

Products from Oxidation Reactions of the Open-Chain Oligopyrrole 2,2'-Bidipyrrin

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As part of our program to explore the intriguing coordination chemistry of open-chain oligopyrroles related to the porphyrins like the 2,2'-bidipyrrins **1** we recently observed the serendipitous formation of manganese(III) complexes of corroles **2**, the one-carbon short analogues of the porphyrins.^[1] As further studies of this novel macrocyclization revealed, the reaction is not necessarily depending on the use of manganese(II) precursors, but occurs also in the presence of excess copper(II) salts, yielding copper(III) complexes in this case. In both cases the reaction was found to be dependant on molecular dioxygen as well as reaction temperatures of at least 150°C. Despite many attempts, the active oxidant could not be unambiguously identified so far.

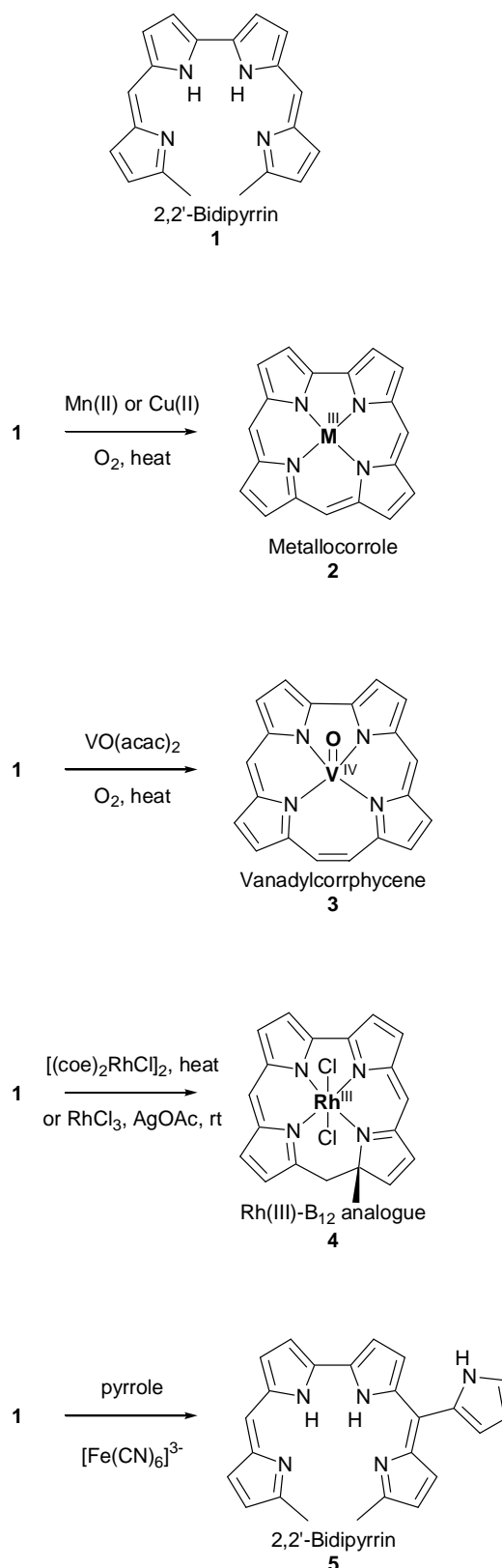
When vanadylacetylacetonate is used as the metal reagent in the reaction, the product formed surprisingly appears to be a corrphycene derivative **3**. Peripheral alkyl substituents also have an influence on whether the 2,2'-bidipyrrin is transformed into a corrole or a corrphycene derivative. Of particular interest is the fact, that even a highly reduced metal precursor like [(coe)₂RhCl]₂ is able to induce an oxidative macrocyclization under anaerobic conditions, leading to a rare example of a Rh-B₁₂ analogue **4**.^[2] Other metallo-2,2'-bidipyrrins^[3,4] also yield macrocycles when oxidized by Ag(I) salts; these products are actually under investigation.

In all examples shown above the terminal groups are the site of oxidation. However, this is not always the case. When **1** is treated with excess pyrrole and [Fe(CN)₆]³⁻ under alkaline conditions a C-C bond formation is observed leading to **5**.

While the reagent based oxidation reactions produce an intriguing variety of novel compounds, the electrochemical investigations of all simple metallo-2,2'-bidipyrrins show a very cleanly reversible one-electron oxidation step without sequential reactions.^[3,4] The ET is unambiguously located at the ligand. The talk will present the current data and try to explain this discrepancy by mechanistic arguments.

Literature:

- [1] M. Bröring, C. Hell, *Chem. Commun.* **2001**, 2336-2337.
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 [3] M. Bröring, C. D. Brandt, J. Lex, H.-U. Humpf, J. Bley-Escrigh, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2001**, 2549-2556.
 [4] M. Bröring, C. D. Brandt, J. Bley-Escrigh, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2002**, 910-917.



Scheme 1. Different products of oxidative macrocyclization reactions starting from 2,2'-bidipyrrin **1**.