Communications to the Editor

Formation of an Iron(III) Porphyrin Complex with a Nitrene Moiety Inserted into a Fe–N Bond during Alkene Aziridination by [(Tosylimido)iodo]benzene Catalyzed by Iron(III) Porphyrins

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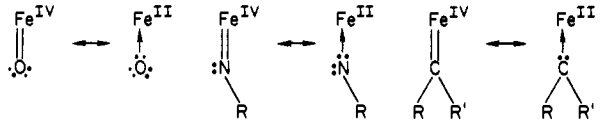
Iron(IV)–oxo porphyrin complexes have been prepared and identified by different spectroscopic techniques.[1] Examples of their nitrogen[2] and carbon[3] analogues have been described.



The complexes derived from these species by one-electron oxidation, formally $Fe^{V}{=}X$ or Fe(III) $\leftarrow{:}X$ species, should be much more reactive and have only been obtained at −80 °C in the case of X = O, either by oxidation of the corresponding $Fe^{IV}{=}O$ complex[4] or by reaction of Fe(III) porphyrins with PhI=O.[5] The one-electron oxidation product of the carbene complex Fe^{II}[TPP[6]] [$C{=}C(C_6H_5Cl)_2$] is not the corresponding Fe(III) carbene complex but an Fe(III) complex where the carbene moiety is inserted between the iron and a pyrrole nitrogen atom.[7] Such a nucleophilic participation of a porphyrin nitrogen atom to help the highly electrophilic $Fe^{V}{=}X$ center has also been proposed to stabilize a $Fe^{V}{=}O$ or (porphyrin)$^{+\cdot}Fe^{IV}{=}O$ species[7a,8] or to be involved in its oxidative degradation at room temperature.[7b] The nitrogen analogue, formally an $Fe^{V}{=}NR$ entity, has never been described, but could be involved as an active intermediate in the transfer of the N-tosyl moiety of [(tosylimido)iodo]benzene (PhI=NTs) (**1**) to alkanes[9] or alkenes[10] catalyzed by Fe(III) porphyrins.

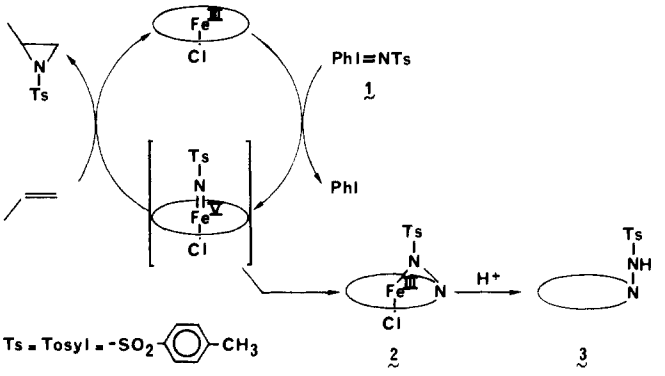
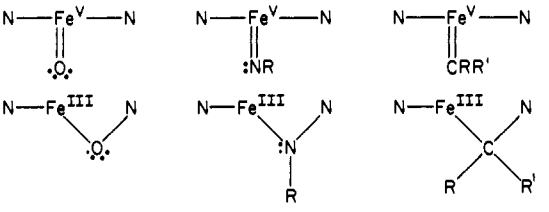


Figure 1.



This paper reports that, upon aziridination of alkenes by PhI=NTs (**1**) catalyzed by Fe(III) tetraarylporphyrins, the starting porphyrin is totally converted into a Fe(III) complex where the N–Ts nitrene moiety is inserted between the iron and a porphyrin nitrogen atom. It also describes the isolation and the spectroscopic and catalytic properties of this first porphyrin complex containing a Fe^{III}–NR–N moiety.

Reaction of PhI=NTs (**1**)[11] with cyclooctene in the presence of Fe(TPP)(Cl) (molar ratio 2000/20/1) in anhydrous CH_2Cl_2 leads to the *N*-tosylaziridine of cyclooctene (17%), as well as tosyl–NH_2 (80%). During this reaction the catalyst is progressively transformed into a porphyrin complex exhibiting peaks in the UV–visible at 422, 520, 560, and 691 nm. When the same reaction is performed in the absence of alkene, the formation of the new porphyrin complex **2** is complete within 15 min at 20 °C. After precipitation by pentane and recrystallization from CH_2Cl_2/CH_3OH (2:1), purple crystals of complex **2** are obtained (80% yield). This complex is stable for days toward O_2. Its mass spectrum (220 °C, chemical ionization with NH_3, negative ions) shows a M − 1 peak at m/e = 871 and a major fragment at m/e = 836 corresponding respectively to Fe(TPP)(NTs)(Cl) and Fe(TPP)(NTs). Elemental analysis (C, H, N, S, Cl) is in agreement with such a formula where an *N*-tosyl moiety has been inserted into Fe(TPP)(Cl). Its magnetic susceptibility measured by the Evans method,[12] 5.8 ± 0.1 μ_B at 34 °C, is indicative of a high-spin (S = 5/2) = 5/2) Fe(III) structure. The EPR spectrum exhibits a signal at g = 4.3 at 4 K which confirms this spin and oxidation state and indicates a rhombic symmetry. The ^{1}H NMR

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spectrum of complex **2** is very similar to those of previously reported high-spin Fe(III) porphyrin complexes with a C_s symmetry such as Fe^{III}(*N*-alkylTPP) complexes.[13] The assignment of the different signals of this ^1H NMR spectrum was made by comparison of the spectrum of complex **2** with those of its analogues prepared from $TPPH_2$ deuterated either on the pyrrole ($TPPH_2$-d_8) or mesophenyl ($TPPH_2$-d_{20}) rings or from tetrakis(*p*-chlorophenyl)porphyrin. Because of the C_s symmetry, the pyrrole protons appear as four signals at −28.4, 81.7, 84.5, and 89.5 ppm (each 2H) and the mesophenyl protons at 6.85, 3.92 (each 2 H, H para), 12.7, 11.22, 10.93, 10.30 (each 2 H, H meta), and 6.10 and 4.10 ppm (each 2 H, very broad H ortho[14]). Two resonances for the *N*-Ts moiety appear at 13.71 (CH_3 + 2 Ar H) and 14.32 ppm (2 H). The great similarity of this ^1H NMR spectrum with those of Fe^{III}(*N*-alkylTPP) complexes suggests two possible structures for complex **2**: either a bridged FeIII–NTs–N or a FeIII–N–NHTs–TPP structure. Accordingly, demetalation of complex **2** by CF_3 COOH under anaerobic conditions leads to the *N*-(tosylamido)tetraphenylporphyin (**3**)[15] (Figure 1). The elemental analysis (C, H, N, S, Cl) of complex **2**, which is in perfect agreement with the Fe(TPP)(NTs)(Cl) formula corresponding to the bridged structure of Figure 1, allows one to discard a Fe^{III}(NNHTsTPP) structure corresponding to a $[Fe(NNHTsTPP)(Cl)]^+X^-$ formula with X^- being Cl^- or another counterion such as OH^-. Moreover, conductimetry measurements performed on complex **2** agree with the bridged structure but are completely inconsistent with the ionic structure (conductivity of **2** 10^{-3} M in CH_3CN almost equal to that of pure CH_3CN). Finally, the great stability of complex **2** at room temperature and its $g = 4.3$ EPR signal indicative of a rhombic symmetry are in agreement with the bridged structure but not with a Fe^{III}–N–NHTsTPP structure since $[Fe^{III}$(*N*-alkylTPP)(Cl)$]^+X^-$ complexes, which should be similar to $[Fe^{III}(NNHTsTPP)(Cl)]^+X^-$, were described as stable only below −40 °C and to exhibit $g = 5.66$ and 2.1 signals indicative of an axial symmetry.[13] Taken altogether these data clearly show the bridged structure of Fig. 1 for complex **2**.

Since complex **2** which derives from the insertion of the N–Ts moiety into a Fe–N bond of Fe(TPP)(Cl) was formed during reaction of PhI=NTs with alkenes catalyzed by Fe(TPP)(Cl), it was of interest to determine whether **2** was able to transfer its NTs moiety to an alkene or to catalyze aziridination by PhI=NR. Complex **2** alone in anhydrous CH_2Cl_2 containing 100 equiv of cyclooctene gave no aziridine after 20 h at 20 °C. However, when used instead of Fe(TPP)(Cl) under the conditions previously described for cyclooctene aziridination by PhI=NR, it acted as a catalyst leading to a similar yield of aziridine (17%).

Complex **2** is the first example of a nitrogen analogue of the $Fe^{III}(TPP)[C{=}C(p\text{-}ClC_6H_5)_2](Cl)$ compound derived from the insertion of the $C{=}CAr_2$ moiety into a Fe—N bond of Fe(TPP)(Cl).[7] Although an intermediate Fe(III) ($S = {}^3/_2$) spin state was found for the latter,[7c] a high-spin Fe(III) state is observed for complex **2**. This is presumably related to the greater strength of the Fe–C bond relative to the Fe–N bond as previously observed from a comparison of the spin states of $Fe(TPP)(NNR_2)$, Fe(II) ($S = 2$),[2] and $Fe(TPP)(C{=}CAr_2)$, Fe(II) ($S = 0$).[3d]

From the aforementioned results, it is likely that the active intermediate formed during alkene aziridination by PhI=NTs catalyzed by Fe(TPP)(Cl), which could be formally written as a Fe^V=NTs complex, either transfers its NTs moiety to the alkene or undergoes an intramolecular isomerization leading to **2** (Figure 1). Even though complex **2** is not able to transfer its NTs moiety to alkenes, it is still active in catalyzing alkene aziridination by PhI=NTs.

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Photochemical and Chemical Enzyme Catalyzed Debromination of *meso*-1,2-Dibromostilbene in Multiphase Systems

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Enzyme-catalyzed reactions in multiphase systems are of substantial interest in organic synthesis.[1] Various reactions were accomplished by using sepharose-supported enzyme systems in organic solvents.[2] Incorporation of enzymes as catalysts in photochemical reactions has been proven to be a promising synthetic tool.[3,4] Recently, we examined photosensitized electron transfer reactions in water–oil two-phase systems using amphiphilic electron acceptors.[5-7] We have shown that photoreduction of *N,N'*-dioctyl-4,4'-bipyridinium, C_8V^{2+}, in the aqueous phase results in the extraction of the reduced photoproduct, $C_8V^{+\cdot}$, into the organic phase. This photoproduct undergoes induced disproportionation (eq 1) to the two-electron charge relay *N,N'*-di-

$$2C_8V^{+\cdot} \rightleftharpoons C_8V + C_8V^{2+} \quad (1)$$

octylbipyridylidene, C_8V, due to opposite solubility properties of the disproportionation products in the two-phase system. Here we wish to report on the photochemically and chemically induced debromination of *meso*-1,2-dibromostilbene to *trans*-stilbene using enzyme-catalyzed systems supported on sepharose beads. In these processes ethanol, lactic acid, alanine, and formate act as electron donors for the debromination process.

In the photochemical systems ethanol, lactic acid, and alanine were used as electron donors. Sepharose beads were soaked in 0.35 mL of an aqueous solution (pH 8.2) that includes the sensitizer ruthenium(II) tris(bipyridine), $Ru(bpy)_3^{2+}$ (1.4×10^{-3} M), *N,N'*-dioctyl-4,4'-bipyridinium (octylviologen), C_8V^{2+} (2.8×10^{-3} M), as electron acceptor, nicotinamide adenine dinucleotide, NAD^+, (1.2×10^{-2} M), and ethanol (0.5 M), lactic acid (0.35 M), or alanine (0.5 M). The system where ethanol is used as electron donor included the enzyme alcohol dehydrogenase (E.C. 1.1.1.1 horse liver, 1.5 units), the system with lactic acid included L-lactic dehydrogenase (E.C. 1.1.1.27 rabbit muscle, 100 units), and with alanine as donor, L-alanine dehydrogenase (E.C. 1.4.1.1. *Bacillus subtilis*, 0.4 units) was introduced.[8] These orange beads were suspended in 4 mL of ethyl acetate that included *meso*-1,2-dibromostilbene (**1**), (3.2×10^{-3} M). The systems were deaerated and illuminated with visible light ($\lambda > 400$ nm). Analysis of the organic phase reveals that dibromostilbene is debrominated and *trans*-stilbene (**2**) is formed.[9] The rate of **2** formation as a function of illumination time is depicted in Figure 1, for the different donors. With ethanol as electron donor 100% conversion of **1** to **2** is accomplished. Ethanol is oxidized in the

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