

Fig. 3. Classement des éléments selon leurs potentiel rédox en milieu acide, d'après Sanderson [3]

carbone et non aux colonnes extrêmes (fig. 3).

La classification des éléments n'est pas périodique, mais bien évolutive. La meilleure représentation du fameux ta-

bleau est sans doute celle de Bohr [4]. Cet éminent physicien a compris ce que nous devrions vérifier tous les jours en chimie: la réactivité des éléments se différencie, se spécialise d'une période à l'autre en s'ap-

pauvrissant. Comme l'hydrogène, le carbone est très riche en possibilités de réactions, le silicium beaucoup moins et le plomb assez pauvre. Les terres lanthanidiques sont connues pour leur ressemblance entre elles.

De telles considérations font aussi l'objet du cours de chimie générale, à l'intention des futurs biologistes et médecins, dont nous avons la responsabilité à la faculté des Sciences de l'Université de Lausanne.

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The Discovery and Future Prospects of Artificial Porphyrins: Molecular Batteries Functioning with the Reversible Formation and Cleavage of Cyclopropane Units

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Abstract. The absence of the *meso*-hydrogen atoms in *meso*-octaalkylporphyrinogens enable the generation of novel forms of the oxidized porphyrinogen, 'artificial porphyrins'. A stepwise four-electron oxidation of *meso*-octaalkylporphyrinogen transition-metal complexes led to an unusual aromatization of the porphyrinogen with the loss of four hydrogen atoms and the introduction of one, followed by two cyclopropane units into the porphyrinogen frame. Such oxidized forms of porphyrinogen function as two-electron shuttles *via* the formation and cleavage of the cyclopropane unit. Furthermore, the appropriate site opening of the cyclopropane may lead to important modifications of the porphyrinogen frame.

1. Introduction

Porphyrin is an ubiquitous molecular framework which may be obtained naturally or synthetically [1]. In both cases this framework originates from a porphyrinogen precursor (compound 1), *via* a six-electron oxidation involving the removal of four H-atoms from the *meso*-positions to give a compound of type 2. Although this is a well-known transformation, neither its chemical nor biochemical mechanism has been fully elucidated. The absence of the *meso*-H-atoms in *meso*-octaalkylporphyrinogens may provide information on the mechanism of aromatization of porphyrinogens to porphyrins and simultaneously enable the generation of novel forms of the oxidized porphyrinogen, 'artificial porphyrins'. We discovered that a stepwise four-electron oxidation of *meso*-octaalkylporphyrinogen transition-metal complexes led to an unusual

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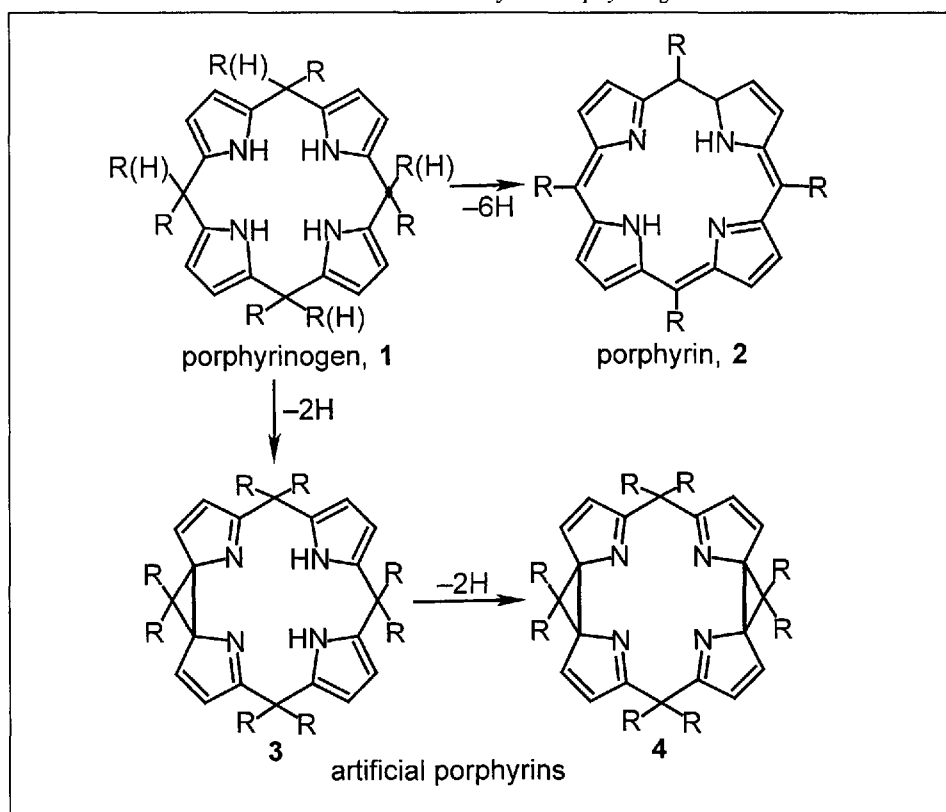
aromatization of the porphyrinogen with the loss of four H-atoms and the introduction of one, followed by two cyclopropane units into the porphyrinogen frame (compounds **3** and **4**) [2]. The oxidized forms, **3** and **4**, have a number of peculiar properties, among them: *i*) Redox processes based on the facile formation and cleavage of a cyclopropane moiety occurring with a two-electron exchange; the cyclopropane unit can, therefore, function as a 'molecular battery', in which the storage and release of electrons is assured by the reversible formation and cleavage of a C-C bond rather than from a conventional change in the oxidation state of a metal. *ii*) The appropriate site opening of the cyclopropane may lead to a ring-contracted corrinoid-type skeleton [3] (see vitamin B₁₂), or to other modifications of the porphyrinogen frame, such as removal of the *meso*-C-atoms.

2. Artificial Porphyrins: Oxidized Forms of Porphyrinogen Other Than Porphyrins

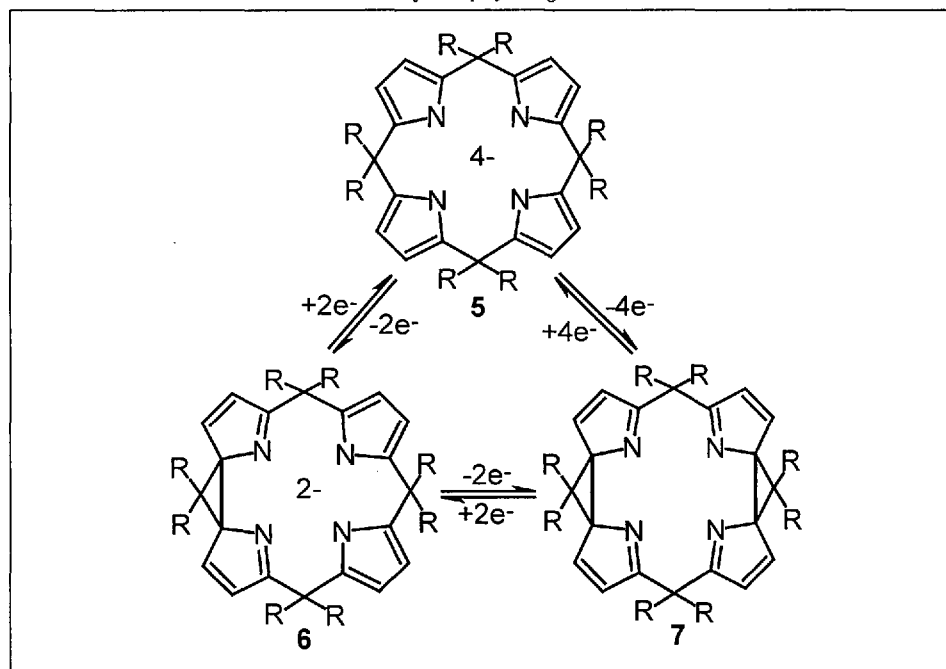
It is very difficult to understand the so-called oxidative aromatization of the porphyrinogen to the porphyrin skeleton (see *Scheme 1*), because such a process can be formally viewed as the result of two molecular actions, namely, the removal of six electrons followed by the removal of six protons. The key part of this process is the removal of four H-atoms from the *meso*-positions. We were interested in answering the following questions in order to understand the porphyrinogen-porphyrin transformations: 'what happens when there are only alkyl groups in the *meso*-positions?', 'can we identify partially or fully oxidized forms other than porphyrins?', and 'is it possible to follow the pathway leading to these species'. Our results are shown in *Scheme 1* and displayed using the standard convention for illustrating the oxidation of the porphyrinogen skeleton. They show the formation of a conventional porphyrin, **2**, from the six-electron oxidation of the *meso*-tetraalkyltetrahydroporphyrinogen and the formation of artificial porphyrins, **3** and **4**, from the two- and four-electron oxidation of the *meso*-octaalkylporphyrinogen.

Two- and four-electron-oxidized forms of porphyrinogen, like those shown in *Scheme 1*, would have no chance of being trapped in the case of *meso*-tetraalkyltetrahydroporphyrinogen, although they may be eventually identified in the *meso*-octaalkyl form. *Scheme 2* gives a more clear picture of the oxidation of

Scheme 1. The Four- and Six-Electron Oxidation of the Porphyrinogen Skeleton



Scheme 2. The Four-Electron Oxidation of Porphyrinogen Skeleton



meso-octaalkylporphyrinogen tetraanion by two and four electrons in which no removal of atoms is required.

Such a redox scheme is correct if one assumes that the tetraanion is bound to the transition metal, which should assist the oxidation (*vide infra*) of the porphyrinogen skeleton. We anticipated that oxidation by two electrons leads to the formation of a cyclopropane unit, which can

undergo the reverse reduction with the cleavage of the same C-C bond. Therefore, each cyclopropane unit within the artificial porphyrin acts as a two-electron shuttle. Let us first discuss the overall metal-assisted pathway and the reaction conditions leading to the generation of 'artificial porphyrins' [2].

meso-Octamethylporphyrinogen was discovered by A. Baeyer in 1886 [4], and

until recently the molecule and its homologues have been almost ignored by chemists [5]. In this report, we consider the octaethyl derivative, $[\text{Et}_8\text{N}_4\text{H}_4]$, **8**, and examine its remarkable transformations, which are assisted by transition metals (Scheme 3).

The lithiated form of **8**, $[\text{Et}_8\text{N}_4\text{Li}_4(\text{thf})_4]$, (thf = tetrahydrofuran) a complex aggregate lithium which is η^5 -, η^3 -, and η^1 -bonded to different pyrrolyl units, provides a suitable compound to enable an investigation of the transition-metal complexation by *meso*-octaethylporphyrinogen in aprotic conditions [6]. The redox chemistry of *meso*-octaethylporphyrinogen skeleton will be exemplified using complexes **9** ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). Each complex contains a transition metal in the

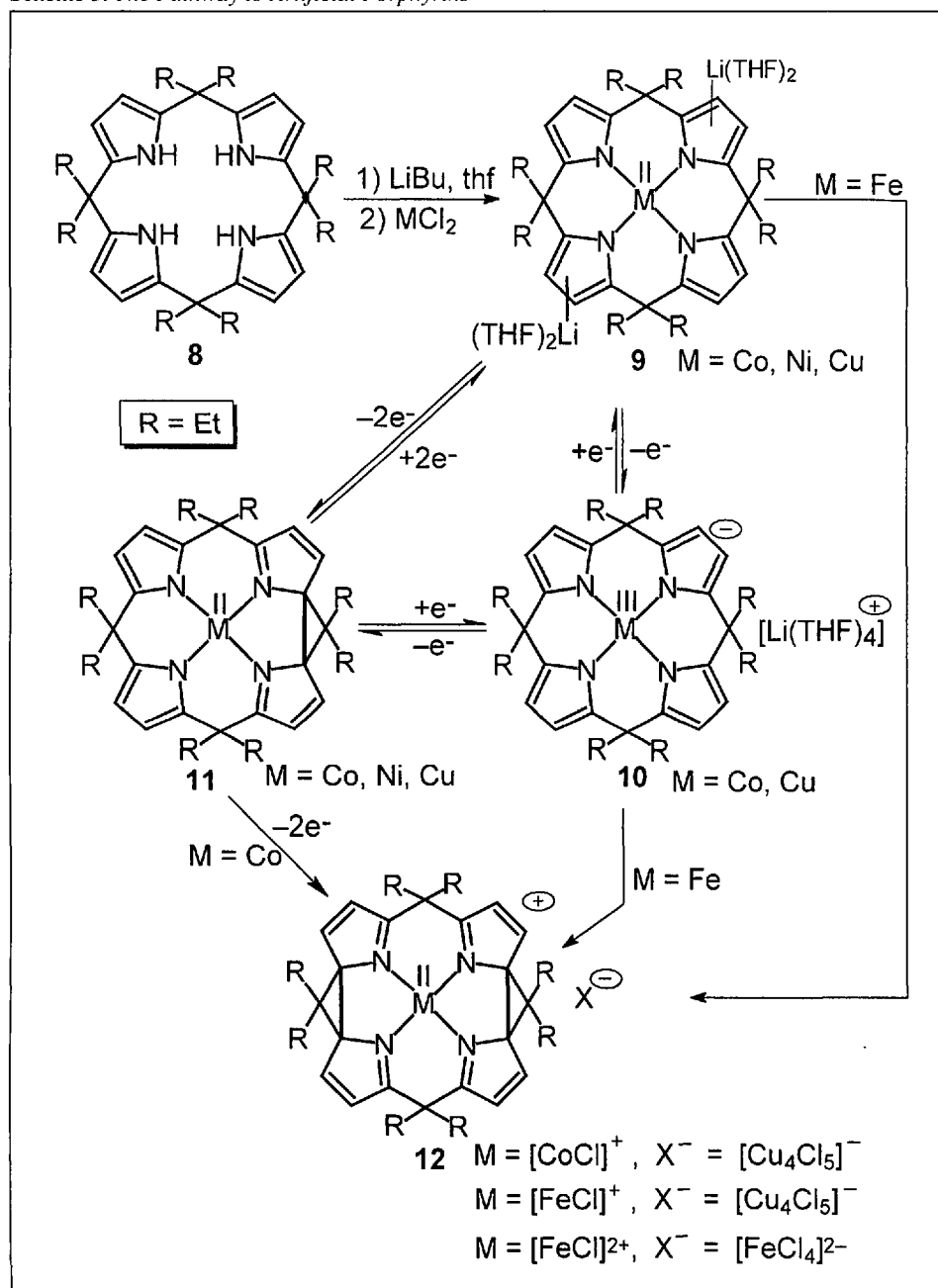
center while each lithium cation is η^3 -bonded to a peripheral pyrrolyl anion [2][4][7]. The reaction of **9** ($M = \text{Co}, \text{Ni}, \text{Cu}$) with *p*-benzoquinones is a two-electron oxidation leading to the introduction of a cyclopropane ring, as shown in complex **11**, $[\text{Et}_8\text{N}_4(\Delta)\text{M}]$ (Δ = cyclopropane, $M = \text{Co}, \text{Ni}, \text{Cu}$). Although the formation of a cyclopropane unit is an overall two-electron oxidation (see Scheme 2), it proceeds *via* two monoelectronic steps, the first being the metal(II)-to-metal(III) oxidation (see complex **10**) followed by the formation of a cyclopropane unit and the concomitant reduction of metal(III) to metal(II) [2c]. The monoelectronic pathway has been elucidated by using CuCl_2 as oxidizing agent in the case of Cu^{II} and Co^{II} , which have an accessible +3 oxida-

tion state [2c]. The monoelectronic pathway emphasizes the effectiveness of the metal-to-ligand intramolecular electron transfer. In addition, we can reasonably assume that the cyclopropane unit is masking a +2 oxidation state for the bound metal.

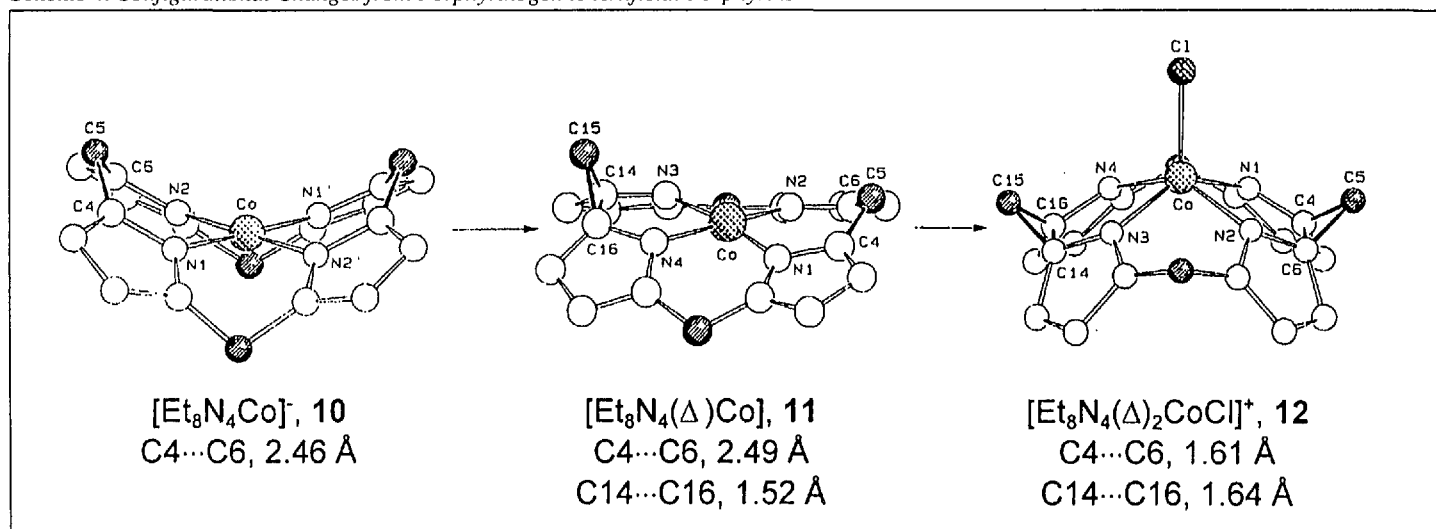
We have also discovered an important redox relationship which exists between the metal and the ligand, as a function of the solvent only [2c]. In toluene, complex **10** disproportionates to complexes **9** and **11**, a reaction which does not occur when Li is complexed by 12-crown-4. Complex **10** forms quantitatively in the reverse reaction by mixing equimolar amounts of complexes **9** and **11** in coordinating solvents like thf . These facts emphasize the role of the Li cation in assisting intermolecular redox processes as a function of the binding ability of the solvent. A number of examples of alkali cations which are bound to the periphery of metal-porphyrinogen units have been structurally characterized. However, in our case, the redox relationship between **9**, **10**, and **11** can also be observed in the stepwise monoelectronic reduction of **11** to **10**, then to **9**, with Li metal. The fully oxidized form of *meso*-octaalkylporphyrinogen containing two cyclopropane units, and using CuCl_2 as oxidant, has only been obtained for Co and Fe. The use of CuCl_2 gives the inconvenient cluster $[\text{Cu}_4\text{Cl}_5]^-$ as a counteranion for **12** bonded to the four pyrrolic C=C bonds [2d]. However, $[\text{Cu}_4\text{Cl}_5]^-$ does not impart any extra stabilization to the bicyclopropane form, as evidenced by the isolation of **12**· $[\text{FeCl}_4]^{2-}$ [2d].

Although their exploitation is at an early stage, these preliminary accounts on the discovery of 'artificial porphyrins' allow one to catch a glimpse of the potential of such molecules in electron-transfer processes. A few facts should be emphasized: *i*) unlike for the porphyrinogen/porphyrin couple, in the *meso*-octaalkylporphyrinogen/artificial porphyrin couple the redox interconversion between the two forms is energetically quite easy. It is particularly attractive to follow the small conformational changes which parallel the conversion of porphyrinogen into artificial porphyrins, as shown in Scheme 4 for the case of a cobalt/porphyrinogen complex. Such small conformational changes may be one of the reasons for the easy porphyrinogen/artificial porphyrin interconversion; *ii*) the cyclopropane unit functions as a two-electron shuttle, thus the C-C bond formation and breakage behave as a molecular battery; *iii*) the metal-to-ligand synergism allows one to use the cyclopropane to mask high oxidation states of the metal,

Scheme 3. The Pathway to Artificial Porphyrins



Scheme 4. Configurational Changes from Porphyrinogen to Artificial Porphyrins



each cyclopropane unit having a contribution of +2 *per metal*; *iv*) the redox processes can be tailored to occur exclusively at the metal, at the ligand, or at the metal-ligand sites; *v*) the cleavage and formation of cyclopropane can be used for planning long-range electron-transfer processes; *vi*) the appropriate site opening of the cyclopropane may lead to a ring-contracted corrinoid-type skeleton, or to other modifications of the porphyrinogen frame.

3. Future Prospects

The work that is described has only been briefly sketched. The future prospects for this field are quite exciting, and some of major directions may be:

- i*) the exploitation of the artificial porphyrins;
- ii*) the chemistry of the porphyrinogen-metal complexes allowing the development of systems whose redox chemistry is associated to the formation and cleavage of C–C bonds, as in the artificial porphyrins;
- iii*) the use of transition metal/porphyrinogen complexes as carriers for polar organometallics, ion-pairs, and salts leading to the development of novel synthetic methodologies in organic chemistry [8].

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