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Structure of a one-electron oxidized Mn(III)bis(phenolate)dipyrrin Radical Complex and Oxidation Catalvsis **Control via Ligand-centered Redox Activity.**

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The tetradentate ligand dppH₃, which features a half-porphyrin and two electron-rich phenol moieties was prepared and chelated to manganese. The mononuclear Mn(III)-dipyrrophenolate complex 1 was structurally characterized. The metal ion lies in a square pyramidal metal ion, the apical position being occupied by a methanol molecule. Complex 1 displays two reversible oxidation waves at 0.00 V and 0.47 V vs. Fc⁺/Fc, which are assigned to ligand-centered processes. The oneelectron oxidized species 1^+ SbF₆⁻ was crystallized, showing an octahedral Mn(III) center with two water molecules coordinated at both apical positions. The bond distance analysis and DFT calculations disclose that he radical is delocalized over the whole aromatic framework. Complex 1^+ SbF₆ exhibits an ($S_{tot} = 3/2$) spin state due to the antiferromagnetic coupling between Mn(III) and the ligand radical. The zero field splitting parameters are D = 1.6 cm⁻¹, E/D = 0.18(1), $g_{\perp} = 1.99$ and g_{\parallel} = 1.98. The dication $\mathbf{1}^{2+}$ is an integer spin system, which is assigned to a doubly oxidized ligand coordinated to a Mn(III) metal center. Both 1 and 1^{+} SbF₆ catalyze styrene oxidation in the presence of PhIO, but the nature of the main reaction product is different. Styrene oxide is the main reaction product when using 1, but phenylacetaldehyde is formed predominantly when using $\mathbf{1}^{+}$ **SbF**₆. We examined the ability of complex $\mathbf{1}^{+}$ **SbF**₆ to catalyze the isomerization of styrene oxide and found that it is an efficient catalyst for the anti-Markovnikov opening of styrene oxide. The formation of phenylacetaldehyde from styrene therefore proceeds in a tandem E-I (epoxidation-isomerization) mechanism in the case of 1^{+} SbF₆. This is the first evidence of control of the reactivity for styrene oxidation by changing the oxidation state of a catalyst based on a redox-active ligand.

Introduction

The design of highly active catalysts employing earth-abundant transition metal ions for oxygenation reactions is one of the most active research fields in inorganic chemistry. Perhaps the most extensively studied inorganic platforms for this purpose are Mn(salen) (in particular Jacobsen's catalyst, see Scheme 1) and Mn(porphyrin) complexes.^[1] In the generally accepted mechanism the Mn(III) precatalyst reacts with an oxygen atom donor (PhIO) to form a high-valent manganese oxo species (or PhIO adduct), which is directly involved in the epoxidation reaction.^[2] We and others established in related Mn(III),^[3] Fe(III),^[4] Co(II),^[5] Cu(II),^[6] and Ni(II)^[7] salen complexes that the ligand can be redox non-innocent when the phenol moieties are functionalized by electron-donating groups. Thus, the electronic hole can be located on the ligand instead of at the

complex without participating in the electron transfer.[14-15] t-Bi t-Bu t_R t-Bi t-Bu Jacobsen's catalyst X = CH₃OH, 1

Scheme 1. Formula of the Jacobsen's catalyst and 1

We recently reported on the coordination chemistry of a bis(phenol)dipyrrin ligand, which incorporate tert-butyl groups

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[†] Electronic Supplementary Information (ESI) available: Spin density plots, TD-DFT assignment of the NIR bands, EPR spectra, X-Ray crystallographic files. See DOI: 10.1039/x0xx00000x

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at both the *ortho* and *para* positions of the phenol moieties.^[16] We established by combined X-Ray diffraction and spectroscopy that the neutral nickel and cobalt complexes are indefinitly stable Ni(II) and Co(II)-radical species. We herein extend this study to the manganese ion, with a newly designed ligand. While the phenol groups still harbour two *tert*-butyl substituents, which are essential to stabilize the high oxidation states of the complex, the dipyrrin is functionalized in meso position by a triaryl moiety. We envision that this new feature will prevent the dimerization, as observed by Aukauloo *et al.*^[17] in a related manganese complex, while keeping labile coordination sites essential for catalysis.

We establish that **1** undergoes two oxidative redox processes, producing the persistent radical species 1^+ and the dication 1^{2+} . We investigate the catalytic activity of both **1** and 1^+ for styrene oxidation in the presence of PhIO.

Results and discussion

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Synthesis of the ligand and characterization of 1

The ligand dppH₃ was prepared following a two-step sequence. First, two equivalents of 2-(3,5-di-*tert*-butyl-2methoxyphenyl)pyrrole^[18] were condensed on 2,6-diphenyl benzaldehyde^[19] in the presence of trifluoroacetic acid. Subsequent oxidation with an equimolar amount of 2,3dichloro-4,5-dicyano-*p*-benzoquinone afforded the di-*O*methylated precursor dppHMe₂ in a 84% yield after purification. Deprotection of the phenol moieties with sodium dodecylthiolate gave the targeted dppH₃ in a satisfactory 69% yield.



Figure 1. X-Ray crystal structure of A) 1 and B) 1^* SbF₆⁻ at the 30 % ellipsoid probability (H atoms omitted for clarity except those of the coordinated water molecules).

The manganese complex 1 was prepared by reacting dppH₃ and 2 equiv of Mn(OAc)₃.2H₂O in the presence of NEt₃ under an argon atmosphere, followed by exposure to air. The crystal structure of 1 (Fig. 1A) displays a mononuclear complex, with a manganese ion that lies in a square pyramidal geometry, in which the O1, O2, N1, N2 atoms of the ligand defines the equatorial plane, and the apical position (O3) occupied by a methanol molecule. The coordination bond distances (Table 1) are indicative of a high spin Mn(III) ion.^[17] The Mn-O3 bond length of 2.270(4) Å confirms that the methanol ligand is not deprotonated upon coordination.^[20] The C1-O1 and C22-O2 bond lengths are 1.336(4) Å and 1.332(5) Å, respectively. These values are similar to those reported for Mn^{III}bis(phenolato) complexes,^[17] attesting that the ligand is in its tri-anionic closed-shell electronic configuration. Furthermore, DFT calculations accurately predict the coordination sphere bond lengths (≤ 0.03 Å for the S = 2 state, see Table S2).

| Table 1. Selected bond lengths in 1 and 1^* SbF ₆ (from the crystal structures) | | | | | | | | | |
|--|----------|--|--------|----------|--|--|--|--|--|
| | 1 | 1 ⁺ SbF ₆ ⁻ | | 1 | 1 ⁺ SbF ₆ ⁻ | | | | |
| Mn-N1 | 1.956(3) | 1.955(7) | 01-C1 | 1.336(4) | 1.304(13) | | | | |
| Mn-N2 ^[a] | 1.963(3) | 1.955(7) | C2-C3 | 1.386(6) | 1.326(20) | | | | |
| Mn-01 | 1.870(3) | 1.868(7) | C3-C4 | 1.394(6) | 1.442(20) | | | | |
| Mn-O2 ^[a] | 1.857(3) | 1.868(7) | C9-C10 | 1.415(5) | 1.471(11) | | | | |
| Mn-O _{ax} ^[b] | 2.270(4) | 2.295(6) | C8-C9 | 1.369(6) | 1.298(12) | | | | |
| Mn-O _{ax} ^[b] | - | 2.295(6) | C6-C7 | 1.451(6) | 1.437(12) | | | | |

^a N2 refers to N1* in 1^{*} SbF₆⁻. Mn-Oax corresponds to one Mn-O3 bond in 1 (square pyramidal) and both Mn-O3 bonds in 1^* SbF₆⁻ (octahedral).

Complex **1** was found to be EPR silent in CH₂Cl₂ at 10 K. This feature is reminiscent of complexes having an integer spin ground state with zero field splitting (zfs) parameters larger than the X-Band energy quantum ($\approx 0.3 \text{ cm}^{-1}$) and wherein the symmetry in the zfs interaction is close to axial.^[21] High spin Mn(III) complexes are the archetype of such systems, which are usually difficult to characterize by perpendicular X-band EPR spectroscopy.^[21] Indeed, under these conditions the conventional spin allowed $\Delta Ms = \pm 1$ transitions are not possible since the energy required is much larger than 0.3 cm⁻¹.



Figure 2. UV-Vis-NIR spectra of CH_2CI_2 solutions of **1** (black), **1**^{*} (red) and **1**^{2*} (blue). *T* = 298 K. The TD-DFT calculated transitions are indicated as vertical bars.

Spectro-electrochemistry

The electrochemical behavior of the ligand dppH₃ and **1** has been investigated by cyclic voltammetry (CV). The CV curve of 1 in CH₂Cl₂ (0.1 M TBAP solution) is characterized by two reversible oxidation waves at $E_{1/2}^1 = 0.00 \text{ V} (\Delta E_p = 0.097 \text{ V})$ and $E_{1/2}^{2} = 0.47 \text{ V} (\Delta E_{p} = 0.104 \text{ V}) \text{ vs. Fc}^{+}/\text{Fc}$ (Fig 3). Both correspond to one-electron redox couples and are assigned to ligandcentered oxidation processes (see below). These potential values are lower than those measured for the free ligand dppH₃ in CH₂Cl₂ ($E_{1/2}^1$ = 0.19 V, $E_{1/2}^2$ = 0.61 V and $E_{1/2}^3$ = 0.92 V), most likely because of the deprotonation of the oxygen donors. Conversely, the first oxidation wave in the complex, which corresponds to the dpp^{2-}/dpp^{3-} redox couple, is anodically shifted by ca. 0.5 - 0.6 V in comparison to related Ni(II) and Co(II) bis(phenolate)dipyrrin complexes (reduction wave in these cases since the complexes were isolated under their radical forms).^[16] We interpret this shift by the higher formal charge at the metal center in the manganese case. The $\Delta E_{1/2}$ value ($\Delta E_{1/2} = E_{1/2}^2 - E_{1/2}^1$) is 0.47 V, thus within the range of those calculated for the Ni(II) and Co(II) bis(phenolate)dipyrrin complexes ($\Delta E_{1/2} = E_{1/2}^{ox} - E_{1/2}^{red}$ in these cases), which are $\Delta E_{1/2}$ = 0.51 and 0.60 V, respectively. $^{[16]}$ This analogy suggests similar assignment of the redox waves, *i.e.* ligand-centered processes. It is interesting that the $E_{1/2}$ value is lower for 1 than for the dinuclear manganese complex reported by Aukauloo et al.^[17] This shift likely results from both the absence of tert-butyl groups in ortho and para positions of the phenolate moieties, as well as the bridging nature of the phenolato donors in their case ($E_{1/2}^{1}$ = 0.67 V vs. SCE in CH₃CN).^[17] Altogether, these data support ligand participation in the redox processes.



Figure 3. Cyclic voltammetry curve of 1 in CH_2Cl_2 (containing 0.1 M TBAP) at a carbon electrode. T = 298 K. Scan rate = 0.1 V s⁻¹. The potential values are given versus the Fc⁺/Fc reference couple.

Bulk electrolysis at a controlled potential produces the cations $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ quantitatively, which were characterized by EPR and Vis-NIR spectroscopies.

The Vis-NIR spectrum of the electrochemically generated $\mathbf{1}^+$ differs markedly from that of the neutral precursor $\mathbf{1}$ (Fig. 2). The most salient features are the attenuation of the main transition at 730 nm and the appearance of several NIR features that are indicative of the formation of a radical species (see below for details). The dication $\mathbf{1}^{2+}$ also displays intense NIR bands, but its spectrum is distinct from that of the cation, suggesting the formation of a quinone-like species.

The X-band EPR spectrum of $\mathbf{1}^+$ (Fig. 4) displays a set of resonances at g_{eff} = 5.4, 2.9, 2 and <1.6, which are indicative of an $(S_{tot} = 3/2)$ ground spin state of the complex. This spectrum could be interpreted by considering either antiferromagnetic coupling between the ligand radical spin $(S_{rad} = \frac{1}{2})$ and the high spin Mn(III) centre $(S_{Mn} = 2)$, [3,22,23] or alternatively by considering a d³ Mn(IV) ion coordinated to closed-shell ligand.^[24] However, both the UV-Vis-NIR spectroscopy and the solid state structure of $\mathbf{1}^+$ (see below) clearly rules out the latter formulation. Thus, complex $\mathbf{1}^{\dagger}$ is a magnetically coupled Mn(III) radical species, and the ⁵⁵Mn hyperfine lines that are well resolved in the low field resonance (A₁= 0.008 cm⁻¹ and A_{II}= 0.005 cm⁻¹), are further indicative of interaction between the radical and the metal center. The following Spin Hamiltonian parameters were obtained from simulation: $D = 1.6 \text{ cm}^{-1}$; E/D = 0.18(1); $g_{\perp} = 1.99$; g_I= 1.98. Since the D value is larger than the X-band energy quantum, it could be only roughly estimated and the value 1.6 cm⁻¹ represents a lower limit.

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Figure 4. X-band EPR spectrum of a CH_2CI_2 solution of 1^* **SbF**₆ (black lines) and simulation using the parameters given in the text (red lines). T = 10 K. *: Impurity in the cavity.

In contrast to $\mathbf{1}^{+}$ the dication $\mathbf{1}^{2+}$ was found to be mainly X-Band EPR silent at 10 K in perpendicular mode (B₀ _|_ B₁). By using a parallel polarization mode (B₀ // B₁), a resonance could be easily detected at g = 8. This strongly supports an integer ground spin state for $\mathbf{1}^{2+}$ (Fig S4). According to the literature,^[23,25] this low field resonance is assigned to a transition within the Ms = ±2 doublet of an (S_{Mn} = 2) Mn(III) ion. It must be stressed that this spectrum is clearly different than that reported for anilinyl-Mn(IV) radical complexes.^[26] Thus, $\mathbf{1}^{2+}$ is consistently assigned to a high spin manganese(III) complex involving a doubly oxidized, and subsequently closedshell, ligand dpp⁻.

Geometric and electronic structures of the oxidized species

The monocation $\mathbf{1}^+$ was synthesized on a preparative scale by using AgSbF₆, i.e. a one-electron oxidant that is not an oxygen donor. Brown single crystals of $\mathbf{1}^+$ **SbF**₆⁻ were grown by slow diffusion of pentane into a dichloromethane solution of the complex. The dication $\mathbf{1}^{2+}$ could not be isolated similarly, in part due to its lower stability.

The X-ray crystal structure of 1^+ SbF₆⁻ is shown in Fig. 1B and selected bon distances summarized in Table 1. The geometry of the metal ion in 1^+ SbF₆⁻ is octahedral, with two water molecules that occupy the axial positions. We ruled out both deprotonation of the axial ligands and the presence of a Mn(IV) center since the Mn-O3 and Mn-O4 bond distances would be much shorter than those experimentally measured (2.295 Å): The expected bond lengths are indeed 1.67± 0.03 Å for a $Mn^{V}=0$ core, and 1.839(2) Å for $Mn^{V}-OH$ or $Mn^{V}-OCH_{3}$ core.^[3,27] Furthermore, each O3 atom resides at an H-bonding distance of an SbF₆⁻ counter ion (shortest O3-F3 distance at 2.75 Å). Within the pyrrole ring the C8-C9 bond length decreases from 1.369(6) to 1.298(12) Å upon oxidation from 1 to 1⁺, while the C9-C10 bond extends from 1.415(5) to 1.471(11) Å. Further, the C2-C3 bond shortens from 1.386(6) to 1.326(20) Å while the C3-C4 bond lengthens from 1.394(6) to 1.442(20) Å upon oxidation. This bonding pattern unambiguously shows that $\mathbf{1}^{+}$ is a genuine Mn(III) complex featuring a hybrid "phenoxyl-pyrroyl" radical. [16,28] DFT calculations at the B3LYP level of theory support this assignment, by showing spin density distributed over the metal center (3.91), and delocalized over both phenoxyl rings (-0.24 and -0.28 each) and the dipyrrin framework (-0.59, Fig. 5a). The ($S_{tot} = 3/2$) spin state, due to antiferromagnetic coupling between Mn(III) and the ligand radical, is correctly predicted to be the lowest in energy (2.9 kcal mol⁻¹ below the $S_{tot} = 5/2$ state).



Figure 5. Spin density plots for (a) 1^+ and (b) 51^{2+} .

The electronic structure of the dication $1^{2^{*}}$ has been investigated by DFT calculations, by considering two axially bound water molecules (Fig 5b). Both the (S = 2) (${}^{5}1^{2^{+}}$) and (S =3) (${}^{7}1^{2^{+}}$) spin states were calculated, but only the first is relevant (more stable by 9.4 kcal mol⁻¹). The spin density is mainly localized on the metal center in ${}^{5}1^{2^{+}}$, supporting a nonradical character of the ligand. Thus, DFT calculations correctly predict the dication to be a high spin Mn(III) complexes coordinated to a doubly-oxidized closed-shell ligand.

Vis-NIR spectroscopy and TD-DFT calculations

The manganese complex **1** exhibits distinct Vis-NIR spectra depending on its oxidation state (Table 2).

| Table 2. Vis-NIR spectroscopic data. [a] | | | | | | |
|--|--|--|--|--|--|--|
| | λ [nm] (ε [M ⁻¹ cm ⁻¹]) | | | | | |
| 1 | 475 (13100), 675 sh (9110), 730 (20000), 955 (540), 1080 (560) | | | | | |
| 1 ⁺ | 425 (12475), 455 (12575), 495 (12580), 515 (13430), 680 (5040), 720 | | | | | |
| | (4340), 945 (6710), 1060 sh (2950), 1390 (2860) | | | | | |
| 1 ²⁺ | 430 (14750), 520sh (8830), 560 sh (7000), 595 sh (5840), 715 (4405), | | | | | |
| | 960 (4380), 1140 (6010), 1340 (7600) | | | | | |
| 2 ^[b] | 417 (14 710), 507 (9520), 645 (6780), 934 (4360) | | | | | |
| a Solvo | nt: anhudrous CH Cl | | | | | |

^e Solvent: anhydrous CH₂Cl₂.

 $^{\rm b}$ oxomanganyl species generated by adding 1.1 molar equivalent of $\mathsf{Phl}(\mathsf{OAc})_2$ to 1, see below.

The Vis-NIR spectrum of the electrochemically generated $\mathbf{1}^+$ is characterized by low energy bands at 1390 nm (2860 M⁻¹ cm⁻¹), 1060 (2950 M⁻¹ cm⁻¹) and 945 nm (6710 M⁻¹ cm⁻¹). In order to gain insight into the nature of the NIR electronic transitions, TD-DFT calculations were undertaken. Three NIR bands are predicted, in agreement with the experimental spectra (Fig. 2

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and 6). The NIR band of highest intensity is predicted at $\lambda_{calcd} = 1318 \text{ nm}$ ($f_{osc} = 0.0583$), and corresponds to a α -HOMO $\rightarrow \alpha$ -LUMO transition. From orbital composition analysis it is assigned to a phenoxyl \rightarrow dipyrrin ligand-ligand charge transfer transition (LLCT) (Fig. 6). The two other low energy bands are predicted at 1075 nm ($f_{osc} = 0.0263$) and 858 nm ($f_{osc} = 0.0242$) and again correspond to CT transitions.

The dication 1^{2^+} also displays intense NIR bands, but their intensities are distinct from those in the cation: 1340 nm (7600 M⁻¹ cm⁻¹), 1140 nm (6010 M⁻¹ cm⁻¹) and 960 nm (4380 M⁻¹ cm⁻¹). The three lowest energy electronic excitations are calculated at 1324 nm ($f_{osc} = 0.0296$), 1191 nm ($f_{osc} = 0.0462$) and 1042 nm ($f_{osc} = 0.0223$), showing again a good agreement between theory and experiment. In this case numerous contributions from many sets of orbitals are involved (see ESI).



Catalytic activity of 1 and 1^+ SbF₆⁻ towards styrene oxidation

Having established that the oxidation state of the ligand differs in 1 and $\mathbf{1}^{+}$ SbF₆, we examined the ability of both complexes to oxidize styrene, a classical olefinic substrate, in the presence of an oxygen atom donor (Table 3). Due to its low stability and difficulties in isolating 1^{2+} at the solid state we refrained to extend the catalytic investigation to the dication. Thus, 1 (1 mol%) catalyzes the reaction between the olefinic substrate and a molar equivalent of iodosylbenzene to afford mainly styrene oxide in a 31% yield (31 turnovers, Table 3, entry 1). It is worth noting that 10 turnovers were obtained for the epoxidation of cyclooctene with the related manganese described by Aukauloo et al., [17] albeit with different conditions. Trace amounts of phenylacetaldehyde and benzaldehyde were also detected. No reaction was observed in the absence of 1. Increasing the PhIO loading to 2 equiv led to a decrease in the epoxide yield while the amount of

aldehyde remained unchanged (Table 3, entry 2). It is noteworthy that under anaerobic and anhydrous conditions the epoxide formed in a slightly lower 19% yield (Table 3, entry 3). Notwithstanding, we ruled out a role of dioxygen in the reaction since no reaction occurs in the absence of PhIO (Table 3, entry 4).

The catalytic properties of $\mathbf{1}^+$ **SbF**₆ were then investigated. Remarkably, replacing **1** with 1^{+} **SbF**₆⁻ dramatically affected the product distribution of the reaction. Indeed, the reaction between styrene and 1 equiv of PhIO in the presence of 1⁺ SbF₆ affords predominantly phenylacetaldehyde in 22% yield, together with a small amount of benzaldehyde (Table 3, entry 5). Unexpectedly, no epoxide was detected. As observed with 1, a higher amount of PhIO had an inhibitory effect on catalysis (Table 3, entry 6), whereas the reaction outcome remains unaffected under inert conditions (Table 3, entry 7). Thus, both **1** and $\mathbf{1}^{\dagger}$ **SbF**₆ are capable of oxygen insertion in the presence of PhIO. However, only $\mathbf{1}^{\dagger}$ **SbF**₆ allows the anti-Markovnikov oxidation (the addition does not occur through the formation of the most substituted carbocation) of styrene into phenylacetaldehyde. Changes in product distribution have been reported for some catalysts based on manganese salan complexes, but not to such an extend and for catalysts that differ by their substituents instead of oxidation state.^[29]

| Table 3. Oxidation of styrene by 1 and $1^* \mathbf{SbF_6}^{[a]}$ | | | | | | | | | | |
|---|--|------|-----------------------------|------------------------------|---------------------------|--|--|--|--|--|
| $\bigcirc \frown$ | [Mn] (1 mol% PhIO CH ₂ Cl ₂ , rt | 6) | + | | 10 | | | | | |
| Entry | [Mn] | PhIO | Epoxide (%) ^b | PhCH₂CHO (%) ^⁵ | PhCHO (%) ^b | | | | | |
| 1 | 1 | 1 | 31 | 3 | 7 | | | | | |
| 2 | 1 | 2 | 19 | 2 | 7 | | | | | |
| 3 ^c | 1 | 1 | 19 | 3 | 5 | | | | | |
| 4 | 1 | - | 0 | 0 | 0 | | | | | |
| 5 | 1 ⁺ SbF ₆ ⁻ | 1 | 0 | 22 | 12 | | | | | |
| 6 | 1 ⁺ SbF ₆ ⁻ | 2 | 0 | 12 | 20 | | | | | |
| 7 ^c | 1 ⁺ SbF ₆ ⁻ | 1 | 0 | 19 | 11 | | | | | |

^a Conditions: Styrene (0.1 M), [Mn] complex (1 mM), PhIO (0.1 or 0.2 M), CH₂Cl₂ (2 mL), 25°C, 20h. ^b Yields are the mean of 2 runs and were determined by GC analysis using biphenyl (5.10⁻² M) as internal standard. ^c Run performed under argon and anhydrous conditions.

Catalytic activity of 1⁺ SbF₆⁻ towards isomerization of styrene oxide

In order to gain insight into this unique reactivity, we examined the ability of $\mathbf{1}^+$ **SbF**_6^- to catalyze the isomerization of styrene oxide under air (Table 4). In the absence of PhIO phenylacetaldehyde was the sole product detected (Table 4, entry 1). Repeating the reaction with 1 equiv of PhIO afforded a mixture of benzaldehyde (23 %) and phenylacetaldehyde (30 %) (Table 4, entry 2). In both cases the yield of phenylacetaldehyde was higher than in any other experiments, showing that $\mathbf{1}^+$ **SbF**_6^- is an efficient catalyst for the anti-Markovnikov isomerization of styrene oxide. The formation of phenylacetaldehyde from styrene therefore proceeds in a

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tandem E-I (epoxidation-isomerization) mechanism, where $\mathbf{1}^{\mathsf{T}}$ **SbF**₆ acts as a bifunctional catalyst.



 a Conditions: Styrene oxide (0.1 M), 1^{\star} SbF_6^- (1 mM), PhIO (0.1 M), CH_2Cl_2 (1 mL), 25°C, 20h.

Reactivity of 1 and 1⁺ SbF₆⁻ with oxygen atom donors

We next examined by spectroscopy the reactivity of 1 and 1 SbF_6 with PhI(OAc)₂, an oxygen atom donor whose solubility is higher than that of PhIO. The addition of 1.1 eqt of PhI(OAc)₂ to 1 and 1^+ SbF₆⁻ induces clean spectral changes, supporting a transfer of an oxygen atom to the pre-catalyst, leading to the adduct 2 (Fig. 7, Table 2). After one hour no more significant evolution is observed and the spectrum, whether the starting material is 1 or 1^+ SbF₆, is identical. The evolution observed in the case of 1 is remarkably similar to that reported upon conversion of a related Mn(III) complex to its Mn(V)-oxo counterpart.^[30] Hence, it consists of transitions at 337 (18 265), 417 (14 710), 507 (9520), 645 (6780) and 934 nm (4360 M^{-1} cm⁻¹). Owing to its thermal stability, the species 2 could be characterized by ESI-MS. After mixing 1 with PhI(OAc)₂ the molecular peak of the initial material shifts by 16 units (m/z = 848.4), indicative of Mn(V)=O formation (Fig. 7, insert). The reaction of **1** and $\mathbf{1}^{\dagger}$ **SbF**₆ with an oxygen atom donor was also monitored by EPR spectroscopy. The spectrum remains silent in the case of 1, confirming its conversion into a species having an integer spin system. After 20 min reaction of PhIO with $\mathbf{1}^{\dagger}$ **SbF**₆ at room temperature (in CH₂Cl₂) the EPR spectrum still exhibits the features of an (S = 3/2) system, but the intensity is three times lower (Fig S7), consistent with its slow conversion into an oxomanganyl species. Thus, these spectroscopic data support a progressive conversion of both Mn(III) complexes (1 and 1^+ SbF₆) into a high valent metal oxo species.



Figure 7. Spectral evolution after mixing a CH_2CI_2 solution of the Mn(III) precatalysts with 1.1 molar eqt of PhI(OAc)₂ at 302 K. (a) **1** and (b) **1**⁺. The arrows indicate the spectral changes as a function of time (one spectrum each minute). Insert: ESI-MS profile after mixing **1** with 10 molar eqts of PhI(OAc)₂.

Thus, both **1** and $\mathbf{1}^{\dagger}$ **SbF**₆ are converted into an oxomanganyl species 2 in the presence of PhIO. This oxomanganyl complex is the active oxygen atom donor responsible for styrene oxidation to styrene oxide. Its formation likely proceeds more slowly with PhIO than with PhI(OAc)₂ due to the limited solubility of the former. This suggests the simultaneous presence of both 2 and the Mn(III) pre-catalyst (1 or 1^+ SbF₆) in solution, at least in the early stage of catalysis. The difference in the product distribution of the oxidation reaction by **1** and $\mathbf{1}^{\dagger}$ **SbF**₆ can be rationalized by the relative Lewis acidity of the metal center modulated by the ligand oxidation state. Under its trianionic closed-shell electronic configuration, the ligand is a strong donor. The relatively weak Lewis acidity at the metal center disfavours isomerization of the bound epoxide.^[29] In $\mathbf{1}^{+}$ **SbF**₆⁻ the ligand adopts a dianionic open-shell electronic configuration, with enhanced Lewis acidity at the metal. The reaction then evolves towards isomerization into phenylacetaldehyde.

Experimental section

Materials and instruments

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All operations were performed under anaerobic conditions under a pure argon atmosphere using a glovebox or standard techniques. Anhydrous toluene, DMF Schlenk and triethylamine were distilled over CaH₂ under an argon atmosphere Anhydrous prior to use. acetone. dichloromethane, acetonitrile, methanol were purchased from Acros. 2-(3,5-Di-tert-butyl-2-methoxyphenyl)pyrrole and 2,6diphenylbenzaldehyde were prepared according to reported procedures.^[18,19] All other chemicals were purchased from Acros, Alfa-Aesar, Sigma-Aldrich or TCI and were used as received. NMR spectra were recorded on a Brüker Avance 300 (¹H at 300 MHz, ¹³C at 75 MHz). Chemical shifts are given relative to solvent residual peaks. Mass spectra were recorded on a Brüker Esquire 3000 (ESI/Ion Trap) equipment. Microanalyses were performed by the Service Central d'Analyze du CNRS (Lyon, France). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with an ATR sampling accessory. UV/Vis visible spectra at 298 K were recorded on a Varian Cary 50 spectrometer. X-band EPR spectra were recorded either on an EMX plus spectrometer equipped with an Oxford Helium cryostat. Spectra were treated using the Bruker SIMFONIA software. Cyclic voltammetry curves were recorded on a CH Instruments 620 potentiostat in a standard three-electrode cell under argon atmosphere in CH₂Cl₂ solutions containing 0.1M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. An Ag/AgNO₃ (0.01 M) reference electrode was used. All the potentials given in the text are referred to the regular Fc⁺/Fc redox couple used as an internal reference. A glassy carbon disc electrode (5 mm diameter), polished with 1 μm diamond paste, was used as the working electrode. Electrochemical oxidations were performed on an EG&G PAR 273A potentiostat, under an argon atmosphere at 298 K, using a carbon foam working electrode.

Synthesis

dppHMe2. Under argon, 2,6-diphenylbenzaldehyde (113 mg, 0.437 mmoles, 0.5 equiv.) $^{[18]}$ and TFA (10 $\mu\text{L},$ 0.131 mmoles, 15 mol%) were added to a stirred solution of 2-(3,5-di-tert-butyl-2-methoxyphenyl)pyrrole (500 mg, 0.876 mmoles, 1.0 equiv.)^[19] in CH₂Cl₂ (5 mL) at room temperature. After 24 hours stirring, DDQ (99 mg, 0.436 mmoles, 0.5 equiv.) was added in small portions. The resulting mixture was allowed to stir 2.5 more hours at room temperature before saturated aqueous NaHCO₃ was added dropwise. The organic phase was separated and the aqueous one was extracted with CH₂Cl₂. The combined organic phase was dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The remaining residue was triturated in MeOH, filtrated through a frit and dried under vacuum to give the desired compound as an orange-red solid. Yield: 84%. ¹H NMR (300 MHz, CDCl₃): δ (ppm)= 7.59 (dd, J = 8.2, 6.7 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.37-7.27 (m, 8H), 7.14 - 7.03 (m, 6H), 6.49 (s, 4H), 3.18 (s, 6H), 1.36 (s, 18H), 1.28 (s, 18H); 13 C NMR (75 MHz, CDCl₃): δ (ppm)= 155.8, 153.4, 145.3, 143.3, 142.8, 142.1, 141.9, 135.9, 135.1, 129.3, 129.7, 128.6, 128.5, 127.6, 127.1, 126.5, 124.9, 124.7, 119.0, 61.0,

dppH₃. Under argon, NaH (293 mg, 7.3 mmol, 4.0 equiv.) was added to a solution of n-dodecanethiol (1.75 mL, 7.3 mmol, 4.0 equiv.) in DMF (20 mL) at 5°C. The temperature was allowed to warm to 25°C and the mixture was stirred during 1 hour. dppHMe₂ (1.46 g, 1.8 mmol, 1.0 equiv.) was then added and the reaction was heated at 110°C during 4 hours. After cooling to rt, saturated aq. NH₄Cl, H₂O and EtOAc were added. The organic layer separated and the aqueous one was extracted with EtOAc. The combined organic phase was dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The remaining residue was purified by crystallization in a MeOH/CH₂Cl₂ mixture afforded the ligand as dark red needles. Yield: 69%. ¹H NMR (300 MHz, CDCl₃): δ (ppm)= 7.60 (dd, J = 8.3, 7.0 Hz, 1H), 7.47-7.44 (m, 4H), 7.31 (d, J = 2.4 Hz, 2H), 7.25-7.21 (m, 4H), 7.19-7.08 (m, 6H), 6.76 (d, J = 4.4 Hz, 2H), 6.60 (d, J = 4.4 Hz, 2H), 1.49 (s, 18H), 1.33 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm)= 153.8, 153.0, 143.3, 141.8, 141.4, 141.2, 135.9, 135.5, 135.3, 129.8, 129.4, 129.0, 128.6, 127.8, 127.0, 125.4, 123.0, 118.1, 116.6, 35.0, 34.5, 31.7, 30.4. MS (ESI): m/z= 781.6 $[M + H]^+$. IR: v (cm⁻¹) = 3626, 3449, 2958, 2905, 2867, 1559, 1476, 1242. Anal. Calcd for C₅₅H₆₀N₂O₂.CH₃OH: C, 82.72; H, 7.93; N, 3.45. Found: C, 82.42; H, 7.96; N, 3.30.

Complex **1.** Under argon, Mn(OAc)₃.2H₂O (34 mg, 0.13 mmol, 2.0 equiv.) and Et₃N (45 μ L, 0.32 mmol, 5.0 equiv.) were added dropwise to a stirred solution of dppH3 (50 mg, 0.064 mmol, 1.0 equiv.) in a CH₂Cl₂/MeOH (3:1, v:v) mixture (15 mL). The reaction was heated at 50°C and was completed within 2 hours (TLC monitoring; Eluent: CH₂Cl₂/pentane; 1:1, v:v). After cooling to r.t. the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography (CH₂Cl₂/pentane; 1:1, v:v) to give the desired complex. Dark brown powder, yield: 74%. Dark crystals were grown by slow diffusion of pentane in a CH₂Cl₂ / MeOH solution of the complex. MS (ESI): m/z= 832 [M - H]⁻. IR: v (cm⁻¹) = 2946, 2904, 2867, 1546, 1486, 1397, 1287, 1017, 859, 695. Anal. Calcd for C₅₅H₅₇MnN₂O₂, 3 CH₃OH: C, 74.98; H, 7.48; N, 3.02. Found: C, 74.73; H, 7.45; N, 3.09.

Complex **1**⁺ **SbF**₆⁻. Under argon, AgSbF₆ (9.9 mg, 0.03 mmol, 1.2 equiv.) was added to a solution of 1 (20 mg, 0.025 mmol, 1.0 equiv.) in CH₂Cl₂ (10 mL). After 10 min stirring at r.t., the mixture was filtrated on Celite[®] and the resulting filtrate was concentrated to a volume of about 1 mL. Addition of pentane under vigorous stirring at 5°C formed a precipitate. Filtration through a frit gave a dark red powder. Yield: 97%. Blue crystals of **1**⁺ **SbF**₆⁻ were grown by slow diffusion of pentane in a CH₂Cl₂ solution of the complex. MS (ESI): m/z= 832.5 [M - SbF₆]⁺. IR: v (cm⁻¹) = 3462, 2949, 2901, 2867, 1530, 1518, 1429, 1397, 1363, 1252, 1103, 1014, 960. Anal. Calcd for C₅₅H₆₁MnN₂O₄, 2 CH₂Cl₂: C, 53.71; H, 5.14; N, 2.19. Found: C, 54.13; H, 5.27; N, 2.11.

Catalytic experiments

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Reactions were carried using stock solutions containing 0.1 M of styrene and 5.10⁻² M of biphenyl (internal standard) in CH₂Cl₂. A typical run was performed as follows: in a vial, PhIO (1 or 2 equiv) and the desired complex **1** or $\mathbf{1}^{+}$ SbF₆ (1 mol%) were successively added to 2 mL of the stock solution. The mixture was stirred at room temperature during 20h, filtrated through coton and analyzed by GC. GC analyses were done on a Shimadzu GC-17A apparatus equipped with a BPX5 capillary column (30 m x 0.25 mm). Analytical method: Injector temp.: 250°C, Detector temp.: 250°C, Column temp.: 75°C during 5 min then 10°C/min until 250°C then 250°C during 5 min).

Computational Details

Geometry optimizations were performed using the Gaussian 09 program (Revision D.01),^[31] the B3LYP^[32] functional and the 6-31G(d) basis set on all atoms. The X-ray crystal structures of **1** and $\mathbf{1}^{\dagger} \mathbf{2} \cdot \mathbf{H}_2 \mathbf{O}$ were used as a starting point for all geometry optimizations. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single point calculations for the complexes were performed using the B3LYP^[28] functional with a polarized continuum model (PCM) for CH_2Cl_2 (dielectric ϵ = 8.94)^[33], and the TZVP basis set of Ahlrichs on all atoms.^[34] The intensities of the 30 lowestenergy electronic transitions for $\mathbf{1}^{+}$ were calculated by TD-DFT^[35] at the B3LYP/TZVP level with a PCM for CH₂Cl₂. AOMix^[36] was used for determining atomic orbital compositions employing Mulliken Population Analysis.

Crystal structure analysis

The collected reflections were corrected for absorption (SADABS)^[37] and solved by direct methods and refined with Olex software.^[38] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters. CCDC-1449350 and 1482036 contains the supplementary crystallographic data for this paper; these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Conclusions

In summary we prepared the Mn(III)-bis(phenolate)dipyrrin complex 1. We establish that 1 undergoes two oxidative ligand-centered redox processes, producing the persistent radical species $\mathbf{1}^+$ and the dication $\mathbf{1}^{2+}$. We structurally characterized an unique Mn(III)-phenoxyl radical $(1^{+} SbF_{6})$ and report the first evidence of control of the reactivity for styrene oxidation by changing the oxidation state of a catalyst based on a redox-active ligand. Both **1** and $\mathbf{1}^{+}$ indeed catalyze styrene oxidation in the presence of PhIO, but the nature of the main reaction product is controlled by the initial oxidation state of the precatalyst: Styrene oxide is the main reaction product when using 1, but phenylacetaldehyde is formed predominantly when using 1⁺.

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Graphical abstract:

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One electron-oxidation produces a structurally characterized Mn(III) radical complex, which catalyzes the isomerization of epoxides in addition to the epoxidation of olefins in the presence of PhIO.

