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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 NMRof proposed manganese(v) intermediates should be relatively straightforward, since d² metalloporphyrins with strong π donor ligands are expected to be diamagnetic. The first ¹H 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

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result of the introduction of the electron-poor 5,10,15tris(pentafluorophenyl)corrole $(H_3(tpfc),^{[10]}tpfc = the trian$ ion). The iron, manganese, and rhodium complexes of H₃(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}(PPh₃), Cr^V(O), and Mn^{III}(OPPh₃) 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) NaN₃, $h\nu$, b) $1/2X_2$ (X = Cl, Br), c) excess Br₂/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-Bu₄N⁺Br⁻ to **1**, corresponding to the metal-centered couple [Mn^{IV}–Br]/



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 CH₂Cl₂ at 130 K; solid at room temperature). The magnetic moment of $3.80 \,\mu_{\rm B}$ and the EPR data (broad g = 4.3 signal and a g = 1.99 signal with resolved Mn hyperfine structure, $a_{\rm Mn} = 85$ 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



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

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}(tpf-c)(OPPh₃)] (1.916 Å),^[12c] but this is because of very large differences in the out of plane displacements of the manga-

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nese 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.

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 NaN₃ in CH₃CN 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. $^1\mathrm{H}$ NMR and UV/Vis spectra of 4 in CD₃CN 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 Br₂ 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 Br₂ 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

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E/V versus SCE

Figure 4. Cyclic voltammetry of [Mn(tpfc)] (1) and [Mn(Br₈tpfc)] (5), in CH₂Cl₂ 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 H₃(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 Br₂ (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 (CH₂Cl₂) 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 benzene as hemi-solvate $(C_{37}H_8BrF_{15}MnN_4) \cdot \frac{1}{2}(C_6H_6)$: 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)°, V = 3517.5(2) Å³, Z = 4, T = 110 K, $\rho_{calcd} = 1.827$ g cm⁻³, $\mu(Mo_{K\alpha}) = 1.63 \text{ mm}^{-1}$, 6636 unique reflections, R1 = 0.053 for 4854 observations with $F_0 > 4\sigma(F_0)$, R1 = 0.082 (wR2 = 0.148) for all unique data, $|\Delta \rho| = 1.31 \text{ e} \text{\AA}^{-3}$.
- [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 (CH₂Cl₂) 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 $(C_{37}H_8ClF_{15}MnN_4) \cdot 2(C_6H_6)$: formula weight 1040.08, triclinic, space group $P\bar{1}$, a = 8.547(1), b = 13.488(1), c = 19.675(1) Å, a = 71.08(1), $\beta = 85.59(1), \gamma = 73.88(1)^{\circ}, V = 2061.1(2) \text{ Å}^3, Z = 2, T = 110 \text{ K}, \rho_{\text{calcd}} =$ 1.676 g cm⁻³, μ (Mo_{Ka}) = 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, $|\Delta \rho| = 0.55 \text{ e} \text{Å}^{-3}$. 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(Br₈tpfc)] 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_2Cl_2) λ_{max} [nm] 402 (4.73), 422 (4.70), 490 (4.38), 612 (4.24); ¹⁹F NMR (CDCl₃): $\delta = -138$ (two overlapping brs, 6F), -152.3 (brs, 1F), -153.2 (brs, 2F), -160.5 (brs, 2F), -161.4 (brs, 4F).

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