1618 *Inorg. Chem.* **2000,** *39,* 1618−1620

The Mn(OESPz) ($OESPz^{2-}$ = 2,3,7,8,12,13,17,18-Octakis(ethylsulfanyl)-5,10,15,20-tetraazaporphyrinato Dianion) Complex as an in Situ Regenerative Defluorinating Agent

Giampaolo Ricciardi, Sandra Belviso, and Francesco Lelj*

Dipartimento di Chimica, Università della Basilicata,
via N. Sauro 85, 85100 Potenza, Italy

Received September 17, 1998

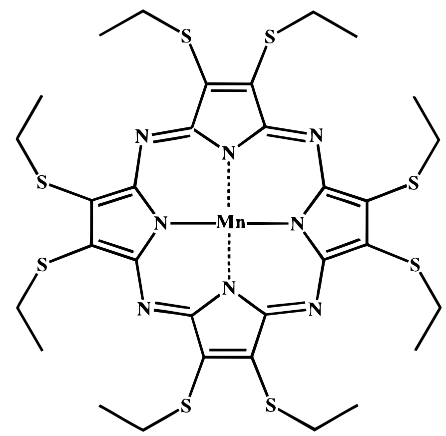
Electrochemical or chemical reduction of the Mn(OESPz)(F) complex restores the original manganese(II) species and affords the F^- ion, suggesting an application of manganese (alkylsulfanyl)tetraazaporphyrins as defluorination catalysts. The reaction is proposed to involve oxidative addition of an $F^\bullet$ radical to the Mn^{II} center and release of an organic radical.

The considerable interest in the oxidative addition of organohalides to titanium,[1] iron,[2] nickel,[3] and especially cobalt porphyrins[4] and to corrins and phthalocyanines[5] stems from its relevance to the understanding of the mode of action of dehalogenase enzymes possessed by methanogenic bacteria,[3a] the development of new synthetic routes to organic compounds,[1] and the catalytic detection and destruction of organohalide pollutants.[1−5]

The porphyrin-like $Mn^{IV}(salpn)Cl_2$ ($salpn^{2-}$ = *N,N′*-salycilidene-1,3-propanediaminato dianion) complex is known to halogenate alkenes, and Mn^{II} tetrapyrroles are, in turn, useful catalysts for the oxidative degradation of aromatic organohalides.[6] However, to the best of our knowledge, there are only rare examples, if any, of oxidative addition of organohalides and, in particular, of organofluorides to Mn^{II} tetrapyrroles.[7]

We recently showed that, in the Mn^{II}(OESPz) complex (see Chart 1), an unusually powerful nucleophile which undergoes a very rapid $Cl^\bullet$ radical oxidative addition upon treatment with C_1-chlorinated hydrocarbons, the Mn^{III}/Mn^{II} redox couple is ∼400 mV anodic with respect to Mn(OEP) (OEP^{2-} = octaethylporphyrinato dianion) due to the larger electronic stabilizing effects of the OESPz ring, in comparison with OEP, on the Mn(II) state.[8] Both the fast reactivity with organochlorides and the facile accessibility of the (II) state make this complex a suitable candidate for the reductive dehalogenation of organohalides. As a matter of fact, it is known that the catalytic activity of the nickel, iron, and cobalt tetrapyrrole complexes in the reductive dehalogenation of organohalides is hampered, in part, by the rather negative potentials required to generate the coordinated metal in its (I) state, which are of −1 V (vs SCE) or more. Redox tuning via chemical alteration of the ring may be effective, but more positive redox potentials imply, in general, lessened reaction rates.[4] Therefore, we were encouraged to check for the response of the Mn(OESPz) complex in activating carbon−halogen bonds other than the C−Cl bonds in chlorinated hydrocarbons, including even the scarcely reactive C−F bonds. The preliminary results of this investigation concern the use of Mn(OESPz) in the chemical and electrochemical reductive defluorination of perfluorodecalin and 1,2-difluorobenzene (hereafter denoted **1** and **2**, respectively,; see Scheme 1), taken as prototypes of saturated and aromatic fluorinated organic compounds, respectively, and are the subject of this paper.

Chart 1



Mn^{II}(OESPz)

The complex Mn(OESPz) shows a remarkable reactivity toward perfluorodecalin, **1**, a well-studied fluorinated saturated substrate,[11] leading to the Mn(OESPz)(F) derivative and to defluorinated organics. Reaction of Mn(OESPz) (0.024 mmol) with a large molar excess of **1** (0.45 mmol) in THF (3.0 mL) at 20.0 ± 0.1 °C results, for instance, in the quantitative conversion (∼95%) of the title complex in the fluoromanganese(III) porphyrazine and in the production of two partially defluorinated compounds, $C_{10}F_{14}$ and $C_{10}F_{13}$, in nearly equal amounts, as quantified by GC and GC/MS. The formation of partially defluorinated and, hence, unsaturated **1** derivatives was deduced from the UV spectrum of the reaction mixture showing intense

---

(1) Wang, X.; Woo, L. K. *J. Org. Chem.* **1998**, *63*, 356.

(2) (a) Elliot, C. M.; Marrese, C. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *119*, 395. (b) Rusling, J. F.; Nassar, A. E. F. *J. Am. Chem. Soc.* **1993**, *115*, 11891.

(3) (a) Krone, U. E.; Laufer, K.; Thauer, R. K.; Hogenkamp, H. P. C. *Biochemistry* **1989**, *28*, 10061. (b) Arai, T.; Kondo, H.; Sakaki, S. *J. Chem. Soc., Dalton Trans.* **1992**, 2753. (c) Lewis, T. A.; Morra, M. J.; Habdas, J.; Czuchajowski, L.; Brown, P. D. *J. Environ. Qual.* **1995**, *24*, 56. (d) Kadish, K. M.; Franzen, M. M.; Han, B. C.; Araullo-McAdams, C.; Saxon, D. *Inorg. Chem.* **1992**, *31*, 4399. (e) Lahiri, G. K.; Schussel, L. J.; Stoltzenberg, A. N. *Inorg. Chem.* **1992**, *31*, 4991.

(4) (a) Dobson, D. J.; Saini, S. *Anal. Chem.* **1997**, *69*, 3532. (b) Kadish, K. M.; Lin, X. Q.; Han, B. C. *Inorg. Chem.* **1987**, *26*, 4161. (c) Rusling, J. F.; Miaw, C. L.; Couture, E. C. *Inorg. Chem.* **1990**, *29*, 2025. (d) Steiger, B.; Ruhe, A.; Walder, L. *Anal. Chem.* **1990**, *62*, 759. (e) Blaser, H.-U.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 1684.

(5) Iwunze, M. O.; Hu, M.; Rusling, J. F. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *333*, 353.

(6) (a) Law, N. A.; Machonkin, T. E.; McGorman, J. P.; Larson, E. J.; Kampf, J. F.; Pecoraro, V. *J. Chem. Soc., Chem. Commun.* **1995**, 2015. (b) Labat, G.; Seris, J.-L.; Meunier, B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1471. (c) Bernadou, J.; Fabiano, A.-S.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1994**, *116*, 9375.

(7) For a comprehensive review of C−F activation by metal reagents, see: Kiplinger, J. L.; Richmond, T. J.; Ostenberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

(8) Ricciardi, G.; Bavoso, A.; Bencini, A.; Rosa, A.; Lelj, F.; Bonosi, F. *J. Chem. Soc., Dalton Trans.* **1996**, 2799.

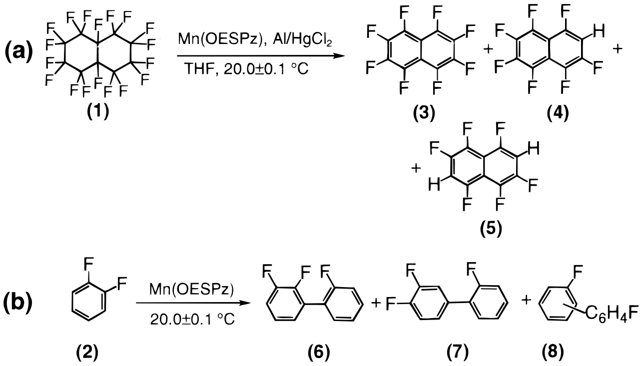
(9) Perrin, D. D.; Armarego, W. L. F. *Purification of laboratory chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

(10) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods—Fundamentals and Applications*; John Wiley & Sons: New York, 1980.

(11) Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805.

10.1021/ic981120z CCC: $19.00

Scheme 1



absorptions, typical of unsaturated hydrocarbons, at 260 and 285 nm.[11]

Voltammetric experiments showed that the Mn^{III}/Mn^{II} couple exhibits catalytic behavior with respect to the reductive defluorination of **1**. Significant results of these experiments are depicted in Figure 1. In the absence of **1**, the voltammogram exhibits in the range +400 to −300 mV (vs Ag/AgCl) a wave featuring the Mn^{III}/Mn^{II} couple. This is chemically and electrochemically reversible, $E_{1/2}$ being 0.115 V, in 0.15 M $(TBA)ClO_4/DMF$. Upon addition of **1** (whose first, irreversible reduction wave is located, as shown by our independent measurements, at −0.97 V in 0.15 M $(TBA)ClO_4/DMF$), the Mn^{III}/Mn^{II} cathodic wave increases with the amount of added **1** and loses reversibility. Very similar behavior is observed in $(TBA)ClO_4/THF$. These results indicate that the Mn^{II}(OESPz) species, once restored by the one-electron reduction of Mn(OESPz)(F), is reoxidized by **1**, still present in the reaction mixture and, hence, that a catalytic sequence of reactions is operative at the Mn^{III}/Mn^{II} couple. This was supported by spectroelectrochemical experiments and preparative-scale electrolysis. UV−vis spectra obtained upon electrolysis at −0.3 V (vs Ag/AgCl) on a platinum grid electrode of a 0.1 M $(TBA)ClO_4/THF$ solution containing ∼1.0×10^{-4} M Mn(OESPz)(F) were indicative of a complete Mn^{III}(OESPz)(F) → Mn^{II}(OESPz)(F^-) conversion. The depletion of the Mn^{III}(OESPz)(F) species (red-violet) and the concomitant formation of the Mn^{II}(OESPz) species (dark blue) were indicated indeed by the decrease of the intensity of the Q bands at 711 and 530 nm typical of the Mn^{III} porphyrazine and by the onset of a Q band at 590 nm diagnostic for the Mn^{II} species.[8] Upon addition of an excess of **1**, the features of the optical spectrum of the fluorinated complex, Mn^{III}(OESPz)(F), were restored. Bulk, controlled-potential electrolysis at −0.3 V of an Mn(OESPz)/THF solution in the presence of **1** (see Experimental Section in the Supporting Information) led to a rather complicated distribution of fluorinated compounds from which we were able to isolate and characterize by GC/MS and ^{19}F NMR spectroscopy octafluoronaphthalene, **3**, in a ∼17% yield, based on **1**. From this result we calculated that more than 700 fluorine atoms were abstracted per Mn^{II} porphyrazine unit. Interestingly, the catalytic, reductive defluorinating capability of the system could be equally realized if electrons for the $Mn^{III} \rightarrow Mn^{II}$ conversion were provided by a chemical source, such as activated Al or Mg. For instance, stirring a mixture of **1** and Mn(OESPz) in THF in the presence of Mg turnings and $HgCl_2$ resulted in the formation of **3**, heptafluoronaphthalene (**4**), and hexafluoronaphthalene (**5**) in 11.0%, 3.0%, and 1.0% yields (based on perfluorodecalin), respectively, as quantified by GC/MS and ^{19}F NMR spectroscopy (the ^{19}F NMR spectra were assigned on the basis of refs 12a,b). Using Al in the place of Mg, the Mn(OESPz) complex still reductively defluorinated **1** to give **3**−**5**. The reaction was significantly slower, but the yields were very similar: 12.7%, 2.5%, and 1.5% for **3**−**5**, respectively. In both cases, we calculated that more than 600 F atoms were removed per Mn^{II} unit and a turnover >60 was obtained. Notably, the catalyst only slightly deteriorated, as it could be recovered from the reaction mixture (as Mn(OESPz)(F)) in a ∼65% yield.

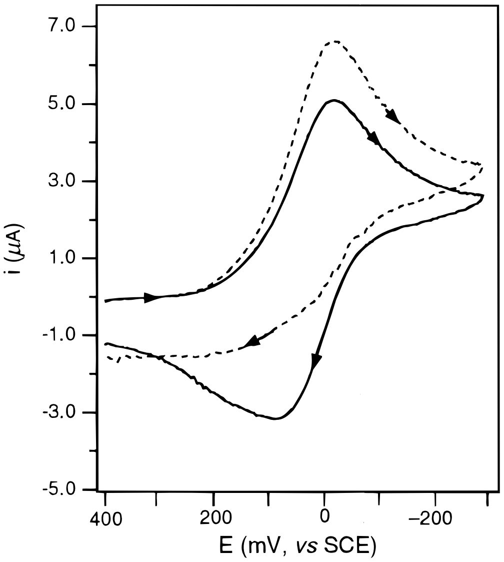


Figure 1. Cyclic voltammograms at a Pt electrode at 0.2 V s^{-1} in 0.15 M $(TBA)ClO_4/DMF$: (solid line) 0.5 mM Mn(OESPz); (dashed line) 0.5 mM Mn(OESPz) + 0.175 M perfluorodecalin. (CV scans are the first scans beginning at +0.4 V on freshly polished electrodes.)

That this chemistry is due to the catalytic role played by the title complex, rather than to the defluorinating capability of the activated metals used, is in line with literature data[11] and confirmed by our control experiments.

While it is known in fact that activated Mg does not show any reactivity with **3** under mild conditions, it has been found that it may react at room temperature with saturated fluorohydrocarbons containing tertiary C−F bonds such as **1**.[11] Control experiments performed by us in the absence of Mn(OESPz) showed that activated Mg started however to induce formation of detectable amounts of **3** after 3 h of stirring at room temperature. Since **3**−**5** formed in considerable amounts, in the presence of Mn(OESPz), in the time regime in which the catalytic activity attributable to activated magnesium was not operative (the reaction in the presence of Mn(OESPz) was stopped after 2 h of stirring; see the Supporting Information), the independent catalytic activity of the Mn(OESPz) complex is clearly demonstrated.

As for the possible, and concurrent, contribution of activated aluminum to the defluorination reaction, we found, in agreement with previous experimenters,[11] that activated aluminum did not react at all with **1** or **3** at room temperature. In all, these findings indicate unambiguously that Mn(OESPz) catalytically mediates the reductive defluorination of perfluorodecalin.

We note that significant similarities can be found between the reductive defluorinating action of the Mn(OESPz)(F)/Mn(OESPz) system and reductive defluorination and mild hydrogenation of aromatic carbon−fluoride bonds mediated by nascent low-valent metallocene species, the Cp_2ZrCl_2 + Mg/$HgCl_2$ system being a working example.[11] The hydrogens in compounds **4** and **5** obtained by the reductive defluorinating action of the Mn(OESPz)(F)/Mn(OESPz) system should result, as found in the case of the metallocene systems, from H atom abstraction from the THF solvent.[11]

The neat reaction of Mn(OESPz) with **2** resulted in the quantitative formation of Mn(OESPz)(F) (~93%, based on the Mn^{II} complex) and a very interesting distribution of organic products. As can be inferred from the gas chromatogram of the reaction mixture (see the Supporting Information), three chromatographic peaks, with t_R values of 10.47, 10.55, and 10.59 min, respectively, together with that of unreacted **2** with $t_R = 2.85$ min, account for the major reaction products. By MS analysis, the chromatographic peak with $t_R = 10.47$ min showed a molecular peak at $m/e = 190$. The remaining two peaks with $t_R = 10.55$ and 10.59 min showed a single molecular peak at $m/e = 208$ but two different fragmentation patterns. In all, GC and MS data seemed to be consistent with the formation of bicyclic fluoro derivatives (whose structures are tentatively proposed in Scheme 1). The generation of these compounds can be rationalized by considering that fluorine atom abstraction from **2** implies the formation of the $C_6H_4F^{\bullet}$ radical, which may in turn recombine (to give **8**) or react with **2** (to give **6** and **7**) and an $H^{\bullet}$ radical. The observed larger abundance of the heavier isomers **6** and **7** relative to **8** correlates with the considerably larger availability of **2** compared to the $C_6H_4F^{\bullet}$ radical in the reacting system.

Summarizing, we have shown that the Mn(OESPz)/Mn(OESPz)(F) system is capable of reductive defluorination of saturated and aromatic fluoroorganics. Our results indicate that the system can exploit an electrochemical or chemical source of electrons to catalyze the reductive defluorination of fluorinated substrates. We have shown that the chemical route is somewhat more efficient and selective than the electrochemical one. It was found that the neat reaction of Mn(OESPz) with 1,2-difluorobenzene may represent, de facto, a radical-trapping reaction where the radical trap is provided by the reactant itself. This suggests a possible use of the complex in organic syntheses. Studies on these and related topics, which include the reaction of the title complex and other metalloporphyrazines with haloorganics, are in progress in our laboratory.[13]

Acknowledgment. We thank Mr. C. Barlabà for technical support and Prof. A. Degl'Innocenti (University of Florence, Italy) for the ^{19}F NMR measurements and for valuable discussions. Financial support provided by the Advanced Materials Laboratory (LaMI) under the auspices of the European Union and Regione Basilicata and by the Ministero della Ricerca Scientifica e Tecnologica (MURST) is gratefully acknowledged.

Supporting Information Available: Text giving experimental procedures and details, spectroscopic data for known organic products, and characterization data for the Mn(OESPz)(F) complex and a figure showing GC/MS spectra for compounds **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981120Z

---

(12) (a) Bolton, R.; Sandell, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1978**, 746. (b) Bailey, W. I.; Kotz, A. L.; McDaniel, P. L.; Parees, D. M.; Schweighardt, F. K.; Yue, H. J.; Anklin, C. *Anal. Chem.* **1993**, *65*, 752.

(13) Ricciardi, G.; Belviso, S.; Lelj, F. Manuscript in preparation.