High-Valent Manganese Corroles and the First Perhalogenated Metallocorrole Catalyst[**]

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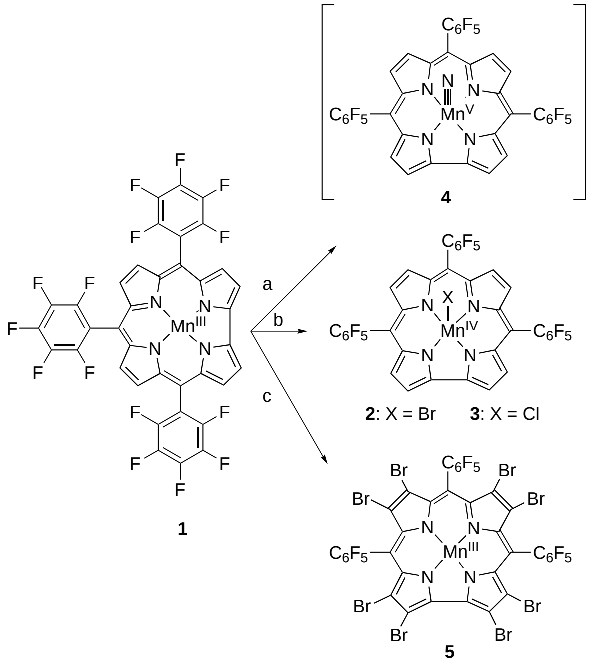
Two major goals of research on the manganese(III) porphyrin catalyzed oxygenation of hydrocarbons are improved activity/lifetime profiles and the identification of reaction intermediates.[1] Increasingly more active catalysts have been obtained by replacing tetraphenylporphyrin with halo-phenyl analogues, and then with derivatives in which the β-pyrrole carbons are halogenated as well.[2] Interestingly, this effect is more pronounced for manganese than for iron porphyrins.[1a, 2b] Spectroscopic identification—particularly by NMR—of proposed manganese(V) intermediates should be relatively straightforward, since d^2 metalloporphyrins with strong π-donor ligands are expected to be diamagnetic. The first ^{1}H NMR spectroscopic characterization of a (nitrido)manganese(V) complex indeed dates from 1983,[3] but the spectrum of an (oxo)manganese(V) porphyrin was obtained only very recently.[4] Manganese(IV) porphyrins are more stable: X-ray structures have been reported for several $[Mn(por)(OR)_2]$ complexes (e.g., $R = CH_3$, C_6H_5I, por = porphyrin);[5] but so far the characterization of high-valent manganese porphyrins with oxo or halo ligands is limited to spectroscopic methods.[6]

Corroles are known to be superior to porphyrins in stabilizing high oxidation states of various transition metals,[7] but until recently only trivalent complexes were reported for manganese.[8, 9] Furthermore, the oxidation state assignment of the *formally* manganese(III) and manganese(IV) complexes of octaalkylcorroles remained ambiguous because of some indications that the corrole is oxidized.[8, 9] In addition, octaalkylcorrole metal complexes have never been examined in oxidation catalysis, probably because *meso* aryl substitution is almost always required in the related porphyrin-based catalysts. However, this situation is changing dramatically as a result of the introduction of the electron-poor 5,10,15-tris(pentafluorophenyl)corrole (H_3(tpfc),[10] tpfc = the trianion). The iron, manganese, and rhodium complexes of H_3(tpfc) have been shown to be potent catalysts for the oxygen and carbene transfer to olefins and alkanes,[11] with a readily observed (oxo)manganese(V) intermediate in epoxidation catalyzed by [Mn(tpfc)] (**1**).[11b] In addition, the Fe^{IV}(Cl), $Rh^{III}(PPh_3)$, Cr^{V}(O), and $Mn^{III}(OPPh_3)$ complexes have been fully characterized by a combination of spectroscopic methods and X-ray crystallography.[12] In all these complexes there were no indications for oxidation of the corrole, as opposed to the ambiguity in the case of the iron and manganese octaalkylcorroles.[8, 9, 13] We now show that **1** can be functionalized at both the metal and the corrole centers, which leads to the isolation and full characterization of two manganese(IV) corroles, a stable (nitrido)manganese(V) corrole, and a perhalogenated manganese(III) corrole (Scheme 1). Preliminary results for the perhalogenated manganese(III) corrole demonstrate its superior activity as an oxidation catalyst.



Scheme 1. a) NaN_3, $h\nu$, b) $1/2X_2$ (X = Cl, Br), c) excess Br_2/MeOH.

Cyclic voltammetry of **1** reveals a redox potential of 0.71 V (vs. standard calomel electrode (SCE)), suggesting that mild oxidants could be used for the isolation of novel high-valent manganese corroles. Indeed, treating a green hexane solution of the highly soluble **1** with bromine or tris(4-bromophenyl)-aminium hexachloroantimonate results in the immediate and quantitative precipitation of [Mn(tpfc)(Br)] (**2**) and [Mn(tpfc)Cl] (**3**), respectively.[14, 15] The electronic spectra of these complexes (each exhibits a single Soret band) are very similar to those of manganese(IV) porphyrins,[4–6] suggesting that the oxidations are metal rather than corrole centered. Reduction of **2** (Figure 1) produces a UV/Vis spectrum that is identical to that obtained by adding n-$Bu_4N^+Br^-$ to **1**, corresponding to the metal-centered couple $[Mn^{IV}{-}Br]$/

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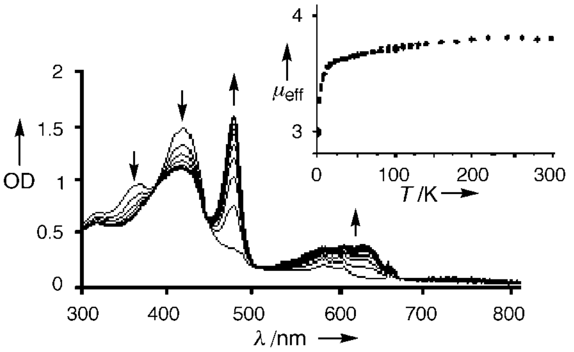


Figure 1. Spectroelectrochemical reduction of **2** at 0.4 V and a plot of the magnetic moment versus *T* for **2**.

$[Mn^{III}{-}Br]^-$. Also consistent with the reduction of the metal center is the large dependence of the reduction potential on axial ligation; $E_{1/2} = 0.69$ and 0.41 V for **2** and **3**, respectively. This proposal was further supported by magnetic susceptibility measurements (SQUID, Figure 1, inset) on **2** and its EPR spectra (not shown, frozen CH_2Cl_2 at 130 K; solid at room temperature). The magnetic moment of 3.80 μ_B and the EPR data (broad $g = 4.3$ signal and a $g = 1.99$ signal with resolved Mn hyperfine structure, $a_{Mn} = 85$ G) confirm an isolated $S = 3/2$ system, in line with the electronic structure of other manganese(IV) complexes.[16] The alternative formulation of **2** and **3** as manganese(III) corrole radical complexes is expected to result in much more complex magnetic data and EPR spectra.[6b]

X-ray crystallographic analysis of **2** and **3** (Figure 2) reveals a pronounced doming of the corrole framework in both structures, with all four pyrrole nitrogens lying significantly above the 19-membered carbon ring (average out of plane distance of 0.065 Å in **2** and 0.21 Å in **3**). As expected, the manganese(IV)–halide bond lengths of 2.428 and 2.312 Å in **2** and **3**, respectively, are shorter (by approximately 0.05 Å) than those found in analogous manganese(III) porphyrin complexes.[17, 18] The average Mn–N bond lengths in **2** (1.925 Å) and **3** (1.932 Å) are longer than those in $[Mn^{III}(tpfc)(OPPh_3)]$ (1.916 Å),[12c] but this is because of very large differences in the out of plane displacements of the manganese atom. Corresponding deviations from the N4 and corrole planes are 0.42 and 0.47 Å in **2**, 0.43 and 0.58 Å in **3**, but only 0.29 and 0.29 Å in $[Mn^{III}(tpfc)(OPPh_3)]$.[12c] Interestingly, the Mn–Cl and Mn–N bond lengths in **3** and [Mn(oec)(Cl)] are very similar,[9] despite the large structural and electronic differences between the corroles.

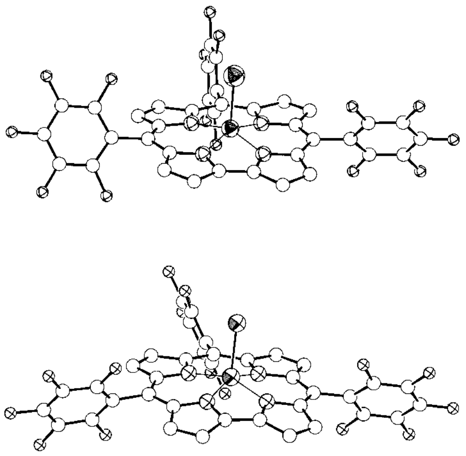


Figure 2. ORTEP views of [Mn(tpfc)(Br)] (**2**; top) and [Mn(tpfc)(Cl)] (**3**; bottom).

In the course of these studies, we noted two other unique features of **1**, both of which could be exploited for preparation of novel manganese corroles. First, the aforementioned high affinity of **1** for Br^- was also applied to N_3^-, which led to a one-pot version of the known protocol for preparation of (nitrido)metal complexes:[19] irradiation of a mixture of **1** and NaN_3 in CH_3CN resulted in very clean conversion into $[Mn^V(tpfc)(N)]^-Na^+$ (**4**). This complex, which is stable at room temperature in solution or as a solid, was identified by a combination of spectroscopic methods (Figure 3). Both the sodium ion and the nitrido ligand are apparent in the mass spectrum (MS); sharp resonance signals in the NMR spectrum are consistent with a diamagnetic manganese(V) center; and the UV spectrum of **4** is very similar to that of analogous neutral (nitrido)manganese(V) porphyrins.[3]

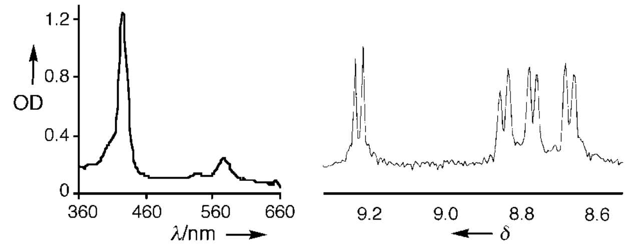


Figure 3. ^1H NMR and UV/Vis spectra of **4** in CD_3CN at room temperature.

Second, we noticed remarkably facile pyrrole-substitution during the aforementioned metal-based oxidation of **1**. In fact, the first two crystal structures of **2** and **3** were obtained with partially halogenated (Br, Cl) corroles. This phenomenon was exploited by treating **1** with an excess of Br_2 in MeOH, which allowed isolation of the fully brominated complex,[20] $[Mn(Br_8tpfc)]$ (**5**), in high yield. In contrast, the preparation of analogous porphyrins requires four synthetic steps: metallation of the porphyrin by zinc, bromination of the zinc complex with NBS (1-bromo 2,5-pyrrolidinedione), not Br_2 as with the corrole, removal of the zinc, and metallation by manganese.[2] The transformation of **1** to **5** causes a 0.37 V shift of the Mn^{III}/Mn^{IV} couple in the cyclic voltammogram (Figure 4), which is the reason that **5** is isolated in the manganese(III) oxidation state, despite the fact that the first equivalent of bromine oxidizes **1** to **2**. To assess differences in reactivity between the "second and third generation" manganese(III) corroles,[2a] **1** and **5** were compared as catalysts for oxygenation of three representative substrates (Scheme 2). Both complexes catalyze the oxidation of styrene by iodosylbenzene in very high yield, but with a very large difference in reaction time: 10 h with **1** compared to 15 min with **5**. These differences were amplified with the less reactive substrates: yields of 100% versus 40% for *trans*-stilbene and 100% versus only 11% for cyclohexene catalyzed by **5** (15 min) and

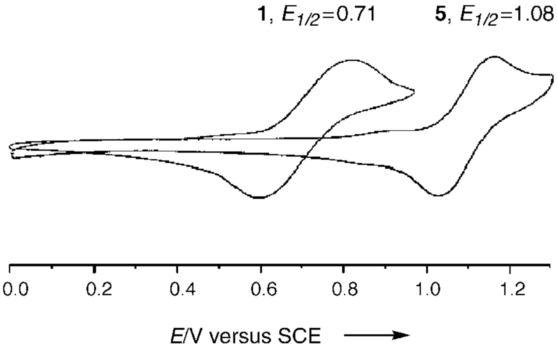
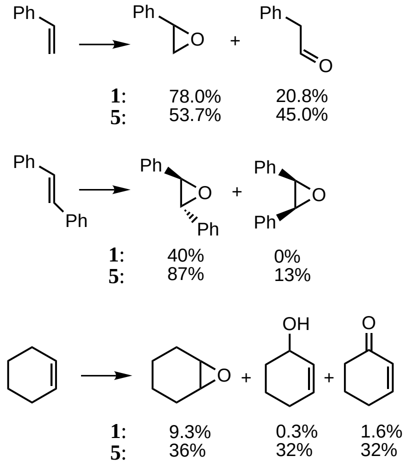


Figure 4. Cyclic voltammetry of [Mn(tpfc)] (**1**) and [Mn(Br$_8$tpfc)] (**5**), in CH$_2$Cl$_2$ with 0.1M TBAP.



Scheme 2. **1** and **5** as oxygenation catalysts, reaction conditions: substrate (1.2 mmol), iodosylbenzene (0.12 mmol), catalyst (1.2 μmol), benzene (1 mL) at room temperature under Ar, for 15 min with **5** and 10–12 h with **1**.

1 (12 h), respectively. Most significantly, **5** *was not bleached* at the end of all reactions, while this is only true for **1** in the reaction with styrene.

In conclusion, we have demonstrated that functionalization of the manganese(III) complex of H$_3$(tpfc) provides a facile route to various high-valent manganese corroles and to the first perhalogenated corrole-based catalyst, all in very simple one-pot syntheses. The very large increase in catalytic activity upon β-pyrrole bromination of **1** to **5** will be fully investigated.

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[14] **2**: A hexane solution of **1** (10 mg, 11.8 μmol) was treated with a hexane solution of Br$_2$ (5.9 μmol), which resulted in quantitative precipitation of **2** as a red-brown solid. MS$^-$: e/z (%): 927 (40) [M^-], 848 (100) [M^- – Br], UV/Vis (CH$_2$Cl$_2$) λ_{max} [nm] (lg ε) 368 (4.63), 416 (4.72), 582 (3.74); elemental analysis (%) calcd for $C_{37}H_8BrF_{15}MnN_4 \cdot 2H_2O$: C 46.08, H 1.25, N 5.81; found: C 45.76, H 1.38, N 6.20. Recrystallization from benzene/heptane resulted in X-ray quality crystals. [Mn(tpfc)(Br)], crystallized as benzene hemi-solvate ($C_{37}H_8BrF_{15}MnN_4$)·½(C_6H_6): formula weight 967.38, monoclinic, space group $P2_1/c$, $a = 13.425(1)$, $b = 23.629(1)$, $c = 11.208(1)$ Å, $\beta = 98.38(1)^\circ$, $V = 3517.5(2)$ Å^3, $Z = 4$, $T = 110$ K, $\rho_{calcd} = 1.827$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.63$ mm^{-1}, 6636 unique reflections, $R1 = 0.053$ for 4854 observations with $F_o > 4\sigma(F_o)$, $R1 = 0.082$ ($wR2 = 0.148$) for all unique data, $|\Delta\rho| = 1.31$ e Å^{-3}.

[15] **3**: A hexane solution of **1** (2.5 mg, 3 μmol) was treated with a dichloromethane solution of tris(4-bromophenyl)aminium hexachloroantimonate (2.5 mg, 3 μmol), which resulted in quantitative precipitation of **3** as a red-brown solid. MS$^-$: e/z (%): 883 (25) [M^-], 848 (100) [M^- – Cl]; UV/Vis (CH$_2$Cl$_2$) λ_{max} [nm] 362, 414 (Soret), 582 (Q band). Recrystallization from benzene/heptane resulted in X-ray quality crystals. [Mn(tpfc)(Cl)], crystallized as dibenzene solvate ($C_{37}H_8ClF_{15}MnN_4$)·2(C_6H_6): formula weight 1040.08, triclinic, space group $P\bar{1}$, $a = 8.547(1)$, $b = 13.488(1)$, $c = 19.675(1)$ Å, $\alpha = 71.08(1)$, $\beta = 85.59(1)$, $\gamma = 73.88(1)^\circ$, $V = 2061.1(2)$ Å^3, $Z = 2$, $T = 110$ K, $\rho_{calcd} = 1.676$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.50$ mm^{-1}, 7056 unique reflections, $R1 = 0.062$ for 4274 observations with $F_o > 4\sigma(F_o)$, $R1 = 0.128$ ($wR2 = 0.147$) for all unique data, $|\Delta\rho| = 0.55$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147467 (**2**) and CCDC-147468 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[20] [Mn(Br$_8$tpfc)] **5**: A solution of bromine (5 mL, 0.2 g, 1.2 mmol) and **1** (10 mg, 12 μmol) in methanol was stirred overnight, after which the methanol and excess bromine were removed under vacuum. Recrystallization from ethanol/water afforded 14.8 mg (85% yield) of **5**. MS$^-$: e/z (%): 1479 (100) [M^-], 1399 (10) [M^- – Br]; UV/Vis (CH$_2$Cl$_2$) λ_{max} [nm] 402 (4.73), 422 (4.70), 490 (4.38), 612 (4.24); ^{19}F NMR (CDCl$_3$): $\delta = -138$ (two overlapping brs, 6F), -152.3 (brs, 1F), -153.2 (brs, 2F), -160.5 (brs, 2F), -161.4 (brs, 4F).