Oxidations Catalyzed by Metallocorroles

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Abstract: Metallocorroles, in particular those containing chromium, manganese, and iron, have been found to be efficient catalysts for oxidation reactions. This review deals with work on hydrocarbon oxidations after the 1999 advance made in corrole synthesis that sparked the Technion-Caltech collaborative program.

Keywords: catalytic oxidation; chromium; dioxygen activation; manganese; metallocorroles

1 Introduction

Corroles are tetrapyrrolic macrocycles related to the cobalt-chelating corrin in vitamin B_{12} and the iron-chelating porphyrin in heme.[1] Early work focused on synthetic aspects and elucidation of the fundamental coordination chemistry of metallocorroles.[2,3] The first report coupling corroles to porphyrins and related macrocycles in regard applications appeared in1999.[4] The renaissance in corrole chemistry in the late 1990s (Figure 1) was driven by the discovery of facile methodologies for the preparation of derivatives with aryl groups on the three *meso*-carbon atoms (triarylcorroles).[5,6] A major outcome of the easy accessibility of these molecules is that many of the corresponding metal complexes were found to be efficient catalysts for a variety of reactions,[7–10] notably including oxidations, the focus of this short review.

In one mode of oxygen-atom-transfer catalysis, the metal ion M^n is oxidized to an (oxo)metal intermediate $(O)M^{n+2}$ that in turn oxidizes the substrate and returns to the reduced M^n state (Scheme 1). The most extensively investigated systems are based on porphyrin complexes with trivalent 3d metal ions, where the efficiency increases in the order manganese > iron >> chromium.[11] This order reflects the reactivity of the $(O)M^{n+2}$ intermediates, as may also be appreciated by the year in which each of the corresponding porphyrin complexes was first isolated: (oxo)chromium(V) in 1979,[12] (oxo)iron(V) [actually a porphyrin-radical complex of (oxo)iron(IV)] in 1981,[13] and (oxo)manganese(V) as late as 1999.[14] For corroles, only the (oxo)chromium(V) complex of a β-alkylated and *meso*-unsubstituted derivative was reported,[15] and there were no publications on metallocorrole-based catalytic systems until 1999.

2 Chromium Complexes

One significant difference between corroles and porphyrins is that high-valent metal ions are generally more

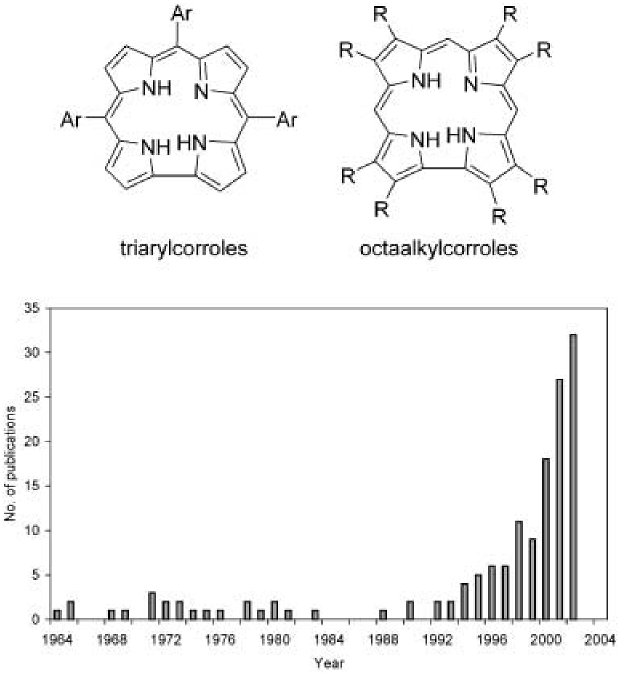
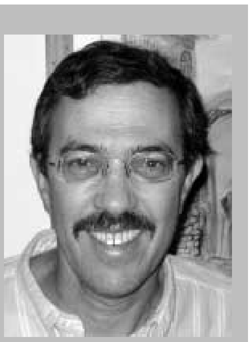


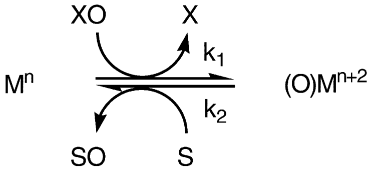
Figure 1. Corrole publications per year since the report by Johnson and Kay in 1964.



Zeev Gross completed his Ph. D. degree in 1988 at Bar-Ilan University under the direction of Professor Shmaryahu Hoz in the field of Physical Organic Chemistry. He then spent two years as a Fulbright postdoctoral fellow in Professor John T. Groves' group at Princeton University, working on several aspects regarding the chemistry of porphyrins and their metal complexes. In 1990 he accepted a position as lecturer at the Technion, where he is currently Professor of Chemistry and head of the field of organic and inorganic chemistry. His main research activities in the first years were concerned with mechanistic aspects of metalloporphyrin-catalyzed reactions and utilization of chiral porphyrins as asymmetric catalysts. Since 1999, when his group discovered the first facile synthesis of corroles from obvious starting materials, the focus of his research is on disclosing unique features of corroles and utilization of their metal complexes in many applications.

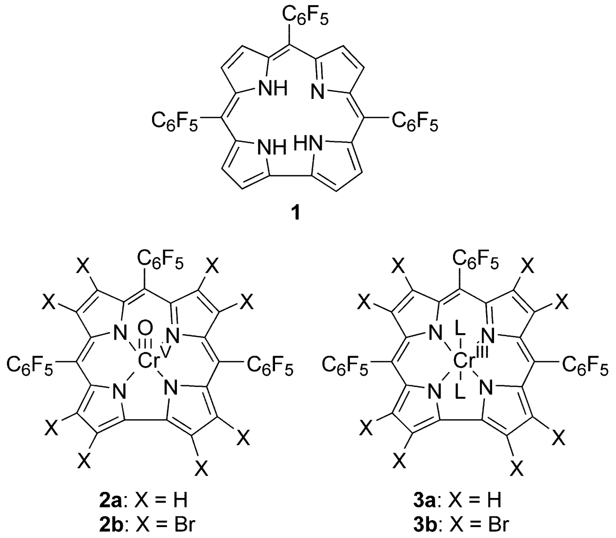
Harry Gray is the Arnold O. Beckman Professor of Chemistry at the California Institute of Technology. After receiving a Ph. D. from Northwestern University and spending a postdoctoral year at the University of Copenhagen (1960–1961), he joined the chemistry faculty at Columbia University, where his main interests centered on the electronic structures and reactions of inorganic complexes. Starting in 1966, he built up a group in bioinorganic chemistry at Caltech, where much of his research has been aimed at understanding electron transfer in proteins. In recent years he has enjoyed working with Zeev Gross in attempts to understand the very rich physical and chemical properties of metallocorroles.

stable in the former complexes.[16] This aspect was investigated by Meier-Callahan et al. for the triarylcorrole **1** (Scheme 2),[17] whose (oxo)chromium(V) complex **2a** was characterized by magnetic susceptibility, EPR, electrochemistry, and X-ray crystallography. The Cr(V) oxidation state in **2a** was clearly evident from the magnetic moment of 1.72 μ_B and the highly characteristic EPR spectrum of a d^1 oxo complex. Complex **2a** was found to be remarkably stable, which accords with its reduction potential of 0.11 V (*vs.* Ag/AgCl), 0.6 V more negative than the potentials of otherwise analogous porphyrin complexes. A comparison of EPR coupling constants of **2a** relative to those of other (oxo)chromium(V) complexes revealed unusually high unpaired spin densities on the nitrogen atoms but low density on the metal ion. Examination of the structure of **2a** revealed that the (oxo)chromium(V) bond length (1.57 Å) is identical with that in (oxo)chromium(IV) porphyrin, while the Cr–N bonds are much shorter and the out-of-plane displacement of the metal atom from the N_4 plane is much larger. This combination of a relatively long Cr–O bond, short Cr–N bonds, and large out-of-plane displacement of the metal also is found in one of the very stable tetraamido-(oxo)chromium(V) complexes reported by Collins and coworkers,[18] while a more reactive salen complex displays a shorter Cr–O bond [1.545(2) Å] and much longer Cr–N bonds.[19] Altogether, we concluded that strong σ-donation by the trianionic corrole (or similarly, by tetraanionic tetraamido ligands) is responsible for the unusually high stability of (oxo)chromium(V) in **2a**.



Scheme 1. Oxygen-atom transfer from exogenous oxidant XO to reduced catalyst M^n and from oxidized catalyst $(O)M^{n+2}$ to substrate S to form oxidized substrate SO, with $k_2 >> k_1$ in most cases.

In a follow-up investigation, Meier-Callahan et al. defined conditions for isolation of chromium corroles in



Scheme 2. 5,10,15-Tris(pentafluorophenyl)corrole and its chromium complexes (L = pyridine or triphenylphosphine oxide).

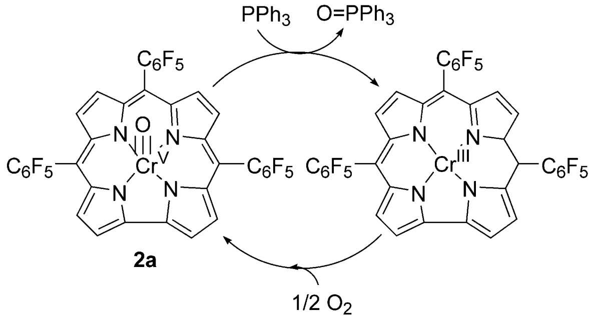
four different oxidation states and found that that chromium(III) complex **3a** is oxidized by air to the (oxo)chromium(V) complex **2a**.[20] This remarkable finding of dioxygen activation by chromium(III) [normally achieved only by chromium(II) complexes] prompted Mahammed et al. to use chromium corroles as catalysts for aerobic oxidations of organic substrates (Scheme 3).[21]

Of course, the aforementioned stability of the (oxo)chromium(V) corrole **2a** – oxygen is bound to chromium by a triple bond, $(d_{z^2}+p_z)^2$, $(d_{xz}+p_x)^2$, $(d_{yz}+p_y)^2$ – limits the range of potential substrates. Nevertheless, with triphenylphosphine as substrate, we demonstrated that oxygenation catalysis ($X{-}O{=}O_2$ in Scheme 1) can be achieved by the system: up to 33 catalytic turnovers were obtained by using only catalyst and molecular oxygen (> 95% incorporation of labeled oxygen from $^{18}O_2$), without external oxidizing or reducing agents. An important observation was the operation of a very significant solvent effect of acetonitrile on the kinetics of the two crucial oxygen-atom-transfer steps shown in Scheme 1, from dioxygen to catalyst (k_1: more than ten-fold faster than in THF) and from (oxo)chromium(V) to substrate (k_2: minutes in CH_3CN *vs.* weeks in THF). The reactivity of the (oxo)chromium(V) complex could be increased to the level required for epoxidation of a reactive olefin (norbornene) *via* substitution of the corrole β-pyrrole carbon atoms by bromine (**2b**, Scheme 2). However, the chromium(III) complex of that corrole (**3b**) was not readily reoxidized by dioxygen to the (oxo)chromium(V) state.

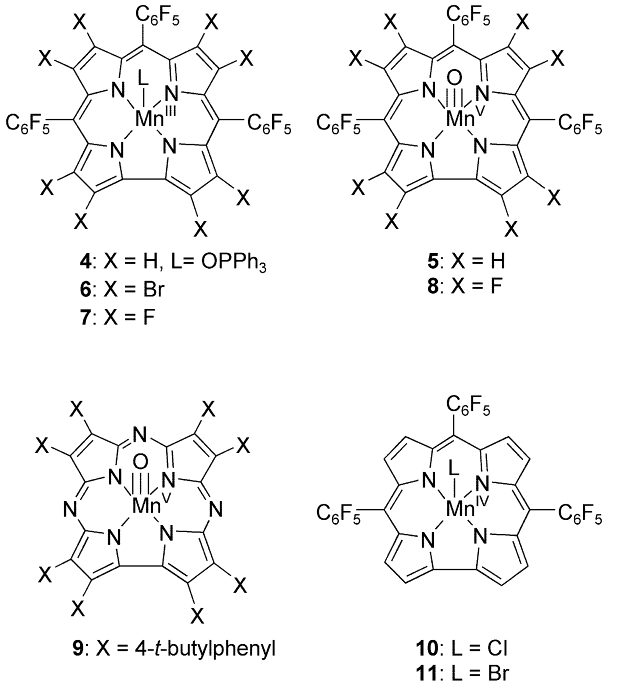
3 Manganese Complexes

In the first investigation of manganese triarylcorroles,[22] Gross et al. demonstrated that catalytic amounts (1 mol %) of the manganese(III) complex **4** (Scheme 4) promote the oxidation of styrene by iodosylbenzene to a mixture of styrene oxide and phenylacetaldehyde in about 80% and 20% yields, respectively (Scheme 5). This result resembles those obtained with manganese(III) and iron(III) porphyrins, except that catalysis by **4** was less efficient. The novelty of the corrole-based system is that the rate-limiting step appears to be oxygen-atom transfer from oxidized catalyst to olefin and not from exogenous oxidant to reduced catalyst, i.e., $k_1 >> k_2$ in Scheme 1. This enabled the isolation of the oxidized form of the catalyst (**5**, Scheme 4), which was characterized by spectroscopy as a genuine (oxo)manganese(V) corrole. A main characteristic feature of **5** is its diamagnetism, consistent with a $(d_{xy})^2$ manganese(V) ion chelated by a closed-shell corrole and bound *via* a triple bond (three 2-e bonds, σ: $d_{z^2}+p_z$, π_y: $d_{xy}+p_y$, π_x: $d_{xy}+p_y$) to the oxo ligand. Similar results were obtained by Mandimutsira et al., who isolated the (oxo)manganese(V) complex of a triazacorrole (corrolazine **9** in Scheme 4) and found it to be even more stable (and less reactive) than **5**.[23]

A puzzle regarding catalysis by **4** is that the *isolated* (oxo)manganese(V) complex **5** does not transfer its oxygen atom to olefins under stoichiometric conditions.[22] Differences in competitive epoxidation of styrene and cyclooctene as a function of the exogenous oxidant led Collman et al. to conclude that the oxygen-transferring intermediate is the precursor of **5**, the iodosylarene-coordinated complex **4**.[24] The relative inertness of **5** could be related to its low-spin ground state, an issue that was addressed in the DFT calculations by de Visser et al. on (oxo)manganese complexes of (non-substituted) trianionic corrole and dianionic porphyrin.[25] Their investigation revealed that the corrolato ligand (but not the porphyrinato ligand) raises the energy of the d_π orbitals to higher levels than that of the metal-d_{xy} and the ligand's HOMO. Electronic



Scheme 3. Chromium corroles as catalysts for aerobic oxidations.



Scheme 4. Isolated manganese complexes of triarylcorroles and triazacorrole (corrolazine).

configurations involving higher metal-based spin multiplicities (proposed for salen complexes)[26] and/or ligand oxidation (found for the porphyrin complex) were predicted at higher energies. The absence of low-lying states with higher spin multiplicities in corroles seems to correlate both with the low oxygen-transfer reactivity and the low selectivity (*vide infra*).

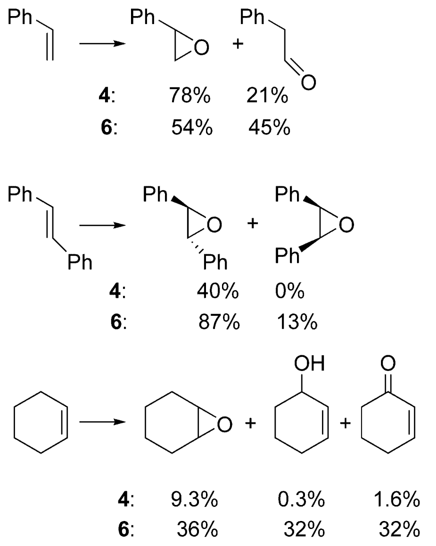
A very large increase in catalytic activity was achieved by Golubkov et al. *via* the facile bromination of all β-pyrrole carbon atoms of **4**, resulting in complex **6** (Scheme 4).[27] Comparisons between the oxidation reactivities of three substrates with either **4** or **6** as catalysts revealed that with the latter complex the reaction times were shortened from 10–12 h to 15 min, the chemical yields were much larger (quantitative for **6**), and **6** was not bleached even when less reactive substrates were employed (Scheme 5). However, the epoxidation selectivity decreased dramatically with the more potent catalyst. In fact, oxidation of cyclohexene gave equimolar amounts of cyclohexene oxide, cyclohexene-3-ol, and cyclohexene-3-one. The most surprising result is that a significant amount (13%) of *cis*-epoxide was formed in the epoxidation of *trans*-stilbene, which to our knowledge is unprecedented. This finding clearly deserves further attention, especially since it could be related to the low-spin state of the (oxo)manganese(V) intermediate, as proposed by the groups of Shaik and Houk based on DFT calculations of the reaction profiles of (oxo)iron porphyrins and (oxo)-manganese salens with olefins.[26,28]

Similar results were obtained by Liu et al.,[29] who prepared manganese(III) complex **7** (Scheme 4) with fluorine rather than bromine substituents (as in **5**) on the β-pyrrole carbon atoms of **4**. These authors demonstrated that **7** is an efficient oxidation catalyst, similar to **5**. In terms of accessibility, however, complex **7** requires the quite tedious preparation of 3,4-difluoropyrrole, while the bromination of **4** to **5** is straightforward. Importantly, the authors also have characterized the corresponding (oxo)manganese(V) complex **8**.

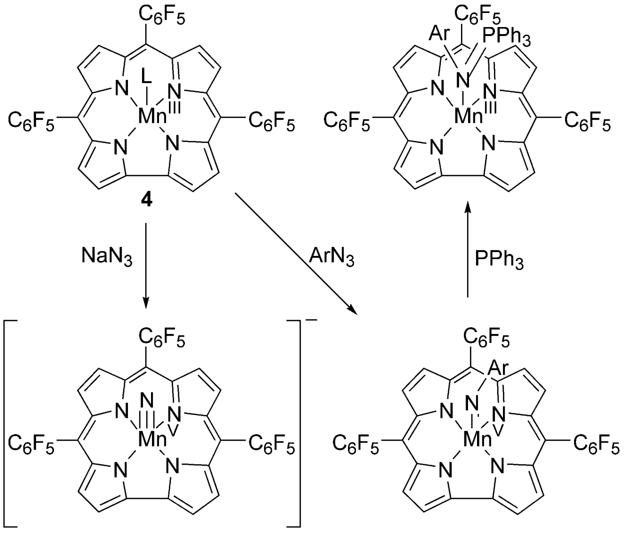
Other catalytic processes have not yet been described for manganese corroles, but several unique complexes and two interesting stoichiometric reactions have been reported. Manganese(III) corrole **4** was further characterized by X-ray crystallography and high-field (high frequency) EPR by Bendix et al.,[30] while Golubkov et al. isolated and fully characterized the stable (chloro)manganese(IV) and (bromo)manganese(IV) complexes **10** and **11** (Scheme 4).[27] What is more, the latter authors also prepared a stable (nitrido)manganese(V) corrole (**12**) *via* the reaction of **4** with sodium azide (Scheme 6).[27] Using organic instead of inorganic azides, Eikey et al. have prepared and fully characterized the (arylimido)manganese(V) corroles **13** and **14**.[31] These authors have further demonstrated that the nitrene moiety in **13** and **14** can be transferred to triphenylphosphine. More recently, Golubkov and Gross have shown that the nitrogen atom of very stable (nitrido)manganese(V) salophen and salen complexes can be transferred to the manganese (unpublished results) and chromium complexes of corrole **1** in reactions that serve as synthetic routes to **12** and **13**, respectively (Scheme 7).[32] These findings are dramatic demonstrations of corrole stabilization of high valent metal ions.

4 Summary and Future Outlook

The potential of metallocorroles as oxidation catalysts has only begun to be exploited and there are many



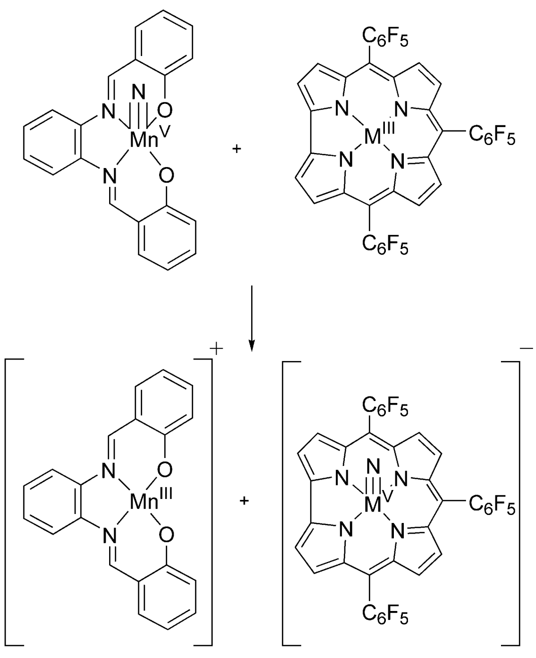
Scheme 5. Products of oxidations using manganese corroles **4** and **6** as catalyst.



12

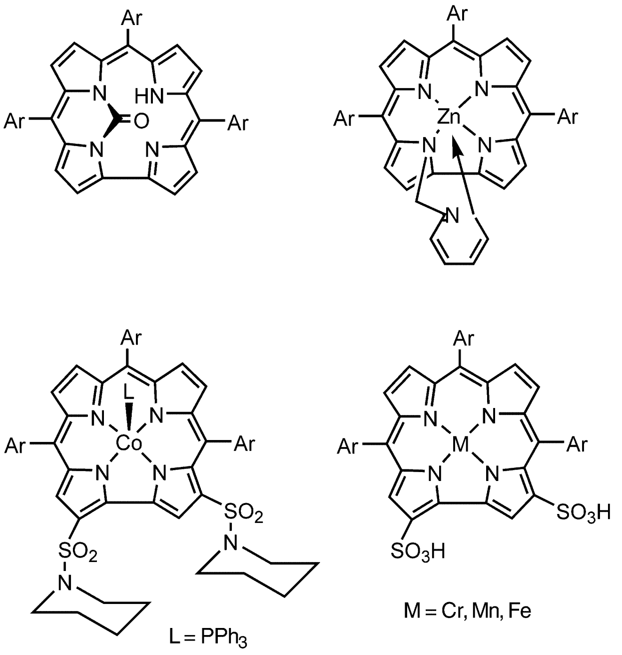
13: Ar = mesityl
14: Ar = 2,4,6-trichlorophenyl

Scheme 6. Synthetic routes to (nitrido)- and (imido)manganese(V) corroles and nitrene transfer by the latter.



12: M = Mn
15: M = Cr

Scheme 7. Nitrogen-atom transfer from (nitrido)manganese(V) salophen to chromium(III) and manganese(III) corroles.



Scheme 8. Three types of chiral corroles and the bis-sulfonated corrole that associates strongly with proteins.

questions to be resolved. Although an iron corrole was used in the first demonstration of corrole-based oxidation catalysis, there were no follow-up reports. Most intriguing is the unique activation of molecular oxygen by iron(III) corroles:[33] can this phenomenon be used in the design of catalytic systems for aerobic oxidations of substrates, and will it be possible to isolate new oxygen-containing intermediates? Another metal that certainly deserves attention is ruthenium, which in porphyrins uniquely catalyzes aerobic oxidation of hydrocarbons without the intervention of exogenous oxidizing or reducing agents.[34] The recent isolation of the first mononuclear ruthenium corrole opens the way for examination of such species as oxygenation catalysts.[35]

A different yet unexplored topic is asymmetric catalysis, for which corroles could be superior to porphyrins because of their intrinsically lower symmetry. The validity of this principle has recently been proven: a variety of chiral metal complexes were prepared (and fully characterized) by approaches that are unique to corroles (Scheme 8).[36,37] It may be expected that some of these will be used for inducing asymmetric oxidation reactions in the near future. A quite different approach aimed at the same goal is biomimetic catalysis by corroles. A breakthrough that paves the way for work in this area is the discovery by Mahammed et al. that sulfonation of corroles proceeds with very high selectivity to the bis-sulfonated corrole shown in Scheme 8.[36a] Various metal complexes of this water-soluble corrole have already been reported and we have found (unpublished results) that they associate strongly with proteins due to their amphiphilicity.[38] Performing heme enzyme-like catalysis by such conjugates, with emphasis on asymmetric oxidation, is one natural extension of this project.

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