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First catalysis by corrole metal complexes: epoxidation, hydroxylation, and cyclopropanation

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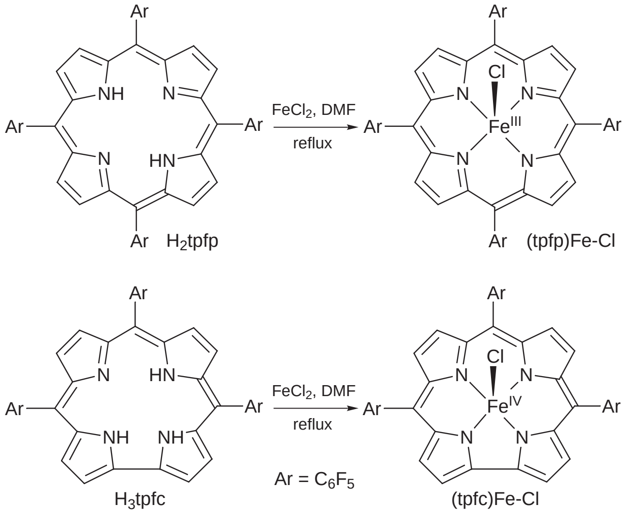
The first ever application of corroles shows that their metal complexes are good catalysts, almost as potent as the corresponding metalloporphyrins in the oxygenation of hydrocarbons by iodosylbenzene and superior for the cyclopropanation of olefins by carbenoids.

Modified porphyrins have received increased attention in recent years, with emphasis on their syntheses, characterizations, and potential applications.[1] Some of these macrocycles form complexes with metal ions, which due to the alteration of the ligand's structure have quite different properties compared with the analogous metalloporphyrins.[2] The most interesting ligands in this respect are corroles, the one-carbon atom contracted porphyrin analogs, which may also be considered as the aromatic version of corrin—the cobalt's ligand in Vitamin B_{12}.[3] Similar to porphyrins, the corroles provide an equatorial tetradentate coordination plane, which is however trianionic and somewhat contracted (see Scheme 1). These last two properties have some remarkable effects on the coordination chemistry of corrole metal complexes (metallocorroles),[4] among which the stabilization of exceptionally high metal oxidation states is the most outstanding. The recent isolation of iron(IV) corroles[4a] and of an iron(IV) corrole radical[4b] could be relevant to catalysis by heme-enzymes and synthetic iron porphyrins, in which the analogous complexes are key intermediates.[5] But, there is still no information about corroles or their metal complexes in catalysis or in any other potential application. Presumably, it is only the lack of obvious procedures for the synthesis of corroles which prohibits such research. Thus, the first *meso*-substituted corrole—*meso*-aryl substitution is a prerequisite for a reasonable oxidation catalyst—was reported as late as 1993,[6] almost 30 years after the first reported corrole.[7] Also, in spite of the significant recent progress in corrole synthesis, even the most simple procedures reported to date require the preparation of non-commercially available starting materials.[8]

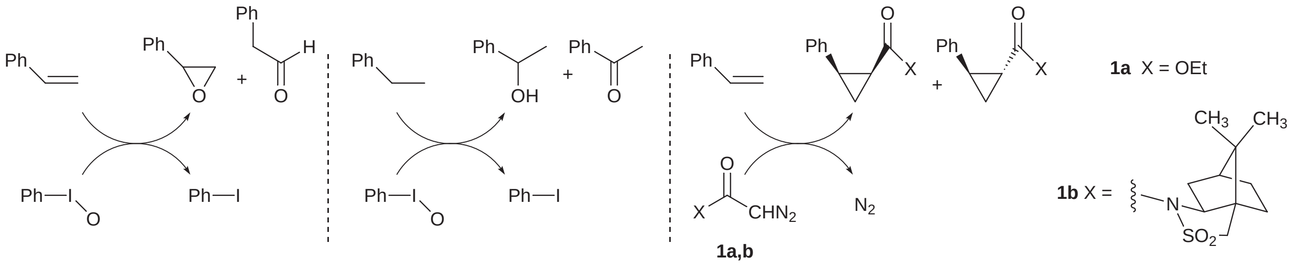


Scheme 1 Structures of *meso*-aryl substituted porphyrin and corrole, and of their iron complexes (note the different oxidation states of the metal).

We have very recently contributed to this field by disclosing the first synthesis of corroles by the direct reaction of pyrrole with aldehydes.[9] In particular, 5,10,15-tris(pentafluorophenyl)-corrole (H_3tpfc, Scheme 1) is now routinely prepared in our laboratory by this very simple and fast methodology. The structure of H_3tpfc is very similar to that of H_2tpfp, whose iron(III) complex is among the most active porphyrin-based catalysts.[10] Accordingly, we have now decided to compare the iron complexes of these two ligands as catalysts for the three main reactions catalyzed by metalloporphyrins.[11] These are the epoxidation of olefins and the hydroxylation of alkanes by iodosylbenzene, and the cyclopropanation of alkenes by carbenoids (Scheme 2).[12]

The results shown in Table 1 clearly demonstrate that (tpfc)Fe–Cl is a good catalyst in all three reactions. Still, it is not as effective as (tpfp)Fe–Cl for the epoxidation and hydroxylation of hydrocarbons. This is reflected in the higher yields of oxygenation products with (tpfp)Fe–Cl, as well as from the fact that at the end of the reactions the corrole complex, but not the analogous porphyrin complex, is completely bleached. However, for the cyclopropanation of styrene by **1a** (Scheme 2), (tpfc)Fe–Cl is superior. In addition, the catalyst is stable under the cyclopropanation conditions.

These results are reasonably accounted for by considering the proposed key intermediates in these processes, metal–oxo in oxygenation and metal–carbene in cyclopropanation.[5,12] It is well known that for iron(III) porphyrins, oxygen atom transfer from iodosyl benzene results in an oxoiron(IV) porphyrin radical intermediate, whose protection against self-destruction relies on the steric crowding of the four *meso*-aryl groups. By analogy, the oxygenation of (tpfc)Fe–Cl—an iron(IV) complex—will lead to an even more reactive intermediate. In addition, the



Scheme 2 Three catalytic transformations examined with (tpfc)Fe–Cl and (tpfp)Fe–Cl as catalysts.

Table 1 A comparison of (tpfc)Fe–Cl and (tpfp)Fe–Cl as catalysts for the processes shown in Scheme 1 with **1a**

	Epoxidation of styrene[a]		Hydroxylation of ethylbenzene[b]		Cyclopropanation of styrene[c]	
Products	Epoxide	Aldehyde	Alcohol	Ketone	*trans*	*cis*
With (tpfc)Fe–Cl as catalyst[d]	66%	21%	6.6%	4.2%	46%	20%
With (tpfp)Fe–Cl as catalyst[d]	90%	10%	15.7%	8.9%	40%	7%

[a] 0.36 mmol catalyst, 36 mmol iodosylbenzene, 360 mmol styrene, and 36 mmol nitrobenzene (internal standard), in 1 mL benzene, at RT for 3.5 h and 45 min, respectively. [b] 0.45 mmol catalyst, 50 mmol iodosylbenzene, 500 mmol ethylbenzene, and 50 mmol nitrobenzene (internal standard), in 1 mL benzene, overnight at RT. [c] 0.3 mM catalyst, 0.15 M **1a**, 1.5 M styrene, in 4 mL CH_2Cl_2, for 2.75 h at RT. 34 and 18% of olefins (diethyl maleate and traces of fumarate) were obtained in the reactions catalyzed by (tpfc)Fe–Cl and (tpfp)Fe–Cl, respectively. [d] Yields with regard to the limiting reagent were determined by GC relative to the internal standard.

Table 2 The results for cyclopropanation of styrene by **1a** and the unichiral carbenoid **1b**, catalyzed by the iron porphyrin complex (tpfp)Fe–Cl and the iron, cobalt, and rhodium complexes of H_3tpfc[a]

	With **1a**		With **1b**			
Catalyst	% Yield[b]	*trans*:*cis*	% Yield[c]	*trans*:*cis*	% de *trans*	% de *cis*
(tpfp)Fe–Cl	24	5.5	10	2.6	67 (*1S,2S*)	63 (*1S,2R*)
(tpfc)Fe–Cl	71	1.8	41	0.9	25 (*1S,2S*)	66 (*1S,2R*)
(tpfc)Co–PPh_3	8	2.1	[d]			
(tpfc)Rh–PPh_3	87	2.0	56	1.0	60 (*1R,2R*)	10 (*1S,2R*)

[a] 0.25–0.28 mM catalyst, catalyst : **1** : styrene = 1 : 100 : 1000, in 2 mL CH_2Cl_2, at RT under Ar. [b] Combined yields of the *trans*- and *cis*-cyclopropyl esters after 1 h, except for (tpfc)Co–PPh_3 (24 h). With (tpfc)Fe–Cl and (tpfc)Rh–P(Ph)$_3$, the reactions are complete after 1 h (the rest of **1a** is transferred into its dimerization products), while with (tpfp)Fe–Cl the reaction continues (43% yield after 3 h). [c] Combined yields of the *trans*- and *cis*-isomers after 24 h, except for (tpfp)Fe–C1 (48 h). [d] Not determined.

absence of the fourth aryl ring in (tpfc)Fe–Cl leads to reduced steric protection. Accordingly, the lower efficiency and the greater bleaching of (tpfc)Fe–Cl during catalysis may be rationalized on both electronic and steric grounds, whose relative importance still needs to be resolved. On the other hand, both factors seem to be beneficial for the cyclopropanation process. It is known that the active oxidation state in catalysis by iron(III) porphyrins is iron(II), which for (tpfp)Fe–Cl is formed *via* reduction by **1a**.[13] Thus, the results suggest that the reduction of the iron(IV) corrole is easier and that the absence of the fourth aryl group is favorable for formation of the relatively large metal–carbene intermediate. The last effect is also reflected in the relatively small *trans*:*cis* ratio of the cyclopropyl esters, 2.3 with (tpfc)Fe–Cl *vs.* 5.7 with (tpfp)Fe–Cl.

Because of the superiority of (tpfc)Fe–Cl in cyclopropanation catalysis, we turned our attention to other metal complexes of H_3tpfc, as well as to the unichiral carbenoid **1b**.[14,15] Table 2 summarizes the results of the reaction of styrene with **1a** and **1b**, catalyzed by (tpfp)Fe–Cl, (tpfc)Fe–Cl, (tpfc)Co–P(Ph)$_3$, and (tpfc)Rh–P(Ph)$_3$. Several aspects are clearly evident. First, the larger activity of the iron corrole relative to the analogous porphyrin in cyclopropanation by **1a** is further amplified in the reaction with the much bigger **1b**. Secondly, within the series of the corrole metal complexes the catalytic efficiency increases in the order of Co $<<$ Fe $<$ Rh, similar to what is obtained with metalloporphyrins.[13] Finally, quite low *trans*:*cis* ratios are obtained for all metallocorroles, together with modest diastereomeric excesses (% de) in the reactions with **1b**. By analogy to our recent studies with the related metalloporphyrins,[14a] we anticipate that a significant increase in diastereoselectivity might be achieved by utilizing metal complexes of corroles with larger *o*-phenyl substituents. We have one such derivative,[9] but we still have to improve the synthetic methodology for its preparation.

In conclusion, this is the first report of catalysis by corrole metal complexes, and actually the first ever application of corroles. We have demonstrated that metallocorroles are good catalysts for the reactions which are traditionally investigated with metalloporphyrins. We trust that these promising preliminary results will encourage further exploration of the chemistry of corroles and their metal complexes.

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