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Manganese as a template: a new synthesis of corrole

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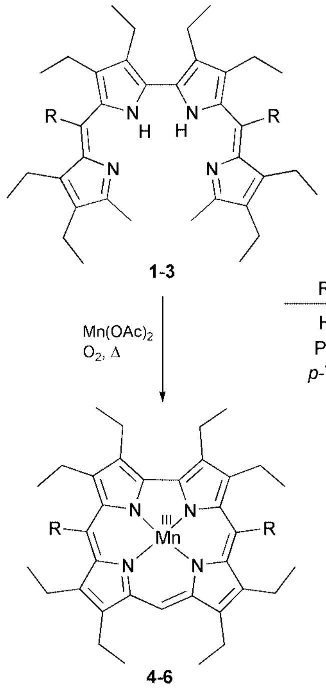
The reaction of 2,2′-bisdipyrrins 1, 2, and 3 with manganese(II) acetate tetrahydrate and molecular dioxygen yields the manganese(III)corroles 4, 5 and 6, which are readily demetalated to the respective free-base corroles.

The chemistry of corrole, the one-carbon short analogue of porphyrin, is currently one of the most flourishing fields in the porphyrin area.[1] Ever since the unexpected observation by Vogel *et al.* in 1994, that this trisanionic ligand stabilises unusually high oxidation states of transition metal centers like Fe(IV), Cu(III), and Co(IV),[2] the interest in this particular macrocycle has continuously increased. The synthetic pathways leading to corroles, however, are still rather small in number, albeit a large body of work has been conducted in recent years towards general approaches to differently substituted corroles, mainly by the groups of Paolesse[3] and Gross.[4] Very recently, the first applications of corroles as ligands in catalytically active transition metal complexes have appeared in the literature,[5] and the first multi-macrocyclic architectures using corroles as building blocks have also been achieved.[6] Today, the major methods used for the preparation of corroles are the oxidative cyclization of α,ω-didesoxybiladienes-*a*,*c* as described by Murakami,[7] and the strategy of Gross *et al.*, who developed the non-catalysed condensation of pyrrole and aromatic aldehydes as a one step procedure.[4] In the course of studies towards a synthetic entry into the corrole and corrin field, Johnson *et al.* attempted to cyclize 2,2′-bisdipyrrin complexes of Pd(II) as early as 1960, but received a palladium(II)-10-oxacorrole instead.[8] Here we report, that by simply changing the metal ion to manganese the desired formation of corroles from 2,2′-bisdipyrrins[9] can in fact be observed.

As 3,3′,4,4′,8,8′,9,9′-octaethyl-10,10′-dimethyl-2,2′-bisdipyrrin **1** is treated with manganese(II) acetate tetrahydrate under aerobic conditions in boiling DMF, varying amounts of **4** build up over the course of several hours. Purging the hot reaction mixture with dioxygen accelerates the reaction significantly, so that within five minutes the cyclization is complete. After chromatography and recrystallization from diethyl ether–*n*-hexane, **4** is obtained as violet crystals in 23% yield (Scheme 1). The material obtained this way is identical in every respect with the manganese(III)octaethylcorrole reported earlier.[10] When applying the very same conditions to other α,ω-dimethyl-2,2′-bisdipyrrins,[9] substituted manganese(III)corroles can be prepared. For example, *meso*-diphenyl- and *meso*-di-*p*-tolyl-2,2′-bisdipyrrins **2** and **3** are cyclized to the manganese(III)-5,15-diarylcorroles **5** and **6** in 18 and 19% yield, respectively.[11,12]

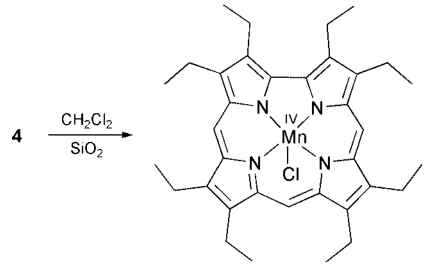
As we experienced at an initial stage of the project, the manganese(III)corroles appear remarkably prone to oxidation by chlorinated solvents (Scheme 2). Thus, simply performing the chromatographic work-up of **4** on silica with a dichloromethane–methanol mixture as the eluent directly gave the known chloro-manganese(IV) complex **7**[1b] as the only product, albeit in diminished yield (17%). This observation provides yet another example for the ease of stabilisation of high oxidation states through the trisanionic corrole ligand.

Free base corroles are readily released from the manganese complexes by simple acid induced demetallation. For example, treatment of **4** with HBr in acetic acid yields the well-known octaethylcorrole **8** quantitatively within 10 min (Scheme 3).[7] This clean demetalation protocol makes the newly found manganese induced cyclization a useful synthetic tool towards



R	bisdipyrrin	Mn corrole
H	**1**	**4**
Ph	**2**	**5**
p-Tol	**3**	**6**

Scheme 1



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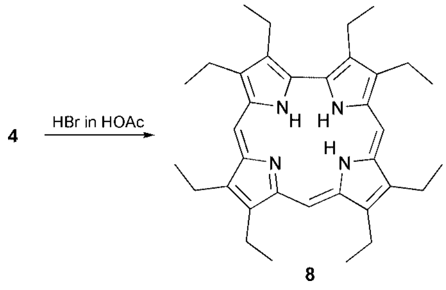
Scheme 2



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Scheme 3

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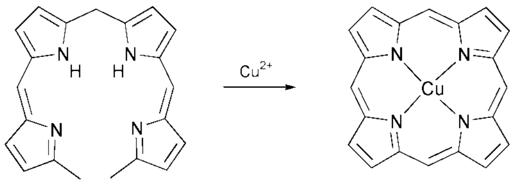

9 **10**

Scheme 4

substituted corrole ligands, some which are hardly or not at all accessible by any other of the corrole forming reactions known today.

Although the mechanistic details of the Mn(II)–O_2 induced cyclization of 2,2′-bisdipyrrins are still in question, the formation of **4–6** points to an analogous oxidative transformation in the porphyrin field, namely the reaction of *a*,*c*-biladienes **9** with several metal salts or oxidants to yield porphyrins **10** (Scheme 4). This valuable transformation, initially found by Johnson *et al.*,[13] has been thoroughly investigated and mechanistically explained by Smith.[14] It appears highly probable, that a related sequence of steps occurs also in the case of 2,2′-bisdipyrrin cyclization. As a major difference to the macrocyclization of *a*,*c*-biladienes we believe, that in our case a templating action of the metal ion—prior to or after partial oxidation—is crucial to the reaction. Most probably, the 2,2′-bisdipyrrin unit will not stabilise the tense, helical conformation necessary for ring closure on its own, but rather retain the ability of an almost free rotation around the central pyrrole–pyrrole axis. Additionally, it is quite questionable, whether the terminal methyl groups of a 2,2′-bisdipyrrin in a closed, quasi-macrocyclic conformation would have sufficient overlap without being forced by a central metal ion.

Further studies towards an understanding of the C_1 extrusion, the use of other metal ions and/or co-oxidants, and the application of the new macrocyclization in the synthesis of tailor-made and functionalized corroles and metallocorroles are currently in progress.

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11 *Spectroscopic data* for **5**: mp. 252 °C (decomp.); MS (FAB): *m*/*z* 726.4, M^+; calc. for $C_{47}H_{51}N_4Mn$: C 77.66, H 7.07, N 7.71; found: C 77.21, H 7.25, N 7.53%.

12 *Spectroscopic data* for **6**: mp. 294 °C (decomp.); MS (FAB): *m*/*z* 754.5, M^+; calc. for $C_{49}H_{55}N_4Mn$: C 77.96, H 7.34, N 7.42; found: C 77.97, H 7.52, N 7.44%.

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