Reductive demetallation of Cu-corroles—a new protective strategy towards functional free-base corroles†

Thien Huynh Ngo, Wim Van Rossom, Wim Dehaen* and Wouter Maes

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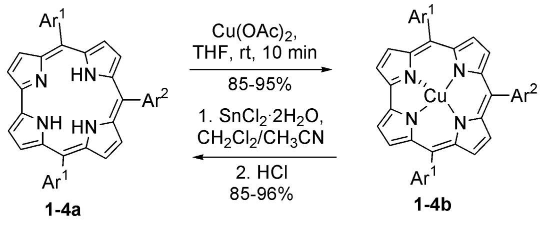
A novel procedure for the reductive demetallation of Cu-*meso*-triarylcorroles has been disclosed. The reversible sequence copper metallation/demetallation was proven to be an effective protection/deprotection strategy towards sophisticated functionalized free-base corroles.

Corroles, ring contracted porphyrin analogues lacking one *meso*-carbon atom, have recently evolved from rare macrocycles to widely studied and attractive porphyrinoids with particular applications.[1] The renewed interest in corroles and their properties has been initiated and facilitated by the vast amount of progress that has been achieved for the synthesis and functionalization of *meso*-triarylcorroles during the last decade.[2] Post-macrocyclization functionalizations of the corrole skeleton, either elaborations of the *meso*-groups or the introduction of substituents on the β-pyrrolic positions, are often performed on the generally more stable metallocorroles rather than their free-base (Fb) counterparts, to protect the trianionic corrole cavity from (de)protonation or to avoid extensive (oxidative) fragmentation of the rather fragile corrole framework.[2] For certain applications, it might however be required to obtain a functionalized Fb corrole, *e.g.*, to benefit from its (enhanced) fluorescence. Functionalized Fb corroles would also enable the introduction of particular desirable metal ions, resulting in paramagnetic metallocorrole complexes, at the final stage of the synthetic protocol only, allowing NMR verification at every step throughout the reaction sequence. In porphyrin chemistry, this problem is commonly solved by the reversible coordination of metal ions in the porphyrinato ligand. Unfortunately, removal of a metal from the corrole cavity after functionalization is often problematic, and no general corrole demetallation strategies have been established yet. To date, only demetallations of Mn-, Ag-, and, very recently, Cu-corroles have been reported under acidic conditions, but the general scope of these procedures remains very limited.[3,4]

meso-4,6-Dichloropyrimidin-5-yl-substituted porphyrinoids are versatile building blocks for the preparation of sophisticated functionalized porphyrinoids and macrostructures, due to the ease and broad scope of post-macrocyclization synthetic modifications, *e.g.*, nucleophilic aromatic substitution (S_NAr) and Pd-catalyzed cross-coupling reactions, that can be performed on the dichloropyrimidinyl moieties.[5,6] The synthesis of *meso*-pyrimidinyl-substituted A_2B-corroles has recently been optimized and various functionalization reactions have been performed on the Cu-metallated pyrimidinylcorroles in high yields.[6b] However, when the same reactions were performed on the Fb analogues, a significant drop in the yield of the substituted pyrimidinylcorrole derivatives was observed, due to decomposition of the less stable Fb corroles. Hence, it might be advantageous to perform all functionalization steps on the Cu-metallated pyrimidinylcorroles and remove the copper metal, after its protective action, from the corrolato ligand in the last step.

Copper is often used as the metal of choice for the synthesis and functionalization of metallocorroles, due to its easy insertion, the absence of a (labile) axial ligand and its diamagnetic ground state.[6b,7] Cu-metallation of corroles has usually been performed with copper(II) acetate as the metal source in pyridine at room temperature,[6b,7a,d–h,j–l] and Cu-corroles are often oversimplified to Cu(III)-species with a thermally accessible paramagnetic triplet excited state.[7] The electronic ground state of Cu-corroles has been revisited recently.[8]

During the course of our continuing studies on pyrimidinylcorroles, it was discovered that copper insertion can also be performed in tetrahydrofuran in an even more efficient way. The procedure involves the use of 3 equivalents of anhydrous copper(II) acetate, which is simply stirred with the Fb corrole in THF for 10 minutes under an inert atmosphere, and this method could easily be extended to other *meso*-triarylcorroles. The desired Cu-corroles were obtained in excellent yields ranging from 85–95% after flash column chromatographic purification (Scheme 1).†



1 Ar^1 = mesityl, Ar^2 = 4-aminophenyl
2 Ar^1 = mesityl, Ar^2 = 4-cyanophenyl
3 Ar^1 = mesityl, Ar^2 = 4,6-dichloro-2-thiomethylpyrimidin-5-yl
4 Ar^1 = Ar^2 = 2,6-dichlorophenyl

Scheme 1 Cu-metallation and demetallation of *meso*-triarylcorroles **1–4**.

Inspired by the straightforward demetallation of metalloporphyrins, several attempts were undertaken to demetallate Cu-pyrimidinylcorroles with different (mixtures of) acids. After using TFA/H_2SO_4, HCl (aq) or BBr_3 in dichloromethane, slow partial demetallation was observed by electrospray mass spectrometry (ESI-MS), but, unfortunately, no satisfying method resulting in

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Molecular Design and Synthesis, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001, Leuven, Belgium. E-mail: wim.dehaen@chem.kuleuven.be; Fax: +32 16327990; Tel: +32 16327439

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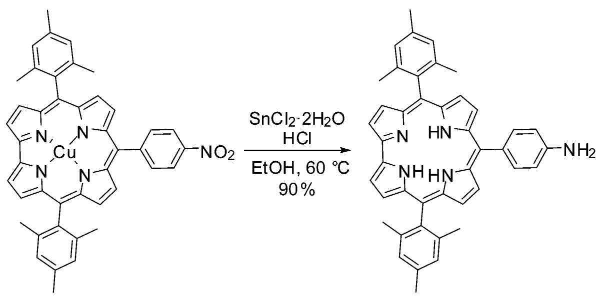
the successful isolation of the Fb analogues in an acceptable yield could be established. Very recently, Paolesse and co-workers reported the (almost complete) removal of Cu (and also Mn and, to some extent, Fe) from 5,10,15-triphenyl- and β-octaalkylcorroles under rather harsh acidic conditions (H_2SO_4 in $CHCl_3$).[3c] When their procedure was, however, applied to Cu-pyrimidinylcorrole **3b**, in our hands, no smooth demetallation was obtained. Although partial copper removal was observed by ESI-MS, TLC analysis showed a mixture of (non-fluorescent) products.

A solution to our quest for appropriate demetallation conditions was provided in a serendipitous way. Upon reduction of Cu-10-(4-nitrophenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole (**5b**), again easily obtained from the Fb analogue **5a**[9,10] by our $Cu(OAc)_2$/THF protocol (95% yield), to the *p*-aminophenyl-functionalized analogue, according to a standard method ($SnCl_2{\cdot}2H_2O$ and concentrated aqueous HCl in ethanol at 60 °C) described for the Fb nitrocorrole **5a**,[11] simultaneous demetallation and reduction of the nitro group was observed and Fb aminocorrole **1a**[11,12] was obtained in 90% yield (Scheme 2).



5b

1a

Scheme 2 Reduction and simultaneous demetallation of *meso*-*p*-nitrophenyl-substituted A_2B-corrole **5b**.

After this initial result, it was tried to extend the Cu-demetallation method to other *meso*-triarylcorroles. First of all, the demetallation conditions were applied to Cu-5-(4,6-dichloro-2-thiomethylpyrimidin-5-yl)-A_2B-corrole **3b**,[6b] which was easily synthesized from the Fb derivative **3a** in 94% yield (Scheme 1). When the demetallation procedure was performed in ethanol or acetonitrile, a sluggish reaction and incomplete copper removal were observed. To ensure sufficient solubility of both the tin salt and the Cu-corrole, the solvent system was changed to an acetonitrile/dichloromethane mixture (2:1). On stirring **3b** with 10 equivalents of $SnCl_2{\cdot}2H_2O$ in the presence of HCl at room temperature, complete demetallation was observed after 10 minutes and, after work-up and flash column purification, Fb analogue **3a** was obtained in an excellent 94% yield. No demetallated corrole could be obtained on omitting the reductant or HCl from the reaction mixture, both components are essential for a successful demetallation. The reductive conditions seem to destabilize the corrolato copper complex resulting in the (protonated) Fb corrole. Similar reductive demetallation of Cu(II)-porphyrins has been known for quite some time.[13] On the other hand, various electrochemical studies have indicated that Cu-corroles undergo a reversible metal-centered one-electron (first) reduction, formally assigned as a Cu(III)–Cu(II) process, while the (first) oxidation is corrole-centered.[7b,d,f,g,j–l,14] Cu(III)–Cu(II) reduction could also be achieved chemically.[7g] Based on these observations, a Cu(III)–Cu(II) transition is likely to be involved in the initial step of the demetallation reaction. Demetallation of Cu-corroles has, however, never been observed during chemical or electrochemical reduction studies.

The demetallation progress was monitored by UV-vis spectroscopy (Fig. 1). No changes in the absorption spectrum were observed on addition of $SnCl_2{\cdot}2H_2O$, while 10 minutes after the addition of HCl a shift in the Soret-band from 404 to 419 nm was noticed, in accordance with the protonated Fb corrole. The reaction seems to occur completely and no traces of the Cu-corrole were detected.

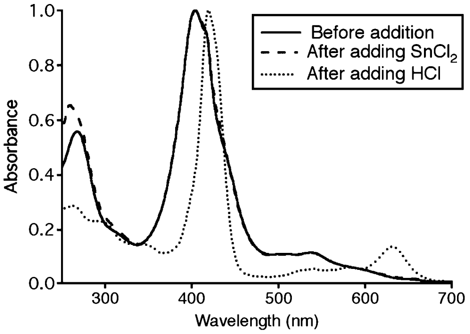
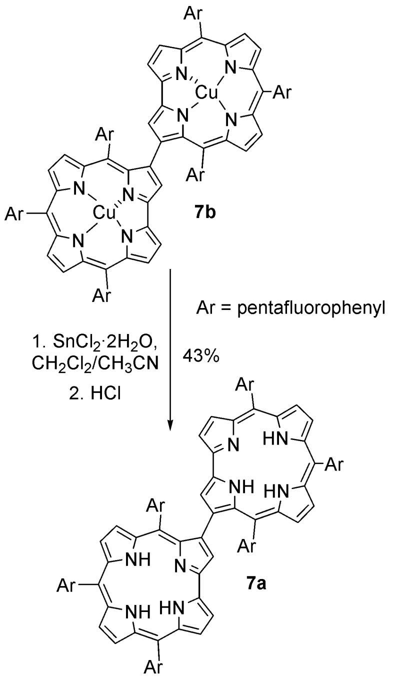


Fig. 1 UV-vis absorption spectra taken during demetallation of **3b**.

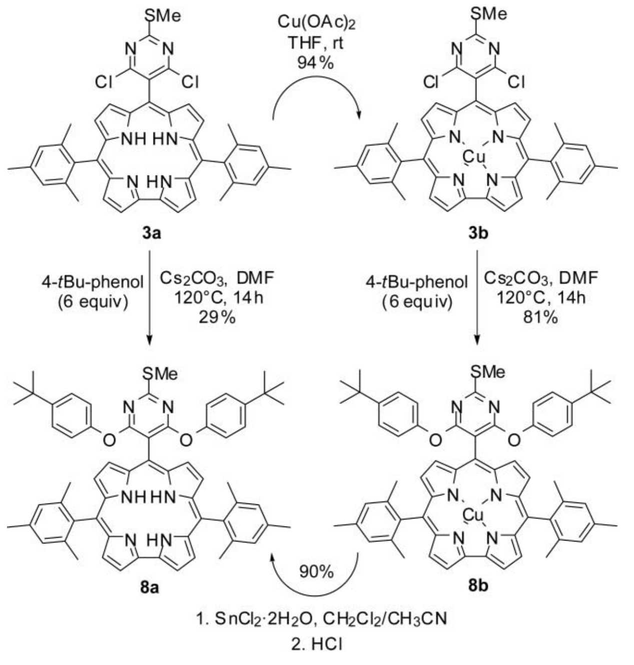
The demetallation method could easily be extended to other, more generally applied Cu-triarylcorroles, *e.g.*, **1b**, **2b**, **4b** (Scheme 1).†‡ The obtained yields were very high to nearly quantitative (85–96%). Completion of the demetallation reaction can be verified by ESI-MS or TLC, since the Fb corroles show a (slightly) lower R_f value, and a colour change from dark brown to green, illustrative for the protonated Fb corrole, can be observed.§ For none of the conducted demetallation reactions, isocorrole species, as reported by Paolesse *et al.* for the removal of copper under acidic conditions,[3c] could be detected (by ESI-MS).

A particular case is formed by 5,10,15-tris(pentafluorophenyl)corrole (tpfc),[15] the most intensively studied corrole to date. According to a previous study by Gross and co-workers, metallation of H_3(tpfc) **6a** with $Cu(OAc)_2{\cdot}H_2O$ (3 equiv) in pyridine at reflux temperature for 10 minutes affords 30% of Cu-corrole **6b**, while 40% of the corresponding dinuclear 3,3′-corrole dimer **7b** is obtained.[7g] The Cu(II) π-cation radical character of Cu-corroles is likely to be responsible for this dimerization process.[16] The same reaction carried out at room temperature in pyridine for 30 minutes produces only traces of the bis(corrole) **7b** and Cu(tpfc) **6b** is isolated in 73% yield. When the metallation of H_3(tpfc) **6a** was carried out in THF at room temperature, **6b** was obtained in 82–91% yield, together with small amounts of dimer **7b**, varying from 1–7%. Demetallation of Cu(tpfc) **6b** under the general conditions afforded H_3(tpfc) **6a** in 54% yield. The lower demetallation yield compared to all other investigated corroles seems to reflect the modest stability of Cu(tpfc).[7g] Care has to be taken to perform both the metallation and demetallation reaction for tpfc as quickly as possible. As for pyrimidinylcorroles, application of the demetallation conditions reported by Paolesse and co-workers did not give satisfying results for Cu(tpfc) either.[3c]

On applying the demetallation conditions to bis(Cu-corrole) **7b**, the demetallated derivative **7a** was obtained in 43% yield after flash chromatographic purification (Scheme 3). The modest yield



Scheme 3 Demetallation of bis(Cu-corrole) **7b**.



Scheme 4 Nucleophilic aromatic substitution followed by demetallation.

could again be attributable to the limited stability of the (Cu-) corrole dimer. It has to be noticed, however, that this metallation/demetallation procedure is still superior to the previously reported method affording the same β,β′-dimer **7a** (H_3(tpfc) in 1,2,4-trichlorobenzene at 200 °C for 6 h, 2% yield of the 3,3′-dimer).†[16c]

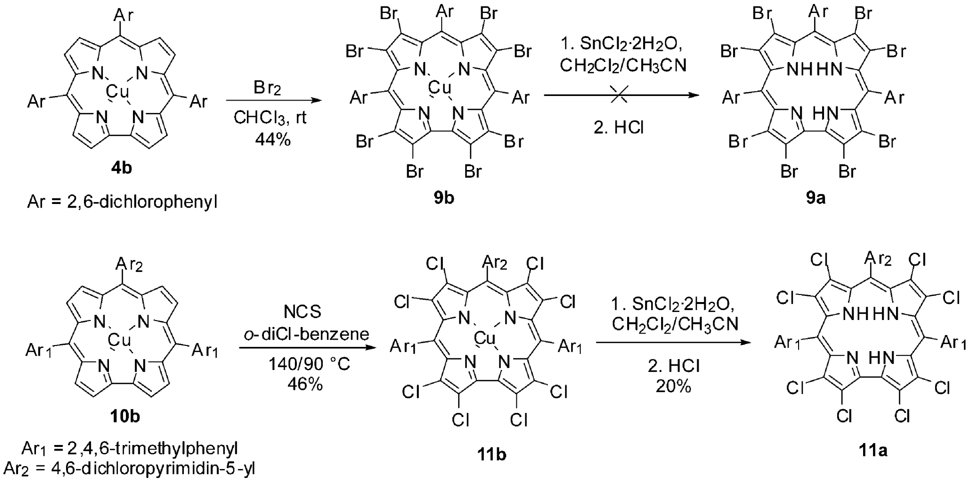
As mentioned above, most of the post-macrocyclization functionalizations of corroles have been performed on metallocorroles due to their improved stability compared to their Fb analogues. Moreover, a number of Cu-catalyzed reactions, *e.g.*, the Liebeskind-Srogl reaction on pyrimidinylcorroles,[6b] inevitably result in copper insertion when performed on Fb corroles, limiting the synthetic accessibility of functionalized Fb corroles. However, since demetallation of Cu-corroles can now smoothly be achieved, the copper metallation/demetallation sequence can be used as a protection/deprotection strategy towards previously difficultly accessible or even inaccessible Fb corroles. As a proof-of-principle, nucleophilic and electrophilic aromatic substitution reactions were carried out on Cu-metallated *meso*-triarylcorroles, followed by demetallation to obtain novel functionalized Fb corroles.

After S_NAr on the *meso*-dichloropyrimidinyl moiety of Cu-corrole **3b** with 4-*tert*-butylphenol (81% yield), according to our previously optimized conditions,[6b] the general demetallation procedure was used to obtain substituted Fb corrole **8a** in 90% yield (Scheme 4).† The overall yield for the three-step procedure involving subsequent metallation, S_NAr and demetallation is as high as 68%. When the S_NAr reaction was carried out directly on Fb corrole **3a**, only 29% of the pursued Fb corrole **8a** could be isolated.

The introduction of substituents on the β-pyrrolic peripheral positions of corroles has already been performed on both metal-free and metallocorroles, and often shows a high degree of regioselectivity not seen for analogous porphyrins.[7d,m,17] The scope of electrophilic aromatic substitution (S_EAr) reactions on Fb corroles is rather limited due to their inherent lower stability and Fb corroles often show a different and distinct reactivity. In some cases, however, Fb corroles were still preferred since demetallation was hard to achieve.

To prove the usefulness of our demetallation strategy for the synthesis of β-substituted Fb corroles, corrole bromination was initially chosen as an example. The bromination of corroles has been found to provide higher yields for metallocorrole derivatives rather than their Fb analogues.[7d,17b,d,f,i,j,l] Moreover, a corrole-isocorrole equilibrium has been observed for bromination of Fb corroles.[17b] Cu-tris(2,6-dichlorophenyl)corrole (Cu(tdcc) **4b**) was converted to the octabrominated derivative **9b** according to a procedure reported by Ghosh *et al.* (44% yield, Scheme 5).[7d] In the UV-vis spectrum, both absorption bands show a bathochromic shift of 23 nm upon full bromination.[7d] Demetallation of **9b** under the general conditions resulted, however, in simultaneous reductive demetallation and partial debromination, affording a mixture of polybrominated (mostly tetra- and pentabromo) Fb corroles. Similar partially brominated metallocorroles have recently been obtained by bromination of Ge-triphenylcorrole.[17l] Sequential reductive debromination of octabrominated Cu-corroles has also been observed electrochemically, albeit at much more negative potentials than the Cu(III)-Cu(II) reduction process.[14b]

We then turned our focus to octachlorinated Cu-corroles, hoping that the β-C–Cl bonds would be more resistant towards the applied reductive conditions. Chlorination of corroles has, to our knowledge, not been reported yet for aromatic corroles.[16d] On applying standard chlorination conditions previously used for metalloporphyrins (*N*-chlorosuccinimide in *o*-dichlorobenzene at high temperature),[18] fully chlorinated Cu-A_2B-pyrimidinylcorrole **11b** was prepared in 46% yield. Running the reaction overnight at 140 °C with a higher excess of *N*-chlorosuccinimide resulted in partial overhalogenation, probably due to chlorination of the mesityl moieties. The Soret band of **11b** is red-shifted by 14 nm (to 417 nm) upon octachlorination. The polychlorinated



Scheme 5 Octahalogenation and subsequent demetallation of Cu-corroles **4b**, **10b**.

pyrimidinylcorrole was subjected to the demetallation conditions and again partial dehalogenation was observed. The reaction time and (the amount of) the reducing agent (*e.g.*, $CrCl_2$) were varied, but at every trial a mixture of Cu-corrole **11b**, Fb corrole **11a** and partially dechlorinated corroles was observed. The desired Fb octachlorocorrole could be isolated from this mixture in varying amounts by preparative TLC and shows a broad Soret-like band at 430 nm. When only one equivalent of $SnCl_2{\cdot}2H_2O$ was used, dechlorination could essentially be avoided and 20% of Fb corrole **11a** could be isolated after purification by column chromatography, while 70% of the starting corrole **11b** could be recovered.†

In summary, a new reductive demetallation strategy for Cu-*meso*-triarylcorroles has been established, that is more generally applicable and affords higher yields than other recently available procedures, and its beneficial use in synthetic strategies towards various complex functionalized corrole structures has been demonstrated.

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Notes and references

‡ General procedure for the demetallation of Cu-*meso*-triarylcorroles: To a solution of the respective Cu-corrole (0.05 mmol) in acetonitrile/dichloromethane (2:1; 15 mL), $SnCl_2{\cdot}2H_2O$ (113 mg, 0.5 mmol, 10 equiv) was added and the resulting mixture was stirred for 10 min at rt under Ar. Subsequently, concentrated aqueous HCl (1 mL) was added and stirring was continued for 10 min at rt under Ar. The completion of the demetallation process was monitored by ESI-MS and TLC.§ The mixture was diluted with diethyl ether, washed with water till neutral, dried over Na_2SO_4 and the drying agent was filtered off. The solvent was evaporated under reduced pressure and the pure Fb corroles were obtained as purple solids after flash column chromatography (silica, eluent CH_2Cl_2/heptane mixtures).

§ In a control experiment, it was verified that residual amounts of Cu-corrole **10b** can be detected in the presence of an excess of the analogous Fb corrole **10a** in ratios up to at least 1:20 by ESI-MS (±) (limit of detection 2–5 mol%).

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