Porphyrinoids

Deutsche Ausgabe: DOI: 10.1002/ange.201503624
Internationale Ausgabe: DOI: 10.1002/anie.201503624

The Corrole Radical

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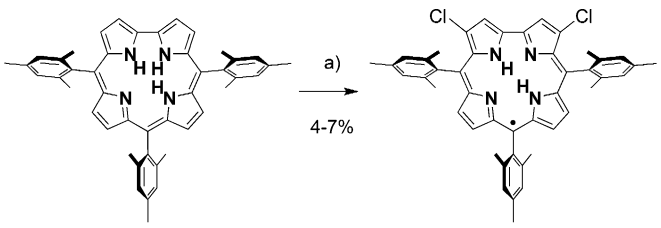
Abstract: *The reaction of 5,10,15-trimesitylcorrole (H_3cor) with tungsten hexachloride and tungsten hexacarbonyl resulted in the unexpected formation of the 3,17-dichloro-5,10,15-trimesitylcorrole radical (H_2cor*) as an air-stable product. X-ray crystallography proved the planarization of the corrole radical structure, which was rationalized by the reduced steric hindrance of two versus three hydrogen atoms inside the N_4 cavity. Although the aromaticity was lost, no specific changes in C–C or C–N bond distances could be observed. The regioselectivity of the two-fold chlorination is the result of the nucleophilic attack of chloride ions to an oxidized corrole macrocycle, and is supported by DFT results. The corrole radical acts as a dianionic ligand and allows the insertion of the divalent zinc(II) cation, which usually does not form neutral corrole complexes.*

Organic radicals currently experience a renaissance in porphyrinoid chemistry. Attempts to investigate and stabilize porphyrin complexes with radical ligand character have been reported in studies related to the natural occurrence of species such as Compound I in the catalytic cycles of heme-dependent monooxygenases and peroxidases.[1] Stable radicals have now been reported for contracted and expanded porphyrinoids,[2] pointing to a new realm in porphyrinoid research. Corroles are one-carbon-atom-short analogues of porphyrins.[3] One of the most intriguing characteristics of corrole ligands is the non-innocent or radical character evident in many coordination compounds. Corrole radical dianions have been found as ligands in copper, nickel, manganese, and iron complexes of corrole, simulating the stabilization of high-valent transition-metal ions.[4] Despite the many cases of metal-stabilized corrole radical dianions, the respective ligand radical H_2cor has thus far remained elusive.

During our investigations of the coordination chemistry of metal porphyrinoids,[5] we observed an unexpected product **2** from the reaction of 5,10,15-trimesitylcorrole (H_3cor, **1**),[6] tungsten hexachloride, and tungsten hexacarbonyl.[7] When compound **1** in benzonitrile was heated at reflux for 8 h in the presence of an excess of the metal reagents, the product formed in 4–7% yield. It was isolated from the reaction mixture by column chromatography on silica gel, on which it appeared as a nonpolar amber-colored band. Crystallization from dichloromethane/methanol gave the new compound as black microcrystals (Scheme 1). When we repeated the experiment, we found that traces of water are required for the successful formation of the product.



1 **2**

Scheme 1. Formation of the 3,17-dichloro-5,10,15-trimesitylcorrole radical **2** from corrole **1**. a) WCl_6, $W(CO)_6$ (2:1), benzonitrile, 200 °C, 8 h.

The new compound was analyzed by different techniques. ESI(+) mass spectrometry provided an $[M^+]$ ion with a mass of $m/z = 719$ u and a characteristic signal pattern for the presence of two chlorine atoms. From the obtained mass, the formula $C_{46}H_{41}Cl_2N_4$ resulted, which indicated the loss of one hydrogen atom. The EPR spectrum of the new compound (X-band, 292 K) provided clear evidence for a typical organic π radical H_2cor* (**2**) with $g_{iso} = 2.0032$ (see the Supporting Information).

Single crystals of **2** suitable for X-ray diffraction were obtained by recrystallization from chloroform/*n*-hexane. Different views of the molecular structure are shown in Figure 1. Only two NH groups are present in the cavity of the macrocycle. The *trans* arrangement of the protons is evident from the differences of the C–N bond length, which are alternatingly short and long at the imino nitrogen atom positions N1 and N3, but aligned for N2 and N4. The C–C bond lengths of **2** show no localization of the radical and are similar to those found in other free-base corroles.[8]

A second feature of the molecular structure of **2** is the high degree of planarity, which is a consequence of the absence of the third proton inside the N_4 cavity. A comparison with known structures of free-base corroles proved to be instructive (Figure 2, Table 1). The angles χ, ψ, and ψ', which define the nonplanar distortions[9] in the macrocycle, are decreased to a maximum value of 2.5° in **2**, while at least two of these angles are larger than 10° in all other corrole structures. Figure 3 shows this phenomenon in a linear display of the corrole framework.

The regioselectivity of the substitution at positions 3 and 17 of the macrocycle follows the same pattern as described for reactions of corroles in the presence of the oxidants Ag^+ and $N(4\text{-}BrC_6H_4)_3SbCl_6$.[10] In contrast, the electrophilic substitution leading to formyl or sulfonyl derivatives usually results in

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503624.

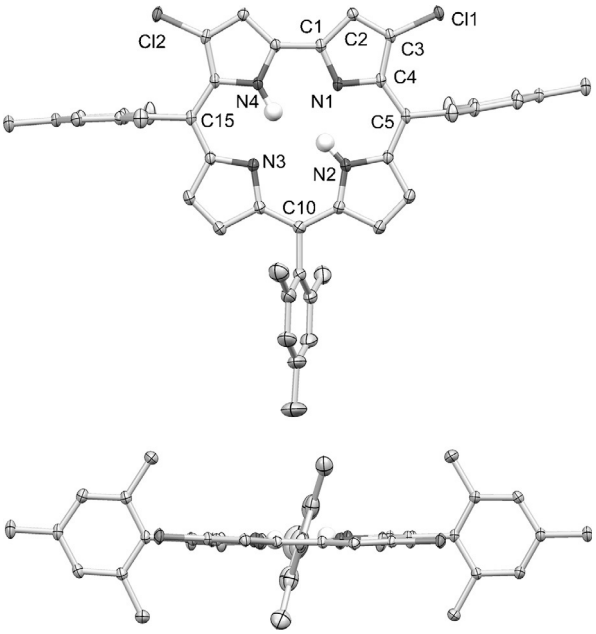


Figure 1. Molecular structure of corrole radical **2** (different views; carbon-bound hydrogen atoms removed for clarity; thermal ellipsoids set to 50% probability). Selected bond lengths [Å] and angles [°]: N1–C1 1.3378(17), N1–C4 1.3757 16), N2–C6 1.3689(17), N2–C9 1.3667(18), N3–C11 1.3678(18), N3–C14 1.3775(17), N4–C16 1.3726(17), N4–C19 1.3444(17), C2–C3 1.3732(18), C7–C8 1.373(2), C12–C13 1.371(2), C17–C18 1.3803(19), C1–C19 1.4395(17), C4–C5 1.3917(18), C5–C6 1.4294(19), C9–C10 1.415(2), C10–C11 1.4188(19), C14–C15 1.4285(18), C15–C16 1.4049(19), C3–Cl1 1.7163(13), C17–Cl2 1.7119(13); C1-N1-C4 109.47(11), C6-N2-C9 109.66 (12), C11-N3-C14 108.09(11), C16-N4-C19 110.94(11), C4-C5-C6 121.34(12), C9-C10-C11 126.52(13), C14-C15-C16 121.22(12).

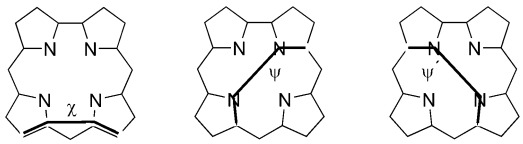


Figure 2. Definition of angles χ, ψ, and ψ' used to describe the nonplanar distortion of corroles.[8]

Table 1: Angles χ, ψ, and ψ' of radical **2** and of selected triarylcorroles.

Compound	χ [°]	ψ [°]	ψ' [°]
radical **2**	1.4	0.2	2.5
5,10,15-tri(C_6H_5)corrole[8a)]	37.5	23.5	7.4
5,10,15-tri(C_6F_5)corrole[8b)]	14.1	18.2	13.7
5,10,15-tri(C_6F_5)corrole[8c)]	14.6	7.8	14.3
5,10-di(C_6F_5)-15-(4-MeOC_6H_4)corrole[8c)]	31.5	4.5	13.0
5,10-di(C_6F_5)-15-(4-MeOC_6H_4)corrole[8c)]	26.7	26.7	21.3
5,10,15-tri(2,6-$C_6F_2H_3$)corrole[8d)]	15.6	8.1	11.0
5,10,15-tri(C_3F_7)corrole[8e)]	31.7	21.8	8.3
5,15-di(C_6F_5)-10-(3-$H_3C_2C_6H_4$)corrole[8f)]	36.8	2.4	34.3
5,15-di(C_6F_5)-10-(3-thienyl)corrole[8g)]	40.6	6.2	15.3

3,18 regioisomers.[10c)] Therefore, we propose a stepwise radical mechanism for the formation of **2**, consisting of two turnovers of an initial oxidation of the macrocycle followed by chloride attack and subsequent abstraction of a hydrogen atom (Scheme 2).

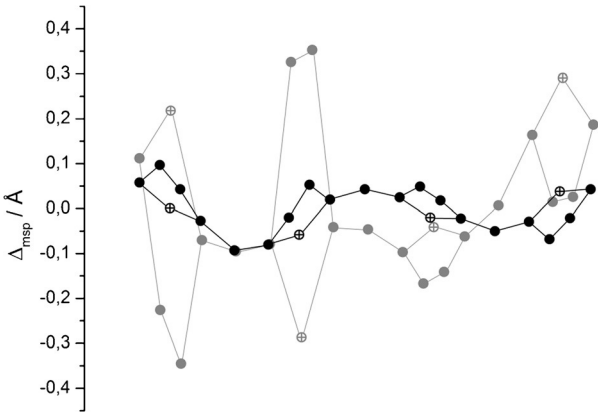
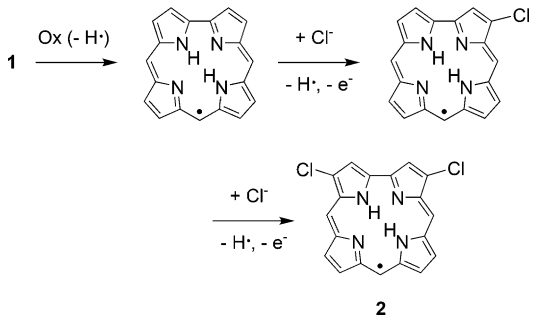


Figure 3. Linear display of the deviations of the macrocycle atoms of radical **2** (black) and of *meso*-triphenylcorrole[8a)] (grey) from the $C_{19}N_4$ least-squares planes.



Scheme 2. Mechanistic proposal for the regioselective formation of **2**.

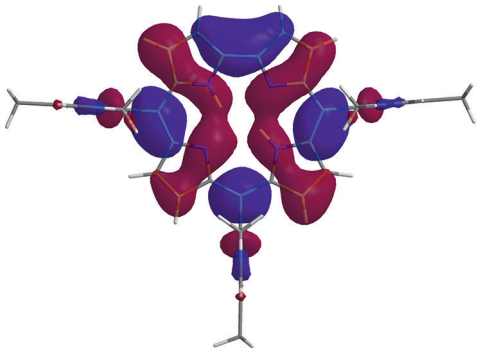
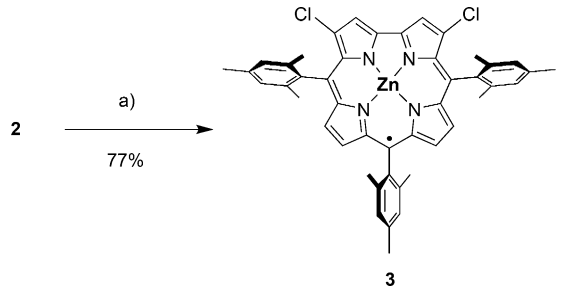


Figure 4. Graphical representation of the singly occupied molecular orbital (SOMO) from DFT calculations (B3LYP/6-311G(d,p))[11] on **2**.

DFT calculations on the H_2cor* radical **2** led to the singly occupied molecular orbital (SOMO) shown in Figure 4. The C–Cl positions are characterized by the large coefficients of this orbital. The question as to why the chlorination of the corrole radical stops after the second substitution cannot be fully answered. The results of the calculation indicate that further attack of a chloride ion on the electrophilic radical (or its protonated form) should take place on the already substituted positions, so that no higher chlorinated compounds can form on the pathway postulated in Scheme 2.

The divalent nature of radical **2** tempted us to investigate the formation of the elusive neutral zinc(II) corrole.[12] Treatment of **2** with zinc acetate dihydrate in pyridine resulted in a color change from amber to olive. Chromatography and recrystallization from dichloromethane/*n*-hexane resulted in the desired zinc corrole **3** in 77% yield as a dark solid (Scheme 3). Comparable to **2**, the radical zinc complex **3** turned out to be remarkably stable in air, even at ambient temperature, and decomposed only slowly during crystallization attempts.



Scheme 3. Metalation of **2** with zinc acetate dihydrate. a) $Zn(OAc)_2{\cdot}2\,H_2O$, pyridine, 50 °C, 2 h.

The signal pattern of the ESI(+)-MS molecular ion $C_{46}H_{39}Cl_2N_4Zn^+$ indicates the binding of a zinc ion in the N_4 cavity. The radical nature of the complex was not affected, which was verified by a signal at $g_{iso} = 2.0029$ in the X-band EPR spectrum. The optical spectrum of **3** shows a split Soret band as for **2** with a slight red shift of 13 nm, in addition to weak and undefined Q bands between 500 nm and 800 nm (Figure 5).[13] Other than in the porphyrin series, where the Soret band of zinc complexes is very intense with ε values of 400 000 $L\,mol^{-1}\,cm^{-1}$ and more,[14] the absorption coefficient of the zinc chelate **3** is in the same range as for the free-base radical **2**.

The corrole ligand has now conquered significant areas of the periodic table of elements. As part of this development, the bonding interactions to a series of lanthanides and 5d metals (Hf, W, Os, Pt, and Au) have been reported in recent

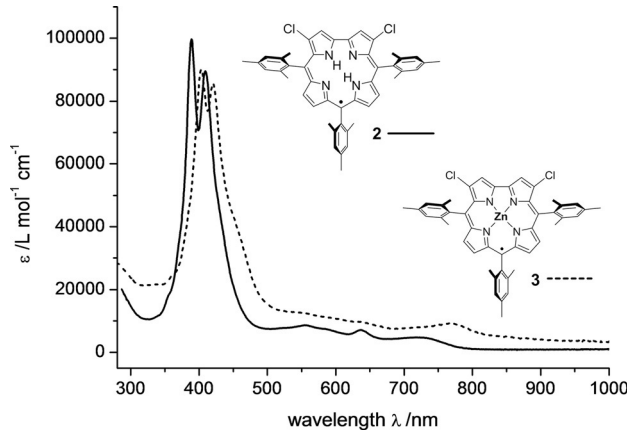


Figure 5. Optical spectra (CH_2Cl_2) of the free-base radical **2** and the radical zinc corrole **3**.

years.[6,15] With the stable, free-base radical **2** and the zinc chelate **3**, we were now able to close two further prominent gaps in the systematic exploration of this fascinating macrocycle, and could pave one more avenue to the field of potential corrole materials and catalysts.[16]

Keywords: corroles · macrocycles · nitrogen ligands · porphyrinoids · radical

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 8213–8216
Angew. Chem. **2015**, *127*, 8331–8334

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Received: April 21, 2015
Published online: June 12, 2015

