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Spin Transition in a Manganese(III) Porphyrin Cation Radical, Its Transformation to a Dichloromanganese(IV) Porphyrin, and Chlorination of Hydrocarbons by the Latter

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Chemical oxidation of (TMP)Mn^{III}(Cl) (TMP = the tetramesitylporphyrinato dianion) by Fe(ClO$_4$)$_3$ leads to the porphyrin-oxidized product (TMP$^{\bullet+}$)Mn^{III}(ClO$_4$)$_2$. Magnetic measurements and EPR spectroscopy show that the total spin of the complex changes from $S = {}^{5}/_{2}$ at high temperature to $S = {}^{3}/_{2}$ at low temperature. Ligand exchange of the perchlorato ligands in (TMP$^{\bullet+}$)Mn^{III}(ClO$_4$)$_2$ by chloride anions is accompanied by a change of the oxidation site from porphyrin to metal, resulting in (TMP)Mn^{IV}(Cl)$_2$. This high-valent-metal complex can effect chlorine atom transfer to olefins, as well as to dimedone and chlorodimedone, natural substrates of chloroperoxidases.

Introduction

The fascinating chemistry of heme-dependent enzymes has initiated the search for synthetic systems which should be capable of mimicking the reactions catalyzed by the enzymes.[1] Thus, very efficient cytochrome P-450 like systems for oxygenation of hydrocarbons have been developed, based on the combination of catalytic amounts of either iron(III) or manganese(III) porphyrins together with a mild oxidant.[2] An integral part of the research in this field has been the isolation of the high-valent metalloporphyrin intermediates involved in the process.[3−6] One intrinsic complexity in the redox chemistry of metalloporphyrins is that both the metal and the porphyrin are potential candidates for oxidation. For iron porphyrins, all possibilities were isolated and characterized, and their electronic features are quite well understood. These include porphyrin-oxidized iron(III) porphyrin cation radicals,[3] metal-oxidized oxoiron(IV)[4] and other iron(IV) porphyrins,[5] and derivatives in which both the iron and the porphyrin are oxidized. The last mentioned intermediate is the oxoiron(IV) porphyrin cation radical,[6] which is closely related to compound **I**, the most important intermediate in catalysis by heme-dependent enzymes.[7]

The situation for manganese porphyrins is much more complex. Among the postulated intermediates with reactivity toward hydrocarbons are oxomanganese(V),[2c,8] oxomanganese(IV),[9] bis(iodosylbenzene)manganese(IV),[10] bis(hypochlorito)manganese(IV)[11] and other bis-ligated manganese(IV) porphyrins,[12] and oxomanganese(IV) porphyrin cation radicals.[13] Regarding the porphyrin-oxidized derivatives, it is well-known that the products of controlled one-electron oxidation of manganese(III) porphyrins are the corresponding cation radicals ((P$^{\bullet+}$)Mn(X)$_2$).[14] But, in contrast to the situation for iron(III) derivatives, only one manganese(III) porphyrin cation radical complex has been structurally characterized.[15] Furthermore, several spectroscopic features of that complex were contradic-

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Table 1. Physical Data for Previously Isolated Manganese(III) Porphyrin Cation Radicals

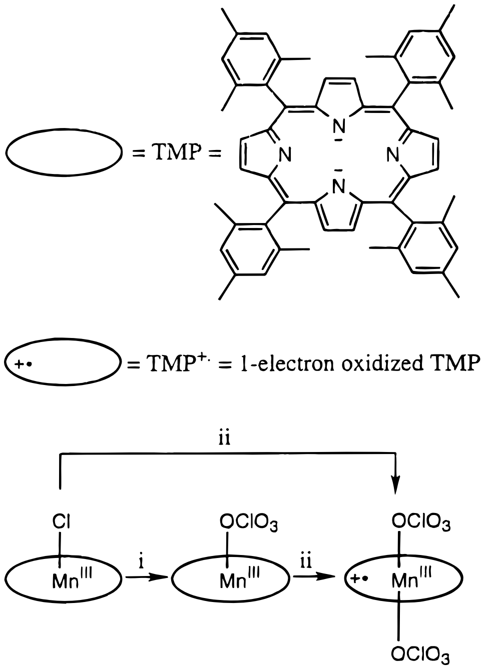
	$(tpp^{\bullet+})Mn(Cl)(ClO_4)$	$(tpp^{\bullet+})Mn(Cl)(SbCl_6)$	$(tpp^{\bullet+})Mn(CF_3SO_3)_2$	$(tmp^{\bullet+})Mn(Cl)(SbCl_6)$	$(tmp^{\bullet+})Mn(ClO_4)_2$
magnetic moment, μ_{eff} (μ_B)	4.7 (soln)	4.9 (solid) 5.7−6.7 (soln)	3.9 (solid, low T) 4.9 (solid, high T)	not reported	3.7−3.9 (solid, low T) >5.0 (solid, high T)
NMR (ppm) (pyrrole H)	−40	not reported	not reported	−40 (^{2}H)	−48 (^{1}H and ^{2}H)
IR (cm^{-1})	not reported	1280, but from solvent	not reported	not reported	1280
EPR	only $g = 2$	EPR silent	$g = 3.9$, $g = 2$ (low T) EPR silent (high T)	not reported	$g = 4$ (low T) $g = 6$ (high T)
ref	16	15	31	13a	this work

tory to reports of similar complexes.[13a,16] The intrinsic interest in manganese(III) porphyrin cation radicals is due to the desire for a better understanding of intramolecular interactions between unpaired electrons on the metal and the porphyrin radical. In addition, since these complexes are formally at the same oxidation state as manganese(IV) porphyrins, i.e. $(P^{\bullet+})Mn^{III}(X)_2 \leftrightarrow (P)Mn^{IV}(X)_2$, it should be possible to shuttle between the two formulations as a function of the axial ligands, X. Generally, complexes with ligands which are known to stabilize high oxidation states on metals are more stable as $(P)Mn^{IV}(X)_2$. Thus, the treatment of manganese(III) and iron(III) porphyrin cation radicals with methoxide ions resulted in their transformation to dimethoxomanganese (IV) and iron(IV) porphyrins.[12a,15,5b] Similarly, the reaction of the former complexes with a suitable source of hydroxyl anions produced oxomanganese(IV) and oxoiron(IV) porphyrins.[9,17,4a] Finally, a unique property of systems based on manganese(III) porphyrin catalysis is the presence of halogenated products in addition to the oxygenated hydrocarbons.[2b,c,18] This phenomenon could be related to the enzymes which are responsible for chlorination of organic substrates in biological systems, the chloroperoxidases (CPO).

Many mechanistic aspects of chlorination under CPO catalysis have been long known.[19] It is clear that the resting state of the enzyme is a cysteinate-coordinated hemin, which upon interaction with H_2O_2 is converted to an oxoiron(IV) porphyrin cation radical (compound **I**).[20] The chlorinating agent is produced via the reaction of compound **I** with chloride anions. Depending on reaction conditions and on characteristics of the organic substrate, chlorine atom transfer proceeds through either free Cl_2 or HOCl or through a metal-bound intermediate.[21] The commonly proposed structure of the metal-bound intermediate is $(P)Fe^{III}{-}O{-}Cl$, in which the chlorine atom is not directly bound to the metal.

As part of our research on oxidized metalloporphyrins,[4a,6d,22] we decided to attempt isolation of an authentic dichloromanganese(IV) porphyrin and to study its reactivity in chlorination of hydrocarbons. The porphyrin-oxidized manganese(III) tetramesitylporphyrin complex $(TMP^{\bullet+})Mn(ClO_4)_2$ was chosen as a possible synthetic precursor of $(TMP)Mn^{IV}(Cl)_2$, since we anticipated that ligand exchange of ClO_4^- by Cl^- would be accompanied by a change of the oxidation site from porphyrin to metal (Schemes 1 and 2). Because of conflicting reports about the characteristics of Mn(III) porphyrin cation radicals, a thorough spectroscopic investigation of $(TMP^{\bullet+})Mn(ClO_4)_2$ was carried out. This disclosed a significant variation of the total spin of the complex with temperature. Up to about 35 K, the characteristics of a complex with only three unpaired electrons ($S_{total} = {}^3/_2$) were observed, while, at high temperature, the total spin approached ${}^5/_2$. This intriguing phenomenon provides a plausible explanation for the wide range of magnetic moments and different EPR results which were previously reported for similar complexes. We also show in this study that the synthetic strategy described in Scheme 2 was successful, as treatment of $(TMP^{\bullet+})Mn(ClO_4)_2$ with chloride anions afforded $(TMP)Mn^{IV}(Cl)_2$. The latter complex is quite stable in the solid state and in benzene solutions, which allowed an investigation of its reactions with hydrocarbons. The results demonstrate that $(TMP)Mn^{IV}(Cl)_2$ has a pronounced reactivity toward olefins and the natural substrates of CPO, dimedone and chlorodimedone.

Scheme 1



1 **2** **3**

Reagents and Conditions: i. Treatment of **1** at RT with either $HClO_4$, or $AgClO_4$, or Bu_4NClO_4, or $Fe(ClO_4)_3$ for 2 min. ii. Reaction with $Fe(ClO_4)_3$ for 15 min at RT.

Results and Discussion

The Porphyrin-Oxidized Manganese(III) Porphyrin $(TMP^{\bullet+})Mn^{III}(ClO_4)_2$. The spectroscopic features and magnetic moments of the few reports of isolated manganese(III) porphyrin cation radicals $(P^{\bullet+})Mn(X)(Y)$—where X and Y

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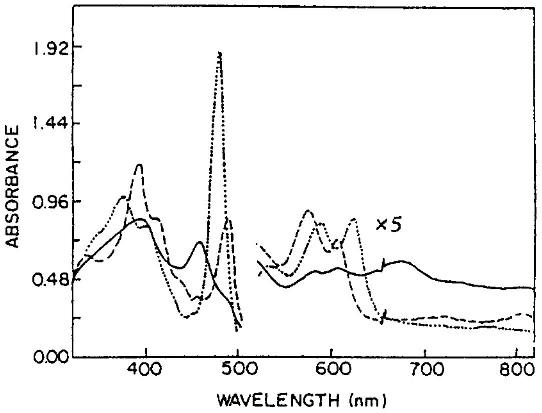

Figure 1. UV−vis spectra (the region after 500 nm is increased 5 times) of the species involved in the reactions described in Scheme 1: (a) complex **1** in CH_2Cl_2 (···) (b) complex **2**, obtained 2 min after the addition of solid $Fe(ClO_4)_3$ to the previous solution (---); (c) complex **3**, obtained by stirring the previous solution an additional 15 min (—).

represent the two axial ligands which are either identical or different—are summarized in Table 1. Examination of the table clearly shows that in no case were the complexes characterized by all relevant methods. In addition, some of the reports about the seemingly very similar complexes are contradictory. Accordingly, we isolated the porphyrin-oxidized complex of (TMP)MnCl with special attention to the identity of the axial ligands and examined the product by UV−vis, IR, ^{1}H and ^{2}H NMR, EPR, and magnetic susceptibility measurements.

The characteristic features in the electronic spectra of porphyrin cation radicals compared to those of neutral porphyrins are a diminished intensity Soret band ($\approx$ 420 nm) and the appearances of new visible bands at 600 −700 nm.[23] These criteria are not so straightforward in the case of $(P^{\bullet+})Mn(X)_2$ since the electronic spectra of manganese(III) porphyrins are much more complicated than those of regular porphyrins.[24] This complication is also demonstrated by the following observations. To ensure the identity of the axial ligands in the desired $(TMP^{\bullet+})Mn(ClO_4)_2$ (**3**), we first prepared $(TMP)MnOClO_3$ (**2**) by treating (TMP)MnCl (**1**) with $HClO_4$ (Scheme 1 and Figure 1). This conversion was accompanied by a color change from green to deep red and very significant changes in the electronic spectrum. Surprisingly, the spectrum of **2** (trace b in Figure 1) was almost identical to the published spectra of oxidized (TPP)-MnCl, formulated as $(TPP^{\bullet+})Mn(Cl)(ClO_4)$.[16] The possibility that **1** was oxidized by excess $HClO_4$ was eliminated by the fact that identical results were obtained when **1** was treated with 1 equiv of $AgOClO_3$ or excess tetrabutylammonium perchlorate (Bu_4NClO_4). Furthermore, when **2** was oxidized by $Fe(ClO_4)_3$ or by electrochemical means, the color changed from deep red to brilliant green, the expected color of porphyrin cation radicals.[6] The major changes in the electronic spectrum associated with this conversion of **2** to **3** were the broadening of the 380−420 nm region, shift of the band at 486 nm to 456 nm, and the appearance of a new band at 674 nm (trace c in Figure 1). At the end, we found that it is actually possible to produce **3** directly from **1** by treatment with $Fe(ClO_4)_3$. When a green solution of **1** was treated with excess $Fe(ClO_4)_3$, the color changed to red within 2 min, accompanied by the spectral changes corresponding to the formation of **2** (traces a and b in Figure 1). That spectrum changed spontaneously (vigorous stirring) to that of **3** after about 15 min (trace c in Figure 1), during which the solution turned brilliant green. Thus, the faster reaction is transformation of **1** by $HClO_4$ from the acidic $Fe(ClO_4)_3$ into **2**, which is oxidized to **3** in the slower step (Scheme 1).

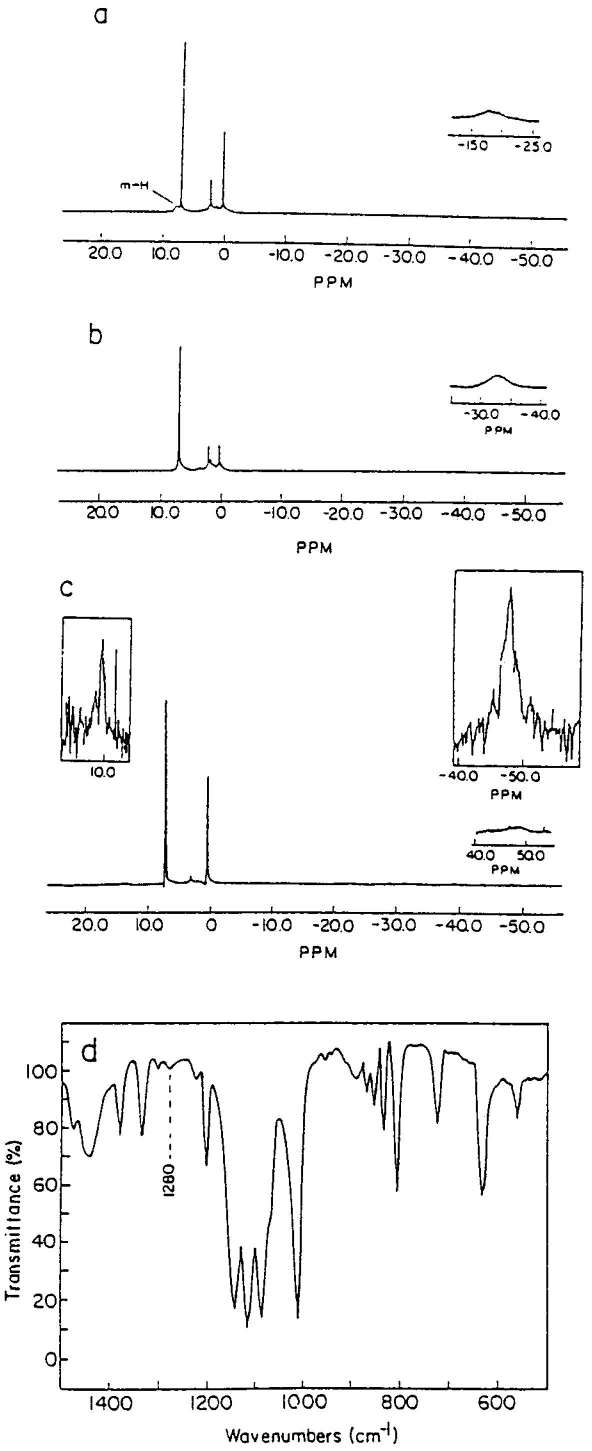

Figure 2. 200 MHz ^{1}H NMR spectra in benzene-d_6 at RT: (a) (TMP)-MnCl (**1**); (b) $(TMP)Mn(ClO_4)$ (**2**); (c) $(TMP^{\bullet+})Mn(ClO_4)_2$ (**3**). Insets: 61 MHz ^{2}H NMR spectra of the meta-d_8 and pyrrole-d_8 derivatives in benzene at RT. Part d shows the FT-IR spectrum of a polycrystalline sample of **3** in KBr.

In the FT-IR spectrum of **3**, a weak band at 1280 cm^{-1} was found for freshly prepared material (Figure 2d). Bands in that range of wavenumbers are usually considered as characteristic for porphyrin cation radicals,[25] but Spreer *et al.* have assigned similar bands of $(TPP^{\bullet+})Mn(Cl)(SbCl_6)$ as originating from solvent molecules, $CHCl_2CHCl_2$.[15] In our case, this band was

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not present in **1** or **2** or in the solvent CH_2Cl_2, and furthermore, it was lost after a few hours, indicating the reduction of the cation radical. Thus, the band at 1280 cm^{-1} can confidently be assigned as a characteristic porphyrin cation radical band, in accord with other studies of manganese porphyrin cation radicals.[26] Additional features in the IR spectrum of **3** are the strong bands at 1091, 1124, and 1150 cm^{-1}. These bands provide clear evidence for metal-coordinated perchlorato anions in **3**, as similar bands were also identified in the spectra of (TPP)Fe(ClO_4) and ($TPP^{\bullet+}$)Fe$(ClO_4)_2$,[3] while uncoordinated ClO_4^- has a single band at about 1090 cm^{-1}.[27]

The NMR spectra of **1**−**3** are compared in Figure 2. They illustrate that the chemical shift of the pyrrole β-hydrogens is sensitive to the axial ligand in the neutral precursors **1** (Cl) and **2** (ClO_4) ($\delta = -18$ and -33 ppm, respectively) and to the oxidation of the porphyrin ring in **3** ($\delta = -48$ ppm). The oxidation of the porphyrin also causes a dramatic increase in line width of the same signal (half-height line width of 2400 Hz for **3**, vs 900 Hz for both **1** and **2**). The assignment of the chemical shifts was confirmed by ^{2}H NMR of selectively deuterated complexes,[28] as shown for complex **3** in the insets of Figure 2c. The only two other relevant complexes whose NMR spectra were previously reported are ($TPP^{\bullet+}$)Mn(Cl)(ClO_4) (^{1}H NMR, −39 ppm, "very broad")[16] and ($TMP^{\bullet+}$)Mn(Cl)($SbCl_6$) (^{2}H NMR, −40 ppm).[13a] Thus, the chemical shift of the pyrrole β-hydrogens in the porphyrin-oxidized complexes with two different axial ligands are very similar, but that of **3**, with two identical ligands, is quite different. It is well-known that upfield shifts of pyrrole proton resonances in manganese porphyrins are due to delocalization of unpaired electrons from the d_{xz} and d_{yz} metal orbitals with the filled 3e π porphyrin orbitals via porphyrin to metal spin transfer.[29,30] The much larger upfield shift experienced by **3** is readily rationalized by the better overlap between the relevant orbitals when the metal ion is located in the plane defined by the porphyrin ring due to its two identical ligands than in cases where the metal is displaced out of plane toward the stronger of its two different ligands. In addition, the chloride ligand in the other complexes is expected to raise the energy of the metal d_π orbitals by π-donation. This will increase the energy difference between the d and π orbitals and decrease the extent of porphyrin to metal spin transfer.

The largest diversity in the reports of porphyrin-oxidized manganese(III) porphyrins concerns their magnetic moments, which vary between 4.7 and 6.7 μ_B.[15,16,31] For iron(III) porphyrin cation radicals, the magnetic interactions between the single electron on the porphyrin and the metal electrons were shown to be governed by symmetry, ferromagnetic in derivatives with two identical axial ligands and antiferromagnetic when the iron has two different ligands.[3a] If the same rules hold for manganese(III) porphyrin cation radicals, a value of 5.9 μ_B would be expected for $S_{total} = {}^5/_2$ in **3**, due to a ferromagnetic interaction of the four Mn(III) electrons with the single porphyrin radical. We first determined the solution magnetic moments of **3** by the Evans method, but the results varied from one sample to the other, in the range $\mu_{eff} = 4.5-6.3$ μ_B. The solid state SQUID measurements of polycrystalline samples shed some light on this irregular behavior. The results which are presented in Figure 3 for two different samples show that the magnetic moment is *T* dependent. Normally, in a plot of μ_{eff} vs *T*, a plateau is expected after 15−50 K, as was indeed the case for the precursor of **3**, (TMP)MnCl (**1**, data not shown). But for **3**, only a shoulder or a "semiplateau" was observed in the 15−35 K range, corresponding to $\mu_{eff} = 3.7-3.9$ μ_B, after which the magnetic moment still increased without reaching a new plateau even at 250 K. The extrapolated value at 300 K was 5.0, significantly higher than that of **1**, for which the experimental value was between 4.5 (solid) and 4.7 (solution). Thus, the magnetic moment of **3** at low *T* is very close to expectation for a spin-only $S = {}^3/_2$ system ($\mu_{cal} = 3.87$ μ_B), while at high *T* it exceeds that of an $S = 2$ system and approaches that of an S $^5/_2$ system ($\mu_{cal} = 4.90$ and 5.92 μ_B, respectively).

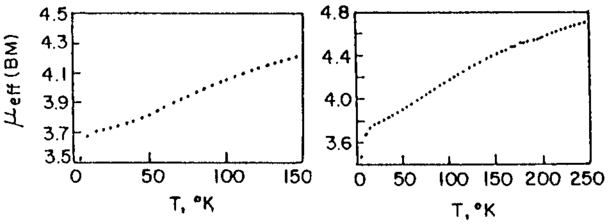

Figure 3. Results of SQUID susceptibility measurements for two polycrystalline samples of ($TMP^{\bullet+}$)Mn$(ClO_4)_2$ (**3**) presented as plots of μ_{eff} as a function of the temperature.

The results at high *T*, i.e. the large magnetic moment of **3**, are in line with expectations for such a complex. An ideal D_{4h} symmetry can be safely assumed for **3**, due to its identical axial ligands and the bulky mesityl groups in the meso position of the porphyrin ring. These expectations are indeed fulfilled in the related crystallographically characterized ($TPP^{\bullet+}$)$Fe^{III}(ClO_4)_2$ complex,[3a] which is even less sterically restricted. The magnetic orbital (the HOMO of the porphyrin, which becomes singly occupied after oxidation) in all metal complexes of ($TMP^{\bullet+}$) is of a_{2u} symmetry,[32] which due to its *ungerade* character is devoid of any orbital overlap with the *gerade* d orbitals of the metal. This eliminates the possibility of spin coupling, the so-called antiferromagnetic interaction. Since the porphyrin a_{2u} orbital acquires some metal character via interaction with the metal p_z orbitals (either filled 3p or empty 4p) which have the same symmetry, the spins of the porphyrin radical and the metal electrons must be parallel, resulting in the so-called ferromagnetic interaction. The total spin in such a case is $S_{total} = 2$ (Mn(III), d^4) + $^1/_2$ ($P^{\bullet+}$) = $^5/_2$. We may thus conclude that, at high *T*, complex **3** behaves as a ferromagnetically coupled Mn(III) porphyrin cation radical. The reason that, at low *T* the same complex has a magnetic moment corresponding to a total spin of $^3/_2$ is however much less obvious.

Further confirmation for the *T*-induced spin transition suggested by the magnetic susceptibility measurements was obtained by EPR. Since both spin states of **3**, $S_{total} = {}^3/_2$ and $S_{total} = {}^5/_2$, are odd spin, they should be detectable by EPR. No signals were however detected in solutions (CH_2Cl_2 and benzene), in accord with all other reports. But, powdered solid samples of **3** revealed *T*-dependent EPR spectra, which are shown in Figure 4 (the spectrum of **3** in frozen benzene solution at 120 K was practically identical to that of the powdered sample). The EPR spectrum at 300 K is a superposition of signals at $g = 6$ (major, 80%), $g = 4$ (minor, 20%), and $g = 2$

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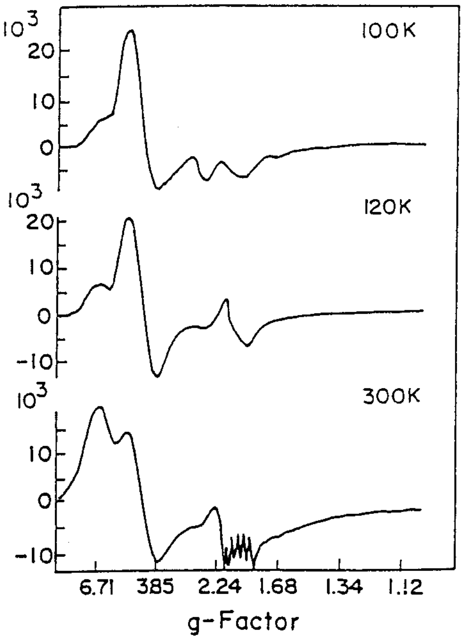

Figure 4. EPR spectra of a polycrystalline sample of $(TMP^{\bullet +})Mn(ClO_4)_2$ (**3**) at the indicated temperatures.

with characteristic ^{55}Mn ($I = {}^{5}/_{2}$) hyperfine splitting.[33] As T is lowered, the $g = 6$ signal loses intensity (only 20% at 120 K), while the $g = 4$ signal increases and eventually becomes the major component (99% by integration) at 100 K. Signals at $g = 6$ and $g = 4$ are exactly what is expected for $S_{total} = {}^{5}/_{2}$ and ${}^{3}/_{2}$, respectively. Thus, the EPR results support the conclusions from the magnetism measurements, claiming spin transition from $S = {}^{3}/_{2}$ at low T to $S = {}^{5}/_{2}$ at high T. It must be emphasized that these spectral changes are completely reversible and that there was no UV−vis evidence for the presence of any (easily detectable) Mn(II) porphyrin which is also an $S = {}^{5}/_{2}$ system.

There are at least three possible mechanisms for the temperature-induced change of S_{total} in complex **3**: (a) The interaction between the metal and porphyrin radical electrons changes from ferromagnetic ($S_{total} = 2 + {}^{1}/_{2} = {}^{5}/_{2}$) to antiferromagnetic ($S_{total} = 2 - {}^{1}/_{2} = {}^{3}/_{2}$). (b) The Mn(III) ion changes from HS to LS, while the interaction remains ferromagnetic ($S_{total} = 1 + {}^{1}/_{2} = {}^{3}/_{2}$). (c) Intramolecular oxidation occurs from the Mn(III) porphyrin radical to the LS Mn(IV) porphyrin. The first possibility, change in the *mode* of the intramolecular interaction between the electrons of the metal and the porphyrin radical as a function of *T*, is not reasonable. In this highly symmetric complex there is simply no symmetry-allowed overlap between the relevant orbitals (*vide supra*). Even if "freezing" of a conformation with low symmetry due to deformation of the porphyrin ring is considered, this should be reflected by EPR as an averaging process causing significant changes in EPR line shapes (broadening or narrowing), rather than simultaneous observation of both complexes at all temperatures. Furthermore, although in a D_{2d} saddle conformation the porphyrin radical and d_{xy} become b_2,[34] this interaction must be very weak, as the d_{xy} orbital is not directed toward the porphyrin nitrogens. Distinguishing between the two other possibilities is much harder. Spreer *et al.*, who noted a similar phenomenon in $(TPP^{\bullet +})Mn^{III}(trif)_2$, assigned the $S = {}^{3}/_{2}$ EPR spectrum at low *T* to $(TPP)Mn^{IV}(trif)_2$.[31] Our data are however not supportive of $(TMP)Mn^{IV}(ClO_4)_2$, since both the brilliant green color and the UV−vis spectrum of complex **3** ($\lambda_{max} = 458$ nm) did not change upon cooling to liquid nitrogen temperatures. This is in contrast to the case of all known Mn(IV) tetraarylporphyrins, which are red and have a single Soret band at $\lambda_{max} = 420$ nm,[9−13] a region where complex **3** has a minimum. On the other hand, proposing LS Mn(III) with perchlorato ligands seems contradictory to the fact that spin pairing in Mn(III) requires very strong field ligands.[35] We note, however, the many examples of similar phenomena in iron(III) porphyrins. In contrast to the case of halo-coordinated Fe(III) porphyrins, which are purely high spin ($S = {}^{5}/_{2}$), in all perchlorato derivatives the metal is intermediate spin to some degree, ranging from $S = {}^{5}/_{2}$, $S = {}^{3}/_{2}$ spin admixtures to purely $S = {}^{3}/_{2}$.[36] Furthermore, the same is also true for bis(perchlorato) complexes of Fe(III) porphyrin cation radicals.[37] This effect, which cannot be explained by simple ligand field considerations,[38] could also be responsible for the small differences between the high- and low-spin states in the present case. Unfortunately, we were not successful in obtaining X-ray data for complex **3**, which could aid in the understanding of its interesting magnetic properties.[39,40]

In conclusion, we have isolated and extensively characterized the Mn(III) porphyrin cation radical $(TMP^{\bullet +})Mn(ClO_4)_2$. The most outstanding feature of this complex is its temperature-dependent spin transition. Although similar phenomena are quite common in iron porphyrins and at least one example was previously reported for a non-porphyrinic Mn(III) complex,[41] this is generally overlooked in manganese porphyrins. It seems reasonable that some of the conflicting reports about Mn(III) porphyrin cation radical complexes, especially with regard to their magnetism, are due to spin transition.

The Metal-Oxidized Manganese(III) Porphyrin from the Porphyrin-Oxidized Derivative. The conversion of trivalent metalloporphyrin cation radicals into tetravalent metalloporphyrins by ligand exchange of the original axial ligands by hydroxide, methoxide, or fluoride[5c] ions was demonstrated for both iron and manganese derivatives. Groves and Stern utilized hydroxide anions for conversion of a manganese(III) porphyrin radical into an oxomanganese(IV) species,[9] while Spreer *et al.* showed that an isolated manganese(III) porphyrin radical was converted to a dimethoxomanganese(IV) porphyrin by treatment with methoxide anions.[15] We also have treated **3** with methoxide anions in a similar fashion, which resulted in a color change from green to red and the appearance of a Soret band at about 420 nm, characteristic of Mn(IV) porphyrins. Surpris-

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(39) The bond length between the metal and the pyrrole nitrogens is most distinctive for differentiation between high-spin (Fe−N ≥ 2.06 Å) and intermediate- or low-spin (Fe−N ≤ 2.00 Å) iron(III) porphyrins.[37a,40a] This is however not expected in the present case, since the $d_{x^2-y^2}$ orbital is not occupied in both high- and low-spin Mn(III). It is well documented that the metal−nitrogen bond lengths are very similar (Mn−N ∼ 2.00 Å) in 5- and 6-coordinated Mn(III) porphyrins[40a,b] in a Mn(III) porphyrin cation radical[15] and even in Mn(IV) porphyrins.[40c]

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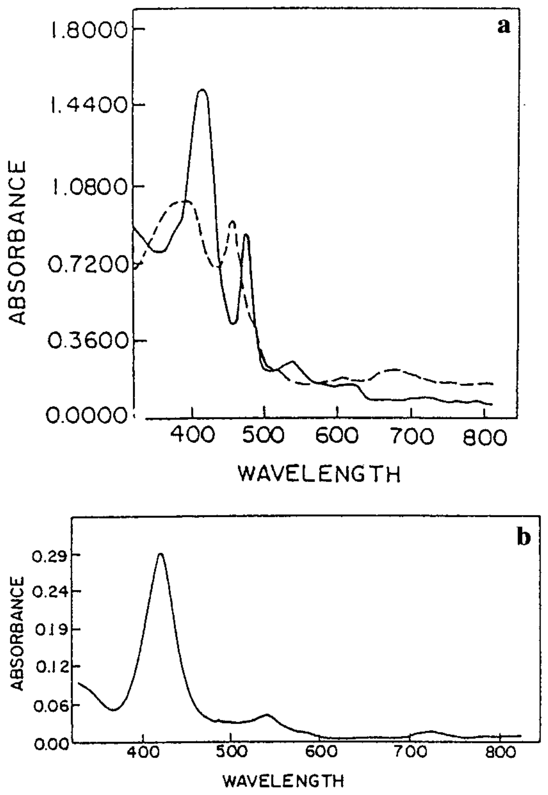
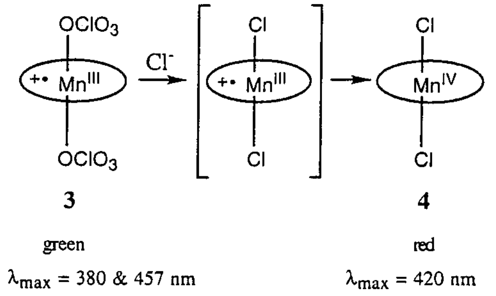


Figure 5. (a) UV−vis spectra at RT of the transformation of a CH_2Cl_2 solution of $(TMP^{•+})Mn(ClO_4)_2$ (**3**, ---) to $(TMP)Mn(Cl)_2$ (**4**, −) by addition of solid Et_4NCl. The maximum at 480 nm is due to (TMP)Mn(Cl) (**1**) from fast decomposition of **4** in this solvent. (b) UV−vis spectrum of isolated **4** in benzene.

Scheme 2



ingly, however, the control experiment with (TMP)MnCl (**1**) gave the same result. This finding is in excellent agreement with the reports of Bruice *et al.*, who showed that manganese(III) porphyrins with basic ligands are not stable toward disproportionation, resulting in either manganese(IV) ($\lambda_{max} \approx$ 420 nm) or manganese(II) ($\lambda_{max} \approx$ 440 nm) derivatives as a function of the solvent system.[13a] In contrast to the results with methoxide anions, treatment of CH_2Cl_2 solutions of **3**, *but not of* ***1***, with tetraethylammonium chloride (Et_4NCl) converted them into a new derivative (**4**) with an electronic spectrum characteristic of manganese(IV) porphyrins (Figure 5, Scheme 2). This conversion was also accompanied by a color change from green to reddish brown.

Complex **4** was very unstable in CH_2Cl_2 and toluene solutions at room temperature and was converted to the manganese(III) chloride complex **1** within a few minutes ($t_{1/2}$ for conversion of **4** to **1** in CH_2Cl_2 is 77 s). At low temperatures, **4** was much more stable, but its isolation was difficult because of the high solubility of the tetraethylammonium salts even at low temperatures. Furthermore, we were interested in testing the reactivity of **4** toward hydrocarbons at ambient temperatures. Since the protons in CH_2Cl_2 and toluene are quite reactive, we decided to investigate benzene as a possibly more inert solvent. Indeed, similar to previous observations in the isolation of $(TMP)Fe^{IV}(O)$,[4a] the stability of **4** in benzene was very high. This allowed the isolation, characterization, and reactivity studies of **4**.

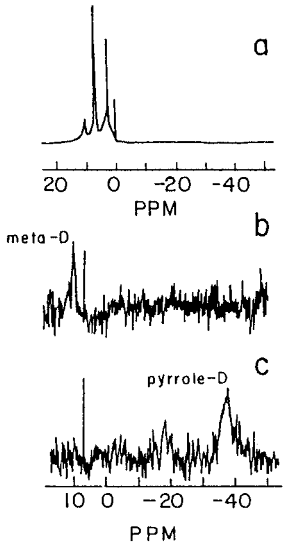
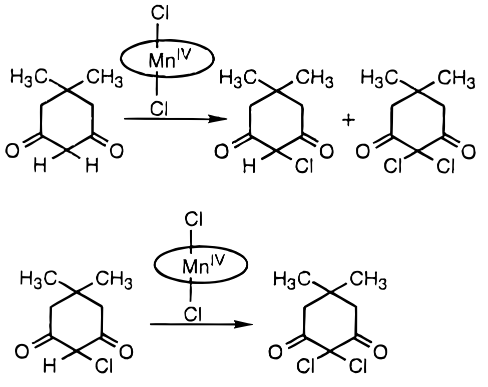


Figure 6. 200 MHz ^1H NMR and 61 MHz ^2H NMR spectra at RT in C_6D_6 and C_6H_6, respectively, of $(TMP)Mn^{IV}(Cl)_2$ (**4**) and its meta-d_8 and pyrrole-d_8 derivatives.

Scheme 3



Isolation of complex **4** from reactions of **3** with Et_4NCl in CH_2Cl_2 at low *T* or in benzene at RT (room temperature) resulted in a red solid, which was characterized as $(TMP)Mn^{IV}(Cl)_2$ by the following methods. The molecular formula was proven by elemental analysis and MS, in which the presence of two chloride ligands was clearly evident. The Mn(IV) oxidation state was proven by the single Soret band at 420 nm in its UV−vis spectrum (Figure 5b) and its $S = {}^3/_2$ EPR spectrum with $g_\perp = 4$ and $g_\| = 2$. The magnetic moment of **4** was also indicative of the $S = {}^3/_2$ system ($\mu_{cal} = 3.87\ \mu_B$), 3.7 μ_B in solution and 3.6 μ_B in the solid state. In the ^1H NMR spectrum of **4** in C_6D_6 at RT, only the meta-H signals of the mesityl groups at 10.56 ppm were identified, but by utilization of ^2H NMR of selectively deuterated samples of **4**, the pyrrole-D signals were identified at −38 ppm and the assignment of the meta-H signals was confirmed (Figure 6). Solid samples of **4** were stable at RT for a few hours, and a UV−vis examination of a benzene solution revealed that after 1 h at RT only one-third of the material was converted to **1**, corresponding to a $t_{1/2}$ of 2 h.

Reactivity of $(TMP)Mn^{IV}(Cl)_2$, 4. The relatively long lifetime of **4** in benzene permitted the investigation of its reactivity toward hydrocarbons. The experiments were per-

Scheme 4

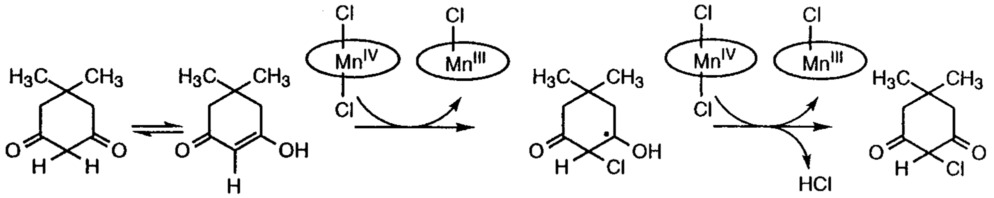


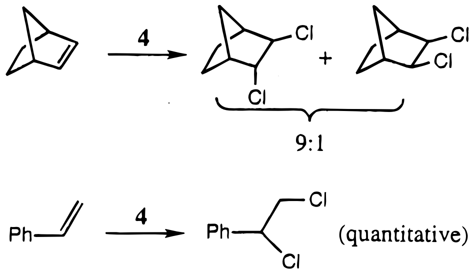
Table 2. Yields of Dichlorostyrene Formation in Reactions between (TMP)Mn^{IV}(Cl)$_2$ (**4**) and Styrene at Different Ratios[44]

reacn time (h)	2[dichlorostyrene]:[**4**]$_0$		
	[styrene]$_0$:[**4**]$_0$ = 1:2	[styrene]$_0$:[**4**]$_0$ = 2:2	[styrene]$_0$:[**4**]$_0$ = 6:2
1	56	48	15
2	70	71	17
3	87	82	22
4	96	75	20
5	99		19
6	99.8		18
7	90		

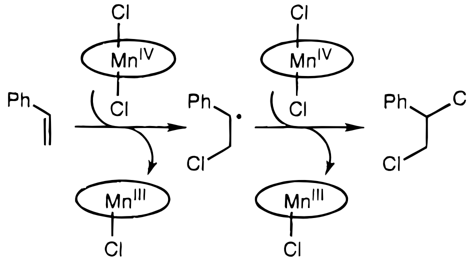
formed by dissolving 2−4 mg of **4** in 1−2 mL benzene at 25 °C and subsequent addition of the organic substrate (0.5−3 equiv). The color change from red (**4**) to green (**1**) took only minutes, but usually the reaction products were examined after 1 h to ensure completion. The natural substrates of CPO—dimedone (5,5-dimethyl-1,3-cyclohexanedione) and chlorodimedone (2-chloro-5,5-dimethyl-1,3-cyclohexanedione)—were examined first (Scheme 3). Chlorodimedone and dichlorodimedone (2,2-dichloro-5,5-dimethyl-1,3-cyclohexanedione) were obtained in a 13:4 ratio in the reaction of dimedone with **4**. With chlorodimedone as substrate, dichlorodimedone was formed as the major product. This is in complete analogy with the CPO-catalyzed chlorination of the same substrates.[42] Reaction of ethylbenzene resulted in only traces of α-chloroethylbenzene, suggesting that the much higher reactivity of dimedone has a specific origin not present in ethylbenzene.

The high acidity of dimedone is known to be related to the high stability of its enolic form, which in benzene at equilibrium consists of 11% (in water it is 95%).[43] It thus seems possible that the much higher reactivity of dimedone compared to ethylbenzene is due to the enolic form of the former. In other words, this suggests that dimedone reacts as an olefin rather than as an alkane, as shown in Scheme 4. To test this hypothesis, we investigated the reaction of **4** with two olefins, styrene and norbornene. In both cases, the corresponding dichloro olefins were identified as major products (Scheme 5). In the reaction of **4** with styrene, we also noticed an intriguing phenomenon: *decrease* in the reaction yields as the concentration of styrene was *increased* (Table 2). At a 3-fold molar excess of styrene, the yield was 22%, at equimolar ratios it was 82%, and at a 2-fold excess of **4**, the yield approached 100%.[44] Interestingly, the highest yield was achieved at the perfect ratios predicted by the balanced chemical equation. We assume that the reason for the lower yields with excess styrene is that the reaction consists of two elementary steps, monochlorination by 1 equiv of **4**, followed by chlorination of the radical produced in the first step by an additional 1 equiv of **4** (Scheme 6). In the reactions with excess styrene, all equivalents of **4** are used for the first step and the second step does not occur.

Scheme 5



Scheme 6



Further evidence for the suggested radical mechanism was provided by the reaction of **4** with the second olefin, norbornene (Scheme 5). It is well-known that very different products are formed by chlorination of norbornene by radical or by ionic mechanisms. Whereas *trans-* and *exo-cis*-1,2-dichloronorbornane with large trans:cis ratios are formed as the major products in the former case,[45] skeleton-rearranged products are the major chlorination products under ionic conditions.[46] In the reactions of norbornene with **4** in the ratios of 1:3 and 3:1, the unrearranged products were formed in 30% and 20% yields, respectively, with only traces of other chlorinated products (GC/MS). Furthermore, the trans:cis product ratios were 9:1 in both reactions, very similar to results which were obtained in a recent example of chlorination of norbornene by a non-porphyrin *trans*-dichloro complex which was also proposed to proceed via a radical mechanism.[47] This allows the conclusion that the reaction of **4** with olefins proceeds stepwise, in each step by radical addition of one chlorine atom from **4** to the double bond.

Summary and Conclusions

In this study, we have developed synthetic pathways for preparation of a dichloromanganese(IV) porphyrin and a manganese(III) porphyrin cation radical with two perchlorato ligands, (TMP$^{\bullet+}$)Mn(ClO$_4$)$_2$ (**3**). To our knowledge, **3** is the first manganese(III) porphyrin cation radical which was characterized by all standard methods. The EPR and magnetic susceptibility examinations of **3** revealed a spin-crossover process, proposed to be due to a high-spin/low-spin transtion of the Mn(III) ion.

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(43) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216.

(44) All yields are reported relative to **4**, taking into account that 2 equiv of **4** is required for 1 equiv of dichlorinated olefin.

(45) Tanner, D. D.; Gidley, G. C. *J. Org. Chem.* **1968**, *33*, 38.

(46) (a) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4293. (b) Uemura, S.; Okazaki, H.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3568.

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In addition, **3** was a suitable synthetic precursor for (TMP)-$Mn^{IV}(Cl)_2$ (**4**). Isolation and full characterization of **4** relie on this synthetic strategy, in which utilization of very potent oxidants such as Cl_2 or OCl_2 is avoided.[48] Complex **4** was able to effect chlorination of dimedone, chlorodimedone, styrene, and norbornene. We have shown that the reactions of **4** with the olefins proceeds by a radical pathway and suggest that the chlorination of the "alkanes" dimedone and chlorodimedone actually proceed trough their "alkene" forms, the enols. The demonstrated ability of an authentic chloro-ligated high-valent metalloporphyrin to effect chlorination of hydrocarbons could have a significant impact on the research of chloroperoxidase-catalyzed chlorinations.

Experimental Section

Physical Measurements. The ^1H NMR spectra were recorded on a Bruker AM 200, operating at 200 MHz, and the ^2H NMR spectra were recorded on a Bruker AM 400, operating at 61 MHz for deuterium. Chemical shifts are reported relative to residual hydrogens in the deuterated solvents and the natural-abundance deuterium for the ^2H spectra (7.20, 7.26, and 5.32 ppm for benzene, chloroform, and dichloromethane, respectively). The EPR spectra were recorded on a Bruker EMX 220 digital X-band radiospectrometer equipped with a Bruker ER 4121VT temperature control system operating within the temperature range 100−700 K. The typical conditions were microwave frequency 9.39 GHz, nonsaturated microwave power 20 mW, receiver gain 10^6, a100 kHz modulation amplitude of 2 G. Spectra processing and parameter calculations were performed using WIN-EPR software. An HP 8452A diode-array spectrophotometer was used for the electronic spectra. Gas chromatographic analysis were performed on an HP-5890 GC with a DB-5 capillary column and FID detector, linked to an HP Chem-Station (HP-3365). For the separation of chlorodimedone, and dichlorodimedone, a DB-210 column was required. GC/MS analyses were performed on a Magnum mass spectrograph, linked to a Varian-3400 with a DB-5 column. Magnetic susceptibility measurements were performed by the Evans method for solutions and by a liquid-He-cooled Quantum Design SQUID MPMS-5S for polycrystalline samples.

Materials. Dichloromethane (Lab-Scan, HPLC grade) was dried by distillation over CaH_2. Benzene (RDH, thiophene free) was further purified by repeated washings with concentrated H_2SO_4, until the aqueous layer was colorless, followed by washing with aqueous K_2CO_3 and water. The material was dried with $MgSO_4$ and distilled twice over Na. DMF (Merck, GC grade), dimedone, chlorodimedone, C_6D_6, $CDCl_3$, and CD_2Cl_2 (Aldrich products) were used as received. Styrene and norbornene were purified by distillation and sublimation, respectively. Bu_4NClO_4 was crystallized twice from EtOH. Et_4NCl, $AgClO_4$, and $Fe(ClO_4)_3$ were dried under high vacuum.

Synthetic Methods. *Caution! The perchlorato complexes **2** and **3** must be handled as potentially explosive compounds.*

(5,10,15,20-Tetramesitylporphyrinato)manganese(III) Chloride, 1. This known complex was prepared by a routine method by metalation of tetramesitylporphyrin (300 mg, 0.38 mmol) with $Mn(OAc)_2{\cdot}4H_2O$ (300 mg, 1.22 mmol, added in two portions) in reagent grade DMF (reflux for 4 h).[49] Green crystals of **1** were obtained in 89% yield (300 mg, 0.34 mmol) after recrystallization from CH_2Cl_2−hexane (1:1). ^1H NMR (RT, C_6D_6; δ, ppm): −17.5 (pyrrole-H), 7.8 (meta-H). ^1H NMR (RT, CD_2Cl_2, δ, ppm): −21.8 (pyrrole-H), 7.9 (meta-H).

(5,10,15,20-Tetramesitylporphyrinato)manganese(III) Perchlorate, 2. A benzene solution of **1** (80 mg, 0.09 mmol) was extracted twice with 10% perchloric acid (25 mL) and once with distilled water (30 mL), dried over $MgClO_4$, and evaporated to dryness. Red-purple crystals of **2** were obtained (60 mg, 71% yield) after recrystallization from benzene and vacuum-drying. Similar results were obtained by heating benzene solutions of **1** with 1.2 equiv of $AgClO_4$ under Ar until the color of the reaction mixture changed from green to reddish-brown, followed by filtration of the AgCl salts. ^1H NMR (RT, C_6D_6; δ, ppm): −32.8 (pyrrole-H), 7.3 (meta-H). UV−vis (RT, C_6H_6; λ_{max}, nm): 390, 400, 480 (Soret), 512, 572, 608.

$(tmp^{\bullet+})Mn^{III}(ClO_4)_2$, 3. Solid $Fe(ClO_4)_3$ (200 mg, large excess) was added to well-stirred benzene solutions of **1** (5−10 mg in 2 mL). The color of the reaction mixture changed from green to red in 1−3 min. Stirring was continued for additional 10−15 min until the color changed again to brilliant green and no more changes were apparent in the electronic spectrum (see Figure 1). The solution was filtered directly into a vial with 2 mL of −20 °C pentane. The dark-green solids which formed in quantitative yields by this procedure were filtered off, washed with cold pentane, dried in *vacuo*, and recrystallized from CH_2Cl_2−pentane (1:1) at −20 °C. ^1H NMR (RT, C_6D_6; δ, ppm): −48.5 (pyrrole-H), 12.8 (meta-H). ^2H NMR (RT, C_6H_6; δ, ppm): −48.3 (pyrrole-H), 12.85 (meta-H). EPR: variable with *T*; see Figure 4. UV−vis (RT, C_6H_6; λ_{max}, nm): 380, 456 (Soret), 674. Identical spectra were obtained at 176 K in CH_2Cl_2 and for a film, generated by evaporating a concentrated CH_2Cl_2 solution on glass by N_2, in a liquid-nitrogen-cooled cell (the measured *T* inside the cell was 85 K). FT-IR (KBr pellets, 1 mg of **3** in 130 mg of salt; cm^{-1}): 1091, 1124, 1150, 808, 637 (Mn-coordinated ClO_4), 1280 (oxidized porphyrin).

***trans*-Dichloro(5,10,15,20-tetramesitylporphyrinato)manganese(IV), 4. (a) In CH_2Cl_2.** A solution of 5.2 mg (6 μmol) of (TMP)Mn(Cl) in 1.5 mL of CH_2Cl_2 was treated with excess $Fe(ClO_4)_3$ (0.25 g, 700 μmol) at room temperature, which caused a fast color change (minutes) from green to red due to the formation of (TMP)-$Mn^{III}(ClO_4)$, followed by a slower color change (10−30 min) to brilliant green, characteristic of $(TMP^{\bullet+})Mn^{III}(ClO_4)_2$. The *in situ* formed solution of $(TMP^{\bullet+})Mn^{III}(ClO_4)_2$ was filtered and immediately cooled in a dry ice−acetone bath. Addition of tetraethylammonium chloride ((TEA)Cl, 2 mg, 12 μmol) resulted in a color change from green to red. The product was precipitated by warming the reaction mixture to −40 °C and adding 1.5 mL of cold acetonitrile. After filtration of the precipitate, washing with cold hexane (−40 °C), and drying under high vacuum at −78 °C for 6 h and at RT for an additional 15 min, 5 mg (5.5 μmol, 92% yield) of (TMP)$Mn^{IV}(Cl)_2$ was obtained as a purple-red solids.

(b) In Benzene. A solution of 5.2 mg (6 μmol) of (TMP)Mn(Cl) in 1.5 mL of benzene was treated with excess $Fe(ClO_4)_3$ (0.25 g, 700 μmol) at room temperature, which caused a fast color change (minutes) from green to red due to the formation of (TMP)$Mn^{III}(ClO_4)$, followed by a slower color change (20−30 min) to brilliant green, characteristic of $(TMP^{\bullet+})Mn^{III}(ClO_4)_2$. The solution was filtered from excess $Fe(ClO_4)_3$, and (TEA)Cl (2 mg, 12 μmol) was added at RT. After the color change from green to red was complete and the visible spectra showed a single Soret band at 420 nm (about 5 min), the solution was filtered (the solubility of (TEA)Cl in benzene is very low). Evaporation of the solvent resulted in 5 mg (5.5 μmol, 92% yield) of (TMP)-$Mn^{IV}(Cl)_2$. Elemental analysis of the product from the CH_2Cl_2 procedure indicated the presence of residual (TEA)Cl, which was not the case for the product from the benzene procedure. Anal. Calcd for $C_{56}H_{52}Cl_2N_4Mn{\cdot}4H_2O$: C, 68.69; H, 6.21; Cl, 7.24; N, 5.72. Found: C, 68.52; H, 6.18; Cl, 6.96; N, 5.73; MS (CI^+, isobutane): *m/z* 906 (3%, $[MH]^+$, for $(^{35}Cl)_2$ and two additional peaks at *m/z* 908 and 910 for the ^{35}Cl, ^{37}Cl, and $(^{37}Cl)_2$ isotopes, respectively), 870 (38%, $[M]^+ - Cl$, for ^{35}Cl and one additional peak at *m/z* 872 for the ^{37}Cl isotope), 835 (100%, $[M]^+ - 2Cl$). MS (CI^-, isobutane): *m/z* 904 (9%, $[M - H]^-$, for $(^{35}Cl)_2$ and two additional peaks at *m/z* 906 and 908 for the ^{35}Cl, ^{37}Cl, and $(^{37}Cl)_2$ isotopes, respectively), 870 (100%, $[M]^- - Cl$, for ^{35}Cl and one additional peak at *m/z* 872 for the ^{37}Cl isotope), 835 (85%, $[M]^- - 2Cl$). UV−vis (benzene, RT; λ_{max}, nm): 420 (Soret band), 540, 724 (Q bands). ^2H NMR (benzene, RT; δ, ppm): 10.56 (meta D of a selectively deuterated complex), −38 (pyrrole β-D of a selectively deuterated complex).

Chlorination Procedures. A 2−5 mg sample of **4** was dissolved in 1−2 mL of benzene containing a known amount of iodobenzene or nitrobenzene as internal standard. A 0.5−3 equiv amount of substrate was added at once, causing a fast color change of the solution from red to green. Without substrate, the red color persisted for more than 3 h. Inspection of the reaction mixtures by UV−vis served to confirm that the color change was due to transformation of **4** to **1**. Product

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analysis by GC was performed 1 h after the addition of substrate, except for the conditions of Table 2. Chemical yields were determined from calibration of the products with the internal standard (determination of the relative response factors) and are reported by taking into account the stoichiometry of the reactions (two molecules of **4** for formation of one molecule of dichlorostyrene etc.). No yields are reported for the reactions of dimedone and chlorodimedone because of unreliable response factors.

The chlorination products of the reactions of **4** with the hydrocarbons were identified by GC and GC/MS comparison to authentic samples. 2-Chloro-5,5-dimethyl-1,3-cyclohexanedione (chlorodimedone) was purchased from Aldrich, while the other compounds were prepared by literature procedures, as follows. 2,2-Dichloro-5,5-dimethyl-1,3-cyclohexanedione (dichlorodimedone) was prepared by the action of chlorine on an ice-cold solution of dimedone in $CHCl_3$ and recrystallized from dilute alcohol.[50] *cis*- and *trans*-dichloronorbornane were prepared by the procedure of Bellesia et al.[51] The products were obtained after purification by distillation in a *trans:cis* ratio of 85:8. Styrene dichloride was prepared by treating an ice-cold solution of styrene in carbon tetrachloride with less than equimolar amounts of chlorine, followed by fractional distillation.[52]

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