, is still rarely encountered and, in our opinion, unjustifiably underestimated.[40-44]

In this context we would like to shed some light on a specific class of reactions which may constitute a set of remarkable synthetic tools useful in the redesigning of macrocyclic frames. Although all reactions described in the review differ strikingly in terms of their mechanisms, they possess a common denominator which is, generally speaking, regioselectivity towards the central core of the macrocycle. These reactions will be, in the following sections, described as the core transformations of porphyrinoids. In addition, the review covers a group of transformations which, albeit targeting a macrocyclic perimeter, lead to a distinct change in the chemical identity of molecules.

For the sake of clarity and transparency, we have limited our description of core chemistry to transformations of porphyrinoids built of four carbocylic/heterocyclic subunits which readily resemble the structure of porphyrin or porphyrin isomers. The molecular frameworks of the discussed compounds have been summarized in Scheme 1. Nevertheless, it is worth noting that the chemistry of expanded porphyrins provides a plethora of spectacular transformations which may also be classified as core chemistry.[41;45-51]




Scheme 1. a) Molecular skeletons and trivial names of chosen porphyrinoids, b) trivial names of carbaporphyrinoids with appropriate moiety incorporated.

## 2. Chemistry inside macrocyclic cores

The architecture of a porphyrinoid framework (Scheme 1) may be, in general, described as consisting of a macrocyclic perimeter built of α, β and meso carbon atoms and – located inside the macrocycle – the central cavity, traditionally described as the coordination core. The peculiar molecular structure of porphyrinoids, especially the existence of a well-defined vacant space inside the molecules, encourages perceiving this group of compounds as a special instance of molecular flasks which are known to alter or modify the specific reactivity of encapsulated reagents (Figure 1).[52] The striking difference in the behavior of these two kinds of systems is that porphyrinoids or metalloporphyrinoids act not only as a platform but, in most cases, they play the role of active reactants, changing their specific chemical identity.

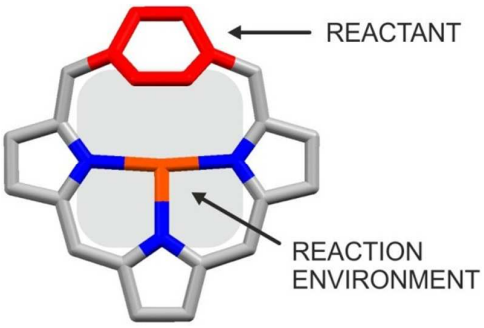



Figure 1. Porphyrinoids as a sub-class of molecular flask systems.

## Molecular stimuli

The predispositions of macrocyclic structures, which may be seen as convoluted reactivity-governing factors operating in the chemistry of porphyrinoids, have been formally systemized into three groups: geometric, electronic and tautomeric, as described below.

### 2.1. Geometric factors

The binding of reaction agents inside the core of the macrocycle through weak interactions (e.g. hydrogen bonds) is expected to facilitate transformations as the distance between the reagents becomes close enough for a given reaction to run. In the case of metalloporphyrinoids, the proximity between metal or metalloid cations and other atoms located inside the coordination core is commonly within the limits necessary to create a bond activation effect which triggers intramolecular reactivity (Figure 2). In addition, generally porphyrinoids are endowed with a noticeable conformational flexibility. The abilities to distinctively change their conformation and the spatial arrangement of their subunits were identified as crucial reactivity determining factors.

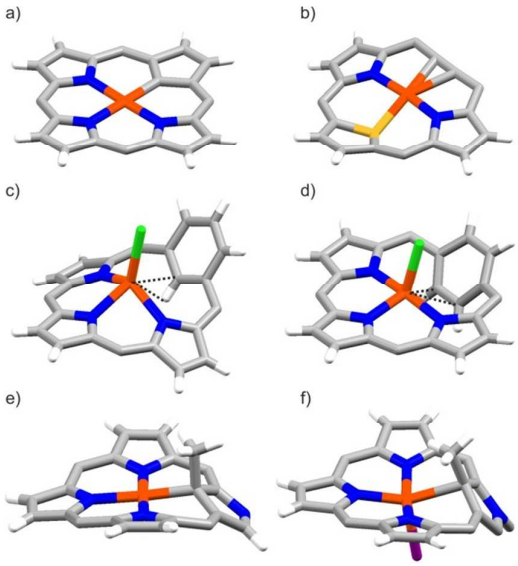
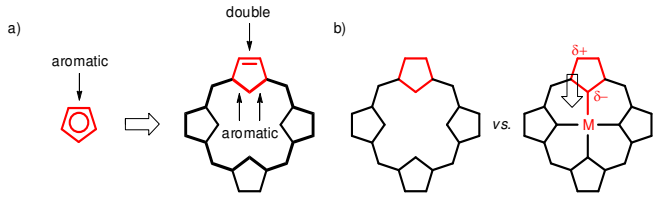



Figure 2. Different modes of metal ion coordination inside a carbaporphyrinoid core: a) M-C($sp^2$) σ bond,[27] b) M-$\eta^2$-CC bond,[53] c) M···[C-H] agostic bond,[54] d) M···$\eta^2$-CC interaction,[54] e) M-C($sp^3$) σ bond,[55] f) M···C($sp^2$) side-on interaction,[55]. Meso substituents have been omitted for clarity.

**2.2. Electronic factors**



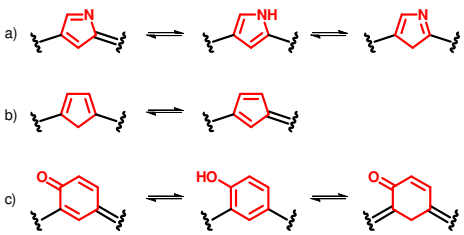

Scheme 2. Electronic factors governing core chemistry: a) a change of bond nature after the incorporation of a selected moiety into a macrocyclic frame, b) a metal coordination-triggered redistribution of electron density.

Typically, porphyrinoids and metalloporphyrinoids demonstrate a distinct aromatic characteristic. An incorporation of heterocyclic, carbocyclic or acyclic subunits into a macrocyclic structure with a connectivity variant that allows for a cyclic conjugation may affect the distribution of electron density inside any incorporated entity (Scheme 2a).

An incorporation of a metal cation into the coordination core causes a redistribution of electron density not only at donor atoms but the effect extends to the whole macrocycle being controlled by the nature of the cation, including its charge and size (Scheme 2b). Both geometric and electronic factors may contribute synergistically and influence specific regions of macrocyclic structures resulting in umpolung-like changes of core reactivity. Significantly, at least two oxidation states of the macrocycle are accessible for several porphyrinoids which specifically contribute to individual steps of the reactions.

**2.3. Tautomeric and isomeric factors**

Evidently, the coordination core of porphyrinoids may be perceived as adaptive. For instance, a given favored metal coordination mode may require a formal prearrangement of the most stable porphyrinoid tautomer into a less stable one to be eventually stabilized via coordination. Noticeably, considering the mechanism of metal ion insertion, one can include a preorganization step envisaged by a transformation, whereas the tautomeric structure of a ligand meets all requirements imposed by an inserted metal cation. These, sometimes energetically demanding, structural adjustments contribute essentially to the overall activation energy of metal insertion. The following tautomeric transformations, evidently influencing the course of the processes, can be considered as representative for such adaptive mechanisms as the amine-imine of pyrrolic rings (N-confused porphyrin),[16;17] cyclopentadiene tautomerism (carbaporphyrins and benzocarbaporphyrins),[56-62] and the keto-enol equilibrium in oxypyri-,[63] oxybenzi-[64-70] and oxynaphthiporphyrins[59;71] (Scheme 3). A more detailed analysis of tautomerism and conjugation-related effects has been described by Stępień and Latos-Grażyński.[72]

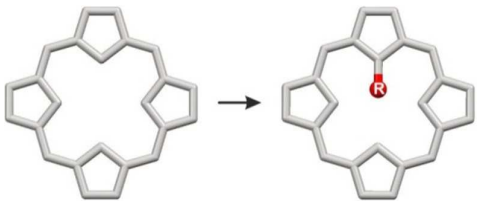



Scheme 3. Tautomeric processes involved in macrocyclic prearrangements : a) imine-amine of N-confused pyrrole, b) tautomerism of cyclopentadiene entrapped in a carbaporphyrin, c) keto-enol tautomers of 2-hydroxybenziporphyrin.

## 3. Core reactivity types

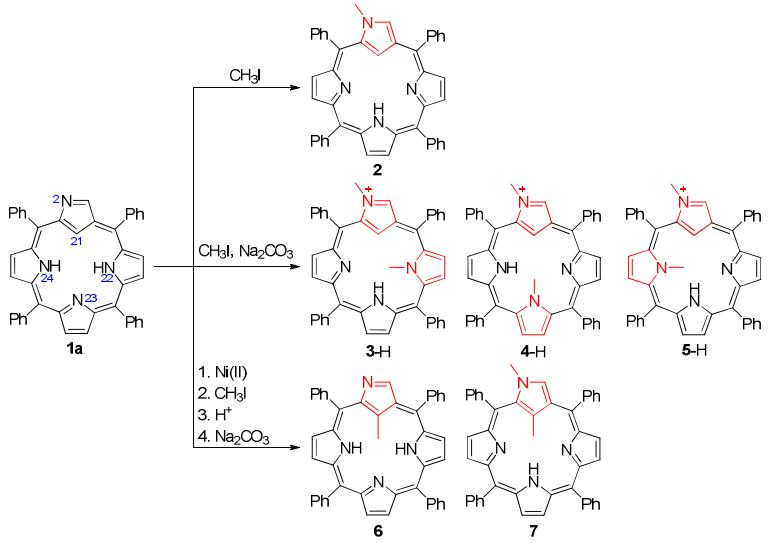
To simplify the reading all reactions reflecting the core reactivity have been rather formally grouped as outlined previously into nine categories distinguished by the principal type of transformation. Still, in several instances the process reflects a convolution of two or more clearly distinct but rationally inseparable steps. In such cases, the classification of the dominant one has been arbitrarily chosen in accordance with the authors' preferences.

### 3.1. Alkylation and arylation



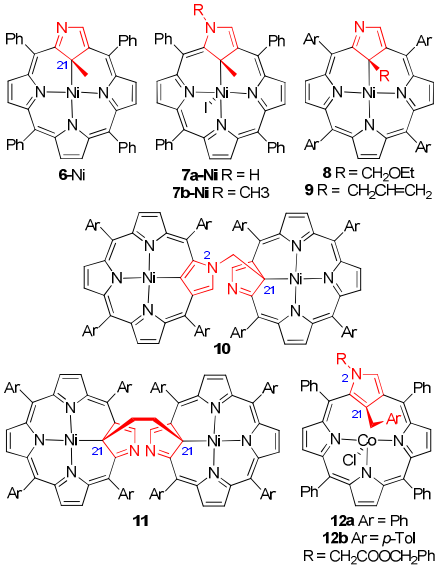

Alkylation or arylation of core atom(s) can be classified as the conceptually simplest modifications of a porphyrinoid cavity (Scheme 4). N-confused porphyrin (2-aza-21-carbaporphyrin) **1**[16;17] reacts regioselectively with methyl iodide in the absence of a base, and transforms into 2-aza-2-methyl-21-carbaporphyrin **2** almost quantitatively (Scheme 4).[73] The addition of acid-neutralizing sodium carbonate allows for conducting the second methylation step, resulting in the mixture of monoprotonated *N*,*N*'-dimethyl derivatives **3**-H – **5**-H.[74] The internally methylated N-confused porphyrins have also been prepared from an N(2)-protected macrocycle. A strategy consisting of 1) methylation and 2) deprotection of the N(2) atom

allowed to prepare N(2)-unsubstituted derivatives of **1** methylated at the N(22) and N(24) atoms.[75]




Scheme 4. Methylated derivatives of N-confused porphyrin.[55;73;74]

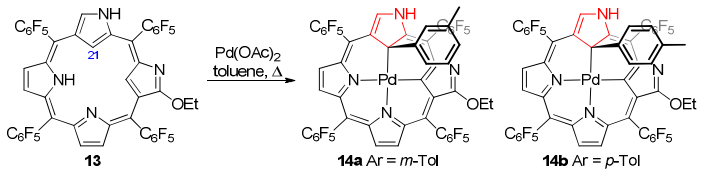
In contrast to free-base N-confused porphyrin, the first methylation step of nickel(II) N-confused porphyrin involves the activated C(21) carbon atom affording C(21)-methylated derivatives: diamagnetic nickel(II) 2-aza-21-methyl-21-carbaporphyrin **6-Ni** and paramagnetic **7a-Ni** (Scheme 5).[55] This variant of alkylation is accompanied by $sp^2$ to $sp^3$ rehybridization of the C(21) atom. The regioselectivity of the methylation reflects the activation effect of nickel(II) coordination. The methylated pyrrole is bound to nickel v*ia* a pyramidal carbon atom in the $\eta^1$-fashion (Figure 2). Subsequently, presuming inner core methylation has been accomplished, the perimeter-localized N(2) atom can be methylated, yielding paramagnetic nickel(II) 2-aza-2-methyl-21-methyl-21-carbaporphyrin **7b-Ni**. This first structurally characterized paramagnetic organonickel(II) complex presents unique structural features related to its electronic structure. The acid demetallation of **6-Ni** and **7b-Ni** affords 2-aza-21-methyl-21-carbaporphyrin **6** and 2-aza-2-methyl-21-methyl-21-carbaporphyrin **7**, respectively (Scheme 4).




Scheme 5. Products of nickel(II) or cobalt(II) N-confused porphyrin alkylations.[55;76;77]

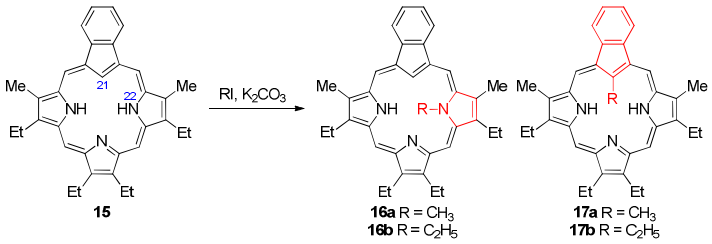
The replacement of the methyl iodide with dihaloalkanes in base-promoted alkylations takes place in the presence of alcohols provided with a group of alkylated products similar to **8** (Scheme 5).[76] Significantly, the C(21)-N(2) dimers **10** were formed under alcohol-free conditions. The reaction of nickel(II) N-confused porphyrin and 1,2-dibromoethane afforded the C(21)-C(21)-diporphyrinic molecule **11,** in which the $CH_2CH_2$ group links two porphyrinic moieties. These transformations follow ionic mechanisms but the identification of some specific by-products suggests some involvement of radical-type mechanisms as well. The core alkylation of **1**, which is accompanied by the rehybridization of the internal carbon atom, were detected during the metallation of the N(2)-protected macrocycle with cobalt(II) chloride in the presence of toluene or *p*-xylene (Scheme 5; **12a**, **12b**).[77]

To the best of our knowledge, only a single example of N-confused system core arylation has been reported (Scheme 6).[78] Thus, the insertion of palladium(II) into the doubly N-confused porphyrin **13** in toluene is accompanied by regioselective arylation centered at the C(21) position. Two toluene addition products – **14a** and **14b** (*meta*- and *para*-substituted) – were identified.



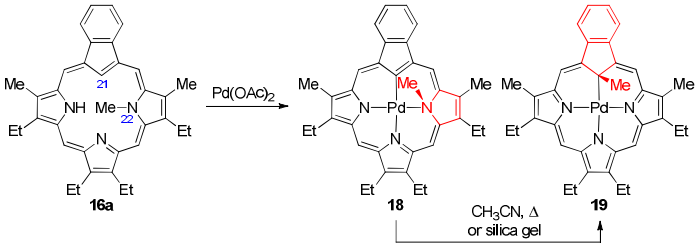

Scheme 6. Arylation of doubly N-confused porphyrin in the course of palladium(II) insertion.[78]

Benzocarbaporphyrin **15** contains three reaction centers susceptible to alkylation. Until now, only N(22)- and C(21)-alkylated derivatives have been identified and isolated (Scheme 7).[79] Compounds **16** and **17** were obtained in a ca. 6/1 ratio (in the case of methylation), reflecting the preference for N-alkylation under the applied conditions.



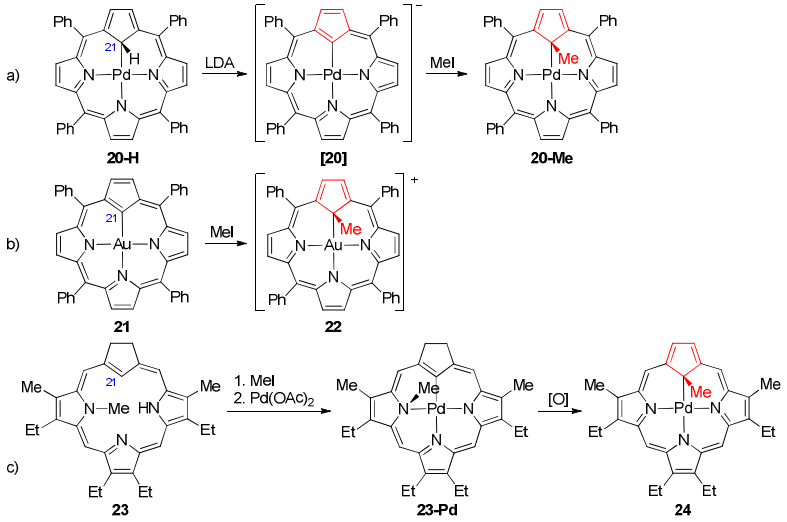

Scheme 7. Alkylation of benzocarbaporphyrin **15**.[79]

The insertion of palladium(II) into 22-*N*-methylbenzocarbaporphyrin **16a** produces palladium(II) 22-*N*-methylbenzocarbaporphyrin **18** and palladium(II) 21-methylbenzocarbaporphyrin **19** with the methyl group attached to the C(21) carbon atom core (Scheme 8).[79] The formation of **19** implies a peculiar inner core N(22)→C(21) methyl migration.




Scheme 8. Methyl group migration in the course of benzocarbaporphyrin metallation.[79]

Palladium(II) and gold(III) tetraaryl-21-carbaporphyrins **20-H** and **21** react regioselectively with methyl iodide, yielding 21-methyl substituted derivatives (Scheme 9).[80] Palladium(II) complex **20-H** requires base-promoted deprotonation prior to the reaction with an electrophile.



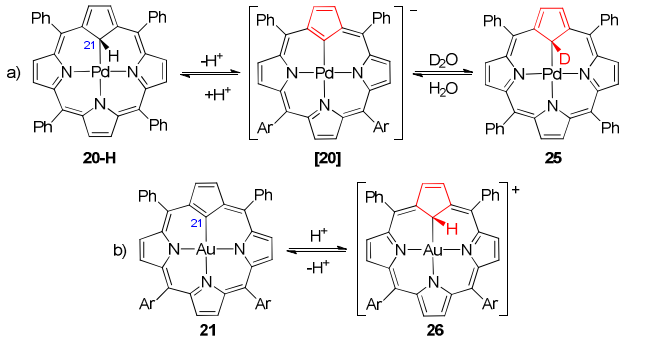

Scheme 9. Methylation of a) palladium(II), b) gold(III) tetraphenyl-21-carbaporphyrins and c) formation of palladium(II) N-methylated β-alkylated 21-carbachlorin and C-methylated β-alkylated 21-carbaporphyrin.[80;81]

Interestingly, C(21)-methylated palladium(II) β-substituted 21-carbaporphyrin **24** has been obtained from the corresponding 21-carbachlorin in a similar procedure as described for benzocarbaporphyrin (Scheme 9).[79;81] The reaction of N(22)-methyl carbachlorin **23** –

prepared in the first step from β-substituted carbachlorin – with palladium(II) acetate led to a metalation followed by oxidation and alkyl group migration which produced **24**.

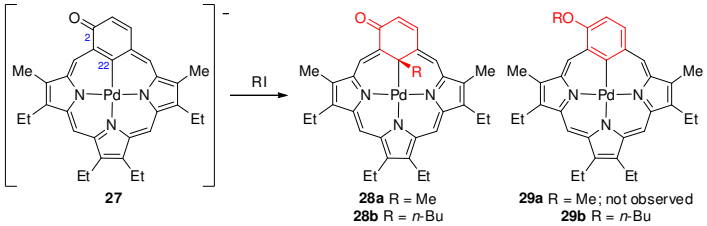
21-Carbaporphyrinoids reveal a peculiar flexibility in their molecular and electronic structures, readily adjusting the anionic character of their coordination cores to the oxidation state of the coordinated metal ion. Thus, the predisposition of 21-carbaporphyrin complexes to react with electrophiles at the C(21) position seems to be a general feature and is most likely related to facets of cyclopentadiene moiety. Accordingly, the tetrahedral-trigonal rearrangement originating at the C(21) atom controls a macrocyclic π-conjugation.

After the addition of $D_2O$, the H(21) hydrogen atom of palladium(II) 21-H-21-carbaporphyrin **20-H** is readily exchangeable with deuterium, yielding palladium(II) 21-D-21-carbaporphyrin **25** (Scheme 10a).[28] It is likely that the reaction goes through the anionic intermediate palladium(II) 21-carbaporphyrin **[20]** (Scheme 10a) with the trigonally hybridized C(21) atom. The rehybridization of the C(21) atom was directly observable during the reversible protonation of gold(III) 21-carbaporphyrin **21** followed by $^1$H NMR, whereas gold(III) 21-H-21-carbaporphyrin **26** has been unambiguously identified in the presence of TFA (Scheme 10b).[27]




Scheme 10. Rehybridization at the C(21) position: a) proton-deuteron exchange of palladium(II) 21-H-21-carbaporphyrin **20-H**,[28] b) reversible protonation of gold(III) 21-carbaporphyrin **21**.[27]

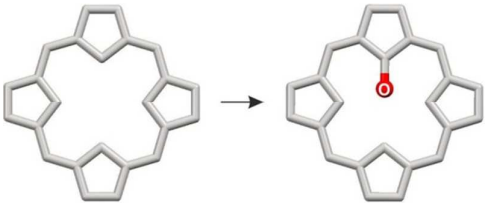
The reactivity of the core carbon atom toward electrophiles has been described in detail for palladium(II) 2-oxybenziporphyrin **27** (Scheme 11).[64] The reaction of anionic complex **27** with methyl iodide nearly exclusively produced the 22-methylated derivative **28a**. The regioselectivity of the reaction depends on the structure of the alkylating agent since the use of 1-iodobutane instead of iodomethane yielded the 1/1 mixture of products **28** and **29** alkylated in positions C(22) and O(2).




Scheme 11. Alkylation of 2-oxybenziporphyrin.[64]

Lash and co-workers have shown that alternatively to C(22) methylation also N-methylation is achievable in the group of benziporphyrins. Treatment of 3,4-dihydro-3-hydroxy-4-oxo-2-oxybenziporphyrin with methyl or ethyl iodide under basic conditions produced mixtures of diastereomers of N-alkylated products.[70]

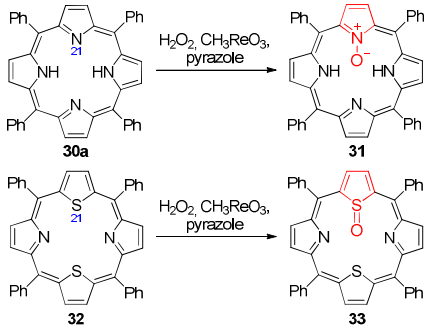
### 3.2. Oxidation and oxygenation



#### 3.2.1. Oxygenation of heteroporphyrins and X-confused porphyrins

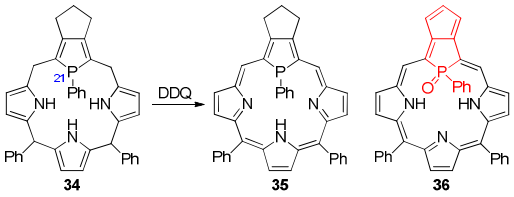
The core atoms of porphyrinoids are susceptible to reactions with donors of the oxygen atom. For instance, porphyrins **30**a are converted into the appropriate N-oxides **31** in the course of reactions with hypofluorous or peroxy acids. The flaw of these methods is the low yield of corresponding N-oxides.[82-86] Brückner and co-workers described an efficient oxidation method based on the reaction of porphyrins with hydrogen peroxide in the presence

of the methyltrioxorhenium/pyrazole system (Scheme 12).[87] This approach also afforded chlorin N-oxides and the first S-oxide of dithiaporphyrin **33**.



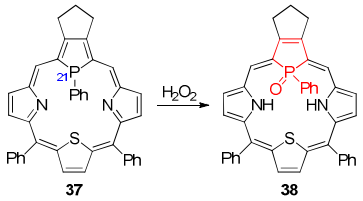

Scheme 12. Oxygenation of porphyrin **30a** and dithiaporphyrin **32**.[87]

Matano and co-workers reported the oxygenation of phosphaporphyrins[88-91] centered at the 21-phosphorus atom.[92] Phosphaporphyrinogen **34** subjected to 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) yielded two products: phosphaporphyrin **35** and π-extended phosphaporphyrin **36** with an oxygenated phosphorus atom (Scheme 13). The reaction of **34** with *m*-chloroperoxybenzoic acid (*m*CPBA) resulted in the oxygenation of the phosphorus atom only, conserving the porphyrinogen framework.



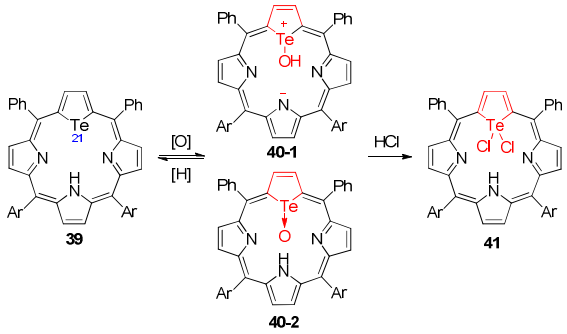

Scheme 13. Oxidation and oxygenation of phosphaporphyrinogen **34**.[92]

Oxygenation of 21-phospha-23-thiaporphyrin **37** with hydrogen peroxide yielded **38** leaving the fused cyclopentane ring untouched (Scheme 14).[93]



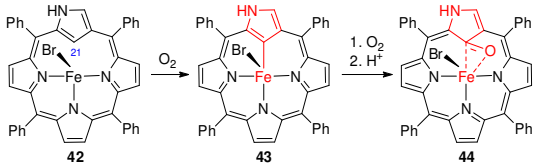

Scheme 14. Oxygenation of 21-phospha-23-thiaporphyrin **37**.[93]

The reaction of 21-telluraporphyrin **39** with a variety of oxidants (air, *m*CPBA[94] or hydrogen peroxide[95]) produces 21-oxotelluraporphyrin **40** (Scheme 15). The *trans* located subunits of tellurophene and pyrrole point out of the $C_4$ meso plane, while the tellurium-oxygen bond is almost perpendicular to that plane. The crystallographic studies revealed that the more appropriate molecular structure for Te-oxide derivative **40** is the one with separated charges (**40-1**) rather than **40-2**. Treatment of **40** with hydrochloric acid produces 21,21-dichloro-21-telluraporphyrin **41**.[96]




Scheme 15. Oxygenation of 21-telluraporphyrin **39**.[94;96]

Several examples of the oxygenation of the C(21) carbon atom have been reported for N-confused porphyrin. Iron(II) N-confused porphyrin **42** reacts with dioxygen affording the product of one-electron oxidation, i.e. the appropriate iron(III) N-confused porphyrin **43** with the direct iron-carbon bond (Scheme 16).[97] Under aerobic conditions, the oxygen atom is subsequently incorporated into the Fe-C(21) bond of **43** producing 21-oxoderivative **44**.




Scheme 16. Oxidation and oxygenation of iron N-confused porphyrin **42**.[97]

An alternative route of core oxygenation has been described for dimer **45** built of two iron(III) N-confused porphyrin units (Figure 3a).[98] The reaction between **45** and dioxygen caused the C(21)-hydroxylation of each porphyrin, forming 21-hydroxy-N-confused porphyrin-related ligands. The reaction is accompanied by the formation of a μ-hydroxy bridge which links two iron(III) centers. The dimeric structure **46** is additionally stabilized by a $[Na(THF)_2]^+$ group bound to the N(2) atoms of both units (Figure 3b).

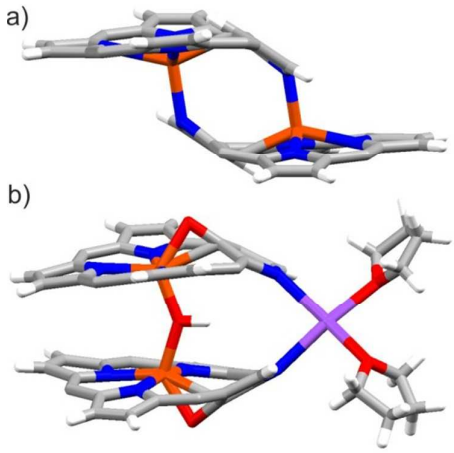
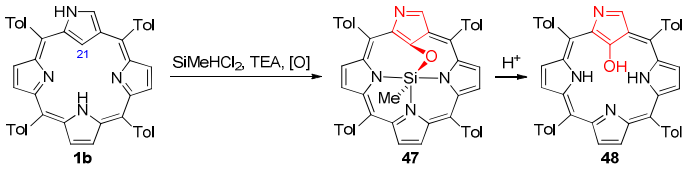



Figure 3. X-ray structures of a) dimer **45** built of two iron(III) N-confused porphyrin units, and b) its oxygenation product **46**. Meso substituents are omitted for clarity.[98]

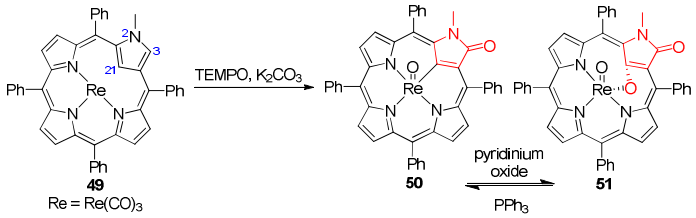
The formation of 2-aza-21-hydroxy-21-carbaporphyrin was also observed during silicon(IV) insertion into N-confused porphyrin **1b** (Scheme 17).[99] Acid-catalyzed removal of the silicon(IV) from **47** produced free-base 21-hydroxy-N-confused porphyrin **48**. The

replacement of **1** with 2-methyl-21-carbaporphyrin resulted, after an analogous two-step procedure, in 21-hydroxy-3-oxo-N-confused porphyrin.



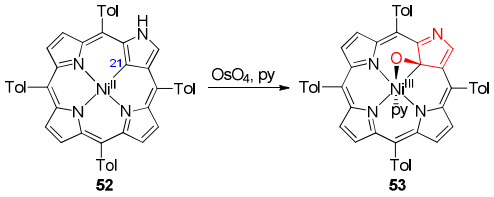

Scheme 17. C(21)-hydroxylation observed during silicon(IV) insertion into **1b**.[99]

The rhenium(I) complex of 2-methyl-N-confused porphyrin **49** oxidized with *tert*-butyl hydroperoxide or TEMPO under basic conditions generates oxorhenium(V) 2-methyl-3-oxo-21-hydroxy-21-carbaporphyrin **51** (Scheme 18).[100] The intermediary species involved in the oxygenation (oxorhenium(V) 2-methyl-3-oxo-21-carbaporphyrin **50**) implements a direct σ carbon-rhenium bond. Importantly, complexes **50** and **51** undergo interconversions in reaction with triphenylphosphine and pyridinium oxide, respectively.



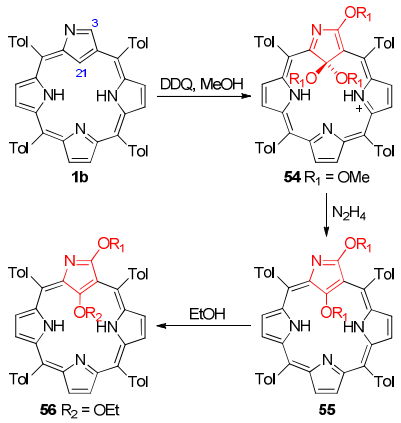

Scheme 18. Oxygenation of rhenium(I) N-confused porphyrin **49**.[100]

The oxygenation of nickel(II) N-confused porphyrin **52** with osmium(VIII) oxide is accompanied by nickel(II) to nickel(III) oxidation and results in nickel(III) 2-aza-21-hydroxy-21-carbaporphyrin **53,** where the C(21) carbon atom acquires a tetrahedral geometry (Scheme 19).[101]



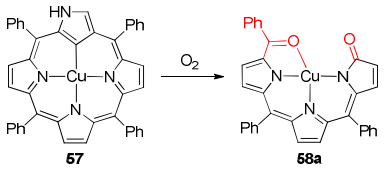

Scheme 19. Oxidation and oxygenation of nickel(II) N-confused porphyrin **52**.[101]

The oxidation of N-confused porphyrin yielding a framework with a tetrahedral inner C(21) carbon atom was also described for free base **1b**.[102] The oxidative addition of alcohol to **1b** produces trialkoxyderivative **54** (Scheme 20). In the $CDCl_3$ and $CD_2Cl_2$ solutions, cationic **54** creates an ionic pair with a semiquinone-type anion radical $DDQ^{\bullet-}$ generated by a one-electron reduction of DDQ. Ketal **54** may be readily transformed into bis-alkoxysubstituted **55** with a trigonal C(21) atom by reduction with hydrazine hydrate. Interestingly, the internal alkoxy substituent is susceptible to a transetherification reaction.



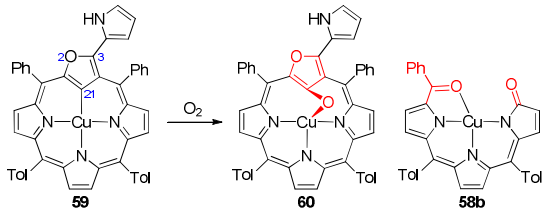

Scheme 20. Alkoxylation of N-confused porphyrin **1b**.[102]

An attempt to probe the reactivity of copper(II) N-confused porphyrin **57** with dioxygen demonstrated an oxidative ring cleavage and the formation of copper(II) tripyrrinone **58a** (Scheme 21).[103] In the course of oxygenolysis, the N-confused pyrrole fragment with the adjacent $C_6H_5$-C unit was extruded.




Scheme 21. Oxidative cleavage of copper(II) N-confused porphyrin **57**.[103]

It was also demonstrated that the copper(II) complex of O-confused oxaporphyrin is also sensitive to oxidative conditions.[104] The degradation of copper(II) 2-oxa-3-(2-pyrrolyl)-21-carbaporphyrin **59** to copper(II) tripyrrinone **58b** was considered to be a peculiar case of dioxygen activation in a porphyrin-like environment (Scheme 22). The reaction of **59** with hydrogen peroxide, performed under biphasic conditions, resulted in quantitative and regioselective hydroxylation centered at the internal C(21) atom yielding **60**. Treatment of **60** with acid resulted in demetalation, forming the nonaromatic 2-oxa-3-(2-pyrrolyl)-21-hydroxy-21-carbaporphyrin.

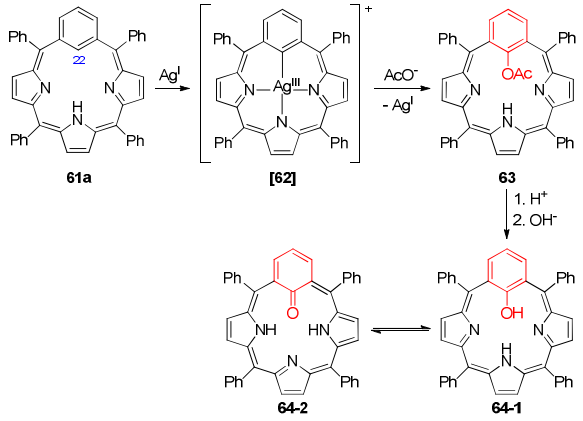



Scheme 22. Reactivity of copper(II) 3-(2-pyrrolyl)-O-confused oxaporphyrin **59** to dioxygen.[104]

### 3.2.2. Oxidation and oxygenation of carbaporphyrinoids

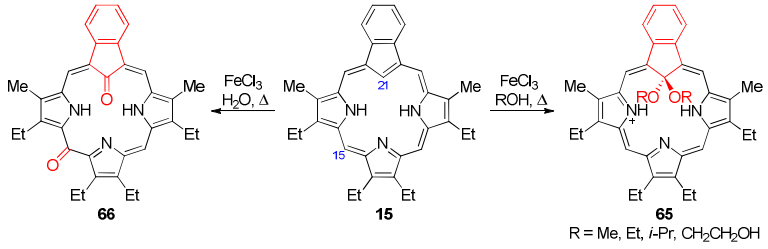
*m*-Benziporphyrin **61** in the presence of silver(I) acetate undergoes regioselective acetoxylation in the C(22) position yielding **63** (Scheme 23).[105] The suggested intermediate of this transformation is silver(III) *m*-benziporphyrin [**62**]. The acid-catalyzed hydrolysis of the ester group afforded 22-hydroxy-*m*-benziporphyrin **64**, which in the solution exists as an

equilibrium mixture of two tautomers, i.e. **64-1** and **64-2**.[66;106] 2,4-Dimethoxy-*m*-benziporphyrin, described by Lash and co-workers, reacts in an analogous fashion.[107;108]




Scheme 23. Hydroxylation of *m*-benziporphyrin **61a**.[66;106]

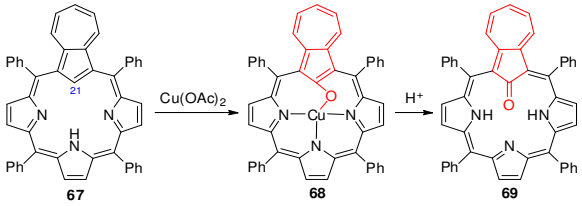
Oxygenation of the inner carbon atom has also been described for benzocarbaporphyrins (Scheme 24).[60] Benzocarbaporphyrin **15** when dissolved in alcohols, in the presence of iron(III) chloride, undergoes the oxidative regioselective addition of two alcohol molecules producing the protonated ketal **65**. The use of a water solution of iron(III) chloride and longer reaction times resulted in further oxidation of the macrocyclic framework affording diketoderivative **66**.




Scheme 24. Oxygenation of benzocarbaporphyrin **15**.[60]

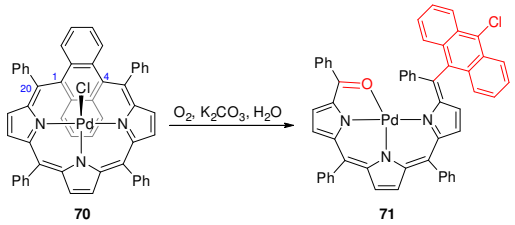
The oxygenation of the cyclopentadiene unit was observed in the course of an attempted azuliporphyrin **67** metallation (Scheme 25).[109] The reaction between **67** and copper(II) acetate

conducted under aerobic conditions yielded copper(II) 21-hydroxyazuliporphyrin **68**. Acid-catalyzed demetallation of **68** provided 21-ketoazuliporphyrin **69**.



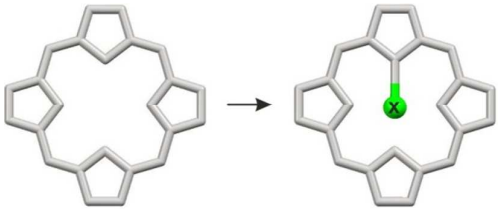

Scheme 25. Oxidative metallation of azuliporphyrin **67**.[109]

An untypical oxygenation reaction has been described for palladium(II) 9,10-anthriporphyrin **70** (Scheme 26).[110] Complex **70** reacts with dioxygen yielding the product of C(1)-C(20) bond cleavage **71**. This step is accompanied by the transfer of a chloride anion from the palladium to the anthracene unit and the oxidation of the meso C(20) carbon atom.



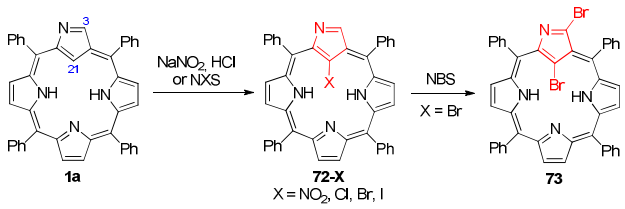

Scheme 26. Oxygenation of palladium(II) *meso*-anthriporphyrin **70**.[110]

### 3.3. Various substitution reactions




The incorporation of a group other than the alkyl or hydroxyl into the macrocyclic core has also been reported for N-confused porphyrin and several porphyrinoids. Thus, the reactions between N-confused porphyrin **1** and N-halosuccinimides run under mild conditions are highly regioselective, providing an efficient synthetic tool for inner core or perimeter directed functionalization (Scheme 27).[111] For example, the use of one equivalent of NBS in the bromination reaction of N-confused porphyrin results in 21-bromoderivative **72-Br**. The use

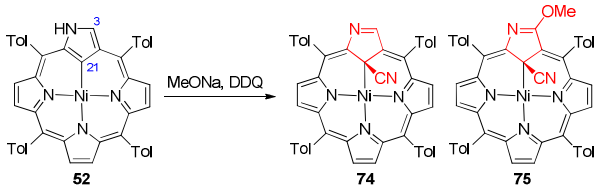
of two equivalents produces 3,21-dibromoderivative **73** as an additional product. The chlorination of the internal C(21) carbon atom was observed during the oxidation of N-confused porphyrin with DDQ under oxidant-deficient conditions.[102]




Scheme 27. Substitution reactions in the core of N-confused porphyrin **1**.[111;112]

N-confused porphyrin **1** is transformed into the 21-nitrosubstituted derivative **72-NO$_2$** in the course of the reaction between **1** and sodium nitrite under acidic conditions (Scheme 27).[112] The C(21)-nitro substituent was easily reduced to an amino group with the use of tin(II) chloride.[113]

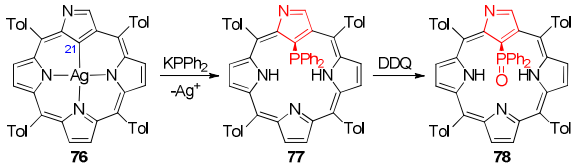
The unique modifications of the N-confused porphyrin core are available after coordination. Thus, the reaction of nickel(II) N-confused porphyrin **52** with DDQ in the presence of sodium methoxide resulted in nickel(II) 21-cyano-N-confused porphyrin **74** (Scheme 28).[114] The addition of cyanide is accompanied by a change in the C(21) atom hybridization from $sp^2$ to $sp^3$. The subsequent nucleophilic addition of methoxide followed by oxidation with DDQ produces **75**.




Scheme 28. Cyanide addition to nickel(II) N-confused porphyrin **52**.[114]

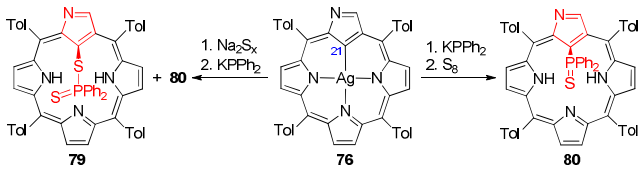
Silver(III) N-confused porphyrin **76** reacted with potassium diphenylphosphide to form macrocyclic derivatives C(21) substituted with diphenylphosphanyl **77** or diphenylphosphoryl

**78** moieties attached at the C(21) position (Scheme 29).[115] A similar reactivity was described for silver(III) carbaporpholactone. A phosphorylation reaction was carried out for free base **1** but under evidently harsher conditions. Regioselectivity changes at a higher temperature as the preferred product is C(3)-substituted. Phosphorylation at C(21) was detected solely for the perimeter diphenylphosphorylated species.



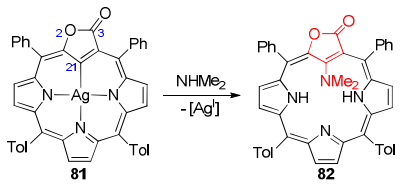

Scheme 29. Phosphorylation of silver(III) N-confused porphyrin **76**.[115]

The order of the addition of diphenylphosphide and elemental sulfur (or sodium polysulfide) to silver(III) N-confused porphyrin **76** plays a significant role in the formation of 21-substituted derivatives (Scheme 30). When **76** was treated with sodium polysulfide and subsequently reacted with diphenylphosphide, the phosphinodithioic acid residue was introduced into the 21-position (**79**). The alternative procedure consisting of the treatment of **76** with diphenylphosphide and then with elemental sulfur $S_8$ yielded 21-diphenylthiophosphoryl derivative **80**. The use of free base **1** instead of silver(III) complex **76** resulted in the formation of carbaporphothiolactam.



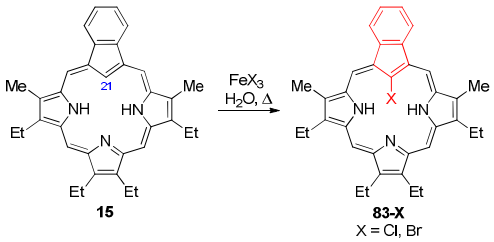

Scheme 30. Reactivity of silver(III) N-confused porphyrin **76** with diphenylphosphide in the presence of sulfur sources.[115]

Silver(III) complexes of N-confused porphyrin **76** and carbaporpholactone **81** react with methylamine and *N*,*N*'-dimethylamine yielding C(21)-aminated products (Scheme 31).[116] The reactions are accompanied by silver(I) extrusion. Non-metallated macrocycles are unreactive under similar conditions.



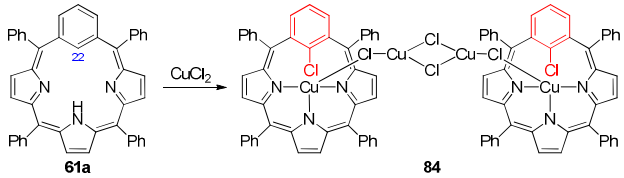

Scheme 31. Amination of silver(III) carbaporpholactone **81**.[116]

Benzocarbaporphyrin **15** undergoes halogenation at the C(21) carbon atom with the aqueous solution of iron(III) chloride or bromide (Scheme 32).[60] This method was used to produce C(21)-chlorinated **83-Cl** and brominated **83-Br** derivatives. The longer reaction times cause lower yields of **83**-X due to the competitive oxidation.



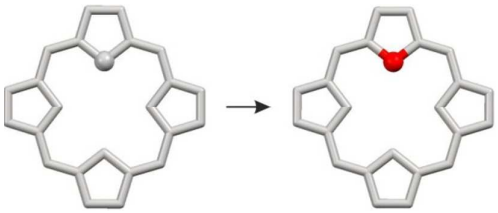

Scheme 32. Halogenation of benzocarbaporphyrin **15**.[60]

The chlorination of *m*-benziporphyrin **61** at the inner C(22) carbon atom accompanies the copper(II) insertion (Scheme 33).[117] In fact, the reaction between **61** and copper(II) chloride run under anaerobic conditions generated a dimer of copper(II) 22-chloro-*m*-benziporphyrin **84** with a bridging $[Cu_2Cl_4]^{2-}$ unit.

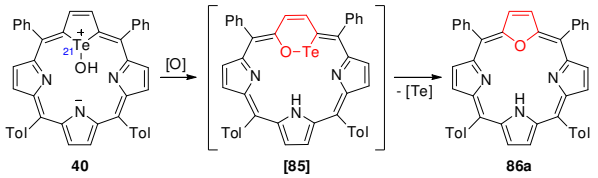


Scheme 33. Copper(II) insertion and halogenation of *m*-benziporphyrin **61a**.[117]

### 3.4. Replacement of the core-heteroatom

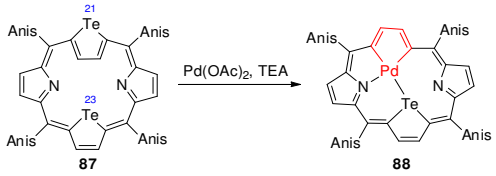


21-Telluraporphyrin **39** undergoes an untypical heteroatom-replacement reaction in the presence of dioxygen or *m*CPBA (Scheme 34).[94] The first step consists of the oxygenation of the tellurium atom of tellurophene to afford tellurium-oxide in order to form **40** (See section **3.2.1**). An excess of the oxidant (e.g. *m*CPBA) forces the replacement of tellurium with an oxygen atom to afford 21-oxaporphyrin **86a**. A plausible reaction mechanism includes the intermediacy of transient porphyrinoid **[85]** containing the six-membered 1,2-oxatellurine ring which is prone to transform into furan as a result of tellurium extrusion.



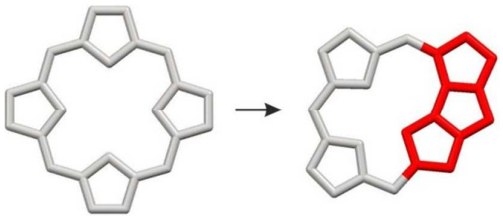

Scheme 34. Conversion of the Te-oxide of 21-telluraporphyrin **40** into 21-oxaporphyrin **86a**.[94]

21,23-Ditelluraporphyrin **87** undergoes a spectacular transformation in the presence of palladium(II) (Scheme 35).[118] The reaction affords an exchange of tellurium for the palladium atom yielding an unprecedented metallaporphyrinoid – 21-pallada-23-telluraporphyrin **88**. Palladium(II) 21,23-ditelluraporphyrin, which adopts the side-on coordination mode, has been identified as the first species in the reaction sequences to be eventually transformed into **88** after the addition of a base.

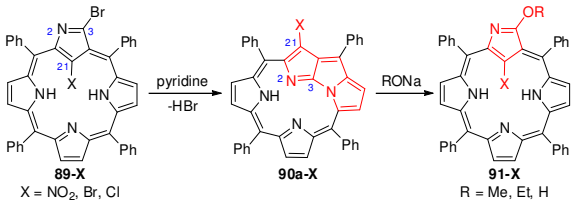



Scheme 35. Formation of 21-pallada-23-telluraporphyrin **88**.[118]

### 3.5. Macrocyclic fusion



One of the most specific and synthetically useful reactions of N-confused porphyrin is its transformation to encompass the N-fused motif.[7;119] 3,21-Disubstituted N-confused porphyrins **89-X**, when heated in pyridine, undergo a fusion reaction which yields 21-substituted N-fused porphyrins **90-X** (Scheme 36).[111;120] Mechanistically, the intramolecular oxidative cyclization is preceded by the inversion of a confused pyrrole unit, which locates the C(3)-Br bond adjacent to a pyrrolic nitrogen, eventually affording a substitution to yield a fused system of three five-membered rings.

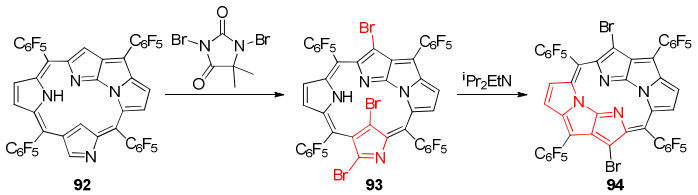



Scheme 36. Synthesis and reactivity of N-fused porphyrin **90-X**.[111;120]

Although the framework of **90** strikingly differs from N-confused porphyrin **1**, it possesses several features which are typical for porphyrins, such as planarity, macrocyclic aromaticity and affinity towards metal cations. N-fused porphyrin **90** is stable under acidic conditions; however, in the presence of hydroxides and alkoxides, it undergoes a ring-opening reaction

which yields 3,21-disubstituted N-confused porphyrin **91-X**. The use of several N-confused porphyrins with different substituents yielded a series of differently functionalized N-fused porphyrins.[111] Thanks to systematic studies on macrocycles with substituents which differ in their electronic nature, it was established that the electron-donating groups in meso positions of N-confused porphyrin increase the rate of fusion reactions.

Bromination of N-confused N-fused porphyrin **92** with 1,3-dibromo-2,2-dimethylhydantoin yielded tribromoderivative **93** (Scheme 37).[121] The subsequent fusion reaction of **93** in the presence of *N*,*N*'-diisopropylethylamine resulted in the doubly N-fused porphyrin **94**. The species is stable under an inert atmosphere, while under aerobic conditions it undergoes an opening reaction yielding N-confused N-fused porphyrin.




Scheme 37. Synthesis of doubly N-fused porphyrin **94**.[121]

The development of synthetic methods, providing appropriately functionalized N-confused porphyrins, allowed for incorporating this motif into dimeric structures. The homocoupling of 21-bromo-N-fused porphyrin **90-Br** with the use of a silver(I) acetate produced the impressive C(21)-C(21') coupled dimer **95**, which – once appropriately opened – yielded dimeric N-confused porphyrin **96** (Figure 4).[122;123] A similar type of dimer was recently prepared in the course of benzonorrole oxidation.[124]

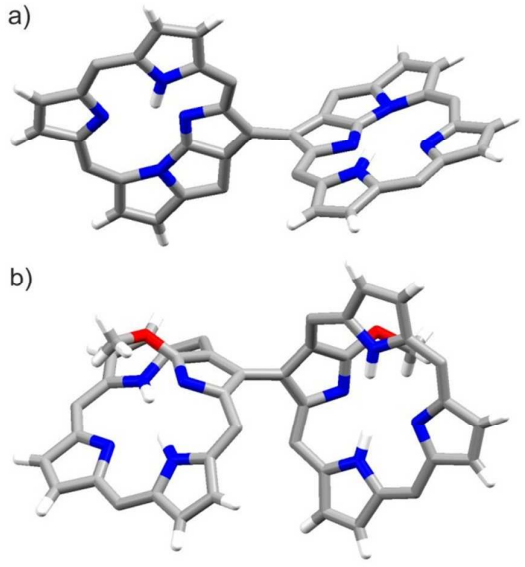
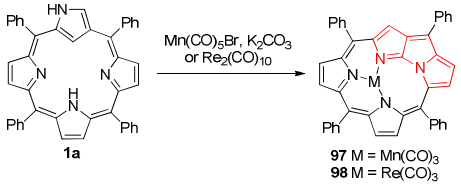



Figure 4. Molecular structures of dimers of a) N-fused porphyrin **95** and b) N-confused porphyrin **96**. Meso substituents have been omitted for clarity.[123]

The opening of N-fused porphyrin **90**, based on the reaction with alkoxides, possesses one flaw as the resulting macrocycles are substituted at the C(3) position. To circumvent the difficulties in further modifications, studies on alternative methods of opening were undertaken. The most effective one relies on an arylthiols-mediated reaction followed by desulfurization with in situ generated nickel boride $Ni_2B$.[125]

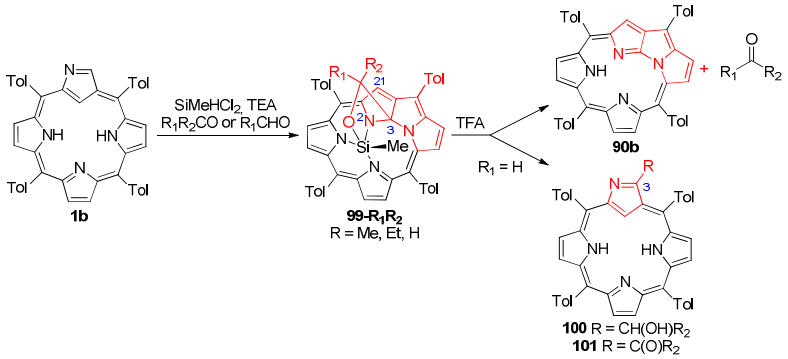
The fusion was also observed during the insertion of metal cations into N-confused porphyrin (Scheme 38). Metallations of **1a** with dirhenium(0) decacarbonyl[126;127] or manganese(I) pentacarbonyl bromide[128] yield the appropriate rhenium(I) or manganese(I) N-fused porphyrins **97** and **98**. In the case of **98,** the fusion is particularly efficient when the ligand macrocycle is substituted with electron-donating groups at the C(21) position. It was also noticed that the fusion is stimulated by bulky substituents which create a steric hindrance impeding the competing dimerization. Such substituents facilitate the conformational rearrangement of **1** necessary for the fusion to appear. Thus, the required inversion of N-confused pyrrole was proved to be feasible as explicitly demonstrated for bis(iridium(I)) N-

confused porphyrin.[129] The demetallation of **97** was performed with the use of the molar excess of amine N-oxides.[128]




Scheme 38. Rhenium- and manganese-mediated fusions of N-confused porphyrin **1a**. [126-128]

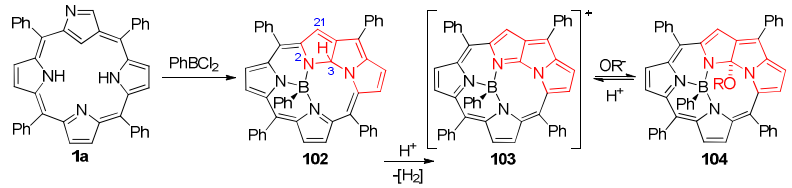
N-fusion was also detected during silicon(IV) insertion into N-confused porphyrin **1**.[99] In contrast, the insertion of silicon(IV) carried out in the presence of aldehydes or ketones afforded derivatives of silicon(IV) N-fused porphyrin **99-$R_1R_2$** (Scheme 39). Formally, these compounds may be classified as the methylsilicon(IV) complexes of N-fused porphyrin substituted at the inner C(3) position by a hydroxyalkyl moiety, which is derived from aldehyde or ketone.




Scheme 39. Synthesis and reactivity of silicon(IV) N-fused porphyrins **99-$R_1R_2$**.[99]

The acid-triggered desilylation of ketone derivatives **99-$R_1R_2$** produces equimolar amounts of N-fused porphyrin **90b** and ketone, whereas that of alkanal compounds **99-$R_1R_2$** ($R_1$ = H) yielded two aromatic N-confused porphyrin derivatives – **100** and its oxidation product **101**. It is worth mentioning that these transformations are the only opening reactions of the N-fused porphyrin-like macrocycle that may be performed under acidic conditions.

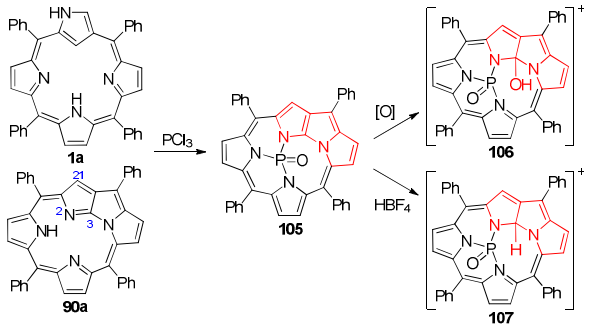
A similar fusion was also observed when **1a** was reacted with phenylboron chloride in toluene.[130;131] The reaction yields two boron(III) complexes with the fused inner phlorin **102** and fused porphyrin **103** (Scheme 40). The latter may also be generated by protonation of **102** or in the course of the reaction between fused porphyrin **90a** and phenylboron chloride. **103** acts as an efficient electrophile. In the presence of alkoxides, **103** reacts quantitatively yielding **104** in which the alkoxy- group is attached to the C(3) position of the fused unit. The addition is reversible as protonation causes the conversion of **104** into **103**.




Scheme 40. N-Fusion reaction accompanying boron insertion to N-confused porphyrin **1a**.[130;131]

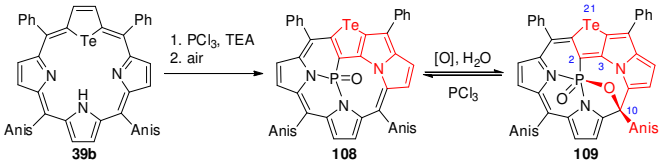
The insertion of phosphorus into N-confused and N-fused porphyrins gives analogous results, although the identified product of fusion can be described as oxophosphorus(V) fused *iso*-phlorin **105** (Scheme 41).[131] During chromatography on basic alumina, species **105** is two-electron oxidized and subsequently undergoes the removal of the PO unit from the core yielding **90a**. The controllable oxidation of **105** results in an almost quantitative conversion to C(3)-hydroxylated phosphorus(V) N-fused inner phlorin **106**. Chlorination at the C(21) position takes place when **106** reacts with excess DDQ. An analogous bromination reaction

may be performed with the use of bromine or NBS. An interesting reactivity pattern was observed when **105** was subjected to fluoroboric acid. The irreversible protonation which takes place in the C(3) position yields inner phlorin **107** stabilized by phosphorus(V) coordination. The proton attachment causes the $sp^2$ to $sp^3$ rehybridization of the inner C(3) carbon atom.



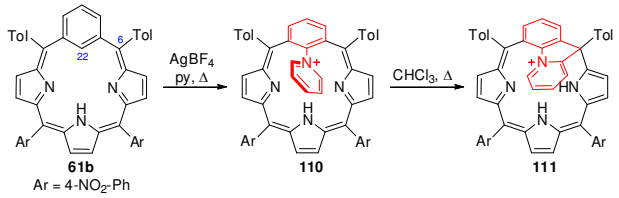

Scheme 41. Fusion accompanying phosphorus(V) insertion to **1a**.[131]

N-fused telluraporphyrin **108** – the only example of N-fused heteroporphyrins – was prepared from 21-telluraporphyrin **39b** in reaction with phosphorus(III) chloride (Scheme 42).[132] The rearranged fused macrocycle acts as a trianionic tridentate ligand. Therefore, the insertion of phosphorus into **39b** prompted the inversion of the tellurophene ring, a two-electron reduction of the macrocycle and the formation of antiaromatic **108**, in which the contracted CNN core of the N-fused telluraporphyrin provides a favorable match for the small radius of phosphorus(V). The oxidation of **108** with *m*CPBA, DDQ or Ag(I) salts in the presence of water yields the nonaromatic phosphorus(V) complex of N-fused telluraphlorin **109**.



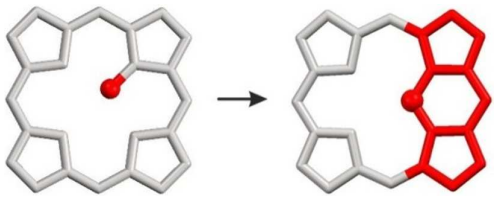

Scheme 42. Fusion reaction accompanying phosphorus(V) insertion to 21-telluraporphyrin **39b**.[132]

A strikingly different fusion inside the coordination core has been identified for *m*-benziporphyrin **61b**, when reacted with pyridine and silver(I) tetrafluoroborate yielding 22-pyridiniumyl-*m*-benziporphyrin **110** (Scheme 43).[133] The regioselectivity of the transformation implies the intermediacy of silver(III) *m*-benziporphyrin, which undergoes subsequent reductive elimination combined with silver(I) extrusion. The 22-pyridinium ring of **110** reacts further with the adjacent meso carbon to form a fused *m*-benziphlorin **111** containing a 10*H*-pyrido[1,2-*a*]indolium fragment.



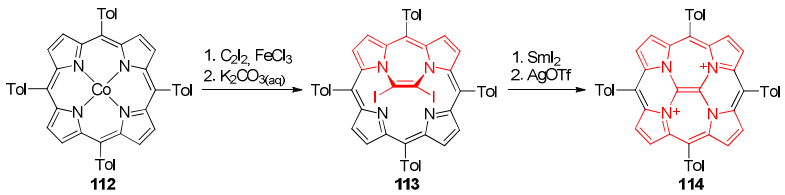

Scheme 43. Pyridination of *m*-benziporphyrin **61b**.[133]

### 3.6. Core bridging



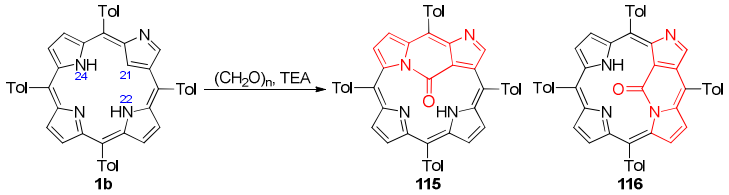
Fusions may be perceived as a special case of a wider class of reactions which result in the cyclization of a molecular fragment inside the coordination core. In general, such transformations consist of the creation of a bridge through linkers connecting at least two subunits of the macrocycle. These will be described as bridging reactions.

The transformation of the macrocyclic framework, which constitutes a particularly apt illustration of the concept of bridging reactions, was described by Vaid (Scheme 44).[134] The reaction of cobalt(II) porphyrin **112** with diiodoacetylene produced the partially fused macrocycle **113**. The subsequent C-N coupling followed by oxidation with silver(I) triflate resulted in the fully condensed aromatic **114,** in which an ethylene linker connects two dipyrromethene units of the porphyrin ring. The compound **114** may also be, in analogy to B-B single-bond diboranyl complexes,[135] recognized as an ethylene complex of porphyrin.




Scheme 44. Bridging by an ethylene linker.[134]

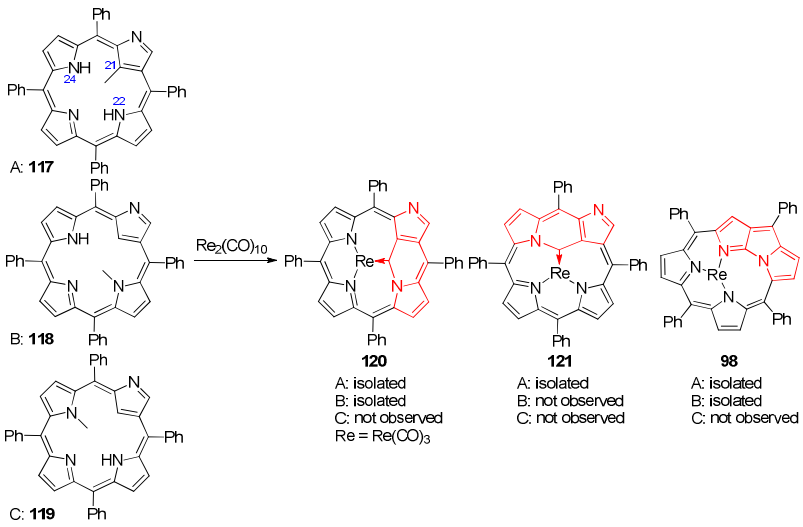
Several reactions affording inner-core bridged N-confused porphyrin have been reported, although the nature of the linker differs distinctively in each case. N-confused porphyrin **1b** reacts with formaldehyde producing the two internally carbonylated products **115** and **116** (Scheme 45).[136] A strong preference was observed in favor of **115** as the molar ratio, established on the basis of the $^1$H NMR spectra, amounting to 10:1.




Scheme 45. N-confused porphyrin bridged by a carbonyl linker.[136]

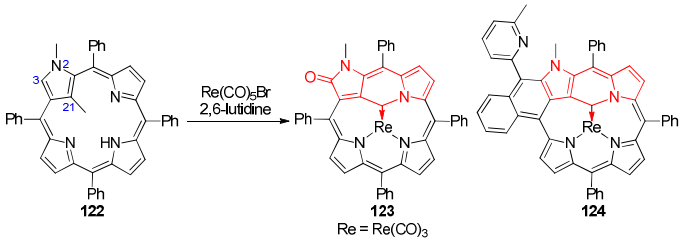
The insertion of rhenium(I) into C(21)- or N-methylated N-confused porphyrins using dirhenium(0) decacarbonyl resulted in the formation of C(21)-N(22) and C(21)-N(24) bridges (Scheme 46).[137] The structure of the product is definitely determined by the specific variant of

the initial methylation. Thus, 22-*N*-methyl-N-confused porphyrin **118** affords, among others, the rhenium(I) complex of N-fused porphyrin **98** and the internally bridged complex **120**. In analogous conditions, 24-N-methylated derivative **119** does not react at all, while 21-C-methyl-N-confused porphyrin **117** produces **120** and its isomer **121**. An N-heterocyclic carbene motif can be identified for **120** and **121**. The addition of acid to **120** and **121** solutions results solely in the protonation of the external nitrogen atoms preserving their macrocyclic frameworks.



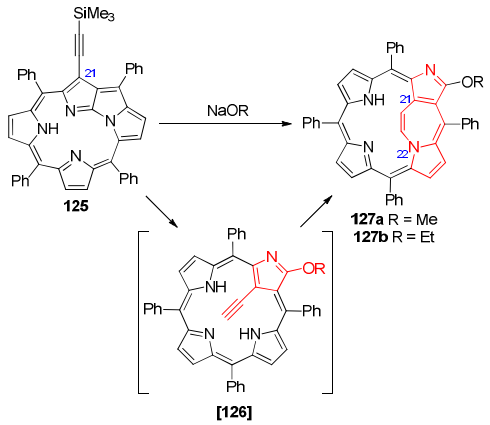

Scheme 46. Rhenium(I)-triggered bridging of internally methylated N-confused porphyrins through a carbene linker.[137]

Rhenium(I) insertion into 2,21-dimethyl-N-confused porphyrin **122** resulted in the two rhenium(I) complexes **123** and **124** containing N-heterocyclic carbenes in their coordination cores (Scheme 47).[138] The formation of inner carbenes was accompanied by reactions at the perimeter with the creation of a lactam unit (**123**) or an unusual π–electron extended porphyrinic system (**124**) due to 2,6-lutidine incorporation.




Scheme 47. Rhenium(I)-triggered bridging of 2,21-dimethyl-N-confused porphyrin **122**.[138]

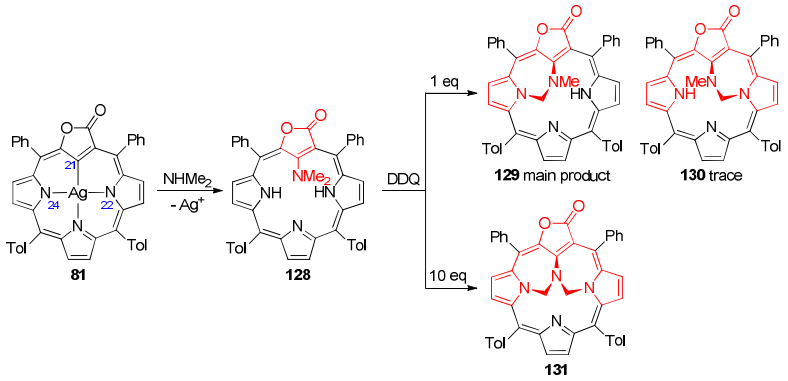
The rational approach afforded the ethylene-bridged N-confused porphyrin **127** starting from 21-(trimethylsilyl)ethynyl N-fused porphyrin **125** (Scheme 48).[139;140] The opening reaction of **125** performed with sodium alkoxides, followed by the rotation of the N-confused ring of [**126**], created the internally-bridged **127** in which two neighboring pyrrolic subunits are linked through a C=C bond. The reaction is regioselective and only one of the possible C(21)-N isomers was detected and isolated. Thus, 21-ethynyl-N-confused porphyrin **[126]**, which locates the highly reactive ethynyl group in the core, is an intermediate of the transformation.




Scheme 48. Synthesis of ethylene-bridged N-confused porphyrin **127**.[139;140]

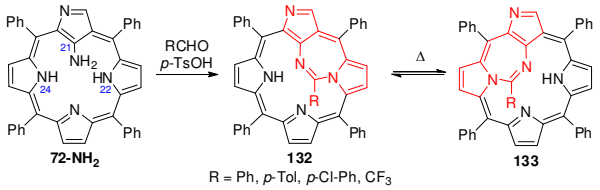
Silver(III) complexes of N-confused porphyrin **76** and carbaporpholactone **81** react with methylamine and dimethylamine producing 21-aminosubstituted derivatives (Scheme 49).[116] Free bases are unreactive under these conditions. The amination reaction is

accompanied by the extrusion of the silver(I) cation. The oxidation of 21-(*N*,*N*'-dimethylamino)carbaporpholactone **128** with one equivalent of DDQ resulted in the two isomers **129** and **130** with a $NMeCH_2$ bridge between the furanone and pyrrole rings. When the amount of oxidant was increased to ten equivalents, the doubly-bridged macrocycle **131** was obtained. This macrocycle may also be prepared by a further oxidation of **129**. A similar reaction carried out with N-confused porphyrin **1** afforded solely mono-bridged forms.



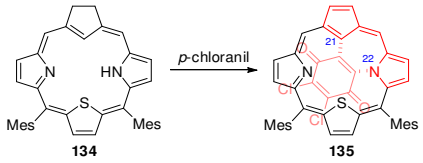

Scheme 49. Amino-bridged carbaporpholactones.[116]

Internally imino-fused N-confused porphyrins **132** and **133** were prepared starting from 2-aza-21-amino-21-carbaporphyrin **72-NH$_2$**, readily obtained from the appropriate nitro-derivative **72-NO$_2$**[112] by reduction with tin(II) chloride.[113] The reaction of **72-NH$_2$** and benzaldehyde produced the two isomeric, internally-bridged macrocycles **132** and **133** (Scheme 50). Presumably, the high reactivity of 21-imino-N-confused porphyrin – a primary condensation product – warrants the subsequent formation of C(21)—N(22) and C(21)—N(24) bridges. Isomers **132** and **133** interconvert when heated in toluene and the rate of the conversion increases once electron donating groups have been attached to the imine carbon atom.




Scheme 50. Bridging of N-confused porphyrin by imine linkers.[113]

Recently, an unexpected bridged carbaporphyrinoid was reported as an identified side-product in the synthesis of 21-carba-23-thiachlorin **134** (Scheme 51).[141] The internally-bridged 21-carba-23-thiaporphyrin **135** in which the carbon atoms of cyclopentadiene and pyrrolic nitrogen are linked through a 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-diyl unit was formed from **134** presumably *via* substitution of two chloro substituents of *p*-chloranil used as a mild oxidant applied in order to convert **134** into 21-carba-23-thiaporphyrin.

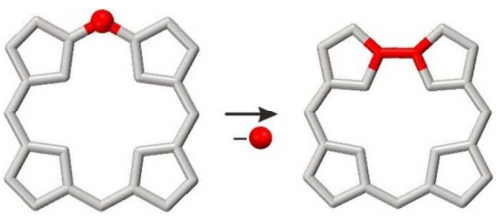



Scheme 51. Formation of internally-bridged 21-carba-23-thiaporhyrin **135**.[141]

### 3.7. Ring contraction

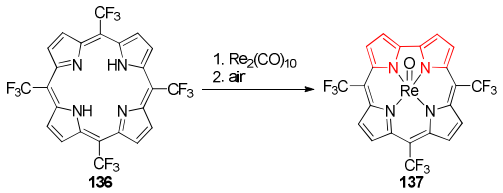
One of the most unusual transformations discovered for porphyrinoid frameworks is ring contraction. It may be further properly separated into two groups reflecting 1) macrocyclic or 2) subunit ring contraction.

#### 3.7.1. Macrocyclic contraction



In principle, a contraction of macrocyclic rings may be realized through the removal of one of

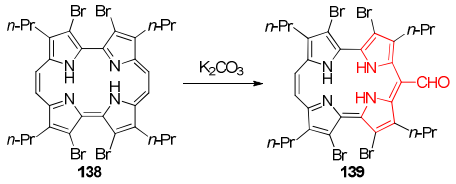
the meso carbon atoms together with its substituent. For instance, such a transformation was identified in the course of tetrakis(trifluoromethyl)porphyrin **136** metallation with dirhenium(0) decacarbonyl (Scheme 52).[142] The insertion of rhenium(V) prompts a removal of the $C_{meso}$-$CF_3$ unit adjusting the size of the macrocyclic crevice to the demands of a very small cation, which corresponds to porphyrin-to-corrole contraction.




Scheme 52. Rhenium-triggered porphyrin-to-corrole contraction.[142]

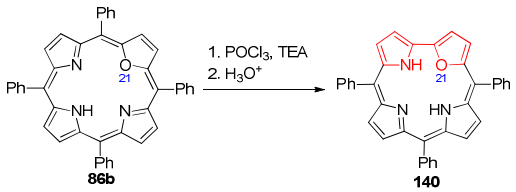
A similar contraction was encountered by Callot and co-workers during the benzoylation of nickel(II) tetraarylporphyrin with benzoic anhydride.[143;144] Structurally, the macrocyclic core of corrole is better suited for the coordination of small metal cations than the porphyrin cavity which seems to be a driving force for any porphyrin-to-corrole rearrangements.

A unique contraction was detected for the porphyrin isomer – porphycene.[145] Heating of the solution of tetrabromoporphycene **138** in DMF under basic conditions and an inert atmosphere yielded a contracted macrocycle – isocorrole **139** (Scheme 53). One of the meso carbon atoms of ethylene bridges in **138** was extruded from the macrocyclic framework and transformed into a formyl *meso*-substituent in **139**.



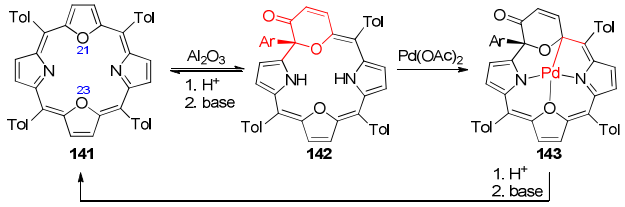

Scheme 53. Porphycene-to-isocorrole contraction.[145]

Macrocyclic contractions were also reported for 21-heteroporphyrins. The reaction between 21-oxaporphyrin **86b** and phosphoryl chloride yields, in addition to the phosphorus(V) complex of **86**, the contracted product – 21-oxacorrole **140** (Scheme 54).[146] The use of $POCl_3$ was crucial for the reaction as its replacement with other phosphorus sources ($PCl_3$, $PCl_5$, $POBr_3$) impedes the contraction. The transformation has been limited solely to 21-oxaporphyrin as other ($N_4$), ($N_3S$) and ($N_2SO$) porphyrinoids conserved porphyrinic skeletons under analogous conditions.



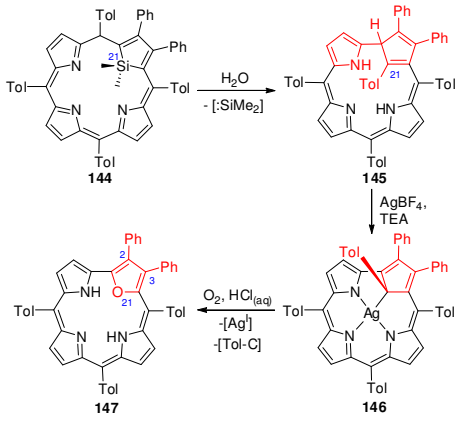

Scheme 54. Oxaporphyrin-to-oxacorrole contraction.[146]

The Achmatowicz rearrangement in a macrocyclic environment has been encountered for 21,23-dioxaporphyrin **141** which undergoes conversion on basic alumina to the contracted flexible macrocycle **142** with the 3-pyranone subunit built into the skeleton (Scheme 55).[147] The insertion of palladium(II) into **142** triggers ligand rearrangement accompanied by the formation of a palladium(II)-carbon bond. The reaction is reversible as **141** may be recovered from **143** by acid addition.



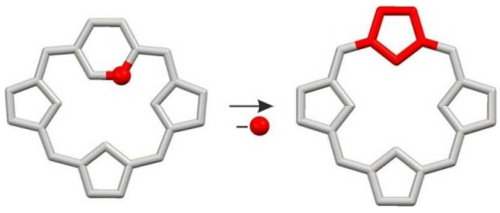

Scheme 55. Intramolecular Achmatowicz rearrangement of 21,23-dioxaporphyrin resulting in macrocyclic contraction.[147]

A unique contraction was also identified in transformations of 21-silaphlorin **144**.[148] In the presence of DDQ, **144** rearranges yielding the nonaromatic *iso*-carbacorrole (isomer of hypothetical 21-carbacorrole) **145** (Scheme 56). Presumably, the transformation requires the initial oxidation of **144** to 21-silaporphyrin to be followed by a reaction with water centered at the Si(21) silicon atom. The macrocyclic contraction results in the formal conversion of the (SiNNN) core of **144** into the (CNNN) one of **145**. The rearrangement involves an extrusion of silylene from **144**, yielding a frame of *iso*-carbacorrole **145**. The insertion of silver(III) or copper(III) into **145** prompts the conversion to carbacorrole trapped in such a peculiar structure solely by coordination to silver(III) or copper(III). Silver(III) carbacorrole **146** undergoes reactions with dioxygen in the presence of aqueous HCl. In the course of oxygenolysis, the benzylic C(21)-*p*-tolyl fragment and the silver(I) cation are extruded to yield 2,3-diphenyl-21-oxacorrole **147**.

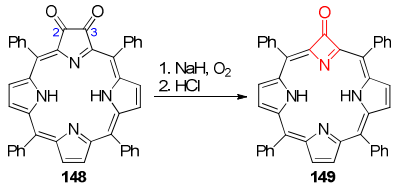



Scheme 56. Contraction of 21-silaphlorin **144**.[148]

### 3.7.2. Subunit contraction

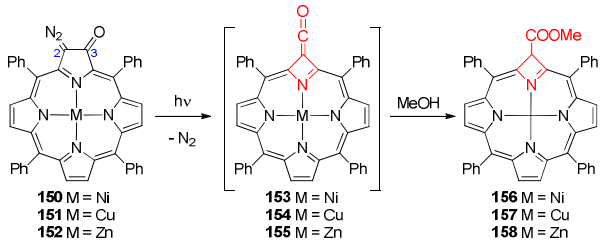


The prototypic contraction of a porphyrinoid subunit was described by Crossley and King in 1984.[149] The reaction of 2,3-dioxochlorin **148** with sodium hydride under aerobic conditions followed by acidification with hydrochloric acid yielded a minor macrocyclic product containing an azetine moiety – azeteoporphyrin **149** (Scheme 57). The same type of subunit contraction was encountered during the oxidation of copper(II) and nickel(II) complexes of **148** with benzeneselenic anhydride.[150]




Scheme 57. Contraction of dioxochlorin **148** to azeteoporphyrin **149**.[149;150]

The photo-Wolff rearrangement was applied to prepare similar contracted macrocycles – azeteochlorins.[151;152] The photolysis of nickel(II), copper(II) and zinc(II) complexes of 2-diazo-3-oxochlorin **150**-**152** resulted in ketenes which, in the presence of alcohol, undergo addition to eventually form metal(II) azeteochlorins **156**-**158** (Scheme 58).

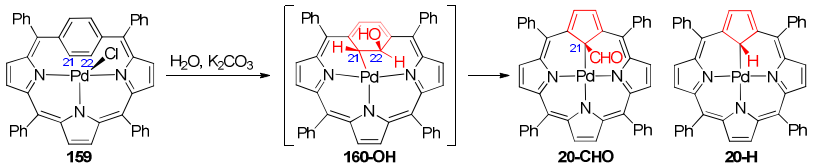



Scheme 58. Photo-Wolff rearrangement of metal(II) 2-diazo-3-oxochlorins to azeteochlorins.[151;152]

In these representative examples, the perimeter β-pyrrolic region of the macrocycle was targeted for chemical transformations. Contractions of carbocyclic subunits which take place inside the carbaporphyrinoid can be categorized as the specific class. So far such peculiar

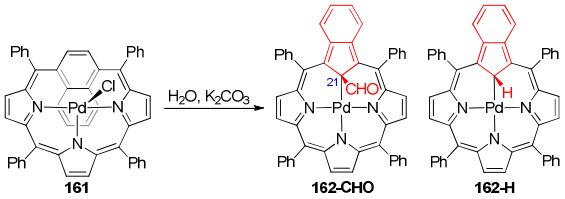
reactivity was described only for *p*-benziporphyrin,[153] and its benzologue – 1,4-naphthiporphyrin.[71;154]

Chloropalladium(II) *p*-benziporphyrin **159** dissolved in acetonitrile under basic conditions undergoes contractions of the *p*-phenylene subunit resulting in two palladium(II) complexes of tetraaryl-21-carbaporphyrin **20-CHO** and **20-H** (Scheme 59).[28] The first step of the reaction consists of the addition of a palladium(II) cation and hydroxide to the CC bond of **159** and yields 22-hydroxycyclohexadieneporphyrin **160-OH**. The latter was obtained and fully characterized with the use of low-temperature NMR measurements as it is stable in 220 K. In order for the contracted products **20-CHO** and **20-H** to be formed, the intermediate **160-OH** must undergo dihydrogen elimination followed by a 1,2-hydride shift or the cheletropic extrusion of carbon monoxide. Recently, β-substituted 21-carbaporphyrin and palladium(II) 21-methyl-21-carbaporphyrin **24** (Scheme 9) have been reported by Lash and co-workers.[81]



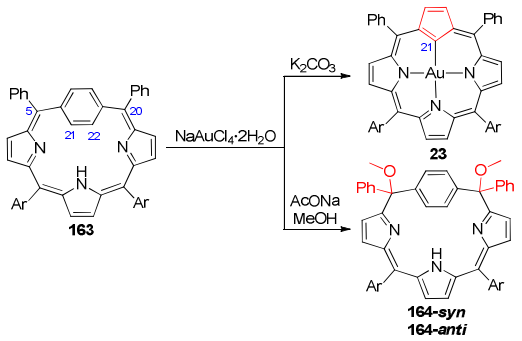

Scheme 59. Contraction of palladium(II) *p*-benziporphyrin **159** to palladium(II) 21-carbaporphyrins **20-H** and **20-CHO**.[28]

An analogous reaction was described for the palladium(II) complex of 1,4-naphthiporphyrin **161** (Scheme 60).[154] The products, obtained from the contraction reaction conducted under conditions previously optimized for benziporphyrin, were two palladium(II) benzocarbaporphyrins **162-CHO** and **162-H**, which differ in the substituent attached to the C(21) atom in the core.




Scheme 60. Contraction of chloropalladium(II) 1,4-naphthiporphyrin **161** to palladium(II) benzocarbaporphyrins **162-CHO** and **162-H**.[154]

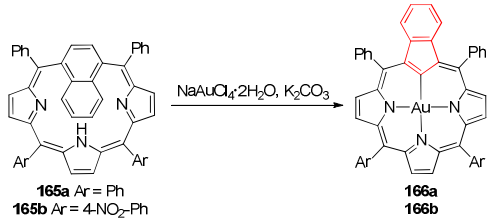
Similarly *p*-benziporphyrin **163** reacts with gold(III) salts, although the course of the reaction strongly depends on the solvent (Scheme 61).[27] Macrocycle **163** dissolved in dichloromethane in the presence of sodium tetrachloroaurate(III) dihydrate and potassium carbonate undergoes the contraction of the benzene unit producing 21-carbaporphyrin gold(III) complex **23**. The addition of methanol and the replacement of $K_2CO_3$ with sodium acetate redirects the reactivity towards *p*-benziporphodimethenes **164** (*syn* and *anti* stereoisomers) produced by methoxide additions into *meso*-positions neighboring the 1,4-phenylene ring. Similar transformations were observed during silver(I) insertion to *m*-benziporphyrin,[155] and *adj*-azulibenzocarbaporphyrin.[156]




Scheme 61. Reactivity of *p*-benziporphyrin **163** with gold(III) salts.[27]

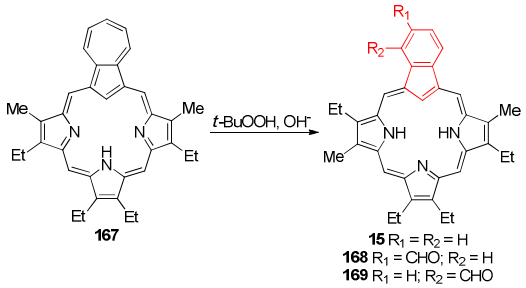
As in the case of the palladium(II)-mediated contraction of **163,** an analogous transformation was observed for 1,4-naphthiporphyrin **165** yielding gold(III)

benzocarbaporphyrin **166** (Scheme 62).[27] The latter compound was previously obtained by a rational metallation of the benzocarbaporphyrin ligand.[157]




Scheme 62. Gold(III)-mediated contraction of 1,4-naphthiporphyrin **165** to gold(III) benzocarbaporphyrin **166**.[27]

The last example of subunit contraction differs distinctively from the above-described as the reaction takes place at the perimeter of the carbocycle which is not directly incorporated into the inner circuit of the porphyrinoid (Scheme 63). Azuliporphyrin contraction was originally recognized by Breitmaier and co-workers, who identified benzocarbaporphyrins **15**, **168** and **169** among the products of the attempted synthesis of **167**.[56] Subsequently, the mechanism of this transformation, based on the oxidative contraction of the tropylium ring, was elaborated by Lash and co-workers.[158] The reaction of basic solutions of azuliporphyrin **167** and hydrogen peroxide or *tert*-butylperoxide produces a mixture of macrocycles including benzocarbaporphyrins **15**, **168** and **169** (Scheme 63). The azuliporphyrin-to-benzocarbaporphyrin contraction is synthetically useful and this method of synthesis was applied to prepare thia- and selena- derivatives of benzocarbaporphyrin.[159]



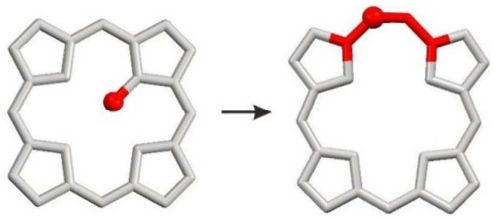

Scheme 63. Contraction of azuliporphyrin to benzocarbaporphyrins.[56;158]

In the original contribution addressing 1,4-naphthiporphyrin, we made the point that two isomers – 1,4-naphthiporphyrin **165** and azuliporphyrin **67 –** undergo conceptually-related transformations. This involves the ring contractions appropriately of azulene (seven-membered ring) or naphthalene (six-membered ring) units, affording eventually an isoindene moiety built into the common transformation target – benzocarbaporphyrin.[154]

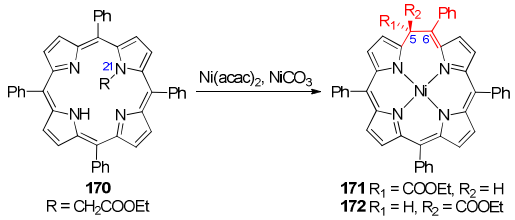
### 3.8. Ring expansion

Apart from the described contractions of porphyrinoids, the opposite direction of macrocyclic ring transformations was also successfully elaborated. These reactions apply an expansion principle of 1) macrocyclic rings or 2) its appropriate subunits.

#### 3.8.1. Macrocyclic expansion

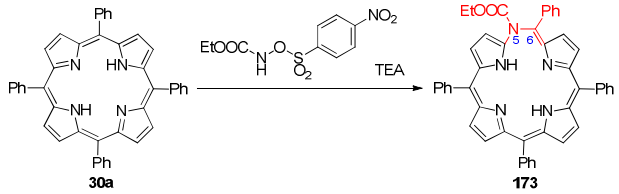


In their pioneering contribution, Callot and co-workers described reactions resulting in the expansion of the porphyrin ring of N-substituted porphyrins (Scheme 64).[160] Metallation of 21-(2-ethoxy-2-oxoethyl)porphyrin **170** with the mixture of nickel(II) acetylacetonate and nickel(II) carbonate yielded, apart from the regular metal complex, two unexpected products – nickel(II) expanded porphyrins **171** and **172**. The substituent previously attached to one of the nitrogen atoms is transferred into a *meso*-position constituting the expansion of porphyrin to homoporphyrin. The transfer of the N-substituent engages the metallic center.



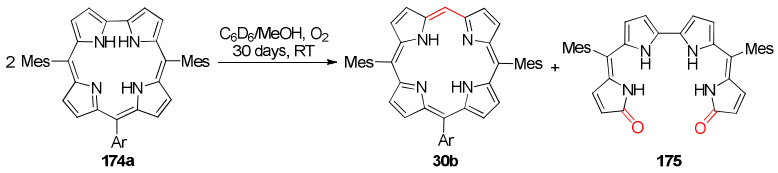

Scheme 64. Expansion of N-substituted porphyrin **170** to homoporphyrins **171** and **172**.[160]

The reaction of tetraarylporphyrin **30a** with the appropriately chosen nitrene source provided a different expansion product – azahomoporphyrin **173** (Scheme 65).[161] Ring transformations of porphyrins, including contraction and expansion reactions yielding homoporphyrins, as well as the chemistry of these interesting macrocycles, have been impressively explored by Callot and co-workers and summarized in their comprehensive review.[162]



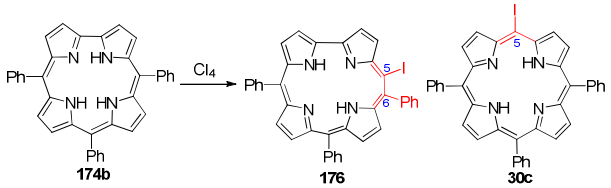

Scheme 65. Expansion of porphyrin **30a** to azahomoporphyrin **173**.[161]

Macrocyclic expansions were also observed in the group of porphyrin analogues, e.g. corroles. Triarylcorrole **174a** left in a solution of benzene-$d_6$ and methanol undergoes ring expansion to porphyrin (Scheme 66).[163] The mechanism consists of [2+2] cycloaddition between two corrole molecules resulting in a spiroderivative intermediate. The subsequent oxygenolysis produces porphyrin **30b** and biliverdine **175**.




Scheme 66. Expansion of corrole **174a** to porphyrin **30b**.[163]

A peculiar example of corrole ring expansion was described by Paolesse and co-workers.[164] The reaction of triphenylcorrole **174b** with tetraiodomethane in DMF afforded two ring-expanded macrocycles: 5-iodo-6,11,16-triphenylhemiporphycene **176** (major product) and 5-iodo-10,15,20-triphenylporphyrin **30c** (traces) (Scheme 67).

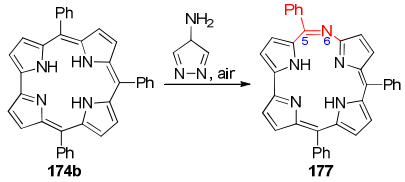



Scheme 67. Expansions of corrole to porphyrin and hemiporphycene.[164]

The corrole-to-hemiporphycene expansion is synthetically relevant as the hemiporphycene framework is built in one step, while rational syntheses required multistep procedures.[165] A similar corrole ring expansion yielding 5-substitued hemiporphycene accompanies the reaction of 5,10,15-tris(4-tert-butylphenyl)corrole and its copper(II) complex with 2,3-bis(bromomethyl)pyrazine.[166] The picturesque term “corrole ring breathing” has been used to reflect the merits of the transformation and to point out that the strain release in the macrocyclic ring is the reactivity governing factor.

During the attempted amination of silver(III) 3-nitrocorrole with 4-amino-4*H*-1,2,4-triazole under aerobic conditions, a ring-expanded product was identified.[167] Under the basic conditions of the reaction, the macrocycle underwent demetallation followed by an expansion to a 6-azahemiporphycene framework. Further work proved that the reaction does not depend

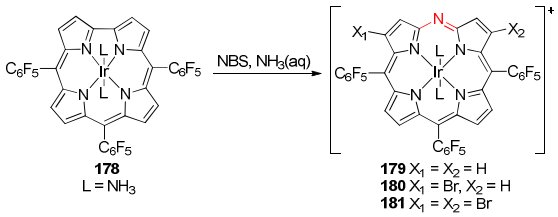
on the metallation of the core or the substitution of corrole with the nitro group and was also successfully conducted on free-base corroles with several variants of substitution in the *meso*-positions (Scheme 68).[168] The regioselectivity of the reaction is different than previously reported for carbon atom insertion as a nitrogen atom was exclusively inserted into the 6 position in each case.




Scheme 68. Expansion of corrole **174b** to 6-azahemiporphycene **177**.[167;168]

The skeletal transformation of corrole into 6-azahemiporphycene has also been reported by Gross and co-workers as accompanying the oxidation of manganese(III) corrole with sodium hypochlorite.[169]

The alternative route of corrole ring expansion, which takes place by nitrogen atom incorporation between two directly bound pyrrolic units, has also been described.[170] The products of the reaction of iridium(III) corrole **178** with NBS in the presence of ammonia were identified as azahomoporphyrins **179**-**181** (Scheme 69). The use of $^{15}$N-labeled ammonia determined the nitrogen atom source.

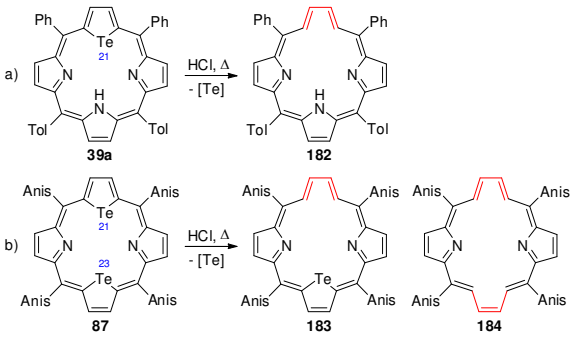



Scheme 69. Expansion of iridium(III) corrole to iridium(III) monoazaporphyrins.[170]

According to Sessler's definition of expanded porphyrins, these are macrocycles which possess at least 17 atoms at the inner circuit.[36;171] Taking this classification into consideration,

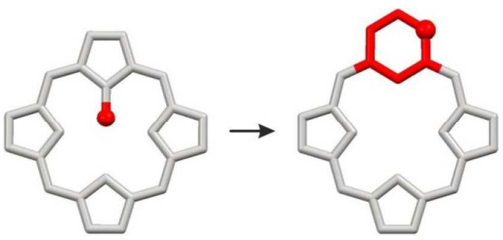
we noticed that tellurium extrusions from telluraporphyrins providing vacataporphyrins may be perceived as a unique case of expansion.[172;173] Refluxing 21-telluraporphyrin **39a** in highly boiling solvents with concentrated hydrochloric acid produces 21-vacataporphyrin ([18]triphyrin(6.1.1)) **182**.

In fact such an expansion results from the tellurium extrusion. This step enlarges the coordination core to seventeen atoms (Scheme 70).[172] An analogous transformation which starts with 21,23-ditelluraporphyrin **87** results in the formation of two expanded porphyrinoids – 21-vacata-23-telluraporphyrin ([18]telluratriphyrin(6.1.1)) **183** and 21,23-divacataporphyrin ([18]diphyrin(6.6)) **184**.[173] The identical macrocyclic motif has already been realized in 7,8,17,18-tetraphenyl-21,23-dideazaporphyrin (7,8,17,18-tetraphenyl-divacataporphyrin) by rational synthesis using the McMurry reaction.[174]

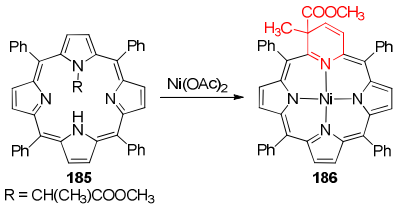



Scheme 70. Vacatization of a) 21-telluraporphyrin **39a** and b) 21,23-ditelluraporphyrin **87** as special cases of macrocyclic expansion.[172;173]

### 3.8.2. Subunit expansion

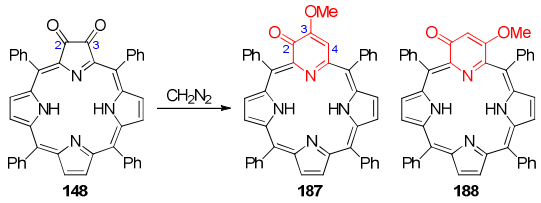


Callot and Schaeffer clearly demonstrated that apart from homoporphyrins the metallation of an N-substituted porphyrin may afford the expansion of one pyrrolic unit of a macrocycle producing nickel(II) pyrichlorin analogue **186** (Scheme 71).[175] Due to the limited scope of this overview, we refer the reader interested in this chemistry to the comprehensive reviews by Callot[162] and Brückner et al.[4]




Scheme 71. Nickel(II)-mediated expansion of porphyrin **185** to nickel(II) pyrichlorin **186**.[175]

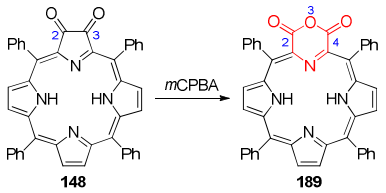
The subunit expansion of 2,3-dioxo-*meso*-tetraphenylchlorin **148** yielding oxypyriporphyrins **187** and **188** has been described by Pandey et al.[176] The reaction of **148** with the excess of diazomethane produced a mixture of three macrocyclic products – two of which (**187** and **188**) incorporate a methoxypyrridinone moiety (Scheme 72). The ring enlargement reaction was also conducted on tetraoxobacteriochlorin which led to the formation of di(oxopyri)porphyrins.




Scheme 72. Ring expansion of dioxochlorin **148** yielding oxypyriporphyrins **187** and **188**.[176]

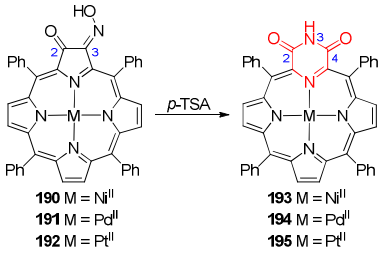
2,3-Dioxochlorin **148** reacts with *m*CPBA yielding the Baeyer-Villiger oxidation product **189** which possesses a morpholine unit (Scheme 73).[149] The same product was obtained in the procedure previously described for azeteoporphyrin **149** based on the reaction of **148** with sodium hydride under aerobic conditions followed by acidification. Similarly, a

morpholinodithiachlorin system was prepared by diol cleavage of *meso*-tetraaryldithia-7,8-dihydroxychlorin.[177]




Scheme 73. Baeyer-Villiger oxidation resulting in subunit expansion.[149]

The reactions of 2,3-dioxochlorin complexes ($Ni^{II}$, $Pd^{II}$ and $Pt^{II}$) with hydroxylamine hydrochloride provided the monooximes **190**-**192**.[178] Their treatment with *p*-toluenesulfonic acid forced the Beckmann rearrangement, causing the expansion of the oxime unit into the appropriate six-membered imide moiety (Scheme 74). Macrocyclic complexes **193**-**195** undergo demetallation in the presence of concentrated sulphuric acid producing free-base *meso*-tetraphenylpyrazino-2,4-dioxoporphyrins.



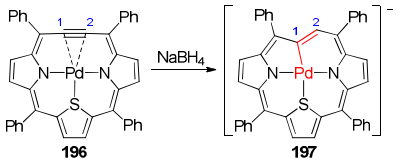

Scheme 74. Beckmann rearrangement of oximes **190-192** resulting in subunit expansion.[178]

### 3.9. C-H and C-C bonds activation

In conducting this review of porphyrinoid core transformations, an effort has been made to shed some light on the reactions which may be generally described as bond activation processes. Evidently, it would be possible to include each of these reactions into previously described ones. However, in our opinion their distinction is crucial to draw the readers'

attention to a particularly important factor, i.e. to the surrounding promoted interaction between the metal ion and adjacent porphyrinoid fragments.

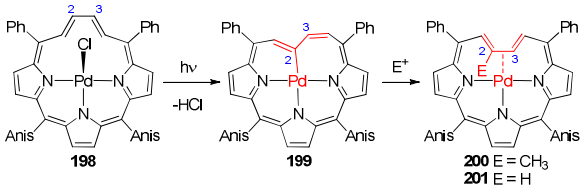
The reaction described for palladium(II) 20-thiaethynoporphyrin **196** provides a revealing example of such an activation of the C-C multiple bond (Scheme 75).[53] Formally, the triple CC bond of aromatic **196** is reduced to a double one in **197** in the course of the reaction with sodium borohydride. The reduction-triggered transformation of the whole frame alters the Pd···$\eta^2$-CC coordination mode to the regular σ Pd-C($sp^2$) bond. The regioselectivity of the reaction is explained by the strong activation effect of the C(1)–C(2) triple bond by the metal ion. The distances between the palladium and carbon atoms with a triple bond equal 2.289(3) Å and 2.315(3) Å, and are distinctively shorter than the appropriate van der Waals contacts (3.3 Å).[179] Although the molecular skeletons of complexes **196** and **197** differ strikingly, the aromatic nature of the macrocyclic framework is preserved after the reaction.




196 197

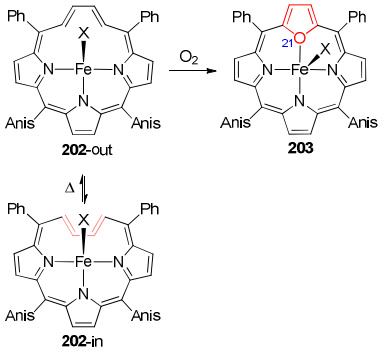
Scheme 75. Regioselective reduction of palladium(II) 20-thiaethynoporphyrin **196**.[53]

Unusual reactivity reflecting the proximity of the metal cation and carbon chain was also described for vacataporphyrin.[180] In the presence of light, chloropalladium(II) vacataporphyrin **198** undergoes conversion to organometallic **199**, forming a direct Pd-C($sp^2$) σ bond (Scheme 76). The newly formed **199** can be methylated with methyl iodide in the presence of silver(I) tetrafluoroborate yielding **200**. The regioselective alkylation is accompanied by the cleavage of the Pd-C(2) bond. The reaction of **199** with acid causes the protonation of the C(2) position. The process is reversible and the heating of the solution of **201** with methanol shifts the equilibrium toward **199**.




Scheme 76. Reactivity of palladium(II) vacataporphyrin **198**.[180]

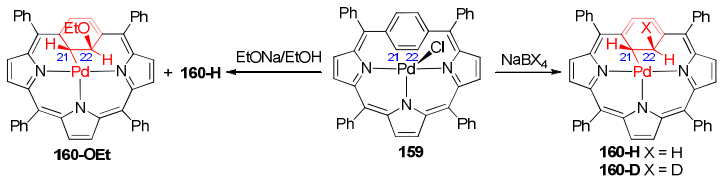
The activation of the butadiene unit by a metal ion is particularly well exemplified by iron(II) vacataporphyrin **202** reactivity.[181] **202** exists in the solution as a mixture of **202**-in and **202**-out, which differ in the relative arrangement of the butadiene unit to the core of the macrocycle (Scheme 77). A reaction with dioxygen causes a slow conversion of **202**-out into the iron(II) complex of 21-oxaporphyrin **203,** while **202**-in isomer remains unreactive under these conditions.[182]




Scheme 77. Reactivity of iron(II) vacataporphyrin **202**.[181]

Other carbaporphyrinoids undergo reactions which are also stimulated by the interaction between core atoms and a metal cation. The relevant activation effect on the phenylene ring of *p*-benziporphyrin has been described above (See section **3.7.2**). The addition of a hydroxy group to palladium(II) *p*-benziporphyrin **159** is an example of a more general type of reactivity observed for **159**.[28] Although the interaction between the palladium(II) ion and the C(21)-C(22) bond directed toward the core is relatively weak (Pd-C = 2.83 and 2.85 Å, sum of van der Waals radii ~3.3 Å), it has distinct consequences in the reactivity of **159** (Scheme

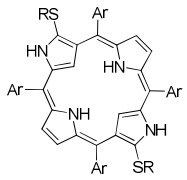
78). The transformation involves the addition of palladium(II) and a nucleophile to the inner C(21)C(22) bond of the *p*-phenylene unit. An analogous reaction in the presence of sodium borohydride or borodeuteride produced the appropriate palladium(II) cyclohexadieneporphyrins **160-H** and **160-D**. The reaction with sodium ethoxide yielded the mixture of 22-ethoxycyclohexadieneporphyrin **160-OEt** and **160-H**. The phenylene ring reduction was surprising at first but it can be explained as a result of reducing activity of ethoxide since acetaldehyde was identified spectroscopically as the byproduct of the reaction.



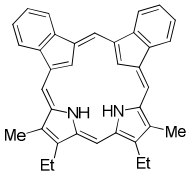

Scheme 78. Reactivity of the palladium(II) complex of *p*-benziporphyrin **159**.[28]

## 4. Conclusions and outlook

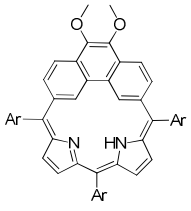
Core alteration affording heteroporphyrinoids (XNNN) and carbaporphyrinoids (CNNN) has emerged as an original and rewarding strategy for modifications of the properties of porphyrins and metalloporphyrins. Such an approach allows for the exploration of new frontiers consisting of porphyrin-like or porphyrin-unlike coordination chemistry introducing a fundamental concept of macrocyclic "equatorial" organometallic chemistry. The set of organometallic derivatives formed by a combination of a variety of metal cations and appropriately tuned carbaporphyrinoids can serve as a perfect molecular flask to explore innovative organometallic chemistry in remarkable porphyrin-like surroundings. The flexibility of the coordination environment around inner carbon donor(s) seems to be a crucial advantage and prompts the exploration in search for original architectures represented by macrocyclic newcomers such as doubly N-confused isophlorin **161**, *adj*-dibenzocarbaporphyrin **162** and phenanthriporphyrin **163**.[183-185]




**161**




**162**




**163**

Heteroporphyrinoids and carbaporphyrinoids fulfill all vital conditions for pursuing new research possibilities at the crossroads of organic, organometallic and inorganic chemistry, aimed at achieving a fundamental understanding of principles in areas relevant for catalysis, sensors or molecular switches. The observation of the unusual reactivity detected inside porphyrinoid or metalloporphyrinoid cores affects the perception of transformations or reactions, including those metal-stimulated which take place in such size-restrained chemical flasks.

**Acknowledgements**

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